

Nuclear Development

**Accelerator-driven Systems (ADS)
and Fast Reactors (FR) in
Advanced Nuclear Fuel Cycles**

A Comparative Study

NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

3. COMPARATIVE ANALYSIS

3.1 Principal fuel cycle schemes

3.1.1 Basis for the selection

A consistent comparison of transmutation systems implies an analysis of the systems using a single nuclear data library, a single reactor code system, and consistent input data for reactor and fuel cycle parameters. It is clear that such an exercise cannot comprehend all possible systems and hence involves a selection of representative systems or “schemes”. The selection was guided by the rationale for introducing P&T in future advanced fuel cycles with emphasis on basically different approaches. The applied criteria and assumptions can be summarised as follows:

- The comparative analysis is restricted to actinide transmutation systems based on *critical and accelerator-driven fast reactors*. Most of the currently proposed transmutation systems belong to this category. Actinide burners with a thermal neutron spectrum are described in Chapter 9.
- A particular goal of the study is to compare *evolutionary and innovative approaches* to the transmutation of actinides, characterised by the separate handling or the co-processing of plutonium and minor actinides, respectively.
- Since, in the medium-term, resource efficiency will probably not become an issue of primary importance, LWRs can be expected to remain important components of all advanced nuclear energy systems. The burner reactors of the fuel cycle schemes are therefore optimised for a high burning efficiency so that they can support a *large fraction of LWRs*.
- Assuming radiotoxicity reduction to be the primary goal, only TRU and minor actinide burners with *fully closed fuel cycles* are considered although such systems cannot be expected to be operational on industrial scales before several decades. (Systems with partially closed fuel cycles cannot achieve such high radiotoxicity reductions as systems with fully closed fuel cycles).
- Since the start-up and the shut-down phase in transient nuclear energy scenarios depend on many boundary conditions which are subject to large uncertainties, the analyses of the schemes are restricted to steady-state conditions, meaning that the results apply only if the reactor park is operated for a very long time (transients aspects are briefly discussed in Chapter 2, Section 2.8.1).

Six principal fuel cycle schemes are found to be sufficient to illustrate and quantify the essential features of FR- and ADS-based systems for the burning of plutonium and the transmutation of minor actinides. These include an LWR-once through scheme as a reference case, a plutonium burning scheme, three transmutation schemes in which critical and sub-critical fast reactors perform specific functions, and a pure fast reactor scheme which represents the long-term goal of the nuclear development. Other transmutation approaches as e.g. the heterogeneous recycling of americium and

curium are considered as variants of the six principal schemes (cf. Section 3.3). For convenience, the six principal fuel cycle schemes will be referred to as follows:

1) *LWR once-through*

A strategy based on modern PWRs with direct disposal of the spent fuel. This is the reference case for the comparisons.

2) *Plutonium burning*

A representative plutonium burning strategy based on LWRs and fast reactors. An LWR-MOX stage is incorporated in the scheme, because MOX recycling in LWRs is already a standard practice in Europe. MOX-fuelled fast reactors with a low conversion ratio are used to maximise the LWR-to-FR ratio (an accelerator-driven plutonium burner is not considered, since plutonium burning is not in the focus of the present study).

3a) *TRU burning in FR*

A “two component” transmutation system based on normal LWRs and ALMR-type critical fast reactors. The top-up fuel of the latter contains fertile uranium such that the passive safety regime and applicability of fuels irradiation database remain valid. This precludes reducing the breeding ratio below about 0.5 (the LWR-to-FR ratio is a function of the FR breeding ratio).

3b) *TRU burning in ADS*

Same strategy as scheme 3a with the difference that the fast reactor is replaced by an ATW-type sub-critical fast system. The capability of the latter to burn pure transuranics improves the LWR-to-FR ratio.

4) *Double strata*

A second, so-called P&T stratum with accelerator-driven, dedicated minor actinide burners is added to the plutonium burning scheme. A particular advantage of this “three component” transmutation system is that the investment in innovative reactor and reprocessing technology is minimised.

5) *Fast reactor strategy*

A fast reactor strategy featuring a fully closed fuel cycle and natural uranium top-up. This strategy represents the long-term goal for the nuclear development, since it fulfils the resource-efficiency and environmental friendliness requirements simultaneously.

3.1.2 Reactor and fuel cycle characteristics

The fuel cycles of the principal schemes are sketched in Figures 3.1 to 3.6. The figures contain information on the net electric power installed in the reactor components (all reactors are assumed to be electricity producers), the fuel cooling and storage time before reprocessing and after fabrication, and the reprocessing method (“wet” or “dry”). Additional information on the fuels (composition, burn-up, fuel management, etc.) is given in Table 3.1. It should be noted that the actinide mass flows in the fuel cycles determine the support ratios, and that the values for the latter refer to net electric power delivered to the grid, i.e. account for the electricity recycled in the accelerator of an ADS. The fuel cooling and storage times - the fabrication is assumed to take place immediately after

the reprocessing – determine the out-of-pile time of the fuel and hence influence the total actinide inventory of the fuel cycle.

The fuel cycle parameters, especially the fuel burn-up and the reprocessing losses, strongly influence the results of the comparative analysis. The adopted values represent a consensus of experts from the major OECD countries with reprocessing experience. The value of 0.1% for the reprocessing losses is an extrapolation from the current technology to a technology which can be expected to work at a time when transmutation systems could be introduced on a larger scale. The extrapolation is based on expected and partly at laboratory scale proven advances in the wet and dry reprocessing technology. The assumptions are comparable to assumptions which have been made in other national and international transmutation studies.

The schemes involve the following reactor components:

- *LWR-UOX*

Fuel as discharged from a French N4 pressurised water reactor. The UOX fuel is irradiated to a burn-up of 50 GWd/tHM.

- *LWR-MOX*

N4 reactor with a 100% MOX core. The initial plutonium vector is that of the discharged UOX fuel, and the MOX fuel is irradiated to a burn-up of 50 GWd/tHM.

- *Plutonium burner*

EFR-type reactor with MOX fuel. Low conversion ratio, high burn-up CAPRA core [24]. The plutonium is recycled indefinitely, and the plutonium-to-uranium ratio of the top-up fuel is adjusted to obtain $k_{\text{eff}} = 1$ at EOEC assuming a six-batch core. The plutonium feed is the plutonium separated from the LWR discharged MOX fuel. The maximum plutonium enrichment of the fuel for the equilibrium core is 44% at beginning-of-life.

- *Critical TRU burner*

ALMR-type actinide burner with a conversion ratio of 0.5. The reactor model is the same as that used in the 600 MW(e), metal-fuelled, multiple recycle burner core benchmark exercise of the NEANSC Working Party on Plutonium Recycling [25]. The TRU-to-uranium ratio of the top-up fuel is adjusted to obtain $k_{\text{eff}} = 1$ at EOEC assuming a five-batch core. The TRU feed consists of the TRU in the LWR discharged UOX fuel, the U feed is depleted uranium. The TRU content of the fuel for the equilibrium core is 33% at beginning-of-life.

- *Accelerator-driven TRU burner*

The reactor model is based on the ANL design of a lead-bismuth cooled sub-critical TRU burner [26]. The actinide-to-zirconium ratio of the metal fuel is adjusted to obtain a k_{eff} of about 0.97 at BOEC assuming a six-batch core. The top-up fuel consists of undiluted TRUs as discharged from the LWRs. Since the fuel is uranium-free, the reactor has a low heavy metal inventory.

- *Accelerator-driven MA burner*

Modular concept which is compatible with the dimensions the ALMR Reference Model A design [27] and, except for a smaller core radius, resembles the lead-bismuth cooled system proposed by JAERI [20]. The reactor model is the same as that used in the NEANSC comparison calculations for an accelerator-driven minor actinide burner [28]. A pure minor

actinide top-up as produced by the first stratum of the plutonium burning scheme (scheme 2) is assumed. Following the Japanese preference, the fuel consists of actinide mononitrides. The actinide-to-zirconium ratio is set to give a k_{eff} of about 0.95.

- *Fast reactor*

ALMR-type fast reactor. The reactor model is the same as that for the critical TRU burner with the difference that the lower steel reflector and the outermost fuel element ring are replaced by uranium blankets. The fuel and the blankets are reprocessed together, the new blankets are fabricated from reprocessed uranium, and the new fuel is fabricated from reprocessed TRU, reprocessed uranium and a natural uranium top-up. The actinide-to-zirconium ratio is adjusted to give a conversion ratio of 1.0 and a k_{eff} of 1.0 at EOEC assuming a five-batch core.

It should be noted that the TRU burners, the MA burner and the fast reactor have fully closed fuel cycles, i.e. all actinides are recycled until the fuel composition reaches an equilibrium.

Figure 3.1. **Once-through strategy (scheme 1)**

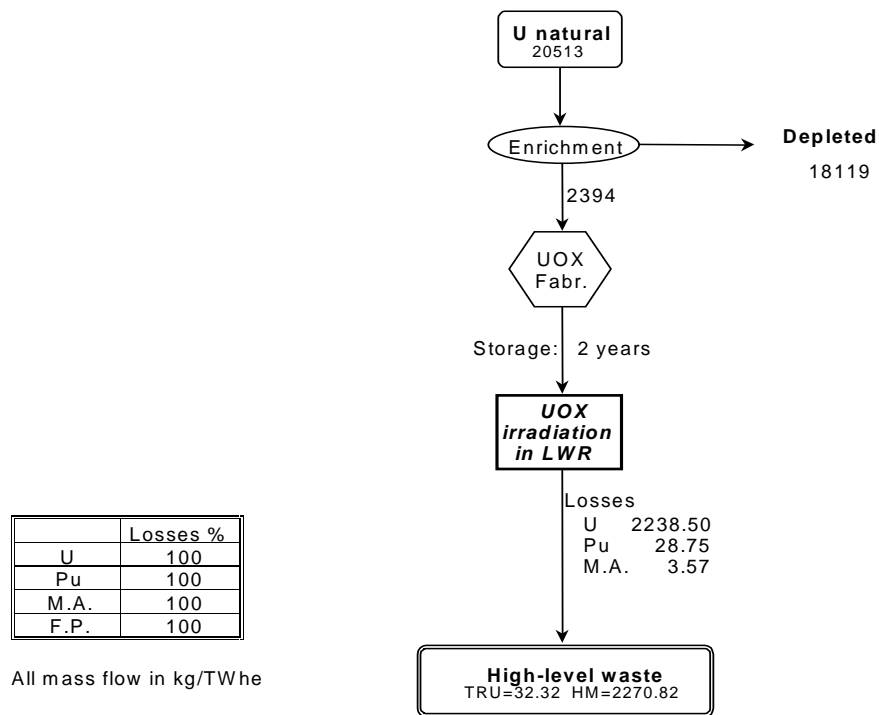


Figure 3.2. Plutonium burning strategy (scheme 2)

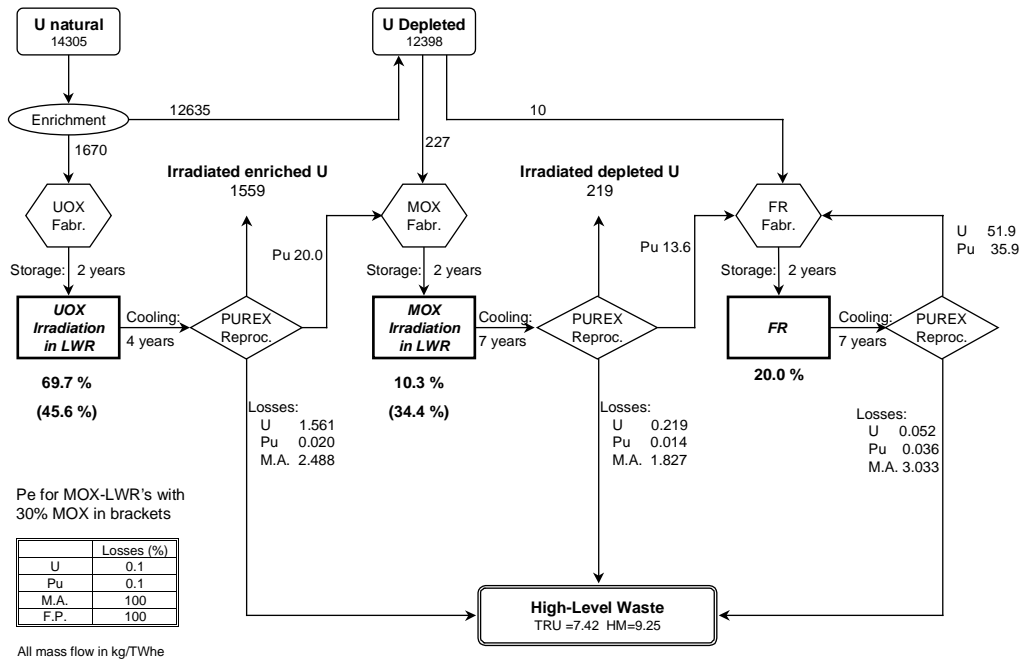


Figure 3.3. Double strata strategy (scheme 4)

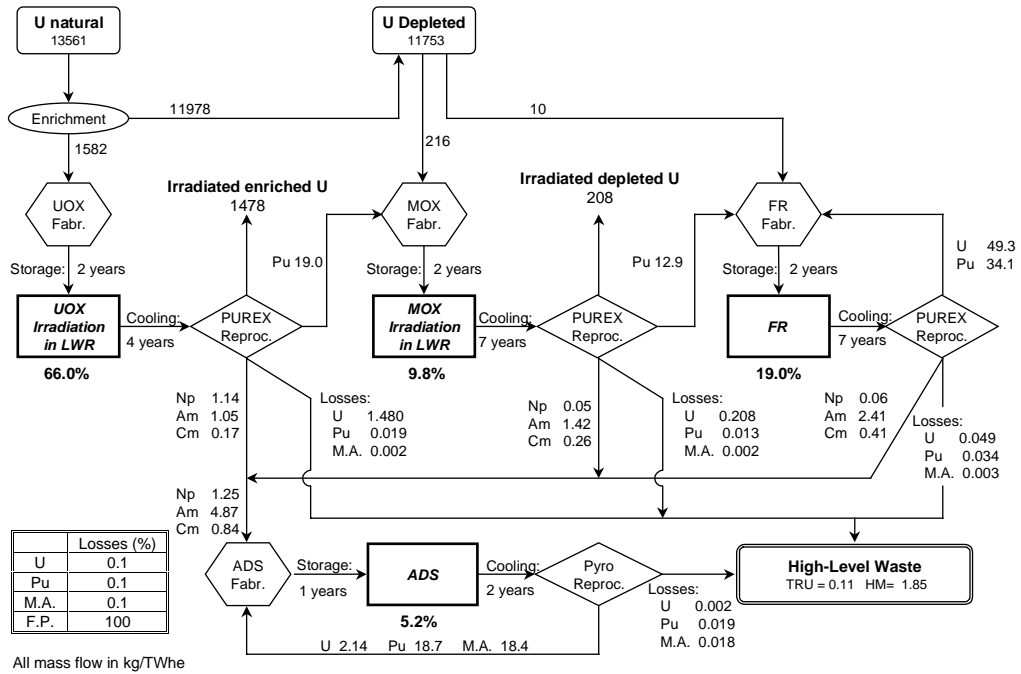


Figure 3.4. TRU burning in fast reactor (scheme 3a)

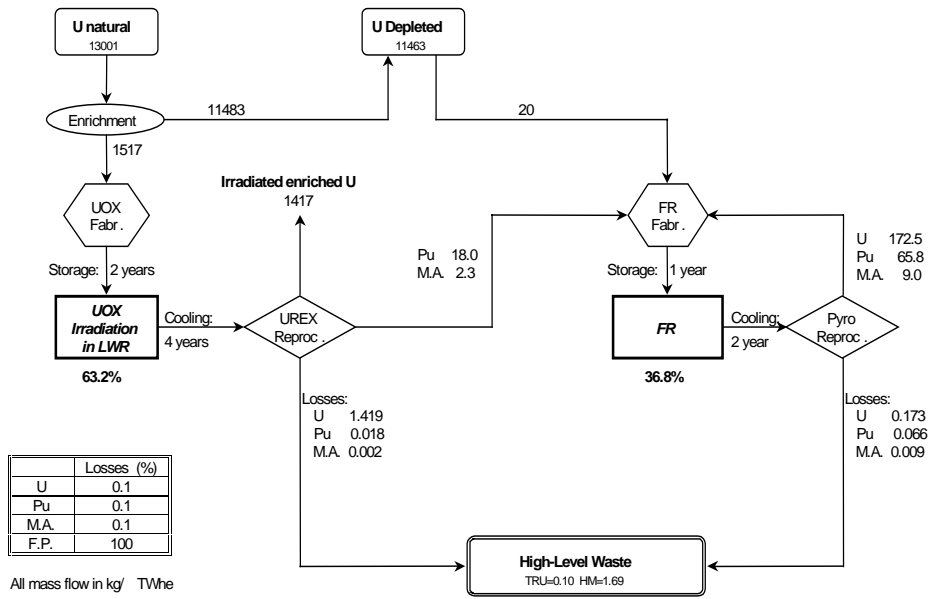


Figure 3.5. TRU burning in ADS (scheme 3b)

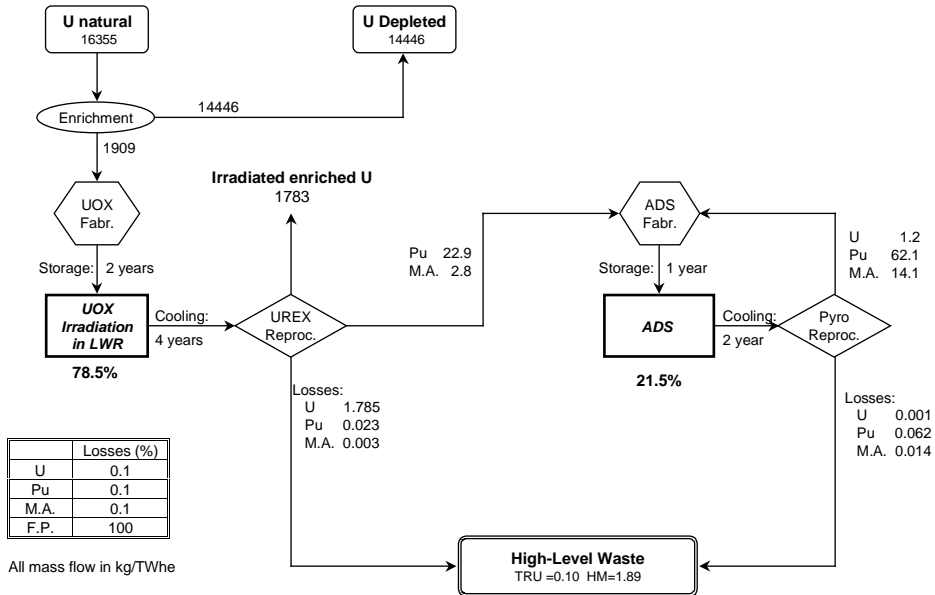


Figure 3.6. Fast reactor strategy (scheme 5)

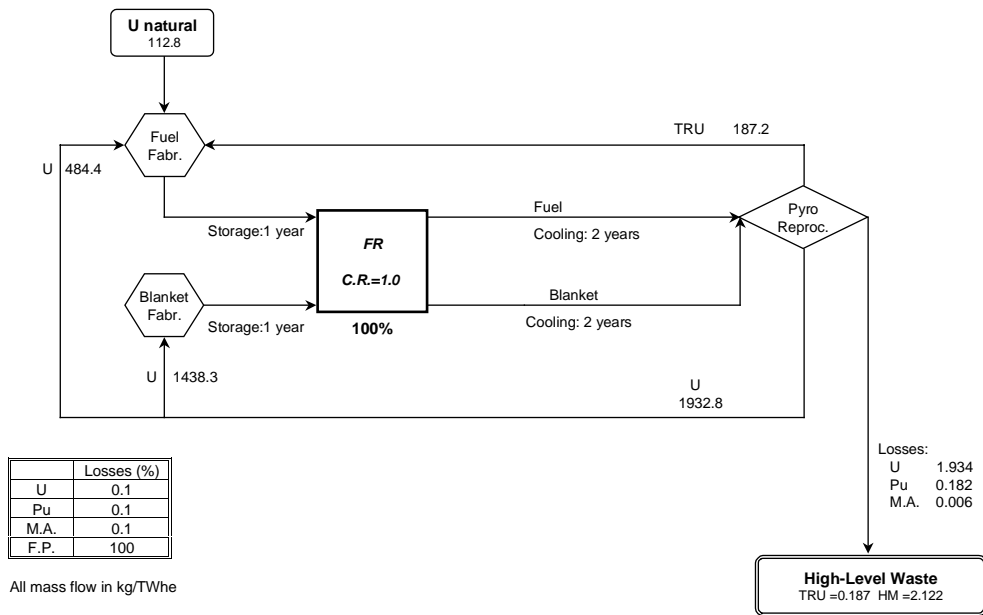


Table 3.1. Design parameters of fast-spectrum systems

Design parameter	Pu burner (FR)	TRU burner (FR)	TRU burner (ADS ¹)	MA burner (ADS ¹)	Fast reactor
Thermal power (MW)	3 600	1 575	840	377	1 575
Net electric power (MW)	1 450	600	275	119	600
Load factor (%)	85	85	80	85	85
Coolant	Na	Na	Pb-Bi	Pb-Bi	Na
Fuel	MOX	⁷⁸ Ac- ²² Zr	²⁵ Ac- ⁷⁵ Zr	²⁹ AcN- ⁷¹ ZrN	⁷⁹ Ac- ²¹ Zr
HM Inventory, BOL (kg)	25'690	17'551	2 923	3 145	17'732 ³
Fuel burn-up (GWd/tHM)	185	139	250	149	127 ³
In-pile time (d)	1 553	1 825	1 093	1 460	1 825
No. of batches	6	5	6	1	5
TRU in top-up fuel (%) ²	57.6	50.0	100	100	0

1. For the accelerator and the target the following assumptions are made:
electrical efficiency = 45%, proton energy = 1 GeV, neutrons per proton = 42.
2. Content of top-up fuel in transuranic actinides.
3. Core without blankets.

3.2 Comparative assessment

3.2.1 Calculation methods

This section overviews the calculation methods used in the analyses of the principal fuel cycle schemes. More detailed information regarding methods and results can be found in [29].

The analyses involved the following well-validated computer code systems:

- *Light water reactors*

The analyses were performed by CEA Cadarache using the deterministic thermal reactor analysis code system Apollo1-Cesar [30].

- *Fast-spectrum systems*

The analyses were performed at PSI Villigen using version 1.2 of the European fast reactor analysis code system ERANOS [31] in combination with the reference ERALIB I libraries, based on JEF 2.2 basic nuclear data. The code system had previously been tested for actinide burner applications in the framework of the NEANSC comparison calculations described in [28].

- *Spallation neutron source*

The PSI version of the high-energy Monte Carlo code HETC was used. HETC simulates the interactions in the target above a cut-off energy of 20 MeV and edits a spatially dependent external neutron source for use with multi-group transport calculations below the cut-off energy. A proton energy of 1 GeV was assumed.

The fast-spectrum systems were modeled in R-Z geometry and analysed using S₄ neutron transport theory with 33 broad energy groups below 20 MeV. The broad group cross-sections were obtained from fundamental-mode cell calculations with 1968 fine energy groups, taking the cell heterogeneities into account. For the sub-critical systems, in-homogeneous reactor calculations with the HETC source were performed and from these the level of the external source for the given thermal power of the systems was evaluated. The equilibrium fuel compositions were calculated using detailed chains including 29 actinides up to ²⁴⁸Cm and 80 explicit fission products.

The evaluation of the equilibrium fuel composition required repeated burn-up calculations with subtraction of the reprocessing losses and addition of the top-up fuel after each iteration. The shut-down times for fuel reloading between reactor cycles and the fuel storage and cooling times were correctly simulated throughout this iterative procedure, and the procedure was repeated until equilibrium was reached, i.e. the differences between two successive fuel compositions were smaller than 0.05% for all relevant nuclides.

For determining the end-of-life fuel composition, it was sufficient to carry out the equilibrium calculation for a single batch core. The neutron multiplication factors for the multi-batch cores were calculated for average fuel compositions which were evaluated as follows: the composition of the fuel at BOEC was obtained by averaging the equilibrium fuel composition at appropriate burn-ups, and this fuel composition was then irradiated during one reactor cycle to obtain the average fuel composition at EOEC.

In an ideal critical reactor, the neutron multiplication factor reaches 1.0 at EOEC. In the core simulations, this was achieved by adjusting the uranium-to-TRU ratio of the top-up fuel. For the sub-critical systems of schemes 3b and 4, this is not possible because the top-up fuel consists of pure TRU. In these cases, the k_{eff} was adjusted by slightly modifying the actinide-to-zirconium ratio of the fuel. This allowed to conserve the geometry of the benchmark models.

The long-term evolutions of the waste activity were calculated with the ORIHET 3 code, an adaptation of the code ORIGEN which uses a decay data library based on NUBASE data. The activities were converted to ingestion doses using the dose conversion factors from [32] (see also

Annex D). The near-field release rates for the vitrified waste arising in schemes 2 and 4 and from an LWR once-through vitrification strategy were calculated by Nagra, Wettingen, using an improved version of the near-field analysis code STRENG.

The decay heat and the neutron source strength of the fuel was calculated with the MECCYCO code [33] which uses nuclear data from JEF. As the 80 explicit fission products used in the establishment of the equilibrium for the actinides were found to be insufficient for accurate decay heat predictions, an additional cycle of the fuel was simulated with 160 explicit fission products. An improvement had also to be applied to the neutron source strength calculations: To account for neutron source contributions from spontaneous fissions in ^{250}Cf and ^{252}Cf , which are significant for the multi-recycled TRU and minor actinide burner fuels, neutron source strength calculations using a special chain library which contains berkelium and californium isotopes had to be carried out.

3.2.2 Equilibrium core characteristics

The principal neutronic parameters of the equilibrium cores, including the k_{eff} at the end of the equilibrium cycle (EOEC), the burn-up reactivity drop during the cycle, the external neutron source strength, the median energy of the core-averaged neutron spectrum, and important safety parameters, are compiled in Table 3.2. Figure 3.7 shows the evolution of the k_{eff} during the equilibrium cycle.

Table 3.2. Equilibrium core characteristics

Core parameter	Pu burner (FR)	TRU burner (FR)	TRU burner (ADS)	MA burner (ADS)	Fast reactor
k_{eff} , EOEC	1.005	1.005	0.920	0.932	0.999
Δk_{eff} , BOEC-EOEC	0.045	0.044	0.051	0.019	0.041
Ext. neutron source (n/s) ¹	–	–	$6.36 \cdot 10^{18}$	$2.53 \cdot 10^{18}$	–
Neutron source importance ²	–	–	0.959	0.843	–
Void effect (pcm) ³ , core	2 245	1 775	-3 302	2 861	1 397
Core and upper reflector	1 904	-1 758	-4 933	2 263	-2 025
Fuel Doppler effect ⁴	1 908	555	308	75	806
β_{eff} at BOEC (pcm)	318	323	260	161	346
Median energy (keV) ⁵	132	242	189	173	228

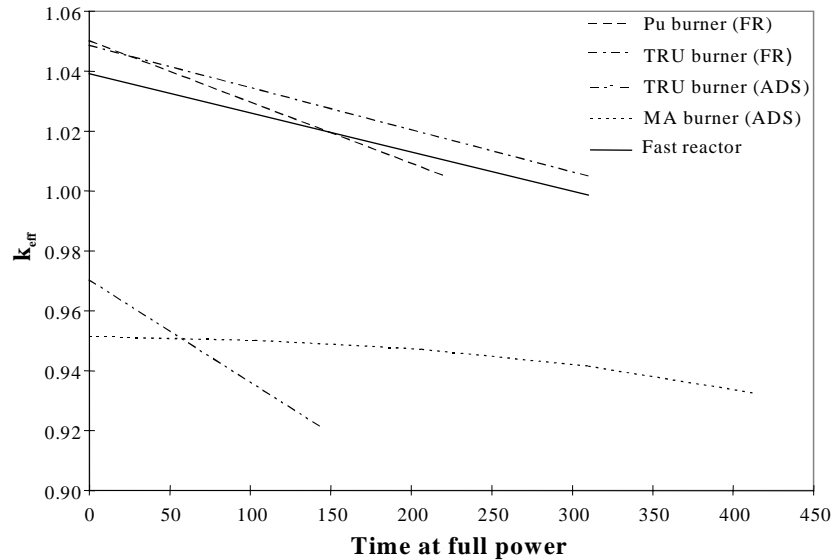
1. No. of source neutrons per second below 20 MeV to maintain design power at EOEC.
2. Neutron source importance at EOEC evaluated as $(1/k_{\text{eff}}-1)/(1/k_{\text{source}}-1)$.
3. Coolant void reactivity effect at BOEC calculated as $(k_{\text{eff}}(\text{voided}) - k_{\text{eff}}(\text{reference}))/k_{\text{eff}}(\text{reference})$.
4. Fuel Doppler effect at BOEC calculated as $10^6 (k_{\text{eff}}(T_{\text{ref}}) - k_{\text{eff}}(T_{\text{ref}}+600\text{K}))/k_{\text{eff}}(T_{\text{ref}}) k_{\text{eff}}(T_{\text{ref}}+600\text{K})$.
5. Median energy of the core-averaged neutron spectrum at BOEC.

The burn-up reactivity drop depends on the reactor type, the fuel burn-up and the core reloading fraction at the end of a reactor cycle. For the critical cores, the latter was optimised to obtain similar reactivity drops and hence excess reactivities at the beginning of the cycle (BOEC). Due to the steeper reactivity gradient, the plutonium burner core has, therefore, a shorter cycle length than the other critical cores. Assuming the plant availability not to be much influenced by the somewhat different cycle lengths, a constant load factor of 85% was used in the analyses of all critical cores.

It is interesting to compare the different neutronic behaviour of the two ADS cores. Whereas the conversion of fertile into fissile actinide species stabilises the k_{eff} of the minor actinide burner core to the extent that it can operate easily with a single batch core, the fertile-free, sub-critical TRU burner core exhibits the steepest reactivity gradient and hence the shortest cycle length of all cores. In the

analyses, the unusually short cycle length of the sub-critical TRU burner was accounted for by a 5% reduction in the load factor; the limited availability of the accelerator, however, suggested not to credit the load factor of the minor actinide burner for the long cycle length of the single batch core.

Figure 3.7. **Evolution of effective multiplication factor during equilibrium cycle**
(time unit: 3 days for MA burner, 1 day for other systems)



The external neutron source strength at EOEC is important because it determines the accelerator design power. The energy which is recycled to the accelerator increases during the burn-up; its average value amounts to 11.6% for the TRU and 12.6% for the minor actinide burner. It is interesting to note that, due to the different burn-up reactivity behaviour of the two sub-critical cores, the minor actinide burner features a higher recycled energy fraction, but a lower accelerator design power (-8% for the same net electrical output, evaluated from the external sources in Table 3.2).

A comparison of the median energies does not confirm the relevance of the often-cited spectrum hardening effect due to the external spallation neutrons. For example, among the metal-fuelled systems, the ADS has the softest neutron spectrum. This, at first, unexpected result is mainly a consequence of the requirement to reduce the fuel density in transmuters with a diluent such as zirconium (see fuel compositions in Table 3.1). It is clear that, although a very hard neutron spectrum cannot be considered a salient feature of a transmuter, the overall neutron balance condition discussed in Chapter 2, Section 2.4.1, which favours the use of fast neutrons especially for the transmutation of minor actinides, must nevertheless be respected.

As to the safety parameters of the cores, the analyses confirm the well-known fact that they deteriorate with increasing minor actinide contents of the fuel. Consequently, the minor actinide burner core features the least favourable coolant void and fuel Doppler reactivity effects, and the effective fraction of delayed neutrons, β_{eff} , for this core is about halved compared with that of a normal fast reactor. The low β_{eff} value would make the control of a critical minor actinide burner core very delicate and suggests the operation of such a core at substantial sub-criticality (the k_{eff} was adjusted to achieve at any time a sub-criticality level of about 5%). In the case of the accelerator-driven TRU burner, which also features a lead-bismuth cooled core, the safety parameters are much more benign, meaning that the incentive to operate the core in a sub-critical state is reduced.

3.2.3 Actinide waste production

A detailed balance of the actinide waste production, including a breakdown by reactor components, is given in Table 3.3. Important features of this balance are illustrated in Figures 3.8 and 3.9.

Since the actinide waste production depends on the fuel burn-up (see Chapter 2, Section 2.3.2) and the burn-up capability of different types of MA- and TRU-dominated fuels has not yet been verified experimentally and is therefore uncertain, the actinide waste production of the fast-spectrum systems using metal and nitride fuels was scaled so that it corresponds to a fixed reference burn-up of 140 GWd/tHM (using the notation of Section 2.3.2, the scaling factor is $\delta(B_{\text{ref}})/\delta(B_{\text{nom}})$, where B_{ref} and B_{nom} are the reference burn-up and the nominal burn-up in Table 3.1, respectively). This means that the observed trends are characteristic for the scheme and not for the burn-up of the metal and nitride fuels. It is clear that, for any fuel type, an increase in the burn-up results in a reduction of the fuel losses. For each scheme, the actinide waste production is normalised such that it corresponds to 1 TWhe of energy produced by the reactor park.

It can be seen that all recycling strategies reduce the plutonium waste mass at least by a factor of 150 compared with the once-through case. The plutonium-burning scheme is more effective than any of the transmutation schemes in eliminating the plutonium, but has the disadvantage of producing 3 to 4 times more americium and curium than the once-through scheme (about half of the americium and curium is generated by the fast plutonium burners). Its tendency to convert plutonium into minor actinides limits the TRU waste mass reduction potential to the modest factor of 4.4.

The importance of a fully closed fuel cycle is highlighted by the fact that the transmutation schemes and the fast reactor scheme achieve TRU waste mass reduction factors of at least 175 relative to the once-through case. Among the innovative transmutation schemes, scheme 3a and scheme 3b, the former appears to have a small advantage due to the higher uranium and hence lower TRU fraction in the fuel (the compensation of the difference in the TRU waste production between the two schemes would require an increase in the average burn-up of the ADS fuel from 140 to 270 GWd/tHM). The double strata scheme performs nearly as well as scheme 3a.

The fast reactor scheme is a special case because it represents a breeding strategy and the generation of plutonium is part of this strategy. It is interesting to note that, nevertheless, it achieves similar TRU and heavy metal waste mass reduction factors as scheme 3b; for the elimination of the minor actinides, it is more effective than any other scheme. The unique features of the fast reactor scheme appear, again, in the isotopic composition presented in Figure 3.9. Due to the breeding of new plutonium in the blankets, the plutonium vector is strongly dominated by ^{239}Pu . The absence of thermal-spectrum systems in the reactor park and the small abundance of the higher plutonium isotopes in the fuel explain the low minor actinide content of the waste.

It can be noted that all recycling strategies reduce the heavy metal waste mass by a factor of 1 100 or more compared with the once-through reference case. The variation in this factor of only 15% is mainly due to the different fractions of fast-spectrum systems in the reactor park: since the fuel in the fast-spectrum systems reaches about three times the burn-up of that in the thermal-spectrum systems, a high fraction of fast-spectrum systems is associated with a lower actinide waste production.

Depleted and reprocessed uranium, which is produced by all LWR-based schemes, does not appear in Table 3.3 because it is considered as a resource. The non-negligible long-term radiological impact of uranium is discussed in Section 3.4.4.

Table 3.3. Actinide waste production for principal fuel cycle schemes (g/TWhe)

O-T	Pu burning			TRU burning in FR			TRU burning in ADS			Double strata			FR strategy			
	LWR	FR	Total	LWR	FR	Total	LWR	ADS	Total	LWR	FR	ADS	Total	Fuel	Blanket	Total
²³⁴ U	11.19	0.06	0.24	0.01	0.62	0.63	0.01	1.65	1.66	0.06	0.22	1.57	1.85	0.23	0.46	0.70
²³⁵ U	18356	13.07	0.07	11.63	0.18	11.81	14.63	0.39	15.03	12.39	0.07	0.37	12.84	0.48	0.68	1.16
²³⁶ U	13207	9.28	0.14	8.37	0.24	8.61	10.53	0.51	11.04	8.80	0.14	0.35	9.28	0.49	1.22	1.71
²³⁸ U	2207E3	1757.9	51.5	1398.7	171.5	1570.2	1759.5	0.0	1759.5	1666.5	48.8	0.0	1715.3	493.6	1264.2	1757.9
²³⁸ Pu	1006	1.39	0.88	0.64	3.55	4.19	0.80	10.66	11.46	1.32	0.83	6.84	8.99	2.08	0.02	2.10
²³⁹ Pu	14915	15.57	10.03	9.45	25.49	34.94	11.89	22.95	34.84	14.76	9.51	1.56	25.83	77.88	34.20	112.09
²⁴⁰ Pu	6847	8.91	15.75	4.34	24.86	29.20	5.46	57.25	62.71	8.44	14.94	7.83	31.21	42.49	1.13	43.62
²⁴¹ Pu	3711	4.39	2.22	2.35	3.31	5.66	2.96	9.98	12.94	4.16	2.11	0.89	7.15	4.25	0.02	4.27
²⁴² Pu	2274	3.43	7.06	1.44	8.56	10.00	1.81	26.27	28.09	3.25	6.70	2.95	12.90	3.52	0.00	3.52
²³⁷ Np	1724	1257.2	65.6	1.09	1.61	2.70	1.37	3.64	5.01	1.19	0.06	2.57	3.83	1.02	0.19	1.21
²⁴¹ Am	909.8	1626.5	1394.6	0.58	2.55	3.13	0.73	6.59	7.32	1.54	1.32	4.84	7.71	2.29	0.00	2.29
^{242m} Am	0.0	6.7	32.4	0.00	0.18	0.18	0.00	0.49	0.49	0.01	0.03	0.45	0.49	0.14	0.00	0.14
²⁴³ Am	670.3	964.7	1112.1	0.42	2.22	2.65	0.53	7.51	8.04	0.91	1.05	4.47	6.44	0.70	0.00	0.70
²⁴² Cm	0.0	0.02	0.09	0.00	0.01	0.01	0.00	0.03	0.03	0.00	0.00	0.01	0.01	0.01	0.00	0.01
²⁴³ Cm	0.0	2.60	6.01	0.00	0.02	0.02	0.00	0.08	0.08	0.00	0.01	0.05	0.06	0.01	0.00	0.01
²⁴⁴ Cm	239.4	396.54	373.95	0.15	1.86	2.01	0.19	7.93	8.12	0.38	0.35	5.39	6.12	0.51	0.00	0.51
²⁴⁵ Cm	23.9	56.77	45.67	0.02	0.35	0.36	0.02	1.54	1.56	0.05	0.04	1.12	1.22	0.09	0.00	0.09
U	2238E3	1780.3	52.0	1418.7	172.5	1591.2	1784.7	2.6	1787.3	1687.7	49.3	2.3	1739.3	494.8	1266.6	1761.4
Pu	28753	33.68	35.95	18.22	65.78	84.00	22.92	127.12	150.04	31.93	34.08	20.08	86.08	130.23	35.37	165.60
Np	1723.8	1257.2	65.6	1.09	1.61	2.70	1.37	3.64	5.01	1.19	0.06	2.57	3.83	1.02	0.19	1.21
Am	1580.1	2597.9	2539.1	1.00	4.95	5.95	1.26	14.59	15.85	2.46	2.41	9.77	14.64	3.13	0.00	3.14
Cm	263.4	455.93	425.72	0.17	2.24	2.41	0.21	9.57	9.78	0.43	0.40	6.57	7.41	0.62	0.00	0.62
TRU	32320	4344.7	3066.4	20.48	74.57	95.06	25.77	154.92	180.69	36.02	36.95	38.99	111.96	135.00	35.57	170.57
HM	2271E3	6125.0	3118.4	1439.2	247.1	1686.3	1810.5	157.5	1967.9	1723.7	86.2	41.30	1851.2	629.8	1302.2	1932.0

Figure 3.8. TRU waste production per heavy element

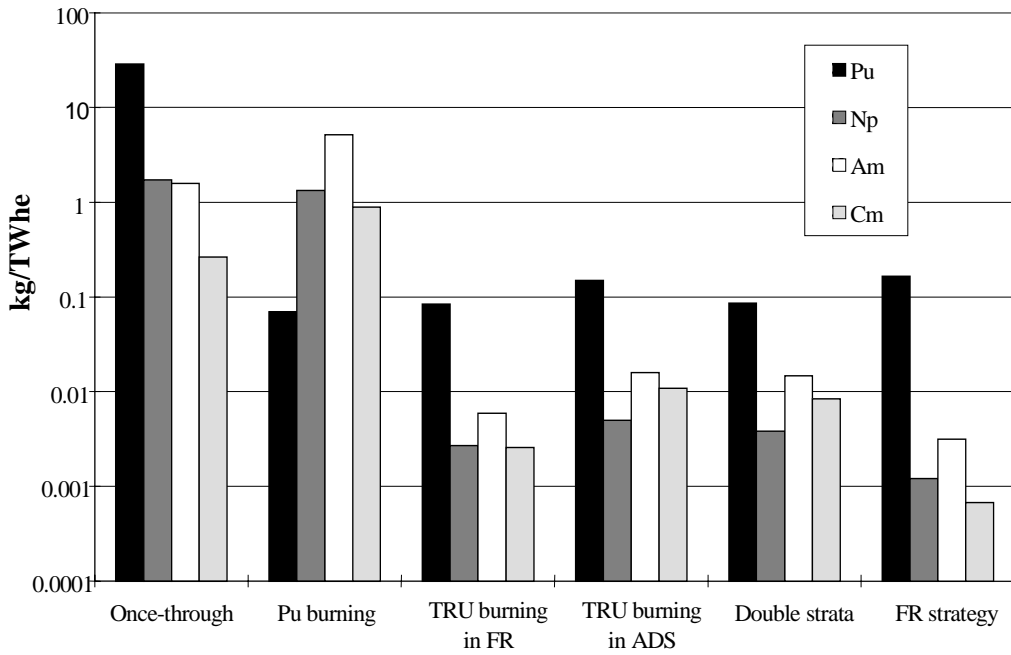
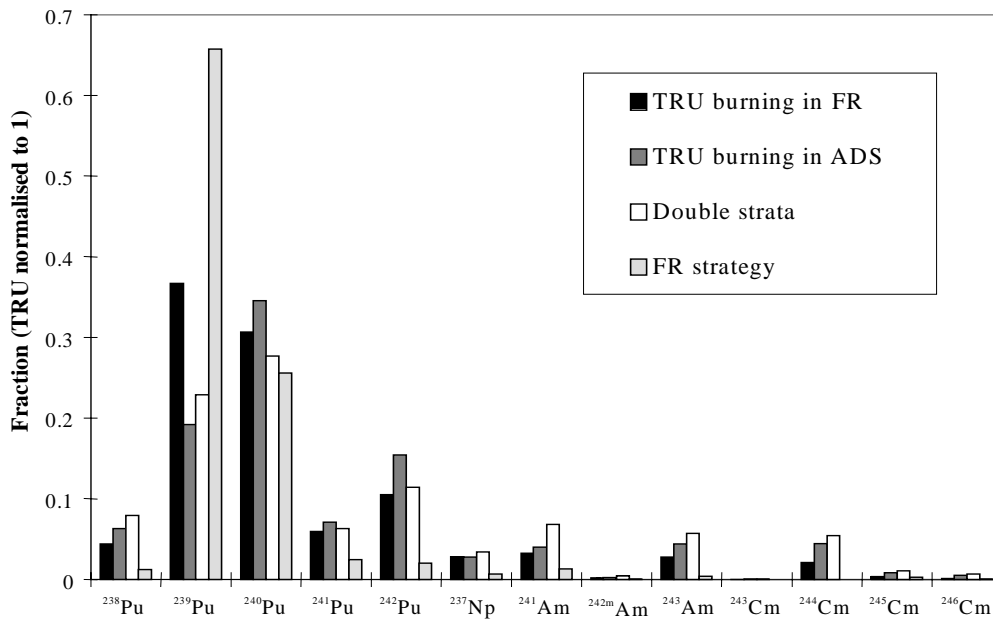


Figure 3.9. Isotopic composition of TRU waste



3.2.4 Radiotoxicity reduction

The actinide waste radiotoxicity is shown in Figure 3.10. It can be seen that, in the important time frame from 10^3 to 10^5 years, all transmutation schemes comfortably meet the goal of a hundred-fold radiotoxicity reduction relative to the once-through fuel cycle. On the other hand, plutonium recycling

alone reduces the radiotoxicity in this time frame only by a factor of about five. This confirms that the plutonium burning strategy cannot qualify as a transmutation strategy.

In the time frame from 10^3 to 10^5 years, schemes 3a and 4 (TRU burning in FR and double strata strategy) achieve the highest radiotoxicity reduction, and beyond 10^5 years the fast reactor strategy achieves the highest radiotoxicity reduction. For all transmutation schemes, however, the differences and fluctuations are relatively small.

To understand the strategy-dependent trends in the time evolution of the radiotoxicity, a decomposition into nuclide contributions is necessary. Figure 3.11 shows that the dominant radiotoxicity contributors are ^{238}Pu up to a few hundred years, ^{240}Pu and ^{239}Pu in the range 10^3 to 10^5 years, and ^{226}Ra (including daughter products) in the range 10^5 to 10^6 years. The latter is predominantly produced by the decay of ^{238}Pu . As this applies to all transmutation schemes, one can expect the trends to be correlated with the ^{238}Pu -to- ^{239}Pu ratio of the fuel. An inspection of the plutonium isotopic composition of the fuels (see Figure 3.9) confirms the existence of such a correlation.

In accordance with the assumptions in Section 3.1.2, the afore-mentioned results apply to fuel losses of 0.1% for all actinides and reprocessing methods. For a single-stratum strategy, the influence of the fuel losses on the transmutation performance can be assessed using the expressions in Chapter 2, Sections 2.3 and 2.5. Figure 3.12 shows parametric results for the radiotoxicity reduction in the case of the double strata strategy. It can be seen that the goal of a hundred-fold radiotoxicity reduction allows the minor actinide losses in the plutonium-burning stratum to be increased by a factor of ten, but that fuel losses of only 0.1% in the minor actinide burning stratum are essential.

Figure 3.10. **Evolution of the actinide waste radiotoxicity**
(Average burn-up of metal and nitride fuel: 140 GWd/tHM)

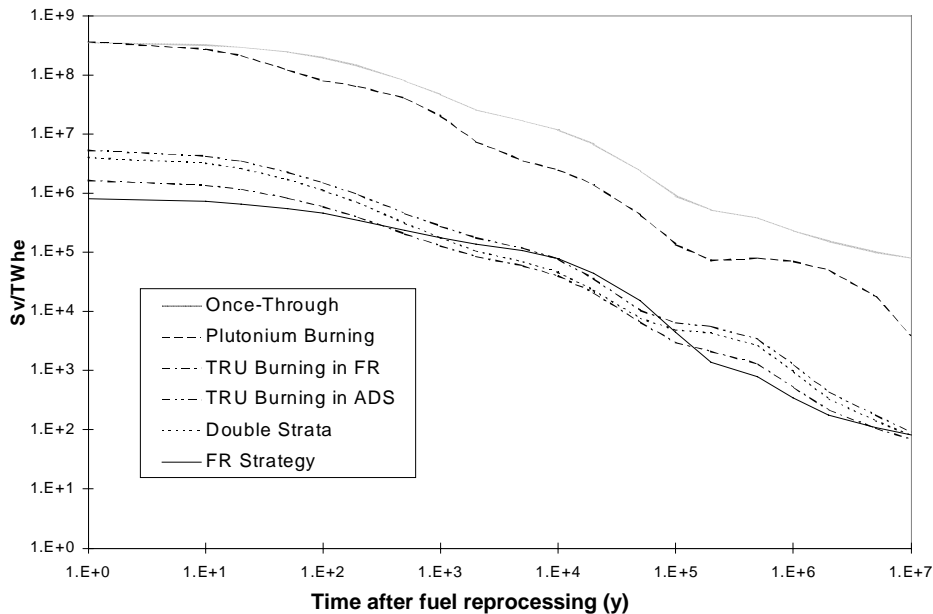


Figure 3.11. Nuclide contributions to the actinide waste radiotoxicity for scheme 3a

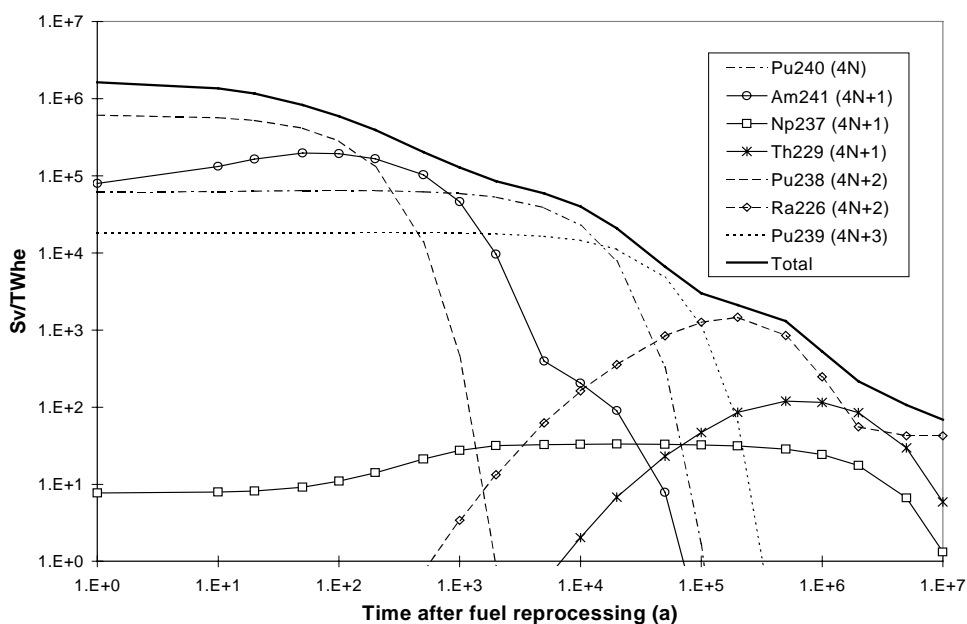
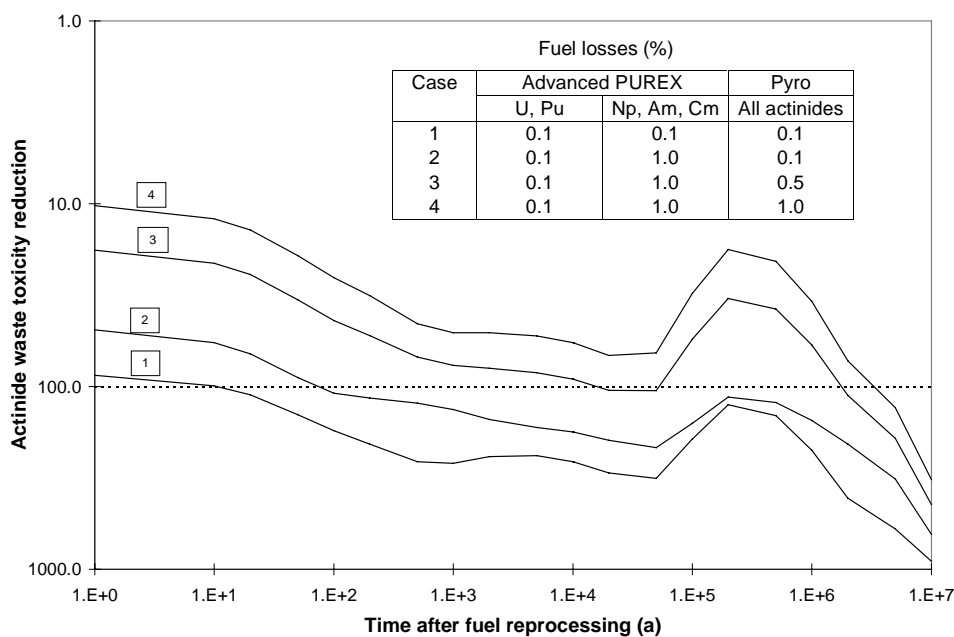


Figure 3.12. Influence of fuel losses on the actinide waste radiotoxicity for scheme 4



3.2.5 Long-term risk

Since the principal fuel cycle schemes involve different waste forms and repository concepts, a comparison of the associated long-term risks is not an easy task.

In principle, three cases can be distinguished:

- For the once-through fuel cycle, the direct storage of the spent fuel elements in geologic repositories is the appropriate disposal concept. Risk analyses for this concept show that the long-lived fission product ^{129}I usually dominates the annual individual dose for the population and that the risk from the actinides is generally smaller than that from the fission products. (In the US study for a repository in tuff, the dominating nuclides up to about 65 000 years are ^{99}Tc and ^{129}I , with ^{237}Np becoming predominant thereafter).
- In connection with wet reprocessing, the vitrification, i.e. the immobilisation, of the fission products and unrecovered actinides in a glass matrix, is the favoured concept. The glass is enclosed in steel canisters and the space between the canisters and the near-field/host rock interface is filled with bentonite. Whereas the nuclide transport properties of the near-field are well-defined, those of the host rock can vary considerably depending on the material (salt, clay or granite) and structure of the host rock. Different studies have identified ^{135}Cs , ^{79}Se , ^{99}Tc and ^{126}Sn as dominant dose contributors. ^{129}I is not contained in vitrified waste because it escapes during the reprocessing. However, the current sea disposal of iodine may no longer be practicable in advanced nuclear fuel cycles, and a special treatment of this nuclide will therefore also be an element of future waste management schemes.
- In the case of dry reprocessing, the unrecovered materials are processed into different waste forms which depend on the particular flow sheet. For the principal fuel cycle schemes with dry reprocessing, respective information will be given in Section 3.5. On the whole, these wastes are very stable; the associated long-term risk, however, is difficult to assess because detailed concepts for the ultimate storage of the wastes have not yet been developed.

Compared with the direct storage of spent fuel elements, the reprocessing of spent fuel has the advantages of reducing the actinide mass and the plutonium content of the HLW. In combination with vitrification, it minimises the risk of a clandestine recovery of fissile material; due to the low mobility of plutonium, it does, however, not significantly reduce the actinide part of the long-term risk of a repository. Drawbacks of the reprocessing are the extra investment in the reprocessing plant and the potential proliferation risk associated with the handling of the separated pure plutonium.

Judging the advantages of the reprocessing to be important and the recovered plutonium to be an asset rather than a risk, several countries have already embarked on a fuel cycle which involves the wet reprocessing of the spent fuel from LWR-UOX reactors, followed by the vitrification and final geologic disposal of the remaining fission products and minor actinides. In this conventional fuel cycle with vitrification (CFC-vitrification), the fate of the recovered plutonium is open; the plutonium will probably be recycled once and the spent MOX will be treated as HLW.

According to [22], a respective canister with vitrified waste contains 320 kg of glass, 48 kg of fission products, 3.5 kg of actinides and 4.5 kg of activation products. This means that the CFC-vitrification strategy reduces the actinide content of the HLW already to a level where the fission products are dominating the waste mass. Since the fission product inventories depend primarily on the number of fissions, i.e. the energy, released in the fuel, it is obvious that the HLW mass cannot be further reduced by moving from a CFC-vitrification to a transmutation strategy. Such a move, however, affects the actinide releases from the waste repository.

Since the repository behaviour for the CFC-vitrification strategy has been assessed in the framework of different national waste management projects, it is interesting to make a comparison with the plutonium burning and the double strata strategies which also involve vitrification. In the latter case, a direct comparison is possible, if the HLW from the dry reprocessing, which contributes

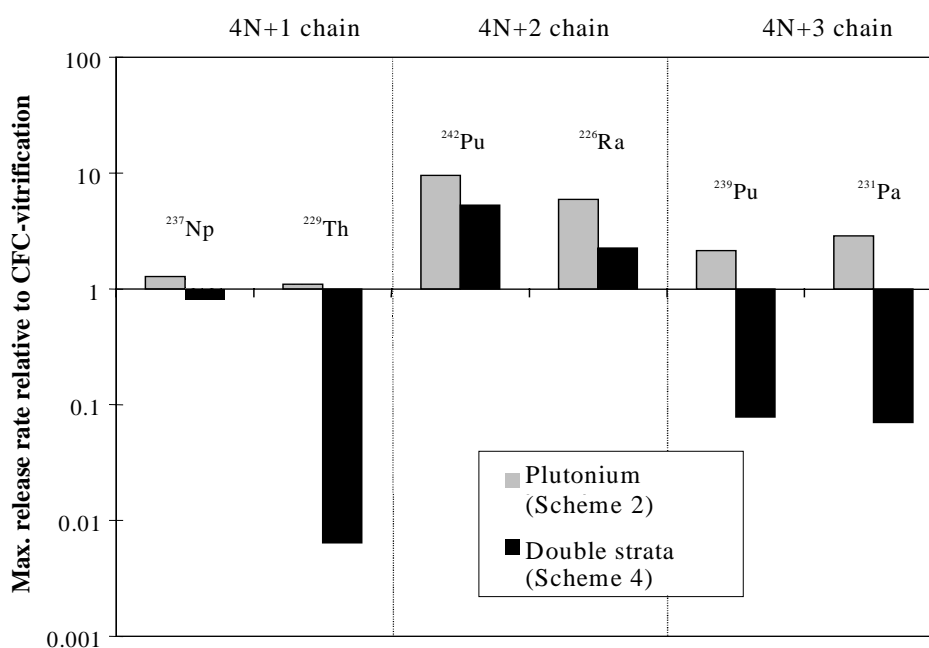
35% to the TRU going to waste (see Table 3.3), can be neglected. This is a reasonable approximation because the waste form bearing actinides from dry reprocessing is at least as stable as vitrified waste.

Taking into consideration that the geosphere and biosphere responses are site-specific and vary considerably between projects, it is advantageous to perform the comparison on the basis of the maximum release rates of potentially troublesome actinides from the repository near-field. Potentially troublesome actinides which can contribute to the annual individual dose beyond about one million years are ^{231}Pa , ^{237}Np and their respective daughter products ^{227}Ac and ^{229}Th , ^{226}Ra , a decay product of ^{238}Pu and ^{234}U , and the long-lived plutonium isotopes 239 and 242. Respective release rates were calculated for the plutonium burning, the double strata and a consistent CFC-vitrification strategy using the same near-field characteristics and nuclide properties as in the Kristallin-I safety assessment study [12].

The relative maximum release rates in Figure 3.13 confirm the expected strongly non-linear relationship between release rates and actinide concentrations in the glass. In particular, it can be seen that:

- Compared with the CFC-vitrification strategy, the plutonium burning strategy generally increases the maximum release rates (this is not surprising, since, in the reference case, most of the plutonium is recovered before vitrification).
- The addition of the P&T cycle results in a reduction of the maximum release rates for the more important, but not for all potentially troublesome actinides.
- Nuclides from the same decay chain can behave very differently (the maximum release rate for ^{237}Np , which has a very low solubility in the glass, is practically unchanged, whereas there is a large benefit for its radiologically more hazardous daughter product ^{229}Th).

Figure 3.13. **Maximum near-field release rates for fuel cycles with HLW vitrification**
(Near-field assumptions as in the Kristallin-I safety assessment study [12])



With regard to the long-term risk arising from the fission products, it is important to note that the fission product inventory depends primarily on the number of fissions, i.e. the energy, produced in the fuel, and that the fission product risk can, therefore, not be much influenced by the actinide transmutation strategy.

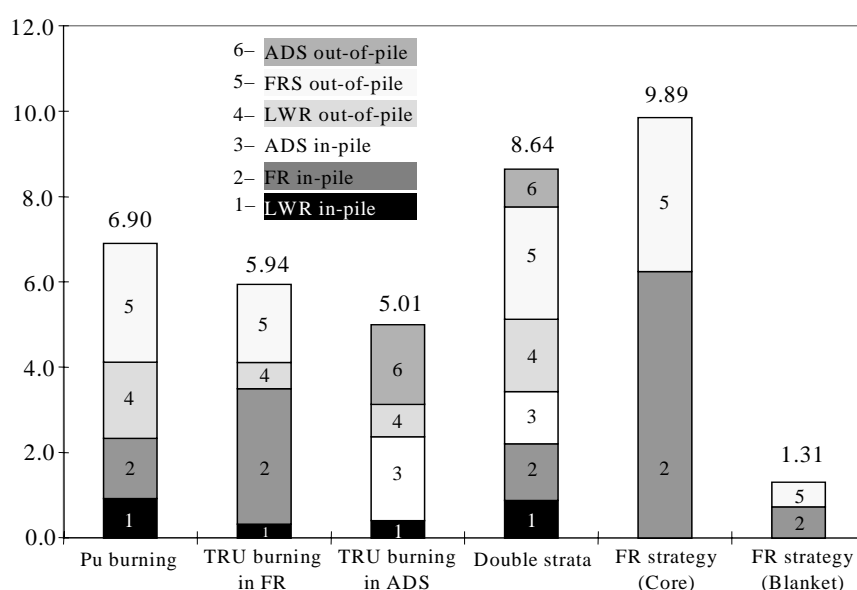
As already noted, the energy released in the fuel determines the fission product inventory and, in a reprocessing strategy, the mass of the high-level waste. Since the dependence of the cumulative fission product yields on the reactor- and fuel-type is small, the fission product release rates of a vitrified waste repository are practically proportional to the released fission energy. Neutron-spectrum dependent variations in the fission product composition and hence release rates can, however, arise from the in-situ transmutation of fission products. For example, capture of thermal neutrons in the precursor ^{135}Xe reduces the ^{135}Cs production in an LWR by as much as 70% [34].

3.2.6 Consequences for the fuel cycle

Whereas the principal transmutation schemes perform similarly with respect to the important goal of the TRU waste mass and radiotoxicity reduction, different requirements and consequences arise for the establishment of the fuel cycles. In this context, important parameters are the in-pile and out-of-pile TRU inventories, the throughput requirements for the fuel cycle facilities, and the decay heat and neutron source strength of the fuels. The TRU inventory has safety implications and plays a role in the shut-down phase of a nuclear energy strategy (see Chapter 2, Section 2.8), the fuel throughput determines the capacity of the fuel cycle facilities, the decay heat affects and limits the applicability of different reprocessing methods, and the neutron source strength has consequences for the shielding and the remote handling of materials.

Figure 3.14 shows that, among the transmutation schemes, the TRU burning in ADS scheme and the double strata scheme feature the lowest and highest total TRU inventories, respectively. This implies that the TRU burning in ADS strategy can respond more flexibly to unexpected changes in nuclear energy scenarios than other transmutation strategies.

Figure 3.14. In-pile and out-of-pile TRU inventories



The reprocessing and fuel fabrication requirements in terms of heavy metal throughput are compiled in Table 3.4. Regarding the reprocessing, the ADS-based transmutation schemes (TRU burning in ADS and double strata strategy) have the advantage of a modest demand for innovative (pyro-) reprocessing. Except for the FR strategy which is fully pyro-based, the schemes require a comparable wet reprocessing capacity, either PUREX or UREX. A similar situation exists on the side of the fuel fabrication, where the ADS-based transmutation schemes have the lowest demand for advanced fuel fabrication (metal and nitride fuel). This applies particularly to the double strata strategy which is, however, penalised by an increased MOX fuel demand for the plutonium burner.

Table 3.4. **Reprocessing and fuel fabrication requirements**

	Pu burning	TRU burning in FR	TRU burning in ADS	Double strata strategy	FR strategy
Reprocessing requirements (kgHM/TWhe)					
PUREX for LWR-UOX	1 583	–	–	1 501	–
PUREX for LWR-MOX	234.7	–	–	222.9	–
Adv. PUREX for FR-MOX	90.9	–	–	86.4	–
UREX	–	1 439	1 810	–	–
Pyro	–	247.3	77.5	39.3	2 122
Fuel fabrication requirements (kgHM/TWhe)					
LWR-UOX	1 669	1 517	1 909	1 583	–
LWR-MOX	247.4	–	–	2 34.5	–
FR-MOX	111.5	–	–	105.7	–
Ac-Zr	–	288.0	103.2	–	2 233 ¹
AcN-ZrN	–	–	–	46.2	–

1. Including 1 438 kg/TWhe of uranium for the blankets.

Tables 3.5 and 3.6 provide information on the activity, decay heat and neutron source strength of the fuels after cooling (cooling times as indicated in Figures 3.1 to 3.6) and after fuel fabrication, which is assumed to take place immediately after the reprocessing. In general, the decay heat is dominated by the actinides and lies beyond the operating limits of existing fuel cycle facilities.

Experience with pilot plants in the UK and France shows that the PUREX-type aqueous reprocessing can be considered as valid for the FR-MOX fuel of schemes 2 and 4. Reprocessing of this fuel within short cooling times and with the required high recovery yield of 99.9%, however, will require measures to improve the plutonium dissolution yield and modifications of the PUREX flowsheet. An interim solution for schemes 2 and 4 could be the blending of the irradiated LWR-MOX and FR-MOX fuels before reprocessing. Such blending would reduce the decay heat of the FR-MOX fuel by a factor of about two.

The decay heat of the ADS fuels arising in schemes 3b and 4 lies well beyond the limit for which the radiation stability of the organic extractant in the aqueous process can be guaranteed. For these and all other systems with fully closed fuel cycles, the pyrochemical reprocessing is the appropriate reprocessing method because it circumvents unnecessary separation processes (only fission products are extracted) and can handle highly active product streams without major radiation degradation. Figure 3.15 shows that the decay heat decreases only slowly with increasing cooling time and that very long cooling times – resulting in very large out-of-pile fuel inventories – would be required to mitigate the problem and facilitate the use of aqueous reprocessing methods.

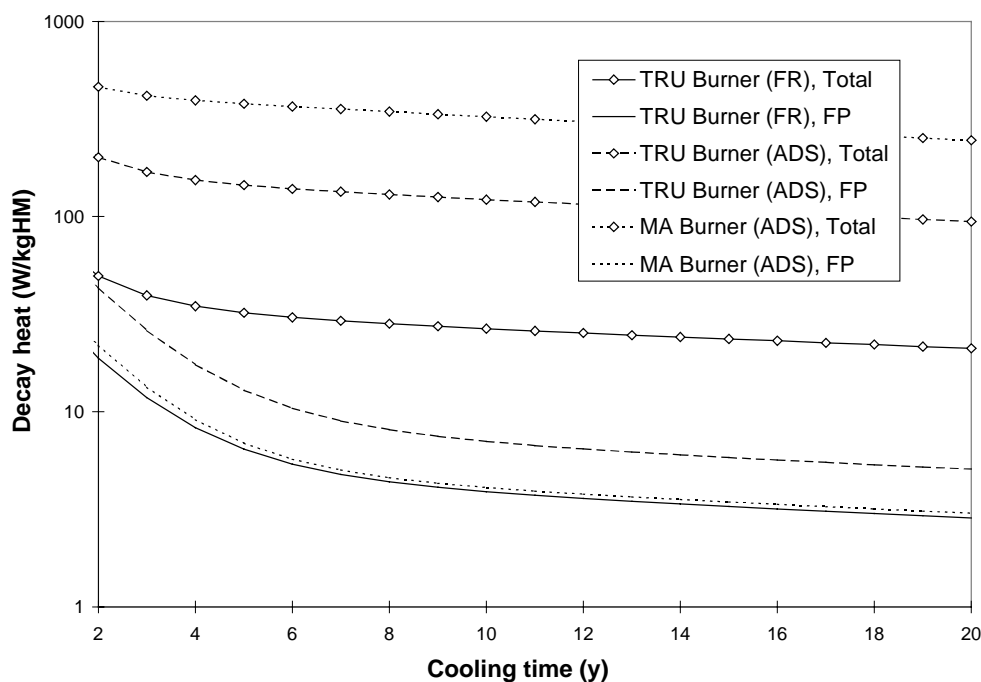
Table 3.5. Activity, decay heat and neutron source strength of fuel after cooling

	LWR-UOX	LWR-MOX	Pu burner (FR)	TRU burner (FR)	TRU burner (ADS)	MA burner (ADS)	Fast reactor
Fuel cooling time (a)	4	7	7	2	2	2	2
Activity (10^{12} Bq/kgHM)							
Actinides and FPs	36.24	50.30	157.0	232.4	691.7	725.4	160.4
FPs	30.15	17.26	62.38	155.3	342.0	183.7	131.7
Decay heat (W/kgHM)							
Actinides and FPs	3.48	6.31	21.77	46.00	192.6	455.1	18.56
α	0.52	4.86	16.76	30.51	156.4	435.4	5.63
β	1.63	0.66	2.32	11.38	27.12	14.83	9.34
γ	1.34	0.79	2.67	4.09	8.96	4.42	3.58
FPs	2.96	1.41	4.86	15.34	35.50	18.02	12.88
β	1.62	0.63	2.21	11.28	26.64	13.83	9.31
γ	1.34	0.79	2.65	4.07	8.88	4.19	3.58
Neutron source strength (10^6 n/s kgHM)							
Total	0.97	10.93	39.28	86.08	649.1	1 812	9.76
Spontaneous fission (α,n)	0.95	10.77	38.72	85.02	643.6	1 797	9.57
	0.02	0.16	0.56	1.06	5.46	15.22	0.19

Table 3.6. Activity, decay heat and neutron source strength of fuel at fabrication

	LWR-UOX	LWR-MOX	Pu burner (FR)	TRU burner (FR)	TRU burner (ADS)	MA burner (ADS)	Fast reactor
Activity (10^{12} Bq/kgHM)							
Actinides	$1.53 \cdot 10^{-5}$	38.28	148.1	111.5	470.6	598.2	28.89
Decay heat (W/kgHM)							
Actinides	$1.1 \cdot 10^{-5}$	1.94	9.64	33.79	168.1	489.3	5.79
α	$1.1 \cdot 10^{-5}$	1.91	9.49	33.60	167.2	487.4	5.74
β	$4.4 \cdot 10^{-8}$	0.03	0.13	0.14	0.59	1.14	0.03
γ	$9.0 \cdot 10^{-8}$	$1.0 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	0.02	0.09	0.30	$4.3 \cdot 10^{-3}$
Neutron source strength (10^6 n/s kgHM)							
Total	$2.07 \cdot 10^{-5}$	0.10	0.66	92.05	669.9	1992	9.76
Spontaneous fission (α,n)	$2.06 \cdot 10^{-5}$	0.04	0.37	90.89	664.0	1975	9.57
	$1.32 \cdot 10^{-7}$	0.06	0.29	1.16	5.82	17.04	0.19

Figure 3.15. Evolution of the decay heat of the fuel



Due to the strong source of spontaneous neutrons, the fuel fabrication will have to adapt its handling technology to reduce the radiation doses to the workers in the plant and during the transport of the fuel assemblies. The increased requirements for shielding during transport also speak for the pyrochemical reprocessing method which is applicable in small facilities in the immediate vicinity of the reactors, whereas the aqueous process favours large centralised facilities which imply shipment of fuel over long distances.

In summary, it appears that all transmutation strategies with fully closed fuel cycles will have to rely on pyrochemical reprocessing. The ADS-based schemes have the advantage of modest throughput requirements, but rely on the development of the technology for fuels with very high decay heats.

3.3 Other fuel cycle schemes

3.3.1 TRU burning with preceding MOX recycling

A country which has already committed itself to the conventional reprocessing of LWR spent fuel with recovery of the plutonium and vitrification of the HLW, or plans to introduce plutonium recycling as an intermediate step before actinide burners become commercially available, could be interested in a TRU burning strategy with an LWR-MOX stage between the normal LWR and the TRU burner. Figure 3.16 shows the ADS variant of this strategy which, in the following, will be referred to as scheme 3c. The strategy represents a mix between the evolutionary and the innovative approach to transmutation and has the advantage that it does not depend on the installation of MOX-fuelled fast plutonium burners and requires a smaller number of fast-spectrum systems than any of the afore-mentioned transmutation schemes. However, due to the presence of a plutonium separation stage, the strategy is not a pure co-processing strategy as in the other TRU burning cases.

Table 3.7. Actinide waste production for scheme 3c (g/TWhe)

	LWR-UOX	LWR-MOX	ADS	Total
²³⁸ Pu	0.75	0.70	9.33	10.78
²³⁹ Pu	12.71	4.28	8.81	25.79
²⁴⁰ Pu	5.97	5.15	35.53	46.65
²⁴¹ Pu	2.42	1.95	6.70	11.06
²⁴² Pu	1.32	1.66	17.03	20.01
²³⁷ Np	1.73	0.03	2.98	4.74
²⁴¹ Am	0.61	1.09	5.99	7.70
^{242m} Am	0.00	0.01	0.48	0.49
²⁴³ Am	0.38	0.49	6.58	7.46
²⁴² Cm	0.00	0.00	0.04	0.04
²⁴³ Cm	0.00	0.00	0.08	0.08
²⁴⁴ Cm	0.16	0.14	6.12	6.42
²⁴⁵ Cm	0.01	0.01	2.05	2.08
<hr style="border-top: 1px dashed black;"/>				
Pu	23.16	13.74	77.40	114.29
Np	1.73	0.03	2.98	4.74
Am	1.00	1.59	13.05	15.65
Cm	0.18	0.16	9.98	10.31
<hr style="border-top: 1px dashed black;"/>				
TRU	26.06	15.52	103.41	144.99

3.3.2 Heterogeneous recycling of americium and curium

As discussed in Section 3.2.5, the homogeneous recycling of minor actinides in the fuel implies very hot fuels which are also strong neutron emitters and consequently necessitates considerable investments in improved and new reprocessing technologies as well as remote handling and shielding of materials. To avoid the contamination of the fuel cycle with minor actinides, it has been proposed to separate americium and curium from the spent fuel, fabricate them into separate targets with a neutron-inert support material like MgAl₂O₄ (spinel), “incinerate” the targets, and dispose of the spent targets without further reprocessing. The targets could be placed in special fast reactor subassemblies containing a neutron moderator such as ¹¹B₄C, ZrH₂ or CaH₂ which enhances fission [36].

For neptunium, the homogeneous recycling is the generally preferred method, although a large fraction of the neptunium in the fuel is converted to ²³⁸Pu, an alpha emitter with a half-life of only 88 years. The resulting heat load and neutron emission from (α,n) reactions could still have economic consequences for the fabrication, transportation and storage of the fuel.

The heterogeneous recycling concept for americium and curium could be implemented either in a pure fast reactor scheme (scheme H1), or a two-component scheme which consists of a mix of UOX-fuelled LWRs and fast reactors (scheme H2). Actinide mass balances for both schemes have been calculated by CEA under the following assumptions [37]:

- The fast reactor is the 1 450 MWe European Fast Reactor (EFR) with a MOX core which is optimised for an average fuel burn-up of 140 MWd/tHM [38]. In scheme H1, the reactor is self-sustaining in plutonium thanks to thin uranium blankets; in scheme H2 the reactor operates as a plutonium burner without blankets. The average plutonium content of the fuel is

about 20% in the former and about 23% in the latter case, meaning that it is close to that of a normal MOX-fuelled fast reactor.

- The LWR in scheme H2 is the 1 450 MWe European Pressurised Reactor (EPR) with an average burn-up of 60 GWd/tHM [39]. The plutonium and minor actinide mass balance for an optimised EFR core with target subassemblies restricts the fraction of LWRs in the two-component scheme to about 44%, meaning that this scheme features the least favourable support ratio of all investigated schemes.

In the case of scheme H1, it was found that an EFR core which consists of 42 target and 346 fissile sub-assemblies allows to incinerate 90% of the minor actinides in the targets. The necessary residence time of the targets is about 10 years to be compared with a 6-year residence time for the fissile subassemblies. In the case of scheme H2, it was found necessary to complement the 42 target subassemblies in the core with a complete ring of 78 target subassemblies at the core periphery, i.e. in the place of the radial blanket region of the self-sustaining core configuration.

It is worth noticing that the moderator in the target subassemblies has a beneficial effect on the fuel Doppler and the coolant void reactivity effect (the former increases and the latter is reduced). Moreover, it has been ascertained that, in spite of the long residence time of the targets, the limit of 200 dpa for the radiation damage to the structural material is not exceeded.

The two-component scheme is illustrated in Figure 3.17. It can be seen that the neptunium from the spent fuels is fabricated into new (U,Pu,Np)O₂ fuel for the EFR, and the americium and curium from the spent fuels is separated and fabricated into targets which are disposed of after irradiation. The assumptions for the recovery yield (99.9% for Pu, Np, Am and Cm) and the fuel cooling and storage time before reprocessing and after fabrication are consistent with the respective assumptions for the principal fuel cycle schemes.

Table 3.8 gives the resulting actinide waste production under equilibrium conditions in units which allow a direct comparison with the results in Tables 3.3 and 3.7. In particular, it can be seen that scheme H2 allows to reduce the TRU mass in the waste by a *factor of about 60* compared with the LWR once-through reference case. The analyses performed by CEA show that the TRU mass reduction factor is nearly the same for scheme H1, and drops to about 40, if americium only is separated and incinerated in the targets while curium is directly rejected to waste.

A TRU waste mass reduction factor of 60 may already be attractive, but is modest compared with a factor of at least 175 achieved by the principal fuel cycle schemes (see Section 3.2.3). However, as pointed out in [40], this limitation of the heterogeneous recycling concept should be balanced against the advantages that:

- The fabrication, irradiation and final disposal of the highly active americium and curium targets is disconnected from the uranium-plutonium fuel cycle which is that of a normal fast reactor.
- The advanced PUREX process with americium and curium separation is valid for the reprocessing of the fuel and the development of the pyrochemical reprocessing method and ADS technology is not required.
- By abstaining from the reprocessing of the targets, the minor actinide mass flows can be reduced significantly (40% for Am, factor 3 for Cm) with a corresponding cost benefit compared with the homogeneous recycling concepts based on fully closed fuel cycles.
- At the initial stage of development, americium only could be loaded into the targets.

- The remaining technological uncertainties, which relate mainly to the behaviour of the targets, are small and alternatives are available (for example, the coated particle concept [41] can be considered as an alternative to the inert matrices).

In summary, it appears that heterogeneous transmutation systems as described in this section are less performant than systems with fully closed fuel cycles. On the other hand, the heterogeneous systems have the advantage that they could be deployed earlier than other systems because they are mostly based on existing technology.

Figure 3.17. **Heterogeneous recycling of americium and curium (scheme H2)**

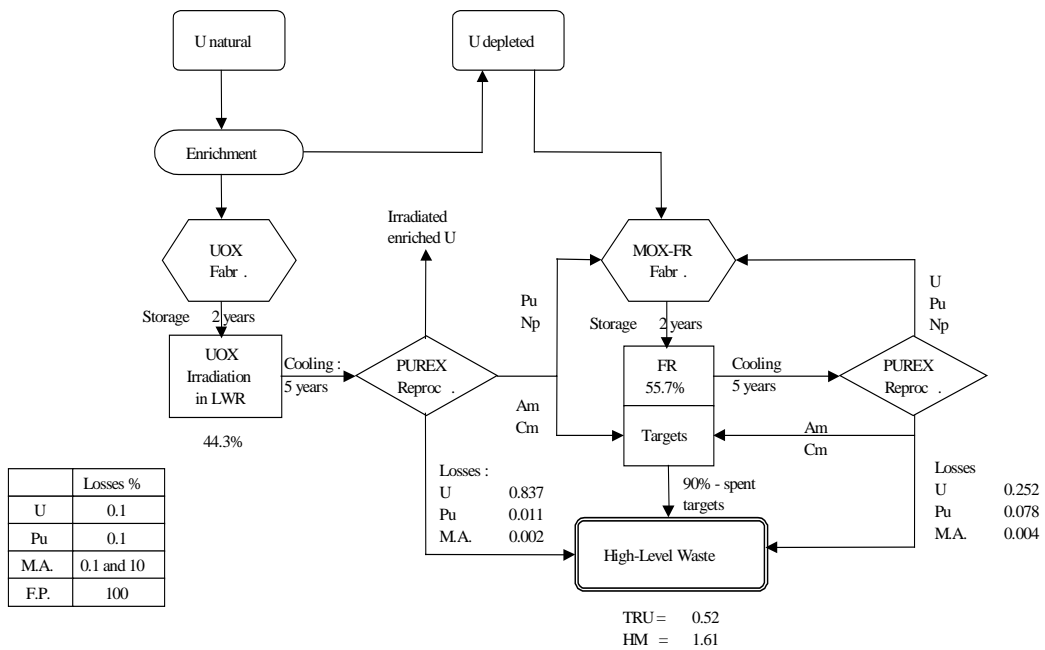


Table 3.8. **Actinide waste production for heterogeneous scheme H2 (g/TWhe)**

	LWR-UOX	FR	Targets	Total
U	837.5	252.5	2.5	1 092.5
Pu	11.4	78.0	150.0	239.4
Np	0.8	1.2	—	2.0
Am	0.7	2.8	37.5	40.0
Cm	0.1	0.3	235.0	235.4
TRU	13.0	82.3	422.5	516.8
HM	850.5	334.8	425.0	1 609.3

3.4 Fuel cycle issues and challenges

The previous Sections 3.2 and 3.3 highlighted the fuel cycle schemes under consideration and indicated in Section 3.2.6 the consequences for the fuel cycle. The following sections will address these consequences in some more detail and will highlight the technological challenges faced by the

fuel cycle operations in order to achieve the performance as supposed in the previous fuel cycle schemes.

Four topics will be highlighted in that respect:

- Fuel and target fabrication.
- Reprocessing.
- Secondary waste arising.
- The management of depleted and reprocessed irradiated uranium.

3.4.1 Fuel and target fabrication and behaviour

Several studies have been undertaken in the recent past addressing the different aspects of fuel and target fabrication and behaviour. The reports by JAERI, the European Commission as well as the Roadmap-reports on ATW and by the European Technical Working Group on ADS include comprehensive reviews of fuel/target technologies for application in transmutation systems, and the interested reader is referred to those documents for details [42,8,9]. In the latter report, the focus is limited to non-fertile (i.e. not uranium-bearing) fuels and to transmutation targets containing ^{99}Tc and ^{129}I . Here, the consideration is somewhat broader, with the various fuel cycle schemes including fertile (schemes 2, 3a, 5) and non-fertile (schemes 3b and 4) fuels, plutonium recycle only (scheme 2), and recycling with co-processing (schemes 3a, 3b, 5) or separation (scheme 4) of plutonium and minor actinides.

3.4.1.1 Oxide fuels and targets.

The schemes under consideration use uranium-bearing oxide fuels and $(\text{Am}+\text{Cm})\text{O}_2$ inert matrix targets. Considerable experience exists with the performance of mixed-oxide (MOX) fuels to high burn-up levels in both thermal and fast reactor applications, with plutonium fractions ranging from 4 to as high as 30 weight percent. The design of MOX fuels for any of the pertinent fuel cycle schemes of this report is therefore a well-founded technology. On the other hand, fabrication of MOX fuels containing recycled plutonium (i.e. with large percentages of ^{240}Pu and higher Pu isotopes) requires a high degree of automation and remote operation of fuel fabrication processes that is not currently in common practice. Innovations in MOX fuel fabrication technology will be necessary to ensure worker protection and the economic viability of the fuel cycle. This may require a departure from the standard powder synthesis, cold pressing and sintering process.

Very little experience exists for fertile oxide fuels containing representative quantities of the minor actinides neptunium, americium and curium. The French SUPERFACT experiment comprised eight fuel pins with $(\text{U},\text{PuO}_2\text{-NpO}_2/\text{AmO}_2$ and $\text{UO}_2\text{-NpO}_2/\text{AmO}_2$ fuel pellets, irradiated to modest burn-up (4.5-6.5 atom percent) in the Phénix reactor. Post-irradiation examination showed nominal performance of the fuel pins, with evidence of the onset of fuel-cladding mechanical interaction due to fuel swelling in those pins containing higher minor actinide fractions. Greater helium production, well in excess of fission gas generation, was observed in the americium-containing fuel and attributed to the high specific alpha activity of the americium daughters ^{242}Cm and ^{238}Pu . At the burn-up levels thought to be needed for efficient performance of a minor actinide transmutation system, it will be necessary to provide accommodation for internal pressurisation and fuel swelling by reducing fuel smear density and increasing plenum volume. A trade-off study between desired core performance and fuel burn-up is clearly needed. Also of concern is the fabrication of minor actinide-bearing oxide fuels.

As curium isotopes build up with repeated recycling, the limitations on fuel handling and facility operation will be challenged. Alpha decay and neutron emission from curium isotopes may impose a need for chemical separation of curium from the other transuranics and storage of the curium until some of its isotopes decay to lower transuranics. This issue requires further study, as the storage of curium poses criticality and heat removal problems.

Non-fertile TRU oxide fuels (targets) use an inert matrix material as a diluent to maintain specific heat generation levels within the proper range. Desired properties of the matrix material are: (1) chemical compatibility with the reactor coolant, (2) chemical and physical compatibility with the fuel, (3) resistance to radiation damage, and (4) a low neutron absorption cross-section. Both metal and ceramic matrix materials have been considered for this application. Ceramic materials include zirconia (ZrO_2 , stabilised in the fluorite cubic structure by additions of CaO , Y_2O_3 or MgO), magnesia, and spinels such as $MgAl_2O_4$. A dispersion of TRU oxides in zirconium or in a refractory metal such as molybdenum offers the advantage of a low fuel operating temperature, but provisions must be made to prevent a chemical interaction between the fuel and matrix (e.g. $PuO_2 + Zr \rightarrow ZrO_2 + Pu$) that could lead to undesirable redistribution of the fissile constituents. The ceramic matrix must be stable under irradiation and capable of accommodating the very large quantities of helium produced in minor actinide-bearing fuels.

Fabrication processes for inert matrix oxide fuels include dry powder operations and wet processes such as co-precipitation or sol-gel reactions. There has been some experience with infiltration of a nitrate solution of transuranics into inert ceramic particles, followed by calcinations/denitration and sintering. In all cases, particular care must be taken to avoid the loss of volatile TRU oxides.

3.4.1.2 *Metal fuels*

Considerable experience with uranium alloy metal fuel has been gained in the course of operations with DFR (U-Mo) and EBR-II (U-Fs³⁴, U-Zr) over a number of years. A limited number of U-Pu-Zr fuel elements were irradiated in EBR-II to reasonable high peak burn-up levels, over 20 atom percent. The 33-cm long EBR-II fuel slugs were fabricated by injection casting the molten fuel alloy into quartz tubes. After solidification, the quartz molds were broken and separated from the fuel. Because the fuel rods were designed for about 75% smear density, with liquid sodium serving as a thermal bond between the fuel and cladding, the fuel slugs could be used in the as-cast condition with little concern for minute dimensional variations. In only one experiment was there made an attempt to incorporate minor actinides in the injection casting process, with the result that most of the americium was lost by vaporisation. It may be possible to suppress such losses by over-pressurisation of the casting system, but this remains a major limitation to the use of minor actinide-bearing metal alloy fuel. Powder metallurgy methods may provide the means for avoiding americium losses. The performance of metallic fuel is well-established; it offers many safety advantages provided that steady-state fuel temperatures are kept below the temperature range for the formation of a low-melting eutectic composition with iron that is present in the cladding alloy.

3.4.1.3 *Nitride fuels*

It is generally accepted that the use of nitride fuels in accordance with contemporary environmental standards would require the use of nitrogen highly enriched in the isotope ^{15}N , to avoid the production of ^{14}C from (n,p) reactions with the more common ^{14}N isotope. Nitride fuels offer a number of advantages: (1) high thermal conductivity, (2) extensive mutual solubilities of the actinide

34. Fs: "fissium", the designation given to a collection of transition metal fission products remaining in the uranium recovered in the original EBR-II melt-refining process.

nitrides, (3) a single common valence state of the actinide nitrides, and (4) very low (and sometimes negative) values for void worth. No nitride fuel performance results are available at high burn-up levels, with past experience limited to burn-ups in the range of 6.5-8 atom%. Nitride fuels can be operated at low temperatures, and this gives some reason for optimism in their ability to reach the high burn-ups required for efficient transmutation systems. There is a concern that, under accident conditions in which the nitrogen over-pressure in a fuel pin is lost, the nitride can decompose rapidly, leading to extensive core damage. This concern should be ameliorated in an inert-matrix fuel in which the matrix is ZrN or Zr (this applies, e.g. to the fuel of the minor actinide burner in scheme 4).

Fabrication processes for nitride fuels commonly involve powder pressing and sintering, with the powders produced either by direct nitridation of metals or by carbothermic reduction of oxide powders followed by nitriding. Losses of americium by volatilisation of the nitride are a problem during high-temperature sintering of minor actinide-bearing fuels.

3.4.1.4 Other fuel types

Carbide fuels and coated-particle fuels are also candidates for application in transmutation systems. Carbide fuels may be of less interest because they do not offer substantial advantages over the other fuel types while presenting some specific complications such as the formation of complex phases and the potential for significant chemical and mechanical interactions with the fuel cladding. Coated-particle fuels, on the other hand, may be favoured in a nuclear system in which a key component is a high-temperature gas-cooled converter reactor, by providing a commonality of fuel cycle processes. These fuels are known to be capable of very high burn-ups and, by virtue of high mechanical integrity coatings, are able to retain the large amounts of helium and fission products generated.

3.4.1.5 Long-lived fission product targets

Important studies of the transmutation of ^{99}Tc and ^{129}I have been carried out within the framework of the EFTTRA program [43]. The general consensus arising from this and other studies is that ^{99}Tc is best transmuted to stable ^{100}Ru in the metal form, while the preferred form for ^{129}I is as a metal iodide. Sodium iodide may become the target of choice due to the nature of the process whereby it is recovered from the dissolver solution during aqueous reprocessing. Irradiation experiments have not been carried to high fractional transmutation levels, but results indicated that the metallic technetium targets are well behaved. The technetium experiments also have shown the importance of target geometry, for exploitation of neutron absorption at resonant energy levels. The behaviour of sodium iodide targets (or silver iodide or lead iodide) may not be so benign, because ^{129}I is transmuted to stable ^{130}Xe , with attendant build-up of gas pressure internal to the target capsule. Meanwhile, as ^{129}I is transmuted, the remaining cations form free metal which can interact with the capsule material, potentially leading to capsule failure through corrosion or formation of low-melting compounds. Capsule material composition is a factor that is often overlooked in transmutation studies. Because the objective of transmutation is a substantial reduction in the radiotoxicity of nuclear wastes to be disposed, it is important that the process not generate more radiotoxic waste than is destroyed. The use of common stainless steel capsules, for example, can lead to the generation of activation products that are more radiotoxic than the technetium or iodine originally present if irradiation is carried out in a thermal flux.

Clearly, long-term irradiation tests and materials compatibility studies are needed for successful implementation of a regime for the transmutation of long-lived fission products.

3.4.2 Reprocessing techniques

3.4.2.1 Aqueous reprocessing

Introduction to aqueous reprocessing

Aqueous reprocessing is based on the use of the PUREX process, which has been since the mid-1950s the industrial technique to separate uranium and plutonium from spent fuel. PUREX is a solvent extraction process that takes advantage of the multi-valent nature of the actinides. When present in nitric acid solution, uranium and plutonium exist in the U(VI) and Pu(IV) states, which are readily extracted into an organic molecule such as tributylphosphate (TBP, typically mixed with a kerosene or dodecane diluent) that is brought into contact with the acid solution. Americium, neptunium and curium are not extracted, and remain in the aqueous phase. Plutonium can then be reduced to the Pu(III) state and stripped out of the organic phase, accomplishing the desired separate recovery of plutonium and uranium. The minor transuranic elements in spent fuel (Np,Am,Cm) typically have long half-lives and/or high toxicity, and are commonly mixed with the fission products and treated as waste in a vitrification process following PUREX reprocessing. The discharge burn-up of LWR fuel has been increased over the years from 33 to 50 GWd/t, with a resulting increase of the decay heat in spent fuel assemblies and the occurrence of higher concentrations of trans-plutonium elements.

Fast-reactor based plutonium-burning technologies, such as that entailed in the French CAPRA program, require an increase in the plutonium content of fuels to as much as 50 weight percent and an increase in goal burn-ups to levels as high as 210 GWd/tHM or more. This makes aqueous reprocessing more difficult, because of the low solubility of plutonium and the radiation damage to the organic extractant (tributyl phosphate). Industrial “pilot” scale work (at research sites in Dounreay, Scotland and Marcoule, France) has shown that with the introduction of advanced technologies (such as pin-choppers and centrifugal contactors), aqueous reprocessing can be considered as valid for fast reactor and future ADS fuel if the decay heat can be mitigated by longer cooling periods or by dilution with LWR fuel.

Special chopping or shearing systems have been developed for fast reactor fuel (e.g. for the reprocessing of FFTF fuel, although the process was never used) in order to replace the single or multiple pin shearing process with a more economical complete bundle shearing approach. Laser cutting of PFR ducts was employed at the Dounreay reprocessing facility.

Many proposals for P&T technology rely on the aqueous reprocessing of spent fuel as a preliminary step preceding minor actinide partitioning. In the case of pyrometallurgical processing of TRU’s (the US ATW Roadmap project), a mechanical head-end and an aqueous processing step (called UREX) for the prior removal of uranium, as the main fertile element, precedes the sequence of pyrometallurgical separation steps. Spent fuel arising from a composite reactor park (70% LWR-UOX, 10% LWR-MOX, 20% FR-MOX) must be reprocessed in order to facilitate plutonium recycle and the stabilisation of the transuranic inventory; aqueous reprocessing methods are favoured in such scenarios. According to the Pu burning scheme (scheme 2, see Figure 3.2), the spent fuel generation rate from a 100 GWe composite reactor system leads to the outputs shown in Table 3.9.

Table 3.9. **Spent fuel discharge rates for components of scheme 2**

Fuel type	Burn-up GWd/tHM	Electrical output GWe	Spent fuel discharge tHM/y
LWR-UOX	50	69.7	1 387
LWR-MOX	50	10.3	206
FR-MOX	185	20.0	80

The reprocessing operations supporting such a system are presumed to be carried out 4 to 7 years after discharge of spent fuel from the reactors. The residual decay heats for these types of fuel are summarised in Table 3.10 (See also Tables 3.5 and 3.6).

Table 3.10. **Residual decay heats for scheme 2 fuel types**

<i>Fuel type (cooling time, y)</i>	Burn-up, GWd/tHM	Total decay heat, kW/tHM	Fission products, kW/tHM	Actinides, kW/tHM
LWR-UOX (4)	50	3.48	2.96	0.52
LWR-MOX (7)	50	6.31	1.41	4.90
FR-MOX (7)	185	21.77	4.86	16.91

In conventional aqueous reprocessing of LWR-UOX fuel, the fuel elements are chopped into small pieces and transferred to the dissolver. Large LWR fuel elements contain between 450 and 500 kg of UO₂ or MOX. For simplicity, we will consider two fuel elements per tHM, which are dissolved in 5 m³ HNO₃. Conceptually we will consider the ratio 1:1.8 between the aqueous HNO₃ feed solution and the organic (30% TBP-diluent) extractant phase. The throughput of a typical plant is about 200kg HM chopped spent fuel per hour or 4.8 tHM/day (800-960 tHM/year) depending on the plant load factor. In this case, we assume the contact time between the aqueous and organic phase to be 1 hour. The radiation damage in the extractant is proportional to the contact time of the highly radioactive aqueous feed solution and the TBP-solvent mixture.

Radiation damage to solvent

The radioactive decay energy dissipated by the feed solution into the extraction mixture as a radiation dose D is calculated as follows:

$$D = 0.35 \text{ kW}/4.8 \text{ m}^3 \cdot \text{hour} = 0.073 \text{ Wh/l}$$

Using this expression and the data given in the previous tables, the following doses are calculated (Table 3.11):

Table 3.11. **Radiation damage to solvent in different fuel cycle schemes**

Fuel type	Dose emitted by aqueous phase (Wh/l)	Dose received by solvent (Wh/l)
LWR-UOX	0.57	0.20
LWR-MOX	1.36	0.48
FR-MOX, 185 GWd/t	6.72	2.40

The main contribution to the radiation dose comes from the alpha decay of the actinides, which is very damaging to organic molecules. For LWR-MOX the alpha radiation represents 60% of the total radioactivity and for the FR-MOX fuel it amounts to 80%. In order to keep the radiation damage to the solvent to the safe limit of 0.1 Wh/l, the residence time for FR-MOX has to be reduced from the conceptual residence time of one hour to 2 or 3 minutes, which cannot be achieved with pulse columns. The use of centrifugal contactors in the first extraction cycle must be investigated as to its feasibility in current reprocessing facilities.

Several other possibilities are open to cope with very high burn-up fuel: (1) dilution of FR-MOX with LWR-UOX and LWR-MOX; (2) special head-end for FR-MOX; (3) installation of fast contactors throughout the reprocessing facility; and (4) very long term cooling.

- *Dilution of FR-MOX with LWR-MOX and LWR-UOX.* In a complex reactor park with 70% LWR-UOX, 10% LWR-MOX and 20% FR-MOX, the bulk mass of discharged spent fuel is given in Table 3.9. An equilibrium flowsheet of an advanced reprocessing plant could be established on the base of a homogeneous throughput of all the fuel types according to their discharge fractions. This option is in any case possible for the mixture of 7 tHM LWR-UOX and 1 tHM LWR-MOX. The total Pu inventory (without burn-up credit) would increase, but the radiation dose to the TBP would only increase marginally. In the case of a joint treatment of all fuel, including FR-MOX, the Pu inventory would drastically increase (by a factor 4.8) and the overall radiation exposure of the solvent would double, with peaks of more than a factor of 10 when FR-MOX is extracted.
- Some 100 tHM have been processed in reprocessing pilot plants after various cooling times and a representative campaign of FR-MOX reprocessing has taken place in the COGEMA UP2-400 plant at La Hague [44]. However, the technology to handle FR fuel in the head-end was different from that of LWR fuel assemblies, due to design differences and to higher fissile content in the irradiated FR fuel. The reprocessing of industrial quantities in a conventional plant will have an impact on the design philosophy of the PUREX extraction (pulse) columns, the slab-tanks and the criticality control devices. These issues are common for conventional PUREX reprocessing and for the newly proposed UREX process (should it be applied to fuel other than LWR spent fuel).
- *Special head-end for FR-MOX.* In order to improve the Pu dissolution yield and to avoid solvent radiation peaks during the extraction, a separate dissolver dedicated to FR-MOX treatment could be installed and connected to the main dissolver by a metering system. By connecting the dedicated FR-fuel dissolver to the main LWR dissolver a constant radiation level can be kept throughout the process campaign. The second dissolver could also serve as a “residue dissolver” by making use of highly oxidizing compounds (e.g. electrochemically-generated Ag(II)) to dissolve the insoluble fraction of the initial Pu inventory (2). Under increased radiolysis of TBP the fission product decontamination factors will decrease, the plutonium losses will increase, and the production of secondary waste (dibutyl phosphate, Na_2CO_3 , ...) will also increase.
- *Installation of fast contactors.* By replacing the pulse columns with fast centrifugal contactors, a gain of a factor three or more, depending on the number of stages and the scheduled contact time per stage, can be expected on the radiolysis of TBP and consequently on the feasibility of using aqueous reprocessing for high-burn-up FR-MOX fuel. Implementation of such a technology requires the complete refurbishment of an existing reprocessing plant. The importance of fast contactors in the first extraction stage warrants additional full-scale hot tests in order to establish whether the design of these components is sufficiently robust that they can be serviced and maintained in a very hostile radioactive environment.
- *Very long cooling times.* The radioactivity concentration in spent nuclear fuel decreases with the mean half-life of the fission products and with the half-life of the “short lived” actinides. The fission product activity decreases with a factor of 2 when delaying the reprocessing from 3 to 7 years. However, in the case of the actinide contribution to radioactivity, which is essentially determined by ^{244}Cm and ^{238}Pu (with half lives of 18 and 87 years, respectively),

the delays have to be much longer to be effective (see Figure 3.15). A long-term storage (~100 years) of separated ^{244}Cm with the formation of ^{240}Pu , has been considered as a strategy for Cm management. The ^{238}Pu contamination of separated plutonium from LWR-MOX and FR-MOX is an issue that must be examined in the framework of Pu purification and fuel fabrication operations.

Recovery of minor actinides

Recovery of minor actinides: neptunium

Although the conventional PUREX solvent extraction process is considered to be a method for extraction of uranium and plutonium from spent fuel, with the remaining actinides and fission products being sent to the waste stream, it is possible to recover neptunium from the dissolver solution by minor modifications to the PUREX flowsheet. Neptunium in the Np(IV) or Np(VI) valence states is reasonably extractable with TBP, while in the Np(V) state it is essentially inextractable. Under process conditions in which plutonium is placed in its extractable Pu(IV) state, neptunium tends to reside in the inextractable Np(V) state. Reagents such as tetravalent uranium, ferrous sulfamate or hydroxylamine can be used to reduce neptunium to the Np(IV) state; nitrite ion or pentavalent vanadium can be used to oxidise Np to the Np(VI) state. Neptunium then is co-extracted with either uranium or plutonium and must be subsequently separated by re-oxidizing it to Np(V) and acid stripping.

Recovery of minor actinides: americium and curium

In the PUREX nitric acid dissolver solution, americium and curium will reside in the +3 valence state, as will the lanthanide elements. The lanthanide fission products comprise about 30% of the total fission product mass in ten-year cooled spent LWR fuel, and their mass is more than ten times that of americium and curium combined. Neither Am(III) nor Cm(III) are extractable with TBP in the PUREX process, and in normal commercial practice there is no need for their recovery. But in a transmutation system that is dedicated to the near-total elimination of the highly radiotoxic transuranic elements, it is necessary to extract these elements. Modification of the valence states of Am and Cm in the mainstream PUREX process through redox reactions adds process complications and could affect other extractions, so the current thinking is to recover these constituents from the PUREX high-active raffinate before that stream is sent to waste processing. The lanthanide fission products complicate the recovery of americium and curium, and a number of processes have been developed for this very complex problem. Because the acidity of the raffinate is rather high, $\geq 2\text{M}$ in HNO_3 , and the radiation level is significant, it has proven challenging to extract americium and curium separately in the presence of a large mass of +3 lanthanides [Ln(III)]. Therefore, initial efforts were directed toward co-extraction of Am and Cm and their subsequent separation. The compromise in such systems is the attendant substantial increase in high-level liquid waste generation.

Co-extraction of americium and curium

Several processes have been developed for the co-extraction of americium and curium from a raffinate solution containing lanthanides and other fission products. The first was the TRUEX process [45], which employs as extractant CMPO [n-octyl(phenyl)-N,N-diisobutyl carbomoylmethylphosphine oxide] in TBP. CMPO is a powerful extractant with high affinity for +3 actinides [An(III)] at high acidities, but it does not discriminate between An(III) and Ln(III). Other processes that feature co-extraction of actinides and lanthanides are TALSPEAK, DIDPA, DIAMEX and TRPO. The TALSPEAK and DIDPA [46] processes utilise an acidic organophosphorous extractant, di-2-ethylhexylphosphoric acid (HDEHP) or diisodecylphosphoric acid (DIDPA), for extraction of An(III) and Ln(III). This extraction is followed by stripping of the An(III) constituents from the solvent with a

combination of a carboxylic acid and diethylenetriaminopentaacetic acid (DTPA). Both the TALSPEAK and DIDPA processes require reduction in the acidity of the aqueous feed solution, either by dilution or by denitration.

The DIAMEX process [47] is based on the use of malonamide extractants such as DMDBDTMA (dimethyldibutyltetradecylmalonamide) in a diluent such as kerosene. Because the DIAMEX extractant contains no metal ions, following the principle of incorporation only of constituents easily converted to innocuous volatile compounds (the so-called “CHON” principle), the waste arising from the DIAMEX process are minimised relative to the previously described processes. The SANEX process can be coupled with DIAMEX for An(III)/Ln(III) separation. The SANEX process selectively extracts the +3 minor actinides from the +3 lanthanides with a BTP extractant, bis-1,2,4-triazinylpyridine, from relatively concentrated aqueous solutions. Recently, extractant mixtures of bis-chlorophenyldithiophosphinic acid and tri-n-octylphosphine oxide (TOPO) have been successfully tested.

The TRPO (trialkylphosphine oxide) process [48] capitalises on the high affinity of trivalent actinides and lanthanides for TRPO in moderately low acid concentrations. The extraction requires additional operations for separation of An(III) and Ln(III). The need for reduction in acidity leads to additional waste generation.

Direct separation of An(III) and Ln(III) has become possible with development of the CYANEX 301 process [49], using bis-2,4,4-trimethylpentylidithiophosphinic acid. Very high An(III) decontamination factors can be obtained with purified CYANEX-301 extractant. A complication of this process is the necessity to dilute the aqueous feed solution to quite low acidity.

Separation of americium from curium

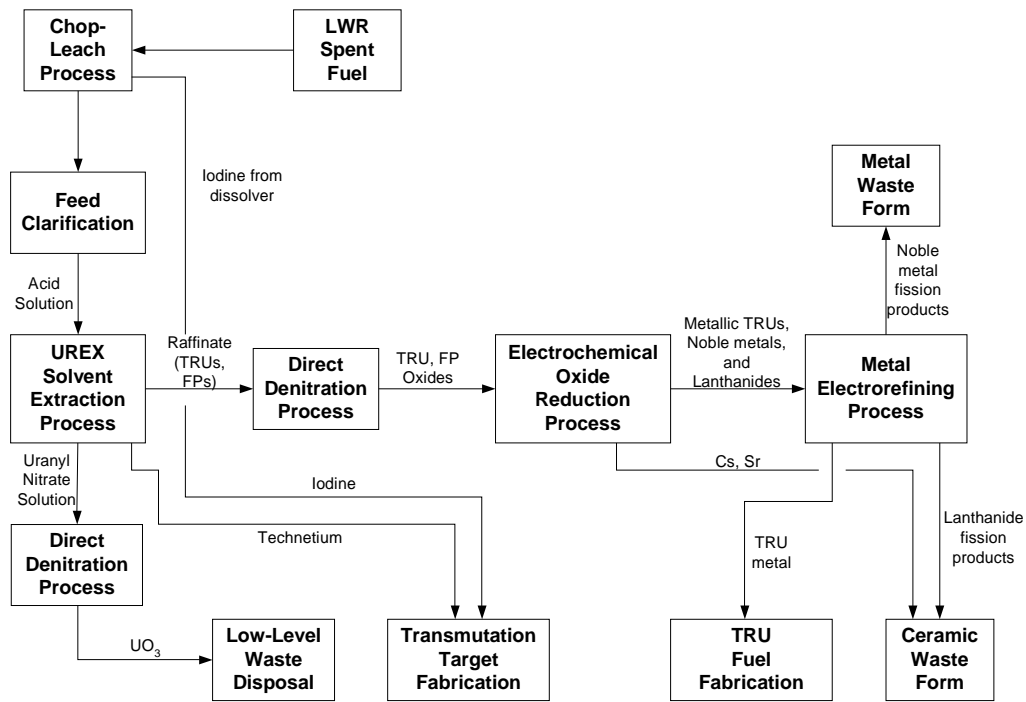
This separation can be accomplished by changing the oxidation state of americium to the extractable (IV) or (VI) states. Curium (III) is very difficult to oxidise to higher states in aqueous solution, making the separation possible. The SESAME process has been developed for this separation. It involves the electrochemical oxidation of americium in conjunction with a complexant to stabilise americium in the higher oxidation state. Potassium phosphotungstate, for example, is a good complexant for tetravalent americium.

A combination of process such as DIAMEX-SANEX-SESAME thus can serve to provide an acceptably efficient separation of americium and curium in pure form, well decontaminated of the lanthanide fission products. Such complete separations can be accomplished, as has been demonstrated, but at a cost of added expense and added high-level liquid waste volume. The question then arises as to the need for separate extraction of all of the actinides present in spent nuclear fuel. The transuranic elements are readily fissioned in the fast neutron spectrum provided by either a fast reactor or an accelerator-driven system. It is possible that certain benefits may accrue in fabrication of the fuel feed to a transmutation system if problems associated with the presence of curium can be avoided. Fabrication of transmuter fuel without the need to account for the neutron emission from curium could provide certain benefits, but at the cost of the need to store curium until its decay is complete (requiring nearly 200 years for ^{244}Cm). It may also prove advantageous to route certain transuranic elements to different transmutation systems optimised for specific elements. It is too early to make a judgement on this question, but the technology for performing any required separations will be available; it is only a matter of cost.

Alternative approaches

An example of a different approach is the hybrid processing system envisioned for the US Accelerator Transmutation of Waste (ATW) program [50], as illustrated in Figure 3.18. In this system, an aqueous solvent extraction process (UREX) is used to extract uranium from spent LWR fuel, using a complexant/reductant such as acetohydroxamic acid (AHA) to prevent the extraction of plutonium and neptunium. In this way, the transuranics are left in the first-stage raffinate solution along with all of the non-volatile fission products. The raffinate is then denitrated and the resulting oxide solids are pyrochemically processed to separate the transuranics from the fission products. The pyrochemical processes proposed will not separate the transuranics one from another, and decontamination of the lanthanide fission products will be low, on the order of a decontamination factor of 20 for individual lanthanides. These are inherent features of the processes selected, and serve the purpose of increasing the proliferation resistance of the overall system.

Figure 3.18. Hybrid processing system utilising aqueous and dry processes for separation of transuranics and long-lived fission products for subsequent transmutation



3.4.2.2 Pyrochemical (dry) processing

Introduction to pyrochemical processing

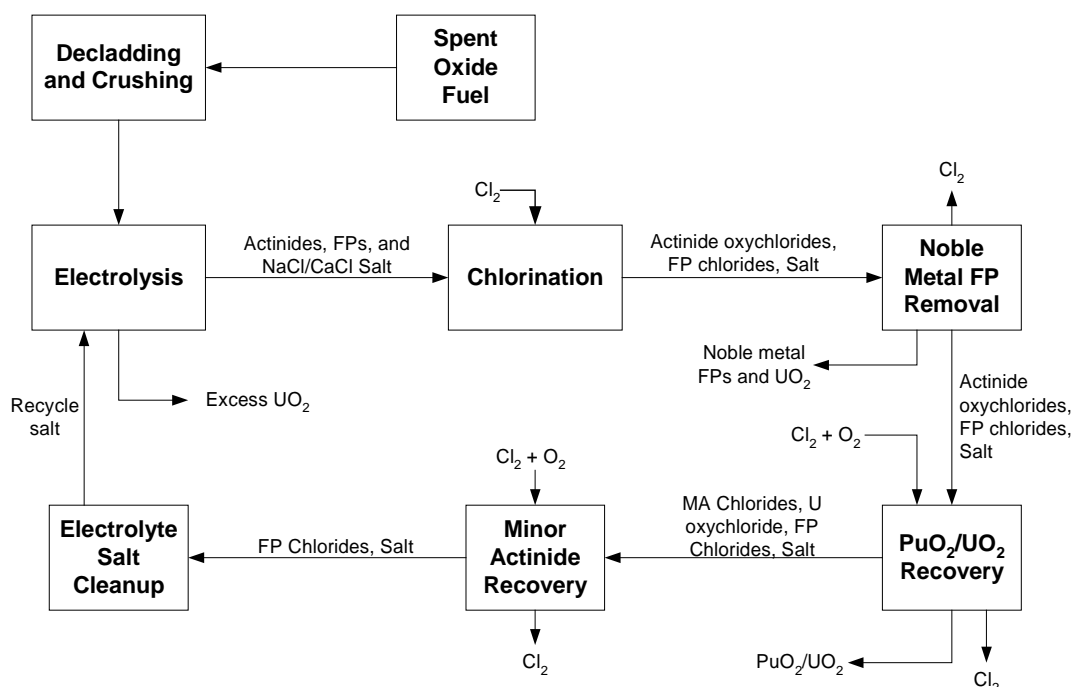
The quest for an alternative to aqueous reprocessing has been underway since the 1960s, when a rudimentary pyrochemical process was implemented for the purpose of processing spent fuel discharged from the U.S. EBR-II reactor. This process, known as “melt-refining,” simply involved the removal of volatile fission products by melting of the fuel material. Plutonium was lost to the melting crucible and later recovered, and the noble metal fission products were collectively recycled with the newly-constituted fuel as a constituent referred to as “fissium”. More recently, an advanced pyrochemical process has been applied to the processing of EBR-II fuel and blanket assemblies. This process, referred to as “pyroprocessing”, involves the electrorefining of the uranium present in the

fuel. Provided that the U:TRU ratio in the electrolyte salt is kept sufficiently high (i.e. >0.5 or so), pure metallic uranium can be electrodeposited at a solid cathode. Recovery of transuranic elements requires the use of a liquid metal cathode such as Cd, which facilitates the deposition of TRU elements by reducing their chemical activity. However, because EBR-II fuel treatment is intended only as a waste management scheme, the uranium is consolidated for storage and the transuranics and fission products present in the fuel/blanket material are left in the electrolyte salt and are subsequently incorporated in a durable high-level waste form. The metallic uranium deposit is freed of adhering electrolyte salt by vacuum melting of the deposit, which results in preferential vaporisation of the salt. This consolidation is normally done at temperatures in the 1 400°C range; at such temperatures the extremely reactive combination of uranium and salt leads to rapid attack of crucible materials.

A related pyrochemical process has been used in Russia for the processing of fast reactor spent oxide fuel. This process, also under development for a number of years [51], is illustrated schematically in Figure 3.19 and is essentially an electrowinning process in which oxide fuel is chlorinated in a chloride salt bath (e.g. NaCl-CsCl) to form oxychlorides (such as PuO_2Cl_2) of the actinide elements. The electrolysis process, typified by the reaction $\text{PuO}_2^{2+} + 2e^- = \text{PuO}_2$, results in the co-deposition of uranium, neptunium and plutonium oxides at the cell cathode and liberation of chlorine at the anode. Some contamination of the deposit with americium and curium occurs. The balance of the americium and curium remain in the salt bath. The cathode deposit is separated from adhering salt by washing with water. The recovered actinide oxides are incorporated into fresh fuel rods by vibratory compaction. Recycle of some oxide fuel elements in the BN-600 reactor has been accomplished.

Figure 3.19. **Oxide electrowinning process for treatment of oxide spent fuel and production of MOX fuel**

Process as developed by RIAR, Dimitrovgrad, Russia. Note that all steps following decladding and crushing are conducted in the same pyrolytic carbon vessel.



Pyrochemical separations processes that would find application in partitioning and transmutation systems must meet demanding requirements on actinide recovery and, in some cases, on long-lived

fission product recovery from spent fuel. The nature of the pyrochemical process to be used in particular applications depends strongly on the fuel composition, both chemical and isotopic. It also depends on economic factors related to the fuel composition and the required plant throughput rate.

Pyrochemical operations, at the present stage of technology development, are batch processes. The cost of such operations is approximately linearly dependent upon the number of batch operations to be run simultaneously. Some economies of scale can be expected from large-volume equipment fabrication, commonality of repair parts, and standardisation of procedures, but the effects are not at all comparable to the considerable economies of scale available with continuous aqueous processing. Furthermore, many pyrochemical processes require the recovery of materials from each batch operation and transport and loading of the materials to the next batch operation; this must generally be done by electromechanical means, as opposed to the simple liquid pumping operations in aqueous processing. All of these handling and transfer operations add complexity to the process, and duplication of complex equipment to provide for multi-batch operations means an increase in the probability for failure somewhere in the system. Intuitively, such considerations must impose a limit on the economic throughput capacity of a pyrochemical separations process. The limited industrial experience with such processes at present precludes a quantitative evaluation of the practical limits to throughput capacity. Nor is it possible to estimate with certainty the capital and operating costs of these processes.

Nevertheless, there are certain applications in which the use of a pyrochemical process is clearly indicated. These processes, typically operated at elevated temperatures, are ideally suited to the treatment of spent fuel that has been cooled for a short time and is generating considerable decay heat. Passively-cooled electrorefining or pyrochemical processing vessels of modest size containing, for example, about 1 m³ of molten salt can accommodate decay heat levels of a few tens of kilowatts. As seen in Table 3.5, decay heat levels encountered with 2-year-cooled fuel in fuel cycle schemes 3b and 4 can be substantial (about 200 and 450 watts per kg heavy metal, respectively). Batch sizes, however, are limited by the amount of TRU product that can be concentrated at any given step in the process, due to criticality concerns. Therefore, even though 200 kg TRU may be critically-safe when distributed in the molten salt or molten metal in the process vessel, it is not possible to amass such a quantity in the TRU product that must eventually be consolidated by melting or other means. Batch sizes with such material must therefore be limited to around 5 kg TRU, corresponding to a batch heat load of 1-2 kilowatts or less. Process vessels must be provided with adequate heating system capacity to maintain the process medium at a constant operating temperature even after extraction of the TRU content of the batch. In addition, redundant heater capacity must be available in the event of heater element failure, and the equipment must be provided with means for expedited heater replacement so that inadvertent freezing of the molten salt can be precluded.

Another factor that can be more limiting in determining the acceptable cooling time before initiation of processing is the need to prevent fuel failure before it is sent to the fuel chopping step. Movement of fuel rods prior to that step generally assumes that the fuel is intact, so the temperature of the fuel cladding must be kept within safety limits to avoid exceeding failure strain levels. This is particularly important when handling complete fuel assemblies where the total amount of TRU elements can be 35-50 kg, sometimes necessitating active fuel assembly cooling.

So, in general, a fuel cooling time of two years is adequate for pyrochemical processing, provided that the fuel can be handled without exceeding temperature limits for the fuel cladding or the handling equipment. High radiation levels (particularly the high levels of α -radiation from the transuranic elements) that would result in serious reagent deterioration in aqueous systems are tolerable in molten salt systems because the reagents are stable. In addition, because of the absence of a moderating agent

(i.e. water), the processes can safely handle large masses of fissile isotopes, thus reducing the size and floor area required for process equipment.

For the ADS-related fuel cycle schemes that produce irradiated fuel with high decay heat levels, the total amount of fuel that must be processed annually, given the design parameters of Table 3.1, is quite small, on the order of one tonne per year for one reactor. Conservatively assuming 100 days productive operation per year, the processing rate in this case need be only 10 kg per day, or two 5-kg batches. This can be easily accommodated in pyrochemical process equipment of very modest size. Following the same rationale, pyrochemical processing operations supporting the three fast reactor based fuel cycle schemes would be presented with much less challenging heat load problems. The comparison, paralleling that from earlier in this chapter, is best seen in Table 3.12, where the calculations are based on the same parameters presented in Table 3.1.

Table 3.12. Process decay heat loads for pyrochemical processing in the various fuel cycle schemes

	Pu burner (FR)	TRU burner (FR)	TRU burner (ADS)	MA burner (ADS)	FR (core)
Fuel discharge, tHM/y	4.9	3.0	0.7	0.7	3.1
Decay heat, W/kgHM	21.8	46.0	192.6	455.1	18.6
Process decay heat load, kW/day	1.3	1.6	3.3	4.1	0.7

Here, it has been assumed that the processing plant operates for 100 days per year. With proper batching and equipment/facility design, these fuels can be processed without difficulty.

A variety of pyrochemical processing methods are available today, the most widely used being (1) molten salt electrochemistry (electrorefining, electrowinning); (2) volatility processes, including vacuum distillation; and (3) molten salt/molten metal reductive extraction processes. More insight in the current technological maturity and R&D needs to develop these processes to an industrial scale will be given in Chapter 7.

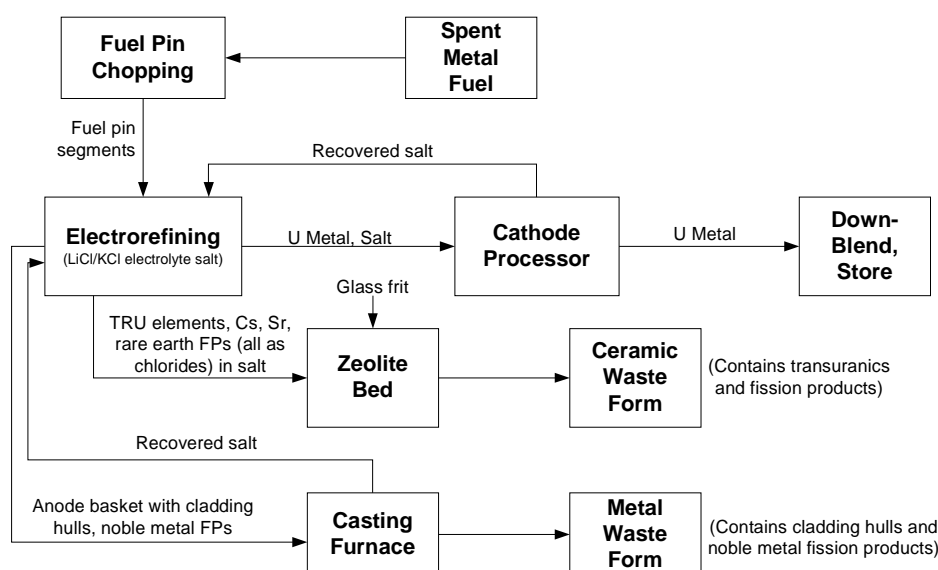
Electrorefining

The electrorefining process can be characterised simply as a process in which an impure material is made as the anode in an electrochemical cell and, with the passage of current in the cell, pure material is deposited at the cathode. In spent fuel treatment applications, the anode contains the spent fuel, generally after chopping to expose the fuel material to the electrolyte salt. The fuel can be either metal, oxide or nitride. It is not necessary to remove the fuel cladding or any other materials internal to the fuel rod. In the case of metal fuel electrorefining in which the fuel material is an alloy of uranium, transuranics and zirconium, the electrolyte salt of choice is a eutectic mixture of LiCl and KCl, operated at a temperature of 500°C. A concentration of about 2 mol% of actinide chlorides is maintained in the electrolyte salt to support electrotransport of the actinides to the cathode. With this concentration of actinide ions in the salt, electrotransport can be sustained at a high rate when a potential of 0.5-1.0 volt is imposed between the solid cathode and the anode. Reduction of the actinide chlorides occurs at the cathode and deposition of an actinide atom is accompanied by dissolution of a corresponding atom from the spent fuel. As anodic dissolution of the chopped fuel proceeds, fission products dissolve by reducing some of the actinide chlorides. This necessitates the occasional addition of a compensating amount of oxidant, usually CdCl₂ or UCl₃. If uranium is present in the spent fuel, and if the ratio of the concentration of UCl₃ to transuranic chlorides in the salt is greater than about

0.1, then only uranium will deposit at the solid cathode. The alkali metal and alkaline earth fission products (e.g. Cs and Sr) will not deposit because their chlorides are much more stable than the actinide chlorides. Similarly, the chlorides of the transuranic elements and the rare earth fission products are more stable than uranium chloride. So, these elements will not deposit at the solid cathode as long as the uranium concentration in the electrolyte salt is sufficient. The transition metal fission products will not be oxidised and will remain in the anode basket as metallic elements. This process is presently in use for the treatment of spent sodium-bonded driver fuel and blankets from the EBR-II reactor and is illustrated schematically in Figure 3.20.

Figure 3.20. **Schematic of pyrochemical process used for treatment of EBR-II spent driver fuel and blankets**

Because this is a waste management system, no attempt is made to recover transuranics for recycle. Recovered uranium is downblended to less than 20% enrichment in ^{235}U before storing.



The transuranic elements can be recovered in the case of the treatment of uranium-bearing fuels by the use of a different cathode, a liquid metal cathode. A common liquid metal cathode consists of a small amount of liquid cadmium contained in a ceramic crucible suspended in the electrolyte salt, with electrical contact made to the cadmium. The transuranic elements will electrodeposit in the liquid cadmium because their chemical activities are reduced by formation of intermetallic compounds such as PuCd_6 . Uranium will also deposit in the cadmium cathode as an intermetallic compound. Even though the rare earth fission products will also form intermetallic compounds with cadmium, their chlorides are more stable than those of the actinides; thus, only small amounts of rare earths are deposited in the cadmium cathode. But it is important to recognise that in this system: (1) the uranium deposited at the solid cathode will be pure; (2) the transuranics deposited in the liquid cathode will be contaminated with 10-30 wt.% uranium and a few percent of the lanthanide elements; and (3) the properties of the transuranic elements are sufficiently similar that they cannot be separated in this process. The cladding materials of the spent fuel will not be dissolved, provided that the cell voltage is maintained below the decomposition potential of the constituents of the cladding.

In the case of non-fertile fuels (no uranium content), the transuranic elements can be electrodeposited directly on a solid cathode. Minor contamination of the transuranics with lanthanide

fission products can be expected, and there will be no separation of the transuranic elements from one another.

If the fuel to be electrorefined is not metallic, one has the option of reducing the fuel to the metallic state, as in the case of oxide fuel using the Direct Oxide Reduction process with calcium as the reductant. Alternatively, it is possible to use the Dimitrovgrad approach and capitalise on the increased electrical conductivity of oxides at elevated temperatures, directly electrodepositing the actinide oxides. Although this process has proven successful with MOX fuel, it requires further development or the use of additional process steps for complete recovery of all of the actinide oxides.

In the case of nitride fuel, actinides can be recovered much the same as with metallic fuel. Actinide elements can be electrotransported to a cathode, with nitrogen gas being liberated at the anode. An off-gas recovery system would be necessary in the case of nitride fuels highly enriched in the ^{15}N isotope to prevent build-up of ^{14}C . Noble metal fission products would remain in the anode basket, and other fission products would form stable chlorides and reside in the electrolyte salt, which could be a LiCl-KCl eutectic mixture. In the processing of non-fertile fuel, transuranic elements could be collected on a solid cathode; with nitride fuels containing uranium, the collection of pure uranium at the solid cathode would not be possible, and the use of a liquid cathode for collection of transuranics may not be necessary. Experimentation is necessary to resolve this question.

Electrowinning

Molten salt electrowinning is simply an electrolysis process in which the material to be recovered is present as a halide compound in an electrolyte salt. For example, a metal or nitride fuel could be chlorinated in a chloride carrier salt to produce chlorides of the actinide elements and most of the non-gaseous fission products (depending on the chlorinating agent). Most fuel types could be fluorinated to produce fluorides in a fluoride carrier salt. The molten salt containing the dissolved spent fuel constituents could then be placed in an electrolytic cell, with a potential applied between the anode and cathode. At the appropriate voltage level (the decomposition potential), which depends on the species to be electrolysed and the cell temperature, actinides can be deposited at the cathode and the halogen gas will be liberated at the anode. Electrowinning can also be important in certain applications of volatility processes.

Volatility processes

The most common of the volatility processes applied in spent fuel processing are chloride volatility and fluoride volatility. Such processes can be extremely useful in the processing of complex fuel types, including inert-matrix fuels. A small-scale fluoride volatility processing system was operated jointly by NRI (Czechoslovakia, now Czech Republic) and RIAR (Russia) in the 1980s. This process was used for treatment of oxide fuel from the BOR-60 reactor. Powdered fuel was fluorinated, converting uranium to UF_6 and most of the plutonium to PuF_6 , both very volatile products. Re-fluorination was necessary to convert the remaining plutonium to the PuF_6 species. Most of the fission products formed non-volatile fluorides, while the noble metal fission products formed semi-volatile fluorides that tended to accompany the uranium and plutonium. After extraction of niobium and ruthenium fluorides, uranium and plutonium fluorides were then condensed at -60 and -80°C . After collection in the condensers, the uranium and plutonium fluorides were reheated, decomposing the PuF_6 to solid PuF_4 , thereby allowing the volatile UF_6 to be separated from the plutonium. Column distillation was then used to purify the UF_6 by separating molybdenum, iodine and technetium fluorides.

Volatility processes have been proposed for application in the various separation schemes envisioned for the US Accelerator Transmutation of Waste (ATW) programme. A chloride volatility process could form the head-end of the treatment process for a fuel consisting of a metallic dispersion of TRU-Zr alloy in a zirconium matrix. Chlorination of the fuel in a LiCl carrier salt is followed by volatilisation of the zirconium as $ZrCl_4$. Digestion of the matrix material then provides physical access to the transuranics and fission products, which are subsequently separated by a reductive extraction process. A direct electrorefining process is currently favoured over the chloride volatility process due to the problem of contamination of the $ZrCl_4$ deposit. Fluoride volatility processing has been proposed for ATW processing of TRISO (pyrolytic carbon coated) fuel [52]. Without question, fluoride volatility processing is a powerful technology; on the other hand, it is a technological challenge to control the process so as to achieve very high efficiency, avoid ancillary recovery steps, and comply with environmental and safety regulations. Much more development is needed to realise the full benefits of this family of process methods.

Reductive extraction processes

Reductive extraction processes exploit certain well-behaved replacement reactions to separate certain fission products and actinides. Molten metal/molten salt systems are particularly useful for application of reductive extraction. An illustrative example is the treatment of chlorinated metallic fuel to separate the actinides from active metal fission products. The fuel can be chlorinated with $CdCl_2$ in a LiCl carrier salt, resulting in the formation of chlorides of the actinides, the Group I/II fission products, and the lanthanide fission products. The noble metal fission products will not form chlorides and will either sink to the bottom of the chlorination vessel or remain in the basket originally containing the fuel. The salt can then be contacted with a molten metal consisting of a dilute solution of lithium in cadmium. Lithium will reduce the actinide chlorides and, to some extent, the lanthanide chlorides. If the process is operated in counter-current mode in a train of high-temperature centrifugal contactors, about eight contactor stages can effect extraction of over 99.99% of the actinide elements into the cadmium phase, with a lanthanide contamination of this product of less than 10% of the lanthanide elements present; i.e. excellent recovery of actinides contaminated with about 10 weight percent lanthanides. Greater purification requires an increased number of contactor stages. The process has been demonstrated with four contactor stages and provided excellent separation [53]. A similar metal/salt reaction process has been reported for removal of noble metal fission products from oxide fuel that has been reduced with hydrogen and then fluorinated, with the noble metal fission product elements being digested in liquid antimony, tin, or zinc.

As described earlier in this chapter, several of the possible fuel cycle schemes can make use of pyrochemical processing methods. Because these methods tend to be non-selective with respect to the transuranic elements, they are applicable in a broad variety of systems. Process selection must be made with full awareness of the potential for contamination of the separated TRU product with traces of lanthanide fission products. If the performance of the FR or ADS fuel is sensitive to the presence of lanthanides, then certain steps, such as the use of several reductive extraction stages, must be called upon to reduce the lanthanide contamination.

Wastes from pyrochemical processing

Pyrochemical processing operations tend to produce little secondary waste because there is little or no reagent degradation. If the processes are properly designed and operated, high-level waste volumes can be minimised by recovery and recycle of salt and metal reagents. There is little published information available on wastes from pyrochemical process operations due to the relative technological immaturity and lack of industrial-scale experience. Therefore, the technology can be assessed only on the basis of extrapolations from laboratory-scale studies, and most of this experience

has been with the electrorefining process used for separations of actinides and fission products in the metallic state.

In the case of the electrorefining process developed at the Argonne National Laboratory in the US, when applied in fuel cycle schemes 3a, 3b, 4 and 5, the high-level waste forms are identical. This is the case regardless of whether the fuel type being treated is metal, oxide or nitride, metmet, cermet, or cercer. Different waste forms would probably arise in the case of coated-particle graphite reactor fuels or in the case where a fluoride salt mixture is utilised in the process, but the discussion will be limited here to the chloride-based processes for the sake of brevity.

In the reference process, then, the active metal fission products (Cs, Sr, etc.) will reside in the electrolyte salt together with trace amount of actinide elements. The transition metal fission products will remain in the anodic dissolution baskets together with the cladding hulls. So, there are two waste streams to deal with, one salt and one metal. Because a chloride salt is not amenable to vitrification, development of a different waste form was necessary. A natural chloride-bearing mineral, sodalite ($\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl}$), exists in the geologic structures of the proposed Yucca Mountain repository in the United States. This mineral can be synthesised by mixing the fission product-loaded electrolyte salt with a zeolite (Zeolite A, $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$) and heating to temperatures near 900°C . The synthesis is catalysed by the presence of borosilicate glass frit, which also serves to encapsulate the sodalite particles, providing an additional barrier to radionuclide release. As is the case with vitrification of high-level waste, the fission product loading of the waste form is constrained by the limiting centerline temperature of the waste form and the total heat generation per unit area acceptable in the high-level waste repository of interim storage site.

The composite glass-ceramic waste form developed by Argonne is limited by the temperature at which transformation of the sodalite to nepheline (a related mineral but one which does not retain fission product cations well) occurs. This restricts centerline temperatures to around 650°C , and because the thermal conductivity of the composite is similar to that of borosilicate glass, the maximum fission product loading is about the same as for glass, around 15 weight percent. The limits on actinide content are higher than for glass (which is limited by the solubility of actinides to around 1 weight percent), but the fission product decay heat limit prevails. Little is known about long-term degradation of the sodalite structure by α -particle damage.

A variety of leach tests conducted with differing leachant chemistries and environmental conditions have shown that the release rate of important radionuclides from the pyrochemical process ceramic waste form is comparable to the releases from the best vitrified waste forms and well over an order of magnitude less than the release from spent fuel under direct disposal conditions. These tests have been carried out in evaluation of the potential behaviour of this waste form in the oxidising environment characteristic of the Yucca Mountain repository. Under reducing conditions, the behaviour is not known.

The metallic waste stream is generated by removing the anode baskets from the system and melting the baskets together with the metallic fission products and the cladding hulls to produce a corrosion-resistant metal alloy. This alloy is dependent in composition on the nature of the cladding material, which dominates the mass of the waste form. A metal waste form based on stainless steel cladding hulls has shown a release rate for technetium that is several orders of magnitude less than than the release of technetium from spent LWR fuel.

The volume of waste emanating from pyrochemical processing operations is somewhat dependent on the nature of the fuel being processed and even more dependent on the complexity of the overall process. Although there is little extended large-scale experience with such operations, it is possible to

estimate the resultant waste volumes on the basis of laboratory-scale testing. Table 3.13 shows estimated waste volumes for the fuel cycle schemes of this report that involve pyrochemical processing (schemes 3a, 3b, 4 and 5). Process wastes, also known as secondary wastes, are difficult to estimate; therefore, a fixed value of 0.2 m³ per tonne was used in this table.

Table 3.13. **Estimated waste volumes from pyrochemical processing operations in fuel cycle schemes 3a, 3b, 4, and 5**

Fuel cycle scheme	Waste stream and type	Est. volume (m ³ /TWhe)
3a	LWR uranium (LLW)	0.20
	LWR ceramic waste form (HLW)	0.27
	LWR metal waste form (HLW)	0.08
	FR ceramic waste form (HLW)	0.20
	FR metal waste form (HLW)	0.01
	Process wastes (LLW)	0.7
3b	LWR uranium (LLW)	0.25
	LWR ceramic waste form (HLW)	0.33
	LWR metal waste form (HLW)	0.10
	ADS ceramic waste form (HLW)	0.07
	ADS metal waste form (HLW)	0.02
	Process wastes (LLW)	0.8
4	LWR-UOX PUREX wastes (HLW)	0.38
	LWR-MOX PUREX wastes (HLW)	0.06
	FR-MOX PUREX wastes (HLW)	0.02
	ADS ceramic waste form (HLW)	0.03
	ADS metal waste form (HLW)	0.002
	Pyrochemical process wastes (LLW)	0.1
	PUREX process wastes (LLW)	2.0
5	FR ceramic waste form (HLW)	0.56
	FR metal waste form (HLW)	0.04
	Process wastes (LLW)	0.2

(HLW: high-level waste; LLW: low-level waste).

3.4.3 Secondary wastes arising in fuel cycle schemes

It is generally acknowledged that in addition to the unwanted fission products, fuel cladding, etc., that would constitute the primary fuel cycle PUREX waste from a P&T scheme, there would be generation of secondary waste. This secondary waste would comprise all insoluble active residues, degraded solvents or salts, ancillary materials, and analytical wastes, etc. that arise during additional fuel cycle operation. It is suggested that the majority of secondary wastes which arise during processing operations would be generated during solvent/salt cleanup and recovery operations [54]. Table 3.14 summarises the potential secondary waste forms that could be generated with the operation of P&T fuel cycles. Note that in this analysis of secondary wastes, construction and decommissioning wastes have not been included. However, it is obvious that the increased number of multistage processes and greater shielding requirements would generate considerably more decommissioning wastes that would include secondary, active, wastes owing to sorption of material onto process surfaces and accumulation of active fines, etc. but these cannot yet be realistically quantified.

3.4.3.1 *Front-end secondary wastes*

The front-end of fuel cycle schemes 1, 2, 3a, 3b, and 4 have common stages associated with the production of UOX-fuel for irradiation in conventional thermal reactors. These fuel cycles will generate wastes during the mining and milling stages, which are reported to represent the major health and environmental hazards of the nuclear industry [55]. Secondary wastes in the form of uranium residues in the tails from milling operations represent a definite anthropological hazard with respect to the in-growth of radioactive progeny. The generation of fugitive dust, from tailings dams can have considerable impact on the localised populations. Additional secondary wastes include sulphuric acid and ammonia that are used during the leaching and purification of uranium ore concentrate, used filter cloths, contaminated solvent extraction raffinate, dilute hydrofluoric and hydrochloric acids and magnesium or calcium fluoride slag. The use of process and ancillary service materials such as petrol and diesel will also generate additional secondary wastes. However, the stages that follow mining and milling generate considerably less waste and have a lower impact on the environment. Conversion and enrichment processes are essentially clean processes that generate very small quantities of secondary waste mostly in the form of scrap metal and analytical wastes.

The power production, or reactor, stage of the nuclear fuel cycle generates relatively little secondary waste. The secondary waste that does arise will be due mainly to the treatment of coolant, such as corrosion products, spent demineralisation resins, filters, ancillary service material and general maintenance and analytical wastes. However, the stages downstream of thermal reactor operation in each of the fuel cycles differ considerably. Analysis of the back-end of the nuclear fuel cycle will show the increased secondary waste generation of P&T schemes becomes more apparent.

3.4.3.2 *Back-end secondary wastes*

It is assumed that final disposal stage would entail long-term storage in a deep geological repository. The primary waste associated with this stage would be the waste rock inventory, which itself is radioactive, generated during construction of the repository. The secondary wastes are difficult to identify, however it seems feasible to assume that similar secondary wastes from the related ancillary services to those generated during mining operations would arise. In contrast, the irradiated fuel from the thermal reactor in the P&T schemes would be subjected to processing following an appropriate post-reactor cooling period. The secondary wastes and the associated increase in dose in most P&T scenarios will arise from the separation and treatment of irradiated fuel components, and their subsequent fabrication into new fuel or transmutation target materials.

PUREX is proposed for the processing of thermal UOX fuel, and it is also proposed that advances in PUREX technology would allow the recovery of Np. It is suggested that a multistage processing operation involving the combination of DIAMEX-SANEX-SESAME technologies is implemented to allow the efficient separation of americium and curium from PUREX HAR and to strip the undesirable lanthanide fraction. The primary wastes produced by this multiplex processing system would comprise HLW of lanthanides, fission products and trace quantities of actinides. The secondary wastes are summarised in Table 3.14. The solvent used in DIAMEX (DMDBTDMA in kerosene or dodecane), conforms to the CHON principle, which implies that the spent solvent would be totally incinerable and as such would reduce the total solid secondary waste arising. However, a solvent waste stream containing up to 11% of the ruthenium in the feed to the DIAMEX process would be generated during solvent processing [56]. The ruthenium fraction could be oxidised to volatile RuO₄ prior to DIAMEX separation although this effectively generates a new RuO₄ secondary waste, which would require scrubbing from the solvent. Iron could accumulate in the solvent phase also, potentially resulting in the formation of a problematic third phase, which would require subsequent removal from the solvent during clean-up processing. Additional scrubbing cycles would be required to remove any residual

ruthenium prior to incineration of the spent solvent. Radiolysis of the solvent would lead to the formation of carboxylic acids, amine, amide-acid and other degradation products, which decreases the solvent extracting properties [47].

SANEX would generate secondary waste from off-gas scrubbing and by radiolysis of the organic solvent. The presence of ^{242}Cm and ^{241}Am would increase the α -level activity and promote solvent degradation. The organic solvent degradation products would depend on which soft donor extractant is used, as several have been suggested (See §3.5.1). Similarly, SESAME would generate waste streams contaminated with trace quantities of Am and Cm from product finishing. The waste solvent could be polluted with activated ^{110}Ag and quantities of waste complexing agents, heteropoly acids such as potassium phosphotungstate, would be generated. The advanced separation processes referred to above are currently in the development stage and as such it is not possible to provide an accurate account of the potential secondary wastes associated with their operation. However, it seems feasible to suggest that implementing such complex multistage processes would generate additional secondary wastes, which would further contribute to the operational dose of the fuel cycle and toxicity of the wastes.

The majority of secondary wastes that arise during processing operations would be generated during solvent cleanup and recovery operations [54]. It is feasible to assume that secondary wastes generated during PUREX processing for thermal UOX compared to FR-MOX fuels would be similar, although probably different in magnitude. Solvent radiolysis or hydrolytic decomposition during PUREX operation would generate the major fraction of secondary wastes, including organic degradation products such as dibutylphosphate (DBP), monobutylphosphate, alkanes, nitro-alkanes, carboxylic acids, carbon dioxide, and phosphoric acid. The α -level associated with recycle FR-MOX fuel would be approximately 30 times greater than the equivalent UO_2 fuel of the same irradiation (See Table 3.5). Consequently, the extraction of FR-MOX fuel that has been subjected to high irradiation would result in increased formation of DBP via solvent radiolysis, due to the increased Pu and MA inventories in the spent fuel (average 140 kg DBP/TWhe for fast reactor fuel). Trace quantities of insoluble crud would be found in solvent wash raffinates. For example, the solvent wash raffinate from the processing of thermal oxide fuel would typically contain around 0.8 g/l U, 8 mg/l Pu and 0.3 mg/l Np. The increased degradation of solvent and diluent expected during the processing of FR-MOX fuel might be accompanied by an increased inventory of insoluble actinide residues, the magnitude of which would depend on the complex interactions of many operating variables such as initial fuel composition, irradiation, dissolution conditions, etc. Distillation of the solvent wash raffinate reduces the volume but generates a higher-boiling residue containing traces of uranium, plutonium, and minor actinides. The recycle of Pu in the FR stage of the fuel cycle would generate quantities of secondary waste subject to accumulation with each cycle.

Secondary waste generation during fast reactor operation would be relatively small in comparison to that from recycling operations. Ancillary service wastes would be expected to be similar to those of the thermal reactor stage; however, the secondary wastes associated with coolant could differ and would depend on the coolant media, e.g. sodium, employed in the fast reactor system. A coolant treatment system would be necessary that would operate on a continuous or periodic basis to remove potential corrosion and activation products.

The operation of an ADS would incur the generation of different secondary wastes to those associated with conventional thermal and fast neutron reactor systems and in greater quantities. The formation of activation and spallation products would have serious safety implications and require continuous or regular periodic removal. The use of Pb or Pb-Bi eutectic (LBE) target and coolant media could result in the generation of isotopes such as ^{202}Pb , ^{205}Pb , ^{208}Bi and ^{210}Po and other possible reaction products (mostly lanthanides). Preliminary calculations have indicated that fission products would account for as little as 10% of the activity in the target [57]. In addition, radiation damage in

structural materials such as the beam tube and beam window could occur due to the formation of spallation and activation products such as isotopes of Fe, Cr, and Ni, depending upon the alloy employed [58]. The generation of gaseous secondary wastes would be expected from sources such as target venting, the coolant system, the supply of an inert operating atmosphere e.g. helium, and beam dumps. Solid secondary wastes associated with the ADS operation would be expected to comprise PPE, HEPA filters, batteries, scrap metals and glass, etc. [59].

The secondary wastes associated with the pyroprocessing of the post-ADS target material would include zeolites, used for ion exchange purification of the process salt medium, and waste eutectic salt and inclusions such as CaCl_2 , FP, MgCl_2 , LiCl , KCl , Li_2O , etc. It has been estimated that 0.3 m^3 of mineral wastes and 0.05 m^3 of metallic wastes would be generated per tonne of reprocessed material [60]. Zeolite ion exchangers would be used for extracting fission products and rare earths, after which they would be collapsed and mixed with anhydrous zeolite to promote salt uptake into the crystalline matrix prior to conditioning for final disposal (See 3.5.2). It is suggested that such waste forms would typically contain around 4 wt% FP. Recycling of the molten salt eutectic mixes could potentially reduce the generation of secondary wastes during pyroprocessing [61]. In addition there would be generation of process fines that would be subject to sorption onto the internal surfaces of equipment, cells and filters. However, the magnitude of secondary wastes generated during pyroprocessing is hypothesised as being relatively low owing to the reduced or negligible reagent degradation, based on extrapolations of current knowledge (See 3.5.2).

Generally, it is proposed that schemes 1 and 5 would generate the smallest secondary waste inventories owing to their relatively simple designs, i.e. fewer multiplex processes. However, scheme 1 generates the greatest secondary waste associated with raw materials extraction and scheme 5 assumes sole use of fast reactor technology and no LWR fuel cycle operations, which does not account for any phase out of current technology. In addition scheme 5 would incur penalties associated with the recycle of TRU cycle including increased criticality risks during FR-MOX dissolution, which would require the construction of dedicated head-end facilities (See §3.5.1). The dose due to recycling of Pu and MA would result in greater handling risks owing to larger inventories of ^{238}Pu and ^{241}Am , which would generate increased neutron and gamma radiation around the glove boxes in fuel fabrication [62]. In addition, further doses would arise through (α , n) reactions in equipment handling ^{238}Pu . This is exhibited in the greater levels of radiation following cooling, and during fabrication, associated with the TRU and MA burner schemes shown in Tables 3.5 and 3.6. Scheme 4 the double strata strategy (Figure 3.4) would generate the greatest quantity of secondary waste owing to its multiplex nature and multiple recycling (See Section 3.1.2).

Categorisation of the secondary waste associated with fuel cycle operation is difficult owing to the uncertainty inherent in any assessment of potential inventories. However, it is possible to suggest that secondary wastes arising from ancillary service materials and secondary liquid effluent treatment, e.g. secondary filter cartridges from steam generator blowdown systems that are contaminated with small quantities of fission products and activation products would be considered LLW. Sludges and concentrates, contaminated with fission products and activation products with trace quantities of actinides would be categorised as ILW. Similarly, material contaminated with activation products, fission products, actinides and neutron-activated products would also be categorised as ILW. In Table 3.14 categories are assigned to the secondary wastes that would potentially arise during the operation of the five principal fuel cycle schemes selected by the expert group.

3.4.4 Depleted and reprocessed irradiated uranium

The management of depleted uranium (DU) and reprocessed irradiated uranium has received relatively little interest over the past years as their environmental impact is very low and, in today's fuel cycles, is overwhelmed by the potential radiological impact from the intermediate and especially high level waste in the long-term. The P&T-schemes under consideration in this study may however reduce the amount of long-lived high-level waste with a significant factor, i.e. a factor hundred or more. Therefore, the management of this depleted uranium and reprocessed irradiated uranium may become a more apparent issue in the future if such P&T-schemes would be deployed.

Table 3.14a. **Summary of secondary wastes arising from fuel cycle front-end and reactor**

FUEL CYCLE STAGE	CATEGORY ^{a)}	SECONDARY WASTES
Mining & milling	LLW	Residual uranic wastes contained in drilling mud and displaced rock.
	LLW	Sulphuric acid, ammonia, used filter cloths, activated solvent extraction raffinate, dilute hydrofluoric and hydrochloric acids, and magnesium or calcium fluoride slag.
	LLW	Emissions from ancillary services.
Enrichment & conversion	LLW	Maintenance wastes: small quantities of coolant, inert gases, scrap metal, polythene, paper towels, etc.
	LLW/ILW	Analytical wastes
	ILW	Conversion: trace uranic quantities from scrub liquor and crud.
	LLW	Conversion: wastes from ancillary services such as polythene, paper towels, carbon and cloth filters, etc.
Power production/ transmutation	ILW	Cooling system maintenance – corrosion products, isotopic activation products
	LLW/ILW	Spent demineralisation resins, and ancillary service material e.g. cooling tower blowdown, sewage, used oil, contaminated oil, wastewater treatment sludge, etc.
	ILW	ADS: Spallation and activation products associated with coolant irradiation, e.g. formation of ²¹⁰ Po from neutron capture in ²⁰⁹ Bi (in LBE coolant / target material), ²⁰² Pb and ²⁰⁵ Pb, ²⁰⁸ Bi. Activation products such as Mo, Ni, Cr, Fe, etc., from irradiation of structural components such as the beam window and beam tube.
	ILW	Corrosion products from mechanical degradation of structural materials
	LLW	Activated air & offgas emissions from: target venting, coolant system, inert purge system, beam dumps
	ILW	PPE, HEPA filters, batteries, scrap metal & glass, etc.

a) Category = radioactive waste category: LLW: Low-level Waste; ILW: Intermediate Level Waste.

Today, the strategy for the long-term management of depleted uranium is based on the consideration that this depleted uranium is a valuable material, which may have various applications, and is not considered a waste. The use of this depleted uranium in fast reactor systems, as shown in

this study, is one of the applications where the re-enrichment is a second potentially valuable source of ^{235}U for LWRs, whilst the remaining ^{238}U may again be used in future fast reactor systems. In the absence of these, or other, large-scale applications, however, final disposition in some form of “repository” would have to be considered.

Table 3.14b. **Summary of secondary wastes arising from fuel cycle back-end**

FUEL CYCLE STAGE	CATEGORY	SECONDARY WASTES
PUREX	ILW	Degraded solvent and wash raffinate containing organic solvent degradation products such as DBP, MBP, alkanes, nitro-alkanes, carboxylic acids, carbon dioxide, and phosphoric acid.
	ILW/HLW	Trace quantities of insoluble U, Pu, FP, and MA dissolver solids, and soluble traces in solvent wash raffinates, e.g. from processing of thermal oxide fuel, typically around 0.8 g.l^{-1} U, 8 mg.l^{-1} Pu and 0.3 mg.l^{-1} Np.
DIAMEX (fission product and transuranic separation)	ILW/HLW	11% initial Ru in solvent wash raffinate, possibly removed in scrub liquor following oxidation to RuO_4 .
	ILW	Possible Fe (corrosion product) accumulation in solvent.
SANEX (Trivalent actinide and lanthanide separation)	ILW	Scrub liquor, from off-gas scrubbing.
	ILW	Organic solvent degradation products – dependent upon extractants, e.g. TPTZ, or <i>di</i> -thiophosphoric acids in combination with TBP.
	ILW	Trace quantities of Am, Cm, from process raffinate.
SESAME (Am/Cm separation)	ILW	Contaminated condensate containing Am and Cm from product streams and associated scrub liquor.
	ILW	Waste solvent (solvent cleanup and recovery operations) possibly containing activated ^{110}Ag and waste heteropoly acid.
	LLW	Acidic wastes, phosphoric acid.
Pyroprocessing (Pu/MA recovery from spent ADS fuel)	ILW	Scrub liquor from off-gas treatment.
	ILW	Cladding hulls, noble metals.
	ILW	Waste eutectic salt & trace inclusions (including the more electropositive FPs).
	HLW/ILW	Ion exchange zeolites, waste crucibles, scrap metallic waste.
Storage (intermediate) & Final disposal (repository)	LLW	Ancillary service wastes.

Depleted uranium, initially occurring as UF_6 , can be stored safely for many decades in steel containers in the open air in storage yards. However, depleted uranium stored in the UF_6 form may represent a potential chemical hazard if not properly managed. Alternatives for the strategic management of depleted uranium therefore include the deconversion of UF_6 stocks to stable forms

more suitable for long-term management. Due to their high chemical stability and low solubility, uranium oxides in general are the favoured form for this. Generally, though not exclusively, storage as U_3O_8 , the most stable oxide, is considered for long-term storage where continued storage as UF_6 is not appropriate. Large-scale storage of compacted U_3O_8 has been undertaken in France since 1984. About 130 000 tU of UF_6 have already been converted into U_3O_8 . The powder is held in about 3 m³ painted mild steel DV 70 type containers stacked three high in “warehouses”.

The radiological characteristics of DU are a consequence of the properties of the three uranium isotopes: ^{238}U , ^{235}U and ^{234}U and their daughter products. DU is safe against criticality under all naturally occurring conditions. The initial activity of DU when it is newly produced is very low, around 23 Bq/g and the toxicity is also low, around 0.75 Sv/g. Whatever the ^{235}U assay of uranium, as time passes, decay products will appear meaning that the activity and the radiotoxicity will increase. The activity and radiotoxicity levels for DU will become the same as for uranium ore (with the same original amount of uranium) after a time period of around 1 million years.

Reprocessed irradiated uranium is currently not systematically recycled in UOX- or MOX-fuel form. The reprocessed uranium distinguishes itself from natural uranium by the occurrence of higher amounts of α -emitting isotopes:

- ^{232}U , not present in natural uranium, has a higher specific activity than ^{235}U and some of the daughter-products are α -emitting, i.e. ^{228}Th with a half-life of 1.9 years, as well as emitting hard γ -rays, i.e. ^{208}Tl . The γ -activity attains a secular equilibrium after about 10 years attaining significant higher values than for natural uranium.
- ^{234}U occurs as a natural α -emitter and is accumulated in this irradiated uranium. In addition, Np and Pu are also occurring in reprocessed irradiated uranium and add to the α -activity.
- Trace amounts of ^{106}Ru occur which increase the γ -activity.

The nuclear industry has in place the facilities that are needed to recycle reprocessed uranium (REPU) on a semi-industrial scale. This includes chemical conversion of REPU, enrichment, fuel fabrication and transport as well as reactor irradiation of REPU-based fuel. In Japan, JNC carried out experiments on the REPU conversion technology at Ningyo-Toge conversion facility. The amount of REPU converted to UF_6 for re-enrichment reached 336 tU. Recycling of REPU from LWR fuel is now demonstrated, albeit limited to a fraction of the available material and to a few numbers of reactors.³⁵ The enrichment of REPU is today based on centrifuge technology and is currently performed in Russia and in the Netherlands. Altogether, the reprocessing plants have delivered more than 12 000 tonnes of REPU where this amount will further grow in the years to come in a pace comparable to the output of a large uranium mine. More recently, an alternative way of REPU reuse has emerged which relies on blending REPU with high-enriched uranium resulting in a reduced ^{236}U -content in the enriched REPU fuel, thus reducing neutron absorption and improving the economy of REPU recycling. If REPU is considered as a by-product from reprocessing, the economics realised in replacing natural uranium by REPU compensate for the extra expenditures related to storage, conversion, enrichment and fabrication depending on the source material. The competitiveness of REPU is strongly related to the cost of reprocessing and of natural uranium, but also to its isotopic composition that varies from a batch to the other. The future of REPU is anticipated to be governed by economic and strategic, e.g. conservation, considerations. Considering the savings which can be made by recycling REPU of relatively good

35. Substantial quantities of REPU from MAGNOX fuel have been re-enriched in the UK to natural level for recycling, while the Doel-1 reactor in Belgium has been operated exclusively with re-enriched REPU for a number of years.

specifications, despite an extremely depressed natural uranium market, it is possible that in the coming years, those utilities having selected reprocessing will also recover uranium through recycling.

In conclusion, as long as LWRs would make up a significant part of the nuclear power plant park in future fuel cycle schemes, an increasing amount of depleted and reprocessed irradiated uranium would emerge. Especially the latter would be of increasing importance, as depleted uranium would be used in fast reactor systems where the recycling of reprocessed irradiated uranium would not compensate for its production. Only the use of this reprocessed irradiated uranium in future all FR-scenarios (scheme 5) may indicate a steady decrease of the build-up inventory of depleted uranium and the reprocessed irradiated uranium. In the very long-term (about 1 million years), disposition of this depleted and reprocessed irradiated uranium results in an activity and radiotoxicity level comparable to natural uranium.

3.5 Conclusions

The results of the comparative analysis of fuel cycle schemes, described in this chapter, can be summarised as follows:

- All transmutation strategies with closed fuel cycles could, in principle, achieve high reductions in the actinide inventory and the long-term radiotoxicity of the waste, and these are comparable with those of a pure fast reactor strategy. With respect to these reductions, the potentials of the FR and the ADS are very similar. The choice of the fuel cycle scheme affects the radiotoxicity reduction factor only within a factor of about two.
- Under the assumptions used in the analysis, these strategies can achieve a more than hundred-fold reduction in the long-term waste radiotoxicity and even higher actinide inventory reduction factors (more than 1 100 for the heavy metal and 175 for the transuranics), compared with the once-through fuel cycle.
- The reduction factors are primarily determined by the fuel burn-up and the reprocessing and fuel fabrication losses. An ambitious goal for the recovery of all actinides (99.9%, as already achieved for uranium and plutonium with aqueous processes) must be set, if the quoted reduction factors are to be realised.
- With regard to actinide waste production and technological aspects, the TRU burning in FR and the double strata strategies are similarly attractive. The former can gradually evolve to a pure fast reactor strategy, but requires a higher initial investment in fast reactor and advanced fuel cycle technology. The latter confines the minor actinides to a small part of the fuel cycle, but calls for particularly innovative technology for this part of the fuel cycle.
- Transmutation systems with partially closed fuel cycles, e.g. heterogeneous transmutation schemes, in which americium and curium are separated from the fuel and recycled in special “target” pins which are disposed of after irradiation, are technologically less demanding than a closed fuel cycle strategy, but are also about a factor of two less effective in reducing the radiotoxicity. They are being explored as a near-term transmutation option which does not depend on an ADS.
- Multiple recycling of plutonium without minor actinide transmutation is useful for the management of plutonium, but cannot qualify as a transmutation strategy because it reduces the long-term radiotoxicity of the high-level waste by only a factor of about five.
- The sub-critical operation of an actinide burner with a fast neutron spectrum offers interesting additional parameters of freedom in the core design. In particular, the possibility of operating

such a burner with a uranium-free (or thorium-free) fuel supply allows the burner effectiveness to be maximised and hence the fraction of specialised transmuters in the reactor park to be minimised.

- A further advantage of the sub-critical operation mode is the tolerance of the system against degradations in the safety characteristics of the core. Both of these advantages are of particular relevance for systems which burn pure minor actinides, i.e. minor actinide burners in a double strata strategy.
- Actinide transmutation implies the handling of unusual fuels with very high decay heats and neutron source strengths. A significant effort is required to investigate the manufacturability, burn-up behaviour and reprocessability of these fuels. This applies particularly to fuels with high minor actinide content, which can probably be reprocessed only with the help of pyrochemical methods. These methods have to be further developed to tolerate from ten to more than twenty times higher decay heat levels than those encountered in the pyrochemical reprocessing of normal fast reactor fuels.
- The introduction of pyrochemical processing techniques at the industrial level will require the development of new process flowsheets and the use of potentially very corrosive reagents at high temperatures. These processes will generate chemical and radiological hazards which will have to be mitigated. A compensating benefit of elevated-temperature operation is the increased reaction rates that prevail. The recovery efficiency of such processes is yet to be proven on an industrial scale.
- The PUREX aqueous reprocessing can be considered as valid for the FR-MOX fuel in the plutonium-burning and double strata schemes. Reprocessing of this fuel within short cooling times and with the required high recovery yields, however, will require the plutonium dissolution yield to be improved and the PUREX flowsheet to be modified.
- Due to the high radioactivity of multiple recycled FR-MOX fuel, its handling will require measures to be taken to reduce the radiation doses in the fabrication plant and during the transportation of the fuel assemblies. The increased requirements for shielding, and preference for short transportation paths, of multiple recycled fuels also favour the pyrochemical reprocessing method.
- All transmutation strategies which include LWRs in the reactor mix produce large streams of depleted and irradiated uranium. If this uranium is not considered as a resource for future fast reactors, its long-term radiological impact has also to be taken into account.