Processing of Used Nuclear Fuel

(Updated September 2014)

- **Used nuclear fuel has long been reprocessed to extract fissile materials for recycling and to reduce the volume of high-level wastes.**

- **Recycling is largely based on the conversion of fertile U-238 to fissile plutonium.**

- **New reprocessing technologies are being developed to be deployed in conjunction with fast neutron reactors which will burn all long-lived actinides.**

- **A significant amount of plutonium recovered from used fuel is currently recycled into MOX fuel; a small amount of recovered uranium is recycled.**

A key, nearly unique, characteristic of nuclear energy is that used fuel may be reprocessed to recover fissile and fertile materials in order to provide fresh fuel for existing and future nuclear power plants. Several European countries, Russia and Japan have had a policy to reprocess used nuclear fuel, although government policies in many other countries have not yet addressed the various aspects of reprocessing.

Over the last 50 years the principal reason for reprocessing used fuel has been to recover unused uranium and plutonium in the used fuel elements and thereby close the fuel cycle, gaining some 25% to 30% more energy from the original uranium in the process and thus contributing to energy security. A secondary reason is to reduce the volume of material to be disposed of as high-level waste to about one-fifth. In addition, the level of radioactivy in the waste from reprocessing is much smaller and after about 100 years falls much more rapidly than in used fuel itself.

In the last decade interest has grown in recovering all long-lived actinides together (*i.e.* with plutonium) so as to recycle them in fast reactors so that they end up as short-lived fission products. This policy is driven by two factors: reducing the long-term radioactivity in high-level wastes, and reducing the possibility of plutonium being diverted from civil use – thereby increasing proliferation resistance of the fuel cycle. If used fuel is not reprocessed, then in a century or two the built-in radiological protection will have diminished, allowing the plutonium to be recovered for illicit use (though it is unsuitable for weapons due to the non-fissile isotopes present).

Reprocessing used fuel[a] to recover uranium (as reprocessed uranium, or RepU) and plutonium (Pu) avoids the wastage of a valuable resource. Most of it – about 96% – is uranium, of which less than 1% is the fissile U-235 (often 0.4-0.8%); and up to 1% is plutonium. Both can be recycled as fresh fuel, saving up to 30% of the natural uranium otherwise required. The materials potentially available for recycling (but locked up in stored used fuel) could conceivably run the US reactor fleet of about 100 GWe for almost 30 years with no new uranium input.

So far, almost 90,000 tonnes (of 290,000 t discharged) of used fuel from commercial power reactors has been reprocessed. Annual reprocessing capacity is now some 4000 tonnes per year for normal oxide fuels, but not all of it is operational.

Between now and 2030 some 400,000 tonnes of used fuel is expected to be generated worldwide, including 60,000 t in North America and 69,000 t in Europe.

World commercial reprocessing capacity[1,2]

(tonnes per year)		
LWR fuel	France, La Hague	1700
	UK, Sellafield (THORP)	600
	Russia, Ozersk (Mayak)	400
	Japan (Rokkasho)	800*
	Total LWR (approx)	**3500**
Other nuclear fuels	UK, Sellafield (Magnox)	1500
	India (PHWR, 4 plants)	330
	Japan, Tokai MOX	40
	Total other (approx)	**1870**
Total civil capacity		**5370**

* now expected to start operation in 2014

Products of reprocessing

Used fuel contains a wide array of nuclides in varying valency states. Processing it thus inherently complex chemically, and made more difficult because many of those nuclides are also radioactive.

The composition of reprocessed uranium (RepU) depends on the initial enrichment and the time the fuel has been in the reactor, but it is mostly U-238. It will normally have less than 1% U-235 (typically about 0.5% U-235) and also smaller amounts of U-232 and U-236 created in the reactor. The U-232, though only in trace amounts, has daughter nuclides which are strong gamma-emitters, making the material difficult to handle. However, once in the reactor, U-232 is no problem (it captures a neutron and becomes fissile U-233). It is largely formed through alpha decay of Pu-236, and the concentration of it peaks after about 10 years of storage.

The U-236 isotope is a neutron absorber present in much larger amounts, typically 0.4% to 0.6% – more with higher burn-up – which means that if reprocessed uranium is used for fresh fuel in a conventional reactor it must be enriched significantly more (*e.g.* up to one-tenth more) than is required for natural uranium[b]. Thus RepU from low burn-up fuel is more likely to be suitable for re-enrichment, while that from high burn-up fuel is best used for blending or MOX fuel fabrication.

The other minor uranium isotopes are U-233 (fissile), U-234 (from original ore, enriched with U-235, fertile), and U-237 (short half-life beta emitter). None of these affects the use of handling of the reprocessed uranium significantly. In the future, laser enrichment techniques may be able to remove these isotopes.

Reprocessed uranium (especially from earlier military reprocessing) may also be contaminated with traces of fission products and transuranics. This will affect its suitability for recycling either as blend material or via enrichment. Over 2002-06 USEC successfully cleaned up 7400 tonnes of technetium-contaminated uranium from the US Department of Energy.

Most of the separated uranium (RepU) remains in storage, though its conversion and re-enrichment (in UK, Russia and Netherlands) has been demonstrated, along with its re-use in fresh fuel. Some 16,000 tonnes of RepU from Magnox reactors in UK has been used[c] to make about 1650 tonnes of enriched AGR fuel. In Belgium, France, Germany and Switzerland over 8000 tonnes of RepU has been recycled into nuclear power plants. In Japan the figure is over 335 tonnes in tests and in India about 250 t of RepU has been recycled into PHWRs. Allowing for impurities affecting both its treatment and use, RepU value has been assessed as about half that of natural uranium.

Plutonium from reprocessing will have an isotopic concentration determined by the fuel burn-up level. The higher the burn-up levels, the less value is the plutonium, due to increasing proportion of non-fissile isotopes and minor actinides, and depletion of fissile plutonium isotopes[d]. Whether this plutonium is separated on its own or with other actinides is a major policy issue relevant to reprocessing (see section on Reprocessing policies below).

Most of the separated plutonium is used almost immediately in mixed oxide (MOX) fuel. World MOX production capacity is currently around 200 tonnes per year, nearly all of which is in France (see page on Mixed Oxide (MOX) Fuel).

Inventory of separated recyclable materials worldwide[3]

	Quantity (tonnes)	Natural U equivalent (tonnes)
Plutonium from reprocessed fuel	320	60,000
Uranium from reprocessed fuel	45,000	50,000
Ex-military plutonium	70	15,000
Ex-military high-enriched uranium	230	70,000

Estimated Savings in Natural Uranium Requirements due to Recycled U & Pu (tU)

	Use of enriched RepU	Use of Pu in MOX	Total Unat replaced
2013	1850	1220	3070
2015	1850	1260	3110
2020	1880	2140	4020
2025	1560	3200	4760
2030	1270	3650	4920

Source: WNA Market Report 2013, Table 5.20 (includes US weapons Pu)

History of reprocessing

A great deal of hydrometallurgical reprocessing has been going on since the 1940s, originally for military purposes, to recover plutonium for weapons (from low burn-up used fuel, which has been in a reactor for only a very few months). In the UK, metal fuel elements from the Magnox generation gas-cooled commercial reactors have been reprocessed at Sellafield for about 50 years[e]. The 1500 t/yr Magnox reprocessing plant undertaking this has been successfully developed to keep abreast of evolving safety, hygiene and other regulatory standards. From 1969 to 1973 oxide fuels were also reprocessed, using part of the plant modified for the purpose, and the 900 t/yr Thermal Oxide Reprocessing Plant (THORP) at Sellafield was commissioned in 1994.

In the USA, no civil reprocessing plants are now operating, though three have been built. The first, a 300 t/yr plant at West Valley, New York, was operated successfully from 1966-72. However, escalating regulation required plant modifications which were deemed uneconomic, and the plant was shut down. The second was a 300 t/yr plant built at Morris, Illinois, incorporating new technology which, although proven on a pilot-scale, failed to work successfully in the production plant. It was declared inoperable in 1974. The third was a 1500 t/yr plant at Barnwell, South Carolina, which was aborted due to a 1977 change in government policy which ruled out all US civilian reprocessing as one facet of US non-proliferation policy. In all, the USA has over 250 plant-

years of reprocessing operational experience, the vast majority being at government-operated defence plants since the 1940s.

The main one of these is H Canyon at Savannah River, which commenced operation in 1955. It historically recovered uranium and neptunium from aluminium-clad research reactor fuel, both foreign and domestic. It could also recover Np-237 and Pu-238 from irradiated targets. H Canyon also reprocessed a variety of materials for recovery of uranium and plutonium both for military purposes and later high-enriched uranium for blending down into civil reactor fuel. In 2011 reprocessing of research reactor fuel was put on hold pending review of national policy for high-level wastes. Currently it is preparing plutonium for use in the new MOX plant at Savannah River.

In 2014, H Canyon completed reprocessing the long-stored uranium-thorium metal fuel from the 20 MWt Sodium Reactor Experiment (SRE), which had a high proportion of U-233. The sodium-cooled graphite-moderated SRE operated in California over 1957-64 and was the first US reactor to feed electricity to a grid. The uranium and actinides will be vitrified.

In France a 400 t/yr reprocessing plant operated for metal fuels from gas-cooled reactors at Marcoule until 1997. At La Hague, reprocessing of oxide fuels has been done since 1976, and two 800 t/yr plants are now operating, with an overall capacity of 1700 t/yr.

French utility EDF has made provision to store reprocessed uranium (RepU) for up to 250 years as a strategic reserve. Currently, reprocessing of 1150 tonnes of EDF used fuel per year produces 8.5 tonnes of plutonium (immediately recycled as MOX fuel) and 815 tonnes of RepU. Of this about 650 tonnes is converted into stable oxide form for storage. EDF has demonstrated the use of RepU in its 900 MWe power plants, but it is currently uneconomic due to conversion costing three times as much as that for fresh uranium, and enrichment needing to be separate because of U-232 and U-236 impurities. The presence of the gamma-emitting U-232 requires shielding and so should be handled in dedicated facilities; and the presence of the neutron-absorbing U-236 isotope means that a higher level of enrichment is required compared with fresh uranium.

The plutonium is immediately recycled via the dedicated Melox mixed oxide (MOX) fuel fabrication plant. The reprocessing output in France is co-ordinated with MOX plant input, to avoid building up stocks of plutonium. If plutonium is stored for some years the level of americium-241, the isotope used in household smoke detectors, will accumulate and make it difficult to handle through a MOX plant due to the elevated levels of gamma radioactivity.

India has two 100 t/yr oxide fuel plants operating at Tarapur with another at Kalpakkam and a smaller one at Trombay, and Japan is starting up a major (800 t/yr) plant at Rokkasho while having had most of its used fuel reprocessed in Europe meanwhile. To 2006 it had a small (90 t/yr) reprocessing plant operating at Tokai Mura.

Russia has an old 400 t/yr RT-1 oxide fuel reprocessing plant at Ozersk (Chelyabinsk), and the partly-built 3000 t/yr RT-2 plant at Zheleznogorsk (Krasnoyarsk) is being redesigned for completion about 2025. An underground military reprocessing plant there is decommissioned.

Reprocessing policies

Conceptually reprocessing can take several courses, separating certain elements from the remainder, which becomes high-level waste. Reprocessing options include:

- Separate U, Pu, (as today).

- Separate U, Pu+U (small amount of U).

- Separate U, Pu, minor actinides[f].

- Separate U, Pu+Np, Am+Cm.

- Separate U+Pu all together.

- Separate U, Pu+actinides, certain fission products.

In today's reactors, reprocessed uranium (RepU) needs to be enriched, whereas plutonium goes straight to mixed oxide (MOX) fuel fabrication. This situation has two perceived problems: the separated plutonium is a potential proliferation risk, and the minor actinides remain in the separated waste, which means that its radioactivity is longer-lived than if it comprised fission products only.

As there is no destruction of minor actinides, recycling through light water reactors delivers only part of the potential waste management benefit. For the future, the focus is on removing the actinides from the final waste and burning them with the recycled uranium and plutonium in fast neutron reactors. (The longer-lived fission products may also be separated from the waste and transmuted in some other way.) Hence the combination of reprocessing followed by recycling in today's reactors should be seen as an interim phase of nuclear power development, pending widespread use of fast neutron reactors.

All but one of the six Generation IV reactors being developed have closed fuel cycles which recycle all the actinides. Although US policy has been to avoid reprocessing, the US budget process for 2006 included $50 million to develop a plan for "integrated spent fuel recycling facilities", and a program to achieve this with fast reactors has become more explicit since.

In November 2005 the American Nuclear Society released a position statement[4] saying that it "believes that the development and deployment of advanced nuclear reactors based on fast-neutron fission technology is important to the sustainability, reliability and security of the world's long-term energy supply." This will enable "extending by a hundred-fold the amount of energy extracted from the same amount of mined uranium". The statement envisages on-site reprocessing of used fuel from fast reactors and says that "virtually all long-lived heavy elements are eliminated during fast reactor operation, leaving a small amount of fission product waste which requires assured isolation from the environment for less than 500 years."

In February 2006 the US government announced the Global Nuclear Energy Partnership (GNEP) through which it would "work with other nations possessing advanced nuclear technologies to develop new proliferation-resistant recycling technologies in order to produce more energy, reduce waste and minimise proliferation concerns." GNEP goals included reducing US dependence on imported fossil fuels, and building a new generation of nuclear power plants in the USA. Two significant new elements in the strategy were new reprocessing technologies at advanced recycling centres, which separate all transuranic elements together (and not plutonium on its own) starting with the UREX+ process (see section on Developments of PUREX below), and 'advanced burner reactors' to consume the result of this while generating power.

GE Hitachi Nuclear Energy (GEH) is developing this concept by combining electrometallurgical separation (see section on Electrometallurgical 'pyroprocessing' below) and burning the final product

in one or more of its PRISM fast reactors on the same site. The first two stages of the separation remove uranium which is recycled to light water reactors, then fission products which are waste, and finally the actinides including plutonium.

In mid-2006 a report[5] by the Boston Consulting Group for Areva and based on proprietary Areva information showed that recycling used fuel in the USA using the COEX aqueous process (see Developments of PUREX below) would be economically competitive with direct disposal of used fuel. A $12 billion, 2500 t/yr plant was considered, with total capital expenditure of $16 billion for all related aspects. This would have the benefit of greatly reducing demand on space at the planned Yucca Mountain repository.

Boston Consulting Group gave four reasons for reconsidering US used fuel strategy which has applied since 1977:

- Cost estimates for direct disposal at Yucca Mountain had risen sharply and capacity was limited (even if doubled)

- Increased US nuclear generation, potentially from 103 to 160 GWe

- The economics of reprocessing and associated waste disposal have improved

- There is now a lot of experience with civil reprocessing.

Soon after this the US Department of Energy said that it might start the GNEP (now IFNEC) program using reprocessing technologies that "do not require further development of any substantial nature" such as COEX while others were further developed. It also flagged detailed siting studies on the feasibility of this accelerated "development and deployment of advanced recycling technologies by proceeding with commercial-scale demonstration facilities."

Reprocessing today – PUREX

All commercial reprocessing plants use the well-proven hydrometallurgical PUREX (plutonium uranium extraction) process. This involves dissolving the fuel elements in concentrated nitric acid. Chemical separation of uranium and plutonium is then undertaken by solvent extraction steps (neptunium – which may be used for producing Pu-238 for thermo-electric generators for spacecraft – can also be recovered if required). The Pu and U can be returned to the input side of the fuel cycle – the uranium to the conversion plant prior to re-enrichment and the plutonium straight to MOX fuel fabrication.

Alternatively, some small amount of recovered uranium can be left with the plutonium which is sent to the MOX plant, so that the plutonium is never separated on its own. This is known as the COEX (co-extraction of actinides) process, developed in France as a 'Generation III' process, but not yet in use (see next section). Japan's new Rokkasho plant uses a modified PUREX process to achieve a similar result by recombining some uranium before denitration, with the main product being 50:50 mixed oxides.
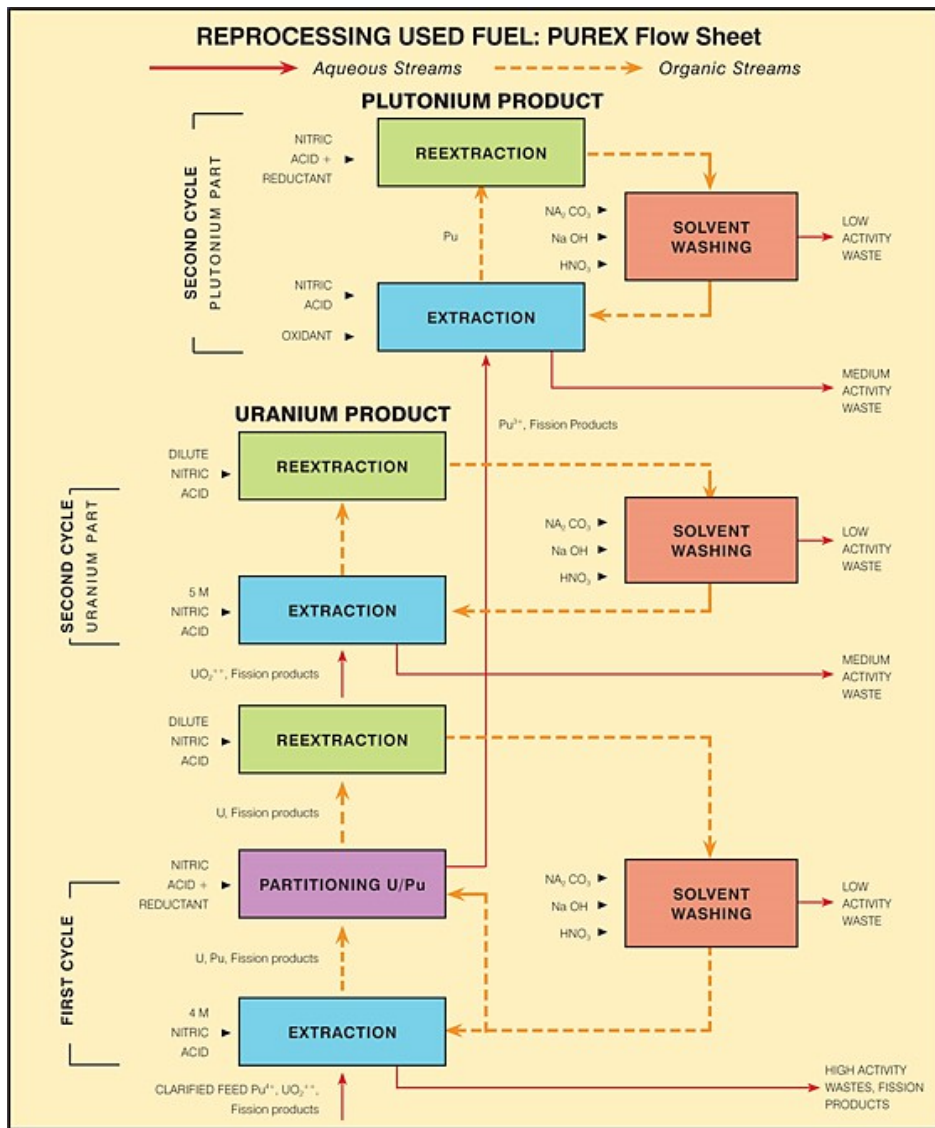
In either case, the remaining liquid after Pu and U are removed is high-level waste, containing about 3% of the used fuel in the form of fission products and minor actinides (Np, Am, Cm). It is highly radioactive and continues to generate a lot of heat. It is conditioned by calcining and incorporation of

the dry material into borosilicate glass, then stored pending disposal. In principle any compact, stable, insoluble solid is satisfactory for disposal.

The Thermal Oxide Reprocessing Plant (THORP) at Sellafield, UK
The smaller black building to the rear is the vitrification plant.
(Sellafield Ltd.)

Chemistry of Purex (see flowsheet below)

REPROCESSING USED FUEL: PUREX Flow Sheet

The used fuel is chopped up and dissolved in hot concentrated nitric acid. The first stage separates the uranium and plutonium in the aqueous nitric acid stream from the fission products and minor actinides by a countercurrent solvent extraction process, using tributyl phosphate dissolved in kerosene or dodecane. In a pulsed column uranium and plutonium enter the organic phase while the fission products and other elements remain in the aqueous raffinate.

In a second pulsed column uranium is separated from plutonium by reduction with excess U^{4+} added to the aqueous stream. Plutonium is then transferred to the aqueous phase while the mixture of U^{4+} and U^{6+} remains in the organic phase. It is then stripped from the organic solvent with dilute nitric acid.

The plutonium nitrate is concentrated by evaporation then subject to an oxalate precipitation process followed by calcination to produce PuO_2 in powder form. The uranium nitrate is concentrated by evaporation and calcined to produce UO_3 in powder form. It is then converted to UO_2 product by reduction in hydrogen.

Developments of PUREX

A modified version of the PUREX that does not involve the isolation of a plutonium stream is the UREX (uranium extraction) process. This process can be supplemented to recover the fission products iodine, by volatilisation, and technetium, by electrolysis. Research at the French Atomic Energy Commission (*Commissariat à l'énergie atomique*, CEA) has shown the potential for 95% and 90% recoveries of iodine and technetium respectively. The same research effort has demonstrated separation of caesium.

The US Department of Energy was developing the UREX+ processes under the Global Nuclear Energy Partnership (GNEP) program (see page on Global Nuclear Energy Partnership). In these, only uranium and technetium are recovered initially (in the organic phase) for recycle and the residual is treated to recover plutonium with other transuranics. The fission products then comprise most of the high-level waste. The central feature of this system was to increase proliferation resistance by keeping the plutonium with other transuranics – all of which are then destroyed by recycling in fast reactors.* However, there are chemical safety problems with the Pu-Np recovery in the aqueous phase, and the process has been abandoned since 2008.

* Several variations of UREX+ have been developed, with the differences being in how the plutonium is combined with various minor actinides, and lanthanide and non-lanthanide fission products are combined or separated. UREX+1a combines plutonium with three minor actinides, but this gives rise to problems in fuel fabrication due to americium being volatile and curium a neutron emitter. Remote fuel fabrication facilities would therefore be required, leading to high fuel fabrication costs and requiring significant technological development. An alternative process, UREX+3, was therefore considered. This left only neptunium with the plutonium and the result is closer to a conventional MOX fuel. However, it is less proliferation-resistant than UREX+1a.

Energy Solutions holds the rights to PUREX in the USA and has developed NUEX, which separates uranium and then all transuranics (including plutonium) together, with fission products separately. NUEX is similar to UREX+1a but has more flexibility in the separations process.

Areva and CEA have developed three processes on the basis of extensive French experience with PUREX:

- The COEX process based on co-extraction and co-precipitation of uranium and plutonium (and usually neptunium) together, as well as a pure uranium stream (eliminating any separation of plutonium on its own). It is close to near-term industrial deployment, and allows high MOX performance for both light-water and fast reactors. COEX may have from 20 to 80% uranium in the product, the baseline is 50%.

- The DIAMEX-SANEX processes involving selective separation of long-lived radionuclides (with a focus on Am and Cm separation) from short-lived fission products. This can be implemented with COEX, following separation of U-Pu-Np. U-Pu and minor actinides are recycled separately in Generation IV fast neutron reactors.

- The GANEX (grouped extraction of actinides) process co-precipitates some uranium with the plutonium (as with COEX), but then separates minor actinides and some lanthanides from the short-lived fission products. The uranium, plutonium and minor actinides together become fuel in Generation IV fast neutron reactors, the lanthanides become waste. It is being demonstrated at ATALANTE and La Hague from 2008 as part of

a French-Japanese-US Global Actinide Cycle International Demonstration (GACID) with the product transmutation being initially in France's Phenix fast reactor (see Transmutation section below) and subsequently in Japan's Monju.

Initial work is at ATALANTE[g] at Marcoule, which started operation in 1992 to consolidate reprocessing and recycling research from three other sites. By 2012, it is expected to have demonstrated GANEX, and fabrication of oxide fuel pins combining U, Pu, Am, Np & Cm. Then work will proceed at La Hague on partitioning and fabrication of minor actinide-bearing fuels without the curium. From 2020 these will be irradiated in the Monju fast reactor, Japan.

All three processes were to be assessed in 2012, so that two pilot plants could be built to demonstrate industrial-scale potential:

- One – possibly based on COEX – to make the driver fuel for the Generation IV reactor planned to be built by CEA by 2020.

- One to produce fuel assemblies containing minor actinides for testing in Japan's Monju fast reactor and in France's Generation IV fast reactor.

In the longer term, the goal is to have a technology validated for industrial deployment of Generation IV fast reactors about 2040, at which stage the present La Hague plant will be due for replacement.

US research in recent years has focused on the TALSPEAK process which would come after a modified PUREX or COEX process to separate trivalent lanthanides from trivalent actinides, but this is only at bench scale so far. Originally in 1960s it was developed to separate actinides, notably Am & Cm from lanthanides.

Another alternative reprocessing technology being developed by Mitsubishi and Japanese R&D establishments is Super-DIREX (supercritical fluid direct extraction). This is designed to cope with uranium and MOX fuels from light water and fast reactors. The fuel fragments are dissolved in nitric acid with tributyl phosphate (TBP) and supercritical CO_2, which results in uranium, plutonium and minor actinides complexing with TBP.

A new reprocessing technology is part of the reduced-moderation water reactor (RMWR) concept. This is the fluoride volatility process, developed in the 1980s, which is coupled with solvent extraction for plutonium to give Hitachi's Fluorex process. In this, 90-92% of the uranium in the used fuel is volatalised as UF_6, then purified for enrichment or storage. The residual is put through a Purex circuit which separates fission products and minor actinides, leaving the unseparated U-Pu mix (about 4:1) to be made into MOX fuel.

Used MOX fuel can be handled through the PUREX process, though it contains more plutonium (especially even-numbered isotopes) and minor actinides than used U oxide fuel. In 1991-92 2.1 tonnes of MOX was reprocessed at Marcoule and 4.7 tonnes was reprocessed La Hague.

Partitioning goals

Several factors give rise to a more sophisticated view of reprocessing today, and use of the term partitioning reflects this. First, new management methods for high and intermediate-level nuclear wastes are under consideration, notably partitioning-transmutation (P&T) and partitioning-conditioning (P&C), where the prime objective is to separate long-lived radionuclides from short-lived ones. Secondly, new fuel cycles such as those for fast neutron reactors (including a lead-

cooled one) and fused salt reactors, and the possible advent of accelerator-driven systems, require a new approach to reprocessing. Here the focus is on electrolytic processes ('pyroprocessing') in a molten salt bath. The term 'electrometallurgical' is also increasingly used to refer to this in the USA.

The main radionuclides targeted for separation for P&T or P&C are the actinides neptunium, americium and curium (along with U & Pu), and the fission products iodine-129, technetium-99, caesium-135 and strontium-90. Removal of the latter two significantly reduces the heat load of residual conditioned wastes. In Japan, platinum group metals are also targeted, for commercial recovery. Of course any chemical process will not separate different isotopes of any particular element.

Efficient separation methods are needed to achieve low residuals of long-lived radionuclides in conditioned wastes and high purities of individual separated ones for use in transmutation targets or for commercial purposes (*e.g.* americium for household smoke detectors). If transumation targets are not of high purity then the results of transmutation will be uncertain. In particular fertile uranium isotopes (*e.g.* U-238) in a transmutation target with slow neutrons will generate further radiotoxic transuranic isotopes through neutron capture.

Achieving effective full separation for any transmutation program is likely to mean electrolytic processing of residuals from the PUREX or similar aqueous processes.

A BNFL-Cogema study in 2001 reported that 99% removal of actinides, Tc-99 & I-129 would be necessary to justify the effort in reducing the radiological load in a waste repository. A US study identified a goal of 99.9% removal of the actinides and 95% removal of technetium and iodine. In any event, the balance between added cost and societal benefits is the subject of considerable debate.

Electrometallurgical 'pyroprocessing'

Electrolytic/electrometallurgical processing techniques ('pyroprocessing') to separate nuclides from a radioactive waste stream have been under development in the US Department of Energy laboratories, notably Argonne, as well as by the Korea Atomic Energy Research Institute (KAERI) in conjunction with work on DUPIC (see section on Recycled LWR uranium and used fuel in PHWRs below). Their main development has possibly been in Russia, where they are to be the mainstay of closing the fuel cycle fully by about 2020. There has been particular emphasis on fast reactor fuels.

So-called pyroprocessing involves several stages including: volatilisation; liquid-liquid extraction using immiscible metal-metal phases or metal-salt phases; electrolytic separation in molten salt; and fractional crystallisation. They are generally based on the use of either fused salts such as chlorides or fluorides (eg LiCl+KCl or LiF+CaF2) or fused metals such as cadmium, bismuth or aluminium. They are most readily applied to metal rather than oxide fuels, and are envisaged for fuels from Generation IV reactors.

Electrometallurgical 'pyroprocessing' can readily be applied to high burn-up fuel and fuel which has had little cooling time, since the operating temperatures are high already. However, such processes are at an early stage of development compared with hydrometallurgical processes already operational.

Separating (partitioning) the actinides contained in a fused salt bath is by electrodeposition on a cathode, so involves all the positive ions without the possibility of chemical separation of heavy elements such as in PUREX and its derivatives. This cathode product can then be used in a fast reactor.

So far only one electrometallurgical technique has been licensed for use on a significant scale. This is the IFR (integral fast reactor) electrolytic process developed by Argonne National Laboratory in the USA and used for pyroprocessing the used fuel from the EBR-II experimental fast reactor which ran from 1963-1994. This application is essentially a partitioning-conditioning process, because neither plutonium nor other transuranics are recovered for recycle. The process is used to facilitate the disposal of a fuel that could not otherwise be sent directly to a geologic repository. The used uranium metal fuel is dissolved in a LiCl+KCl molten bath, the U is deposited on a solid cathode, while the stainless steel cladding and noble metal fission products remain in the salt, and are consolidated to form a durable metallic waste. The transuranics and fission products in salt are then incorporated into a zeolite matrix which is hot pressed into a ceramic composite waste. The highly-enriched uranium recovered from the EBR-II driver fuel is down-blended to less than 20% enrichment and stored for possible future use.

The PYRO-A process, being developed at Argonne to follow the UREX process, is a pyrochemical process for the separation of transuranic elements and fission products contained in the oxide powder resulting from denitration of the UREX raffinate. The nitrates in the residual raffinate acid solution are converted to oxides, which are then reduced electrochemically in a LiCl-Li2O molten salt bath. The more chemically active fission products (eg Cs, Sr) are not reduced and remain in the salt. The metallic product is electrorefined in the same salt bath to separate the transuranic elements on a solid cathode from the rest of the fission products. The salt bearing the separated fission products is then mixed with a zeolite to immobilize the fission products in a ceramic composite waste form. The cathode deposit of transuranic elements is then processed to remove any adhering salt and is formed into ingots for subsequent fabrication of transmutation targets.

The PYRO-B process, has been developed for the processing and recycle of used fuel from a transmuter (fast) reactor. A typical transmuter fuel is free of uranium and contains recovered transuranics in an inert matrix such as metallic zirconium. In the PYRO-B processing of such fuel, an electrorefining step is used to separate the residual transuranic elements from the fission products and recycle the transuranics to the reactor for fissioning. Newly-generated technetium and iodine are extracted for incorporation into transmutation targets, and the other fission products are sent to waste.

The KAERI advanced spent fuel conditioning process (ACP) involves separating uranium, transuranics including plutonium, and fission products including lanthanides. It utilises a high-temperature lithium-potassium chloride bath from which uranium is recovered electrolytically to concentrate the actinides, which are then removed together (with some remaining fission products). The latter product is then fabricated into fast reactor fuel without further treatment. The process is intrinsically proliferation-resistant because it is so hot radiologically, and the curium provides a high level of spontaneous neutrons. It recycles about 95% of the used fuel. Development of this process is at the heart of US-South Korean nuclear cooperation, and is central to the renewal of the bilateral

US-South Korean nuclear cooperation agreement in March 2014, so is already receiving considerable attention in negotiations.

With US assistance through the International Nuclear Energy Research Initiative (I-NERI) program KAERI built the Advanced Spent Fuel Conditioning Process Facility (ACPF) at KAERI. KAERI hopes the project will be expanded to engineering scale by 2012, leading to the first stage of a Korea Advanced Pyroprocessing Facility (KAPF) starting in 2016 and becoming a commercial-scale demonstration plant in 2025.

South Korea has declined an approach from China to cooperate on electrolytic reprocessing, and it has been rebuffed by Japan's CRIEPI due to government policy.

Russian pyroprocessing consists of three main stages: dissolution of the used nuclear fuel in molten salts, precipitation of plutonium dioxide or electrolytic deposition of uranium and plutonium dioxides from the melt, then processing the material deposited on the cathode or precipitated at the bottom of the melt for granulated fuel production. The process recovers the cathode deposits without changing their chemical composition or redistributing the plutonium. All used fuel is reprocessed with the goal of having a complete recycle of plutonium, neptunium, americium, and curium as well as the uranium. This process, combined with vibropacking* in fuel fabrication will be used to produce fuel for the BN-800 fast reactor. The technologies complement one another well and involve high levels of radioactivity throughout, making them self-protecting against diversion or misuse.

* Vibropacked MOX fuel (VMOX) is seen as the way forward. This is made by agitating a mechanical mixture of $(U, Pu)O_2$ granulate and uranium powder, which binds up excess oxygen and some other gases (that is, operates as a getter) and is added to the fuel mixture in proportion during agitation. The getter resolves problems arising from fuel-cladding chemical interactions. The granules are crushed UPuO2 cathode deposits from pyroprocessing. VMOX needs to be made in hot cells. It has been used in BOR-60 since 1981 (with 20-28% Pu), and tested in BN-350 and BN-600.

At MCC Zheleznogorsk which hosts a pyroprocessing module, civil PuO2, ex-weapons metal Pu and DU are combined into granulated MOX. This is sent to the Russian Institute of Atomic Reactors (RIAR) at Dimitrovgrad for vibropacking and producing fuel assemblies for the BN-800 fast reactor. In future fuel for BREST will follow the same route. RIAR has substantial experience in reprocessing used fuel from BOR-60 and BN-350 fast reactors and has developed a pilot scale pyroprocessing demonstration facility for fast reactor fuel.

GE Hitachi is designing an Advanced Recycling Centre (ARC) which integrates electrometallurgical processing with its PRISM fast reactors. The main feed is used fuel from light water reactors, and the three products are fission products, uranium, and transuranics (Np, Pu, Am, Cm), which become fuel for the fast reactors (with some of the uranium). The uranium can be re-enriched or used as fuel for Candu reactors. As the cladding reaches its exposure limits, used PRISM fuel is recycled after removal of fission products. A full commercial-scale ARC would comprise an electrometallurgical plant and three power blocks of 622 MWe each (six 311 MWe reactor modules), but a "full-scale building block" of ARC is a 50 t/yr electrometallurgical plant coupled to one 311 MWe reactor module, with breeding ratio of 0.8.

Recycled LWR uranium and used fuel in PHWRs

The established approach to using RepU is recycling it through conversion and enrichment, for light water reactors. Another approach to used nuclear fuel recycling is directing recycled uranium (referred to as RepU, reprocessed uranium), or actual used light water reactor (LWR) fuel, into pressurized heavy water reactors (PHWRs). This may be directly using RepU, or by blending RepU with depleted uranium to give natural uranium equivalent (NUE), or by direct use of used PWR fuel in CANDU reactors (DUPIC).

PHWRs (such as CANDU reactors) normally use as fuel natural uranium which has not undergone enrichment and so can operate fuelled by the uranium and plutonium that remains in used fuel from LWRs. This might typically contain about 0.5 to 0.9% U-235 and 0.6% Pu-239 but with significant neutron absorbers.

In unit 1 of the Qinshan Phase III plant in China, there has been a demonstration using fuel bundles with RepU from PWRs blended with depleted uranium to give natural uranium equivalent (NUE) fuel with 0.71% U-235[6]. It behaved the same as natural uranium fuel. Subject to supply from reprocessing plants, a full core of natural U equivalent (NUE) is envisaged. Following design, licensing, etc, full core implementation in both China's CANDU reactors is envisaged by the end of 2013. (Recycled plutonium will be used in MOX fuel for fast reactors.)

AECL says that it is also possible to use the RepU directly in CANDUs, without blending it down, and Qinshan III envisages this possibility with recycled uranium (RU) having 0.9% U-235.

With DUPIC, the direct use of used PWR fuel as such in CANDUs, used fuel assemblies from LWRs would be dismantled and refabricated into fuel assemblies the right shape for use in a CANDU reactor. This could be direct, involving only cutting the used LWR fuel rods to CANDU length (about 50 cm), resealing and re-engineering into cylindrical bundles suitable for CANDU geometry.

Alternatively, a "dry reprocessing" technology has been developed which removes only the volatile fission products from the used LWR fuel mix. After removal of the cladding, a thermal-mechanical process is used to reduce the used LWR fuel pellet to a powder. This could have more fresh natural uranium added, before being sintered and pressed into CANDU pellets. It would contain all the actinides and most of the fission products from irradiation in LWR.

The DUPIC technique was promoted as having certain advantages:

- No materials are separated during the refabrication process. Uranium, plutonium, fission products and minor actinides are kept together in the fuel powder and bound together again in the DUPIC fuel bundles.

- A high net destruction rate can be achieved of actinides and plutonium.

- Up to 25% more energy can be realised compared to other PWR used fuel recycling techniques.

- And a DUPIC fuel cycle could reduce a country's need for used PWR fuel disposal by 70% while reducing fresh uranium requirements by 30%.

However, as noted above, used nuclear fuel is highly radioactive and generates heat. This high activity means that the DUPIC manufacture process must be carried out remotely behind heavy shielding. While these restrictions make the diversion of fissile materials much more difficult and hence increase security, they also make the manufacture process more complex compared with that

for the original PWR fuel, which is barely radioactive before use. (NUE would be more radioactive than natural U, due to U-232 in the RU.)

Canada, which developed the CANDU reactor, and South Korea, which hosts four CANDU units as well as many PWRs, initiated a bilateral joint research program to develop DUPIC. This included the reactor physics of DUPIC fuel and the impacts on safety systems. However, as of 2013 plans for DUPIC are on hold.

The Korean Atomic Energy Research Institute (KAERI) has had a development program since 1992 to demonstrate the DUPIC fuel cycle concept. KAERI believes that although it is too early to commercialise the DUPIC fuel cycle, the key technologies are in place for a practical demonstration of the technique. Challenges which remain include the development of a technology to produce fuel pellets of the correct density, the development of remote fabrication equipment and the handling of the used PWR fuel. However, KAERI successfully manufactured DUPIC small fuel elements for irradiation tests inside the HANARO research reactor in April 2000 and fabricated full-size DUPIC elements in February 2001. AECL is also able to manufacture DUPIC fuel elements.

A further complication is the loading of highly radioactive DUPIC fuel into the CANDU reactor. Normal fuel handling systems are designed for the fuel to be hot and highly radioactive only after use, but it is thought that the used fuel path from the reactor to cooling pond could be reversed in order to load DUPIC fuel, and studies of South Korea's Wolsong CANDU units indicate that both the front- and rear-loading techniques could be used with some plant modification.

Transmutation

The objective of transumutation is to change (long-lived) actinides into fission products and long-lived fission products into significantly shorter-lived nuclides. The goal is to have wastes which become radiologically innocuous in only a few hundred years. The need for a waste repository is certainly not eliminated, but it can be smaller and simpler and the hazard posed by the disposed waste materials is greatly reduced.

Transmutation of one radionuclide into another is achieved by neutron bombardment in a nuclear reactor or accelerator-driven device. In the latter, a high-energy proton beam hitting a heavy metal target produces a shower of neutrons by spallation[h]. The neutrons can cause fission in a subcritical fuel assembly, but unlike a conventional reactor, fission ceases when the accelerator is turned off. The fuel may be uranium, plutonium or thorium, possibly mixed with long-lived wastes from conventional reactors. See also page on Accelerator-Driven Nuclear Energy.

Transmutation is mainly initiated by fast neutrons. Since these are more abundant in fast neutron reactors, such reactors are preferred for transmutation. Some radiotoxic nuclides, such as Pu-239 and the long-lived fission products Tc-99 and I-129, can be transmuted (fissioned, in the case of Pu-239) with thermal (slow) neutrons. However, a 2001 BNFL-Cogema study found that full transmutation in a light water reactor would take at least several decades, and recent research has focused on use of fast reactors. The minor actinides Np, Am and Cm (as well as the higher isotopes of plutonium), all highly radiotoxic, are much more readily destroyed by fissioning in a fast neutron energy spectrum (see Table), where they can also contribute to the generation of power.

Transmutation probabilities (%)

Isotope	thermal spectrum	fast spectrum
Np-137	3	27
Pu-238	7	70
Pu-239	63	85
Pu-240	1	55
Pu-241	75	87
Pu-242	1	53
Am-241	1	21
Am-242m	75	94
Am-243	1	23
Cm-242	1	10
Cm-243	78	94
Cm-244	4	33

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One of the main functions of France's Phenix fast neutron reactor in its last two years of operation was test burning fuel assemblies containing high concentrations of minor actinides. From mid-2007 it irradiated four fuel pins containing actinides from the US Department of Energy, two from the CEA, and two from the European Commission's Institute for Transuranics.

Further Information

Notes

a) Used fuel from light water reactors (at normal US burn-up levels) contains approximately:

- 95.6% uranium, over 98.5% of which is U-238 (the remainder consists of: trace amounts of U-232 and U-233; less than 0.02% U-234; 0.5-1.0% U-235; around 0.5% U-236; and around 0.001% U-237 – which accounts for nearly all of the activity)

- 2.9% stable fission products

- 0.9% plutonium

- 0.3% caesium & strontium (fission products)

- 0.1% iodine and technetium (fission products)

- 0.1% other long-lived fission products

- ***0.1% minor actinides (americium, curium, neptunium)***

b) For the Dutch Borssele reactor which normally uses 4.4% enriched fuel, compensated enriched reprocessed uranium (c-ERU) is 4.6% enriched to compensate for U-236.

c) Since Magnox fuel was not enriched in the first place, this is actually known as Magnox depleted uranium (MDU), which assayed about 0.4% U-235. The MDU was converted to UF6, enriched to 0.7% at BNFL's Capenhurst diffusion plant and then to 2.6% to 3.4% at Urenco's centrifuge plant. Until the mid 1990s some 60% of all AGR fuel was made from MDU and it amounted to about 1650 tonnes of low enriched uranium. Although used Magnox fuel continues to be reprocessed, recycling of MDU was discontinued in 1996 due to economic factors.

d) At anything over about 20 GWday/t burn-up the plutonium is considered to be 'reactor grade' and significantly different from weapons grade material. Some figures for the Oskarshamn 3

nuclear unit: with 30 GWd/t burn-up, 69% Pu is fissile; 40 GWd/t, 61% fissile; 50 GWd/t, 55% fissile; and 60 GWD/t, 50% fissile.

e) See Note *c* above

f) ***Minor actinides*** are americium and curium (95 & 96 in periodic table), sometimes also neptunium (93). The major actinides are plutonium (94) and uranium (92).

g) *Atelier Alpha et Laboratoire pour les Analyses de Transuraniens et Etudes de retraitement*, Alpha shop and laboratory for the analysis of transuranics and reprocessing studies.

h) Spallation is the process where nucleons are ejected from a heavy nucleus being hit by a high energy particle. In this case, a high-enery proton beam directed at a heavy target expels a number of spallation particles, including neutrons.

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