6.11 Spent Fuel Dissolution and Reprocessing Processes[☆]

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Abbreviations

ADS   accelerator driven system
AEA   global consulting firm based in the UK
AFCI   advanced fuel cycle initiative
AREVA   international group and world leader in the energy sector
ASTRID   advanced sodium technological reactor for industrial demonstration
ATALANTE   major nuclear cycle R&D facility in Marcoule (France)
BPP   bismuth phosphate process
BTBP   bis-triazine-bis-pyridine
BTP   bis-triazine-pyridine
BUTEX β,β'-dibutyoxydiethyl ether. A process based on a solvation extraction
CANDU   Canada deuterium uranium reactor

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CEA Commissariat à l'énergie atomique et aux énergies alternatives
CMPO n-octyl-phenyl-di-isobutyl-carbomoylmethyl-phosphine-oxide
COEX co-extraction of actinides
CRIEPI Central Research Institute of Electric Power Industry
DIAMEX diamide extraction
DIDPA di-isodecylphosphoric acid
DIREX direct extraction
DMDBTDMA dimethyldibutyltetradecylmalonamide
DMDCHMA dimethyldicylohexanomalonamide
DMDOHEMA dimethyldioctylhexylethoxymalonamide
DMDPhMA dimethyldiphenylmalonamide
DTPA diethylenetriaminepentaacetic acid
DUPIC direct use of pressurized water reactor spent fuel in CANDU
EBR-II Experimental Breeder Reactor-II
EDX energy-dispersive X-ray spectroscopy analysis
ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic Development
EURATOM European Atomic Energy Community
FP7 7th European Research Program
FZ Jülich Forschungszentrum Jülich
GENIV Generation IV
GIF Generation IV International Forum
GNEP Global Nuclear Energy Partnership
HDEHP diethylhexylphospohric acid
HEDTA hydroxyethyl ethylenediamine triacetic Acid
HLLW high level liquid waste
HLW high level waste
IFR integral fast reactor
ILW intermediate level waste
INL Idaho National Laboratory
JAEA Japan Atomic Energy Agency
JNC Japanese Nuclear Cycle Development Institute
JRC Joint Research Center
KAERI Korea Atomic Energy Research Institute

LLW low level waste
LWR light water reactor
MA minor actinides
MELOX MOX fuel manufacturing plant
METAPHIX metallic fuel irradiation ad PHENIX
MOX mixed oxide
NAS National Academy of Sciences
NMR nuclear magnetic resonance
NNL National Nuclear Laboratory
NOx nitrogen oxides
NPT Nuclear Non-Proliferation Treaty
OMEGA options for making extra gains from actinides
ORANO international group for nuclear fuel cycle products and services
ORNL Oak Ridge National Laboratory
P&T partitioning and transmutation
PHENIX French fast reactor
PREFRE fuel reprocessing plant (Tarapur, India)
PUREX plutonium and uranium extraction
PWR pressurized water reactor
QSAR quantitative structure-activity relationship
R&D research and development
REDOX reduction-oxidation reaction
RIAR Research Institute of Atomic Reactors (Dimitrovgrad, Russia)
SANEX selective actinide extraction progress
SEM scanning electron microscope
SETFICS solvent extraction for trivalent f-elements intra-group separation in CMPO-complexant system
SPIN SeParation-Incineration
TBP tributyl phosphate
THORP thermal oxide reprocessing plant
TOPO trioctylphosphinoxid
TPTZ tripyridyltriazine
TRPO trialkyl phosphine oxide
TRU transuranium elements
TRUEX transuranium extraction process
UREX uranium extraction process

6.11.1 Introduction

The first large-scale nuclear reactors were designed for the production of weapon grade Pu during the 2nd world war. It is obvious that the reprocessing technology was focussed on the extraction of Pu from the irradiated fuel. The bismuth phosphate process (BPP) was the first process developed and tested in the early forties at the Oak Ridge National Laboratory (ORNL) and scaled up to the kg scale in 1944 at the Hanford site. This precipitation process was already used in 1942 by Glenn Seaborg to separate microgram quantities of Pu. A recovery of U is not possible.

In the BPP process the irradiated fuel is dissolved in nitric acid and the Pu precipitated with the fission products using sodium phosphate and bismuth nitrate as $Pu_3(PO_4)_4$ after adjustment of the valence with sodium nitrite to Pu(IV). To separate Pu from the fission products the precipitate is re-dissolved in nitric acid, Pu is oxidized to Pu (VI) and the fission products re-precipitated. Several cycles are necessary to achieve a sufficient decontamination.

The first solvent extraction process used in reprocessing is the REDOX process, a continuous process, where both U and Pu are recovered at high yields and with high decontamination factors from fission products. Both uranyl and plutonyl nitrates are selectively extracted from dissolved fuel. After development at the Argonne National Laboratory and tested at the pilot scale at the Oak Ridge National Laboratory from 1948 to 1949, a REDOX plant was built in Hanford in 1951.

The BUTEX process utilizes a dibutyoxydiethyl ether solvent and nitric acid and was developed in the late 1940s at the Chalk River Laboratory and operated at an industrial scale at the Windscale plant in the UK until 1976.

Again at ORNL in 1949, a successful solvent extraction process for the recovery of pure U and Pu was developed initially to separate 239-Pu for military purposes. The PUREX process was invented by Herbert H. Anderson and Larned B. Asprey at the University of Chicago, as part of the Manhattan Project.[1]

The PUREX process is still today the standard method of extraction for the reprocessing of commercial nuclear fuels. The first industrial reprocessing plant for commercial fuels was the UP1 facility at Marcoule in France. During the 1960s and 1970s reprocessing activities were launched in Belgium, France, Germany, India, Japan, the Russian Federation, the UK and the USA. For various reasons however, only some of these plants are still in operation today (see Table 1), namely at the ORANO La Hague site in France, the THermal Oxide Reprocessing Plant (THORP) operated by the British Nuclear Group Sellafield (BNGSL) in Sellafield in the UK, the RT-1 plant in Majak in Russia, the PREFRE facility in Tarapur, India and since 2009 JNFL in Japan started operation of the Rokkasho plant.

THORP in Sellafield has stopped operation in 2018. The RT-1 facility in Majak is the only plant, where fast reactor fuel, from the BN600 and BN800 reactors is reprocessed at large scale. The final start of operation of the Rokkasho plant has been postponed also due to the Fukushima accident and the start is now scheduled for 2021.

The total amount of used fuel cumulatively generated worldwide by the beginning of 2020 is approximately 450,000 tHM, (including $\sim$68,000 t in North America and $\sim$77,000 t in Europe) of which 33,000 t will be stored and 120,000 will be reprocessed.[2]

Worldwide the used fuel generation rate is in the order of 11,000 tHM/year. The not reprocessed fuel inventory is placed into interim storage facilities, mostly on the reactor sites.

6.11.2   Fuel Cycle

The various activities associated with the production of electricity from nuclear reactions are referred to as the nuclear fuel cycle (see Fig. 1). The nuclear fuel cycle starts with the mining of U and ends with the disposal of nuclear waste. When opting for the reprocessing route of used fuel fissile materials will be recycled and remaining waste will be vitrified before final disposal.

Nuclear energy systems of the future, as they were defined by GIF, are supposed to provide a sustainable energy generation for the future.[3] The major benefits for used fuel recycling are the conservation of natural U resources, reduced dependence on foreign fossil fuel, the reduction of the nuclear waste radiotoxicity and the heat load of repositories. Major challenges for the implementation are significant costs, safety and increasing proliferation concerns also affecting the public acceptance of these technologies.

The present reactors use less than 1% of the U available in nature. With such a low efficiency, the U resources identified today worldwide might last only about 100 years with the currently installed nuclear power infrastructure. Depending on the growth rate

Table 1   Major commercial reprocessing plants in operation today

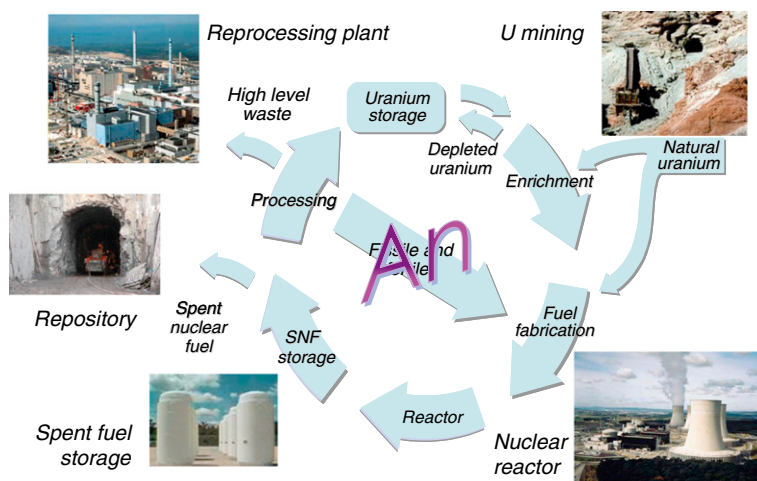| Plant	Country	Site	In operation since	Capacity (tons/year)
UP2	France	La dHague	1990	800
THORP	United Kingdom	Sellafield	1994	1000
RT-1	Russia	Mayak	1976	400
PREFRE	India	Tarapur	1982	150
RRP	Japan	Rokkasho-Mura	2009	800

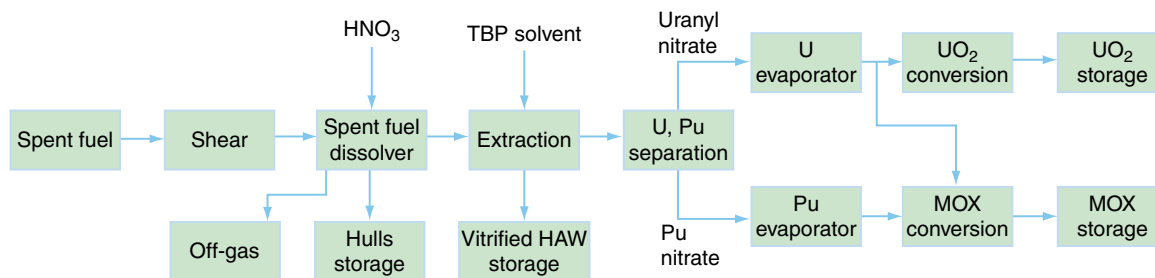**Fig. 1**   The nuclear fuel cycle.

Fig. 2 Simplified PUREX process scheme.

in the future use of nuclear systems, this time span could also be significantly lower. New energy systems using a technology based on the combination of fast neutron reactors with advanced multi-recycling of the fuel would improve the usage of natural U resources by at least a factor of 50 and possibly even higher depending on the scenarios adopted.

The new reactor concepts under development will be able to recycle most of the fertile and fissile U and Pu but also the other long-lived actinides produced in the nuclear fuel. This objective could be achieved with a so-called double-strata concept (see Fig. 2). The first part is the commercial reprocessing of spent fuel using the PUREX Process, the second stratum deals with the separation and transmutation of m the MAs and eventually long-lived fission products such as Tc or I. A drawback is a more complex and difficult fuel refabrication.

The sustainability goals include similar or even improved safety standards, higher economical competitiveness in comparison to other electricity production routes and minimized risks of proliferation. It is obvious that this change to an enhanced sustainability is a progressive process which has already started. Indeed the fuel recycling technologies which are industrially operated today are constantly improved and optimized in view of natural resource utilization and impact on the environment.

6.11.3   Industrial Reprocessing

The reprocessing of used commercial fuel is today exclusively done by the PUREX extraction process. In a reprocessing facility the used fuel is separated into three fractions: U, Pu and waste, which contains fission products and MAs. Reprocessing today enables recycling of U and Pu and possibly in the future also neptunium into fresh fuel.

Since 2007, the commercial reprocessing of nuclear is used by the nuclear industry in several countries to separate and reuse Pu in a mixture with U as mixed oxide fuel (MOX) in electricity producing reactors. The first irradiation of MOX was done in 1960 in the BR3 reactor in Belgium. Today ORANO operates in Marcoule in the South of France the world largest MOX fabrication facility called MELOX with a capacity of $\sim$1500 HM/y.

In some countries reprocessed U is also reused after enrichment as nuclear fuel. The U from reprocessing which typically contains a slightly higher concentration of U-235 than occurs in nature, can be reused as fuel after conversion and enrichment. However, reprocessed U contains also U-236, typically 0.5%, however increasing at higher burn-up. This isotope is a neutron absorber, therefore only reprocessed U from low-burn-up fuel is re-used in LWRs, while that from high burn-up fuel is best used for blending or MOX fuel fabrication.

6.11.3.1   The Irradiated Fuel

Gen-II reactors were typically designed to achieve a burn-up of about 40 GWd/MTU. With an improved fuel technology, these same reactors are now capable of achieving up to 60 GWd/MTU and R&D efforts are ongoing to further increase this burn-up value. The incentive is to reach a better economy of the energy production process. To produce a given amount of energy a lower number of fresh nuclear fuel elements is required and less used nuclear fuel elements are generated; furthermore as a consequence of this the downtime of the reactor for refueling is reduced.

At some stage however, the build-up of fission product neutron poisons achieve values which necessitate the reactor to be shut down and refueled. Used fuel is a highly radioactive and very complex material and contains at an average burn-up of 45 GWd/t about 94% U-238, approximately 1% U-235 that has not fissioned, almost 1% Pu and 4.5% fission products with the following approximate composition:

Rare Earths, Y: 24%
Ru, Tc, Rh, Pd: 16%
Kr, Xe: 15%
Zr, Nb: 14%
Mo: 13%
Cs, Rb, I, Te: 11%
Ba, Sr: 7%

Table 2   Composition (major transuranium elements and some fission products) of LWR fuels at various burnups in comparison to MOX fuel

Fuel type		LWR			MOX
Average burn-up (GWd t^{-1})		33	45	60	45
Constituent	Pu (g tU^{-1})	9.740	11.370	12.990	48.850
	Np (g tU^{-1})	433	611	887	161
	Am (g tU^{-1})	325	521	765	4.480
	Cm (g tU^{-1})	23	92	213	810
	Zr (g tU^{-1})	3.580	4.740	6.280	3.440
	Tc (g tU^{-1})	814	1.085	1.403	977
	Ru (g tU^{-1})	2.165	3.068	4.156	3.924

Depending on their thermophysical behavior during irradiation, the fission products exhibit a totally different behavior. A detailed classification of fission products was published by Kleykamp in 1985.[4]

- Dissolved in the matrix: Rb, Sr, Y, Zr, Nb, Te, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu
- Partly precipitated at grain boundaries (oxides): Rb, Sr, Zr, Nb, Mo, Se, Te, Cs, Ba
- Metallic precipitates: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Se, Te
- Volatiles: Br, Kr, Rb, I, Xe, Cs, Te

Especially at the beginning of the irradiation process when the fission event density is the highest, leading to a maximum linear power a significant relocation of fission products, depending on their volatility, takes place in the fuel. In fact, in an oxide fuel, temperature gradients of at least 500°C between the fuel periphery($\sim$500°C) and the fuel center ($>$1000°C) lead to significant migration and diffusion processes. The grain structure of the fuel initially pressed from UO_2 powder induces a precipitation of some of the fission products at the grain boundaries, noble elements partially form metallic precipitates. The most volatile elements can migrate outside of the fuel pellets where they are deposited or potentially form compounds, also with the cladding material. Parts of the volatiles are found in the fuel rod plenum.

The above mentioned burn-up has also a considerable impact on the content of transuranic elements which are formed by neutron capture of U-238. Table 2 shows the composition (major transuranium (TRU) elements and some fission products) of LWR fuels at various burn-ups in comparison to MOX fuel.

Especially for Cm the content is increased by almost a factor of 10 if the burn-up is increased from 33 to 60 GWd/t. A similar increase is observed between MOX and LWR at the same burn-up of 45 GWd/t.

New generation fast reactors are using MOX fuel with a Pu content before irradiation of about 20% instead of 5% in LWRs and because they are less sensitive to increasing amounts of fission products, burn-ups up to 200 GWd/t are possible. It is obvious that all this will have a major impact on the reprocessing process, especially with respect to radiation issues.

6.11.3.2   The Process Scheme

The well-proven hydrometallurgical PUREX process used by the commercial reprocessing plants involves the dissolution of the fuel elements in 5–6 M nitric acid, the extraction of U and Pu by the TBP solvent, the chemical separation of U and a conditioning of the products (see Fig. 2). The raffinate of the extraction process is a high active waste solution (HAW) which contains the major part of the fission products and the MAs.

U and Pu can be returned to the fuel cycle, the U to the conversion plant prior to re-enrichment and the Pu to MOX fuel fabrication.

6.11.3.2.1   Shearing/dissolution/off-gas treatment

The fuel elements are transferred to the dissolver equipment, where the shearing equipment is used to cut the fuel pins in segment of a few centimeters to ensure effective fuel dissolution. Dissolver systems with a critically safe geometry can be operated in a continuous or in a batch mode. For high throughputs in large scale reprocessing continuous rotary dissolvers are preferred. The sheared fuel falls into the dissolver basket where it is immersed in hot nitric acid, contained in the dissolver.

The following reactions can be written for the direct dissolution of the U oxide fuel pellets (not showing the dissolution of the remaining actinides and fission products):

$$3UO_2 + 8HNO_3 = 3UO_2(NO_3)_2 + 2NO + 4H_2O \tag{1}$$
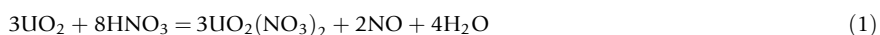
The basket retains the bulk insolubles contained in the fuel and the cladding material also called hulls, allowing them to be removed from the vessel after the dissolution process is complete. Finer insoluble solids, not retained in the basket, are removed with the product liquor and separated subsequently by settling or centrifugation, according to their size. Insolubles are washed before being removed. Also the off-gas containing mainly nitrogen oxides, I, Ru, C-14, fuel dust and aerosols are treated in a dedicated off-gas treatment plant before being either recycled (NOx) or discharged to the atmosphere.

6.11.3.2.2 Dissolver product liquor conditioning

Following its removal from the dissolver, the product liquor containing the dissolved U, Pu, MAs and fission products, clarified from any solid material, together with recovered washings is accurately measured for adherent radioactive material, before further conditioning. Therefore accountancy measurement tanks are fitted with highly efficient mixing systems, multi-level sampling, high accuracy level determination and density instrumentation and very precise tank weighing systems. After accountancy determination the liquor is transferred to conditioning tanks for further adjustments, necessary for the solvent extraction process.

6.11.3.2.3 Hulls and fines handling

The hulls are checked to be free of residual fuel and product liquor using gamma spectrometry and neutron measurement techniques (active and passive). In the unusual case of a high residual fuel content the hulls are returned to the dissolver for further treatment, otherwise they are either compacted or encapsulated in a cement matrix. The insoluble residues removed from the product liquor are added to the calcined high level waste for vitrification.

6.11.3.2.4 Solvent extraction

The central part of the reprocessing is of course the solvent extraction based on the well proven Purex process (see **Fig. 2**). The solvent is tri-butyl phosphate (TBP) diluted with odorless kerosene. The extraction happens through formation of an uranyl nitrato complex with 2 TBP molecules in the organic phase according to:

$$UO_2{}^{2+} + 2NO_3{}^- + 2TBP = UO_2(NO_3)_2 \times 2TBP \qquad (2)$$

For the primary separation cycle to remove fission products and to separate U and Pu a series of pulsed columns is used. The aqueous highly active raffinate containing the fission products from the primary separation cycle is treated by a water steam strip to remove residual solvent. After storage the solution is concentrated and immobilised by vitrification in view of a final disposal. This vitrification process shows high flexibility because also insoluble residues and alkaline effluents from the solvent regeneration can be incorporated in the glass matrix. U and Pu in the solvent phase are separated by adding U IV which acts as a Pu reductant. The reduced Pu is back-extracted into an aqueous phase which is routed to the Pu purification and finishing lines.

Where possible equipment is designed to operate without routine maintenance for the life of the plant, and the contaminated components are kept to the minimum. Equipment in contact with radioactivity can be remotely cleaned and dismantled. In cases where contaminated equipment must be maintained it may be remotely dismantled and rebuilt, or in other cases it is routed to special decontamination plant systems to allow contamination to be removed and also to allow hands-on maintenance. Because of the time involved in this type of activity, duplicate spares are generally provided for units requiring routine removal for decontamination and maintenance. Radioactively contaminated components are consigned for disposal or waste treatment.

Appropriate materials have to be selected according to the requirements of each item of equipment. In addition the integrity of all process equipment in contact with active materials has to be ensured by quality control during manufacturing, installation, inspection and testing, in order to minimize maintenance requirements and plant downtime.

Stainless steel is the standard material used in the construction of the majority of the process systems, with special materials such as titanium or zirconium utilized for particularly demanding applications. All materials to be used in hot cells are subject to checks for reliability in a radiation environment. Radiation sensitive items are either located outside the hot cells or locally shielded to minimize radiation effects. Significant progress has been achieved in the development of suitable materials. However, even more reliable materials are needed and R&D efforts are continuing with a view to enhancing the quality of materials used in modern plants.[5]

6.11.3.2.5 Product finishing

After purification the Pu is precipitated by addition of oxalic acid. The Pu oxide product, which is produced by calcination of the oxalate, is packaged in stainless steel containers. These containers are arranged in a way to provide a criticality safe geometry for storage. The solvent loaded with U from the primary separation cycle passes to purification and the resulting uranyl nitrate solution is evaporated and converted to U trioxide by thermal de-nitration. The U trioxide product is packaged in drums for interim storage in an engineered storage. Both the U and the Pu products are obtained to internationally agreed specifications and in a form suitable for recycling.

6.11.3.2.6 Reprocessing waste management

A number of categories of radioactive waste are defined, each of them requiring a specific management approach. High Level Waste (HLW) is defined as the category of waste where the heat generated by radioactive decay significantly affects the design of the waste management route. Solid Low Level Waste (LLW) is defined as the solid waste with radioactivity levels less than the authorized limits for the shallow land disposal. Intermediate Level Wastes (ILW) are those wastes between HLW and LLW. In addition very low level liquid and aerial effluents are produced, which are discharged to the environment, provided their monitoring shows compliance with discharge authorization values.

6.11.3.2.7   High level waste

The major waste fraction from the radioactivity point of view is the HLW, despite their low volumes. The general management strategy internationally adopted for this type of waste is the storage of the liquor for radioactive decay in storage tanks. The aqueous solution of fission products and MAs is concentrated up to about a factor of 15 before it is vitrified at 1150°C using a borosilicate glass matrix. The fission product content is ranged from 6% to more than 20% depending on waste composition and type of glass; the French R7T7 (R7 and T7 are the names of the vitrification plants in La Hague) glass contains 12%–18% fission products. The glass is poured into stainless steel container with a capacity of 200–500 kg where it solidifies. The vitrified waste from the operation of a 1000 MWe reactor for one year would fill about twelve of these canisters. Commercial vitrification plants in Europe produce about 1000 tonnes per year of such vitrified waste (2500 canisters) and some have been operating for more than 20 years.

The glass properties must be guaranteed to ensure the satisfactory long-term performance of the waste package. The alteration behavior of the glass is therefore assessed against the performance criteria required for interim storage or disposal purposes.

In France a cold crucible vitrification process is currently proposed as a replacement for conventional system, aiming at a simplified single-step process. The waste solution is supplied through a direct liquid-feed system at the same time as the glass frit. This would considerably reduce the size and maintenance requirements of the industrial equipment. Since 2010 this vitrification concept is in operation in the La Hague plant.

6.11.3.3   Safeguarding and Criticality of the Reprocessing

The goal to foster the peaceful uses of nuclear energy based on the Treaty on the Non-Proliferation of Nuclear Weapons (NPT), is achieved through the implementation of a highly efficient safeguarding process at the reprocessing plants. The International Atomic Energy Agency (IAEA) is in charge of inspection and verification of the peaceful uses of nuclear materials world-wide and the European Commission as guardian of the Treaties operates as an effective regional nuclear safeguard system (EURATOM) in close partnership with the IAEA.

The particular interest in bulk-handling facilities like reprocessing plants, where large quantities of Pu are handled is obvious. Nuclear material flows (in or out) are monitored at key measurement points, such as storage areas (tanks, containers, used fuel ponds), the head-end fuel treatment, shearing and dissolution area, and product storage area (Pu, U).

The National Academy of Sciences (NAS) has declared that the large and growing stocks of Pu from weapons dismantlement in the U.S. and the former Soviet Union are a "clear and present danger" to peace and security. Moreover, experts consider, that Pu of any isotopic blend is a proliferation threat, this means of course that Pu produced in the civilian fuel cycle is itself a proliferation threat. Assuring that separated Pu, from dismantled warheads as well as from civilian power programs, is under effective control has (again) become a high priority world-wide. If Pu is considered as an energy resource it is mandatory to safeguard it against diversion, putting it into active use in the civilian power program. The ultimate choice cannot be separated from the long-term strategy for use of peaceful nuclear power.

But also continued use of a once-through fuel cycle will obviously lead to an ever-increasing quantity of excess Pu, requiring safeguarding as well. Alternatively, recycling the world's stocks of Pu in fast reactors, will cap the world supply of Pu and hold it in working inventories for generating power. Transition from the current-generation light water cooled reactors (LWRs) to a future fast-reactor-based nuclear energy supply under international safeguards would, henceforth, limit world Pu inventories to the amount necessary and useful for power generation, with no further excess production.

The Integral Fast Reactor (IFR) in the US foresees a recycling of all actinides as complete as possible, with lowest possible losses to the waste, such that a perpetual safeguards of IFR waste is not necessary. The pyro-recycle process in general and of course also the one of the IFR is more proliferation resistant than the PUREX process because it does not aim at pure actinide fractions. The scale of IFR recycle equipment is compatible with co-location of power reactors and their recycle facility, eliminating off-site transportation and storage of Pu-bearing materials. Self-protecting radiation levels are unavoidable at all steps of the IFR cycle, and the resulting limitation of access contributes to making covert diversion of material from an IFR very difficult and easy to detect.

Another key issue for any reprocessing activity is the criticality. The factors that mainly affect criticality safety are:

- the fissile nuclides (U-235, Pu-238 and to a lesser extent U-233),
- the fraction of fertile nuclide diluting fissile nuclides (U-238 and Pu-240),
- the mass and concentration of fissile nuclides,
- the geometries and volumes of fissile materials in the facility,
- the neutron moderators, reflectors and absorbers,

As already mentioned in the process description section above, the criticality control in the PUREX process is mandatory throughout the process scheme and in this respect Pu is a key element, especially in view of increasing burn-up, the usage of MOX fuel and in the long term the implementation of fast reactor systems. It is obvious that advanced schemes will require similar criticality control.

6.11.4   Advanced Reprocessing

A sustainable energy generation for the future with the major objectives of an effective fuel utilization and waste minimization through recycling of all actinides can only be achieved with the corresponding substantially modified fuel cycles (see **Fig. 2**). The

Table 3   Long-lived radionuclides in used nuclear fuel

Category	Element	Isotope	Period (years)	Mass (g t^{-1})	Isotope content (%)
Minor actinides	Np	237	2 140 000	430	100
	Am	241	432	220	67
		243	7380	100	31
	Cm	243	28.5	0.3	1
		244	18.1	24	94
		245	8530	1	5
Fission products	Se	79	65,000	4.7	9
	Zr	93	1,500,000	710	20
	Tc	99	210,000	810	100
	Pd	107	6,500,000	200	16
	Sn	126	100,000	20	40
	I	129	15,700,000	170	81
	Cs	135	2,300,000	360	10

waste minimization goal is in fact based on a waste management strategy with the main motivation to reduce the long-term radiotoxicity and the repository volumes (the so-called environmental footprint) required. In such a partitioning and transmutation (P&T) scenario studied for many decades already, long-lived radionuclides are recovered (partitioning) and converted into shorter-lived or stable isotopes by irradiation (transmutation). The transmutation efficiency should be as high as possible, an objective which can be achieved in fast reactors or in dedicated reactors such as accelerator driven systems (ADSs), where a subcritical reactor is connected to a cyclotron or linear accelerator. Numerous research activities carried out in P&T have shown, that efficient P&T scenarios can shorten the time needed for isolation of nuclear waste from >100,000 years down to about 500 years. In P&T as from the viewpoint of a radiotoxicity reduction of the actual waste, P&T must first concern with the actinides, particularly Pu and the MAs (mainly Am, Cm), which make up more than 99% of the radiotoxicity already after a few hundred years of storage.[6]

Advanced reactor systems of the IVth generation, especially those using a fast neutron spectrum offer excellent transmutation features. Therefore an inherent P&T scheme can be used to reduce the long-term waste radiotoxicity. On the partitioning side, one can rely on the considerable scientific and technical progress made through domestic and international projects such as SPIN (France),[7] OMEGA (Japan),[8] GNEP/AFCI (USA) (see "Relevant Websites"), bilateral co-operations and EURATOM Framework Programs[9–13] over the last couple of decades.

The most long-lived radionuclides contained in used nuclear LWR fuel are listed in **Table 3**.

Two types of processes can be applied to the separation of long-lived radionuclides: hydro-chemical (wet) and pyro-chemical (dry) processes. Both have advantages and disadvantages, they are not to be seen as competitive options and should be used in a complementary way. The choice of the partitioning process to be applied should depend on the boundary conditions, such as the type of fuel material to be treated. If a double strata concept e.g., also proposed in the above mentioned OMEGA project would be adapted, the well established industrial reprocessing of commercial LWR fuel with a recycling of U and Pu using PUREX extraction should be logically combined in this first stratum with an advanced aqueous partitioning scheme also based on liquid-liquid extraction to separate the long-lived radionuclides. In the second stratum new generation reactors systems should preferably be combined with pyro-reprocessing, because most of the fuels under investigation for advanced reactor systems are more soluble in molten salts, shorter fuel cycles are possible due to a higher radiation resistance and a higher proliferation resistance is due to reduced product purity.

In any case an efficient and selective recovery of the key elements from the spent nuclear waste is absolutely essential for a successful sustainable fuel cycle concept. This necessitates that Am and Cm can be selectively separated from lanthanide fission products, certainly the most difficult and challenging task in advanced reprocessing of used nuclear fuel due to the very similar chemical behavior of trivalent elements. There are three major reasons to separate actinides from lanthanides:

- Neutron poisoning: lanthanides (esp. Sm, Gd, Eu) have very high neutron capture cross sections, e.g., >250,000 barn for Gd-157.
- Material burden: in used LWR fuels, the lanthanide content is up to 50 times that of Am/Cm.
- Segregation during fuel fabrication: upon fabrication, lanthanides tend to form separate phases, which grow under thermal treatment; Am and Cm would also concentrate in these phases.

Also the lanthanide – actinide separation can be derived from aqueous or pyro-chemical partitioning processes of MAs.

6.11.4.1   Advanced Aqueous Reprocessing

For the advanced fuel cycles world-wide efforts are made to use modified versions of the present industrial hydro-chemical PUREX process with the goal to cope with sustainability goals and to improve the economy and the proliferation resistance. The main objective is to separate in addition to Pu also the other TRU elements, mainly Np, Am and Cm.
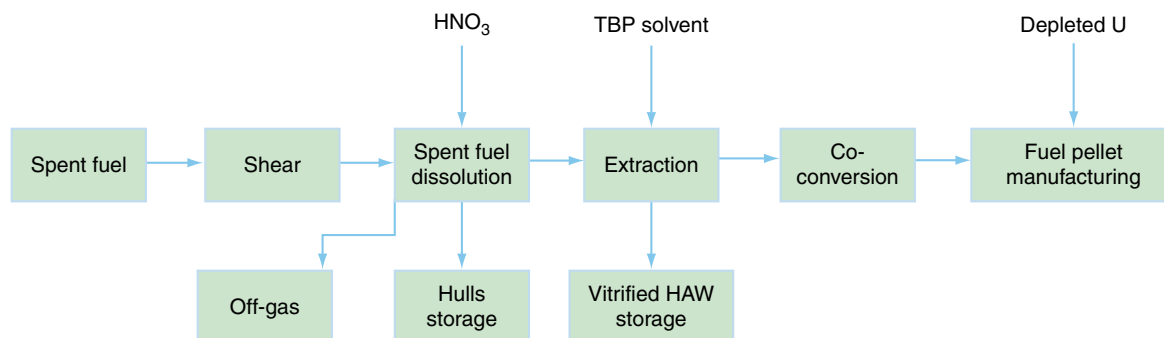
Fig. 3 COEX: a simplified PUREX process scheme.

6.11.4.1.1 UREX

The US Department of Energy proposes the UREX+ process in the frame of their advanced fuel cycle development programs, where only U is recovered and recycled. The central feature of this concept is the increased proliferation resistance by leaving the Pu with other TRUs for a grouped recycling in fast reactors. Several variations of the UREX+ process have been developed, with different options in how the Pu is combined with various MAs, lanthanide and non-lanthanide fission products. A major challenge is the fuel fabrication mainly due to the Am volatility and the fact that Cm is a strong neutron emitter. Remote fuel fabrication facilities would be required, leading to high fuel fabrication costs and significant technological development.

6.11.4.1.2 COEX

Areva and CEA have developed the COEX (co-extraction of actinides) process on the basis of extensive French experience with PUREX (see Fig. 3).

The COEX process is based on co-extraction and co-precipitation of U and Pu (and usually Np) together, as well as a pure U stream but no separation of a pure Pu fraction. This process allows to produce a high quality MOX for both light-water and fast reactors. An industrial deployment for LWR- MOX is foreseen for the near-term. The sodium fast reactor prototype ASTRID could also be based on the COEX process.

In the longer term, the goal is to have a technology validated for industrial deployment of Generation IV fast reactors around 2050, at this stage the present La Hague plant will also be due for replacement around 2050.

The long-term goal is to make a large capacity of spent fuel reprocessing (in the range 2000–3000 t/year) available with a potential to further reduce the reprocessing costs and to address the potentially increasing spent fuel reprocessing needs. Another objective is to enhance the flexibility in material management with a design adapted to treat a wide spectrum of fuel types, i.e., legacy fuel stored for decades, reprocessing of newly discharged fuel, fuels with high fissile isotopes content (MOX fuel, very high burn-up fuels).

Another objective is also to install the spent fuel reprocessing and fresh fuel refabrication on the same site with limited fuel transports and storage needs. Also the implementation of MA reprocessing would be facilitated.

6.11.4.1.3 Super-DIREX

Another alternative reprocessing technology under development by Mitsubishi and Japanese R&D establishments is the Super-DIREX (supercritical fluid direct extraction) process. This technology is designed to cope with U and MOX fuels from light water and fast reactors.[14] The fuel is dissolved in a mixture of nitric acid with tributyl phosphate (TBP) and supercritical CO_2, which results in a complexation and extraction of U, Pu and MAs with TBP.

6.11.4.1.4 PUREX adapted for Np recovery

In the standard PUREX process, Np is partially extracted by TBP, this part follows the U stream, is separated in the second U purification cycle and then added to the HLW and vitrified. In the fuel solutions feeding to the first decontamination cycle, Np is present as a mixture of Np (IV), Np (V) and Np (VI), only Np(IV) is extracted.[15] Therefore in the PUREX process adapted for Np recovery, Np is completely oxidized to the oxidation state VI and then co-extracted with U and Pu in the first decontamination cycle where it follows again the U stream. Finally it is, as in the standard process, recovered through a reducing scrub in the second U cycle. After separation, the Np nitrate, contaminated by β-γ emitters, may be purified by solvent extraction with TBP and finally transformed to oxide by calcination of the oxalate.

6.11.4.2 Extended PUREX Process for MA Recovery

For the separation of MAs the PUREX process has to be modified and extended using also hydro-chemical extraction techniques.[16] Extensive R&D is carried out world-wide to synthesize special extractants and to develop the corresponding process schemes

required for a selective separation of MAs (mainly Am and Cm) from HLLW. The process development requires a good basic understanding on the underlying extraction mechanisms.

6.11.4.2.1 Fundamental studies

As aqueous partitioning is based on liquid-liquid extraction from an acidic solution into an organic phase it is of crucial importance to know about extraction selectivity, thermodynamics, mechanisms and kinetics. In aqueous MA partitioning schemes, two main routes are possible (see **Fig. 4**). The optimal strategy would be of course a process, where MAs are directly extracted from the PUREX raffinate, the high level liquid waste (HLLW). However up to now an extractant, capable of selective and efficient separation of the MAs at high acidities ($>2M\ HNO_3$) in a highly radioactive solution containing all fission products, among them lanthanide elements in a mass excess of 20 times compared to MAs is not available. Partitioning of MAs involving co-extraction of lanthanides and a subsequent separation of the two element groups is therefore the only viable option at present.

6.11.4.2.2 Extraction mechanisms

One of the major questions to be solved for the extraction of lanthanide (III) and actinide (III) from aqueous nitrate solutions concerns the knowledge of the nature of the extracted species. A dual mechanism of extraction would be based on the formation of solvates having the general formula $M(NO_3)_3L_n$, formed according to the following equation:

$$M^{3+} + HNO_3 + nL = M(NO_3)_3L_n + 3H^+$$
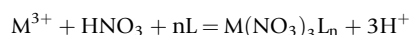
with M(III) = Ln(III) or An(III) and L = organic extractant.

In European research programs the reference organic extractant is based on the diamide molecule with the general formula: $(R(R')NCO)_2CHR''$ (where R, R', and R'' are alkyl or oxyalkyl groups), e.g., N,N′-dimethyl-N,N′-dibutyltetradecyl-1,3-malonamide (DMDBTDMA), shown in **Fig. 5**.

For concentrated aqueous nitric acid solutions, as encountered when extracting U(VI) or actinide (IV) from nitric acid media by monoamide extractants, ion-pairs of formula $[LH^+]n$, $[M(NO_3)_{3+n}]^{n-3n}$ could be present.

Several experiments, involving UV-visible and ^{13}C NMR spectroscopies and solvent extraction, have been conducted to confirm this assumption. From the data obtained so-far one can conclude that, if a dual extraction mechanism exists, the second
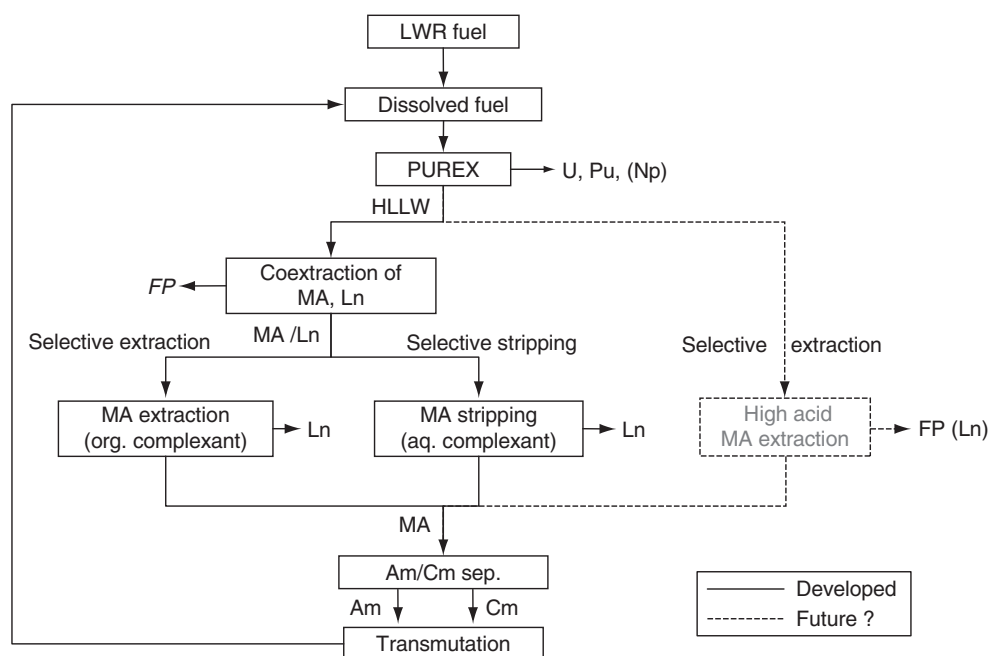

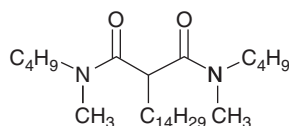**Fig. 4**   Strategies for the separation of the MAs from HLLW.

Fig. 5   N,N′-dimethyl-N,N′-dibutyltetradecyl-1,3-malonamide (DMDBTDMA).
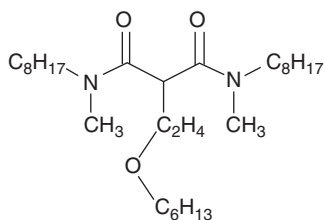
Fig. 6   N,N'-dimethyl-N,N'-dioctylhexylethoxy-malonamide (DMDOHEMA).

mechanism does not seem to be an ion-pair mechanism involving a protonated diamide. It can therefore be concluded that the occurrence of an ion-pair mechanism is unlikely.

A comparison of diamides with different R' groups (butyl, phenyl and chlorophenyl) in their ability to extract An(III) or Ln(III) from aqueous nitrate media shows that a less basic malonamide has better extraction properties of the M(III) nitrate. If in the central R'' position the alkyl group is replaced by a di-octylhexylethoxy group (see **Fig. 6**), the diamide DMDOHEMA exhibits better affinities for M(III) nitrates.

Arrhenius activation energies close to 40 kJ/mol for all M(III) studied, indicate that the extraction is chemically limited at the aqueous/organic interphase. For a diffusion limited kinetic regime, this energy is generally found close to be 20 kJ/mol.

The extraction kinetics of M(III) nitrates by DMDBTDMA were found to be much slower than for the extraction of U(VI) or Pu (IV) nitrates by TBP in the PUREX process.

Crystal structures were determined by X-ray absorption spectroscopy and using synchrotron light for a large number of lanthanide – and actinide – diamide complexes. Molecular modeling studies have been conducted to compare calculated structures and X-ray determined crystal structures and to propose structural explanations for experimental differences observed during extraction of M(III) metallic nitrates by several malonamides.

Using the Quanta/CHARM code, the lowest conformation calculated structures for DMDPhMA, DMDCHMA and BDMDPhMA, were found to be similar to the experimentally determined crystal structures. Also differences between structures of DMDPhMA and BDMDPhMA and that of DMDCHMA were confirmed by calculations. The differences in M(III) extraction efficiency between cyclohexano (DMDCHMA) and phenyl substituted (DMDPhMA and BDMDPhMA) malonamides can be correlated with the difference of the preferred conformations of the malonamide extractants.

Using the Gaussian 94 program, protonation of cyclohexano (DMDCHMA) and phenyl (DMDPhMA) substituted malonamides were studied. Results are equivalent for both malonamides and show that *mono*-protonated malonamide contains an intramolecular hydrogen bond, while the *di*-protonated malonamide does not.

A Quantitative Structure-Activity Relationships (QSAR) study related to the extraction of Nd(III)nitrate by a set of 17 malonamides supported the above mentioned improved M(III) nitrate extracting properties in the presence of an oxygen ether atom in the R'' substituent.

6.11.4.2.3   Separation of trivalent actinides from lanthanides

To explain the great affinity of actinides for nitrogen-bearing molecules, numerous fundamental studies were carried out with a wide range of experimental methods, including spectroscopy. For Ln(III) and An(III) ions the formula, stability, and structure of the complexes were determined both in aqueous solution and in various solvent media. It has been demonstrated that bonds between the nitrogen atoms of these ligands and Ln(III) and An(III) ions include some definite covalence. The covalence observed in bonds with the electron-donor nitrogen atoms of ligands seems higher for An(III) ions than for Ln(III) ions, could be an indication for the greater affinity of these ligands for An(III), however the difference is too small to really explain the sometimes very high differences in the distribution factor.

Theoretical studies in the fields of quantum chemistry and molecular dynamics have provided greater insight into certain crucial aspects of reactions between these metal ions and nitrogen-bearing ligands. In particular, the synergetic extraction mechanism of Ln(III) ions using a mixture of nitrogen-bearing ligand and carboxylic acid has been identified by computer calculations. The calculated synergetic complex seems consistent with the experimental results.

6.11.4.2.4   Process development

Three alternative approaches are proposed. The first is based on co-extraction of trivalent minor actinides (MAs) and lanthanides and in a second step a separation in MA and lanthanides fractions. For the first part the most important processes are:

- The TALKSPEAK process (USA)[17] and DIDPA process (Japan)[18] use acidic organophosphorus extractants.
- The TRUEX process (USA)[19] and SETFICS (Japan)[20] are based on the use of CMPO (n-octyl-phenyl-di-isobutyl-carbomoylmethyl-phosphine-oxide).
- The TRPO process (China) uses a trialkyl phosphine oxide. The hot demonstration of this process using genuine HLLW has been done at the JRC Karlsruhe.[21]
- The DIAMEX (diamide extraction) process using malonamides as extractant[22] has been developed at CEA (France) and is also the reference process under investigation in the European partitioning projects.
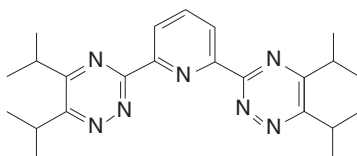
Fig. 7 2,6-bis-(5,6-di-*iso*propyl-1,2,4-triazine-3-yl)-pyridine (*i*Pr-BTP).

For an efficient recycling scheme, losses of the relevant elements should be as low as possible (0.2% or less), therefore a compromise between extraction and back extraction has to be made.

The MA/Ln separation can be achieved by a so-called selective actinide extraction process (SANEX). The major options are:

- The BTP (Bis-Triazine-Pyridine) developed at FZK-INE Germany[23] or BTBP (Bis-Triazine-Bis-Pyridine) capable to achieve the selective extraction of MA's at high nitric acid concentration (2 M).
- The TPTZ (tripyridyltriazine) developed at CEA, France to be used at much lower nitric acid concentrations.[24]
- Variants of the dithiophosphinic acids (ClPh)2PSSH in a mixture with TOPO at FZ Jülich, Germany.[25]

Promising results have been obtained on simulated as well as on genuine solutions at lab-scale. Among many extractants tested world-wide, the combination of DIAMEX and BTP (see **Fig. 7**)[26] is shown to be the best combination for an efficient recovery of MAs from HLLW or transmutation targets.

Diamides do not require feed adjustment, can easily be recycled to the process and do not leave any residue upon incineration. Concerning the separation of MAs from lanthanides, BTP has shown to be the most efficient extractant, giving at the same time the highest separation factor with no feed acidity adjustment required. Separation factors between MAs and lanthanides up to 80 are reached in a single stage extraction. These values are of course considerably increased in a continuous multistage process and a Am/Cm product containing less than 1% of lanthanides can be obtained.[27] Unfortunately due to a high sensitivity to hydrolysis and radiolysis, an industrial application of the BTP molecule requires further investigations to improve these properties.

The second alternative under investigation aims at a direct selective extraction of minor actinides from the PUREX raffinate in a single operation leaving all the lanthanides in the HLLW.

A third option is the co-extraction of actinides and lanthanides with DMDOHEMA (DiMethyl-DiOctyl-HexylEthoxy MalonAmide), as in the extraction step of the DIAMEX process, followed by selective stripping of the trivalent actinides from the loaded diamide solvent using a mixture of HEDTA (actinide-selective polyamino-carboxylate complexing agent) and citric acid.

The scientific feasibility of this type of process has been demonstrated by the CEA in the ATALANTE facility in Marcoule. A MA recovery of $\sim$99.9% and less than 0.3 wt% lanthanides in the MA fraction was achieved with a flowsheet, where the DIAMEX solvent was supplemented by an acidic extractant, diethylhexylphosphoric acid (HDEHP), to ensure effective extraction at pH > 2. Also the so-called EXAm process aiming at recovering Am alone adopts a similar extraction scheme.[27]

In Japan the JAEA has studied an advanced aqueous process combined with a U crystallization process. The main differences to the conventional PUREX are:

- The purification steps of U and Pu in the conventional PUREX are eliminated, resulting in co-extraction of U/Pu/Np, and the simplification of the system. A compact-sized centrifugal type equipment is used to reduce the size of the reprocessing facility.
- The crystallization is used to separate excess U before extraction of U/Pu/Np,

A combination of the SETFICS process, developed by JNC, and the TRUEX process is applied for the recovery of Am and Cm. A recovery ratio of U/TRU has been estimated to be 99.7%, and the decontamination factor of the reprocessed product is higher than 10^2.

Another process developed by JAEA is known as the "Four-Group Separation Process"; it includes:

- An extraction of all TRU elements including Np (V) with DIDPA at 0.5 M nitric acid.
- A separation of Tc and platinum group metals by precipitation through denitration.
- A separation of Sr and Cs by adsorption with inorganic ion exchangers.
- A selective back-extraction of Am and Cm by 0.05 M diethylenetriaminepentaacetic acid (DTPA).

In **Table 4** the separation efficiency and estimated recovery values obtained in the various processes mentioned above are compared to target values for the recovery of TRU elements and some key fission products in advanced reprocessing.

The separation efficiency and the estimated recovery of TRU elements are quite high and almost fulfill the target recovery. The recoveries of Tc and platinum group metals are around 90%–95% which is lower than the expected target recovery. This lower recovery is less important because of a lower potential radiotoxicity contribution of these elements.

In the frame of the European FP7 research project SACSESS (Safety of ACtinide Separation proceSSes[28]), the "EURO-GANEX" process based on the French GANEX scheme[29] has been developed. The goal is the homogeneous grouped recycling of Pu and MAs in a future closed fuel cycle. After an initial U extraction cycle, actinides and lanthanides are co-extracted into an organic phase followed by selective stripping of actinides altogether.[30,31] A suitable organic phase has been formulated and distribution ratios determined for lanthanides, actinides and some problematic fission products under extraction and stripping conditions. The process flowsheet has been successfully tested on surrogate feed solutions and with genuine spent fast reactor fuel. Excellent

Table 4 Target recovery, experimentally obtained separation efficiency, and estimated recovery of elements in the four-group partitioning process

Elements	Target recovery (%)	Separation efficiency (%)	Estimated recovery (%)
Np	99.5	>99.95	99.85
Pu	99.9	>99.99	99.85
Am	99.99	>99.99	99.97
Cm	99.9	>99.99	99.97
Tc	99	~98	~95
Sr, Cs	99	>99.9	>99.9

recoveries of the actinides (~99.9% of the TRU elements) and good decontamination factors from the lanthanides and other fission products were obtained. Less than 0.1% of the lanthanides were found in the product solution, which also contained the major fractions of Zr and Mo.

With respect to aqueous reprocessing in Europe, dedicated larger research facilities are available in France (CEA, Marcoule) and U.K. (NNL, Sellafield), where extensive studies are being performed on used fuel material. Facilities for smaller scale hot-tests are available in other countries and the JRC (Karlsruhe, Germany). In addition, European universities are strongly involved in this research through the European Framework Programs mentioned above, especially in the fields of synthesis of new extractants and for molecular modeling.

6.11.4.3 Pyro-Reprocessing

Pyro-chemical processes rely on refining techniques at high temperature, mainly between 500°C and 900°C depending on the molten salt eutectic used. Typically chloride systems operate at lower temperature compared to fluoride systems. In nuclear technology, the processes are typically based on electrorefining or on extraction from the molten salt phase into liquid metal.

For more than 50 years, pyro-metallurgy has been studied as an alternative strategy in the reprocessing of used fuel. Until now, only two processes have been developed up to the pilot scale, both in chloride media. The first one developed by RIAR in Dimitrovgrad (Russia) is based on oxide fuels and the second one is using metallic fuel and was developed in the US as part of the so-called Integral Fast Reactor (IFR) program. The RIAR process can be operated in an air atmosphere, whereas the metallic process requires a more or less pure Ar atmosphere. Only the metallic fuel process allows however also the treatment of TRU elements and is therefore discussed in more detail in the following paragraphs.

6.11.4.3.1 IFR pyro-process

The electrometallurgical process was applied for the first time as an part of the IFR system in the pyro-chemical separation processes for the recovery of U and to some extent also Pu from EBR II fuel. These processes have been investigated for decades[32,33] and remain the core process in the EBR-II Spent Fuel Treatment Program. Many of the pyro-processing systems presently proposed for further development are spin-offs of this process, shown in **Fig. 8**.

The fuel is recycled using an electrochemical process based on molten chloride salts and liquid metals. The molten salt medium for electrorefining is a solution of a certain amount of UCl_3 dissolved in a LiCl-KCl eutectic. At an operating temperature of about 500°C, chopped used fuel is loaded into the electrorefiner using specially designed stainless steel baskets. The fuel is then electrochemically dissolved a an appropriate potential between the basket used as anodes and a stainless steel electrode in the salt phase serving as cathode. Once the fuel starts to dissolve, U and a small part of the TRU elements are collected on the cathodes. When the fuel is completely dissolved and most of the U is deposited on the solid steel, this cathode is replaced by a liquid-cadmium cathode, and the TRUs can be co-deposited with the remaining U. A liquid-cadmium cathode is a ceramic crucible containing molten cadmium that can be lowered into the salt bath. The cadmium in the crucible is put at cathodic potential.[33] Because of the chemical activities of the TRU elements in cadmium, they can be more easily deposited with U in liquid-cadmium cathodes than on solid cathodes. The cathode products from electrorefining operations are further processed to distill adhering salt and cadmium and to consolidate the recovered actinides. Those are remotely fabricated into new fuel for recycling.

The alkali, alkaline earth, rare earth, and halide fission products remain primarily dissolved in the salt phase. These elements can be separated from the salt phase (e.g., by extraction or precipitation processes) and are eventually conditioned in a ceramic high level waste before being disposed. More than 90% of the noble metal fission products and fuel alloy material are retained in the chopped fuel cladding segments in the anode baskets. This residue can be stabilized into a metal high-level waste to prepare it also for final disposal.

Adaptations of this technology exist for the treatment of both oxide and nitride fuels. The flow sheet for the treatment of nitride fuels is similar to that of the metal fuel. The nitride fuels are also fed directly into the electrorefiner, the actinides are dissolved from the fuel cladding and collected all together electrochemically in liquid cadmium or bismuth cathodes. A specificity of this process is an evolution of nitrogen gas. If during irradiation the formation of ^{14}C (from ^{14}N) should be avoided, the initial nitride fuel should be enriched in ^{15}N. For obvious economic reasons this nitrogen should be recycled; it can be collected and recycled back into the liquid cathodes where actinide nitrides are formed. This process and the fuel re-fabrication are of course quite complex.
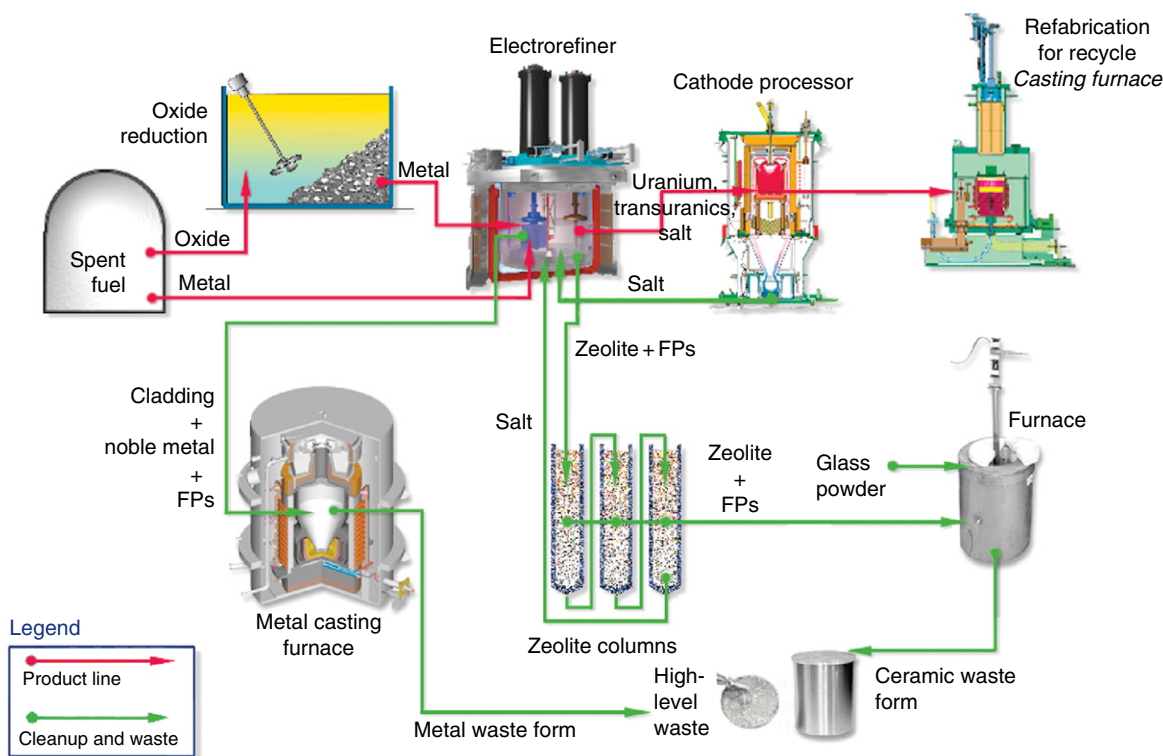
Fig. 8 Metal and Oxide Fuel Pyro-process Flow sheet.

After distillation of the cadmium, the recovered nitrides are separated and then fabricated into new fuel using a vibro-packing step. This process is being developed in Japan.[34]

6.11.4.3.2 European pyro-chemistry projects

The US pyro-metallurgy process has been considered as the reference route for the molten salt reactor fuel treatment, but also as an alternative technology that could be applied to some types of fuels today envisaged for Gen IV systems or ADSs, as complementary reprocessing routes to current hydrometallurgical processes.

Also in the European Research Programs, several pyro-reprocessing projects were run with the following objectives:

- to obtain basic data relevant for the conceptual design and assessment of reprocessing processes suitable for many different types of fuel and targets,
- to assess the feasibility of separating U, Pu and minor actinides from fission products using pyro-metallurgy in a molten chloride or fluoride systems,
- to identify and characterize solid matrices for the conditioning of the wastes issuing from the pyro-processes,
- to carry out system studies for comparing some selected reprocessing of used fuels of advanced nuclear reactors including the ADS,
- to revive and consolidate European expertise in pyro-processing.

As an underpinning support for the pyro-process developments, basic properties of actinides and some fission products in molten salts (chlorides and fluorides) and in liquid metal solvents have been studied extensively.

A very important work was done in the thermodynamic data acquisition in molten chloride media, with a comprehensive study of actinides, lanthanides and some other relevant fission products. In comparison to molten chloride salts, studies in molten fluoride are much less developed. Even if a lot of experiments were carried out in various salts, it seems in this case to be more difficult to get the necessary thermodynamic data, also due to the lack of reliable reference electrodes. Especially for Cm the data available are very scarce.

Two efficient processes for the separation of actinides from lanthanides have been selected as promising core processes: (1) electrorefining process on a solid reactive cathode in molten chloride, (2) liquid-liquid reductive extraction in liquid metal-molten fluoride. As a result of the data collected for a variety of liquid metals, a clear choice of aluminum was made for both the cathode material for the electrochemical process in molten chlorides and as extractant for the reductive extraction process in molten fluorides. Several reference flow sheets have been assessed.

The results were used to optimize the two reference core processes. Moreover, several new experimental installations for process tests have been designed and constructed. In the UK, Nexia Solutions has built a new facility in an alpha-active glove-box and in Italy

ENEA has commissioned the Pyrel II facility for process scale-up and modeling. It became clear, that the construction of a large scale electrolyser for studies in molten salt is a complex and laborious task, which requires a lot of additional efforts to be successful.

A successful recycling should have similar targets for dry and aqueous reprocessing regarding the loss of fissile materials and of long-lived radionuclides to be recovered. A realistic value is below 0.1% for all actinides. Furthermore also the pyro-process should produce the lowest achievable amounts of waste, and the waste produced must be converted in a convenient form for storage or disposal. Here real progress was made in the decontamination of used chloride salts coming from electrorefining, the complementary techniques of zeolite ion-exchange filtration and phosphate precipitation have been selected for their potential to clean up used salt efficiently. A number of specific matrix materials for salt confinement were identified (sodalite, pollucite), however, a lot of work is still to be done also in this field.

The system studies which were performed in the course of the European Research Programs included: (1) double-strata concept (ADS), (2) IFR and (3) Molten Salt Reactor. In a first step the general principles used for the assessment of pyro-chemical separation processes were defined and a common methodology for technical and economical comparisons and the selected flow-sheets was set up. During the second step, the work was focused on detailed flow-sheeting studies and mass balance calculations. The major interest of these studies is the validation of the "process approach", a very useful tool to identify key issues and eventually reorient R&D programs. Nevertheless, as the flow sheets address different scenarios and fuels, it is often very difficult to make a direct inter-comparison in terms of advantages and drawbacks.

6.11.4.3.3   Basic data acquisition

As mentioned in the previous paragraph, a large variety of basic properties of actinides and relevant fission products in molten salts (chlorides and fluorides) and in liquid metal solvents have been studied.[35-37]

In molten chloride media large efforts were made in basic data acquisition, mainly at the JRC Karlsruhe with a comprehensive study of actinides (U, Pu, Np, Am, Cm), lanthanides and key fission products. Thermochemical properties are derived from the electrochemical measurements and from basic thermodynamic data for instance in the case of Np of $NpCl_3$ and $NpCl_4$ in the crystal state.[38,39] It could be demonstrated, that the $NpCl_3$ has a strong non-ideal behavior in a molten LiCl–KCl eutectic. For these experiments a double glove box has been constructed, where the outer glove box is operated under nitrogen and the inner box under a purified argon atmosphere at over pressure condition. In this equipment a precise determination of the required data could be achieved. Auxiliary equipment is devoted to chlorination, material processing and electrochemistry in room temperature ionic liquids, a potential alternative to the high temperature molten salt systems.[40]

6.11.4.3.4   Core processes

Initially three potential chemical routes were identified as candidates for core process development activities. The first one is based on selective precipitation and was also investigated by RIAR in Russia as possible option to selectively separate the TRU elements. However the success of this process is not very encouraging, the decontamination factors that can be obtained are always quite low. The second route is the electrochemical one, which includes electrolysis or electrorefining techniques, either in chloride or in fluoride molten salts. The third one is based on the liquid-liquid reductive extraction between a molten salt and a liquid metal phase.

Therefore only the processes based on electrorefining on solid Al cathode in molten chloride and the one based on liquid-liquid reductive extraction in molten fluoride/liquid Al were extensively studied in the European programs. In parallel some studies were carried out on electrolysis in molten fluoride or liquid-liquid reductive extraction in molten chloride but with a much lower priority.

6.11.4.3.5   Electrorefining on solid Al cathode in molten chloride media

A mentioned already in previous paragraphs, a grouped actinide recycling has several advantages and is therefore also applied in molten salt electrorefining. Special emphasis is given to a selective electrodeposition of actinides with an efficient separation from lanthanide fission products. In contrast to the IFR concept, where U is deposited on a solid stainless steel cathode and TRU actinides on a liquid Cd cathode,[41] the electrorefining processes rely on a co-deposition of all actinides on a solid Al cathode material.

In fact the choice of the cathode material onto which the actinides are deposited in the electrolysis is essential in this context.[42] In contrast to stainless steel or W, Al is a reactive electrode material, i.e., it forms stable alloys with the actinides, thereby avoiding the redissolution of deposited trivalent actinides. Also the redox potentials on solid cathodes show a much larger difference of the reduction potential between actinides and lanthanides. **Fig. 9** shows the reduction potentials for U^{3+}, Pu^{3+}, Am^{3+}, La^{3+} and Nd^{3+} determined by transient electrochemical techniques (mainly cyclic voltammetry and chronopotentiometry) on different cathode materials. On Bi and Cd, the selectivity of the minor actinide recovery is limited due to the small difference in reduction potentials between actinides and lanthanides.

Solid Al has therefore been selected because of two reasons essentially

(1) Stable actinide deposits (alloys) are formed and are consequently very adherent to the cathode; at the same time a redissolution of the trivalent actinides by comproportionation with the trivalent actinides in the salt to form divalent actinides can be avoided according to: Am(III) + Am(0) = 3 Am(II).

(2) The difference in the reduction potentials compared to lanthanides is sufficiently high to avoid their co-deposition and thus allow their separation.
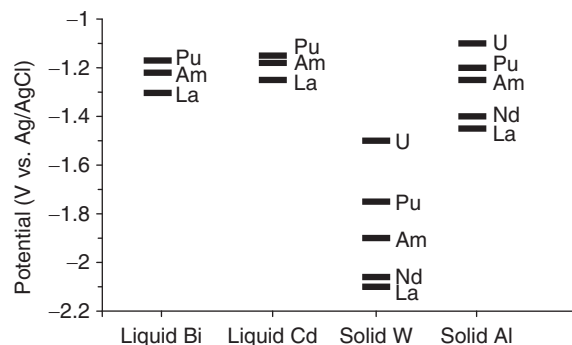
Fig. 9   Reduction potentials of some actinides and lanthanides on different cathodic materials.
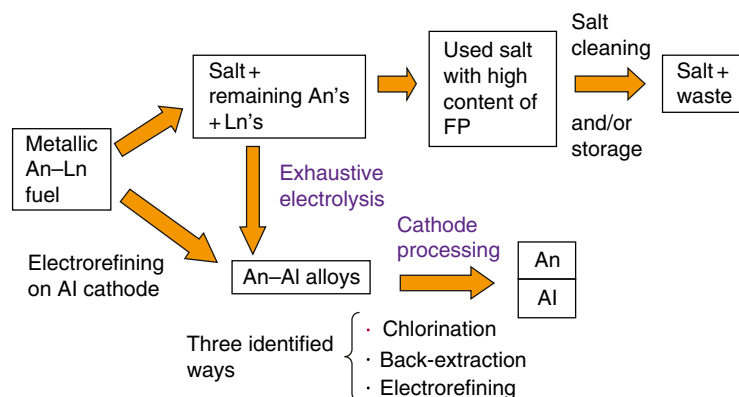

Fig. 10   Process scheme for the electrorefining of metallic fuels.

In these electrolytic processes, the rate of the alloy formation depends on the diffusion of the involved elements in and through the solid alloy phase. Therefore the maximum amount of actinides that can be collected on a single Al electrode has been investigated in constant current electrorefining experiments in which the cathodic potential was maintained at a suitable level for separation of actinides from lanthanides. With increased charged passed, i.e., with the build up of a surface layer of An–Al alloy, the applied current is gradually reduced in order to stay above the cathodic potential limit.

Based on a large set of data obtained for the electrodeposition on Al cathodes, the process scheme is being proposed as shown in Fig. 10.

The electrorefining process as presented here is operated in a batch mode. After multiple use of the eutectic salt bath, an exhaustive actinide electrolysis is required to avoid losses >0.1% to the waste, before the cleaning of the salt bath takes place. It is evident that the lanthanide content in the electro-deposited An- Al alloy in the exhaustive electrolysis contains more lanthanides than in the runs were metallic fuel is deposited and must eventually be recycled. For the cathode processing, three options are possible, chlorination, back-extraction and electrorefining. Among those chlorination is the most promising. This step is needed to recycle the actinides as far as possible quantitatively to the fuel fabrication.

In laboratory experiments it could be demonstrated that 3.72 g of actinides were deposited in 4.17 g Al, corresponding to 44.6 wt% actinides in Al or 68 wt% of the maximal loading, considering that $AnAl_4$ alloys are formed.[43] A successful demonstration of the Am/ Nd separation was carried out using a mixture of 255 mg Am, 281 mg Pu and 140 mg Nd. Am and Pu were co-deposited in two steps on two Al cathodes of 0.8 g each. The cathodes used were made of Al foam to increase the reaction surface area. The Nd content in the deposit of only about 0.5%, proves the feasibility of a selective actinide separation by electrolysis onto Al electrodes.

The results were confirmed in a multiple run experiment inducing an accumulation of lanthanides in the salt. The fuels used for these experiments had already been developed in the frame of the integrated fast reactor (IFR) concept (see previous paragraph) in the mid 1980s in the US. These fuels contain about 15% of Zr in the metallic alloy to stabilize the fuel during reactor irradiation. The same type of fuel is used for transmutation studies initiated by CRIEPI, Japan in collaboration with JRC Karlsruhe, Germany and was irradiated in the METAPHIX experiment in the PHENIX reactor in France.[44] This fuel, containing 2% of Am and lanthanides ($U_{61}Pu_{22}Zr_{10}Am_2Ln_5$) was fabricated in the late 1890s at the JRC Karlsruhe. The remnants of the fuel fabrication campaign were used for the separation studies described here.

In the pyro-reprocessing, the metallic alloy is anodically dissolved in a LiCl-KCl eutectic[45] and the actinides are collected together onto Al cathodes as alloys, leaving lanthanides in the salt phase. It is very likely, that a large-scale pyro-processing by
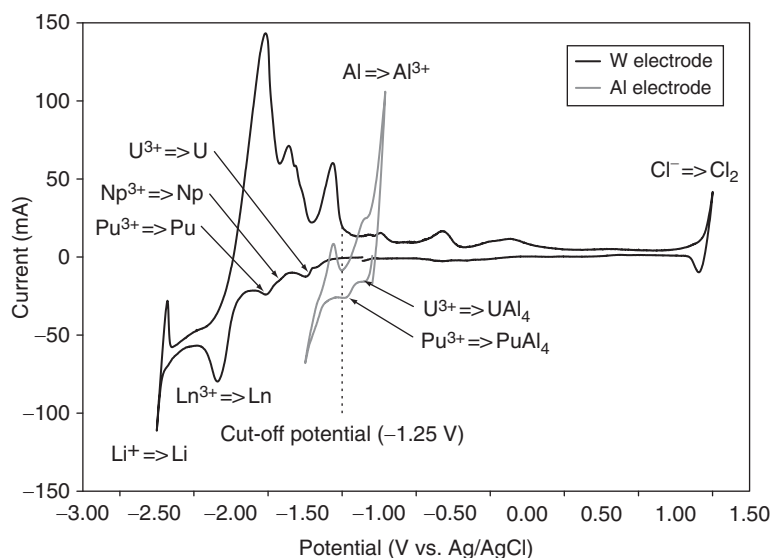
Fig. 11 Cyclic voltammogram of $U_{61}Pu_{22}Zr_{10}Am_2Ln_5$ on W and Al wires. Reference electrode: Ag/AgCl-1 wt%, $v = 100$ mV/s, T $= 450°$C. Salt composition in wt%: U – 0.29, Np – 0.12, Pu – 0.28, Am – 0.06, Zr < 0.07 and Ln – 1.0.

molten salt electrorefining will be operated as a batch process similarly to the industrial Al fabrication process. In view of a large scale development of the process, an experiment of 25 successive runs was carried out to demonstrate the feasibility of a grouped actinide recovery from larger amounts of fuel without changing the salt bath. A total amount of more than 5 g of $U_{61}Pu_{22}Zr_{10}Am_2Ln_5$ fuel was treated in this experiment and various process parameters were studied. **Fig. 11** shows the cyclovoltamogram of the alloy on Al and W electrodes.

The goal of this 25-run test was to find optimal conditions for the recovery of Am. The recovery rate of actinides was difficult to evaluate because new fuel was added in each run. Nevertheless a stable recovery rate $[m_{An}/(m_{ln} + m_{Ln})]$ better than 99.9% was achieved throughout the whole experiment. U, the main constituent of the fuel with a less electronegative electro-deposition potential is preferentially deposited in the earlier runs. At the same time the relative Am content in the actinide deposit and the separation from lanthanides (m_{Am}/m_{Ln}) increases despite an increasing content of lanthanides in the salt. The results are very promising in view of a large-scale development of pyro-reprocessing in advanced nuclear fuel cycles.

6.11.4.3.6 Exhaustive electrolysis

When a salt bath is being used for the electrorefining of large amounts of fuel, the fission products are accumulated in the salt bath and their concentration becomes too high and thereby prevent a selective deposition of actinides on the cathode. Before cleaning the salt, an exhaustive electrolysis aiming at a complete grouped recovery of the remaining actinides on a solid Al cathode was carried out without further fuel dissolution (see **Fig. 10**). The anode basket is therefore replaced by a chlorine electrode. Partial oxidation of the chloride salt to chlorine gas allows the actinide reduction on the cathode side. A scheme of the process is shown in **Fig. 12**.

In order to prove feasibility of the method, two galvanostatic electrolysis were carried out using a mixture of UCl₃-NdCl₃.[46] The potentials of both electrodes were constantly followed and a decrease of the U concentration from 1.7 to 0.1 wt% with no co-deposition of Nd was recovered observed. Although the maximum applicable current densities were relatively low, the results are promising and show high current efficiency and high selectivity.

6.11.4.3.7 Liquid-liquid reductive extraction in molten fluoride/liquid Al

The alternative process to electrorefining in molten chloride salts is the liquid metal molten salt process. This option was extensively studied by CEA in several European Research Programs.[47–49] An experimental device and a process scheme have been developed to study the distribution of actinides and lanthanides between molten fluoride salt and a liquid metal phase. The results obtained with Pu, Am, Ce and Sm in the (Li–AlF₃)/(Al–Cu) medium revealed the excellent potential of the system for separating actinides from lanthanides.

With a salt composition corresponding to the basic eutectic (LiF–AlF₃, 85–15 mol%), up to 99% of Pu and Am could be recovered in a single stage, with Ce and Sm separation factors exceeding 1000 were achieved. The effect of the AlF₃ concentration in the salt has been investigated. The distribution coefficients logically go down as the initial AlF₃ concentration increases. A thermodynamic model to describe the extraction as a function of the fluoroacidity has been developed on the basis of the experimental results for Ce and Sm. The model clearly reveals a difference in solvatation between divalent and trivalent lanthanides in fluoride media.

The results obtained for each element were confirmed by demonstration experiments under more realistic conditions at lab-scale. Two runs were carried out at 830°C using LiF–AlF₃ (85–15 mole%) as a salt phase: one with an Al–Cu alloy (78–22 mole%) as metallic phase, the other with pure Al, to check the influence of Cu on the extraction, both in terms of separation performance and in terms of process implementation (phase separation). The metal phase was contacted with salt of the following composition
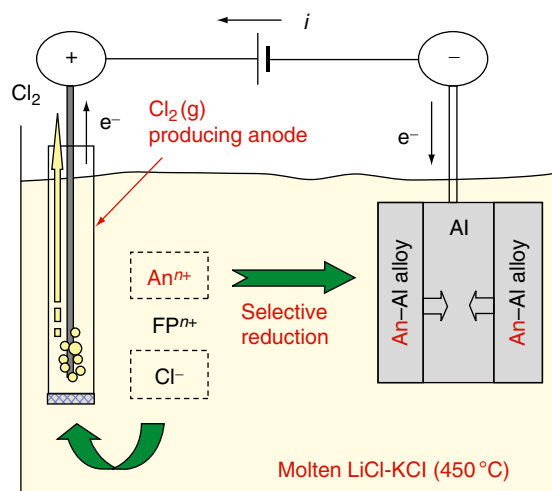
Fig. 12 Principle of the exhaustive electrolysis process.

Table 5   Mass distribution coefficients and separation factors of actinides and lanthanides with and without Cu in the metallic phase

Al–Cu (78–22 mol%)			Al		
Metal	Distribution actor	Separation factor Am/metal	Metal	Distribution factor	Separation factor Am/metal
Pu	197 ± 30	0.73 ± 0.21	Pu	273 ± 126	0.78 ± 0.47
Am	144 ± 20	1	Am	213 ± 30	1
Ce	0.142 ± 0.01	1014 ± 213	Cm	185 ± 31	1.15 ± 0.35
Sm	0.062 ± 0.006	2323 ± 488	Ce	0.162 ± 0.02	1315 ± 289
Eu	<0.013	$>11\ 000$	Sm	0.044 ± 0.004	4954 ± 1139
La	<0.06	>2400	Eu	<0.03	>7100
			La	0.03	7100

(wt%): PuF_3 (11), AmF_3 (0,2), CeF_3 (2,5), SmF_3 (0,5), EuF_3 (0,5) and LaF_3 (0,5). The results show that the distribution ratios of Pu and Am are in the same order of magnitude, similar to the ones previously measured at low concentration without lanthanides.

The results obtained with Al-Cu and Al are very similar, the distribution coefficients of the lanthanides are low and thus the separation from actinides is very efficient. In a test with Al without Cu, the distribution coefficient of Cm (trace concentration in Am starting material) has been measured for the first time; it is very close to the values obtained for the other actinides (U, Np, Pu, Am). In **Table 5** the main test results are summarized.

The results show that the distribution ratios of Pu and Am have similar high values independent from the presence of Cu in the metallic phase and that in all cases high separation efficiency from lanthanides can be achieved.

The actinide back-extraction from the Al phase is of course an important step in view of fuel refabrication. In a bibliographic study three possible routes were identified:

- Electrorefining: main drawback is the complexity of the process which requires 3 steps,
- Volatilization of the Al matrix by a chlorinating reagent: it is a simple and efficient method. Nevertheless, high volumes of chlorination gas have to be managed and an additional step is necessary to convert the $AlCl_3$ to Al metal,
- Oxidizing liquid-liquid extraction in molten chloride.

An extensive experimental study is necessary to select the most efficient option.

6.11.4.3.8   Technical uncertainties of the pyro-reprocessing

In the Spent Fuel Treatment Program at INL the feasibility of many parts of the pyro-process fuel cycle could be demonstrated up to the 100 kg scale. Nevertheless there are still key aspects that have yet to be demonstrated, particularly the recovery of TRUs. Large-scale equipment designed and constructed was never tested beyond the laboratory scale, because of the termination of the IFR program.

The remote fabrication of IFR fuel was not part of the Spent Fuel Treatment Program, but this technology was used to fabricate cold fuel for EBR-II and a demonstration of another pyro-process (melt refining) for recycling EBR-II in the 1960s employed remote fabrication for 34,500 fuel elements.[50]

Another key challenge for a pyro-processing system is the selection of appropriate construction materials for the high temperature processes. Material improvements are needed in order to reduce the formation of dross streams and to increase the material recovery and throughput.

The quantity of waste generated requiring geological disposal from pyro-processing seems to be quite similar to the one generated by present modern commercial aqueous processes. Advancements are being pursued to further reduce the disposal volumes using specially adapted zeolite ion exchange technology, which has at present not yet been demonstrated beyond the laboratory scale.

Most of the radioactive work performed to date has been on the pyro-processing cycle for metal fuel. Laboratory work has been performed on the head-end operations for oxide reduction and on the nitride fuel cycle. Demonstrations of these technologies with actual commercial used fuel have started at a laboratory scale. Additionally for nitride fuels, a demonstration of the above mentioned recycling of nitrogen (^{15}N) is essential for the economic considerations.

6.11.4.3.9 *Head-end conversion processes*

Today all commercial reactors are operated with oxide fuels and advanced reactor systems selected in the GIF roadmap rely also on oxides as the major fuel options at least in the beginning. As mentioned above, the pyro-metallurgical process based on oxides developed in Russia, RIAR, Dimitrovgrad does not allow to recycle MAs. Pyro-reprocessing where all actinides are recycled is based on metallic materials, therefore a head-end reduction step for oxide fuels is needed to convert oxides into metals. This conversion can be performed chemically, e.g., by reaction with Li dissolved in LiCl at 650°C. The recovered metal can directly be subjected to electrorefining and the Li$_2$O converted back to lithium metal by electrowinning. A more elegant method is the so-called direct electroreduction.[51] In this case, the heat generating fission products are removed and the fissile materials are recovered as an alloy, which can be again directly reprocessed by electrorefining.

Numerous experiments are carried out today to study this conversion process. The lithium reduction process using lithium metal as a reductant is carried out in molten lithium chloride. The reduction of UO$_2$[52] and simulated used LWR fuel[53] was studied mainly by CRIEPI in Japan in collaboration with AEA Technology in the UK. The optimized thermodynamic conditions for the reduction of TRU elements[54] and the behavior of major fission product elements[55] were determined. Li is converted into Li$_2$O and constantly removed during the process from the molten salt bath to prevent the re-oxidation of the reduced fuel material. Li is recovered by electrochemical decomposition of the Li$_2$O and recycled to the process.

A simulated used oxide fuel in a sintered pellet form, containing the actinides U, Pu, Am, Np and Cm, and the fission products Ce, Nd, Sm, Ba, Zr, Mo, and Pd, was reduced with Li metal in a molten LiCl bath at 923K. The pellet remained in its original shape, it became porous and shiny metallic color was observed throughout the pellet. The Pu/U ratio did not change during the reduction process. The reduction yield of U and Pu determined by measuring the H$_2$ formed upon reaction of the reduction product with HBr and using a gas burette was more than 90%. A small fraction of Pu has formed an alloy with Pd. The rare earth elements are found in the gap of the porous U-Pu alloy. As expected from the oxygen potential of Ce, Nd, Sm, and Li they remained in an oxide form. A small fraction of the actinide and lanthanides are leached from the pellet into the molten LiCl bath or are found as precipitate on the crucible bottom. A large part of Am in is found in the rare earth oxide phase rather than in the reduced U-Pu alloy. This represents of course a major problem for a grouped actinide recovery. Also the handling of highly reactive Li and problems in developing the corresponding equipment especially for the Li recovery are major drawbacks of this process.

The electrochemical reduction process is clearly the more reliable technique to convert oxides into metal. The difficult handling of Li metal and recycling through reconversion from Li$_2$O can be avoided. The oxide ion produced at the cathode is simultaneously consumed at the anode and thus the concentration of oxide ions in the bath can be maintained at a low level. A more complete reduction of the actinide elements can be achieved and the subsequent electrorefining to separate actinides as described in the previous paragraph can be carried out in the same device.[55]

An electrochemical process is being developed at present mainly in the US at INL in Idaho and in Japan at CRIEPI in collaboration with the EC, DG JRC Karlsruhe, Germany. Both unirradiated and irradiated fuel materials were treated with slightly different concepts.

The oxide fuel is loaded into a permeable stainless steel basket as crushed powder. The basket immersed into a molten LiCl–1 wt% Li$_2$O electrolyte at 650°C is used as the cathode and a platinum wire is used as anode. The reduced fuel is retained in the basket. The oxygen ions liberated at the cathode diffuse to the Pt anode, where they are oxidized to oxygen gas. The corresponding reactions are:

$$\text{Cathode: } M_xO_y + 2y \ e^- = xM + yO^{2-}$$

$$\text{Anode: } yO^{2-} = y/2 \ O_2(g) + 2y \ e^-$$
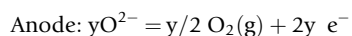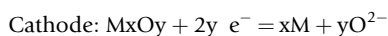
where M = metal fuel constituent

In the INL process, a combined chemical/electrochemical process, Li$_2$O present in the salt is reduced to Li which reduces chemically the fuel oxide.

The molten salt can be either LiCl or CaCl$_2$. In CaCl$_2$ the higher temperature of 1123K in comparison to 923K for LiCl induces a faster diffusion of oxygen ions to the anode. At the same time an increased initial reaction rate leads to the formation of a thin dense metal layer at the fuel surface hampering the diffusion of oxygen ions into the salt.
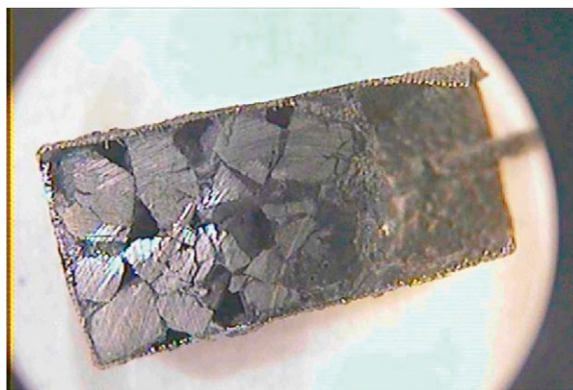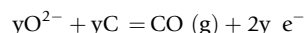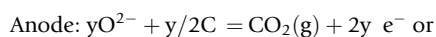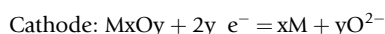
Fig. 13   Schematic layout of an electroreduction process developed by CRIEPI/JRC Karlsruhe.

For the CRIEPI/JRC Karlsruhe process the anode is made of carbon, the fuel is not crushed but loaded as fuel element segments in a cathode basket, i.e., made of Ta. The corresponding cathodic and anodic reactions are:

$$\text{Cathode: } MxOy + 2y\ e^- = xM + yO^{2-}$$

$$\text{Anode: } yO^{2-} + y/2C = CO_2(g) + 2y\ e^- \text{ or}$$

$$yO^{2-} + yC = CO(g) + 2y\ e^-$$

The INL process scheme was successfully demonstrated using irradiated used light water reactor oxide fuel in a hot cell. More than 98% of the U was reduced. Cesium, Ba and Sr were dissolved in the salt phase, as expected. The rare earth and noble metal fission products remained with U and TRUs, Pu and Np were reduced together with U, however about 20% of the Am remain as oxide.

The CRIEPI/JRC Karlsruhe process was tested on various MOX (Pu content 5%–45%) fuels. It could be shown that U and Pu are efficiently co-reduced, but due to the problems mentioned above, the complete reduction requires very long reaction times. The reduction of irradiated fast reactor fuel particles at JRC Karlsruhe was considerably faster and a complete reduction of all fuel constituents including fission products and MAS was achieved. **Fig. 13** shows the reduced fuel particles in the cathode basket.

The analyses of the salt bath used for these experiments, the examination of the reduced product by SEM/EDX and the analysis of the reduced fuel after dissolution allow to establish a mass balance of the electroreduction process. The results show that the fuel is completely reduced, i.e., all actinides are in the reduced product, the light fission products Rb, Mo, Cs, Ba, Se are dissolved in the salt and the lanthanide fission products are divided between the reduced fuel and an oxide precipitate found in the bottom of the salt crucible.

A first experiment has shown that the reduced fuel can be treated similar to the metallic fuels described above and using the same equipment and the same type of salt bath as the one used for the electrorefining tests.

6.11.4.4   The DUPIC Process

Another approach for used nuclear fuel recycling which could be employed by some countries is the DUPIC process[56,57]; it allows direct recycling of used PWR fuel in CANDU reactors.

CANDU reactors use natural U fuel without enrichment and could therefore be fueled with U and Pu from used light water reactor fuel. In the DUPIC process the used fuel assemblies from light water reactors (LWRs) are dismantled and re-fabricated into fuel assemblies for CANDU reactors. This process could involve simple cutting of used LWR fuel rods adapted to CANDU fuel elements (about 50 cm), resealing and re-engineering into cylindrical bundles suitable for the CANDU reactor geometry.

The more likely alternative is a dry reprocessing treatment, where the volatile fission products are removed from the used LWR fuel. No materials are separated during the re-fabrication process. After removal of the cladding, the used LWR fuel is converted into powder by a thermal-mechanical process, fresh natural U is added before CANDU pellets are sintered and pressed.

However, as noted above, used nuclear fuel is highly active and generates heat. The high radioactivity of the materials to be handled in the DUPIC process requires heavy shielding and remote operation. The restricted diversion of fissile materials and hence increased proliferation resistance goes together with a much more complex manufacturing process.

Canada, where the CANDU reactor line has been developed, and South Korea, which hosts four CANDU units as well as many PWRs, have initiated a bilateral joint research program to develop the DUPIC process. The Korean Atomic Energy Research Institute (KAERI) has been implementing a comprehensive development program since 1992 to demonstrate the DUPIC fuel cycle concept.

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 small DUPIC fuel elements for irradiation tests inside the HANARO research reactor in Daejeon, Korea in April 2000 and fabricated full-size DUPIC elements in February 2001. Research is also underway on the reactor physics of DUPIC fuel and the impact on safety systems. A trial period of the technology has started with an irradiation of used LWR fuel in the Qinshan reactor in China.[58]

6.11.4.5 Outlook

Industrial reprocessing as it is in operation today mainly in France, United Kingdom and Japan will continue operation for several decades. New capacities will be installed or extended in China, Russia and India in the near future; France and Japan consider deployment of new or additional capacities in a few decades from now.

If the sustainability goal strongly promoted in the GEN-IV initiative and also in the INPRO program coordinated by the IAEA or the European SNE-TP platform should be inherent to new advanced reactor systems, the waste minimization will require separation of long-lived waste constituents including MAs. As a consequence extended advanced reprocessing technologies have to be implemented at a large scale. As a first step, the actual PUREX process will be adapted to these needs. If advanced fuel materials such as composites, metals, nitrides or carbides are selected for the new reactor systems, adapted reprocessing technologies based on pyro-processes could be complementary options to reprocess these fuels. Considerable efforts are ongoing in South Korea, India, Japan and USA to develop processes at industrial scale. A possible strategy for the second half of this century could be a double strata concept with an advanced aqueous reprocessing of LWR fuel in the first stratum, combined with a fast reactor pyro-process in the second stratum, to reach the sustainability goals.

See also: 6.12 Degradation Issues in Aqueous Reprocessing Systems. 6.15 Waste Glasses

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