

14 ANNEX 2 - RADIOTOXIC EVOLUTION

The radiotoxicity as a function of time is reproduced in figure A2.1 below. This example is for fuel irradiated in a PWR with an initial U235 enrichment of 4%, power rating of 40 MW/t and a burnup of 40 GWd/t. The results have been normalised to 1 TWh of electrical energy produced. The various separation indicating in the diagram takes place five years after shutdown. The time on the abscissa is that from separation, thus a time of 1 year corresponds to 6 years after shutdown. (This offset is also applied to the case of no separation).

No Separation

The radiotoxicity decreases relatively slowly during the first fifty years and is dominated during this period by Sr90, Cs137 and Pu238. These are relatively short-lived nuclides and by 50 years the radiotoxicity begins to decrease at a faster rate. However, the grow-in of Am241 (from the decay of Pu241) begins to become significant at about this time and this nuclide dominates the period to just beyond 1000 years. Pu239 and Pu240 become increasingly dominant after this time, and with the greater half-life of Pu239, it alone comes to contribute the majority to the total radiotoxicity (accounting for almost 90% at 50,000 years). The significance of Pu239 begins to wane at a similar time as the radiotoxicity of the daughters of long-lived decay chains reach their maximal values. From about 140,000 years, Ra226 (and its equilibrium daughters) and Th229 (and its equilibrium daughters) account for the majority of the radiotoxicity out to 10 million years. By 10 million years the radiotoxicity is 0.01% of its initial value.

U and Pu Separation

When uranium and plutonium are removed, the radiotoxicity is reduced by only 25%-50% for the first 50 years due to the dominance of Sr90 and Cs137 during this period. Although the amount of Am241 does not increase from the decay of Pu241 in this case, this nuclide still dominates the radiotoxicity from 50 to 3000 years. After this period, Am243 becomes the most important, followed by Pu239 (having grown-in from the decay of Am243) after about 16,000 years. From 100,000 years, Th229 (and its equilibrium daughters) account for the majority of the radiotoxicity out to 10 million years. Compared to the case of no separation, after about 100 years the radiotoxicity is reduced to below 20% and remains so from then on. The removal of plutonium has by far the largest effect upon the reduction in radiotoxicity.

U, Pu, Np and Am Separation

When uranium, plutonium, neptunium and americium are removed, the period of dominance of Sr90 and Cs137 lasts until 300 years, after which Pu240 (having grown-in from the decay of Cm244) dominates up until 50,000 years. After this period, the long-lived fission products Tc99 and I129 account for the majority of the radiotoxicity out to 10 million years. Compared to the case of no separation, after about 300 years the radiotoxicity is reduced to below about 1% and remains so from then on.

Fate of Uranium

If uranium is not separated and processed, after about 100,000 years its daughters will cause the radiotoxicity to increase to a similar level had no separation of other nuclides occurred due to its daughters. However, the increase is to a similar level to that of the uranium ore used to manufacture the fuel, had it been left undisturbed.

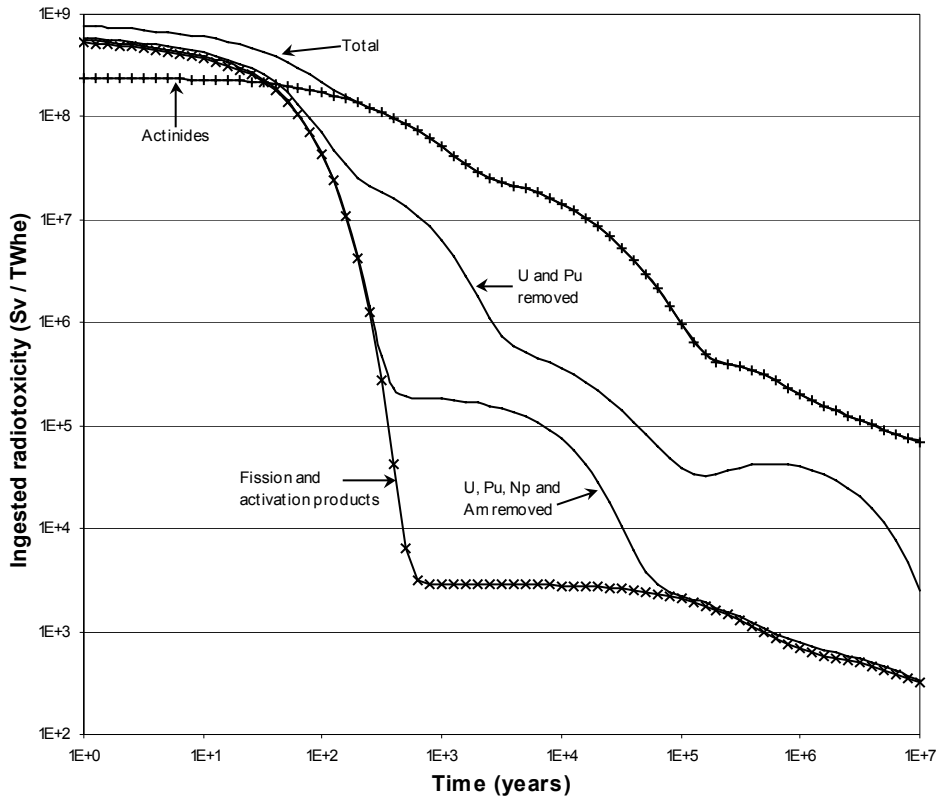


Figure A2.1

15 ANNEX 3 - PARTITIONING CAPABILITIES FOR KEY RADIONUCLIDES

Radionuclide / Element	Partitioning
¹⁴ C	Partitioned in high yield and trapped as a relatively 'high purity waste' as part of current PUREX reprocessing as CO ₂ , and subsequently removed via alkaline scrubbing prior to precipitation. Expected removal efficiency >95%.
³⁶ Cl	Partitioning is difficult and ³⁶ Cl would be contaminated with natural chlorine. It is present as secondary waste contaminant in PUREX reagents but in such small amounts to make separation virtually impossible.
⁷⁹ Se	Partitioning would almost certainly be difficult from HLW. No studies into the partitioning of ⁷⁹ Se have been reported and little is known about selenium speciation.
⁹⁰ Sr	Extraction using cobalt dicarbollide/polyethylene glycol has been suggested by INEEL (USA) and Khlopin Radium Institute (Russia). This is to be investigated further as part of US AFCI work. Developments in the four stage partitioning process proposed by JAERI include the separation of strontium by adsorption with inorganic ion exchangers such as titanate acid, which have estimated recoveries of >99.9%. The SREX (strontium extraction) process, using crown ethers, has been proposed to complement the TRUEX process from strontium removal from acidic highly active liquid waste. The JAERI process is possibly too complicated for industrialisation.
⁹⁹ Tc	Partitioning is performed in present PUREX-based technology but not to the very high efficiencies that would be necessary for a P&T program. Extension to PUREX should allow for recovery of majority of Tc as separate product, however the proportion of Tc in insoluble residues will be more difficult to recover. The US AFCI recognises the possibility of needing to recover Tc from insoluble fission products. Two methods have been developed by JAERI for Tc and platinum group metals (PGM) separation that are reported to achieve between 95% and 99.9% extraction. The method of Tc partitioning that achieves 95% extraction might not be efficient enough but does not generate secondary wastes and therefore may warrant further development.
¹²⁶ Sn	Partitioning is reported to be difficult especially due to the component being present in insoluble residue. The fate of ¹²⁶ Sn during current reprocessing operations is reported as being uncertain, and it has been proposed that the bulk of the material probably goes to the dissolver insolubles. Methods have been suggested for ¹²⁶ Sn separation from an aqueous HLW stream but only 60% recovery was achievable.
¹²⁹ I	Partitioning of ¹²⁹ I is possible with current technologies but problems arise with partial separations due to ¹²⁹ I being volatilised during fuel dissolution operations. It has been suggested that iodine could be immobilised by adsorption on silver impregnated zeolites. However, in current PUREX operations a quantity of iodine (<10%) is transported as colloidal iodine in the aqueous waste stream and would subsequently be distributed amongst different waste streams, making recovery very difficult. Reprocessing operations at La Hague plan to recover >95% of

	iodine and the Tokai Reprocessing facility have developed the use of silver impregnated adsorbents for immobilisation of iodine effluent
^{135}Cs	Partitioning of caesium from HLW has been developed using dicarbolyde or crown ethers (as with ^{90}Sr). The dicarbolyde process involves nitrobenzene, which has a high toxicity and is thus a serious penalty of this method. It has been proposed that Cs and Tc could be co-extracted almost totally free of all other fission products if the aqueous waste is made alkaline prior to vitrification stages but this is problematic because of the increased Na or Ca loading in the glass waste form. As with strontium, the four group partitioning process developed by JAERI is reported to be capable of highly efficient extraction of Cs via adsorption on inorganic ion exchangers.
^{137}Cs	Partitioning of ^{137}Cs would be similar to ^{135}Cs and decay-cool storage is suggested as an alternative to transmutation as it would take about 300 years to achieve a considerable reduction in activity.
^{226}Ra	^{226}Ra is not initially present in large enough quantities to warrant dedicated attempts to separate it. ^{226}Ra is the decay daughter of ^{234}U , which is formed from either ^{238}Pu decay or ^{238}U decay and as such is a long-term problem. The removal of Pu and U from waste streams is achievable at high levels of efficiency and to improve upon them would be difficult.
Uranium	Uranium isotopes are separated with a high yield in the current PUREX process.
Plutonium	Separated with a high yield by current reprocessing using existing technology, e.g. PUREX. US development of UREX process directs Pu (and Np) to HA raffinate from where they are separated from the lanthanides in order to avoid Pu proliferation issues.
^{237}Np	Partitioning of ^{237}Np could be feasible with current technology, but has not yet been developed on an industrial scale. The majority of neptunium is extracted by TBP in current PUREX operations and follows the uranium stream prior to being separated from that during the second uranium purification cycle. At present all the neptunium is sent to vitrification apart from a small fraction that follows the plutonium stream, but it is feasible that neptunium could be separated for incorporation into a transmutation target.
^{241}Am , Cm	Partitioning of ^{241}Am is vital to P&T operations as ^{241}Am is a parent nuclide of ^{237}Np , therefore removal of ^{237}Np without separation of ^{241}Am from HLW would only delay the accumulation of a ^{237}Np inventory. Recovery of ^{241}Am is not possible with current separation technology. However, methods are being investigated for recovery from HLW by aqueous methods but separation from curium and lanthanide isotopes would require further development. Two methods have been suggested for the separation from curium, one that uses the differences between the partition coefficients of americium and curium in the DIAMEX solvent and one that capitalises on the existence of americium in oxidation states higher than III (unlike curium). The SESAME process uses the oxidation states method to separate americium and curium. Progress being made in France with Bis-Triazinyl-Pyridines (BTP) molecules show promise for An/Ln separations but there are still significant issues with respect to their stability.

16 ANNEX 4 - TRANSMUTATION CAPABILITIES FOR KEY RADIONUCLIDES

Radionuclide / Element	Transmutation
¹⁴ C	Transmutation would be difficult due to a low neutron capture cross section and the precipitate resulting from partitioning would be likely to contain considerable quantities of natural carbon. The extremely low capture cross section would result in a very long transmutation half-life time, i.e. the dwell time required in a transmutation system of a given flux for a species exhibiting a given capture-cross section. In addition any oxygen or nitrogen contamination of the targets would produce more ¹⁴ C.
³⁶ Cl	Not practical in the chemical form of Cl ₂ . Additionally, natural chlorine would contain approximately 75% ³⁵ Cl with a large capture cross section that would form extra ³⁶ Cl in a thermal neutron flux. Activation of ³⁷ Cl would generate ³⁸ Ar, which would lead to a pressure build up around the transmutation target that would subsequently require venting to reduce the pressure.
⁷⁹ Se	Problematic due to the long transmutation half-life times of ⁷⁹ Se. Additional ⁷⁹ Se would be formed from the natural ⁷⁸ Se isotope ^{20,21} .
⁹⁰ Sr	Not considered a viable option due to the relatively short half-life of ⁹⁰ Sr. Separation and cool-decay storage are a more likely method of management.
⁹⁹ Tc	Transmutation (to stable ¹⁰⁰ Ru via neutron capture) is possible and ⁹⁹ Tc offers good characteristics as a target material. ⁹⁹ Tc has been studied experimentally as it is generally considered to be one of the main fission products that should be transmuted (the other main fission product being ¹²⁹ I). Transmutation in a fast flux reactor would seem to be the most promising prospect, however ⁹⁸ Tc with half-life of 4.2x10 ⁶ years could form thus incurring a penalty. Different alloys of Tc such as Nb/Tc have been studied but activation products, such as ⁹⁴ Nb, would be problematic ²² . Experimental results in high flux thermal reactors have showed promising results but are presently capacity limited, so the development of large scale HFR in the future could be an alternative. Studies have been performed as part of the Experimental Feasibility of Targets for Transmutation (EFTTRA) program ²³ .
¹²⁶ Sn	Problematic because of the very long transmutation half-life and the eventual

²⁰ Volckaert G., Mallants D., Bush R., Lambers L. 'Long-term environmental impact of underground disposal of P&T waste', Actinide and fission product partitioning and transmutation, Proceedings of the Fifth Information Exchange Meeting, Mol, Belgium, 1998, pp. 463-474.

²¹ Actinide and Fission Product Partitioning and Transmutation Status and Assessment Report, OECD NEA, 1999

²² Cummings R., Crookshanks C.E., McAdams R., Rogers J.M., Sims H.E., Smith-Briggs J.L. (1996) 'An assessment of partition and transmutation against UK requirements for radioactive waste management: Supporting studies', DOE Report No.: DOE/RAS/96.010, 1996

²³ Konings R.J.M., Mühling G., Conrad R., Rouault J., Haas D., Vambenepe G., 'Transmutation of americium and technetium: recent results of EFTTRA', Actinide and Fission Product Partitioning and Transmutation, Proceedings of the Fifth International Information Exchange Meeting, Mol, Belgium, 25-27 November 1998, pp. 207-212, OECD NEA, France.

	<p>production of ^{127}I, which could lead to target failure²² It has been suggested that it might be more beneficial to segregate the insoluble residues and store. However because of its very long half-life (^{126}Sn has a half-life of approximately 10^5 years), this suggestion is problematic and conditioning prior to repository storage may be more realistic.</p>
^{129}I	<p>Could be possible but problems with corrosion and gaseous products such as ^{130}Xe may arise^{20, 22} Transmutation in the chemical form, I_2, would not be suitable so it is most likely that a stable iodide such as NaI or BeI_2 would be used. BeI_2 could be problematic because of the formation of ^{10}Be, which has a half-life of 10^6 years. Gaseous products are a problem that is difficult to avoid and would require venting from the target to prevent pressure build-up. Other problems to consider are the generation of atomic and molecular iodine, which are corrosive and can form volatile iodides.</p> <p>An alternative suggestion is to separate iodine from waste and manufacture Ag^{129}I, which is insoluble (therefore reducing the groundwater release risk) and dispose of in a repository.</p>
^{135}Cs	<p>Transmutation is reported to be infeasible because transmutation of other caesium isotopes would generate additional ^{135}Cs²⁵. The presence of ^{133}Cs renders the transmutation process inefficient.</p>
^{137}Cs	<p>Decay-cool storage is suggested, as an alternative to transmutation as it would take about 300 years to achieve a considerable reduction in activity.</p>
^{226}Ra	<p>No studies into the transmutation of ^{226}Ra. As the problem is posed by the gradual accumulation of ^{226}Ra in the waste it would not be feasible to transmute, as this would require retrieval of disposed waste and extraction of ^{226}Ra. However, there are greater quantities of ^{226}Ra in the depleted uranium residues from fuel enrichment and in Pu from ^{238}Pu decay, which implies that there is a considerable problem related to the fate of ^{226}Ra.</p>
Uranium	<p>Possible but produces transuranic actinides that represent considerable hazards in a repository.</p>
Plutonium	<p>Possible by incorporating the plutonium into mixed oxide fuel for recycle in thermal or fast reactors. Fast neutron flux systems would limit the formation of minor actinides but fuel density constraints would subsequently limit the plutonium loading, which would then increase the number of transmutation cycles required to incinerate plutonium stocks.</p>
^{237}Np	<p>Possible but considerable amounts of ^{238}Pu, a high specific activity alpha emitter, would be generated, which then increases the problem of ^{226}Ra.</p> <p>There are also problems associated with the manufacture of neptunium targets as the decay daughter ^{233}Pa, which would increase the gamma dose and thus require additional shielding around the powder blending glove box²⁴. Transmutation in a fast neutron flux is favoured, or in a very high thermal flux that would form ^{238}Np which would be subsequently fissioned.</p>
^{241}Am	<p>Would be favoured in a fast neutron flux with multiple recycling and</p>

²⁴ Actinide and Fission Product Partitioning and Transmutation Status and Assessment Report, OECD NEA (1999).

	<p>reprocessing as fission of the transmutation products could occur. Penalties would be incurred by the formation of curium²⁵. Transmutation in a thermal flux would generate ²⁴²Am, subsequently decaying to ²⁴²Cm and ²⁴²Pu which would contribute greatly to the long-term hazards of a repository. Studies have been made into the transmutation of americium in an inert matrix as part of the EFTTRA program and it was reported that problems could occur due to the formation of helium from the decay of ²⁴²Cm, and damage to the matrix from fission fragments. Both problems would cause swelling of the fuel.</p>
Cm	<p>Very problematical. The isotopic composition of ex-reactor Cm is dominated by ²⁴⁴Cm which has a half-life of 18.1 years by alpha decay. It also has a relatively large neutron emission rate through spontaneous fission. Construction of Cm bearing fuel after a standard delay of 5 years cooling would produce a fuel which would have a neutron emission rate around twice that of standard LWR MOX fuel and a heat output around 10 times higher. There would be extreme difficulty in handling this fuel. Accordingly the most promising management scheme seems to be storage for a century or so to allow decay of the lower isotopes to plutonium. There is a further difficulty in that the cooled Cm would have to be irradiated in an extremely hard neutron spectrum to avoid producing higher, longer-lived Cm isotopes.</p>

²⁵ Volckaert G., Mallants D., Bush R., Lambers L., 'Long-term environmental impact of underground disposal of P&T waste', Actinide and fission product partitioning and transmutation, Proceedings of the fifth information exchange meeting, Mol, Belgium, 1998, pp. 463-474.