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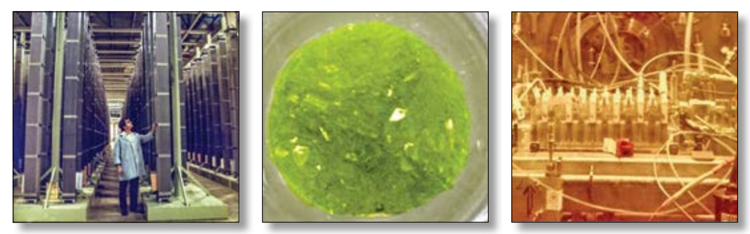
# State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry



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Nuclear Science

# State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry

NEA No. 7267

NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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The mission of the NEA is:

- to assist its member countries in maintaining and further developing, through international co-operation, the scientific, technological and legal bases required for a safe, environmentally sound and economical use of nuclear energy for peaceful purposes;
- to provide authoritative assessments and to forge common understandings on key issues as input to government decisions on nuclear energy policy and to broader OECD analyses in areas such as energy and the sustainable development of low-carbon economies.

Specific areas of competence of the NEA include the safety and regulation of nuclear activities, radioactive waste management, radiological protection, nuclear science, economic and technical analyses of the nuclear fuel cycle, nuclear law and liability, and public information. The NEA Data Bank provides nuclear data and computer program services for participating countries.

# Foreword

Under the guidance of the Nuclear Energy Agency (NEA) Nuclear Science Committee (NSC), and the mandate of the NEA Working Party on Scientific Issues of the Fuel Cycle (WPFC), the Expert Group on Fuel Recycling Chemistry (EGFRC) was established to perform technical assessments of separation processes relevant to recycling technologies for spent nuclear fuel and assessments of separation processes in applications related to the current and future nuclear fuel cycles. The expert group was also mandated to provide recommendations for collaborative international efforts towards the development of further separation processes.

This report presents a comprehensive state of the art on current developments in various separation technologies. It was written in the form of an international review of the different separation processes developed – or under development – in separation chemistry within a number of NEA member countries (France, Japan, Korea, Russia, the United Kingdom and the United States, as well as the European Union).

# Acknowledgements

The NEA Secretariat would like to extend its sincere gratitude to the members of the EGFRC for their contributions to this report, as well as for the valuable time and effort dedicated to this field of work. Special thanks go to P. Baron (France), Chair of the expert group. Thanks are also extended to E. Collins (United States) for his review and helpful suggestions.

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# List of abbreviations and acronyms

| | |
|---|---|
| AGR | Advanced gas-cooled reactor |
| ACPF | Advanced Spent Fuel Conditioning Process Facility (Korea) |
| ACSEPT | Actinide reCycling by SEParation and Transmutation |
| ASTRID | Advanced Sodium Technological Reactor for Industrial Demonstration |
| ADPTZ | Amino diPyridyl-triaZine |
| ADS | Accelerator-driven system |
| AHA | Aceto-hydroxamic acid |
| ALINA | Actinide III-lanthanide intergroup separation in acidic medium |
| ALSEP | Actinide-lanthanide separation |
| AMP | Ammonium molybdophosphate |
| AMP-PAN | Ammonium molybdophosphate-polyacrylonitrile |
| ANL | Argonne National Laboratory (United States) |
| ATR | Advanced test reactor |
| AWP | Ammonium tungstophosphate |
| BNFP | British Nuclear Fuel Processing Plant (United Kingdom) |
| BRC | Blue Ribbon Commission (United States) |
| BTP | Bis-triazinyl-pyridines |
| BTP | Bis-triazinyl-bipyridines |
| BWR | Boiling water reactor |
| CaALG | Calcium alginate |
| CANDU | CANada Deuterium Uranium |
| CARBEX | Carbonate extraction |
| CBP | High-Level Process Shielded Line |
| CCD | Chlorinated cobalt dicarbollide |
| CDTA | Trans-1,2- diaminocyclohexane-N,N,N’,N’-tetraacetic acid |
| CEA | Commissariat à l’énergie atomique et aux énergies alternatives (France) |
| CEPOD | Catalysed electrolytic plutonium oxide dissolution |
| CERS | Continuous electrorefining system |
| CF | Concentration factor |
| ChCoDiC | Chlotinated cobalt dicarbollide |
| CHON | Organic agent containing C,H, O, N |
| CMPO | Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide |
| CNRS | Centre National pour la Recherche Scientifique (France) |
| COEX™ | Co-extraction of actinides |
| CSSEX | Extraction process with crown ethers |
| CST | Sodium titanosilicate |
| CRIEPI | Central Research Institute of Electric Power Industry (Japan) |
| CV | Cyclic voltammetry |
| DR | Distribution ratio |
| DDFHA | 2,2,3,3,4,4,5,5,6,6,7,7- dodecafluorheptyl acetate (DDFHA) |
| DDFHME | 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorheptylmethyl ether |
| DEHDMPA | N,N-di(2-ethylhexyl)-2,2-dimethylpropanamide |
| DEHiBA | N,N-di-(ethyl-2-hexyl)isobutyramide |
| DMDOHEMA | N,N’-dioctyl-hexylethoxy-malonamide |

| | |
|---|---|
| DF | Decontamination factor |
| DFDF | DUPIC Fuel Development Facility (Korea) |
| DGA | Diglycolamide |
| DHOA | N,N-dihexyloctanamide |
| DIAMEX | DIAMideEXtraction |
| DOA | N,N-dioctylamine |
| DODGAA | N,N-dioctyl-3-oxapentane-1,5-amic acid |
| DOE | Department of Energy (United Sates) |
| DOG | Dissolver off-gas |
| DOODA(C12) | N,N,N’,N’-tetradodecyl-3,6-dioxaoctanediamide |
| DOODA(C2) | N,N,N’,N’-tetraethyl-3,6-dioxaoctanediamide |
| DPA | Dipicolinic acid |
| DSNC | DUPIC safeguards neutron counter |
| DTPA | Diethylenetriaminepentacetic acid |
| DUPIC | Direct use of PWR fuel in CANDU |
| Dyp | Dipyridyl |
| EARP | Enhanced Actinide Removal Plant (United Kingdom) |
| EDC | Experimental Demonstration Centre |
| EGFRC | Expert Group on Fuel Recycling Chemistry (NEA) |
| EtTDPA | N,N-diethyl-N’,N’-ditolyl diamides |
| EURATOM | European Atomic Energy Community |
| ExAm | Extraction of americium |
| F-3 | Meta-nitrobenzotrifluoride |
| FaCT | Fuel cycle technology development |
| FNR | Fast neutron reactor |
| FCT | Fuel cycle technology |
| FHA | Formohydroxamic acid |
| FJZ | Forschungszentrum Jülich |
| Formal-2 | 1,1,2,2,3,4,4,10,10,11,11,12,12,13,13-hexadecaflour-6,8-dioxatridecane |
| FP | Fission products |
| FPEX | Fission product extraction |
| FR | Fast reactor |
| FS-13 | Trifluoromethylphenyl sulfone |
| FVM | Fluoride volatilisation method |
| GANEX | Group actinide extraction |
| GDF | Geological disposal facility |
| GIF | Generation IV International Forum |
| GNEP | Global Nuclear Energy Partnership |
| GWd/tHM | Giga watt day/tonnes of heavy metals |
| GWd/tU | Giga watt day/tonnes of uranium |
| HA | Hydroxamic acid |
| HAN | Hydroxylamine nitrate |
| HAR | Highly active raffinate |
| HDBP | Dibutyl phosphoric acid |
| HDEHP | Di-(2-ethylhexyl)phosphoric acid |
| HEDTA | Hydroxyl-ethylene-diamine-triacetic acid |
| HEH[EHP] | Mono-2-ethylhexyl ester [2-ethylhexylphosphonic acid] |
| HFEF | Hot fuel examination facility |
| HHR | High heat radionuclide |
| HLLW | High-level liquid waste |

| | |
|---|---|
| HLW | High-level waste |
| HTP | Hydrogen tetrapropylene |
| HZ | Hydrogen mordenite |
| IAEA | International Atomic Energy Agency |
| IFR | Integral fast reactor |
| IODOX | Iodine oxidation |
| IL | Ionic liquid |
| ILW | Intermediate-level waste |
| INL | Idaho National Laboratory (United States) |
| INTEC | Idaho Nuclear Technology and Engineering Centre (United States) |
| ITU | Institute for Transuranium Elements (EU) |
| JAEA | Japan Atomic Energy Agency |
| JAERI | Japan Atomic Energy Research Institute |
| JFCS | Joint Fuel Cycle Studies |
| KAERI | Korea Atomic Energy Research Institute |
| KCoFC | Potassium cobalt hexacyanoferrate |
| KNiFC | Potassium nickel hexacyanoferrate |
| LiF | Low solubility in the fuel |
| LMFNR | Liquid metal fast neutron reactor |
| Ln | Lanthanides |
| LHR | Low heat radionuclide |
| LLW | Low-level waste |
| LWR | Light water reactor |
| M | Mole/litre |
| MA | Minor actinides |
| MCC | Mining and Chemical Combine (Russia) |
| MDD | Modified direct denitration |
| MOTIE | Ministry of Trade, Industry and Energy (Korea) |
| MFBC | Non-fuel bearing components |
| MLW | Medium level waste |
| MOSART | Molten salt actinide recycler and transmuter |
| MOX | Mixed oxide |
| MSNR | Molten salt neutron reactor |
| MSFR | Molten salt fast reactor |
| MSR | Molten salt reactor |
| MSRE | Molten salt reactor experiment |
| MTTA | Methyltrialkylammonium |
| NE | Nuclear energy |
| NEXT | New extraction system for TRU recovery |
| NFC | Near-field communication |
| NIRAB | Nuclear Innovation and Research Advisory Board (United Kingdom) |
| NIS | Nuclear Information Service (United Kingdom) |
| NFBC | Non-fuel bearing components |
| NSC | Nuclear Science Committee (NEA) |
| NNL | Nuclear National Laboratory (United Kingdom) |
| NOx | Nitrogen oxide |
| NPIA | National Policing Improvement Agency (United Kingdom) |
| NPP | Nuclear power plant |
| NUEX | New uranium extraction process |
| OMEGA | Offshore membrane enclosures for growing algae |

| | |
|---|---|
| ONR | Office for Nuclear Regulation (United Kingdom) |
| OREOX | Oxidation and reduction of oxide fuels |
| ORNL | Oak Ridge National Laboratory (United States) |
| O/W | Organic phase to aqueous phase ratio |
| PAN | Polyacrylonitrile |
| PECOS | Public Engagement Commission on Spent Nuclear Fuel Management (Korea) |
| P&T | Partitioning and transmutation |
| PDC | Pilot Demonstration Centre (Russia) |
| PEF | Polyethylene furanoate |
| PEG | Polyethylene glycol |
| PIE | Post-irradiation examination |
| PIEF | Post-irradiation examination facility |
| PLS | Partial least squares |
| PNC | Power Reactor and Nuclear Fuel Development Corporation (Japan) |
| PNH | Plutonyl nitrate hexahydrate |
| PR/PP | Proliferation resistance/physical protection |
| PRISM | Power Reactor Innovative Small Module |
| PRIDE | PyRoprocess integrated inactive demonstration |
| PUREX | Plutonium and uranium refining by extraction |
| PWR | Pressurised water reactor |
| R&D | Research and development |
| RCONHOH | Alkyl hydroximic acid |
| RE | Rare earth |
| REDC | Radiochemical Engineering Development Centre (United States) |
| REMIX | REgenerated MIXture |
| RHC | Research hot cells |
| RT | Residence time |
| REE | Rare earth element |
| REPA | REprocessing-PArtitioning |
| RIAR | Russian Institute of Atomic Reactors |
| RRC | Russian Research Centre |
| SANEX | Selective actinide extraction |
| SBF | Sodium-bearing waste |
| SESAME | Selective extraction of americium by electrochemical methods |
| SETF | Solvent Extraction Test Facility (United States) |
| SMR | Small modular reactors |
| SFR | Sodium-cooled fast reactor |
| SRL | Scientific readiness level |
| SSA | Specific surface area |
| SF | Separation factor |
| SFAs | Spent fuel assemblies |
| SIXEP | Site ion exchange effluent plant |
| SN | Solvation number |
| SNF | Spent nuclear fuel |
| T2EHDDGA | N,N,N’,N’-tetra(2-ethylhexyl)diglycolamide |
| TALSPEAK | Trivalent actinide-lanthanide separations by phosphorus reagent extraction from aqueous “k”omplexes |
| TBDPA | N,N,N’,N’-tetrabutyl-dipicolinic acid |
| TBP | Tributylphosphate |
| TD | Theoritical density |

| | |
|---|---|
| TDdDGA | N,N,N’,N’-tetradodecyl-diglycolamide |
| TDN | Thermal denitration |
| TEHP | Tris-2-ethyl hexyl phosphate |
| TEF | Transmutation experimental facility |
| THOREX | Thorium extraction |
| TRL | Technology readiness level |
| TEDGA | N,N,N’,N’-tetraethyl-diglycolamide |
| THORP | Thermal oxide reprocessing plant |
| TND | Thermal denitration |
| TOA | Trioctylamine |
| TODGA | N,N,N’,N’-tetraoctyl-3-oxapentane-1,5-diamide |
| TOPEN | N,N,N’,N’-tetrakis((5-octyloxypyridin-2-yl)methylethylenediamine) |
| TOPO | Trioctyl phosphine oxide |
| TPE | Transplutonium element |
| TPH | Total petroleum hydrocarbons |
| TPTZ | TriPyridyl-triaZine |
| TRU | Transuranium |
| TRUEX | Transuranium extraction |
| UDS | Undissolved solids |
| UN | Uranium nitrate |
| UNF | Used nuclear fuel |
| UNH | Uranyl nitrate hexahydrate |
| UOx | Uranium dioxide |
| UREX | Uranium extraction |
| VNIIKHT | Leading Research Institute of Chemical Technology (Russia) |
| VNIINM | A.A. Bochvar High-Technology Scientific Research Institute for Inorganic Materials (Russia) |
| VOG | Vessel off-gas |
| VVER | Water-Water Energetic Reactor (Russia) |
| WAK | Karlsruhe Reprocessing Plant (Germany) |
| WP | Waste package |
| WPFC | Working Party on Scientific Issues of the Fuel Cycle (NEA) |

# Executive summary

The continuous use of nuclear energy as part of a global low-carbon energy strategy will lead to the production of large quantities of used fuel which will need to be treated. Two options are currently being considered for the disposal of this fuel:

- direct disposal in a geological disposal facility (open or once-through fuel cycle);
- reprocessing to recycle in advanced reactors (closed fuel cycle) to recover reusable components. There are many separation and conversion processes that are applicable; some are aqueous processes and some are non-aqueous pyrochemical processes. Combinations may be required.

Many countries are currently using or developing reprocessing and separation technologies. These processes are being developed to address different fuel cycle strategies according to the national context, so as to respond to the specific needs of particular situations.

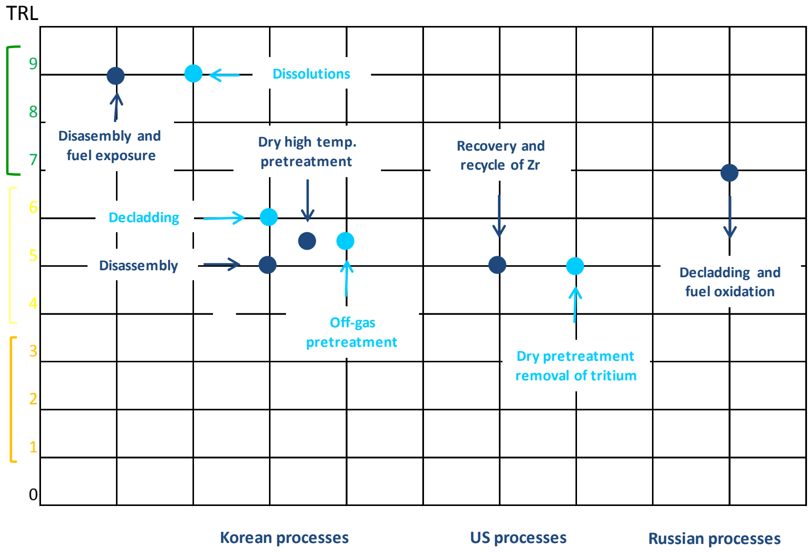
A comprehensive review of the progress of separation technology developments and current achievements was carried out, taking into consideration both the aqueous and pyroprocesses. The different steps of the processes were examined, from the preparation of the used nuclear fuel (head-end processes) to the separation of the different elements. Each process was described according to its purpose: U recovery, U/Pu extraction, co-processing of actinides or TRU extraction. Various options were investigated for the extraction of minor actinide elements (Np, Am, Cm). The separation of other elements such as Zr from cladding, Cs and Sr was also covered. Processes using a nitric media and other media, such as carbonates, are also described.

This review only addresses the stages from spent fuel to the separation of the elements without considering fuel refabrication. Most processes relate to advanced fuel cycles beyond the management of only U and Pu, to allow the management of all materials separated from spent fuel re-use, disposal or further transmutation to help reduce radiotoxicity, heat generation and the burden on geological disposal.

The technical maturity or "technical readiness level" (TRL) (see Figures 1 to 3 – see chapter 4) and state of R&D of the major aqueous and pyrochemical processes are also compared. The processes with higher maturity (higher TRLs) are those based on commercially operated processes, which allow the separation of U/Pu with or without Np. A few new processes are nearing industrial implementation (TRL 7-8). Innovative processes for the separation of U/Pu/Np and/or the separation of other elements are still at an early stage of development (TRL 4-5) and will require further investigation.

Non-aqueous pyroprocesses are less advanced than aqueous processes, and less industrial implementation has been demonstrated thus far. However, the development of advanced fuel cycles has led to a renewed interest for pyro-separations for the treatment of advanced fuels, including metallic and nitride fuels.

## Figure ES 1. Summary of TRLs for head-end processes



## Figure ES 2. Summary of TRLs for aqueous processes

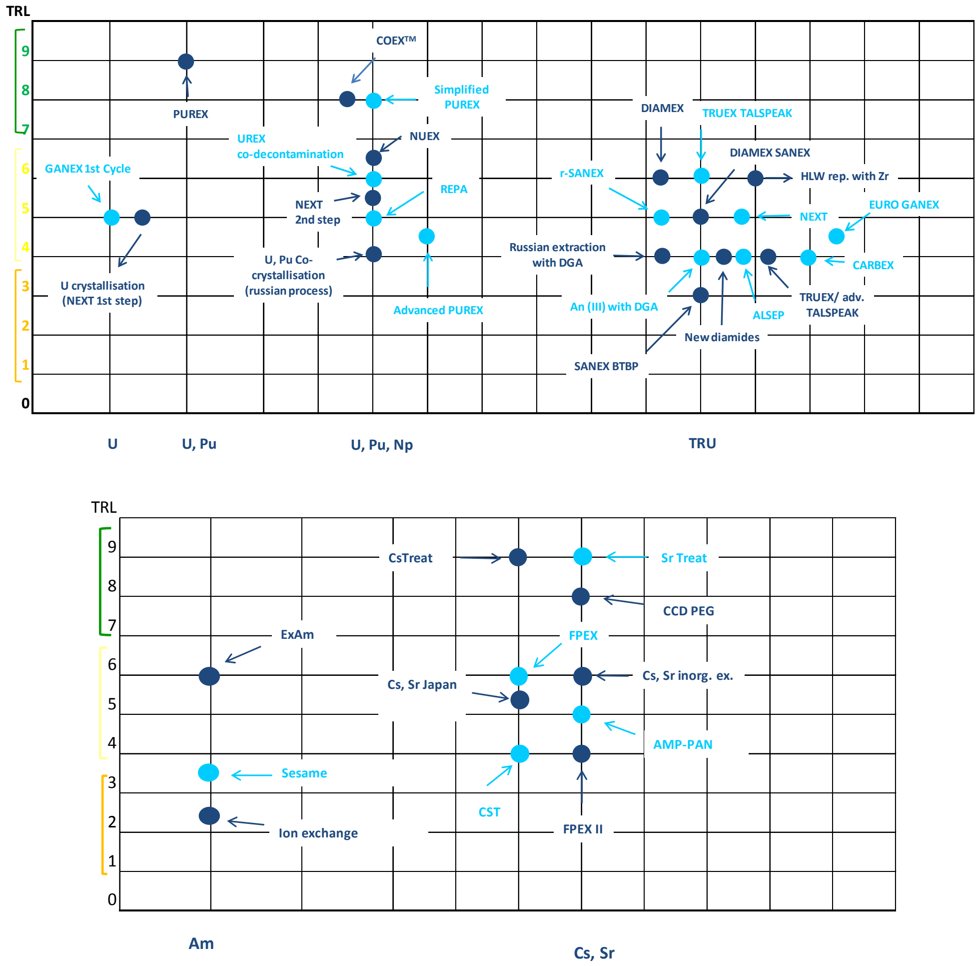
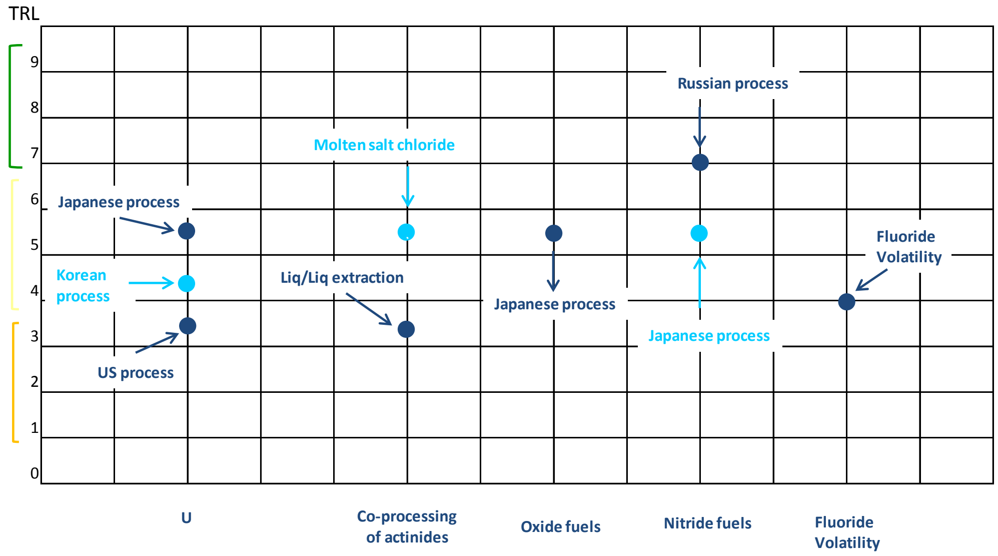


**Figure ES 3. Summary of TRLs for pyrochemical separation processes**



Head-end pyrochemical separations such as dry oxidation processes for removal of volatile components (e.g. tritium), are shown in Figure ES 1.

The choice of different processes according to the types of fuels to be treated and refabricated is also explored. Advanced fuel cycles generally consist of closed fuel cycles, and may include multi-recycling of U and Pu in thermal and fast reactors. In addition to meeting performance criteria, future recycling plants need to meet other requirements, such as lowering cost, increasing efficiency, ensuring safety, managing radioactive waste, and mitigating environmental impact so as to ensure sustainability. The ability to reprocess different types of fuels, in particular for a transition scenario from LWR to FRs with a good understanding of waste management and environmental impact (), is thus an important consideration.

Non-proliferation is a key issue when considering advanced reprocessing technologies. Different strategies have been explored to resolve this issue. One such strategy was the partial separation of actinides or fission products to reduce the "attractiveness" of the fissile components (e.g. UREX, COEX$^{TM}$, NUEX, pyroprocessing), but this strategy was found to be only marginally effective. Safeguards-by-design approaches using co-located and integrated spent fuel storage, reprocessing separations and recycle fuel fabrication within a physically protected facility were found to be an effective safeguard strategy. Physical protection and engineered safeguards are in any case necessary.

The following points are of particular importance to clarify non-proliferation uncertainties:

- The selection of a specific reprocessing separation technology over other technologies can provide only insignificant effects on the safeguard arrangements placed on recycle plants to meet non-proliferation requirements since:
  - Plutonium is a chemically separable component of spent nuclear fuel (SNF), regardless of the processes selected for reprocessing separations and recycled fuel production.
  - A variety of well-known methods can be used to produce separated plutonium, especially for a small-scale, non-commercial operation, which could still be large enough to conduct an undeclared operation of proliferation concern.

- Separated plutonium, partially separated plutonium and unseparated SNF must be protected by physical and other engineered safeguards, including safeguards-by-design. This is essential, whether the plutonium is stored, disposed of in a repository or separated to enable recycling.
- The self-protecting radiation barrier decays exponentially with time. With indecision and continued storage for several decades, stored SNF becomes more vulnerable. This vulnerability can be eliminated by recycling and re-irradiation of the plutonium.
- Continued production of plutonium in nuclear fuels and storage of SNF for multiple decades, together with the exponential decay of the self-protecting radiation barrier, are genuine reasons for international and national proliferation concern.
- Safeguards-by-design, co-location and integration of SNF storage, reprocessing separations, and recycle fuel production, together with the application of multiple engineered safeguards, can provide the "defence-in-depth" necessary to prevent diversion and permit secure recycling of SNF.
- Experience in non-proliferation analyses of several possible methods of separation of SNF components has shown that the various separation technologies that have been proposed for a closed back end of the nuclear fuel cycle do not offer significant non-proliferation differences. Therefore, the technologies to be used should be chosen for reasons such as process efficiency, maturity and cost-effectiveness.

A common perspective for developing future technologies through R&D programmes is the objective of reducing the volume and radiotoxicity of waste and hence the burden on geological disposal. National strategies are described, and they can be divided into three main groups:

- Reprocessing towards a **closed fuel cycle** (France, Japan): The French strategy considers multi-recycling of plutonium based on oxide fuels. In Japan, the priority is partitioning and transmutation (P&T) even after the review of the accident at Fukushima.
- **Open (or once-through) fuel cycle**: Korea, the United Kingdom and the United States are currently operating a once-through fuel cycle, but they are pursuing R&D efforts for a potential future closure of the fuel cycle. In Korea, the priority is to establish a long-term spent fuel management programme or policy to resolve the spent fuel accumulation issues (waste management using pyroprocessing technologies to prepare spent fuel for recycling and storage). An open fuel cycle is envisaged as current investigations include the search for a site for long-interim storage of spent fuel without reprocessing.
- **Open/closed fuel cycle** (Russia): spent fuel will be reprocessed and recycled to operate several fast reactors.

Finally, international collaboration could be an asset in implementing various processes at a commercial scale. It would be particularly beneficial for the less advanced countries hoping to develop similar processes.

# 1. Introduction

The implementation of advanced nuclear systems requires new technologies associated with the back end of the fuel cycle. The separation of minor actinides (MA: Np, Am, Cm) from other fuel components is one of the advanced concepts required to close the nuclear fuel cycle and to improve the long-term effects on the performance of geological repositories. Separating these elements and subsequently converting them by transmutation into short-lived nuclides should considerably reduce the long-term risks associated with nuclear power. R&D programmes worldwide have been launched in order to address this challenge and many processes for partitioning MA have been developed. Improved or new separation techniques such as advanced head-end processes, co-processing solvent extractions, and pyroprocessing are also being investigated in different member states. The role of the NEA Expert Group on Fuel Recycling Chemistry (under the guidance of the Nuclear Science Committee and the mandate of the Working Party on Scientific Issues of the Fuel Cycle [WPFC]) is to share up-to-date information on recent developments in the field of recycling and to perform technical analyses of advanced processing concepts, including technological maturity in design bases for future spent nuclear fuel recycling plants. In this context, members of the expert group have launched an activity to perform a technical assessment of separation processes under development, related to the current and future nuclear fuel cycles, to help recommend collaborative international efforts that will further the development of these separation processes. The objective was to carry out an international review of the different processes developed or under development in separation chemistry within NEA member countries (France, Japan, Korea, Russia, the United Kingdom and the United States, and in the European Union).

Since 2009, experts have worked to produce a report in which they intend to deliver a comprehensive but not exhaustive state of the art of the current R&D status in the field of separation chemistry of used fuel and treatment of minor actinides. The advantages and disadvantages of each process are outlined without taking into account past and current national strategies. Therefore, the report is organised according to the different processes and the role and aim of these technologies. These processes cannot be compared because they were each developed following a specific strategy, with a particular goal, and taking into account the existence or absence of industrial tools. For example, France, Russia and the United Kingdom have established strong industrial tools based on hydrometallurgy, whereas some countries have not yet developed recycling technologies at an industrial/commercial level. In reprocessing technologies, as in all other steps of the nuclear fuel cycle, safety remains a priority. The safety aspect was taken into account during the development of the different separation processes mentioned, although it is not discussed in detail in the report. For every chemical system, the behaviour of the extractants, complexants and diluents (solvent stability) has been studied and the safety issues related to process development have been addressed.

A comprehensive review of the progress of separation technology and current achievements is provided in Chapter 2. This includes head-end processes, hydrometallurgy and pyroprocessing for different types of fuels. Criteria are then suggested to assess the impact of various processes on fuel cycle scenarios for fuel recycling (Chapter 3). Key issues of safeguards and non-proliferation are also considered. The methods member states use to focus their strategic choice are also described. Chapter 4 presents an evaluation of the technical maturity of each process through a technology readiness level (TRL) approach. Finally, national perspectives on future R&D are described in Chapter 5.

# 2. Progress of separation technology and current achievements

## 2.1. Head-end processing

### *2.1.1. Introduction*

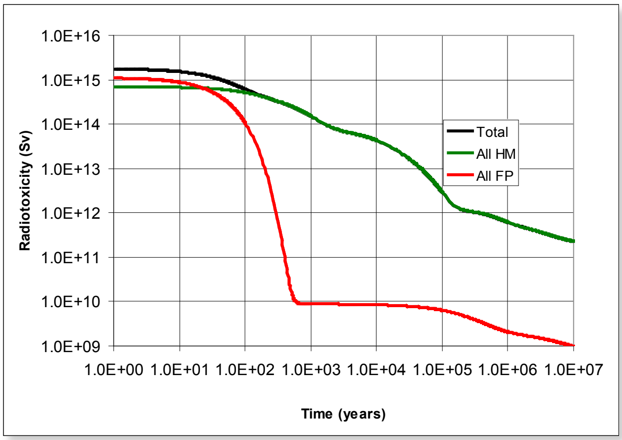
In closed nuclear fuel cycles, the initial role of used nuclear fuel (UNF) reprocessing is to recover the valuable fissile and fertile materials for re-use, thereby improving the sustainability of the nuclear fuel cycle. Another major goal is the reduction of waste volumes, heat loadings and the amount of long-lived radioactivity to be consigned to a geological disposal facility (GDF). In designing advanced reprocessing plants for future fuel cycles, it may be possible that recovery of the minor actinides (MA), neptunium, americium and curium will be required [1]. The recovery of the minor actinides provides potential to reduce the amount of long-lived radioactivity emplaced in the GDF and allows fission energy to be generated during the destruction of the MA. To maximise the reduction in radioactivity, a greater value may be placed upon achieving high recoveries; as illustrated in Figure 2.1.

The head-end processes prepare UNF for component separation. The head end encompasses disassembly and shearing, an optional dry process for volatile fission product removal, off-gas trapping of volatile used fuel components, potential recovery and recycle of zirconium from zircaloy® used fuel cladding and dissolution of the oxide fuel to prepare for subsequent component separations. The head-end processes are coupled with off-gas treatment systems to control the release of radioactive gases arising from the fuel and of harmful chemical vapors arising from the process chemicals.

In comparison with current industrial-scale operations, research, development and demonstration studies have shown progress in improving the capabilities for volatile component release and trapping by means of the advancements made in the dry pyrochemical oxidation processes and associated off-gas trapping, as well as in conversion of the ceramic oxide fuel components to a finely divided oxide powder that is amenable to continuous dissolution. Moreover, systems studies have shown the potential benefits of recycling more of the used fuel components, including uranium, all transuranium elements, zirconium from Zircaloy fuel cladding and several of the valuable fission product components [1].

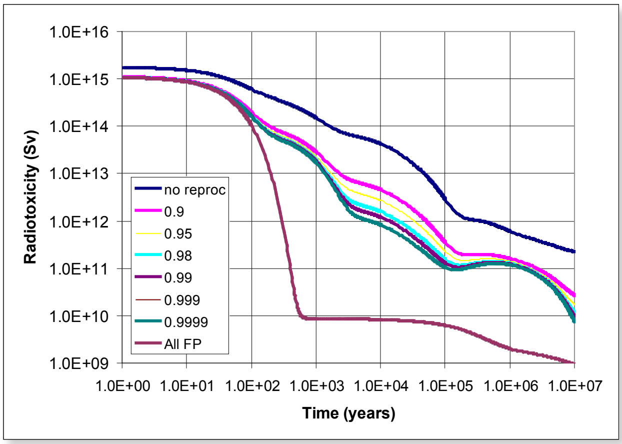
**Figure 2.1. Radioactivity of 4% $^{235}U$ – 40 GWd/tHM, under three scenarios**

a) Used fuel and fission products*

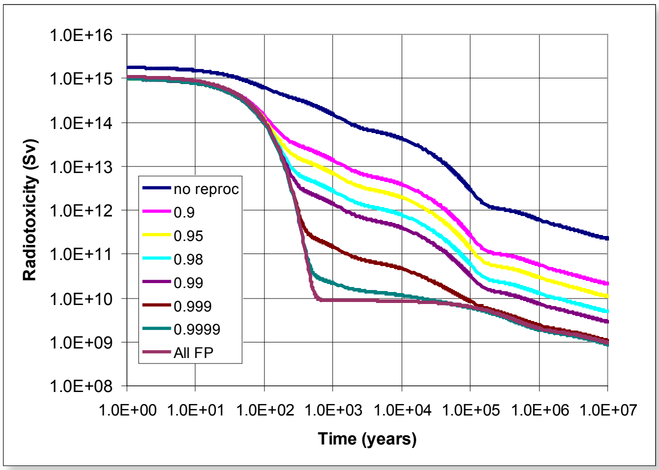


* FP: fission product; HM: heavy metal

b) Reprocessing with varying recovery of uranium and plutonium



c) Reprocessing with varying recovery of uranium, plutonium and minor actinides



### *2.1.2. Current practices*

The United Kingdom has operated four reprocessing plants and currently two are undergoing decommissioning and two are operational (Table 2.1). The Magnox reprocessing plant reprocesses uranium metal fuel from the domestic Generation I Magnox reactors. The Thermal Oxide Reprocessing Plant (THORP) reprocesses domestic and foreign oxide fuel from light water reactors (LWRs).

**Table 2.1. UK reprocessing plants**

| | | |
|---|---|---|
| 1951-1972* | Windscale | Reprocessing plant for metal fuel, early commercial reactor fuel and decontamination of prototype oxide fuel. Currently undergoing decommissioning. |
| 1960-1996** | Dounreay | Reprocessing of a variety of fuel from the fast reactor development programmes. Currently undergoing decommissioning. |
| 1964 - | Magnox | 2nd reprocessing plant at Sellafield reprocesses commercial Magnox clad uranium metal fuel. |
| 1994 - | THORP* | 3rd reprocessing plant at Sellafield reprocesses commercial thermal oxide fuel. |

*With intermediate refurbishment.

**Due to close in 2018.

*Disassembly and fuel exposure*

The different designs of fuel require different fuel preparation. The Magnox uranium metal fuel was declad using a die press, but this was later replaced with a slitter wheel. Dounreay reprocessing plant used, and THORP uses, a hydraulic cutting blade to chop the fuel into short lengths. Due to the high fissile content and low throughput required, the Dounreay plant used a single pin shear. The higher throughput and lower fissile content of THORP requires the shear of entire pressurised water reactor (PWR) and boiling water reactor (BWR) fuel elements or bundles of advanced gas-cooled reactor (AGR) fuel pins.

Many designs for both PWR and BWR fuel assemblies have evolved over time. A typical Westinghouse PWR fuel assembly is shown in Figure 2.2. This type of fuel assembly has a 17 × 17 fuel pin array, of which 264 array positions are occupied by fuel pins and the remaining positions are for control rods. (A BWR fuel assembly typically has an 8 × 8 fuel pin array, of which 63 array positions are occupied by fuel pins.) Eight grid spacers and massive nozzles at the top and bottom of the assembly are clearly visible in the photograph. In terms of mass, one PWR fuel assembly is composed of ~525 kg of $UO_2$ (~461 kg U metal), ~108 kg of zircaloy, and ~26 kg of other steel-based hardware. The nozzles, spider (part holding the control rods), and springs are part of the steel-based hardware. Descriptions of various types of fuel assemblies can be found in DOE/RW-0184 (DOE Rev.1, 1992) [2].

Because UNF is enclosed in chemically resistant metal cladding, the fuel must be exposed for subsequent chemical treatment. Commercial enterprises for processing and recycling the components of UNF utilise a mechanical shear to cut the fuel pins into segments, although other techniques such as laser cutting have been tested and evaluated. Shearing options range from whole-bundle shearing to single-pin shearing. In both cases, the top and bottom nozzles are usually removed as part of a disassembly operation to eliminate these robust metal components. The non-fuel-bearing plenum areas of the fuel pins may be cropped to eliminate additional metal that does not contain fuel material. In whole-bundle shearing, all the fuel pins are held tightly in a compaction device while they are cut with a shear blade that moves perpendicular to the long axis of the pins. Compaction is necessary to prevent closing the ends of the cladding tube by pinching. The grid spacers remain in place and might hold a group of fuel pin segments together. Compaction can cause significant cladding tube deformation along the entire length of a fuel cladding segment and can result in fracture of the fuel pellets, which is beneficial to fuel dissolution. In single-pin shearing, the individual pins are removed so that the grid spacers are also eliminated from the shearing process. No grid spacer remnants remain to hold groups of sheared pin segments together. The cuts may be smooth and result in little fuel fracturing. Therefore, the difference between whole-bundle and single-pin shearing affects the size of the largest “chunk” of material to be processed and the degree of crushing of the fuel pellets. This variation, in turn, has implications for voloxidiser or dissolution process equipment design.

**Figure 2.2. Westinghouse PWR fuel assembly**

Source: ORNL Photo 3897-77.

*Dissolution in the UK reprocessing plants*

All reprocessing plants dissolve oxide fuel in nitric acid, although the dissolver designs differ. The first Sellafield reprocessing plant dissolved declad uranium metal rods in a batch kettle. The sequence of operations was, first, to add the fuel to the dissolver, which was then lidded and heated to temperature. The Magnox dissolver is a large, continuous dissolver where declad uranium metal fuel is added continuously and the dissolved fuel liquor is discharged and fed to the reprocessing plant.

The high fissile content of the fast reactor fuel used at Dounreay required a dissolver that was criticality “eversafe” and for this a thermosyphon dissolver was used. A sheared batch of fuel was placed into a basket which was then inserted into the dissolver vessel. Nitric acid was added for fuel dissolution.

THORP uses a similar method to the Dounreay dissolver; however, fuel is sheared and falls directly via a chute into a basket that is contained in the dissolver vessel.

Fuel is partially dissolved before more fuel is added. After all of the fuel is dissolved, the chute is removed. The dissolver is lidded and heated to the leaching temperature. The dissolvers are large kettle dissolvers that are not, by geometry, of subcritical design. Therefore, gadolinium nitrate is added as a neutron absorber to ensure criticality safety. THORP has three dissolvers that operate in sequence. While fuel is added to one, the second is leaching fuel, and the third dissolver transfers the liquor and hulls to the next processing step and is prepared for the next batch.

Air is added to the reflux condensers of both the Magnox and THORP dissolvers to enable increased conversion of nitrogen oxides (NOx), that are generated from the dissolution of fuel in nitric acid, to the more soluble nitrogen dioxide. This decreases the amount of nitric acid used and the amount of nitrogen oxide released to the dissolver off-gas (DOG) treatment system. This technology is termed “fumeless” dissolution when operated at high efficiencies.

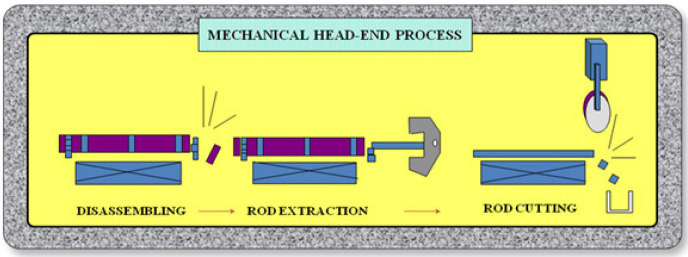
The Magnox swarf from decanning Magnox elements and THORP leached hulls are encapsulated in cement to form an intermediate-level radioactive waste (ILW) waste form.

### 2.1.3. Potential additional process steps for future reprocessing plants

*Korean process for disassembly*

The first step of the head-end process is to disassemble the used PWR fuel assembly and to extract the fuel rods. Rod extraction is followed by cutting the ~4 m fuel rods into sections of proper size for the decladding process. PWR fuel assemblies consist of an upper structure, a lower structure and fuel rods. According to the type of fuel assembly (14 x 14, 16 x 16, 16 x 16 and 17 x 17), suitable disassembling equipment would be applied. KAERI conducted a rod consolidation study in the 1990s, and a dummy spent PWR fuel assembly was used for disassembly, extraction and cutting tests. Additionally, disassembly, extraction and cutting operations on an actual spent PWR fuel assembly have been performed on the laboratory-scale for post-irradiation examination (PIE) and direct use of used PWR fuel in a CANDU reactor (DUPIC) experiment in the post-irradiation examination facility (PIEF). The mechanical head-end process, which is a process for dismantling the spent fuel assembly, has been demonstrated using a mock-up fuel assembly to provide the technical basis for a future pilot-scale fuel recycle and rod consolidation plant. The process consists of an assembly down-ender, a rod extractor, a rod cutter, fuel decladding equipment, a skeleton compactor and a gantry-mounted telescopic manipulator. Figure 2.3 shows the mechanical head-end process flow for disassembly, rod extraction and rod cutting. All the machines were designed and verified using the graphic simulator. Their performance was tested and verified using a mock-up fuel at the mock-up facility. The rod extractor consists of a clamping table, an extraction table, an extraction rotary head, a cradle and a side transfer port. The machine unfastens the securing nuts of the bottom nozzle so that the remote manipulator may remove the bottom nozzle from the fuel assembly. Then the machine automatically extracts one rod at a time from a 17 x 17 PWR fuel assembly mock-up and transfers each rod to the adjacent rod cutter. After removing all the fuel rods, the skeleton compactor is used to compact the non-fuel bearing components (NFBC) of the fuel assembly for permanent disposal by implementing the method of cutting after a compression.

**Figure 2.3. Mechanical head-end process for the spent fuel PWR**



### *Korean process for decladding*

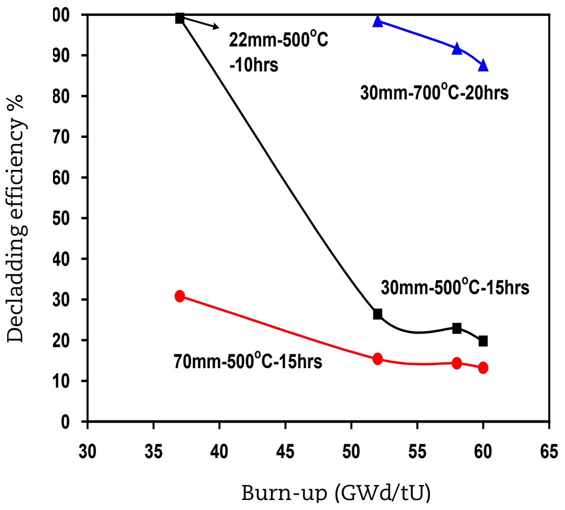
The decladding step in an advanced head-end process for recycling spent nuclear fuel affects the efficiency of the whole process. Issues in developing decladding technology include effective fuel material recovery and increased fission product removal which affects down-stream processes. Several decladding technologies (Table 2.2) for separating a fuel material from cladding tubes have been developed.

**Table 2.2. Notable examples for decladding technologies**

| Decladding technologies | | Organisation (country) | Characteristics | Rod-cut length |
|---|---|---|---|---|
| Mechanical | Roll straighten [3,4] | Kobe<br>steel (Japan) | Straighten and re-round deformed rod-cut by passing the rod-cut through a series roller, cut one end of rod-cut, hammering of rod-cut | 100-200 cm |
| | Hammering [5] | INL (United States) | Hammering of rod-cut | 20 cm |
| | Agitation [4] | CEA (United States) | Tumbling of rod-cut in a ball mill after hammer milling | 7 cm |
| | Slitting [6] | KAERI (Korea) | Axial cutting of rod-cut by blade | 15-25 cm |
| Oxidative | | ORNL [7], INL [8] (United States), JAERI [9] (Japan),<br>KAERI [10] (Korea) | Oxidation of rod-cut at 450-750°C | -ORNL: 2.5 cm<br>-JAERI: 1.15 cm<br>-INL: 2.5 cm<br>-KAERI: 2.5-10 cm |

Decladding by voloxidation treatment of spent fuel is a common head-end technology for reprocessing of spent fuel. Conventional oxidative decladding technology provides an effective removal of fission gases, especially tritium, with high recovery efficiency from low burn-up spent fuel (below 35 GWd/tU) at 500°C. KAERI has developed a mechanical decladding technology for separating fuel material from a cladding tube as fragment type for the DUPIC process. Considering the current trend to extend fuel burn-up in a PWR, the effect of burn-up on fuel recovery in the oxidative decladding technology should be investigated. The oxidative decladding efficiency of high burn-up spent fuel was experimentally evaluated based on the results of a test performed in the hot cell at KAERI. The oxidative decladding test was performed using the Oxidation and Reduction of Oxide fuel (OREOX) furnace without rotational agitation. It was observed that high burn-up spent fuel, over 50 GWd/tU, showed low decladding efficiency (~15%) due to the small fuel-to-clad gap and low oxidation rate (Figure 2.4). Improved decladding efficiency for high burn-up spent fuel requires longer oxidation time (>15 h) at 700°C. Compared to high burn-up spent fuel, low burn-up spent fuel (<40 GWd/tU) showed about 100% decladding efficiency at 500°C for 10 h with short length fuel (<30 mm). Therefore, oxidative decladding equipment with rotational agitation would be required to reduce the oxidative decladding time and obtain the very high decladding efficiency.

**Figure 2.4. Oxidative decladding efficiency according to variation of rod-cut length and burn-up**



Mechanical decladding technology as shown in Figure 2.5 was effective for the recovery of spent fuel material as a fragment type. Decladding efficiency was determined by DUPIC Safeguards Neutron Counter (DSNC) at the DUPIC Fuel Development Facility (DFDF). Decladding efficiency by mechanical slitting was higher than 99% for fuels with burn-up up to 58 GWd/tU. However, total decladding efficiency with a combination of mechanical slitting and subsequent oxidation was higher than 99.6%. Table 2.3 shows the particle size distribution of fuel fragments obtained from processing assemblies with average fuel burn-ups. In the case of mechanical slitting, the fraction of fine fragments <0.2 mm was lower than that produced by other mechanical decladding methods listed in Table 2.2.

**Figure 2.5. Decladding efficiency according to variation of burn-up**

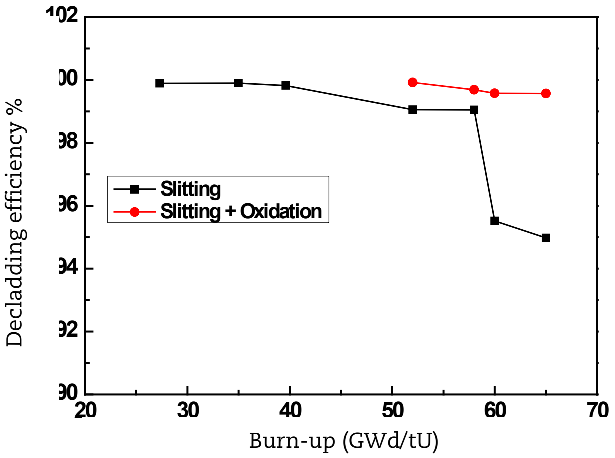


**Table 2.3. Particle size distribution of fuel fragments**

(Unit: weight percent)

| Burn-up (GWd/tU) | Particle size (mm) | | | | | | | Sum |
|---|---|---|---|---|---|---|---|---|
| | > 5 | 2-5 | 1-2 | 0.5-1 | 0.3-1 | 0.2-0.3 | < 0.2 | |
| 34.8 | 0.5% | 63.7% | 22.1% | 8.9% | 1.6% | 1.1% | 2.0% | 100% |
| 54.9 | 0.4% | 57.2% | 25.3% | 11.6% | 1.6% | 1.3% | 2.5% | 100% |

*Russian process for decladding and fuel oxidation*

Thermo-chemical destruction of zirconium cladding is based on the fact that nitrogen is dissolved at high temperatures in zirconium, which, as a result, loses its metallic properties and becomes brittle and break down with small mechanical stress. After separation from the broken cladding, the uranium dioxide fuel is oxidised with oxygen in air. In the course of this treatment, uranium dioxide transforms into $U_3O_8$ with destruction of the $UO_2$ crystal lattice, which is accompanied by tritium evolution. Tritium is trapped in the off-gas cleaning system and fixed in a special matrix, whereas the oxidised fuel is supplied to the acid dissolution and subsequent extraction reprocessing. [11].

The pilot mock up for studying thermochemical head-end operations of SNF reprocessing in the hot cells of the Khlopin Radium Institute is shown in Figure 2.6. This pilot mock-up (so-called “mini Khrust”) was designed at the Sverdlovsk Research Institute of Chemical Engineering. The tests were first performed using unirradiated nuclear fuel and then tests were carried out with the samples of WWER-1000 SNF (~47 MWt*day/kg U burn-up and ~9-year holding time).

**Figure 2.6. “Mini Khrust” pilot set-up (heater, ampoule for spent nuclear fuel and cork are observed)**

The fragments of the fuel elements (25 cm length and ~20 g of $UO_2$) were placed in the pilot set-up and the thermo-chemical destruction of zirconium cladding with subsequent oxidation of the uranium in the fuel was performed. In the course of the tests, the release of the volatile and gaseous fission products (such as tritium, krypton, iodine, cesium, etc.) was analysed.

The thermo-chemical treatment was carried out at a 900-1 100°C temperature range in the nitrogen and oxygen atmospheres. After treatment for 40 minutes at a given temperature, the fragments of zirconium cladding lost their plasticity that is typical for metals and became brittle. zirconium cladding with $UO_2$ pellets before and after heat treatment, are shown in Figure 2.7.

**Figure 2.7. View of zirconium cladding before and after treatment**

Fraction of non-irradiated fuel element (1) and sample after processing with the “mini Khrust” set-up (2)

The photograph of the broken zirconium cladding after mechanical stress (shock) is presented in Figure 2.8.

**Figure 2.8. Broken cladding**

Next, the oxidation of the uranium dioxide fuel was carried out in an oxygen atmosphere at 400-600°C. In the course of oxidation of $UO_2$ to $U_3O_8$, which is accompanied by degradation of the pellets (Figure 2.9), almost complete recovery of tritium and some gaseous nuclides were observed.

**Figure 2.9. Voloxidised uranium dioxide nuclear fuel**

The gaseous phase from the set-up was treated with an aerosol filter to remove volatile fission products ($^{134}$Cs, $^{137}$Cs, $^{99}$Tc, ruthenium isotopes) and then was supplied to the off-gas cleaning system. Tritium, $^{14}$C and $^{129}$I were trapped in three absorbers. First absorber was charged with aqueous NaOH. After this absorber, the afterburners were placed where tritium, present in the HT form, was oxidised on a catalyst and then trapped on a special sorbent. After cooling, the sample of $U_3O_8$ was dissolved in 3 M nitric acid and the resulting solution was analysed.

The experimental data for the SNF samples are listed in the Table 2.4.

**Table 2.4. Experimental data obtained with the "mini Khrust" set-up (recalculated to the sample of WWER-1000 SNF 18.6 g of uranium dioxide)**

| No. | Elements | Operations | | | |
|---|---|---|---|---|---|
| | | Thermo-chemical head processing | | Dissolution of voloxidised SNF | |
| | | Decladding | Voloxidation | Resulting solution | Trapping in the gas system |
| 1 | T | $8.2 \cdot 10^7$ Bq<br>(52.3%) | $7.2 \cdot 10^7$ Bq<br>(46.3%) | $6.4 \cdot 10^5$ Bq<br>(0.4 %) | - |
| 2 | $^{14}$C | $1.45 \cdot 10^5$ Bq<br>(8 %) | $2.0 \cdot 10^5$ Bq<br>(11 %) | - | $18.2 \cdot 10^5$ Bq<br>(81 %) |
| 3 | $^{129}$I | 22 mkg<br>(0.3%) | 410 mkg<br>(5.7 %) | - | 7.2 mg<br>(94 %) |
| 4 | $^{137}$Cs | $1.3 \cdot 10^9$ Bq (0.81%) | | $1.5 \cdot 10^{11}$ Bq (99.2%) | - |

Almost complete removal of tritium was observed in the course of the thermal treatment and subsequent voloxidation. It should be noted that in the course of thermal decladding, only tritium dissolved in the zirconium cladding is recovered; whereas, in the course of voloxidation, tritium dissolved in the SNF is recovered. The other gaseous and fission elements were recovered partially and the fraction of the recovered elements decreases in the following order: $^3$H>Kr=Xe>I. The recovery of Cs from SNF was insignificant.

*US process for recovery and recycle of zirconium from UNF cladding*

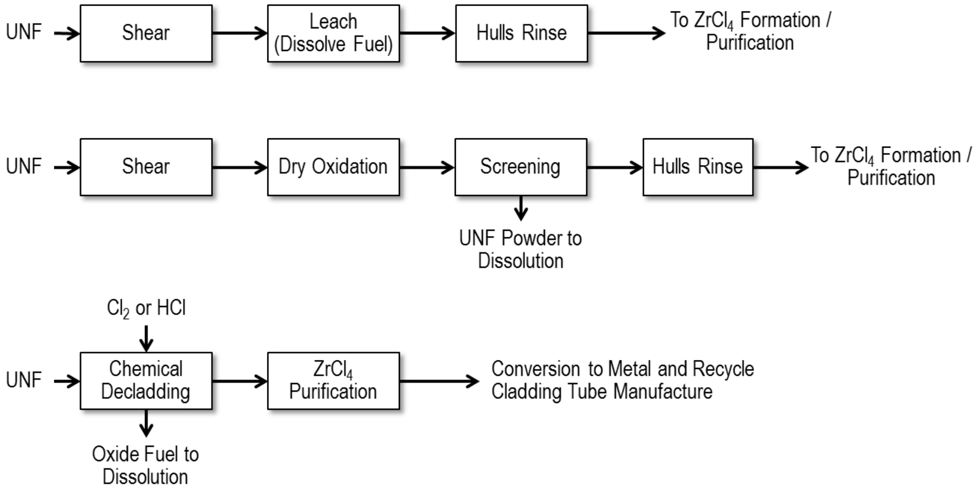
An objective of current research is to determine the feasibility of recovery and recycle of zirconium from LWR used fuel cladding waste. Zircaloy cladding, which contains 98+% of hafnium-free zirconium, is the second largest mass, on average ~25 wt%, of the components in LWR used fuel assemblies [1]. Recovery and recycle of the zirconium would enable a large reduction in geologic waste disposal for advanced fuel cycles. Current practice is to compact [12] or grout the cladding waste and store it for subsequent disposal in a geologic repository.

LWR zircaloy cladding contains zirconium with a natural abundance isotopic composition, and the used fuel cladding contains one radioactive isotope, $^{93}$Zr, formed by neutron capture on natural $^{92}$Zr during irradiation. The recycled zirconium would be radioactive. However, $^{93}$Zr has a low specific activity (half-life is 1.5 million years) and only a weak beta emission, which means that the recycled zirconium would have low radioactivity if it can be decontaminated from other fission and activation product elements.

The zirconium recovery process would be integrated into the advanced fuel cycle head-end process steps for treatment of used fuel assemblies. Figure 2.10 illustrates three options where the cladding may be processed to recover the zirconium: (1) following dissolution of the fuel and rinsing of the cladding to remove fuel bearing-solution,

(2) following the dry oxidation (tritium separation) process, where the fuel components are present in the form of finely divided powder that can be separated easily by screening from the empty, sheared cladding hulls, or (3) substituting for shearing where the cladding is removed chemically to volatilise the zirconium [13].

**Figure 2.10. Typical head-end operations where zirconium recovery may be integrated**



Recent tests with actual used fuel rods (Table 2.5) have shown that most of the residual fuel powder remaining on the cladding hulls after screening can be removed by hull washing with nitric acid. The washed hulls would nonetheless contain residual contamination sufficient to prevent disposal of the clad as low-level waste. The residual contamination would be removed during the zirconium recovery process, along with the alloying constituents, and returned to the UNF reprocessing plant for disposal together with other radioactive waste.

**Table 2.5. Residual contamination after UNF clad washing**

| Element | Removed by cladding wash (wt % of UNF) | Remaining in washed clad (wt % of UNF) | Reduction factor | Residual clad contamination (ppm) |
|---|---|---|---|---|
| U | 0.6 | 0.0037 | 162 | 100.0 |
| Pu | 0.3 | 0.0130 | 23 | 6.0 |
| Am | 0.2 | 0.0130 | 15 | 0.6 |

A process step for clad shredding may be needed to increase the surface area and thereby the efficiency of the zirconium recovery step. Previous tests have shown that approximately half of the tritium remains within the cladding hulls [14]. Therefore, removal and capture of residual tritium released from the cladding should be included in any future radioactive process development studies.

Zirconium in the cladding may be converted to volatile $ZrCl_4$ by reaction with either hydrogen chloride or chlorine. The volatile product can be purified by an additional step of condensation and sublimation. Purified $ZrCl_4$ may be fed to the metal sponge conversion step of the industrial zirconium metal manufacturing process (Figure 2.11).

An issue for an industrial application of the hydrochlorination process in a radiochemical operation may be the hydrogen generated in the off-gas by the reaction:

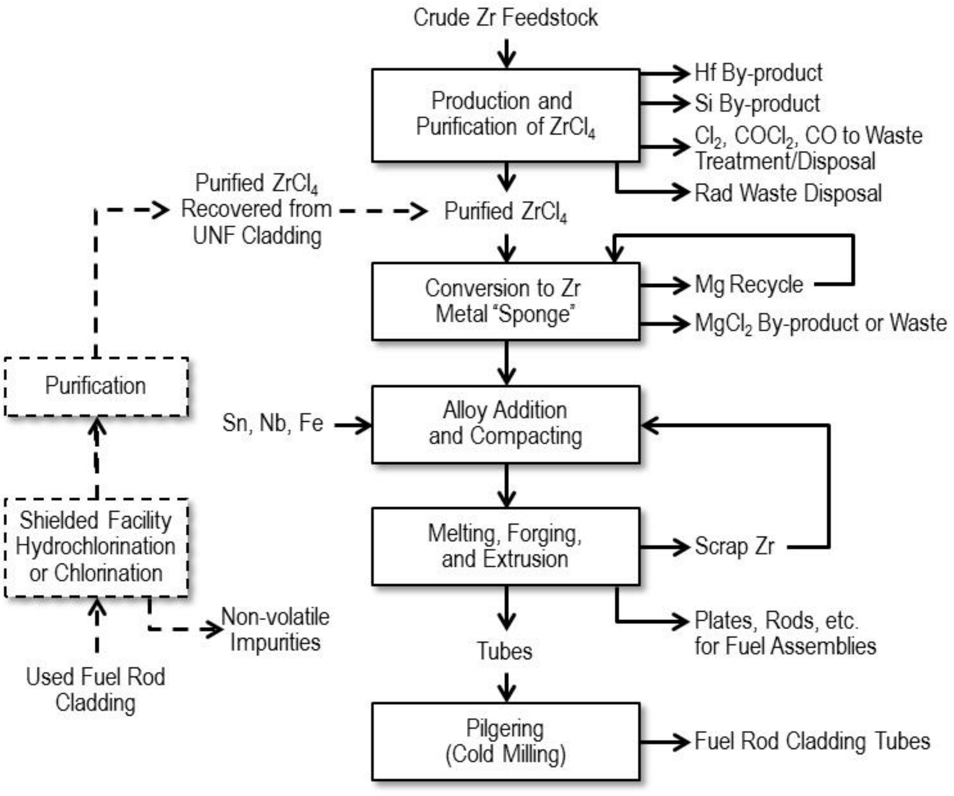
$$\text{Zr clad} + 4\text{HCl} \xrightarrow{350°\text{C}} \text{ZrCl}_4\uparrow + 2\text{H}_2\uparrow$$

whereas hydrogen is not generated by reaction with chlorine:

$$\text{Zr clad} + 2\text{Cl}_2 \xrightarrow{350°\text{C}} \text{ZrCl}_4\uparrow$$

Both methods of chlorination are still being considered, and a two-step recovery/purification may provide the best results. Nonvolatile residues, including radioactive contamination, would be treated to remove residual chlorides, and then returned to the fuel reprocessing plant for disposal with other radioactive waste.

**Figure 2.11. Interfacing zirconium recovery from cladding with tubing manufacture [13]**



### *Removal of volatile fission products*

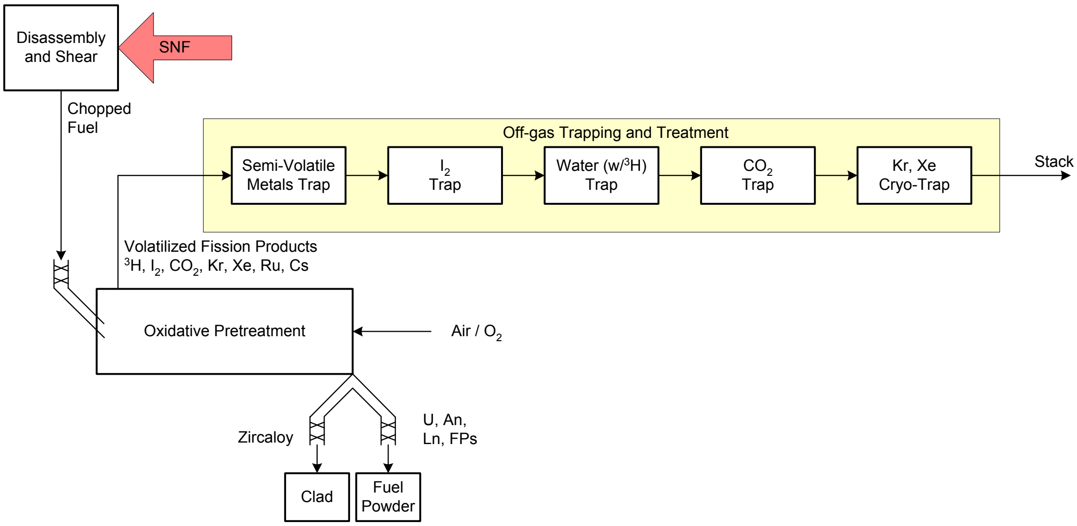
Future reprocessing plants will necessitate the abatement of radionuclides that are currently incompletely or poorly controlled, such as $^{3}$H, $^{14}$C, $^{36}$Cl, $^{85}$Kr, and $^{129}$I. To achieve control of these species, additional process steps may be required. Also, the reprocessing of fuels other than standard oxides may also necessitate the use of additional process steps. Two of the major candidate technologies are high temperature oxidative pre-treatment (voloxidation) and application of electro-mediated dissolution, e.g. using silver (II).

- United States process for dry pre-treatment for tritium management

Dry pyrochemical pre-treatment is a method for removing tritium from used reactor fuel prior to aqueous dissolution and chemical separations of fuel components. This avoids introducing the tritium into the aqueous systems, where it would accumulate or might be released to the environment with gaseous or liquid water discharges. Recent studies have indicated that tritium removal and retention is necessary to meet exposure limits at the reprocessing site boundary [15]. A general schematic of the process is shown in Figure 2.12.

The dry oxidation pretreatment process usually takes place at 480 to 600°C in the presence of air or oxygen. At these temperatures the reaction of $UO_2$ with oxygen to form $U_3O_8$ is rapid enough to be of practical value. Conversion to the higher oxide results in expansion and restructuring of the grain-level crystallite accompanied by crumbling of the monolithic fuel pellet to a fine powder [16]. Comminution increases the available surface area for reaction and releases the fuel from the segments of cladding. Tritium, which may be present in the fuel in elemental form, diffuses to the surface of the particle, where it reacts with oxygen to form water, which enters the gas stream [17]. A fraction of the tritium is associated with the cladding as zirconium hydride ($ZrT_x$). This fraction has been reported at >40% [18]. Indications are that oxidation has little effect on the tritium held in the cladding when processing occurs at a temperature of 480°C for 6 h.

**Figure 2.12. Standard dry oxidation pre-treatment process with off-gas treatment**



The rate of reaction at 480°C is such that >99.9% of the tritium is released from the fuel in about 4 h. Over 99% of the fuel particles are reduced to <20 µm. Powder size distribution depends on the temperature of the oxidation process [19-21] and other factors related to the used fuel characteristics. However, nearly all sizes will be <20 µm [18]. Along with the tritium, about half of the $^{14}C$ and minor fractions of other fission products are volatilised, including ~5% of krypton and xenon; ~1% of iodine and bromine; and <0.2% of the ruthenium, antimony and cesium. With higher temperatures and longer reaction times, larger fractions of the noble gases may be released.

The conversion to $U_3O_8$ may also be desirable for other fuel types, such as carbides and nitrides, because:

- During the dissolution of carbides in nitric acid complex organic products are produced that interfere with solvent extraction processes [22-23].
- The dissolution of nitrides in nitric acid is highly exothermic and conversion to $U_3O_8$ reduces the reactivity. Also, if $^{15}N$ containing nitride fuels are used, the $^{15}N$ being a valuable isotope, it may be necessary to recover it for re-use. An oxidation process would release the nitrogen for simple trapping and recovery, whereas, direct dissolution in nitric acid would cause isotopic dilution, complicating $^{15}N$ recovery [24].

The large difference in particle sizes between the oxidised fuel powder and remaining cladding hulls present the option of mechanical separation of the cladding from the fuel. Over 99% of the fuel may be separated from the cladding by screening. Such a separation benefits the dissolution process because a powder dissolver may be much less complex and more compact. Also, the powder dissolves faster and requires less use of nitric acid. However, high fuel recovery will require washing of the cladding hulls to remove the fines that cling to the surfaces.

During the oxidation pretreatment process, partial release of volatiles and trace release of semivolatiles occur at conditions where the tritium is volatilised. This is not problematic. The tritium is easily removed from the voloxidiser off-gas as tritiated water, and the remaining off-gases may be combined with the dissolver off-gas for treatment to sequester iodine, $^{14}C$ (as $^{14}CO_2$), and the radioactive noble gases (krypton, xenon). The partial release of other radioactive fission products indicates the potential to remove other semi-volatiles from the fuel, especially those that complicate downstream processes or their off-gas treatment systems.

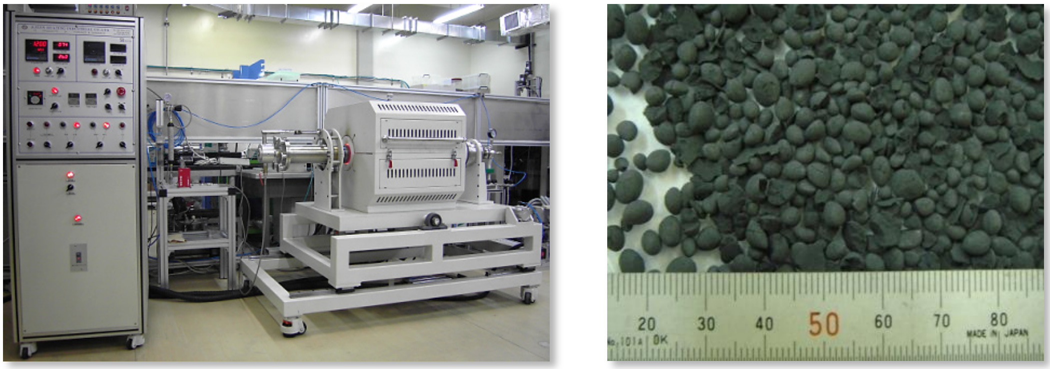
An enhanced oxidation process is being investigated that utilises either higher temperatures or alternative reactants (e.g. ozone, steam, nitrogen dioxide) or a combination of both temperature control and alternative reactants to completely remove other volatile or semivolatile fission products. The targeted species depends on the goals of the process, which depend on the trade-offs between benefits obtained for downstream processes and the costs to implement the process. Preliminary results indicate that iodine may be almost completely removed in an oxidation step using nitrogen dioxide as an oxidant. This possibility would simplify recovery (compared with processing the moisture-laden off-gas from the dissolution step), decrease halogen-enhanced corrosion in downstream processes, and reduce the requirements for iodine emissions controls from multiple points in the plant to a single control point. Similarly, $^{14}C$ and the noble gases are more completely removed.

### ▪ Korean process for dry high temperature pre-treatment

Fission gases and semi-volatile fission products are vaporised and removed by thermal pre-treatment to reduce the burden of fission products on the electrochemical processes. Specifically, the benefits to the electrolytic reduction process obtained by the removal of semi-volatile fission products from fuel material, such as I and Cs, by thermal pre-treatment are Pt anode protection from interaction with I and an extension of the salt replacement cycle due to a very low Cs accumulation rate [25,26]. In addition, the pretreatment makes possible further extension of salt replacement cycle by a post-treatment, a layer crystallisation method to separate Sr and Ba from salt waste generated by electrolytic reduction, which can reduce further the amount of salt waste [27]. Then, the purified salt could be recycled to the electrolytic reduction process. KAERI investigated three kinds of feed forms for the thermal pretreatment: crushed pellet to simulate fuel fragments, granules, and porous pellets.

During fabrication of granules and porous pellets from $U_3O_8$ powder, fission products were considered to be more effectively removed than from fuel fragments. The particles of $U_3O_8$ powder were bonded together during thermal pre-treatment and transformed into aggregates at temperatures above 1 000°C. In 2009, a laboratory scale rotary voloxidiser (max. 1.5 kg $U_3O_8$ powder/batch), as shown in Figure 13, was designed and manufactured to investigate control of particle size during conversion to $U_3O_8$ powder. The characteristics of granules fabricated from 200 g $U_3O_8$ powder was investigated under the conditions of thermal pre-treatment; specifically, a temperature of 1150 to 1200°C in an argon atmosphere, a treatment time of 5 to 15 h and a rotational velocity of 1 to 3 rpm using a rotary voloxidiser. The recovery rate of granules with characteristic dimension >1 mm and composition expressed as $UO_{2+x}$, where $0.25< x <0.67$ (Figure 2.13) significantly increased with increasing temperature, rotation velocity and time of up to 10 h. The typical recovery rate of granules showed about 89% (>1 mm) and 98% (>0.5 mm). The $UO_2$ granule with density of 4.38 g/cm$^3$ (40% of theoretical density [TD]) was fabricated by reduction of $UO_{2+x}$ at 1 000°C for 5 h in 4%$H_2$-Ar atmosphere. The process to fabricate the granules was very simple, but handling of the granules produced fine powder due to the weak bond between the grains in the granules.

**Figure 2.13. A rotary voloxidiser (left) and $UO_{2+x}$ granules (right)**



Porous $UO_2$ pellets with density of 6.78-7.67 g/cm$^3$ (60-70% TD) were fabricated by the traditional sequential process of compaction and thermal pretreatment (sintering) using the $U_3O_8$ powder obtained by oxidation of $UO_2$ pellets. Since the electrolytic reduction process is operated batch-wise, it requires a porous feed form with a high density in order to enhance the processing capacity. Also, a feed form having mechanical stability is required due to the mesh-type basket used in electrolytic reduction. A porous pellet fabricated from $U_3O_8$ powder was considered to satisfy the requirements of density and mechanical stability. KAERI measured release rates of $^{85}$Kr, $^{14}$C, and Cs during the OREOX (Oxidation and Reduction of Oxide fuel) pre-treatment step in the DUPIC fuel fabrication process. From the experimental data obtained, and from published data, release rates of the fission products during high temperature voloxidation are estimated to be 98% of the Cs, and 100% of the Kr, Xe, $^3$H, $^{14}$C, and $^{129}$I. These values may change with further experimental results.

*Off-gas treatment*

The processing or treatment of UNF will result in the release of a number of volatile and semivolatile species. Over the past two to three decades, a number of technologies have been developed to various stages of maturity. Off-gas treatment in a fuel reprocessing plant must address three main gaseous streams. The first is the off-gas from the head-end, which includes the shear, the optional dry pre-treatment, and the dissolver. This collectively is sometimes called the dissolver off-gas (DOG). The second is the vessel off-gas (VOG), which collects in-leakage to all of the process equipment and the instrument air used in bubblers, air sparge discharges, etc. The third is the cell ventilation, which provides confinement to the process cell. Each of these has unique characteristics and processing challenges, although the elements or radionuclides to be captured may be found in one or more of these streams. For this reason it is convenient to discuss capture technology for each of the targeted species.

- Tritium

Tritium may be removed from the off-gas stream with desiccants or molecular sieves. Anhydrous $CaSO_4$ has been reported as a possible desiccant [17]. Molecular sieves exhibit high water capacities: 10 to 20% based on the dry weight of the sorbent [28]. Type 3A desiccants have been shown to also sorb carbon dioxide at temperatures significantly below room temperature [29].

- Iodine

Numerous technologies have been developed for the recovery of airborne $^{129}$I based on scrubbing with caustic or acidic solutions and chemisorption on silver-coated or impregnated adsorbents. However, to achieve the high decontamination factors (DFs) required to meet the regulatory requirement (>500), a critical step is to ensure that the iodine is volatilised into the most concentrated gas stream possible. The distribution of $^{129}$I in gas and liquid process streams has been measured at the Karlsruhe reprocessing plant (WAK) [30] and predicted for the British Nuclear Fuel Processing Plant (BNFP) [30]. These evaluations indicate that about 94 to 99% of the $^{129}$I reports to the DOG, and the remaining is distributed among the high-, medium-, and low-level aqueous waste. While the primary recovery technology is applied to the DOG, the VOG may also require treatment to recover $^{129}$I arising from other processing steps and vessels.

Various types of adsorbents for iodine have been studied and developed over the years. Natural or artificial porous materials such as zeolite, mordenite, alumina, and silica gels have been loaded with metals (e.g. silver, cadmium, and lead) and/or metal nitrates (e.g. $AgNO_3$) and used in performance studies. Commercially available inorganic sorbent materials include silver-exchanged zeolites (i.e. faujasite, AgX, and mordenite, AgZ) and silver-impregnated silicic acid (AC-6120).

Caustic scrubbing for $^{129}$I recovery has been applied at fuel reprocessing plants in the United Kingdom (at Windscale and the Thermal Oxide Reprocessing Plant [THORP] at Sellafield), in France (units UP1 and UP2 at La Hague), and in Japan (Power Reactor and Nuclear Fuel Development Corp. [PNC] Tokai Reprocessing Plant) [31,32]. In the United States, the iodine oxidation (IODOX) technology was developed for application to liquid metal fast neutron reactor (LMFNR) fuel reprocessing where the used fuel would have been processed within 180 days of leaving the reactor and would have required high DFs to control $^{131}$I releases ($>10^4$). The Mercurex process was also developed for the treatment of the DOG that evolved during the processing of very short cooled fuels where very high DFs are required ($>10^5$).

- Krypton

Most of the $^{85}$Kr (>99%) remains in the used fuel until it is sheared and dissolved. $^{85}$Kr is released primarily to the DOG in a concentration range of hundreds of parts per million. Recovery processes are based on physical separation from the off-gas since krypton is chemically inert. The primary technologies for $^{85}$Kr control are cryogenic distillation, fluorocarbon adsorption, and sorption on molecular sieves, charcoal or zeolites. Xenon is also recovered by these processes. The xenon is present at about ten times the concentration of krypton in the gas stream.

Cryogenic distillation, a technology to recover rare gases, has been used commercially for many years. The cryogenic distillation process was successfully used at the Idaho Chemical Processing Plant to recover krypton. Fluorocarbon absorption technology was developed at the Oak Ridge Gaseous Diffusion Plant and at the reprocessing plant located in Karlsruhe, Germany [33-36]. This process uses an organic solvent ($CCl_2F_2$, aka Freon-12 or R12) to selectively absorb noble gases from air or DOG streams; the noble gases are then stripped from the solvent by boiling.

Both activated carbon and zeolites have been studied for their potential to recover krypton from the DOG stream. One possible system uses a bed of synthetic silver mordenite (AgZ) at ambient temperatures to recover xenon. The "xenon-free" gas is then chilled and passed onto a second hydrogen mordenite (HZ) bed operated at about -80°C that absorbs the krypton. Laboratory tests have shown DFs of 400 for krypton and 4 000 for xenon [36].

- Carbon-14

The bulk of the $^{14}C$ found in irradiated nuclear fuel is assumed to be evolved as $CO_2$ into the DOG during fuel dissolution. If the standard dry oxidation pretreatment is used, then approximately 50% of the $^{14}C$ will be released there as $CO_2$. A number of technologies have been developed for $CO_2$ removal. These include caustic scrubbing, molecular sieve adsorption, adsorbent bed fixation, and co-absorption/concentration in conjunction with $^{85}Kr$ recovery followed by fixation.

*Recovery of semivolatile components and particulates*

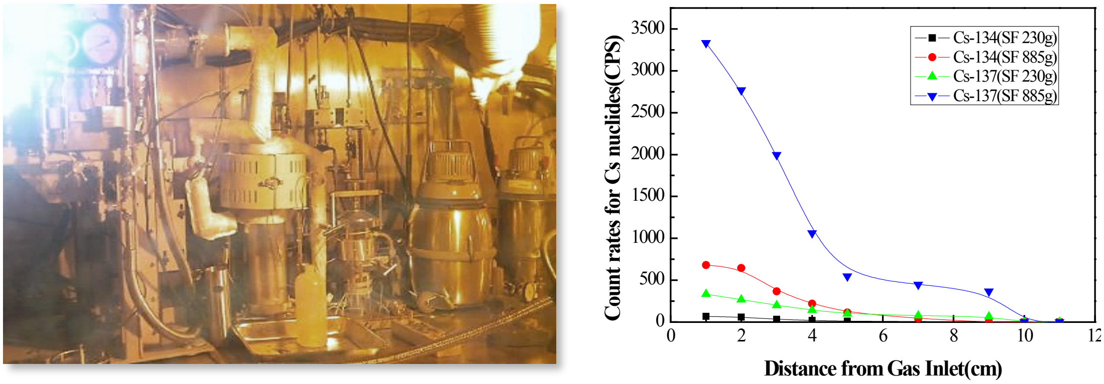
The head-end portion of the fuel reprocessing plant and the waste processing portion presents additional challenges in terms of the composition of the off-gas streams to be treated. In addition to the gaseous species already discussed, a number of "semivolatile" species are released to the off-gas stream. These include oxides of ruthenium, cesium, technetium, tellurium, and antimony. Of these, the most studied are ruthenium and cesium, which also typically require the highest recovery factors. The amount released is highly dependent on the processing conditions. For example, under normal oxidation pretreatment conditions, only very limited fractions of krypton, and iodine are released. Work in Korea has recently shown that, under high temperatures and $O_2$ or $O_3$ oxidising conditions, virtually all of the $^3H$, $^{14}C$, $^{85}Kr$, $^{129}I$, $^{99}Tc$, ruthenium and cesium are released to the off-gas and significant fractions of the tellurium, rhodium, and molybdenum are also volatilised.

In addition, the head-end processes may result in the production of very fine particulates that must also be removed prior to the release of the gas stream to the facility stack. Particulate filtration is for the most part a well-established technology [38-39].

*Korean process for off-gas treatment*

An off-gas treatment system for trapping fission products released from the DUPIC oxide fuel fabrication process is very important for preventing release of nuclides to the environment. In the mid-1990s, research was initiated on the trapping of cesium released from the OREOX and sintering processes used in fabricating DUPIC fuel. The off-gas treatment system for trapping volatile fission gases such as $^3H$ and I arising from the OREOX process and Cs arising from the sintering process has been established at the DFDF and is shown in Figure 2.14(a). It was demonstrated that Cs released from the sintering process was completely trapped by fly ash filters. Figure 2.14(b) shows that approximately 100% of each cesium isotope released was trapped by using a fly ash filter.

**Figure 2.14. Off-gas treatment system for DUPIC sintering furnace in DFDF and gamma spectroscopy measurement results of the fly ash filter**


(a) Sintering off-gas trapping system

(b) Gamma spectroscopy measurement

Engineering-scale equipment for treatment of 50 kg/batch (Figure 2.15) and lab-scale equipment for treatment of 1 kg/batch have been developed to fabricate porous pellets and crushed pellets (fuel fragments) as feed forms for the electrolytic reduction process in the Pyroprocess Integrated Inactive Demonstration (PRIDE) facility and the Advanced Spent Fuel Conditioning Process Facility (ACPF), respectively. In order to fabricate porous pellets in the PRIDE facility, equipment for oxidation, rotary pressing, and thermal pre-treatment was manufactured in 2012. Also, crushing equipment was manufactured to fabricate the crushed pellets. In order to fabricate feed forms in DFDF, equipment for slant-slitting the cladding, oxidative decladding with a rotational device, pressing, and thermal pre-treatment was manufactured in 2012. Feed form fabrication technology has been demonstrated using simulated fuel pellets since 2013.

**Figure 2.15. Equipment for engineering-sclae tests in PRIDE facility**


(a) Crushing

(b) Oxidation

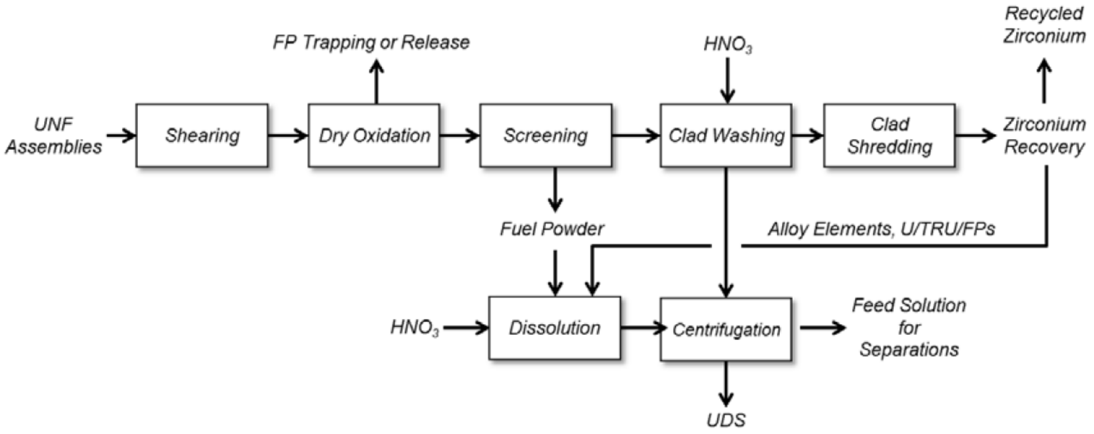
(c) Pressing

(d) Thermal pre-treatment

*Advanced aqueous dissolution*

Currently, dissolved segmented fuel is leached using nitric acid ($HNO_3$) to dissolve the fuel while the cladding hulls are separated from the dissolver solution either in batch-wise fashion as described in Section 2.1.2., or as part of a continuous operation, such as the French rotary wheel-dissolver. In future advanced systems, the dry oxidation pre-treatment process can convert a metal fuel or lower oxide fuel (e.g. $UO_2$) to the higher oxides and reduce the fuel particle sizes. The reduction in particle size can enable use of a screen to separate the cladding hulls from the powdered fuel, and enable continuously operated fuel powder dissolution to be used, as illustrated in Figure 2.16.

**Figure 2.16. Advanced head-end operations**



The fine powder greatly accelerates the rate of dissolution. Higher oxidation states of the uranium reduce the nitric acid requirement and the amount of $NO_x$ evolved. For example, dissolution of $UO_2$ may be described by a combination of two stoichiometries [17].

$$3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO + 4H_2O \quad \text{and}$$

$$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO + 2H_2O$$

An empirical approximation for dissolution of $U_3O_8$ is:

$$U_3O_8 + 7.35HNO_3 \rightarrow 3UO_2(NO_3)_2 + NO_2 + 0.35NO + 3.65H_20$$

Strong oxidants used in voloxidation, such as $NO_2$, can convert the fuel to the uranium trioxide ($UO_3$), which theoretically supports fumeless dissolution:

$$UO_3 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + H_20$$

In practice, small amounts of nitrogen oxides are produced.

Standard voloxidation has been observed to increase the insoluble fraction of the fuel, typically called “undissolved solids” (UDS). The UDS consist primarily of the noble metals, ruthenium, rhodium, palladium, molybdenum, and technetium, which are found in used fuel as micro-precipitates that are formed from solid solution during irradiation [21]. Fuel burn-up is the major factor that determines the amount of UDS with the greater amounts produced at higher burn-up. Removal of the UDS is normally accomplished by clarification (centrifuging or high efficiency filtration) of the dissolved fuel solution.

Some evidence indicates that very small quantities of plutonium are retained within these undissolved residues. The amount is normally insignificant, but for the higher concentrations of plutonium in MOX fuels, or in cases where the prior fuel fabrication includes milling for homogenisation and high temperature treatment, the plutonium is known to be present as plutonium-rich inhomogeneities, and may have lower solubility in the acid dissolvent [40].

In such cases, the use of special dissolution technologies to improve the recovery of plutonium may be particularly useful. Such technologies could be carried out upon the as-dissolved liquor or selectively upon the undissolved centrifuge cake. The dissolution of plutonium-containing residues may be carried out using techniques such as mediated electrochemical oxidation, using, for example, electrochemically generated silver (II) [41]. One disadvantage of these processes is that some fission products present in dissolved fuel and UDS are also oxidised and catalysed by the decomposition of the silver (II).

*Advanced head-end for molten salt dissolution and electrochemical separations*

An advanced head-end process has been developed in many countries for a future nuclear fuel cycle. In recent studies, the effect of feed form on the electrochemical process has been investigated as shown in Table 2.6. KAERI has been developing a feed form fabrication process through electrolytic reduction tests of feed material.

**Table 2.6. Status of feed form development for pyroprocessing**

| Feed forms | Organisation (country) | Fuel material | Applied electrochemical process | Density and size of feed form applied to electrochemical process |
|---|---|---|---|---|
| Rod-cut | ANL (United States) [42] | Unirradiated $UO_2$ pellet | Reduction/refining | -Rod-cut length: 10 mm<br>-Cladding material: stainless steel |
| Fuel fragment (crushed pellet) | ANL (United States) [42] | Unirradiated $UO_2$ | Reduction/refining | -Crushed pellet size: 0.045-4 mm |
| | INL (United States) [43] | Spent LWR fuel, crushed pellet, $UO_2$ | Reduction | -Crushed pellet size: <0.045, 0.045-4.0 mm |
| | CRIEPI (Japan) [44] | Uniraddiated $UO_2$ | Reduction | -Crushed pellet size: 0.053-0.5 mm<br>-Density: 97-98% TD |
| | CRIEPI/JRC-ITU (Japan/Germany) [45] | Spent MOX fuel, $UO_2$ | Reduction/refining | -Fuel fragment: SEM image |
| | KAERI (Korea) [46] | Unirradiated and crushed pellet, $UO_2$ | Reduction | -Crushed pellet density: > 95% TD<br>-Size: 1-9 mm |
| Powder | ANL (United States) [47] | Unirradiated $UO_2/U_3O_8$ | Reduction | - |
| | INL (United States) [48] | Spent LWR fuel, $U_3O_8$ | Reduction | -Powder prepared by oxidative pretreatment |
| | KAERI (Korea) [49] | Uniraddiated $U_3O_8$ | Reduction | -Powder prepared by oxidation |
| Granule | KAERI(Korea) [46,50] | Uniraddiated Simfuel, $UO_2$ | Reduction | -Density: 28.3-40% TD<br>-Size: 1-5 mm |
| Porous pellet | CRIEPI (Japan) [51,52] | Unirradiated $UO_2$ | Reduction/refining | -Density: 62-69% TD<br>-Size: ϕ6.6-6.9 x 10.3-12.5 H (mm) |
| | KAERI (Korea) [46,53] | Unirradiated $UO_2$ | Reduction | -Density: 55-95% TD<br>-Size: ϕ6-10 x 7-12 H (mm) |

### *2.1.4. Summary*

The discussion of progress in advancements for head-end processing of spent fuel can apply to any downstream fuel component separation steps that may be selected. In comparison with current industrial-scale operations, research, development and demonstration studies have shown progress in improving the capabilities for dry volatile component release and emissions control by means of the advancements made in the voloxidation process and associated off-gas trapping methods, as well as in the conversion of the ceramic oxide fuel components to a finely divided oxide powder that is amenable to continuous dissolution in either nitric acid or molten salt. Moreover, systems studies have shown the potential benefits of recycling more of the used fuel components, including uranium, all transuranium elements, zirconium from zircaloy fuel cladding and several of the valuable fission product components [1].

## 2.2. Hydrometallurgy

### *2.2.1. Uranium recovery*

*Introduction*

Over the last few decades, spent fuel management has become one of the challenges associated with the production of nuclear energy. This has led many countries to develop strategies to plan, develop and implement safe and efficient methods of managing spent fuel.

The major constituent of spent fuel is uranium (representing ~95 wt% of the heavy metal components and 65% of the mass of pressurised water reactor fuel assemblies). If separated from other components, uranium can be re-used as fuel in a reactor and therefore reduce the volume of material to be disposed of as high-level waste. Extensive R&D has been carried out in the field of separation chemistry and several processes have been adapted or new processes have been developed using different extractants to selectively and quantitatively or partially recover uranium, often as a first step of a reprocessing process, in order to optimise/simplify the subsequent steps.

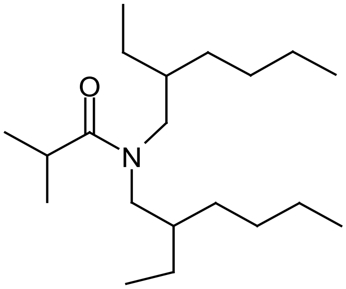
*Selective extraction of uranium*

One example of this strategy is the French GANEX concept (Group ActiNide EXtraction). This process is composed of two extraction cycles following the dissolution of the spent fuel in nitric acid [1]. In this process, uranium(VI) is selectively extracted from the dissolution solution prior to the group separation of transuranic elements (Np, Pu, Am, Cm – see Section 1.2.3.), which occurs in the second cycle prior to the co-conversion step [2]. The preliminary separation of uranium in the first cycle is required in order to recover uranium at a high purity to adjust the U/TRU ratio before the co-conversion of the actinides and to handle the excess of uranium resulting from the reprocessing of fuels unloaded both from existing light water reactors and future fast reactors. Additionally, the separation of the major constituent of the spent fuels is helpful for the hydrodynamics and equipment size of the second extraction cycle.

Uranium is selectively separated by solvent extraction using N,N-dialkylamide, which strongly extracts uranium(VI) from a high nitric acid medium. This extractant has previously been studied as an alternative to tributylphosphate (TBP) for the co-extraction of uranium and plutonium and for the selective separation of uranium [3-7]. Tuning the structure of the monoamide increases significantly the U(VI)/Pu(IV) selectivity. Some branched-alkyl monoamides can selectively extract uranium(VI) without addition of any reducing or complexing agents to avoid co-extraction of plutonium (IV) in the process [5,7]. The monoamide molecules are also good candidates for the development of other hydrometallurgical processes, because of their high solubility in the aliphatic diluents usually used in reprocessing operations, high decontamination factors from fission products, low solubility in aqueous phase, and low synthesis cost. Moreover, most of the time, they form water-soluble degradation products via hydrolysis and radiolysis.

DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide) (Figure 2.17) was selected among different N,N-dialkylamides as the extracting molecule for the GANEX 1st cycle, because it exhibits a good compromise between a quantitative extraction of uranium and a high U(VI)/Pu(IV) selectivity ($SF_{U(VI)/Pu(IV)}$ ~ 80 at 3M $HNO_3$)[7]. In addition, a high loading capacity for uranium [6] can be achieved with this type of extractant.

**Figure 2.17. Structure of DEHiBA**



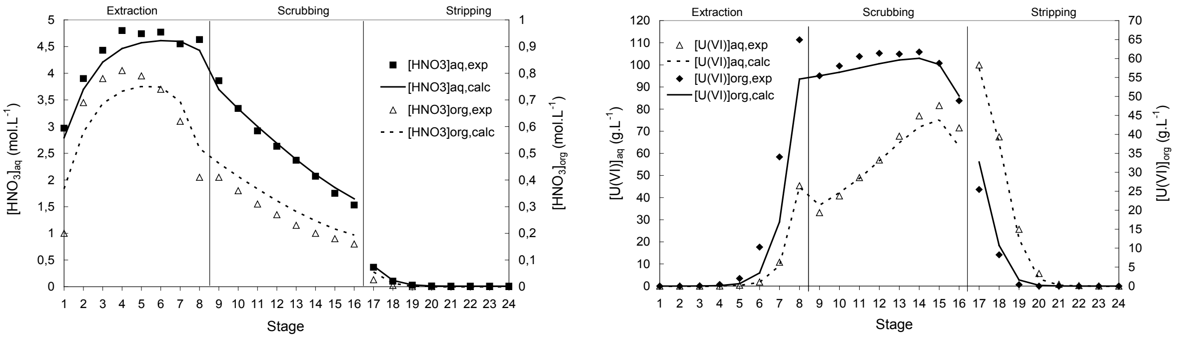
The DEHiBA process development from batch experiments to a high active demonstration required different steps, including the development of a chemical model.

First, distribution data of nitric acid, uranium(VI), neptunium(V,VI), plutonium(III,IV) and technetium(VII) were measured with the 1M DEHiBA-TPH solvent for different aqueous concentrations of nitric acid and uranium loading in the solvent. These experimental distribution ratios were then described with the help of a physicochemical model based on the application of the mass action law on each of the extraction equilibria. Due to the large concentrations of nitric acid and metals, deviations from ideal behaviour cannot be neglected and they were estimated by calculating the activity coefficient of each component in the aqueous phase according to the "simple solutions" concept. This concept exploits the experimental behaviour of isopiestic solutions, first observed by Zdanovskii [8] and confirmed later by Stockes and Robinson [9]. The use of this concept dramatically simplifies the McKay-Perring integral thermodynamic relation [10] to finally obtain the Mikulin relation [11].

The equilibrium constants were optimised to represent the extraction of both nitric acid and uranium(VI) and were integrated into the process simulation software PAREX developed by CEA [12] to design a flowsheet for a demonstration test. Flow rates were optimised and the composition of the scrubbing solution was determined to achieve a recovery yield of uranium exceeding 99.99% with the highest decontamination factors (DF) from FPs and other transuranic elements (Np and Pu in particular) compared to other processes.

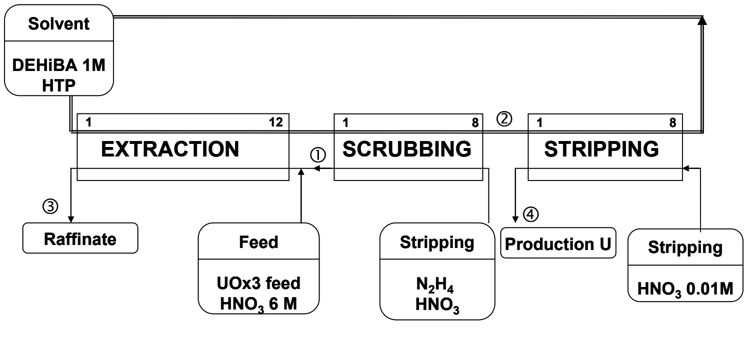
This flowsheet was primarily tested in 2006 on a surrogate uranium(VI)/$HNO_3$ feed solution (200 $g.L^{-1}$ at 4M $HNO_3$) in mixer-settler contactors in order to check the extraction performance of this extracting system in a counter-current process [13]. The uranium separation was performed in three sections of laboratory scale mixer-settlers devoted to the extraction, the scrubbing, and the stripping steps. The counter-current test reached the objective of the GANEX 1st cycle after recovering more than 99.99% of the total amount of uranium. This test confirmed the good performance of DEHiBA for the extraction of uranium from nitric acid. The experimental profiles of uranium and nitric acid concentration in the organic and aqueous phases were measured and compared to the calculated concentrations (Figure 2.18). The model based on the acquisition of experimental distribution data, with corrections for the activity coefficients of the components in the aqueous phase, was confirmed by the agreement between the experimental and calculated profiles.

**Figure 2.18. Aqueous and organic concentration profiles of nitric acid and uranium**



Following the successful "cold" demonstration, the initial flowsheet was adapted in order to route technetium and neptunium to the raffinate with the fission products and the TRU. Hydrazinium nitrate was added in the scrubbing solution to reduce Tc(VII) and Np(VI) and help to strip them from the solvent. The modified flowsheet was tested in 28 mixer-settlers (laboratory-scale) on a genuine High Liquid Waste (HLW) in the CBP hot cell (ATALANTE facility) in June 2008 [14]. The uranium separation was performed in three sections of the laboratory scale mixer-settlers corresponding to the extraction, scrubbing, and stripping steps. The contactor set-up consisted of 3 batteries of mixer-settlers of 12. 8 and 8 stages, respectively. The experimental flowsheet is shown in Figure 2.19. Before introducing the HLW feed, a surrogate uranium (VI)/$HNO_3$ feed ($176\ g.L^{-1}$ at 6M $HNO_3$) was used for ten hours to reach nitric acid and uranium equilibrium. The genuine HLW solution (obtained from the dissolution of an irradiated uranium oxide fuel UOx$_3$ at 70 GWd/t and 6 years cooling time) was then fed and the test ran for 58 hours at steady state.

**Figure 2.19. Flowsheet for the Ganex 1st cycle hot test**



Good hydrodynamic behaviour was observed during the 58 hours of the counter-current test. The main results reported in Table 2.7 show that desired yields for uranium recovery and decontamination factors (DF) were reached. The losses of uranium in the raffinate and in the solvent were estimated at values lower than 0.002% and 0.003%, respectively, corresponding to a recovery yield of uranium higher than 99.99%. The decontamination factors versus Np, Tc and Pu are high enough with the help of hydrazinium nitrate in the scrubbing section. The values of alpha and $\beta$–$\gamma$ decontamination factors in Table 2.7 are, however, under-estimated because of the average contamination of the cell. It is therefore difficult to assess the need for a second purification cycle of uranium after a first extraction cycle using DEHiBA.

**Figure 2.20. Photo of the extraction section of mixer-settlers**

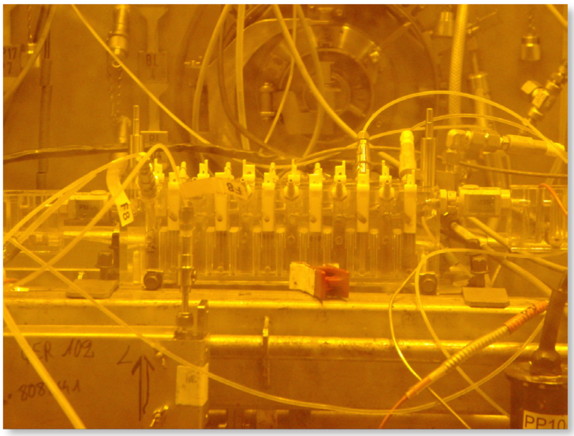
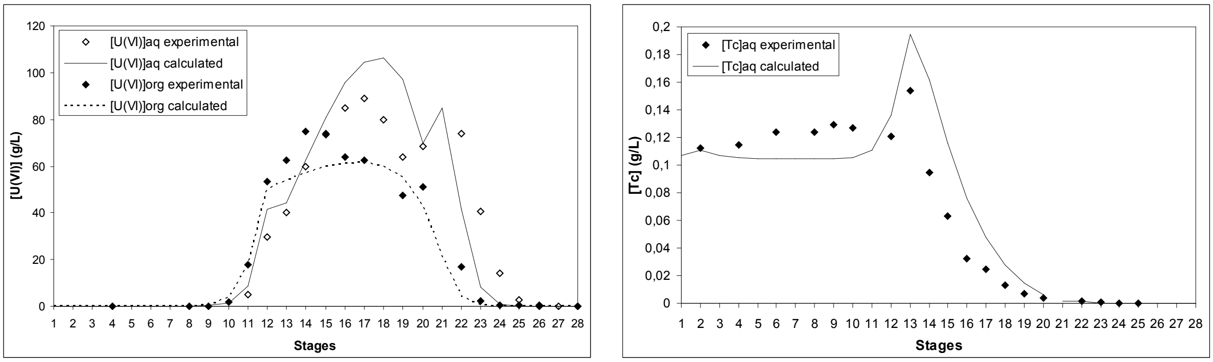


**Table 2.7. Recovery and decontamination factors estimated after the CBP hot test**

| Element | % in raffinate | % in U product | DF | % in solvent |
|---|---|---|---|---|
| U | <0.002% | >99.99% | - | 0.003% |
| Np | 96% | 0.331% | >300 | - |
| Pu | 102% | 0.024% | 4 100 | <0.24% |
| Tc | 103% | 2.4% | 41 | - |
| $^{106}$Ru | 136% | <0.007% | >15 000 | <0.02% |
| $^{137}$Cs | 102% | <0.003% | > 35 000 | <0.0002% |

Uranium and technetium concentration profiles in the aqueous phase (and organic phase for uranium) obtained during the continuous hot test are shown in Figure 2.21 and compared with calculated data for the three sections (extraction, scrubbing, stripping). These predicted values for uranium and technetium reproduced quite well the experimental concentrations, which confirm the validity of the model for uranium and technetium extraction by DEHiBA (extraction constants, kinetics and speciation).

**Figure 2.21. Experimental and calculated profiles of uranium and technetium concentrations in aqueous and organic phases for the three sections**



The agreement between experimental and calculated concentration profiles enables the extrapolation of the decontamination factors of Np, Pu and Tc for a flowsheet with two more scrubbing stages (10 instead of 8). If we consider the hydrazine consumption independent of the number of stages, the decontamination factors would be increased by a factor 3. These high DFs show that the performance of the process could be even better and could avoid the need for further U decontamination cycles.

Degradation studies of the DEHiBA solvent were carried out under hydrolysis and radiolysis. DEHiBA is very stable under hydrolysis but forms some degradation products under radiolysis. The main degradation products (carboxylic acids, amines, amides), identified by gas-chromatography coupled with mass-spectrometry, can be stripped from the solvent by basic and acidic scrubbing (PUREX-like solvent clean-up step). A counter-current test was performed on a uranium solution spiked with fission products using the MARCEL loop for 700 hours with solvent recycling under radiolysis. Up to 329 kGy of integrated dose, extraction of uranium remained stable and only an increase of the extraction of palladium was observed with the increase of the integrated dose of the solvent.

From these results, it appears that the monoamide DEHiBA seems suitable for the selective separation of uranium from a spent fuel solution. Further developments such as a demonstration in continuous contactors (pulsed columns) are however required to definitely assess the process for future industrial implementation.

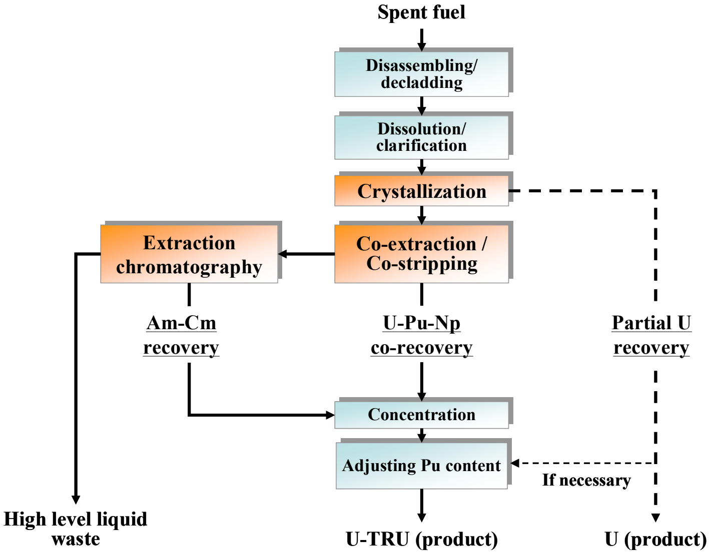
In addition, selective U separation by extraction with monoamide have been studied in Japan for more than ten years [7,15]. N, N-di(2-Ethylhexyl)-2,2-Dimethylpropanamide (DEHDMPA) was selected as an extractant for U [16]. A recent study on counter-current extraction using U, Pu and simulated fission product solution showed more than 99.9% recovery of U with a high decontamination factor from Pu and good agreement in concentration profiles of U and Pu between observed and as calculated by the PARC code, which was developed in JAEA [17].

*Crystallisation for partial recovery of U in the NEXT process*

A second method is the recovery of U through crystallisation in the NEXT (New Extraction System for TRU Recovery) process which has been developed for reprocessing fast reactor spent fuel for the Japan Atomic Energy Agency (JAEA) in the framework of the “Fast Reactor (FR) Fuel Cycle Technology Development (FaCT)” Project [18]. The NEXT process consists of partial recovery of U by the crystallisation of uranyl nitrate hexahydrate (UNH) from dissolver solution, followed by U-Pu-Np co-recovery by solvent extraction with a single cycle flowsheet using TBP (elimination of partitioning and purification section from the conventional PUREX process), and Am and Cm recovery with extraction chromatography, as shown in Figure 2.22 [19,20] (see Sections on JAEA NEXT Process and Russian process for HLW reprocessing for the description of these steps).

In the crystallisation step, about 70% of U in the dissolved solution can be recovered by lowering the temperature of the solution [20] in order to reduce the amount of heavy elements to be treated in the next co-extraction step and to increase the Pu/U ratio in the solution. To recover 70% of the U, the concentration of U in the solution should be increased to more than 400 g/L, which requires effective dissolution of spent fuel. The technique of powderisation of spent fuel was developed for this purpose [21,22].

**Figure 2.22. Schematic flow of the NEXT process [19]**



To avoid co-crystallisation with U(VI), Pu should be in the tetravalent state not in the hexavalent state [23,24] However, Pu(IV) forms a crystalline precipitate of dicesium tetravalent plutonium hexanitrate, $Cs_2Pu(NO_3)_6$, when the concentrations of Pu(IV), Cs and $NO_3^-$ are high enough [24,25]. A very low decontamination factor (DF) for Cs was observed (nearly 1) in the beaker-scale crystallisation test with dissolved solution of FBR MOX spent fuel [24,26]. Refinement of the UNH crystal is being studied to improve the DF for Cs and other fission products [27,28]. The refinement consists of two steps: first, remove liquid impurities (mother solution) contained inside the crystal by sweating and second, separate solid impurities such as $Cs_2Pu(NO_3)_6$ and $Ba(NO_3)_2$ by filtration after melting the UNH crystal. Beaker-scale experiments of the sweating and the melting-filtration were performed with irradiated fuel. Engineering scale tests of the sweating with U and simulated FP were carried out to evaluate its performance [28].

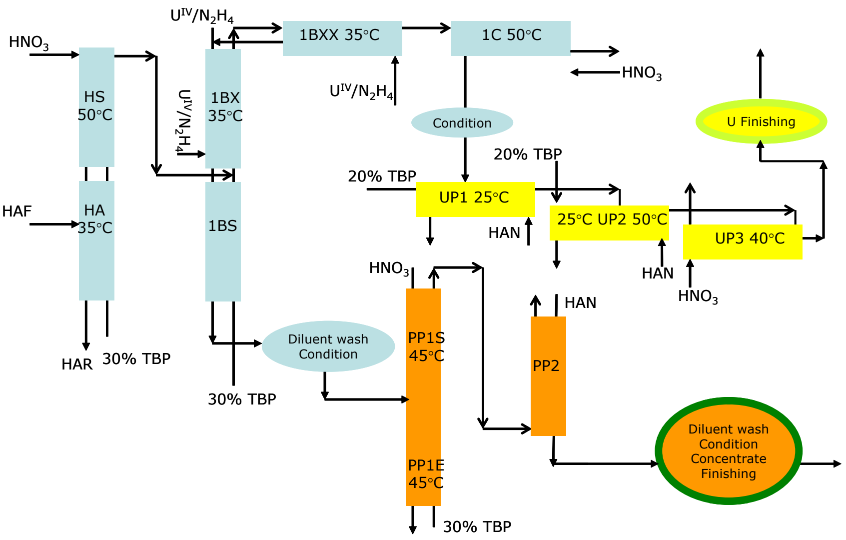
In the study of the main step of crystallisation process, the crystalliser and solid-liquid separator were developed and engineering scale tests were conducted [27,29]. A cylindrical annular type continuous crystalliser was selected and a centrifugal separator with a washing basket and a screw conveyer was adopted for continuous dehydration of the crystal. The feasibility of these equipment was confirmed using U(VI) solution.

### *2.2.2. Options for the co-processing of actinides (U, Pu, Np)*

*Introduction*

In current nuclear fuel reprocessing, as practised at industrial scales in France, the United Kingdom, Russia and Japan, separate high purity U and Pu products are formed following a number (typically three) of solvent extraction cycles, using tri-butyl phosphate (TBP), diluted in a paraffinic diluent as the actinide extractant (the PUREX process). Figure 2.23 shows the solvent extraction flowsheet for the Thorp (Sellafield, United Kingdom) reprocessing plant as an example. Np is partially recovered with the highly active raffinate in the first solvent extraction cycle with the remainder later removed from the U product stream and re-directed with the high-level waste. The trivalent actinide ions (Am, Cm, etc.) are not extractable into the TBP solvent and are left with the fission product waste stream. Ultimately, Np, and the other minor actinides, are vitrified with the high-level waste ready for geological disposal [1]. Later sections in this report deal with the recovery of minor actinides from the high-level waste.

**Figure 2.23. Sellafield Thorp plant – solvent extraction flowsheet**



The possibilities for the co-processing of U with Pu, Pu with Np or U-Np-Pu together are not new concepts. If the Pu-containing product from the reprocessing plant is to be used for production of mixed oxide fuel (MOX), there are obvious benefits of directly co-processing, particularly for a U-Pu product [2]. Some perceived advantages of co-processing are:

- production of a homogeneous U-Pu stream for subsequent conversion to MOX fuel;
- elimination of process steps thus decreasing waste arisings and enhancing plant economics;
- recovery of the minor actinide Np for burning (as part of the "P&T" fuel cycle scenario);
- enhanced security and proliferation resistance of the fuel cycle through the avoidance of separated Pu at any point.

With the anticipated global expansion of nuclear energy, the last point in particular is becoming increasingly important and has led to a renewed interest in co-processing flowsheets for future fuel cycle plants.

Various hydrometallurgical flowsheets have been proposed that include actinide co-processing as part of an anticipated next generation fuel cycle, including those from industrial corporations, such as CEA/Areva's COEX™ [3] and EnergySolutions' NUEX [4] processes, the suite of UREX processes developed by the US national laboratories [5] and similar options from the national laboratories of France, United States, United Kingdom, Japan, India, Russia and elsewhere. All these processes are modifications of the established PUREX process and still use diluted TBP (or related tri-alkyl phosphate) as the actinide extractant.

An alternative approach to co-processing are Grouped ActiNide EXtraction (GANEX) processes that seek to co-recover all the transuranics (TRU = Np-Pu-Am-Cm) together, i.e. to fulfill the so-called homogeneous recycling framework [6]. GANEX recycling plants may remove all or part of the U inventory in a first separation cycle prior to TRU recovery or may seek to recover some U with the TRU elements to enhance the perceived proliferation resistance. GANEX processes require alternative extracting ligands (not TBP) to co-extract the trivalent actinide ions with the tetravalent and hexavalent ions. GANEX processes are discussed in a later section in Chapter 2 of this book.

### *Basis of flowsheets for U-Pu(-Np) co-processing*

Generically, these (PUREX-based) co-processing flowsheets are relatively simple, involving up to four basic steps:

- separation of U-Pu-Np (or U-Pu) from the fission products and higher minor actinides;
- separation of a portion of the U along with all of the Pu or Pu and Np from the bulk of the U;
- purification of the bulk U product, to meet specifications for re-use, storage or disposal;
- purification of the Pu-containing product, to meet specifications for re-use, storage or disposal.

Step 1 is reasonably straightforward in a PUREX flowsheet. U and Pu are easily extracted into the solvent with very high recoveries and decontamination factors from fission products. Current oxide fuel reprocessing plants use 30% TBP/hydrocarbon diluent to extract U and Pu from dissolver product solutions typically containing 200-300 g/L U, ~1 wt.% Pu in ~3 mol/L $HNO_3$. As noted earlier, however, Np recovery is only partial with ~70% Np extracted into the U-Pu solvent product. P&T-based advanced fuel cycles require recovery of >99% Np, hence, significant recent work has focused on Np extraction in the primary separation stage (see Section on Np co-extraction). Future flowsheets must also be sufficiently robust to accommodate higher Pu concentrations from the processing of LWR MOX and Generation IV (Gen IV) reactor fuels.

Step 2 is more complex. It requires maintaining the bulk of the U in the TBP solvent phase while completely stripping the Np and Pu into the aqueous phase. For enhanced proliferation resistance of the flowsheet, a small percentage of the U must be routed with the aqueous Pu stream also. For operational purposes when co-processing it is probably simplest if the U/Pu ratio in the aqueous product in the solvent extraction plant is maintained below a specific level such that it can be diluted down to the required ratio in the finishing process. The main approaches to this partition are:

- Some U can be “leaked” into the Np-Pu aqueous product by an appropriate parameterisation of the flowsheet, for example adjusting the flowrates or number of stages in the 1BS section of the contactor and/or by an engineered modification (e.g. fixed flow diverter).
- Reductive stripping of Np and Pu using hydroxylamine (or similar salt-free reductant) usually in conjunction with a stabiliser such as hydrazine.
- Complexant based stripping of Np and Pu using formo- or aceto-hydroxamic acid without a stabiliser.

The bulk U product is then backwashed into dilute $HNO_3$, usually at an elevated temperature.

Step 3 is routine, simply requiring a further solvent extraction cycle to purify the U stream from residual activity prior to U finishing, which is usually via a thermal denitration (TDN) process.

Step 4 is a further solvent extraction to purify the Pu-containing product from residual fission product activity. This is slightly complicated by the need to keep the actinide species (U-Pu or U-Np-Pu) together through the cycle. If oxalate precipitation is chosen as the finishing route, then a further fission product decontamination factor can be achieved. However, depending on the activity of the spent fuel to be processed within the Recycle Plant, fission product decontamination achieved upstream and the engineered design and shielding requirements in place downstream (finishing and MOX fuel fabrication plants), it may be possible to eliminate this purification cycle from the process.

Furthermore, steps 1 and 2 above can be reversed, thus providing alternative routes to the same products, with the separation of the bulk U carried out first to reduce volumes or to maintain Pu with the fission product stream in the flowsheet. The Japanese NEXT process employs U crystallisation following dissolution to remove bulk U before a simplified TBP co-extraction cycle to recover residual U, Np and Pu (Section on JAEA NEXT Process). The US UREX+ processes may use aceto-hydroxamic acid (AHA) to render Pu and Np inextractable in the primary separation stage, thus isolating U and Tc only in the TBP solvent product. Pu and Np (also Cs, Sr, Am, Cm) would then be separated from the HA raffinate in further solvent extraction cycles (Section on US R&S Studies).

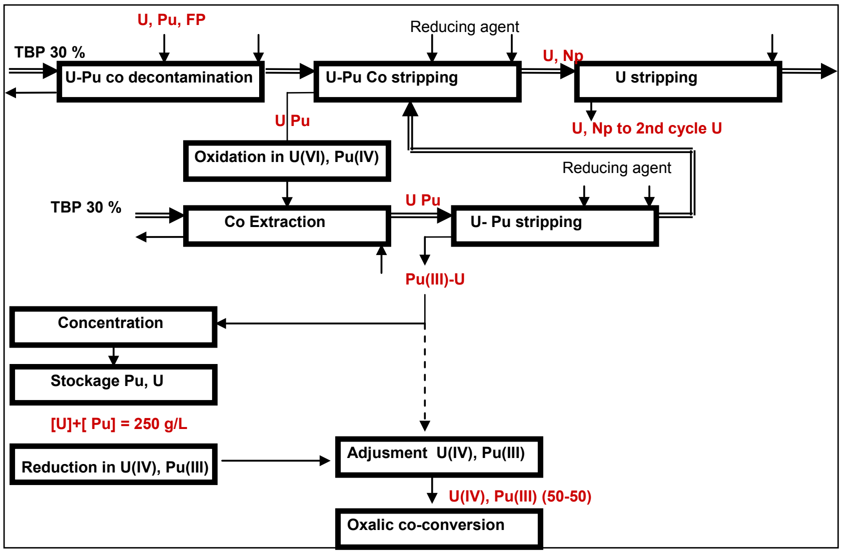
The following sections will describe some leading options for U-Pu recovery (Section on U-Pu co-processing) and U-Np-Pu co-recovery (Section on U-Np-Pu co-recovery) before describing, in some detail, exemplar advanced reprocessing options developed by Russian institutes that co-process (U,Pu) from spent nuclear fuel (Section on Review of new co-processing-based processes developed in Russia). Note that U-Np-Pu-MA co-recovery is dealt with in a later section in Chapter 2 of this report.

*U-Pu co-processing*

- COEX™ process

The COEX™ process is basically an evolution of the conventional PUREX process used at La Hague (France), by modifying it to produce a U + Pu mixture (U/Pu > 20%), rather than pure plutonium [7]. The basic enhancement in COEX™ is thus to avoid full plutonium separation at any point of the process (see Figure 2.24). The advantage of so doing is to reduce proliferation risk "attractiveness levels" and to produce a homogeneous mixed oxide, for the purposes of downstream MOX fuel fabrication, giving enhanced performance.

**Figure 2.24. COEX™ process**



The reference flowsheet involves an initial part that is fairly similar to the first purification cycle, as implemented in the La Hague and Rokkashomura plants. The plutonium stripping part is modified, with regard to the uranium scrubbing function which is changed from a uranium scrub to a neptunium scrub. This enables some uranium to remain in the plutonium stream while allowing neptunium to be extracted from the plutonium stream. The extracted neptunium is directed to the uranium product stream due to the higher distribution coefficient of Np(IV) compared to U(IV) (separation factor ~1.8).

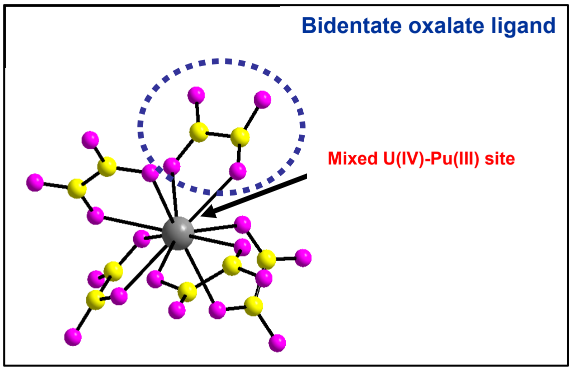
In this version of the COEX™ process, Np is recovered in the raffinate of the U-Pu extraction and in the uranium purification cycle. Variants for the flowsheet have already been suggested to allow for potential evolutions in the near future where neptunium recycling is required. A modification of the U-Pu extraction acidity enables co-extraction of all of the Np, suppression of the neptunium scrub, and use of HAN as reducing agent to co-strip Np and Pu along with part of the U, thus allowing neptunium to follow the plutonium-uranium stream. Then in the Pu-U purification cycle, given some minor flowsheet modifications, neptunium will continue to follow the U-Pu stream through to the co-conversion stage.

The last step of this process is the oxalic acid based co-conversion of uranium and plutonium (and potentially neptunium). Of the possible variants, the current reference route is the U(IV)-Pu(III) (Np(IV)) variant due to the following advantages [8]:

- unexpectedly U(IV) and Pu(III) co-crystallise into a single oxalate structure, thus ensuring homogeneous distribution of the two actinides at the molecular scale (see Figure 2.25 [9]). This structure is an oxalate solid-solution, over a broad range of Pu/(U + Pu) ratios: 0-50 mol/mol;
- this mixed oxalate exhibits very low solubility in a nitric acid solution carrying excess oxalic acid: solubility is about the same as that of the plutonium(IV) oxalate precipitate;
- calcination of this mixed oxalate in an inert atmosphere yields a solid-solution of $(U,Pu)O_2$; the homogeneity of uranium and plutonium distribution at the molecular level is thus conserved from the solution to the oxide;
- conventional technology, similar to that operated in the current plutonium finishing workshops at the La Hague plant, may be used.

A major advantage, for oxalic co-conversion, is to produce mixed oxides exhibiting physicochemical characteristics directly tailored to fuel fabrication, affording in particular, the ability to use this raw material directly with no further specific chemical or mechanical treatment.

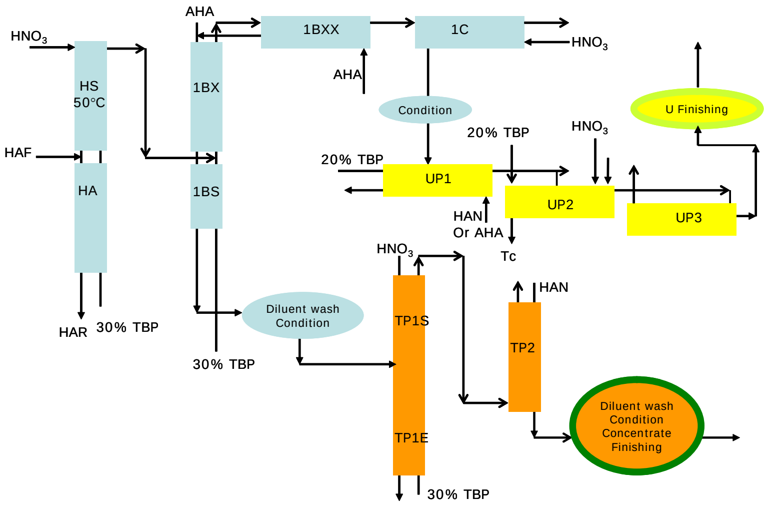
**Figure 2.25. Representation of the co-crystallised U(IV)-Pu(III) mixed oxalate structure**



- NUEX process

The NUEX process, designed for near-term spent fuel recycling applications in the United States by an industrial consortium, led by EnergySolutions [4], is similar in concept to the COEX™ process. It is intended to be a relatively simple evolution from the process used in the Thorp reprocessing plant at Sellafield, United Kingdom, being based on the established three-cycle PUREX process, but again modified to produce a U:Pu co-processed product as well as a pure U product (Figure 2.26). Following solvent extraction, these products would be converted to oxides using thermal denitration (U) and oxalate co-precipitation (U/Pu). The main innovation in this flowsheet is to replace the U(IV)/$N_2H_4$ reductant with acetohydroxamic acid (AHA), thus partitioning U from U/Pu by complexation rather than reduction [10]. Complexant based stripping using hydroxamic acid is described in greater detail in Section on NNL Advanced Process.

**Figure 2.26. NUEX process solvent extraction flowsheet**



*U-Np-Pu co-recovery*

- Np co-extraction

As noted above, current reprocessing plants do not fully recover Np and a substantial portion is lost to the first (HA) cycle raffinate (33% in Sellafield Thorp plant and 25% at La Hague plants [11]). This is due to the complex chemistry of Np, which can exist in a multiplicity of inter-convertible oxidation states in $HNO_3$ [12]. Following dissolution, NOx conditioning and buffer storage in the head-end plant, Np enters the primary separation cycle predominantly as the poorly extractable Np(V) species. To achieve full extraction of Np, therefore, requires the oxidation of Np(V) to the extractable Np(VI) species within the solvent extraction contactor.

In $HNO_3$ Np(V) oxidation occurs via Equation 1 and full extraction of Np(VI) depends on the manipulation of conditions within the flowsheet to promote this reaction.

$$2NpO_2^{+} + 3H^{+} + NO_3^{-} \longleftrightarrow 2\ NpO_2^{2+} + HNO_2 + H_2O \quad (1)$$

The rate and extent of oxidation, therefore, depends on the following flowsheet parameters:

- $HNO_3$ concentration;
- temperature;

- flow rates;
- residence time;
- $HNO_2$ concentration;
- radiation (radiolytic generation of $HNO_2$);
- U saturation of the solvent phase;
- any additional reagents (e.g. V) and inter-actinide reactions.

Various groups are developing flowsheets to maximise Np extraction in the primary contactor, and the approaches are common in nature. Figure 2.27 illustrates the generic nature of these flowsheets and Table 2.8 gives specific conditions proposed by various researchers.

**Figure 2.27. Generic flowsheet layout for Np extraction in the first cycle (HA/HS contactor)**

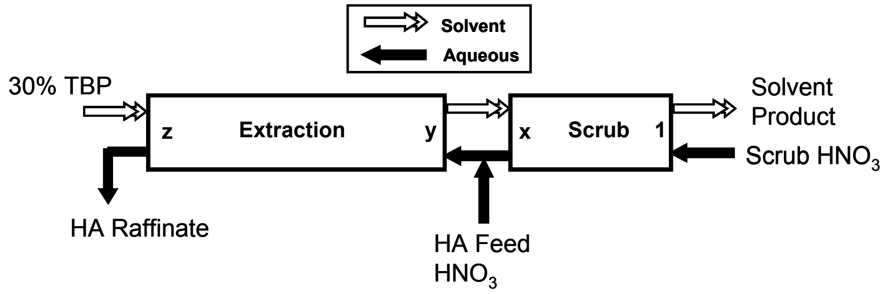


**Table 2.8. Details of Np extraction flowsheets tested by international laboratories**

| | CEA [11,13] | JAEA [14-15] | NNL [16-18] |
|---|---|---|---|
| HAF [$HNO_3$] (M) | 4.5 | 5.2 | 4.5 |
| Scrub [$HNO_3$] (M) | ? | 5 | 4.5 |
| Extract T (°C) | Ambient | 25 | 50 (stages 5-8)<br>25 (stages 9-14) |
| Scrub T (°C) | Ambient | 25 | 50 |
| Scrub stages (x) | ? | 8 | 4 |
| Extract stages (z-y) | ? | 8 | 12 |
| HAF [U] (g/L) | U+Pu=250 | 150 | 250 |
| HAF [Pu] (g/L) | U+Pu=250 | 13 | 0 |
| HAF [Np] (mg/L) | ? | 48.2 | 150 |
| Contactor technology | Pulsed columns | Centrifugal contactors | Centrifugal contactors |
| Feed | UOx (52 GWd/te) | Irradiated JOYO FR fuel | Simulant |

CEA (France) has reported the testing of Np extraction flowsheets in pilot scale pulsed columns (27 mm diameter), obtaining >90% Np extraction with a simulated feed solution. In a fully active test with 15 kg spent UOx fuel (52 GWd/te, 6.5 y cooled), CEA achieved >99.6% extraction of Np in 15 mm diameter pilot scale pulsed columns. Extraction was achieved primarily by raising the feed acidity to 4.5 mol/L. Temperatures are not reported but presumably are ambient (~35°C in spent fuel solution due to self heating). While they anticipated a requirement for an additional $HNO_2$ feed at the base of the extraction column to accelerate Np(V) oxidation, as used in the simulant trial, in the active test this was not required, probably due to the kinetics of the oxidation of Np(V) and the role that radiolytically-generated $HNO_2$ played in their fully active trial [13].

Progress towards full Np recovery has also been made by JAEA (Japan) as part of their NEXT process development. Dissolved irradiated JOYO fast reactor fuels containing 32, 37, 13 and 21 $gL^{-1}$ Pu in 6.2, 5.2, 5.2 and 3.9 mol/L $HNO_3$ respectively were tested in flowsheets using centrifugal contactors (RD = 27 mm). In addition to the high feed acidities, the last two flowsheets also used high-acid scrubs of 5 and 10 mol/L $HNO_3$. Good performances were observed with only 0.9, 1.5, 1.1 and 4.7 % Np lost to the HAR in each case [14-15].

NNL (United Kingdom) has also reported progress towards flowsheets that fully extract Np in the first extraction cycle utilising short-residence-time centrifugal contactors (RD = 10 mm) [16-19]. A simulant feed solution (250 g/L U, 4.5 mol/L $HNO_3$), was fed at stage 5. The flowsheet used a 4.5 mol/L $HNO_3$ scrub and elevated temperatures (45-50°C) in stages 1-8, where it was expected that most of the Np(V) oxidation occurred. To partially replicate the effects of radiolytically generated nitrous acid, $NaNO_2$ was added to the feed and to stage 7. The test was successful with >99% Np extracted [18]; based on CEA experience, it is to be expected tha,t under irradiated conditions with spent fuel solution, neptunium extraction will be even higher [11].

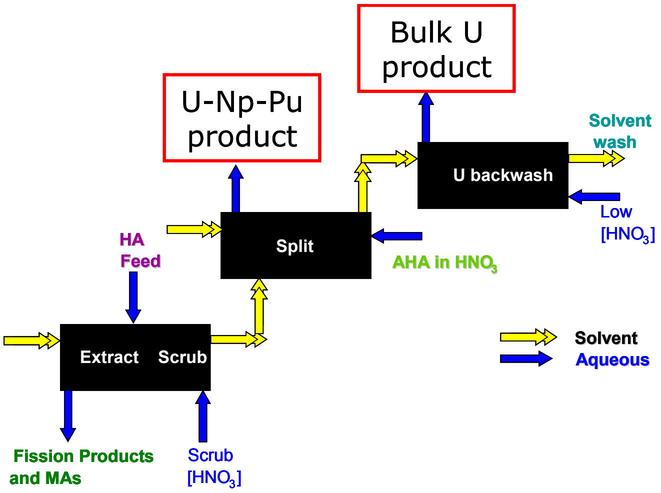
While the most elegant solution to Np recovery is clearly to rely only on adjustments to $HNO_3$ and temperature, it is also possible to condition Np to oxidation state (VI) using added redox reagents. These are usually salts such as V(V) ions, which then contribute to the high-level waste (HLW) generated. Among others, researchers at ANL (United States) have experimented with the use of V(V) ions to achieve Np(V) oxidation within their UREX processes [5].

It is recognised by most researchers that the efficient development of flowsheets to fully recover Np in the first cycle extract/scrub contactors is promoted by accurate modelisation of the complex process chemistry. Models in turn depend on having comprehensive and accurate fundamental data (thermodynamics, kinetics etc.). Both CEA [13] and NNL [17] have reported some details of their models for Np extraction and have pointed out that the reported aqueous phase kinetics of Equation 1 do not adequately represent Np(V) oxidation in the 2-phase system. This is a complex reaction, kinetically catalysed by $HNO_2$ that has been investigated by numerous researchers in aqueous solutions without definitive resolution. Thus, to more accurately model experimental data, CEA using the data of Moulin [20] and Gaquer [21], adjusted the rate constants of the reaction [13] while NNL [17] modified the order of reaction with respect to $[H^+]$ in the kinetic equation given by Koltunov [22]. It is recognised, however, that these data-fitting approaches should be supplemented by a more detailed and fundamental understanding of the redox chemistry in aqueous and solvent phases. The effects of radiation on the system are also highly relevant and under re-investigation [23].

- NNL advanced process

Simplified flowsheets meeting the requirements for advanced thermal or Gen IV fuel cycles have been developed within the United Kingdom by the National Nuclear Laboratory (NNL). A single cycle flowsheet suitable for Gen IV fuel processing is illustrated in Figure 2.28.

**Figure 2.28. Schematic of single cycle Advanced PUREX process suitable for Gen IV fuel reprocessing**



Following co-extraction of U-Np-Pu into 30% TBP/kerosene, Pu and Np are separated from U by use of a hydroxamic acid complexant. This is the major innovation of the NNL Advanced PUREX process. Hydroxamic acids are complexants of general formula RCONHOH, which are predominantly soluble in the aqueous phase when R=H or $CH_3$. Thus, they act as bidentate O,O donor ligands forming hydrophilic complexes with charge-dense metal ions such as $Np^{4+}$ and $Pu^{4+}$. Measurement of stability constants between acetohydroxamic acid (AHA) and various metal ions [24] has shown that AHA forms strong complexes with the tetravalent actinides even in substantially acidic solutions. Much weaker complexes are formed with $UO_2^{2+}$, $NpO_2^{+}$ and $M^{3+}$ ions. Batch distribution experiments show that $Np^{4+}$ and $Pu^{4+}$ ions can be very effectively stripped from the TBP phase into $HNO_3$, with low extraction (or high stripping) coefficients obtained at acidities <1 mol/L $HNO_3$ [25]. U(VI) distribution coefficients are not adversely affected by AHA and high separation factors between Pu(IV) and U(VI) can thus be obtained.

Basic research has also shown that hydroxamic acids are redox active, acting as very fast reducing agents for Np(VI) ions [26] but, while Np(V) is formed very quickly further reduction to Np(IV) is not observed. Reduction of Pu(IV) [27] and Tc(VII) [28] also occurs in the presence of AHA, but both these reactions are slow and can be suppressed with excess AHA at moderate acidities under ambient conditions. Reaction mechanisms are very complex in both cases.

Hydroxamic acids are also rather unstable in acid solution, hydrolysing to the parent carboxylic acid and hydroxylamine and also reacting rather quickly with $HNO_2$ [27]. Formohydroxamic acid (FHA) is significantly more susceptible to hydrolysis than AHA and, coupled with the easy availability of the latter, usually makes AHA the preferred process choice. However, FHA may be more suitable from a waste management viewpoint as it is easily degraded to gaseous products compared with acetic acid from AHA.

Mass transfer kinetics in the presence of AHA have not been studied in detail, but single stage centrifugal contactor work suggests little effect on kinetics and that the kinetics are sufficiently fast for flowsheet applications.

These simple hydroxamic acids, therefore, appear to possess many ideal basic chemical properties for actinide separation processes. Such "Advanced PUREX" flowsheets have been designed and tested at NNL (Sellafield, United Kingdom) under

$\alpha$-active conditions with simulant feeds containing up to 100 g/L Pu in the feed [29]. While the flowsheet designs were not fully optimised, the following conclusions were realised from the R&D work:

- very high U-stream Pu DFs are achievable using AHA;
- the U DF on the Pu stream can be degraded and there are no major barriers to flowsheets designed to co-process U-Pu;
- Np is quantitatively routed with the aqueous (Pu-containing) stream;
- Tc is substantially routed with the U-stream but the factors that affect Tc partitioning need further clarification, particularly with high Pu feeds;
- no stabiliser is required, Pu(IV) reduction is easily avoidable and kinetics are suitable for use with centrifugal contactors;
- degradation of AHA to acetic acid can complicate the recycle of nitric acid in the overall process.

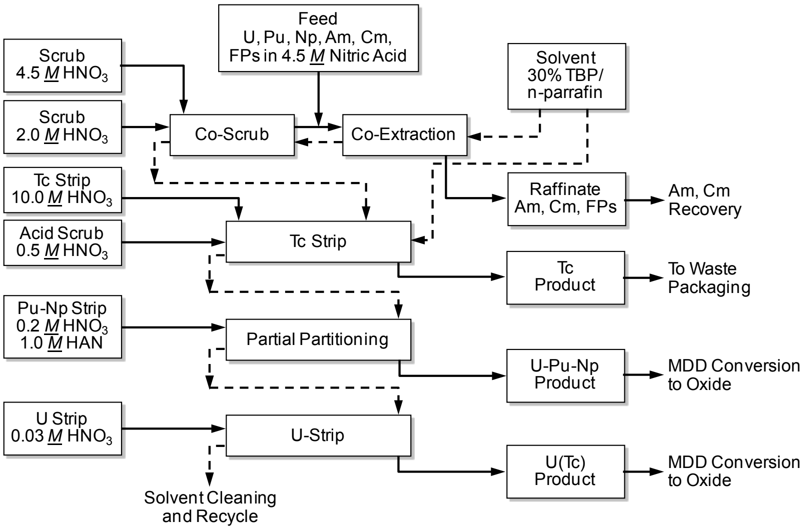
Further flowsheet applications of AHA have been proposed within the US UREX process, for Indian fast reactor reprocessing [30-31] and EnergySolutions NUEX process [4]. However, these are variations on the same basic concepts and process chemistry.

### US R&D studies

The US fuel cycle R&D programme is evaluating multiple approaches and technologies. In the area of developing co-processing capabilities, recent work has included demonstration of the UREX co-decontamination process illustrated in Figure 2.29.

This process has been demonstrated successfully for light water reactor (LWR) used fuels having a wide range of burn-up (20-65 GWd/te) and decay storage prior to separations treatment (4-32 years). Moreover, the process has been operated with and without the "Tc Strip" operation and with the partial partition process varied to produce a U-Pu-Np product containing either ~10% Pu-Np for potential recycle to LWRs or ~30% Pu-Np for potential recycle to fast reactors.

**Figure 2.29. UREX+ co-decontamination process**

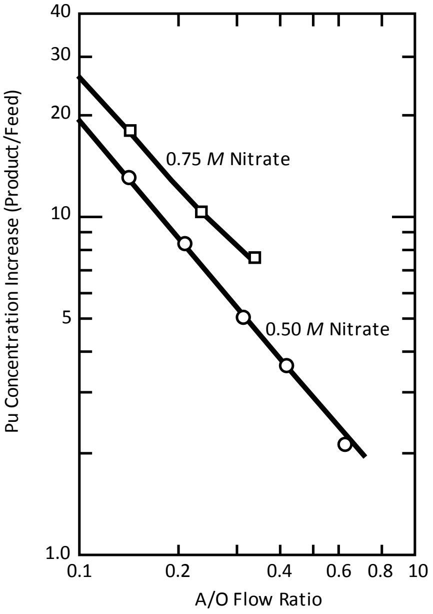


As indicated, many alternatives used fuel separation processes are being considered for development in the US fuel cycle R&D programme. As a part of this programme, recent studies of the solvent extraction process that uses *n*-tributyl phosphate in aliphatic diluent as the organic solvent have elucidated an improved understanding of variables that can provide significant benefits in process effectiveness, simplification and cost reduction. The potential improvements have included: i) conditions needed to enable effective use of hydroxylamine nitrate (HAN) as the reducing agent for plutonium and neptunium during co-partitioning, without the need to use hydrazine as a nitrous acid scavenger, ii) use of excess HAN as a combination reductant and salting agent to enable elimination of the need for a uranium backscrub contactor, iii) soluble technetium behaviour during use of HAN or acetohydroxamic acid (AHA) to enable co-partitioning and, iv) elimination of the need for product purification cycles.

**Effective use of HAN**: An early objective was to establish necessary operating conditions for effective use of HAN and to determine if stabilisation with hydrazine is necessary. Hydrazine is typically used as a holding reductant to protect the reduced species, Pu(III) and Np(V), from re-oxidation by reaction with any nitrous acid that may be generated by radiolysis of nitric acid within the system. Elimination of the need for hydrazine in a reprocessing plant is desirable because of a potential safety hazard – the formation of highly explosive compounds (hydrazoic acid and metal azides). Studies showed that control of the maximum aqueous phase acidity to <1 mol/L within the multistage partitioning contactors is the key variable in ensuring effective use of HAN without the addition of hydrazine. Previous kinetic studies [32] have shown that the rate of reduction of $Pu^{+4}$ by HAN is inversely proportional to the fourth power of the aqueous acidity. Based on measured stripping coefficients and the low aqueous/organic phase ratio normally used in partitioning, a relatively large number of stages are required to strip the plutonium at acidities greater than ~1.5 M; this may be because the rate of reduction is slower than the rate of re-oxidation at the higher acidities. In a multistage counter-current partitioning contactor, $Pu^{+3}$ can be effectively stripped in the region where the aqueous acidity is low enough for HAN to be effective but, if the aqueous strip solution containing $Pu^{+3}$ subsequently passes into a region of the contactor where the acidity is high enough to make HAN ineffective, the rate of re-oxidation and re-extraction may exceed the rate of reductive stripping and cause plutonium refluxing to occur. Therefore, control of the maximum aqueous phase acidity in the partitioning contactor to <1 mol/L is necessary. Excessive acidity can enter the partitioning contactor via the loaded solvent unless a low-acidity (<0.5 M) scrubbing of the loaded solvent is done immediately before entry to the partitioning contactor.

**Elimination of uranium backscrub contactor:** Recent tests have used both low-burn-up, long-cooled BWR used fuel and high-burn-up, short-cooled PWR used fuel to demonstrate a successful co-processing operation without the use of a uranium backscrub contactor. The process was shown to be capable of producing a U-Pu-Np product containing either ~10% Pu-Np for subsequent recycle to LWRs, or ~30% Pu-Np for subsequent recycle to FBRs. The co-partitioning process used in these demonstration tests utilised a method developed at the Savannah River Laboratory [33] in which an excess amount of HAN is used as the reducing agent for Pu(IV) and Np(VI) and as a salting agent to control the portion of uranium that is co-stripped with the plutonium and neptunium. The proportion of uranium co-stripped with the plutonium and neptunium (expressed as "plutonium concentration factor" in Figure 2.30) is dependent on the flow ratio of aqueous strip solution to organic solvent and on the aqueous-phase salting strength provided by the excess amount of HAN.

**Figure 2.30. Calculated plutonium concentration factors (CF) using the SEPHIS code [33]**



After the co-stripping operation has been completed, the U-Pu-Np product solution can be treated with NOx gas to convert the excess residual HAN to nitrogen gases and water, as is done in current industrial plant operations. Elimination of the uranium backscrub contactor can be considered as an engineered safeguard that effectively prevents production of a purified plutonium product.

**Behaviour of soluble technetium during co-partitioning:** Typical loaded solvent contains soluble technetium in addition to uranium, plutonium and neptunium. If the solvent is treated to remove the plutonium and neptunium by reductive stripping using HAN (or AHA) as the reducing agent, ~10 to 30% of the technetium will also be reduced and co-stripped. Limited test data have indicated that part of the technetium will be removed from the stripped product during the subsequent modified thermal denitration process and more may be released during the sintering of the MOX pellets. Thus, the technetium may be further distributed into the plant equipment, requiring multiple recovery and recycle operations. Alternatively, the technetium may be selectively removed from the loaded solvent prior to the co-stripping operation by washing the solvent with concentrated nitric acid, as is done in the La Hague reprocessing plant.

**Elimination of purification cycles:** Systems studies have shown that a number of benefits can be obtained by storing used fuel for ~30-70 years before processing for recycle of uranium, transuranium (TRU) actinide elements and other used fuel components [34]. Radioactive decay of short-lived radionuclides, such as $^{106}$Ru, is sufficiently extensive to eliminate the need for a plutonium (or U-Pu-Np) product purification cycle. Likely, the uranium product purification cycle can be eliminated if the recovered uranium is recycled directly to heavy-water reactors.

- JAEA NEXT process

The NEXT (New EXtraction system for TRU recovery) process being designed by JAEA (Japan) for future fast reactor fuel recycling uses a U crystallisation step following fuel dissolution to partially remove the bulk U content (see Section 2.2.1). Following this crystallisation residual U-Np-Pu are co-recovered using a TBP based extraction cycle. The two main goals of the process development are to obtain a high yield of Np extraction at the co-extraction step and to achieve effective co-stripping of U-Np-Pu in the backwashing step.

Np oxidation and extraction has been described above in some detail. At the co-stripping step, normally 0.02 mol/L $HNO_3$ was used as a stripping solution [35-36]. To enhance U stripping, the temperature of the stripping solution was raised to 45°C. The distribution ratio of Pu(IV) increases with the temperature but this is overcome by increasing the flow rate of the stripping solution [14]. Polymerisation of Pu(IV) was avoided by adding a nitric acid feed to the middle of the stripping section. Engineering scale centrifugal contactors are being developed for the NEXT co-recovery process.

- Flowsheet variations

There are various other proposals for modified hydrometallurgical processes that can co-recover U-Np-Pu, usually employing TBP as the extractant, such as Simplified PUREX[37], described below; SuperPUREX [38] from Russia; the PARC process [39] from Japan and Indian fast reactor reprocessing flowsheets [30-31]. Alternative CHON extractants to TBP for reprocessing have also been considered, including amides such as N,N-dihexyloctanamide (DHOA), which has some promising properties in comparison with TBP for U-Pu co-processing [40].

- Np-Pu co-reduction

From the above examples it is apparent that U co-processing with the Pu product is relatively straightforward in concept, but requiring a mastery of the flowsheet parameters (numbers of stages, flowrates, acidities, saturation etc.) and/or some re-blending of separated U with the Pu-containing product. It is also apparent that the key to these flowsheets remains the development of methods for Pu (and Np) stripping from the solvent phase. Flowsheet modifications to the established U(IV)- or HAN-based reductive partitioning processes, or a move to complexant-based stripping are leading proposals.

While hydroxamic acids are clearly leading candidates for complexant-based Pu stripping, with very few alternatives proposed (e.g. acetate, lactate [41], glycolate, pyruvate [42]), other organic (CHON) reducing agents have been proposed for reductive Pu-Np stripping, of which substituted hydroxylamines such as the ethyl(hydroxy)ethyl derivative [43], oximes [44], ureas [45] and butyraldehydes [46] are perhaps the more interesting examples.

*Review of new co-processing-based processes developed in Russia*

- Introduction

The next part of this section on (U, Pu) and (U, Pu, Np) co-processing options describes in some detail the different processes under development in Russia. These processes are used here to exemplify two aspects of process development. Namely, (a) how advanced reprocessing R&D programmes can take an overall approach to meeting the product and waste specifications for an advanced reprocessing plant, i.e. by integrating objectives of co-processing across head end, separation and conversion stages (the Simplified PUREX process) and (b) to illustrate how other innovative aqueous methods, such as crystallisation, can be incorporated within the reprocessing flowsheet to meet (U,Pu) co-processing objectives (REPA process, co-crystallisation and low-nitrate extraction).

Separation of neptunium during the reprocessing of spent nuclear fuel at the industrial scale already exists in the RT-1 plant (Russia) [47,48]. The technological scheme of the RT-1 plant is essentially a classic PUREX process based on solvent extraction technologies using 30% TBP diluted in light n-paraffin non-aromatic solvent. The process consists of two cycles in the uranium line and the Pu-Np purification cycle. The scheme includes the following flowsheet operations: co-extraction of uranium, plutonium, neptunium and technetium in 30% TBP; extract scrubbing; partitioning of uranium, plutonium, neptunium and technetium from bulk uranium; bulk uranium stripping (using 0.03 mol/L $HNO_3$ at 60°C) and carbonate-based regeneration of the extractant. Re-extraction of uranium (90 g/L) is carried out in the second uranium refining cycle. Re-extraction of plutonium and neptunium is carried out in the Pu-Np purification cycle. The subsequent plutonium and neptunium separation is based on the creation of the Pu(III)-Np(IV) pair using Fe(II) as a reducing agent. After stripping from TBP, neptunium is concentrated by a sorption method.

- Russian “simplified PUREX” process

To process spent nuclear fuel (SNF) from VVER-1000 reactors in the Test Demonstration Centre of the Mining and Chemical Combine (FSOE “MCC”), a version of the PUREX process was developed by the “NPO V. G. Khlopin Radium Institute” in St. Petersburg, Russia; this has been termed “Simplified PUREX” [49, 50]. This process was selected as the baseline process for the Experimental Test Centre being constructed at the site of the Mining and Chemical Combine (FSOE “MCC”), Zheleznogorsk, Krasnoyarsk region [51].

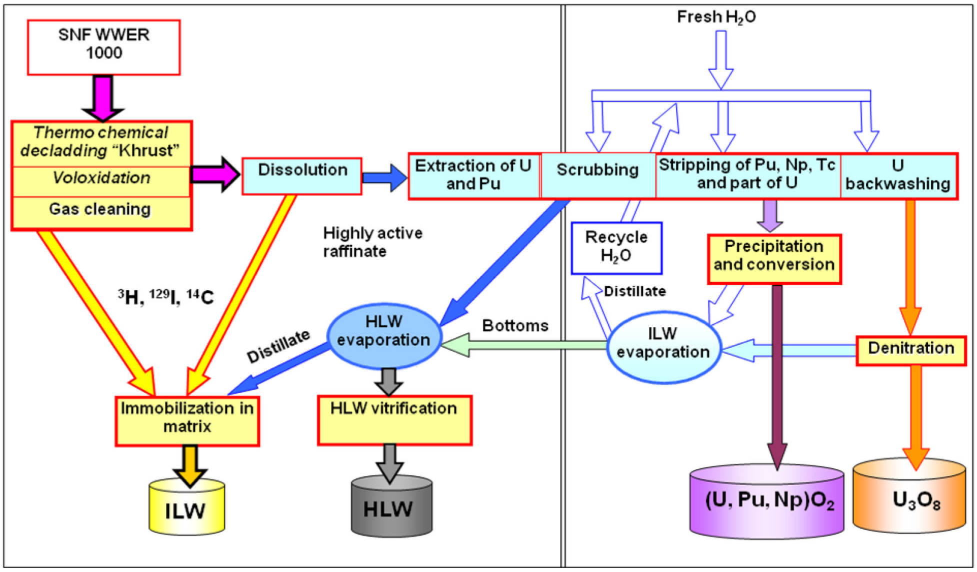
A block schematic diagram of the Simplified PUREX process is shown in Figure 2.31 and includes the following operations:

- thermochemical opening of spent fuel assemblies (SFA) instead of cutting;
- low-temperature voloxidation (tritium and iodine stripping);
- SNF dissolution in nitric acid giving a highly concentrated solution of uranium and plutonium;
- extraction of U, Pu, Np and Tc into a solution of TBP in a hydrocarbon diluent;
- scrubbing section for deeper cleaning of the actinides stream from FP;
- re-extraction of Pu, Np, Tc and part of the uranium;
- precipitation of U, Pu and Np and their conversion into dioxides;
- re-extraction of the bulk uranium component, then denitration to give $U_3O_8$;
- evaporation of the highly active raffinate (HAR) giving a liquid intermediate level waste ILW in the condensate and high-level waste HLW in the form of solid evaporated bottoms;
- solidification of liquid ILW in a cement matrix together with gaseous fission products (FP) $^{3}H$, $^{129}I$, $^{14}C$ that were removed during the voloxidation stage;
- HLW vitrification, storage and disposal;
- liquid ILW evaporation with condensate returning for washing and re-extraction and delivery of evaporator bottoms to HLW evaporation.

The use of the Simplified PUREX process for SNF reprocessing has two important goals:

1. production of U+Pu+Np and pure uranium fractions for recycling fissionable materials;
2. prevention of liquid process radioactive waste discharges into the environment.

**Figure 2.31. Flowsheet for VVER-1000 SNF reprocessing using the basic "simplified PUREX process"**



Solving the first goal allows the elimination of pure plutonium recovery thus increasing the resistance of a recycling process to nuclear materials propagation. Solving the second goal provides an opportunity not only to recycle water within a single technology, but also to reduce sufficiently the costs for liquid radioactive waste processing in comparison with those experienced in the Russian RT-1 plant and RT-2 project.

Important SNF reprocessing operations in the Simplified PUREX process are head-end water-free operations of thermochemical destruction of cladding and voloxidation of fuel. Thermochemical opening is made at ~1 000°C temperature ("Khrust" facility, JSC "SverdNIIKhimash") in a nitrogen-oxygen atmosphere. As the result of a dramatic loss of strength, zirconium cladding is destroyed by gravity with separation of fuel. When the temperature is reduced to 400-600°C, SNF oxidation occurs and, as a result, $UO_2$ (pellets) are transformed into $U_3O_8$ (powder) with more than 90% tritium, 60-80% krypton-85, iodine-129, carbon-14 and some other volatile FP stripped from the fuel. Formation of $U_3O_8$ powder facilitates the subsequent SNF dissolution in nitric acid.

Dissolution of oxidised fuel gives concentrated solutions of uranium containing from 500 g/L to 900 g/L, with residual nitric acid content up to 0.5 mol/L. This provides an opportunity to reduce the volume of the extraction raffinate after U+Pu+Np separation down to 1.6 $m^3$/teU. The raffinate solution can be evaporated in a flow-through evaporator with final vitrification. Liquid intermediate low-level waste (LLW) arising from the process are cemented, thus preventing radioactive waste discharges.

The Simplified PUREX-process for the Experimental Demonstration Centre (EDC) was tested in the hot cells of the Khlopin Radium Institute using 8 kg of WWER-1000 SNF with burn-ups of 50 and 60 GWd/teU with 10 and 3 years storage, respectively. Also, 3 kg of SNF with a burn-up of 70 GWd/teU were processed [52].

As described above, dissolution of $U_3O_8$ made it possible to achieve a high concentration of uranium in the process feed (more than 500 g/L U) at low concentration (1.5-1.8 mol/L) of nitric acid. Comparison of the volumes of the recycled nitric acid and the tritium-containing distillate from HLW evaporation generated by extraction reprocessing of Simplified PUREX feed solutions containing 550 g/L uranium in 1.5 mol/L nitric acid with the conventional PUREX feed solution containing a 250 g/L uranium in 3 mol/L nitric acid) demonstrated that the volume of the distillate for the Simplified

PUREX process will be two times less and the amount of recycled nitric acid four times less than in the conventional PUREX process. Reduction of the tritium-containing distillate volume to less than 2 $m^3$/te of SNF provides its complete immobilisation in cement together with intermediate level waste (ILW). Regenerated nitric acid containing tritium is used for SNF dissolution.

The feed and effluent compositions for extraction processing, obtained after voloxidised SNF dissolution, are presented in Table 2.9, where the average composition of the obtained products is given as well. Extraction processing duration was more than 150 hours. The decontamination factor for uranium was 2 x $10^6$ from $^{134,137}$Cs and 1 x $10^6$ from $^{154}$Eu.

**Table 2.9. Average data, obtained during WWER-1000 SNF reprocessing**

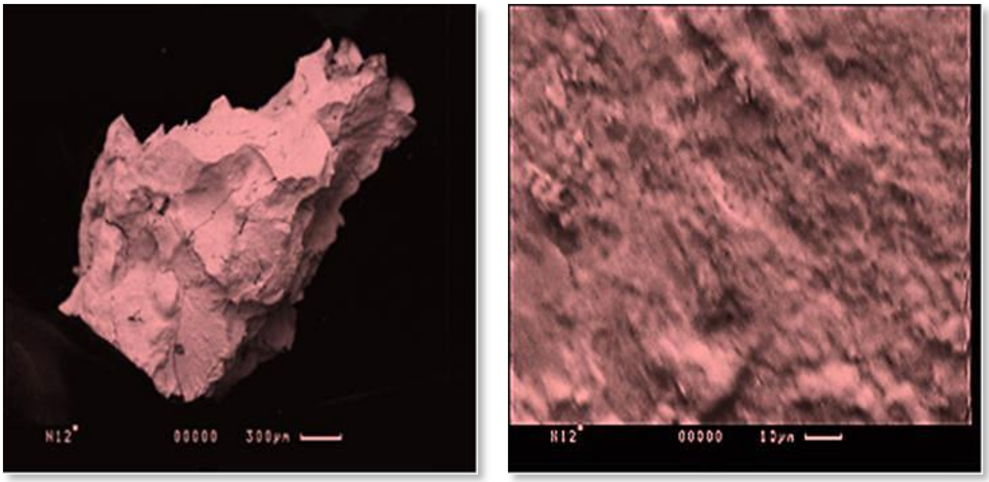
| Product | $HNO_3$ mol/L | U g/L | Pu mg/L | Np mg/L | Tc mg/L | Zr mg/L | $^{134,137}$Cs Bq/L | $^{154}$Eu Bq/L |
|---|---|---|---|---|---|---|---|---|
| Feed | 1.9 | 496 | 5 200 | 392 | 270 | 1 500 | 2.1E+12 | 2.1E+11 |
| Raffinate | 0.7 | 0.03 | 3 | | | <40 | 1.9E+12 | 1.3E+11 |
| Zr strip | 2 | <0.2 | <0.4 | 40 | 50 | 1 600 | 3.0E+09 | 8.0E+08 |
| Pu, Np strip containing U | 0.5 | 12 | 4 600 | 138 | 250 | <10 | 2.3E+07 | 2.1E+07 |
| U backwash | 0.2 | 55 | 0.2 | | <5 | <10 | 1.3E+05 | 2.2E+04 |

During the first extraction cycle, technetium is removed from the feed solution together with the target components (uranium and plutonium as well as neptunium, and zirconium). Back-extraction of technetium is provided together with plutonium and neptunium. Subsequent purification of the actinides from technetium is reached by precipitation of neptunium and plutonium, and precipitation of actinides with ammonia. To achieve the desired decontamination factor, the precipitate is then washed with a solution of ammonia, filtered and calcined. The following decontamination factors of the final product were achieved: $10^7$ from $^{134,137}$Cs; $10^4$ from $^{154}$Eu; $10^2$ from Tc. The packed density of the MOX product was 2.4 g/cm.

Figure 2.32 shows an image of the calcined actinide precipitate obtained by an electron microscope. Two types of particles are visible: lamellar and isomeric, indicating the formation of mixed solid solutions of actinide oxides. The obtained data demonstrates that actinide mixed oxides can be used for fabrication of MOX fuel for actinide transmutation reactors.

The uranium backwash solution was concentrated up to 500 g/L and sent to direct denitration in a spray drier with the spray generation through a nozzle. The product uranium oxide powder is shown in Figure 2.33, and some properties of the powder are presented in Table 2.10. Uranium decontamination at this stage of denitration was ~2.6 from $^{137}$Cs. The off-gases were directed to the system off-gas cleaning, where nitrogen oxides were catalytically reduced to nitrogen.

**Figure 2.32. Electron microscope image of a mixed oxide sample at different magnifications using the back-scattered electron mode**



Note: The size of individual particles is less than 2.1 microns.

**Figure 2.33. Image of the uranium oxide sample after denitration**

**Table 2.10. Properties of uranium oxide powder**

| Sample | $^{137}$Cs Bq/g U | Phase composition | Crystal size Å | Packed density g/mL |
|---|---|---|---|---|
| Initial U strip | 2 600 | - | - | - |
| After denitration | 980 | $\alpha$-$U_3O_8$ | 250 | 1.6 |

- Russian REPA (REprocessing-PArtitioning) process

A diagram of the Russian REPA process [52-58], developed for U-Pu (Np) recycling, is shown in Figure 2.34. In this process, SNF reprocessing comprises the following stages:

- embrittlement of fuel cladding at 800°C with separation of cladding from fuel;
- dry mixing of fuel with sodium hydroxide;

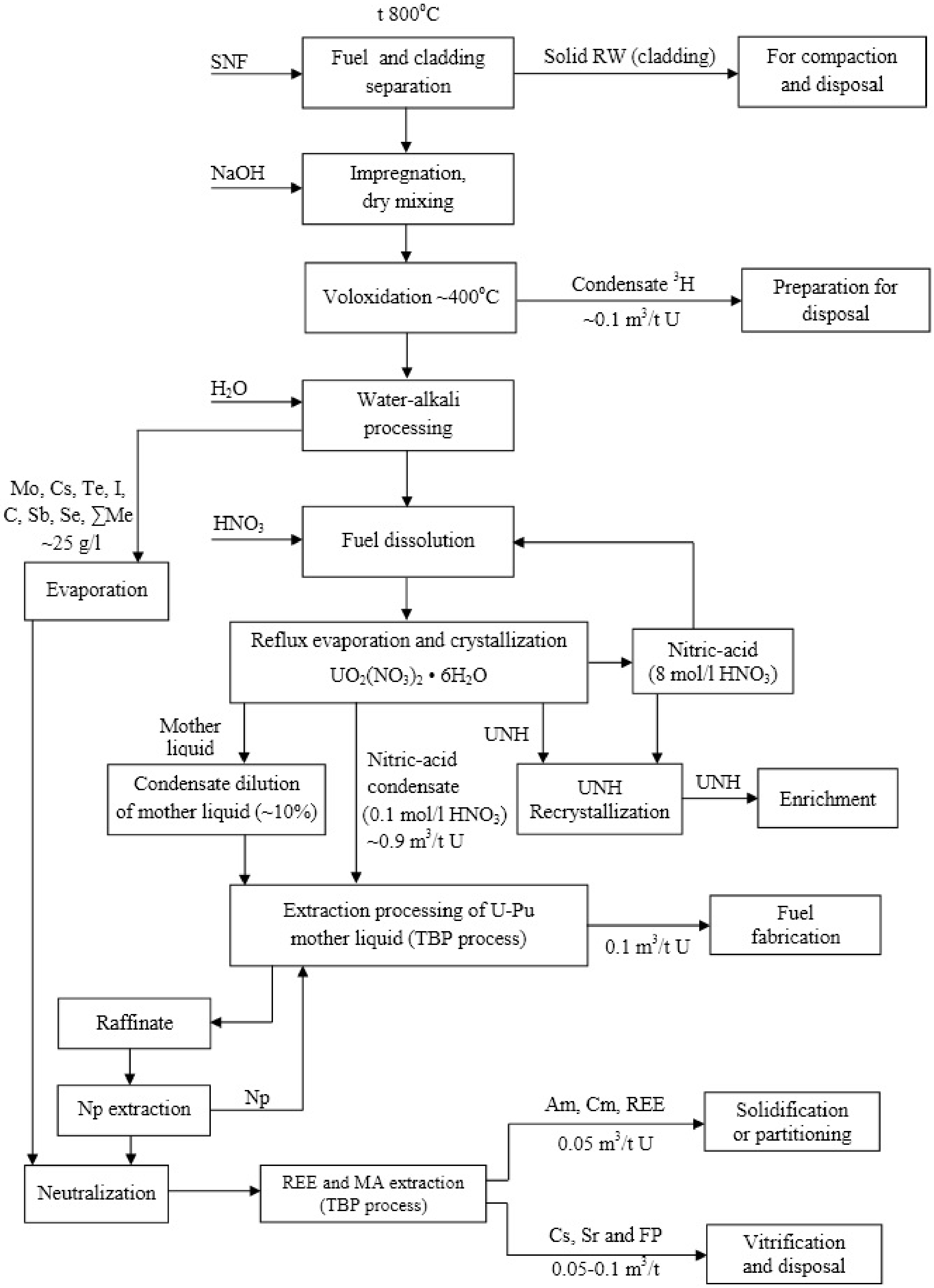
- fuel voloxidation in sodium hydroxide medium at 350-400°C giving separation of tritiated water and some volatile FP;
- water dissolution of surplus alkali and FP soluble in alkaline solutions (Mo, Cs, Tc, I, Sb, Se and others);
- extraction of cesium, technetium and iodine from alkali solutions;
- dissolution of fuel residuals after alkali flushing of FP in nitric acid and reflux evaporation of the obtained solution to increase uranyl nitrate concentration;
- cooling of the evaporated solution leading to UNH (uranyl nitrate hexahydrate) crystallisation;
- separation of UNH crystals and their recrystallisation with output of standard product, i.e. purified uranyl nitrate hexahydrate;
- dilution of the mother liquid from UNH crystallisation with nitric acid condensate;
- U and Pu extraction from diluted nitric acid into TBP solution resulting in the commercial uranium-plutonium product;
- Np extraction from U and Pu extraction raffinates;
- FP fractioning with output of Sr, Am+Cm and REE fractions;
- conditioning of U, Pu, Np, Am and Cm fractions for fuel production and recycling;
- conditioning of Tc+I fraction for production of a transmutation target;
- conditioning of Cs+Sr fraction for controlled storage and rare earth element (REE) and FP fractions for disposal.

The efficiencies of the REPA process are defined by the stage of UNH crystallisation, extraction of the U+Pu fraction and fractionation processes for the actinides, REE and other FP.

To optimise the separation process for UNH crystals, some research was performed on UNH solubility in nitric-acid solutions, the results provided a base to obtain calculated nomographs to define the uranium yield in crystals at different temperatures. Nitric acid concentrations were found to increase the rate of UNH cristallisation into solids and to optimise impurity flushing from the crystals. Thermal expansion of the two-phase system UNH crystals-uranium-saturated solution was studied, and their volume increase was determined. Dependences of expansion ratios on uranium concentration in the two-phase system and dependences of UNH melt viscosity on the system temperature and composition were also determined. Parameters determining the rate of UNH crystal formation in the crystalliser were estimated, as were conditions for crystal separation from nitric-acid solutions and cross-flow flushing to remove impurities from the crystals [53,54].

Co-extraction of uranium and plutonium from the mother liquor solutions from UNH crystallisation into solutions of TBP/hydrocarbon diluent is complicated with high emulsion carry-over into the organic phase; this is caused by the viscosity of uranium-saturated solutions and high concentration of solids [55].

**Figure 2.34. Block schematic diagram of REPA process**



To purify the organic phase from the water-emulsified phase a method was proposed and is based on forced coalescence of the two-phase flow passing through the granular layer in the coalescence units with phase upflow. If the organic to aqueous (o/w) phase volume ratio ranges from 0.02 to 0.075, the concentration of particle in the water flow decreases from 2.1 g/L to 0.003-0.008 g/L, when the solids content in the organic flow ranges between 28 g/L and 105 g/L. Peculiarities of make-up and movement of the two-phase flow in the separator pore space allow the flow to be well-cleaned both from microemulsion and microsuspension contaminants. Application of the separator as an extractor at high o/w ratios gives an opportunity to concentrate and separate plutonium in the water phase from the extraction cycle as a concentrated solution [56].

For precipitation-based separation of REE and minor actinide (MA) from nitric acid solutions, ethylenediamine and ethylenediamine formate are proposed for use [57]. Under optimal conditions in case of formate precipitation, up to 96-98% of the REE+MA fraction precipitates whereas in case of hydroxide precipitation, 99.9% of the same fraction precipitates. 98-99% of the Sr and 99% of the Cs stay in the mother liquor. This provides an opportunity to carry out precipitation-fractioning of the HLW formed after UNH and U-Pu fraction have been separated in the REPA process, using a salt-free precipitator with near complete separation of the REE+MA fraction from the Cs+Sr fraction into their own streams for further individual treatment. Mutual contamination does not exceed 0.6% [58].

Advantages of the proposed REPA process are: i) an early stage separation, prior to dissolution, of a number of volatile FP, particularly tritium, and sediment-forming FP at the alkali flushing stage; ii) an approximately ten-fold reduction in volumes of evaporated solutions; iii) an approximate two-fold reduction in chemicals to be used, and iv) a decrease in volumes and radioactive toxicity of radioactive waste to be disposed. Joint treatment of Pu and U with other actinides complies with requirements of fissionable materials non-proliferation. Recycling of U, Pu, Np, Am and Cm can support a complete scenario of the closed nuclear fuel cycle.

- Russian (U,Pu) co-crystallisation process

The co-crystallisation of uranium and plutonium nitrate hexahydrate in the process of mixture undivided refining crystallisation [59] is under investigation at the Bochvar Institute (VNIINM), Moscow, Russia. Production of mixed uranium-plutonium fuel includes steps of obtaining a master mix $(U,Pu)O_2$ with a ratio of Pu/U ≥0.25 and subsequent "dry" adjustments of this ratio by adding the required amount of $UO_2$. The important issue in manufacturing the master mixture is achievement of maximum homogenisation of $UO_2$ and $PuO_2$ (at a level of a solid-solution). Use of precursor compounds is a prerequisite for such homogenisation. Uranium and plutonium nitrates (UN, PuN) are such compounds. Co-crystallisation of hexahydrates $UO_2(NO_3)_2 \bullet 6H_2O$ and $PuO_2(NO_3)_2 \bullet 6H_2O$ is both a refining operation for obtaining an undivided mixture of uranium and plutonium and the method to achieve the desired chemical form for subsequent conversion into $(U,Pu)O_2$.

Step 1: preparation of the solution with the desired ratio of Pu/U

The source of the uranium-plutonium product for the crystallisation separation and purification is the plutonium re-extract. The choice of this crystallisation method does not affect the back extraction using plutonium reduction other than controlling the ratio of flows in the washing zone of plutonium from uranium. The ratio of U:Pu is a consequence of the apparatus used for reductive back washing of Pu; specifically related to the flow rate of the circulating extractant (Figure 2.35, Table 2.11).

**Figure 2.35. The dependence of U/Pu ratio in the aqueous flow of Pu leaving the washing zone on the ratio of phase flows in the zone**

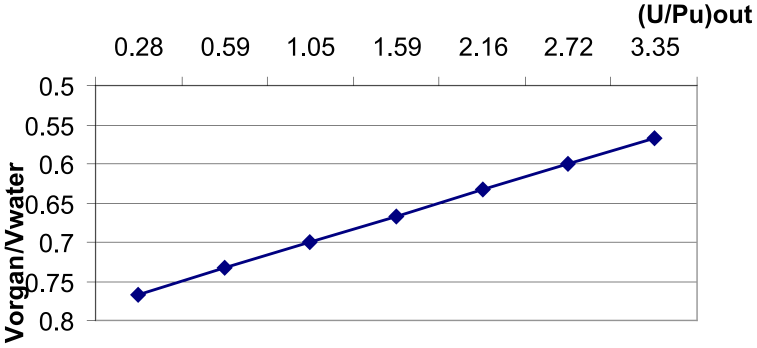


**Table 2.11. Composition of Pu re-extract entering the washing zone**

| U (g/L) | Pu (g/L) | $HNO_3$ (mol/L) |
|---|---|---|
| 73 | 5.5 | 0.4 |

Step 2: evaporation of the solution to high concentrations of metals (to melt)

The methods used in this step were:

- the starting solution was evaporated to a melt;
- condensate was weighed and analysed for nitric acid;
- upon completion of evaporation, the concentrated solution was diluted with water (1:1);
- further evaporation was conducted to remove excess acid, and for the optimisation of the concentrated solution content.

Figure 2.36 shows the experimental set-up and Table 2.12 details the composition after completion of the evaporation.

**Figure 2.36. The laboratory facility for actinide melting showing 1 – a thermocouple in a glass pocket, 2 – an evaporator, 3 – a direct condenser and 4 – a solution of actinide nitrates**

**Table 2.12. Composition after completion of the evaporation**

| Mass of liquid (g) | $UO_2(NO_3)_2$ (% wt.) | $PuO_2(NO_3)$ (% wt.) | $NpO_2(NO_3)_2$ (% wt.) | $HNO_3$ (% wt.) | $H_2O$ (% wt.) |
|---|---|---|---|---|---|
| 268 | 55.8 | 5.7 | 0.32 | 10.31 | 27.7 |

Step 3: stabilisation of U(VI) – Pu(VI) valence pairs

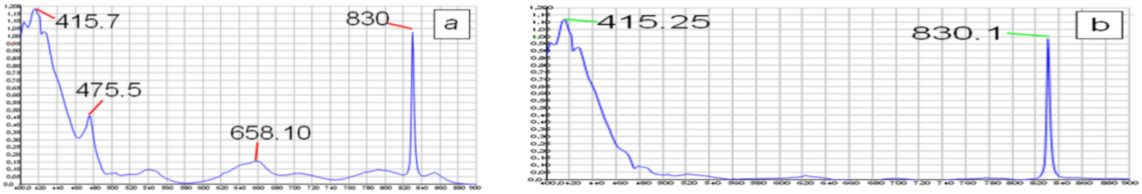
At this step it is necessary to stabilise the U(VI)-Pu(VI) valence pair, i.e. to oxidise Pu contained in solution to the hexavalent state. Two experiments were carried out with a mixed solution of uranium and plutonium (IV) nitrates. The initial solution was evaporated to reduce the volume within specified times. After evaporation of the solution, the Pu valence was spectrally analysed. The results and spectra obtained are shown in Figure 2.37.

Thus, stabilisation of plutonium (VI) can be achieved by a combined process of evaporation and refluxing. The total concentration of nitrate ions, boiling temperature and the time keeping the melt at this temperature all influence significantly the full stabilisation of Pu(VI) (see Table 2.13).

**Table 2.13. Results of U(VI) – Pu(VI) stabilisation experiments**

| | Experiment 1 | Experiment 2 |
|---|---|---|
| | Initial solution | |
| U (g/L) | 182 | 332 |
| Pu (g/L) [100% Pu(IV)] | 38 | 82 |
| $HNO_3$ (mol/L) | 4.9 | 1.5 |
| Multiplicity of evaporation | 5 | 4.8 |
| T (°C) (cub solution) | 135 | 135 |
| | Cub solution | |
| $(U,Pu)O_2(NO_3)_2$ (% wt.) | 68 | 78.25 |
| $HNO_3$ (% wt.) | 5.3 | 0.15 |
| Pu(VI) (%) | 97 | 100 |

**Figure 2.37. Absorption spectra of melts**



Experiment 1

Experiment 2

X-axis is wavelength in nm.

Step 4: adjustment of solution content to provide optimal working conditions for crystallisation of the basic component $UO_2(NO_3)_2 \bullet 6H_2O$

It was observed in the third step that in the crystallisation system (uranyl – plutonyl nitrate) – nitric acid – water, co-crystallisation took place. The coefficient of co-crystallisation is 0.6-0.7, and can be calculated according to Equation 2 where $G_{(tot)}$ is the total mass of elements in the system and $G_{(cr)}$ is the mass of elements in the crystalline phase.

$$K = \frac{G_{Pu(cr)} / G_{U(cr)}}{G_{Pu(tot)} / G_{U(tot)}} = 0.6 - 0.7 \qquad \textbf{(2)}$$

On this basis, the compositions of feed streams were selected in accordance with the solubility diagram of $UO_2(NO_3)_2$-$HNO_3$-$H_2O$ (Figure 2.38) so that these compositions were in the "working" lines sector of crystallisation of uranyl nitrate, i.e. corresponding to a high yield in a crystalline phase. For the equation of the working line (Equation 3), where [UN] and $[HNO_3]$ are uranyl nitrate and nitric acid (% wt.) in the liquid phase of the system, k is the coefficient determining the angle of the working line, the range of k was determined to be within the interval 2.25 ≥ k ≥ 1.50.

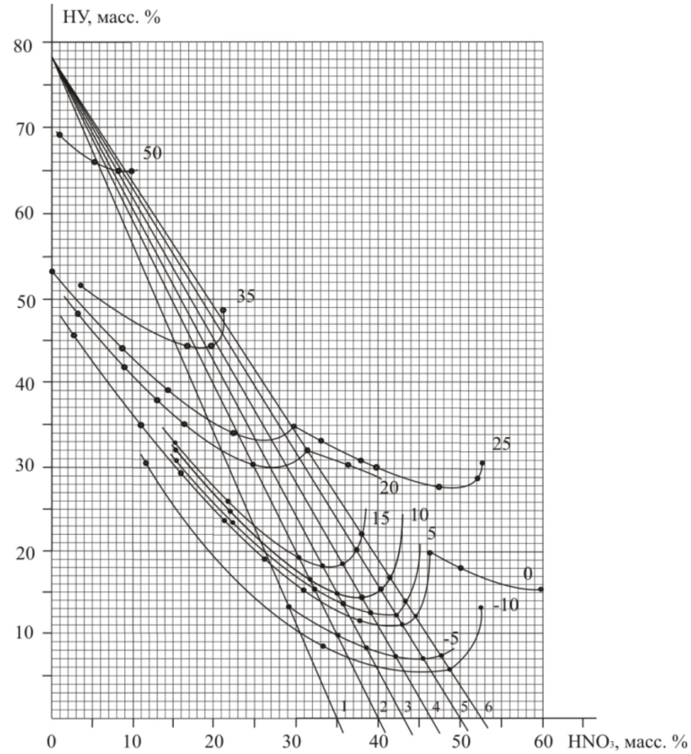
$$[UN]=78.49 - k \cdot [HNO_3] \qquad \textbf{(3)}$$

The samples of plutonyl and uranyl nitrate hexahydrate melts (PNH-UNH) for the crystallisation have compositions lying in the optimum position in the process sector of the working lines (1.60 and 1.98)

Step 5: co-crystallisation of $UO_2(NO_3)_2 .6H_2O$ and $PuO_2(NO_3)_2 .6H_2O$. Determination of the composition of the mother liquor and the operational salts output to the crystalline phase

Based on the patterns in the set, whereby the amount of co-crystallised UNH and PNH goes on almost the same isotherm, that of crystallisation of UNH, the calculation of the process working line was performed by Equation 3. For the calculation it was assumed that $[UN]' = [UN] + [PuN] + [NN]$. That is, the sum of the concentrations of nitrates is the "reduced" concentration of UN in the equation of the working line. In this case, the coefficient *k* = 1.6 (Figure 2.38). The results of spectral analysis showed that in the initial solution plutonium was completely in the hexavalent state. Thus, during evaporation, Pu(IV) is completely oxidised to Pu(VI) (Figure 2.39).

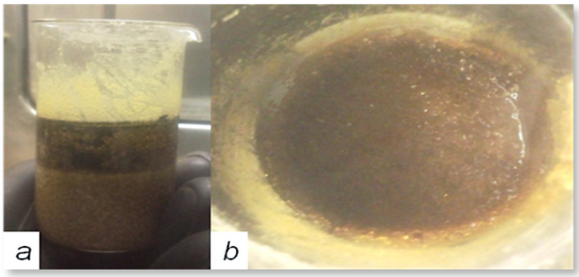
**Figure 2.38. The solubility isotherms of the system $UO_2(NO_3)_2$-$HNO_3$-$H_2O$ and location of the working line zone (A) of the crystallisation process of the UNH**



Values of *k* for the working lines 1, 2, 3, 4, 5 and 6 are 2.24, 1.96, 1.83, 1.69, 1.57, and 1.50, respectively.

**Figure 2.39. Crystals of $(U,Pu,Np)O_2(NO_3)_2 \cdot 6H_2O$**

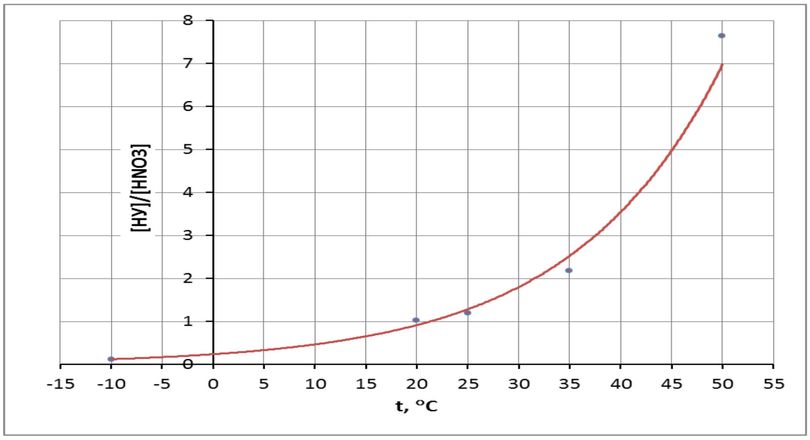
(a) distribution by volume, (b) top view after mother liquor draining



Composition of mother liquor:

It may be noted that the established mother liquor content and the corresponding value of [NU]/[$HNO_3$], where NU is the sum of the concentrations of actinide nitrates, corresponds to a temperature of crystallisation of 16°C (Figure 2.40).

**Figure 2.40. Relationship between the ratio [NU]/[$HNO_3$] in mother liquor from temperature along working line with k=1.6.**



The estimated weight of the mother liquor was 81.2 and the mass of crystals was 186.8 g. The mother liquor composition is given below:

| [U], g/L | [Pu], g/L | [Np], g/L | [$HNO_3$], mol/L |
|---|---|---|---|
| 227 | 40.5 | 8.60 | 9 |

Thus, the yield of actinides to the crystalline phase amounted to uranium: 89.0%; plutonium: 80.7%; neptunium: 44.2%, all by weight.

Step 6: definition of co-crystallisation factors in the direct (crystallisation) and reverse (crystals washing) process

Experiment 1: determination of the co-crystallisation coefficient in the direct process.

Mass of the prepared melt = 12.6 g

Temperature = 65°C

Analysis of an aliquot of the melt showed no other valence forms of plutonium, except for Pu(VI). The chemical composition of melt obtained in Experiment 1 is given below:

| NU, % wt. | NPu, % wt. | $HNO_3$, % wt. | $H_2O$, % wt. |
|---|---|---|---|
| 38.1 | 25.4 | 8.42 | 28.08 |

The appearance of the crystals UNH-PNH, shown in Figure 2.41, is very different from the crystals of the UNH and was found to be an intense red-brown colour. The results of the experimental work carried out led to the following conclusions:

1. The distribution of the amount of nitrates of uranium and plutonium in the crystallisation process between the liquid and crystalline phases is similar to the distribution of the "matrix" component, i.e. uranyl nitrate. This is confirmed by the compositions of the mother and washing solutions.
2. In the processes of crystallisation and washing the crystals in the crystalline phase depleted on each operation and, accordingly, the liquid phase became enriched in plutonium.

3. The coefficients of co-crystallisation for plutonium operations were as follows: crystallisation = 0.68; watching (35% $HNO_3$) = – 0.70; watching (50% $HNO_3$) = – 0.70.

Experiment 2: high plutonium nitrate content experiment

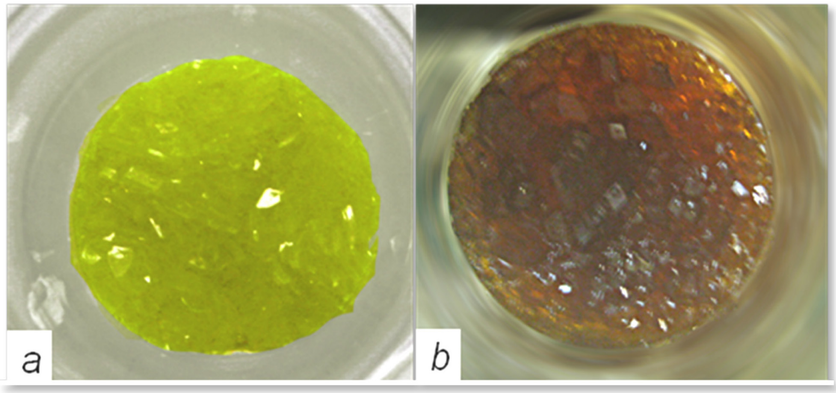
The next experiment was conducted with a high content of plutonium nitrate (absolute or relative) in the melt. Preparation of the melt and the oxidation of plutonium under complete control were also carried out as in the previous experiment, the temperature of crystallisation and crystal washing remained the same (20°C). The melt mass was 39.4 g. Concentrations were as follows:

| NU, % wt. | NPu, % wt. | $HNO_3$, % wt. | $H_2O$, % wt. |
|---|---|---|---|
| 36.3 | 31.8 | 5.55 | 26.35 |

The appearance of the crystals is shown in Figure 2.42. The results of the experimental work carried out led to the following conclusions:

1. As follows from the experimental data, the overall patterns of uranium and plutonium distribution were on the working line "crystallisation- washing the crystals".
2. Coefficients of plutonium co-crystallisation operations were as follows: crystallisation = 0.65; washing = 0.69.

**Figure 2.41. Crystals of (a) $UO_2(NO_3)_2 \cdot 6H_2O$ and (b) $(U,Pu)O_2(NO_3)_2 \cdot 6H_2O$**



- SNF reprocessing in dilute acidic nitrate solutions

A process is currently being developed in Russia (at the Vernadsky and Kurnakov Institutes) to dissolve SNF [57] in low concentrated nitrate solutions (nitric acid at pH ~1). This process should allow the separation of uranium and plutonium from FPs at the fuel dissolution stage. Well developed precipitation methods can be applied at the final stages of U/Pu extractions, using fluoride, carbonate, oxalate or peroxide precipitators. This separation technique aims to decrease the amount of radioactive waste generated during reprocessing [58].

**Figure 2.42. Crystals $(U,Pu)O_2(NO_3)_2{\cdot}6H_2O$ with an increased content of plutonium**

Fuels can be converted into solution using 0.1 mol/L $HNO_3$ aqueous solutions containing trivalent iron nitrate (or chloride) present in sufficient quantity to allow the oxidation of U(IV) to U(VI), since both Fe (III) and $NO_3^-$ ions (redox pairs: Fe(III)/Fe(II) and $NO_3^-/NO_2^-$) have oxidising properties. The use of iron (III) nitrate to dissolve $UO_2$ proved more efficient because of the smaller quantity required in comparison with $FeCl_3$. The dissolution reaction of $UO_2$ can be described as follows (Equation 4):

$$UO_2 + Fe(NO_3)_3 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + Fe(NO_3)_2 + NO_2 + H_2O \quad (4)$$

The rate of $UO_2$ dissolution in iron (III) nitrate solutions at room temperature does not differ from the dissolution rate of the mixture (6 mol/L $HNO_3$ + 0.1 mol/L HF) commonly used as a solvent for actinide oxides. The dissolution rate increases with the temperature. Complete dissolution (without mixing) of SNF model pellets containing 100 g (0.37 mol) of $UO_2$, can be achieved in 40 hours at 60°C and 15 hours at 80°C in 1 litre of aqueous solution containing 290 g $Fe(NO_3)_3.9H_2O$ (0.72 mol) at pH~1. The dissolution of $U_3O_8$ is slower than for $UO_2$. Dissolution slowed down after approximately 6 hours, i.e. the period after the full amount of uranium dioxide has gone into solution as shown in Equation 5.

$$2UO_3 + 4Fe(NO_3)_3 + 6H_2O \rightarrow 2UO_2(NO_3)_2 + 4Fe(OH)_2(NO_3) + 4HNO_3 \quad (5)$$

When the pH of the solution decreased, sparingly soluble iron (III) compounds were formed along with some suspensions. The original pH is reduced from 0.9 to 0.5 and corresponds to an increase of nitric acid concentration from 0.13 mol/L to 0.32 mol/L.

The dissolution of MOX fuel (4.6 wt.% $PuO_2$ in $UO_2$) in $Fe(NO_3)_3$ solution at pH ~1 leads to the formation of Pu(III) compounds formed by the reduction of Pu(IV) with Fe(II) ions (generated from the oxidation of U(IV) with Fe(III) salts) [59]. Solid solutions of mixed oxides $NpO_2$-$UO_2$ and $AmO_2$-$UO_2$ are also soluble in weak nitric acid solutions containing Fe(III) nitrate [60]. Neptunium goes into solution at the oxidation state +5 ($NpO_2^+$ ions), and americium as Am(III) ions.

In summary, dissolution of fuel in low nitrate solution allows not only the dissolution of uranium and plutonium but also minor actinides. However, further precipitation of uranium and plutonium peroxides from such solutions leads to their rather complete separation as shown in Table 2.14. Precipitation was performed using hydrogen peroxide. Co-precipitation of FP with uranium and plutonium peroxides did not exceed 0.05 mass%. Further purification of mother liquors from FP can be performed with hydroxide precipitation of Fe(II) by ferrocyanide ions with separation in the sediment of fragmented lanthanides, technetium, cesium and strontium.

Further processing of uranium and plutonium peroxide sediments is achieved with re-dissolution of uranyl hydroxylaminate in 0.1 mol/L $HNO_3$ and its precipitation with plutonium at a pH ranging from 7 to 11. Hexavalent uranium and plutonium are present in the original nitrate solution. With the addition of hydroxylamine to such solution, Pu(VI) is reduced to Pu(III). After ammonia has been added into the solution up to pH ~7, plutonium hydroxide is precipitated and uranyl dihydroxylaminate is generated. Increase of pH up to 11 leads to precipitation of 98-99% of uranium and plutonium as a mixed residue of uranyl dihydroxylaminate and plutonium hydroxide.

**Table 2.14. Separation of uranium and plutonium peroxides from nitrate solution (pH ~1) and their isolation from related FP [60]**

| Analysed object | Element concentration* (mol/L) | | | | | |
|---|---|---|---|---|---|---|
| | U | Pu | Fe | $Tc^{99}$ | $^{137}Cs$ | $^{85}Sr$ |
| Solution after fuel dissolution | $6.8 \cdot 10^{-2}$<br>(100 %) | $4.4 \cdot 10^{-3}$<br>(100 %) | 0.15<br>(100 %) | $1.8 \cdot 10^{-4}$<br>(100 %) | $1.4 \cdot 10^{-4}$<br>(100 %) | $2.0 \cdot 10^{-3}$<br>(10 0 %) |
| Residue | $6.6 \cdot 10^{-2}$<br>97 % | $4.2 \cdot 10^{-3}$<br>95 % | $6.0 \cdot 10^{-5}$<br>0.05 % | $<10^{-7}$<br>0.05 % | $<10^{-7}$<br>0.05 % | $<10^{-7}$<br>~0.05 % |
| Mother solution | $0.2 \cdot 10^{-2}$<br>3 % | $0.2 \cdot 10^{-3}$<br>5 % | ~0.15<br>99.95 % | $\sim 1.8 \cdot 10^{-4}$<br>99.95 % | $\sim 1.4 \cdot 10^{-4}$<br>99.95 % | $\sim 2.0 \cdot 10^{-3}$<br>~99.95 % |

*Element concentration was determined after dissolution of residue of mixed actinide peroxide in nitric acid.

After further calcination of the residue in air at 300°C, uranium and plutonium powder is generated. Low temperature decomposition of uranyl hydroxylaminate at 300-500°C is accompanied with uranium dioxide formation that does not require application of a reducing atmosphere ($H_2$ or CO) at this stage. X-Ray diffraction analysis of the obtained uranium and plutonium dioxide powder [61] provided evidence for the formation of a solid-solution of plutonium dioxide in the uranium dioxide matrix.

Thus, the proposed method of SNF reprocessing in dilute acidic nitrate solutions containing trivalent iron salts provides opportunities not only to simplify SNF reprocessing but also to reduce fire and explosion hazards of a production process and decrease the volume of liquid radioactive waste, as well as simplifying the manufacturing process of high grade mixed oxide fuel (high solubility in nitric acid solutions due to formation of $PuO_2$ solid solution in $UO_2$ matrix).

### *2.2.3 .TRU Actinide extractions using new solvent systems*

*Motivation*

The separation and recovery of the trivalent minor actinides, americium and curium, is a necessary step in realising the ultimate goals of the sustainable advanced nuclear fuel cycle with P&T (partitioning and transmutation) for waste management. However, this is an extraordinarily difficult chemical problem due to the complex mixture of elements contained within dissolved spent nuclear fuel solution (or the high-level waste [HLW] obtained after the PUREX process is used to recover uranium and plutonium) and because of the chemical similarity between the trivalent actinides and trivalent lanthanides. The tributyl phosphate (TBP) extractant used in the PUREX process is not capable of extracting trivalent actinides; therefore, new solvent systems based on alternative extracting ligands are required to achieve minor actinide recovery. This has been a topic of intensive global research over the last couple of decades and various ligands and solvent systems have been developed and new solvent extraction processes tested. These new processes either tend to be designed to separate minor actinides from PUREX raffinates or are alternative processes that seek to overcome the limitations of the PUREX process by replacing it with systems designed to recover the full series of actinides, including minor actinides, from spent fuel. While there has been significant progress towards this objective, there is however, as yet, no clear consensus on which system should be taken forward to industrial deployment. This section describes some of the trends, solvent systems and solvent extraction processes developed by the international community in the frame of minor actinide separations. Specifically, sub-sections describe developments in European programmes; studies in Japan and Russia on the promising diglycolamide class of extractants; some alternative diamide based ligands; the development of grouped actinide extraction (GANEX) processes capable of managing all TRU actinides together; Russian process development using the zirconium salt of dibutyl phosphoric acid (HDBP) for HLW separations; studies in the United States using TRUEX/TALSPEAK and TRUEX/Advanced TALSPEAK and, finally, two alternative aqueous technologies – respectively the applications of extraction chromatographic methods and a process based on aqueous carbonate media. While this is not an exhaustive review of all ligands and aqueous separation processes proposed for minor actinide separations, it provides an overview of some of the most important, recently emerging, international trends. For more detailed reviews of these processes the interested reader is referred to complementary recently published reviews [1-5].

### *Extraction by new solvents*

#### ▪ Introduction: Why are new molecules needed?

Once the uranium and plutonium have been separated, the minor actinides (americium first, then curium and neptunium) represent the highest contribution to the spent fuel radiotoxic inventory. They are, therefore, top priority target radioelements, and their management is indispensable in order to reduce the radiotoxicity of the final nuclear waste. For example, in France, the laws of December 1991 and June 2006 have set the basis for decades of research programmes carried out by the CEA, in collaboration with the CNRS, universities and nuclear industry partners. The work achieved in the framework of these laws should enable the feasibility of separation and transmutation procedures for minor actinides to be demonstrated.

If the separation of neptunium, jointly with uranium and plutonium, is made possible by an adaptation of the industrial PUREX process, the separation of americium (Am) and of curium (Cm) is almost impossible using this process, as tri-n-butyl phosphate only extracts actinides (An) of oxidation states +IV and +VI. With the know-how acquired from national and international research conducted over more than 40 years in this field, the chemists in different European Institutes gathered in collaborative projects coordinated by the CEA during successive Framework Programmes (FP5 to 7), have fostered the development of new hydrometallurgical processes, based on complexing and/or extracting molecules which could enable more than 99.9% of the Am and Cm to be recovered.

#### ▪ Difficulties in the separation of americium and of curium

After five years of cooling, a tonne of UOX spent fuel with a burn-up of 60 GWd/te contains 785 g of Am, 135 g of Cm and approximately 60 kg of fission products (FP), of which a third are lanthanides (Ln), ), neutron absorbers that are generally thought to reduce An transmutation yields. However, new research in Canada and the United States indicates that the presence of Ln does not prevent effective An transmutation when irradiated in the form of burnable poison rods for HWRs or LWRs. Nevertheless, continued research on separation and removal of at least a portion of the Ln is needed to ensure that their concentration in recycle fuels or targets will not increase.

In nitric acid solution (dissolution matrix for spent nuclear fuel), the two groups of elements Ln and Am+Cm are present at the oxidation state +III and their physicochemical properties are very similar. They are strongly hydrated and their ionic radii are very similar. Considered as "hard acids" in Pearson's "Hard and Soft Acids and Bases" theory, they react preferentially with hard bases, such as ligands with oxygen atoms, via electrostatic interactions (the co-ordination number varies from 6 to 12 depending on the chemical system considered). Therefore, if initiated by a size effect between the metallic cations' radii and the co-ordination site of the oxygen donor ligand the two series of elements can be partially separated.

Nevertheless, the distribution of 5f electrons in the electron clouds of the $An^{3+}$ cations presents a bigger spatial extension than that of the 4f electrons of $Ln^{3+}$. This distinction enables a difference in reactivity to be obtained, by using ligands that bear electron donor atoms that are less "hard" than oxygen (e.g. nitrogen, sulphur), and thus making An(III)/Ln(III) separation possible.

- How can An(III) be separated from Ln(III)?

**First option: Separation of the An(III) by selective extraction**

Given the acidity and the element inventory of PUREX raffinates, selective extraction of minority An(III) would appear to be logical. However, this strategy is complicated by the fact that the organic extracting agent to be developed should be i) very efficient (if the extraction of An(III) is carried out from a high-concentration nitric medium, the « $H^+/An^{3+}$ » competition is very strong) and ii) highly selective, especially in comparison to the fission product transition metal (e.g. Fe, Pd, Mo, Zr) and Ln(III). In order to address the first option more easily, a two-step process approach was proposed by the CEA. In the first step of the process, the trivalent actinide and lanthanide families are selectively co-extracted from the PUREX raffinates by a malonamide extractant, such as N,N'-dimethyl-N,N'-dioctyl-hexylethoxy-malonamide (DMDOHEMA), which is a "hard base" bearing oxygen-donor atom. This first step, named the DIAMEX process, provides the advantage of reducing the acidity of the "An(III)+Ln(III)" product solution, which is introduced to the second step of the process, where the trivalent actinides and lanthanides are separated using "soft donor" extractants, which are more sensitive to acid environments.

**Second option: Separate of the An(III) by selective back-extraction**

It appeared simpler to co-extract the An(III) and Ln(III) into an extractant that does not require a low-acidity aqueous phase, and then to carry out the An(III)/Ln(III) separation by the selective back-extraction of the An(III) in order to overcome the difficulties associated with the concept of An(III) selective extraction as explained above. In this case, a hydrosoluble complexing agent is used to ensure the An(III)/Ln(III) selectivity. Thus, the whole separation process, which has been developed at the CEA Marcoule, can be carried out in one single step as compared to the first option which is a two-step process.

- An(III) separation systems studied at the CEA and in European contracts (FP4-NEWPART, FP5-PARTNEW, FP6-EUROPART, and FP7-ACSEPT projects)

**First step DIAMEX process: An(III)+Ln(III) co-extraction**

Due to their two solvating amide functions separated by a methylene bridge, malonamides are diamides which strongly chelate Ln(III) and An(III). Since these molecules are composed only of C, H, O and N atoms, they have added benefit of not generating mineral ash if disposed after use by incineration treatment. Within this family, the structure of the reference molecule, DMDOHEMA, was optimised:

- the total number of C atoms was increased to raise the solubility of the complexes and limit the risk of splitting of the loaded organic phase;
- the C atoms were more uniformly distributed on the alkyl chains to facilitate the elimination of products formed by hydrolytic and/or radiolytic degradation (basic washes proved to be efficient in eliminating acidic-type degradation products);

- an ethoxy group was inserted in the central chain to increase the affinity of the solvent for An(III) and Ln(III);
- in addition, hydrophilic complexing agents were added to the DIAMEX flowsheet (in the feed and scrubbing solutions) in order to limit any interfering extraction of fission products such as zirconium,molybdenum, iron and palladium. Oxalic acid is recommended for Zr, Mo and Fe, and HEDTA (hydroxy-ethylene-diamine-triacetic acid) for Pd.

Several counter-current tests were carried out from 1999 to 2005 at the CEA Marcoule (France), the Forschungszentrum Jülich (FZJ, Germany) and the Institute for Transuranium Elements (ITU, Karlsruhe, Germany) through successive collaborative projects funded by the European Commission [6]. These tests consisted of:

- surrogate, spiked, or genuine PUREX raffinates, as well as PUREX concentrates, as the feeds [7];
- DMDOHEMA dissolved at 0.65 mol/L in hydrogenated tetrapropylene (HTP), as the solvent;
- mixer-settlers, centrifugal extractors, rotating 'Couette-Taylor' effect columns, and pulsed columns, as the laboratory scale contactors.

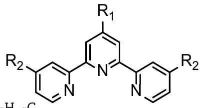
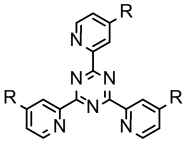
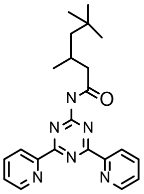
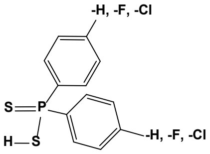
### Second step SANEX process: An(III)/Ln(III) separation

Two types of extracting systems were investigated for this step: synergic nitrogenous or sulphurous systems and BT(B)P-type solvating nitrogenous extracting agents.

- Synergic systems: exploiting synergy of extracting molecules

Two types of synergistic systems were studied: nitrogenous and sulphurous mixtures. Nitrogenous synergistic systems were made of, on the one hand, polyazine ligands (Table 2.15: terpyridine, TPTZ (TriPyridyl-TriaZine) ADPTZ (Amino-DiPyridyl-TriaZine) [8]) incapable of extracting An(III) by solvation) and, on the other hand, cationic exchangers (e.g. carboxylic acids). The sulphurous synergistic mixtures consisted of a diaryldithiophosphonic acid (Table 2.15: $(Cl\phi)_2PSSH$ used in the ALINA process [9] and derived from the very selective CYANEX 301 acid) and monodentate organophosphorous solvating agents (e.g. trioctyl phosphine oxide TOPO, TEHP).

**Table 2.15. Polyazine and dithiophosphorous ligands investigated in Europe for the synergistic extraction of An(III)**

| Terpyridines (terpy) | TriPyridyl-TriaZines (TPTZ) | 2-amino-4,6-di-(pyridine-2-yl)-1,3,5-triazines (ADPTZ) | Bis(halogeno-phenyl)-dithiophosphinic acids |
|---|---|---|---|
|  $R_1$ = -H, -$C_nH_{2n+1}$, $\Phi$–$C_nH_{2n+1}$; R2= H, -$C_nH_{2n+1}$<br>**R-Terpyridines (R-Tpy)** |  $R_1$ = -H, -Me, -$^tBu$<br>**R-Tripyridyltriazines (R-TPTZ)** |  **R-AminoDiPyridylTriazines (TMHADPTZ)** |  **$(R^{\Phi})_2$PSSH** |

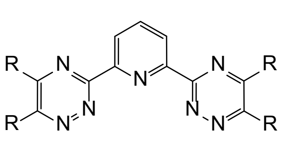
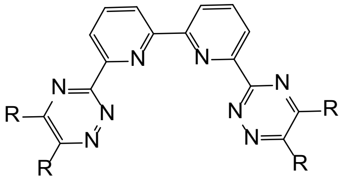
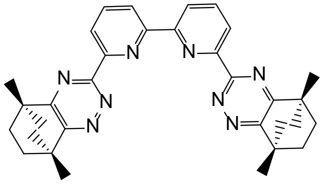
In these synergistic systems, the soft-donor ligands bring the selectivity towards the An(III). For instance, the pre-organisation of the co-ordination sites of the tridentate polyazine ligands proved to be useful in overcoming the hydration of the $An^{3+}$ cations, leading to the desired An(III)/Ln(III) selectivity, whereas the synergists enabled the extraction of the An(III) complexes into the organic phase. However, these synergistic mixtures often required the adjustment of the feed acidity below $[HNO_3] = 0.2$ mol/L. That is the reason why they were basically eliminated from the European strategies for the separation of the trivalent minor actinides.

- Solvating nitrogenous extracting agents: BT(B)P

The tridentate nitrogenous extractants Bis-Triazinyl-Pyridines (BTP, Table 2.16) were discovered in 1997 by Kolarik [10]. They can be distinguished from TPTZ and from ADPTZ by the special asymmetric configuration of their triazines, which gives them a lower affinity for the proton but higher for An(III). They very quickly proved to be efficient in the extraction of An(III) cations, accompanied by their nitrate anions, from relatively concentrated acidic solutions ($[HNO_3] > 1$ mol/L), with an An(III)/Ln(III) selectivity of 100 ($SF_{An/Ln} = D_{An}/D_{Ln}$), as compared to those of TPTZ or ADPTZ, which never exceeded 20.

Many BTPs were synthesised and tested in Europe between 1997 and 2002. The parametric and thermodynamic studies carried out on these molecules revealed that the nature (*e.g.* normal or branched alkyl chains, aromatic rings) and the length, as well as the position of the substituting groups, not only influence the complexing and extracting properties of BTP compounds (An(III)/Ln(III) selectivity and kinetics of extraction), but also their chemical stability. The first molecule used for testing the SANEX process step was 2,6-bis-(5,6-di-n-propyl-1,2,4-triazine-3-yl)-pyridine (nPr-BTP), diluted in a mixture of TPH and n-octanol. Unfortunately, it proved to be chemically unstable during the high-activity test and complementary laboratory studies demonstrated that it degraded in just a few hours under the effect of nitrous acid. Next, 2,6-bis-(5,6-di-isopropyl-1,2,4-triazine-3-yl)-pyridine (iPr-BTP), was tested in 2001 and it required the addition of a phase transfer catalyst, DMDOHEMA, and the use of pure n-octanol as diluent. During the high-activity trial, iPr-BTP was shown to be efficient in terms of An(III) retrieval (99.9%) and purification, as concerns Ln(III), but it degraded during the trial under the effect of radiolysis [11]. This family of nitrogenous extractants was, therefore, abandoned by the CEA in 2002, but is still being investigated within European framework projects, both to further our fundamental understanding of actinide soft donor interactions and to try and develop better optimised processes.

**Table 2.16. Polypyridine-triazine extractants developed for An(III)/Ln(III) separation**

| 2,6-Bis-(5,6-dialkyl-1,2,4-Triazin-3-yl)-Pyridines (BTP) | 6,6'-bis(5,6-dialkyl-[1,2,4]-triazin-3-yl)-[2,2']-bipyridines (BTBP) | Bis-Annulated-Triazine-Bis-Pyridine(BATBP): $CyMe_4$-BTBP |
|---|---|---|
|  |  |  |

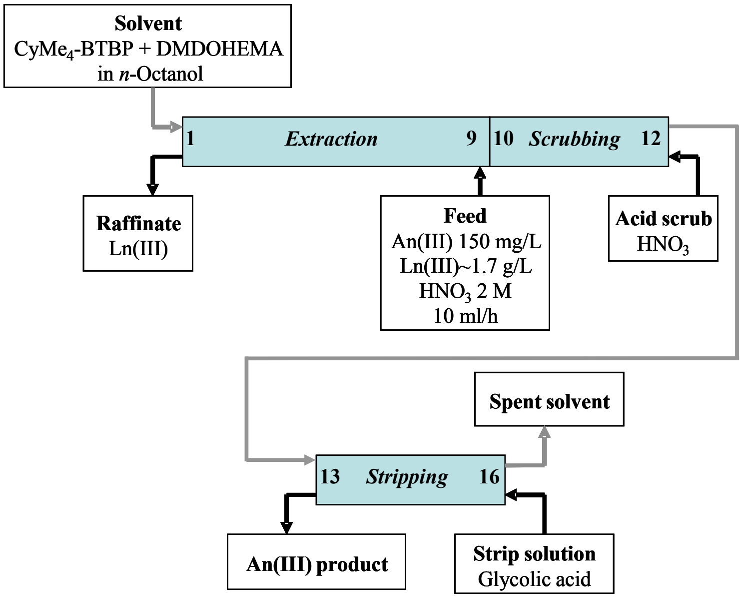
Within the FP6-EUROPART collaborative project, a new class of N-donor polyazines was designed and synthesised to better conform to the requirements of the SANEX process development: the bis-triazinyl-bipyridines (BTBP, Table 2.16). The extraction properties of these tetradentate ligands were investigated and they appeared to differ from those of BTP ligands, in that $M{:}L_2$ complexes were identified instead of $M{:}L_3$ complexes. The selectivity of alkyl-BTBP ligands towards An(III) and their kinetics of extraction are similar to those of alkyl-BTP ligands: the bulkier the alkyl groups are, the slower the mass transfer is, thus requiring a phase transfer catalyst, such as a diamide. In the particular case of the bis-annulated-triazine-bipyridines, $CyMe_4$-BTBP (Table 2.16) appeared less selective towards An(III) ($SF_{Am/Eu} > 100$) than its BTP analogue ($CyMe_4$-BTP, for which $SF_{Am/Eu} > 1000$), certainly due to the formation of $M:L_2$ complexes as opposed to the rigidified $M:L_3$ complexes observed with $CyMe_4$-BTP. This difference in the mass action law of complex formation is somehow beneficial for the development of partitioning processes based on $CyMe_4$-BTBP, in that the impact of the solvent hydrolytic/radiolytic degradation on the extraction performances is reduced: the apparent decrease of extraction efficiency, resulting from the destruction of the extractant, is thus smaller for BTBPs than for BTP extractants.

- SANEX-BTBP process

The formulation of the BTBP solvent was optimised, based on the iPr-BTP solvent formulation (i.e. $CyMe_4$-BTBP and DMDOHEMA, respectively dissolved at 0.015 and 0.25 mol/L in n-octanol [12]), in order to elaborate a SANEX partitioning flowsheet (Figure 2.43) that was successfully tested counter-currently in laboratory scale centrifuges at the ITU (Karlsruhe, Germany) in 2008, using a highly active "An(III)+Ln(III)" solution. Table 2.17 shows the recoveries in the outgoing phases as a percentage of the feed, together with the decontamination factor (DF) for the extraction. The DF is calculated as $Massflow_{Feed}/Massflow_{Raffinate}$. Excellent feed decontamination factors for Am (7000) and Cm (1000) were obtained and the recoveries of these elements were higher than 99.9%. More than 99.9% of the lanthanides were directed to the raffinate except Gd, for which 0.32% was recovered in the product [13]. The total Ln content, however, is still below 0.1%, as the major part is lighter Ln. In addition a small fraction of Y (0.43%) is recovered in the product. If necessary, the scrubbing can be improved in an optimised process by, for example, an increased number of stages. The concentration profiles for Am-241 and $^{244}$Cm were compared to calculated profiles (Figures 2.44 and 2.45). Calculations were made using an in-house flowsheet model developed by JRC-ITU. The concentrations in the extraction section were calculated using kinetic data to estimate the apparent D-ratios (~10-15% of equilibrium D-ratios for Am and Cm) while in the scrub section equilibrium D-ratios were used. No kinetic data was available for the stripping and since the D-ratios are far from equilibrium, values from stage 13 in the experiment were used (constant value for all stripping stages). The calculated concentrations agree well with the experimental for both Am and Cm. The only large deviation was found in the two last stages, where the concentrations were too low to be measured accurately (too close to background).

This test showed that partitioning of trivalent An from Ln, in a SANEX process using the $CyMe_4$-BTBP, is possible with excellent results in a laboratory set-up. The process test gave high recoveries for Am and Cm (>99.9%), which is important for the P&T strategy, and excellent separation from the trivalent lanthanides (total Ln amount <0.1% in the product). The calculated concentration profiles agreed well with experimental results. Some improvements of the organic phase formulation are still necessary. The low flow-rate, caused by the slow kinetics, is a drawback in an industrial process in which large volumes of raffinate solution are to be treated. In addition, the limited loading capacity of the organic phase will be a problem in the treatment of HLW with high MA content. Furthermore, the radiolytic stability of $CyMe_4$-BTBP is still weaker than the stabilities of TBP, CMPO and DMDOHEMA, and the possibility of recycling $CyMe_4$-BTBP solvents has not yet been demonstrated.

### Figure 2.43. SANEX-BTBP process flowsheet tested at the ITU (Germany) on a genuine "An(III)+Ln(III)" feed [13]



### Table 2.17. Main results from the BTBP test

| | Recoveries [% of Feed] | | | DF |
|---|---|---|---|---|
| **Element** | **Raffinate** | **Product** | **Organic** | **Extraction** |
| **Y** | 103 | 0.43 | - | 1 |
| **La** | 113 | <0.01 | - | 1 |
| **Ce** | 107 | <0.01 | - | 1 |
| **Pr** | 117 | <0.01 | - | 1 |
| **Nd** | 103 | <0.01 | - | 1 |
| **Sm** | 100 | 0.01 | - | 1 |
| **Eu** | 100 | 0.08 | - | 1 |
| **Gd** | 100 | 0.32 | - | 1 |
| **Am** | 0.01 | 103 | - | 7 000 |
| **Cm** | 0.09 | 107 | - | 1 000 |

**Figure 2.44. Calculated and experimental concentration profiles for $^{241}$Am**

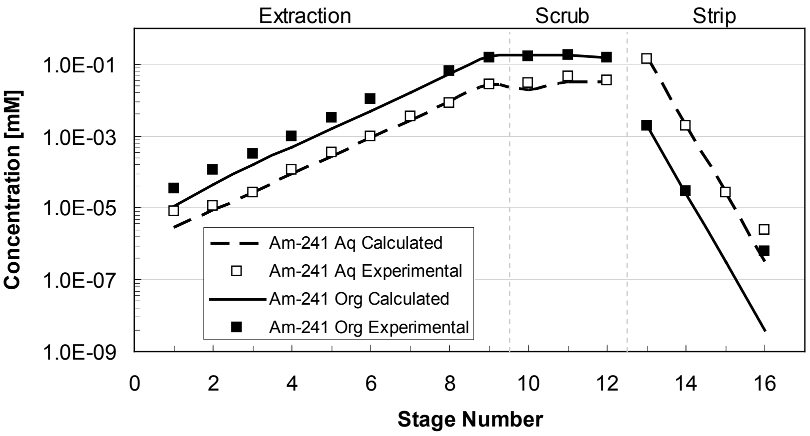
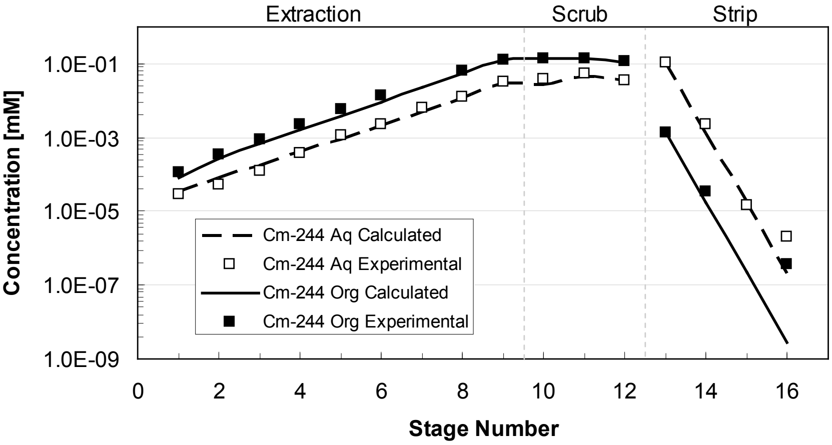


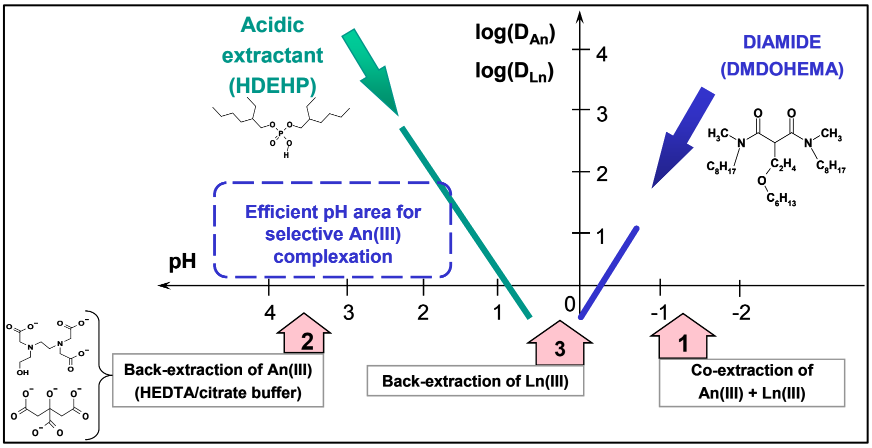
**Figure 2.45. Calculated and experimental concentration profiles for $^{244}$Cm**



- Single-step flowsheet: DIAMEX-SANEX/HDEHP, the CEA's studied option

The possibility of carrying out an An(III)/Ln(III) separation directly from a PUREX raffinate in a single step (see the principle described in Figure 2.46) was imagined by chemists at the CEA Marcoule, by combining in the same solvent DMDOHEMA, which extracts An(III) and Ln(III) at a high acidity, and di-(2-ethyl-hexyl)-phosphoric acid (HDEHP, Figure 2.57b), which maintains the Ln(III) in the organic phase. The An(III) ions are then selectively back-extracted using HEDTA aqueous complexing agent in a buffered stripping solution (pH 2-3). The flowsheet for the DIAMEX-SANEX/HDEHP process is nevertheless complicated by the fact that HDEHP is responsible for the parasitic co-extraction of some d-transition elements, such as Mo, Zr, and Fe (concomitantly with the extraction of the lanthanides), despite the presence of oxalic acid in the feed and scrubbing solutions (as works for the DIAMEX process). Fortunately, the strong loading capacity of the DMDOHEMA/HDEHP solvent prevents third phase formation (an advantage compared to the DIAMEX solvent). The inventory of extracted elements is easily managed through the process, but additional steps are introduced in the flowsheet to remove these elements from the solvent, thus increasing the overall output fluxes: Mo and Ru are back-extracted upstream from An(III) by an aqueous medium at pH 3, while Zr and Fe are back-extracted downstream from the Ln(III) stripping by a specific mixture of complexing agents.

**Figure 2.46. The DIAMEX-SANEX/HDEHP process principle**



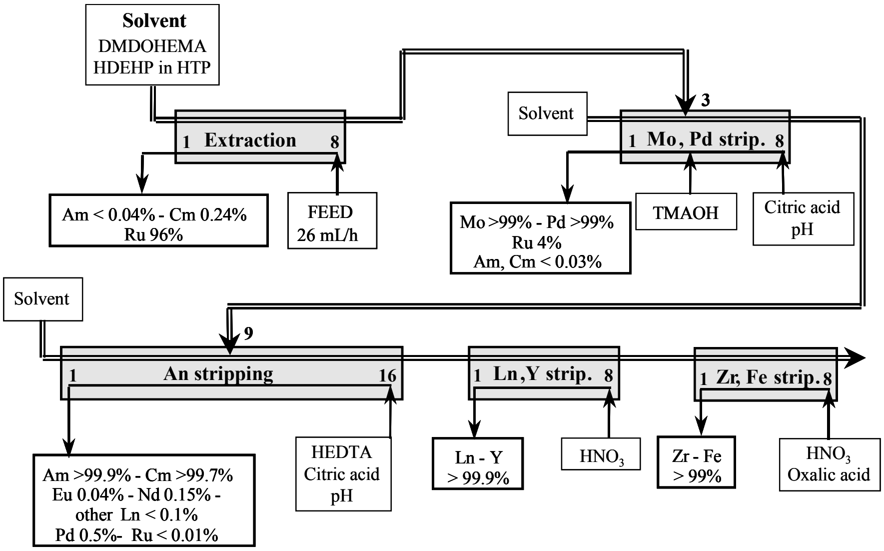
The concept feasibility of this process was first validated by the successful implementation of an inactive counter-current test using 48 stages of laboratory-scale mixer-settlers (6 mL mixing chamber and 17 mL settling chamber) in the G1 facility at the CEA Marcoule. This inactive test was followed by a counter-current hot test, performed on a genuine highly active PUREX raffinate in the hot cells of the ATALANTE facility in 2000 [8]. The main results of this hot test (Figure 2.53) can be summarised as follows:

- satisfactory hydrodynamic behaviour;
- high recovery yields for An(III): >99.9% for Am(III) and >99.7% for Cm(III) (0.2% of Cm(III) remained in the raffinates, but this should be improved by two additional stages in the extraction section);
- satisfactory An(III)/Ln(III) decontamination factors: $DF_{An/Ln}$ >800 (less than 2 wt% of Ln(III) in the An(III) product solution);
- satisfactory An(III)/fission products decontamination factors: only 0.5% of Pd and less than 0.01 % of Ru followed the An(III) fraction.

The DIAMEX-SANEX/HDEHP process was actually implemented twice more: i) in 2005, on a genuine highly active DIAMEX product (An(III)+Ln(III) fraction), as the second step of an An(III)/Ln(III) partitioning scheme in the scope of the technical feasibility validation of minor-actinide separation proposed by the CEA to address the issues of the 1991 French radioactive waste management act, and ii) in 2008, to assess the scientific feasibility of the GANEX 2nd cycle (group extraction of the actinides).

Research, currently running at the CEA, aims at simplifying the DIAMEX-SANEX/HDEHP process, which generates a large volume of effluents. An envisaged optimisation consists of introducing an in-line separation of the two extractants to the process, which would avoid the parasitic extraction of Mo, Zr, and Fe at the first extraction step where the organic phase would contain only the DMDOHEMA extractant (as in the DIAMEX process). These modifications involve the search for a new organophosphorous acid which would offer the advantages of HDEHP, but which could be easily separated from DMDOHEMA by simple aqueous washings.

**Figure 2.47. DIAMEX-SANEX/HDEHP process flowsheet tested at the CEA Marcoule on a genuine PUREX raffinate**



- Conclusion

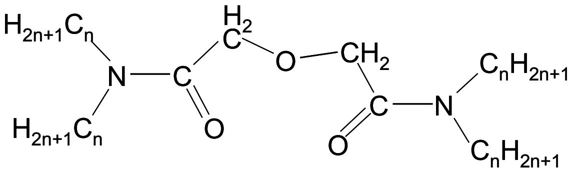
An(III)/Ln(III) separation remains the most complicated step in the recovery of the minor actinides, because of the very similar chemical properties of An(III) and Ln(III). The recommended strategy under the terms of the French law of 1991 was to demonstrate the possibility to carry out two successive steps: (1) co-extraction of An(III) and Ln(III) from PUREX raffinates to reduce the element inventory and the acidity of the feed to be treated, and (2) An(III)/Ln(III) separation, carried out either by the selective extraction of minority An(III) ions by using solvents based on nitrogenous or sulphurous ligands, or by the selective back-extraction of An(III), using a hydrophilic polyamino-carboxylic complexing agent in buffered conditions. For the first step, the DIAMEX process has been extensively studied at the CEA Marcoule as well as within European collaborative projects of the various successive EURATOM Programmes. For the second step, the tridentate nitrogenous extractants Bis-Triazinyl-Pyridines have supplanted the formerly studied synergistic mixtures based on extractents that are similar to TPTZ or CYANEX 301, because of their ability to extract An(III) from acidic media. However, their chemical instability has forced European researchers to modify and strengthen their structure. A new ligand has been developed, $CyMe_4$-BTBP, which was successfully utilised on a highly active test with an "An(III)+Ln(III)" feed at the ITU. Applications of the nitrogenous extractants have been discontinued by the CEA, who have developed an original but robust single-step process, named DIAMEX-SANEX/HDEHP, which carries out the An(III)/Ln(III) partition directly from PUREX raffinates. It combines two extracting agents, operating in different acidity zones. However, this process generates a large amount of effluents and improvements to separate the extractants are in progress to simplify this process.

*Diglycolamide (DGA) extractant studies*

- Japanese studies

Sasaki et al. have developed a new extractant for Am and Cm separation, N,N,N',N'-tetraoctyldiglycolamide (=N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide, TODGA) [14,15], based on a preceding study [16]. TODGA is one of the diamides, fully soluble in n-dodecane, and is tridentate. It gives very high distribution ratios (D) at relatively high nitric acid concentrations (over 1 mol/L) and low distribution ratios at low nitric acid concentrations for Am, Cm and rare earth elements (RE). The generalised structural formula of DGA compounds with alkyl radical groups is shown in Figure 2.48. These compounds can be easily synthesised by diglycolic anhydride and dialkylamine [15,16].

**Figure 2.48. Structural formula of DGA compounds**



Distribution ratios of Sr, one of the most important fission products, are rather high at higher nitric acid concentrations [15,17,18] and, therefore, the nitric acid concentration of the feed solution and scrub solution in the extraction process should be properly selected to achieve the required separation.

Investigation of the radiolytic stability of TODGA showed that the degradation rate of TODGA by gamma-ray irradiation was a little faster than that of the malonamide, but within an acceptable region for practical use in the treatment of HLW [19]. The main degradation products of TODGA irradiated in the presence of nitric acid are N,N-dioctyldiglycolamic acid (=N,N-dioctyl-3-oxapentane-1,5-amic acid, DODGAA) and N,N-dioctylamine (DOA). Since DODGAA is an acidic extractant which gives high distribution ratios at low nitric acid concentrations, back-extraction of Am by diluted nitric acid becomes difficult; this is one of common drawbacks of neutral extractants. However, for TODGA solvent that has been degraded by 400 kGy gamma-irradiation, the DODGAA concentration was still low enough so that the Am extraction coefficient remained lower than 1 at 0.1 mol/L nitric acid, and essentially all of the Am was successfully back-extracted. Therefore, the degradation of TODGA was considered to be tolerable in practical use [20,21].

Extraction capacity, which is the maximum concentration of the extracted element in the solvent without forming a third phase, (of 0.1 mol/L TODGA in n-dodecane diluent) was only about 0.006 mol/L for Nd [22]. When the Nd concentration in the organic phase increased over that level, a third phase was formed. Further studies revealed that the extraction capacity can be increased by adding dialkylamide such as N,N-dihexyloctanamide (DHOA) to the TODGA-dodecane solution [23] or by lengthening the alkyl chain in the DGA molecule. It was found that N,N,N',N-tetradodecyldiglycolamide (TDdDGA, n=12 in Figure 2.48) can extract Nd at the maximum concentration, i.e. one-third of the extractant concentration, without third phase formation [24]. Even when the amount of Nd in the system is increased, the Nd concentration in the organic phase does not exceed the extraction capacity and there is no formation of a third phase becausethe excess amount of Nd remains in the aqueous phase. Modolo et al. use TBP and/or 1-octanol in their studies on separation processes development with TODGA [25,26] to prevent third phase formation.

In JAEA, a counter-current continuous extraction test with 0.1 mol/L TDdDGA in n-dodecane was carried out using a small-scale mixer-settler battery and simulated solution of HLLW containing Am. The flowsheet was based on conditions determined by process simulation calculations, which were based on the results of batch extractions [27,28]. It was reported that the solvent of TODGA with DHOA has two drawbacks: one is the slow rate of the phase separation, and the other is that it gives relatively high distribution ratios of nitric acid, which causes the accumulation of Am, Cm and rare earths (RE) in the stripping step. In the continuous extraction test with TDdDGA, very clear phase separation was observed, without any crud formation during the operation, and quantitative recovery of Nd and Am was obtained. Recovery of Am was more than

99.96%. Important fission products in DGA extraction (Sr, Zr, Pd) were separated from Am and RE by addition of hydroxylethylethylenediaminetriacetic acid (HEDTA) and hydrogen peroxide and by proper control of the nitric acid concentration; however, the process conditions still require further optimisation [27].

In the TDdDGA extraction process, some of the lanthanides are separated from Am and Cm if proper conditions are selected for the extraction-scrub section, and stripping section with diluted nitric acid. Process simulations were perfomed using the PARC-MA code, developed by JAEA, to find optimum conditions. These simulations showed that about one-third of the lanthanides can be separated from Am and Cm in the process while using only nitric acid within two units of 16-stage mixer-settlers [29]. Calculations performed using PARC-MA also revealed that the TDdDGA process can accept much higher concentration of RE in the feed solution. The high extraction capacity of TDdDGA makes this process possible.

Separation performance for actinides, relative to fission products, in the optimised process should still be clarified by continuous counter-current extraction tests. The issues to be further examined would be the behaviour of Np, Pu, U in continuous extraction, and a process test with real HLLW in a laboratory scale solvent washing facility for treatment of the used solvent.

- Russian studies: influences of diluent on DGA extractions
  - Actinides and lanthanides extraction by diglycolic acid diamides in new polar fluorinated diluents [30]

As mentioned above, one of the most well known and studied extractants for co-recovery of actinides and lanthanides is N,N,N',N'-tetraoctyl diglycolamide (TODGA). TODGA contains three oxygen atoms and acts as a tridentate ligand. It is well-soluble in aliphatic n-dodecane and shows very high distribution ratios for extraction of An(III) and An(IV) from concentrated nitric acid into n-dodecane. Many studies on TODGA extraction chemistry have been reported and several processes have been developed and tested. Most of the studies on the metal extraction by TODGA have been performed in dodecane. The extraction of Am and Eu by TODGA from nitric acid into diluents with different dielectric constants were studied at the Khlopin Radium Institute in Saint Petersburg.

1,2-Dichloroethane, 1-octanol, ethyl acetate, chloroform, diethylether, benzene, toluene, tetrachloromethane, n-dodecane, n-hexane and nitrobenzene were tested as diluents. The distribution ratio values (D) were found to increase with dielectric constant values of the diluents. The highest distribution ratios were observed for nitrobenzene and 1-octanol. The low D values for chlorinated (1,2-dichloroethane) and aromatic (toluene) diluents were attributed to their interaction with the donor oxygen atoms of diglycolamide leading to decrease of free diamide concentration.

The problem of extraction a dependence on dielectric constant values is widely discussed. Indeed, diluents with high dielectric constants, with the exception of chlorinated and aromatic diluents, provide high values of distribution ratios. At the same time, the order of distribution ratios and the order of dielectric constants for various diluents are different and independent and the correlation could exist only for diluents of the same nature: only aromatic or only aliphatic.

In previous work, onextraction of metals by diamides of dipicolinic acid, it was found that using polar-fluorinated diluents instead of chloroform or 1,2-dichloroethane, leads to increasing metal distribution ratios and increasing capacity of the extractant.

From these studies, advantages of fluorinated diluents were found, as follows:

- high chemical and radiolytic stability;
- high density, non-flammable;

- high solvate solubility;
- high extraction ability.

The main goal of the recent work summarised here, was to study americium and lanthanides extraction with TODGA in new polar-fluorinated diluents (Tables 2.18 and 2.19), and find the dependence of diamide extraction ability on diluent type. Such an investigation is important for (1) thedetermination of the correlation between diluent structures and solvent properties, (2) and further quantitative description of diluent effects on extraction chemistry.

The extraction of metals from nitric acid solution to the organic phase by neutral ligands is usually accompanied by extraction of nitric acid. Being a part of the extraction system, all diluents can possess extraction capability. Most diluents used for neutral ligands extract nitric acid by formation of hydrogen bonds between acidic protons and oxygen groups of the diluent. The extraction capability when using different types of diluents differs significantly. For instance, the distribution ratios of nitric acid in the case of tributyl phosphate, used as a modifier in the TRUEX solvent, are many times higher than in the case of n-dodecane. The degree of extraction capability of a solvent towards nitric acid is one of the most important technological characteristics and sometimes it depends on the choice of diluent.

The data on extraction of nitric acid by new polar fluorinated diluents are presented in Figure 2.49a. The extraction capabilities of F-3, DDFHME and DDFHA are very close to each other. The diluent, Formal-2, extracts nitric acid much less. At the same time (Figure 2.49b), the extraction of $HNO_3$ by solvents containing new diluents differs significantly. The order of solvents with respect to nitric acid extraction is F-3 > DDFHME > DDFHA > Formal-2 which coincides with the order for pure diluents. During extraction experiments, third phase formation was noted for 0.1 mol/L TODGA in Formal-2 at an initial nitric acid concentration of more than 2 mol/L, and for 0.1 mol/L TODGA in DDHFA at a nitric acid concentration greater than 5 mol/L.

**Table 2.18. Structures of polar fluorinated diluents used**

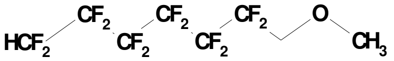
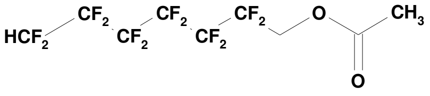
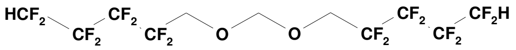
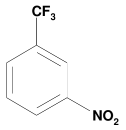
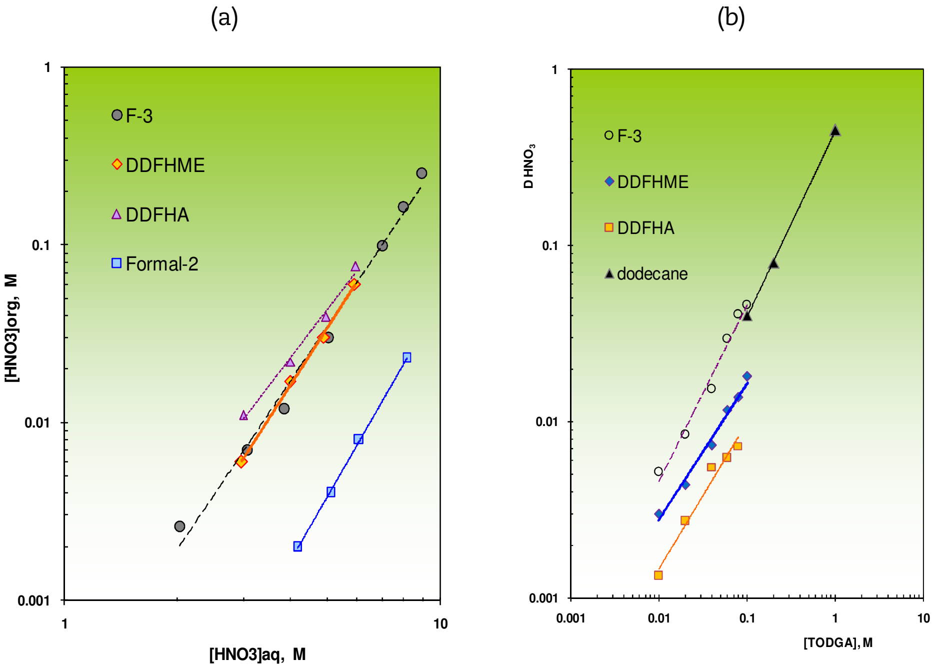
| Structure | Name |
|---|---|
|  | DDFHME |
|  | DDFHA |
|  | Formal-2 |
|  | F-3 |

**Table 2.19. The common physical properties of the studied diluents**

| Diluent | $T_{bp}$, °C | $d_{20,3°C}$, g/cm$^3$ | $\eta_{20}$, mPa·s | $n_D^{20}$ | ε |
|---|---|---|---|---|---|
| DDFHME | 159-161 | 1.651 | 4.1 | 1.314 | 9.73 |
| DDFHA | 184-186 | 1.626 | 6.4 | 1.327 | 6.31 |
| Formal-2 | 112-115 | 1.673 | 13.4 | 1.325 | 7.17 |
| F-3 | 201-205 | 1.436 | 3.02 | 1.472 | 22.3 |
| n-dodecane | 215-217 | 0.75 | 9.0 | 1.421 | 2.0 |

**Figure 2.49. Extraction of nitric acid with (a) polar fluorinated diluents; (b) 0.1 mol/L TODGA in polar fluorinated diluents**



- Extraction of americium and europium

The extraction of americium and europium from nitric acid with TODGA solutions in new diluents was studied. To compare the effect of new diluentswith other traditional diluents on TODGA extraction capability solutions of 0.1 mol/L TODGA in various diluents were tested. This concentration of diamide in solvent is consistent with previous studies devoted to TODGA extraction. It was found that the usage of polar fluorinated diluents provides very high extraction properties for neutral ligands. Metal distribution ratios were > 100 and it was difficult to evaluate and compare the actual extractabilities ofindividual metals. Thus, the concentration of TODGA in subsequent experiments was reduced to 0.01 mol/L.

The data on Am and Eu extraction from nitric acid with 0.01 mol/L TODGA in various diluents are presented in Figure 2.50a. In the case of Formal-2 and DDFHA, the extraction capability of the solvents tends to increase with increasing nitric acid concentration. While using F-3 and DDFHME, there is a maximum of extraction capability at ~ 2-3 mol/L nitric acid and the distribution ratios are >1, even for a solution of 0.5 mol/L nitric acid. The presence of the maximum on the extraction curves could be explained by high extraction capability of solventfor nitric acid. Systems that used F-3 and DDFHME both extracted $HNO_3$ better than other studied diluents (Figure 2.50b). At nitric acid concentrations over 3 mol/L, americium and europium distribution ratios start to decrease due the increasing nitric acid extraction.

All studied solvents effectively extract both Am and Eu from 3 mol/L nitric acid solutionsfrom the fission product elements typically in HLW and europium is extracted many times greater than for americium. The selective extraction of europium is a characteristic feature of TODGA. The usage of polar fluorinated diluents instead of n-dodecane increases the extraction capability of TODGA for Am and Eu but does not change the selectivity of extraction.

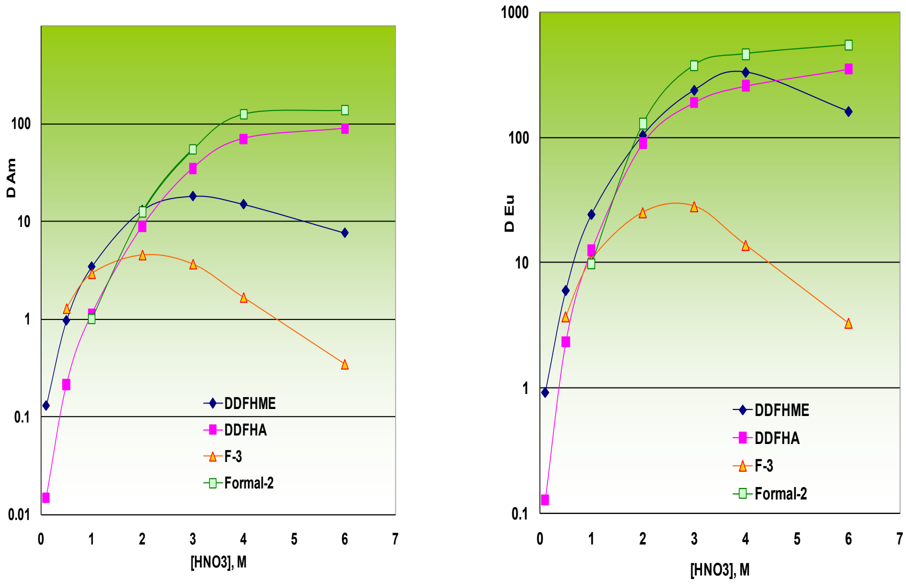
The dependencies of Am and Eu extraction from 1 mol/L $HNO_3$ on the TODGA concentration in diluent are presented in Figure 2.51. The solvation numbers (SN) of americium and europium determined by slope analysis are 2.9 ± 0.003 (DDFHME), 2.7 ± 0.068 (DDFHA), 2.7± 0.022 (Formal-2), 1.9± 0.002 (F-3) and 3.6 ± 0.004 (n-dodecane) for americium compared to 3.4 ± 0.065 (DDFHME), 2.8 ± 0.13 (DDFHA), 2.9 ± 0.018 (Formal-2), 2.6 ± 0.032 (F-3) and 3.7 ± 0.004 (n-dodecane) for europium.

The solvation numbers for other diluents in contrast to F-3 and n-dodecane, are close to 3. The solvation numbers for Am are slightly smaller than those for Eu. The complex formation reaction between TODGA and trivalent metal in various diluents can be described by the following Equation 1:

$$M^{3+} + 3TODGA + 3NO_3^- \leftrightarrow M(TODGA)_3(NO_3)_3 \qquad (1)$$

To find the correlation between extraction capability and diluent physical properties the distribution ratios of Eu were compared (for extraction from 3 mol/L $HNO_3$ with 0.1 mol/L TODGA in diluent) with density, viscosity, refractive index and dielectric constant of the diluents. No exact correlation was found.

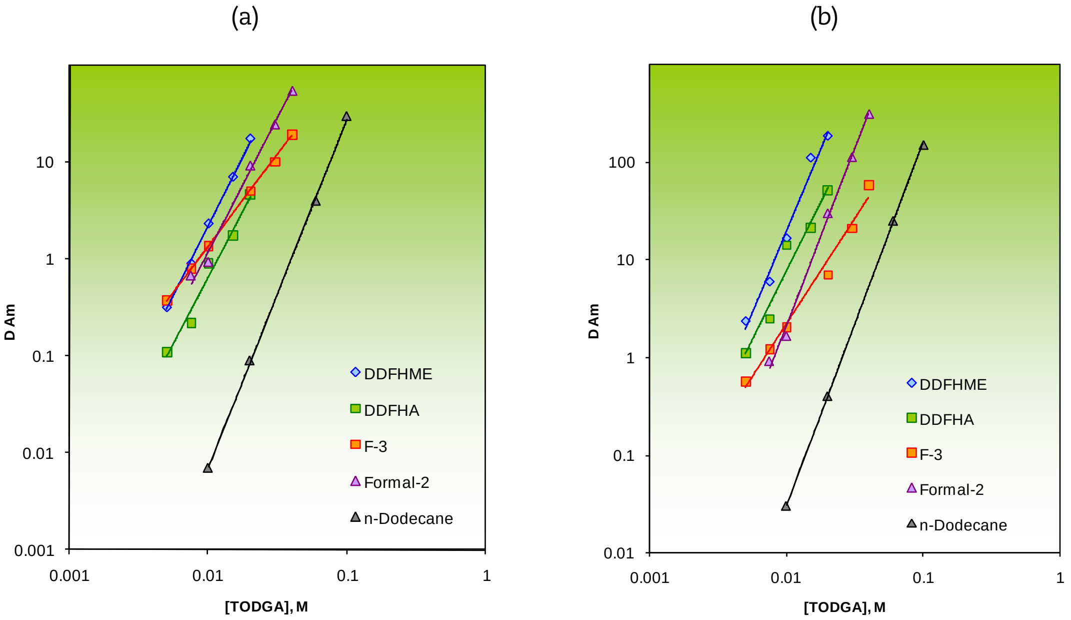
**Figure 2.50. The dependency of (a) Am and (b) Eu distribution ratios values on nitric acid concentration. Solvent – 0.01 mol/L TODGA in diluent**



(a)

(b)

**Figure 2.51. The dependency of (a) Am and (b) Eu distribution ratios on TODGA concentration in diluents with extraction from 1 mol/L $HNO_3$**



- Extraction of lanthanides

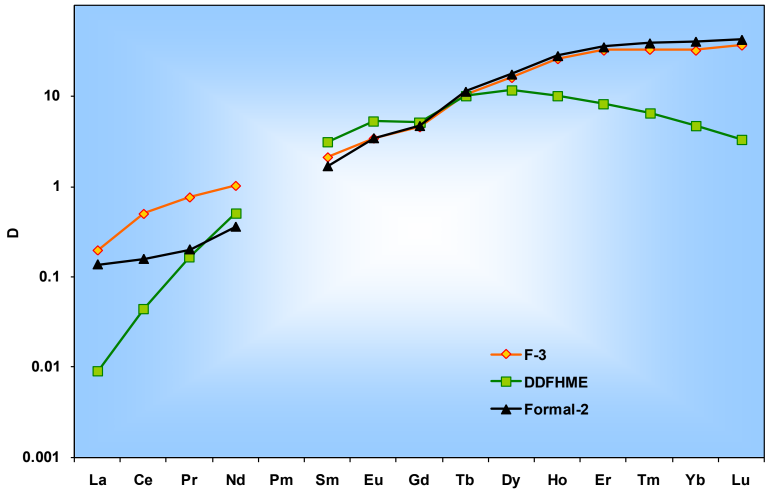
The extraction of all lanthanide metal ions was studied. The data on lanthanide extraction dependence on nitric acid concentration with TODGA using the studied diluents are presented in Figure 2.52. In the case of solvents with F-3 and Formal-2, the lanthanide distribution ratios increase with increasing atomic number. The character of extraction is constant for all studied concentrations of nitric acid. There is a break point for Gd that is common for lanthanide extraction: the distribution ratios increase from La to Eu and then from Gd to Lu. The same break point could be seen for TODGA solution in DDFHME. In the case of DDFHME the extraction ability towards heavy lanthanides decreases from Dy to Lu.

The solvation numbers for other diluents in contrast to F-3 and n-dodecane, are close to 3. The solvation numbers for Am are slightly smaller than those for Eu. The complex formation reaction between TODGA and trivalent metal in various diluents can be described by the following Equation 1:

$$M_3^+ + 3TODGA + 3NO_3^- \rightarrow M(TODGA)_3(NO_3)_3 \qquad (1)$$

To find the correlation between extraction capability and diluent physical properties the distribution ratios of Eu were compared (for extraction from 3 mol/L $HNO_3$ with 0.1 mol/L TODGA in diluent) with density, viscosity, refractive index and dielectric constant of the diluents. No exact correlation was found.

**Figure 2.52. Extraction of lanthanide ions from 1 mol/L HNO3 into solutions of 0.01 mol/L TODGA in diluents: F-3, DDFHME and Formal-2**



- US studies: Minor actinide/lanthanide separation using the Actinide-Lanthanide Separation (ALSEP) Concept

The United States Department of Energy (DOE) –Nuclear Energy (NE) Fuel Cycle Technology (FCT) programme is also developing a hybrid solvent system for the extraction and separation of minor actinide elements from the lanthanide elements in a single solvent extraction cycle [31]. This Actinide-Lanthanide Separation (ALSEP) concept utilises an extractant consisting of either N,N,N’,N’-tetraoctyldiglycolamide (TODGA) or N,N,N’,N’-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) combined with (mono-2-ethylhexyl ester [2-ethylhexylphosphonic acid] (HEH[EHP]-Figure 2.53) for the co-extraction of the trivalent actinides and lanthanides from the raffinate stream resulting from a U/Pu separation process such as the Co-decontamination process. Once extracted, the solvent is scrubbed first with nitric acid, then with citrate to remove co-extracted Mo. Next, the trivalent actinides are selectively stripped from the solvent with a citrate buffered diethylenetriaminepentaacetic acid (DTPA) solution at pH 2.5 to 4. Finally, the lanthanides are stripped from the solvent using a solution of tetraethyldiglycolamide (TEDGA)/nitric acid and co-extracted zirconium is removed with an oxalic acid contact.

To date, proof-of-principle experiments on the ALSEP concept have been complete using simulated feed streams spiked with radiotracers [31]. These tests have demonstrated separation factors of minor actinides from the lanthanides ranging from 20 to 40. Research and development of the ALSEP concept is continuing with the near-term goal of laboratory-scale flowsheet testing in centrifugal contactor or mixer-settler equipment using radiotracer spiked simulant followed by similar testing with actual dissolved spent nuclear fuel.

*Russian studies of other diamides*

- Extraction of lanthanides with diamides of dipicolinic acid (DPA) from nitric acid solutions [32]

The chlorinated cobalt dicarbollide (CCD) anion is an effective phase-transfer reagent. Strongly acidic and hydrophobic, it has a significant synergistic effect in the extraction of polyvalent cations by other chelating or neutral extractants, so it can be then applied at much lower concentrations. Three extraction mixtures of cobalt dicarbollide with diamides of dipicolinic acid (DPA) in a polar diluent FS-13 were investigated for their extractability toward lanthanides and americium (Table 2.20, Figure 2.54). The N,N,N’,N’-tetrabutyl- dipicolinic acid (TBDPA) and three isomers (ortho, meta, para) of N,N-diethyl-N’,N’-ditolyl diamides were included in the study. The effect of position of the methyl group on the tolyl ring of the EtTDPA was investigated. Data on the extraction ability show that the ortho-position is the most favorable and the ethyl-tolyl isomer Et(o)TDPA has the most promising properties because it has the best balanced selectivity between the heavy and light lanthanides. Current studies involve other actinides (U, Th, Pu), fission products (Zr, Mo), and hydrolytic and radiolytic stability of extractants and extracted complexes. Future studies will be focused on structures of these complexes and the speciation of metals in the organic polar phase.

**Figure 2.53. Chemical Structures of TODGA, T2EHDGA and HEH[EHP]**

HEH[EHP] TODGA T2EHDGA

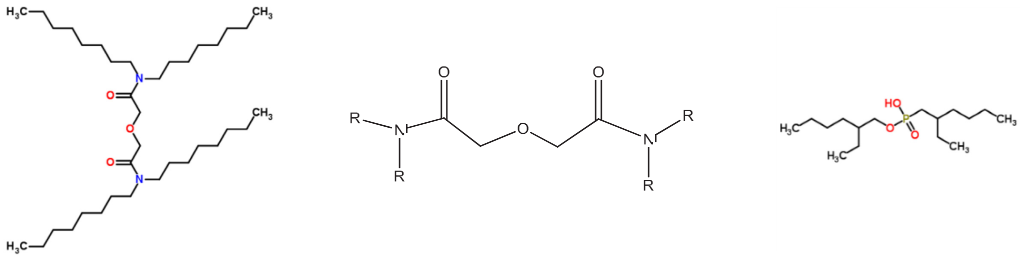


**Figure 2.54. Distribution of Ln and Am as a function of diamide type;**
**Aqueous phase: 3 mol/L $HNO_3$; solvent: 0.02 mol/L CCD + 0.01 mol/L DPA in FS-13**

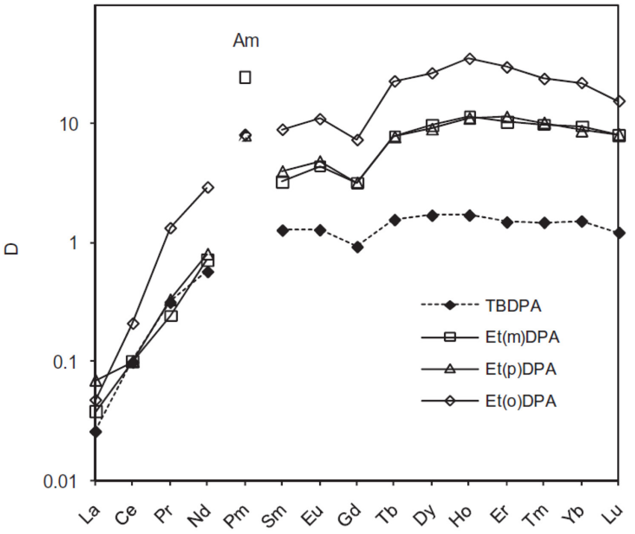


**Table 2.20. Am/Ln separation factors**

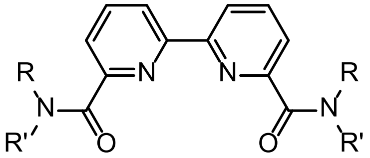
| SF=D(Am)/D(La) | Am/La | Am/Ce | Am/Pm | Am/Nd | Am/Sm | Am/Eu | Am/Gd |
|---|---|---|---|---|---|---|---|
| 1 M $HNO_3$ | | | | | | | |
| TBDPA | >1 000 | 160 | 55 | 23 | 5.6 | 4.8 | 12 |
| Et(o)DPA | 700 | 59 | 18 | 8.1 | 1.8 | 1.6 | 4.4 |
| Et(m)DPA | >1 000 | 190 | 48 | 15 | 1.8 | 1.1 | 5.0 |
| Et(p)DPA | >1 000 | 130 | 33 | 10 | 1.2 | 0.8 | 3.6 |
| 3 M $HNO_3$ | | | | | | | |
| TBDPA | 300 | 80 | 25 | 14 | 6.3 | 6.2 | 8.6 |
| Et(o)DPA | 530 | 120 | 19 | 8.6 | 2.8 | 2.3 | 3.4 |
| Et(m)DPA | 210 | 80 | 33 | 11 | 2.5 | 1.8 | 2.5 |
| Et(p)DPA | 115 | 80 | 24 | 10 | 2.0 | 1.7 | 2.5 |
| 5 M $HNO_3$ | | | | | | | |
| TBDPA | 120 | 44 | 41 | 14 | 2.8 | 1.6 | 1.7 |
| Et(o)DPA | 185 | 93 | 43 | 18 | 2.0 | 1.0 | 1.5 |
| Et(m)DPA | 34 | 27 | 20 | 14 | 2.0 | 0.9 | 0.7 |
| Et(p)DPA | 45 | 29 | 23 | 13 | 1.9 | 0.8 | 0.7 |

- New diamides of 2,2′-dipyridyl-6,6′-dicarboxylic acid for actinide-lanthanide separation [33]

Separation of minor actinides (Am and Cm) from lanthanides is one of the most important and challenging problems due to their chemical similarity. The most powerful agents for separation of trivalent actinides are “soft” donor complexants possessing several nitrogen or sulphur atoms. The combination of hard and soft donors in one structure can lead to effective extraction of actinides and their separation from lanthanides in one stage. The possibility of selective extraction depends on the structure of ligand. For example, phenanthroline-diamides selectively extract Am over lanthanides with a SF of about 10 and terpyridine diamides form complexes only with plutonium.

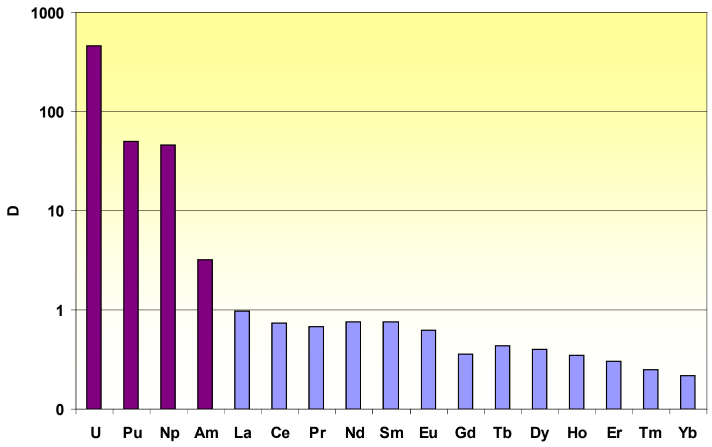
At the Khlopin Radium Institute, the extraction properties of dipicolinic acid and dipyridyl-dicarboxylic acid have been studied. Diamides of 2,2-dipyridyl-6,6-dicarboxylic acid (Figure 2.55) were studied as potential extractants for the separation of minor trivalent actinides from lanthanides (Figure 2.56). High separation factors (>10) were achieved for extraction from 1-4 mol/L nitric acid by diamides of 2,2 -dipyridyl-6,6-dicarboxylic acid solutions in polar fluorinated diluents. Complex composition was calculated by the slope analysis method. Generally, mono-solvates are the most stable adducts, particularly for heavy lanthanides.

**Figure 2.55. Structures of heterocyclic amides**



diamides of 2,2'-dipyridyl-
6,6'-dicarboxilic acid

**Figure 2.56. An-Ln extraction using 0.1 mol/L dyp-7 in F-3 from 3 mol/L $HNO_3$**



*US Studies of Minor Actinide Separation using TRUEX/TALSPEAK and TRUEX/Advanced TALSPEAK*

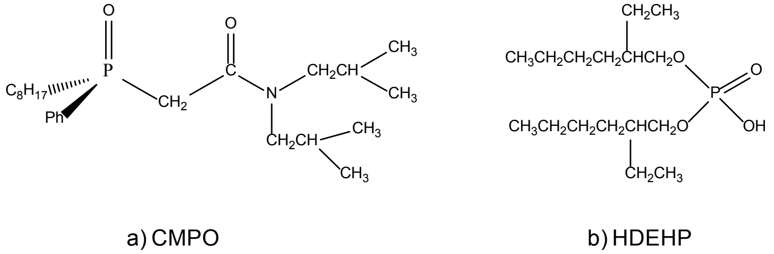
DOE-NE FCT Programme is developing solvent extraction processes for the separation of the trivalent actinides (i.e., Am and Cm) from the fission product lanthanides, and all other fission products in the high-level waste stream from the Uranium Extraction co-decontamination process (UREX+ Co-decon). This involves two distinct process steps; first, the trivalent actinides and lanthanides are co-extracted from the high acidity and non-lanthanide fission products in the UREX+ Co-decon raffinate using the Transuranic Extraction (TRUEX) process. Second, the combined actinide/lanthanide product from the TRUEX process is treated to separate the lanthanides from the actinides using the Trivalent Actinide-Lanthanide Separations by Phosphorus reagent Extraction from Aqueous "K"omplexes (TALSPEAK) process or advanced versions. The 2-step tandem approach of TRUEX/TALSPEAK for recovering the trivalent actinides has been demonstrated with multi-kilogram amounts of spent nuclear fuel.

- The TRUEX process

The TRUEX process was developed at Argonne National Laboratory in the 1980s [34]. This process uses octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), shown in Figure 2.57 to extract the trivalent lanthanides and actinides from nitric acid solution. Tri-butyl phosphate (TBP) is added as a solvent modifier to prevent third phase formation. The CMPO and TBP are dissolved in an aliphatic diluent. A typical TRUEX solvent consists of 0.2 mol/L CMPO plus 1.4 mol/L TBP in *n*-dodecane. Figure 2.58 shows the dependence of the Am(III) distribution ratios on the $HNO_3$ concentration. The maximum $D_{Am}$ value is attained at approximately 2 mol/L $HNO_3$. The trivalent lanthanide elements behave in a similar manner. This extraction behaviour allows the actinides and lanthanides to be co-extracted from several molar $HNO_3$ (e.g., the raffinate from the UREX+ Co-decon extraction cycle).

Figure 2.59 illustrates schematically the TRUEX solvent extraction flowsheet. The process consists of the following basic steps: (1) co-extraction of the lanthanides and actinides, (2) scrubbing, (3) stripping of the lanthanides and actinides, and (4) solvent washing. Based on modelling of the TRUEX flowsheet using the ANL AMUSE code, >99.9% of the transuranic elements (Np, Pu, Am, and Cm) and the lanthanide elements present in the feed stream are extracted into the organic phase. For all other components, >99.9% report to the TRUEX raffinate stream, with the exception of Y, of which 97% is extracted into the TRUEX solvent. The loaded TRUEX solvent passes into the scrubbing stages where three scrubbing steps are applied: first with $H_2C_2O_4/HNO_3$ to remove extracted fission products, especially Zr, second, with $HNO_3$ to remove any other extracted or entrained impurities, third, with dilute $HNO_3$ to reduce the residual $HNO_3$ concentration in the organic phase. Following scrubbing, the lanthanides and actinides are co-stripped into either low acidity nitric acid, or an aqueous solution consisting of diethylenetriaminepentaacetic acid (DTPA) in a lactate buffer at pH 5. Ninety-seven percent of the Y is also carried into the lanthanide + actinide product stream from TRUEX. Using the DTPA/lactate stripping solution provides a lanthanide + actinide product that can be fed to the direct TALSPEAK process with only minor adjustment in the pH. Alternatively, using the low-acidity nitric acid solution provides the lanthanide + actinide product that can be fed to the reverse TALSPEAK process, in which the lanthanides + actinides are extracted into the TALSPEAK solvent and then partitioned by selectively stripping the actinides with DTPA/lactate stripping solution at pH 2.8-3.3. The reverse TALSPEAK provides a more precise method of controlling pH than the direct TALSPEAK. Finally, the TRUEX solvent will go through a series of alkaline and acidic washes, as needed, to remove degradation products before recycling the solvent to the extraction section. There is some uncertainty regarding the TRUEX solvent washing and recycling, since this has not yet been demonstrated at an industrial scale.

**Figure 2.57. The chemical structures of (a) CMPO and (b) HDEHP**



a) CMPO

b) HDEHP

**Figure 2.58. Americium (III) distribution ratios for extraction by 0.2 mol/L CMPO + 1.4 mol/L TBP in normal paraffin hydrocarbons [36]**

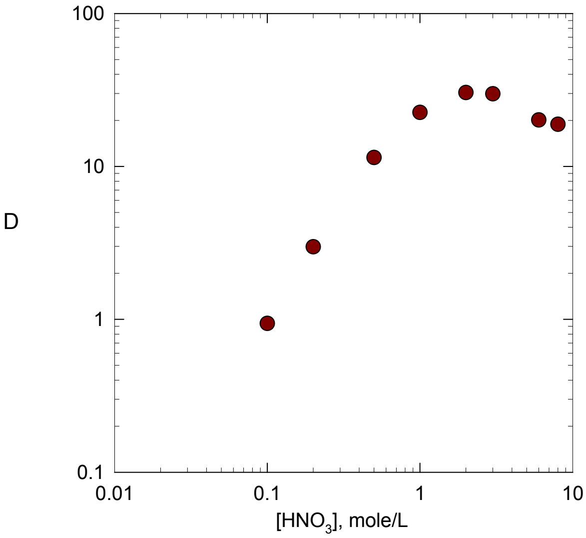
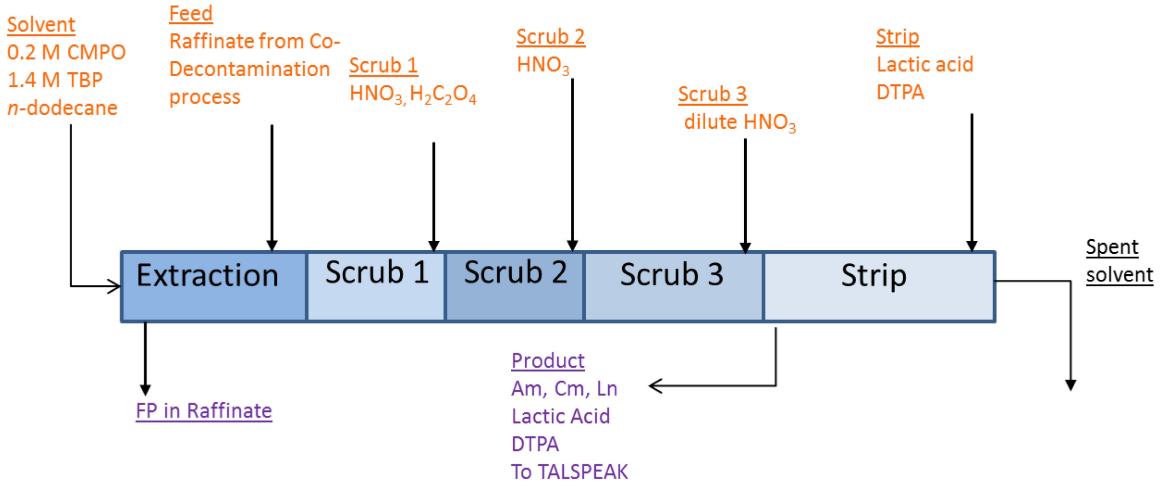


**Figure 2.59. The TRUEX solvent extraction flowsheet**



- The TALSPEAK process

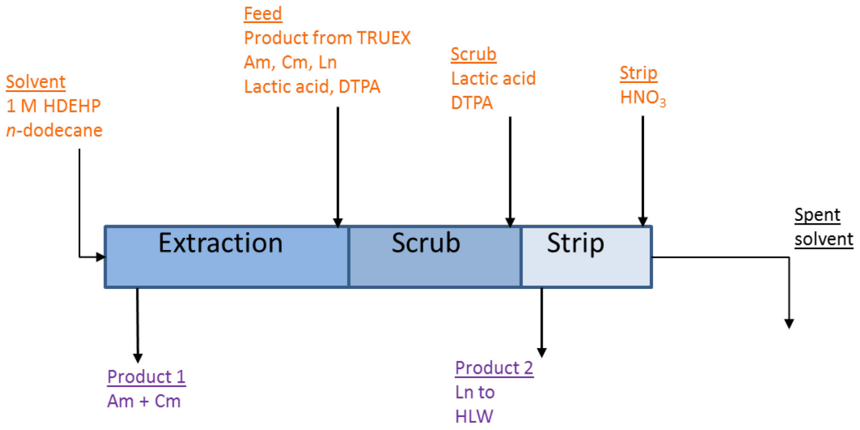
The TALSPEAK process was developed at Oak Ridge National Laboratory (ORNL) in the 1960s [36]. The process is based on the higher affinity of polyaminocarboxylate ligands for trivalent actinides compared to trivalent lanthanides. Addition of DTPA to the aqueous phase results in selective complexation of the actinides, keeping them in the aqueous phase while the lanthanides are extracted into the organic phase with bis-(2-ethylhexyl) phosphoric acid (HDEHP). The configuration of HDEHP is illustrated in Figure 2.57b. The aqueous phase is buffered with lactic acid, primarily to control the pH, but also to improve the extraction kinetics. [37] The TALSPEAK process may be operated in (1) the direct mode, where the DTPA/lactic is added to the feed solution and the pH is adjusted by addition of ammonium ion to the optimum value for separation of Nd and Am, or (2) the reverse mode, where both lanthanides and actinides are extracted into the HDEHP solvent from dilute nitric acid and then the actinides are selectively partitioned by stripping with DTPA/ammonium lactate at the optimum pH (2.8-3.2).

Figure 2.60 illustrates the direct TALSPEAK solvent extraction flowsheet. The process utilises a solvent consisting of 1.0 mol/L HDEHP in n-dodecane and consists of the following basic steps: (1) lanthanide extraction, (2) scrubbing, (3) lanthanide stripping, and (4) solvent clean-up. Before entering the TALSPEAK process, the product from the TRUEX process is adjusted to pH 3.1 by addition of ammonium ion. Based modelling of the TALSPEAK flowsheet using the AMUSE code, >99.9% of the transuranic elements (primarily Am, and Cm; but also trace Np and Pu) remain within the aqueous minor actinide product stream while >99.9% of the lanthanides are extracted into the solvent. The loaded TALSPEAK solvent is scrubbed with DTPA + lactate at pH 3.6. Following scrubbing, >99.9% of the lanthanides (and Y) are stripped into HNO3 and then combined with the rest of the high-level waste.

The TRUEX and TALSPEAK processes have been demonstrated in laboratory scale equipment using actual spent fuel through testing at ANL in 2-cm centrifugal contactors and ORNL using lab-scale mixer-settlers. The ANL tests utilised dissolved irradiated fuel consisting of ATM-105 and H.B. Robinson fuel. The ATM-105 fuel (Cooper Nuclear Power Plant, Nebraska) had an average burn-up of 33 GWd/MTIHM. The Robinson fuel had an average burn-up of 76 GWd/MTU. The process tested included a UREX process for the separation of U and Tc followed by TRUEX and direct TALSPEAK testing. Results from these tests indicated >99.99% recovery of Pu, Np, and Cm and 99.97% recovery of Am [38].

The ORNL tests utilised 3 kg of spent fuel that had been irradiated in the Dresden-1 BWR to a burn-up of ~25 GWd/MT of heavy metal and decayed for 32 years following discharge in 1975. The process tested included a UREX Co-decontamination process, followed by TRUEX and reverse TALSPEAK testing. An overall recovery of 99.8% was obtained for the TRU (approx. 99% for Am, 99.3% for Np, and 99.996% for Pu).

**Figure 2.60. The TALSPEAK solvent extraction flowsheet**

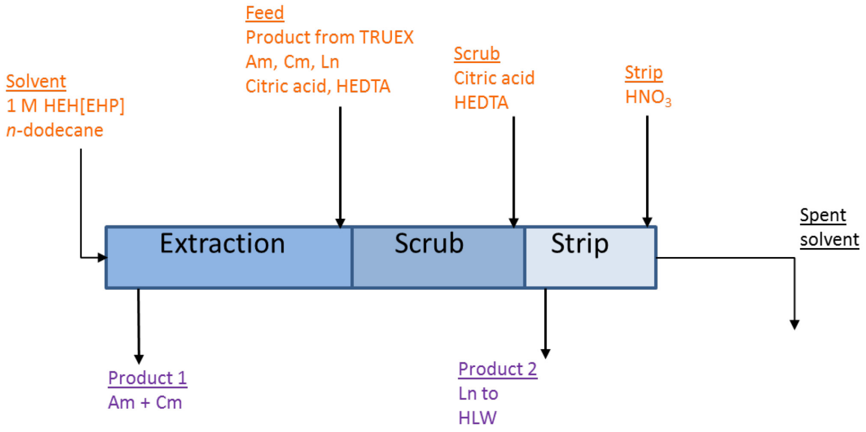


- The Advanced TALSPEAK process

In order to reduce the dependence of the process performance on the aqueous solution pH, and thereby obtain more predictable extraction behaviour, and more rapid extraction kinetics, the Advanced TALSPEAK process is currently being developed by the US DOE-NE FCT Programme. For the Advanced TALSPEAK process, some adjustments are made to the TRUEX process: the DTPA/lactate stripping solution is replaced with a (HEDTA)/citrate stripping solution which is compatible with the Advanced TALPSEAK process.

Figure 2.61 illustrates the Advanced TALSPEAK solvent extraction flowsheet. The flowsheet is quite similar to the TALSPEAK flowsheet, except the extractant formulation (HEH[EHP] instead of HDEHP) and (2) the aqueous feed composition is,, (HEDTA)/citrate instead of DTPA/lactate [38].

**Figure 2.61. The Advanced TALSPEAK solvent extraction flowsheet**



### *TRU recovery in grouped actinide extraction (GANEX) processes*

- Background

Grouped ActiNide Extraction (GANEX) involving the co-processing of all the transuranic actinides (Np – Cm) is a relatively new concept currently under development in Europe [39] aimed in particular for future scenarios with homogeneous recycling of actinides in sustainable (Gen IV) fuel cycles [40]. It should be recognised that homogeneous recycling of actinides requires shielded facilities for product conversion and recycle fuel fabrication, and thereby, is a much more expensive method in comparison to heterogeneous recycling, in which only the minor actinides, Am and Cm, which are present in spent fuel in low concentrations, require shielded target fabrication

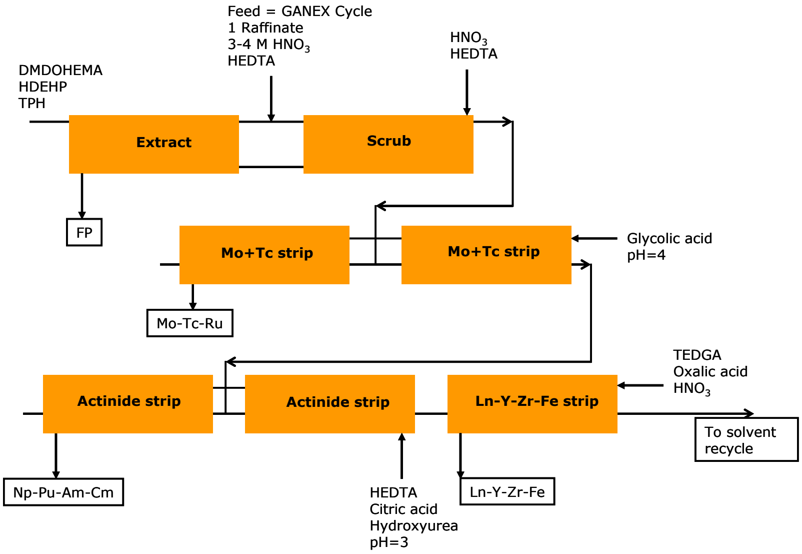
The GANEX process will most probably consist of a first separation cycle to either fully or partially remove U and to reduce the solvent loading capacity required and volumes of liquor to be processed (see previous section in Chapter 1). Miguirditchian and co-workers [41] have shown in a laboratory scale test using mixer-settlers that >99.999% of the U can be recovered using a monoamide, N,N-di-2-(ethylhexyl)isobutyramide (DEHIBA) in HPT hydrogen tetrapropylene),, as a solvent, leaving the TRU elements in the raffinate with the fission products. An alternative approach, similar to U-Pu co-processing flowsheets, would be to allow some small portions of the U to be routed with the TRU elements in the first cycle raffinate (typically <10 wt.%), thus enhancing the perceived proliferation resistance of the flowsheet. Thus, the GANEX 2nd (TRU) Cycle solvent ideally needs to be able to extract all actinides in oxidation states III, IV, V and VI; it is this second cycle that is the key innovation of the GANEX concept. Two parallel programmes for GANEX process development are ongoing in Europe:

- those developed by CEA, France;
- those developed under the European Framework Programme (the ACSEPT project).

- CEA-GANEX process

CEA researchers have proposed the use of a N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide (DMDOHEMA) and bis(2-ethylhexyl)phosphoric acid (HDEHP) based co-solvent, utilising the extractive capacities of the malonamide in strongly acidic and HDEHP in weakly acidic solutions [42,43]. Actinides, lanthanides and a few other fission products (e.g. Mo, Zr, Y) are extracted by DMDOHEMA from the feed solution and the actinides are then selectively stripped at high pH using a complexant/buffer solution,(HEDTA) and citric acid, for Am-Cm stripping and hydroxyurea for Np-Pu reductive stripping. The GANEX 2nd cycle flowsheet tested on spent fuel solution at CEA laboratories is illustrated schematically in Figure 2.62. This test recovered >99.9% of the actinides but suffered from some lanthanide contamination of the actinide product which it is believed can be dealt with by minor optimisations of the acidity and flows ratios across the backwash contactor [44]. Further refinements are in progress.

**Figure 2.62. GANEX process under development at CEA (France)**



- EURO-GANEX process

GANEX process development within the European Framework ACSEPT project [45] was focused on finding suitable mixtures of extractants, phase modifiers and diluents that enable co-extraction of TRU actinides. Two emerging systems show potential:

- solvents based around the CyMe$_4$BTBP (6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl) [2,2′]bipyridine) ligand [46];
- solvents based on diglycolamide ligands, primarily TODGA (N,N,N’,N’-tetraoctyldiglycolamide) [47,48].

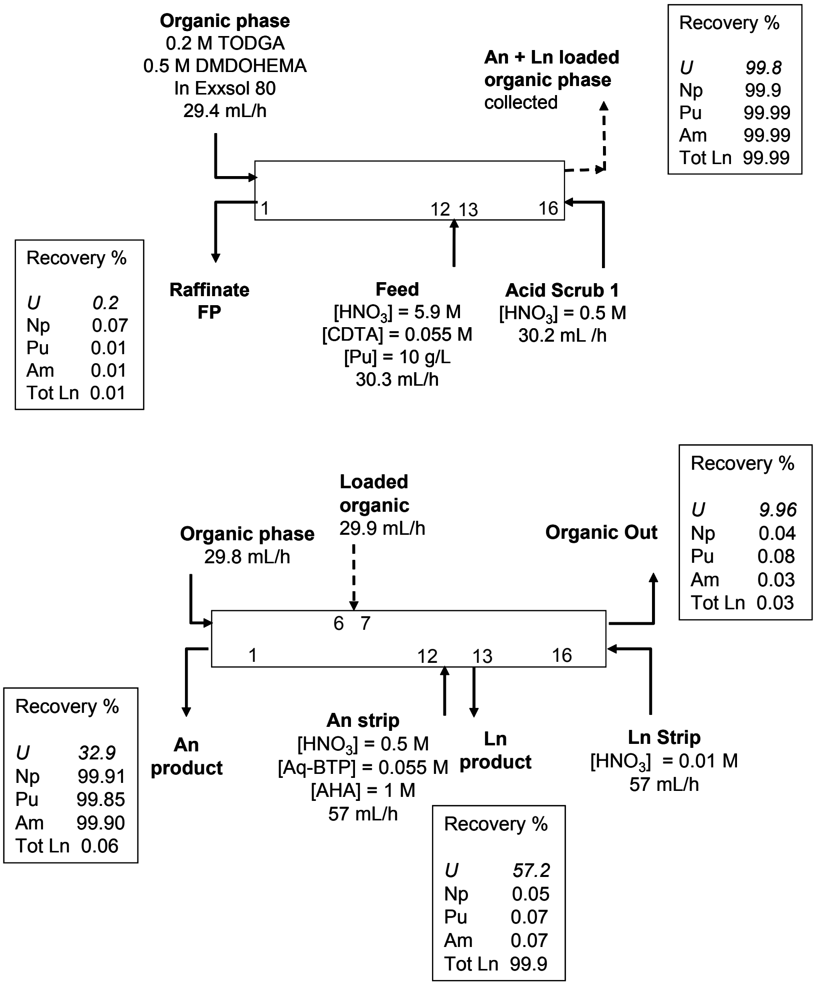
The process being developed by the University of Chalmers (Sweden) uses a combination of CyMe$_4$BTBP and tributyl phosphate (TBP) to selectively co-extract actinides in oxidation states III-VI. Good results have been obtained from batch distribution tests although from the distribution data, some fission product interferences are likely [49]. The radiolytic stability has been tested [50] and the replacement of TBP with a “CHON” ligand appears feasible. Key to this system is the adoption of cyclohexanone as the diluent since cyclohexanone has been shown to substantially enhance the extraction kinetics of the BTBP ligand. However, there are problems with the stability of cyclohexanone in nitric acid and also, indications are that this solvent system has some problems dealing with macro-quantities of plutonium. This process is still at an early stage of development and has not been taken forward to a flowsheet test yet.

An alternative approach, initially proposed by NNL (United Kingdom), is to co-extract the TRU actinides and trivalent lanthanides using TODGA in a kerosene diluent, this being known to be a highly efficient extractant for trivalent and tetravalent actinides [48,51]. TODGA/TBP mixtures have also been shown to be reasonably good extractants for hexa- and penta-valent actinides under specific conditions [52]. TODGA, however, forms precipitates with macro-quantities of Pu(IV) ions [53]. To avoid precipitation, the malonamide DMDOHEMA (N,N‘-dimethyl-N,N‘-dioctylhexylethoxy-malonamide) was found to be an effective phase modifier and co-extractant [53]. A solvent formulation of 0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA in odourless kerosene diluent has been shown to be suitable for plutonium loadings of 10 – 50 g/L between 6 and 1 mol/L $HNO_3$ [54]. Thus ,this conceptual GANEX 2nd (TRU) cycle flowsheet involves the co-extraction of actinides and lanthanides from the aqueous raffinate of the 1st GANEX cycle.

Co-extraction and fission product scrubbing is followed by recovery of the TRU actinides by selective stripping using a suitable combination of hydrophilic complexing agents to separate the TRU actinides from the lanthanides. A sulphonated and, therefore, hydrophilic version of the BTP ligand has been shown to be an excellent selective complexant for stripping trivalent actinides from an organic phase in the presence of lanthanides [55]. This ligand, coupled with aceto-hydroxamic acid (AHA) [56,57], can then be used to selectively strip Np, Pu, Am and Cm from the solvent phase. Results of the initial surrogate testing of the flowsheet have recently been published [58].

This "EURO-GANEX" process has recently been "hot tested" at the European Joint Research Centre Institute of TransUranium elements (ITU). The spent fuel used was a mixture of some legacy fast reactor nitride and carbide fuels originally from Dounreay. After oxidation, dissolution and uranium separation using the GANEX 1st cycle, the aqueous raffinate was adjusted to give an acidity of 5.9 mol/L $HNO_3$ and plutonium content of 10 g/L. The 0.05 mol/L of trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA) was added to retain, as inextractable elements, problematic fission products, zirconium and palladium [59]. The flowsheet design tested at ITU is illustrated in Figure 2.63. Since there were only 16 centrifugal contactor stages in the ITU hot cell, extract/scrub and backwashing were run as separate experiments (on consecutive days).

**Figure 2.63. EURO-GANEX flowsheet tested with spent fuel**



For the extract-scrub section, Table 2.21 lists the measured concentrations of An and Ln in the different fractions at steady state, and recoveries are shown in Figure 2.63.

**Table 2.21. Results from EURO-GANEX, extraction and scrubbing**

| | 1st cycle GANEX Raffinate (mg/L) | Feed (mg/L) | Raffinate (mg/L) | OrgOut (loaded) (mg/L) |
|---|---|---|---|---|
| Np | 12,9 | 97,3 | 0,03 | 87,8 |
| U | 61,5 | 68,1 | 0,1 | 87,8 |
| Pu | 18108 | 10143 | 0,040 | 10201 |
| Am | 245 | 134 | 0,001 | 142 |
| Total Ln | 657,5 | 371,6 | 0,04 | 395,3 |

Using 12 extraction stages, a near-to-complete separation of all An (and Ln) was achieved. In particular, losses of Np to the raffinate were minimal (less then 0.1 %). With regards to the stripping section, concentration of actinides and lanthanides are listed in Table 2.22 and recoveries in Figure 2.63.

**Table 2.22. Results from 2nd cycle GANEX 2, backextraction**

| | OrgOut (extraction) (mg/L) | Loaded Org Feed (mg/L) | An product (mg/L) | Ln Produc (mg/L) | OrgOut (mg/L) |
|---|---|---|---|---|---|
| Np | 87,8 | 69 | 37 | 0,02 | 0,01 |
| U | 87,8 | 23 | 6 | 10 | 2 |
| Pu | 10200 | 11000 | 5800 | 4 | 4 |
| Am | 142 | 155 | 83 | 0,06 | 0,02 |
| Tot Ln | 395,3 | 193 | 0,06 | 99 | 0,03 |

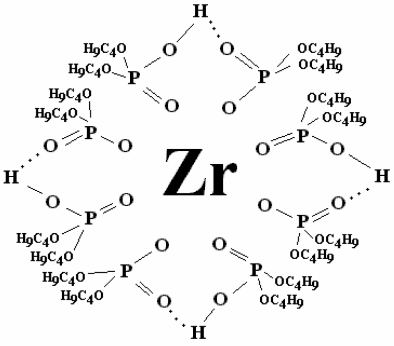
It is evident that the process has been highly successful. An almost complete recovery (99.9%) of Pu, Np and Am has been achieved. Also, the selectivity is excellent with less than 0.1% of the lanthanides in the actinide product. The lanthanides were efficiently back-extracted into the Ln product (recovery > 99.9%), together with less than 0.1% of the actinides. The level of An and Ln impurities in the used solvent is also less than 0.1%. Impurity levels can likely be managed to even lower levels if more stages are added.

In summary, excellent recoveries of TRU actinides were obtained in the flowsheet test (>99.8%) with <0.1% of lanthanides found in the TRU product. The GANEX concept has thus been demonstrated using genuine irradiated fast reactor fuel as feed solution. The Np loss in the first cycle GANEX process was around 3%, which is unexpectedly high, and can probably be managed by flow sheet optimisation. The EURO-GANEX process proved to be both selective and efficient at the high Pu loading involved in reprocessing of fast reactor fuels [60].

*Russian process for HLW reprocessing with zirconium salt of dibutyl phosphoric acid [63]*

Liquid radioactive waste formed as a result of SNF reprocessing by solvent extraction have the most complicated composition, containing several long-lived α-emitting radionuclides (neptunium, americium, curium, trace amounts of plutonium), λ- and β-emitting nuclides with intermediate half-lives (Cs, Sr, Eu and others), precipitate-forming elements and corrosion products (Mo, Zr, Fe, Cr, *etc.*), salt-forming and accompanying elements (Ca, Na *etc.*), as well as decomposition products of organic reagents and solvents used for primary SNF reprocessing. The effective waste treatment requires partitioning of elements into groups and their reliable immobilisation in appropriate matrices with respect to final radioactive waste storage. As each group of radionuclides is characterised by unique chemical behaviours, their processing with a single solvent extraction system is an extremely difficult task. The zirconium salt of dibutylphosphoric acid (ZS of HDBP, Figure 2.64) is an effective extractant for liquid high-level waste (HLW) and medium active level waste (MLW) processing. Zirconium forms adducts with HDBP that are insoluble in water solutions and, among them, the most interesting is the adduct, in which one molecule of zirconium interacts with eight molecules of HDBP.

**Figure 2.64. Structure of zirconium salt of dibutylphosphoric acid (ZS of HDBP)**



The ZS of HDBP allows recovery of transplutonium elements (TPE), residual U, Pu, Np and also Sr, rare earths (RE) and other elements from nitric acid solutions with subsequent separation into individual fractions. The data on extraction of different elements with ZS of HDBP are presented in Figure 2.64. The most promising solvent is the solution of ZS of HDBP (Zr:HDBP = 1:8) in 30% tributylphosphate (TBP), which can be used in processing the complex mixtures found in liquid HLW.

The key goals of HLW processing were as follows:

1. Collection of long-lived radionuclides (TPE together with RE) for subsequent immobilisation and final waste disposal. Long-lived TPE require special management because of their particular hazards in the environment. Since TPE possess high heat generation and neutron emission, it is expedient to dilute the TPE, for example with RE, before inclusion in ceramic matrices.
2. Recovery of beneficial isotopes which could be used in medicine or industry (for example, Sr). This also allows reduction in the volume of radionuclide-containing ceramics for disposal.
3. Isolation of radionuclides, characterised by short life times, which are suitable for direct disposal.
4. Isolation of non-radioactive elements (Fe, Mo and so on) in cement as LLW or ILW.

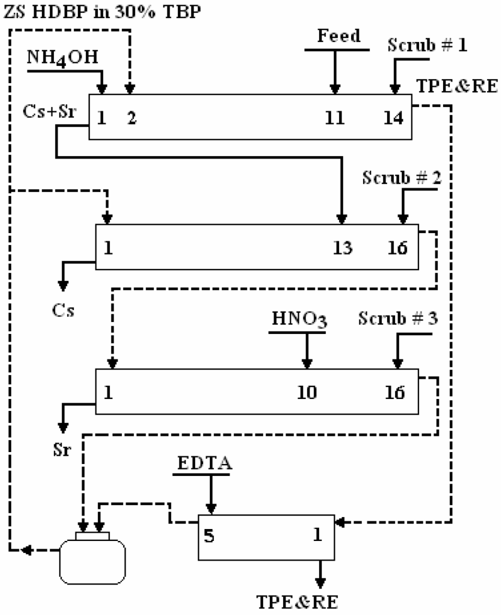
Initially, solutions simulating liquid radioactive waste were used in the investigations that were carried out. The results of experimental testing of the ZS of HDBP for processing of real liquid HLW accumulated at the Khlopin Radium Institute, are presented for the first time here. During the experiment carried out in the hot cells, the ZS of HDBP was, dissolved in 30% TBP with isopar-L as a diluent. The concentration of HDBP was 0.4 mol/L and Zr was 0.022 mol/L.

The reprocessing of liquid HLW was carried out in mixer-settlers with a working volume of 0.1 L. The liquid HLW was a complicated mixture accumulated for a year and they contained TPE (~77 % $^{244}$Cm, the rest being $^{241}$Am and $^{243}$Am), RE, Sr and Cs with total volume activity of 520 MBq/L; the concentration of nitric acid was 2 mol/L, and also the HLW contained residues of the dissolved organic phase and corrosion products of stainless steel. The volume of the HLW treated was 30 L. At the start, the HLW solution was treated with HDBP in ammonium carbonate solution to precipitate Fe and Mo prior to beginning before the solvent extraction process. It should be noted that Fe and Mo precipitation using HDBP did not lead to significant co-precipitation of other radionuclides. The separated precipitate was directed to cementation as an ILW. The HLW extraction processing flowsheet is shown in Figure 2.65 and consisted of four extraction banks. In the first bank of 14 stages, the TPE $\alpha$-nuclides, and RE were extracted and separated from Cs, Sr and other elements.The back-extraction of TPE and Re was realised in the fourth bank of five stages where EDTA was as a complexation and stripping agent; subsequently the aqueous TPE-RE produc was evaporated and then consolidated in a ceramic matrix. The duration of the experiment on the real product was two days. Sampling of effluents was done once every eight hours. Key results are presented in Table 2.23.

**Table 2.23. Compositions of initial feed and product (after 54 hours) solutions from the process test using real HLW**

| Feed/product | $HNO_3$ (mol/L) | TPE (Bq/L) | Cs-137 (Bq/L) | Sr-90 (Bq/L) |
|---|---|---|---|---|
| Initial solution | 2.0 | 2.6E9 | 10E9 | 7.5E9 |
| Cs/Sr raffinate | 0.06 | 1.0E7 | 10E9 | |
| TPE & RE strip | | 6.5E8 | <2E6 | |
| Cs raffinate | 0.45 | | 5.0E9 | 4.2E8 |
| Sr strip | 1.5 | 1.2E5 | 4.0E4 | 1.7E9 |

**Figure 2.65. The process flowsheet used in treating real HLW**



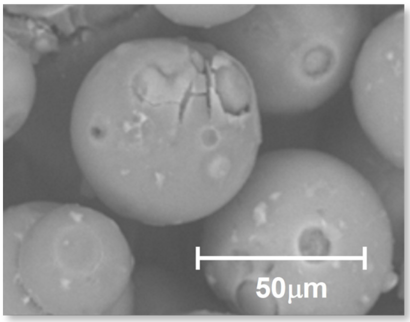
During the HLW processing the decontamination factor of TPE and RE from Cs and Sr was $10^4$, and thedecontamination factor of Sr from TPE and Cs was $10^3$. The results show that the ZS of HDBP can be successfully used in liquid HLW processing for radionuclide separation. Strontium, separated from the HLW, was offered for sale as a medical isotope. Cesium was sorbed on the composite sorbent, FS-2, containing copper potassium ferrocyanide and silica gel, with cesium loading up to a specific activity of the solid phase of ~1011 Bq/g. loaded sorbent was dried and placed into a stainless steel container for disposal. A facility to enable manufacturing of a ceramic matrix waste form (on the basis of zirconium phosphate) for RE and TPE inclusion and subsequent temporary storage, is under development at the present time.

*MA separation process using extraction chromatography developed in Japan*

A separation process for minor actinides (MA) by extraction chromatography has been studied at the Japan Atomic Energy Agency (JAEA) as a part of the NEXT (New Extraction System for TRU Recovery) process, which has been developed for reprocessing of fast reactor spent fuel in the framework of “Fast Reactor (FR) Fuel Cycle Technology Development (FaCT)” Project [64,65]. The NEXT process consists of partial recovery of U by a crystallisation of uranyl nitrate hexahydrate (UNH) from dissolver solution, U-Pu-Np co-recovery by solvent extraction in a single cycle flowsheet using TBP (elimination of partitioning and purification sections from the conventional PUREX process), and Am and Cm (trivalent actinides, An(III)) recovery by extraction chromatography.

The process of extraction chromatography for An(III) separation in the NEXT process utilises adsorbents where the extractants for An(III) are loaded on porous silica particles coated with an inert copolymer of formylstyrene and divinylbenzene ($SiO_2$-P, Figure 2.66) [67].

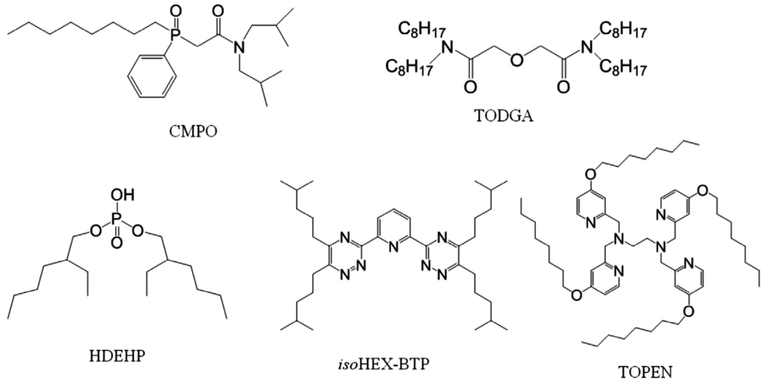
**Figure 2.66. Adsorbent porous silica particles coated with styrene-divinylbenzene polymer**



This type of adsorbent shows rapid adsorption-elution kinetics, high mechanical strength, small swelling and shrinking, and significantly low pressure loss in a packed column, compared with conventional polymer matrix resins [66,67]. One of the most important advantages of extraction chromatography is that it does not have to use diluents, which allows for a wide range of extractant selection. Utilising these advantages, JAEA have developed a process of extraction chromatography for An(III) separation at the engineering scale with a capacity of ca. 750 L(raffinate)/day (ca. 1.7 kg An(III)/day for a 200 teHM/y FBR fuel reprocessing plant), aiming at more than 99.9% recovery of An(III) with a decontamination factor of more than 100 against other elements [67].

Two cycles of separation were examined. In the first cycle, An(III) is recovered together with lanthanides (Ln) from a highly acidic raffinate after U-Pu-Np recovery by TBP, using CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide) or TODGA (N,N,N’,N’-tetraoctyl-3-oxapentane-1,5-diamide) as an extractant to be loaded on the $SiO_2$-P. In the second cycle, An(III) is separated from Ln, using HDEHP (bis(2-ethylhexyl)hydrogen phosphate), i-Hex-BTP (2,6-bis(5,6-dihexyl-1,2,4-triazine-3-ylpyridine) or TOPEN (N,N,N',N'-tetrakis((5-octyloxypyridin-2-yl)methyl)ethylenediamine) [68,69]. Chemical structures of these extractants are shown in Figure 2.67. Various column adsorption experiments were carried out using simulated solutions and the separation performance of the adsorbents with these extractants was investigated.

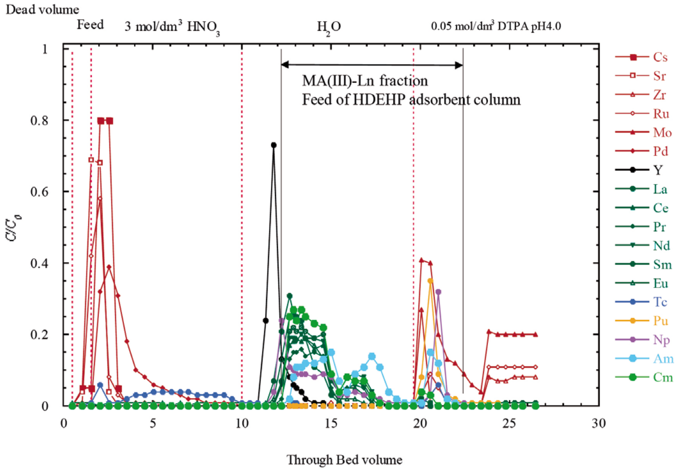
**Figure 2.67. Chemical structures of extractants examined in the development of separation process by extraction chromatography in JAEA**



Figures 2.68 and 2.69 show the chromatograms obtained for the first separation step with CMPO adsorbent (15 $cm^3$ column) and TODGA adsorbent (23.5 $cm^3$ column), respectively [69 Stability of adsorbents against radiation and acid, regeneration of adsorbents and thermal degradation were also investigated from a view point of practical use of the adsorbents [67,68]. From these fundamental studies, TODGA and i-Hex-BTP were selected as optimum extractants for the first and second separation steps, respectively [70].

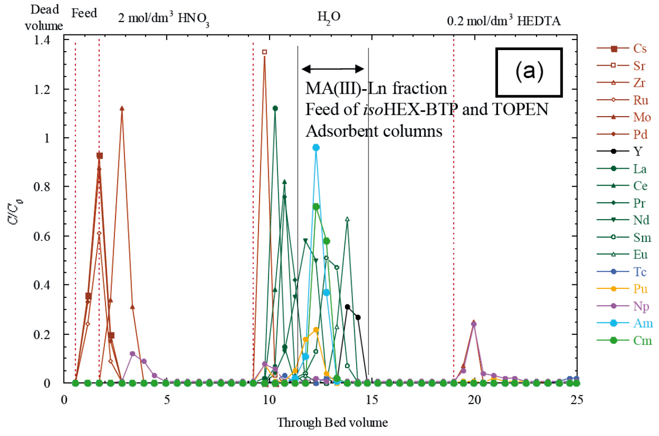
To demonstrate the separation process, experiments with a genuine high-level liquid waste were carried out using a column of 25.5 $cm^3$ bed volume [71]. The chromatogram for TODGA – i-Hex-BTP system showed lower recovery of An(III) than expected and, therefore, further improvement of the flowsheet and adsorbent is necessary.

**Figure 2.68. Chromatogram of simulated raffinate using CMPO/$SiO_2$-P adsorbent [69]**



Bed volume of the adsorbent: 15 $cm^3$

**Figure 2.69. Chromatogram of the simulated raffinate using TODGA/$SiO_2$-P adsorbent [69]**



Bed volume of the adsorbent: $23.5 cm^3$

The engineering of the extraction chromatography system was investigated with a large scale experimental device [72]. Adsorption experiments with a column of 20 cm diameter (ϕ) ×65 cm high (bed volume = 20 L) with CMPO and HDEHP adsorbents were performed and stable separation of elements was obtained in ten times repeated operation [73]. The adsorbents can be regenerated to mitigate radiation damage, which is remarkable for gamma-ray radition compared with alpha [74]. A large-scale slurry-transfer, column bed configuration was developed with steady flow inside the column. This was confirmed using a large-scale column of 48 cm diameter ×65 cm high [70]. Concerning safety, heat transfer and gas generation, these issues are yet to be considered. Heat generated by An(III) and fission products inside the column is adsorbed by the mobile phase and transferred outside the column. Hydrogen generated from radiolysis is also released in a similar manner. Column plugging by solid material as a result of particle entrainment or internal generation must be avoided in order to prevent the accumulation of heat and hydrogen [70]. It was found that foreign particles are caught at the inlet filter or the upper layer of the bed.

The phase I development for the FaCT project has now been terminated, and its evaluation delayed due to the accident of reactors at Fukushima, Japan, although further improvements have been pointed out prior to its industrial scale application.

*SNF reprocessing in carbonate media- the CARBEX process developed in Russia*

- Introduction

In 2006, at the D.I. Mendeleyev University of Chemical Technology of Russia, a concept of SNF reprocessing in carbonate solutions was formulated. This has been called the CARBEX-process [75]. Carbonate media have some distinctive benefits compared with the usual nitric acid media used in aqueous reprocessing, being generally a less hazardous medium. At low values of the metal ion to carbonate ion ratio, the carbonate group is a precipitating agent of many polyvalent metals from solutions, whereas at high ratios it is an efficient acido-ligand conferring a high solubility to carbonate complexes of actinides [76]. This allows regulation of the solubility of SNF components and increased selectivity over FP, many of which are practically insoluble. Moreover, species that are aggressive in nitric-acid media, such as fluoride-ions, do not show high corrosion activity in the carbonate media, but are effective complex formers.

- Overview of the CARBEX process

The concept of the CARBEX (carbonate extraction) process was formulated in 2006, based on results of extraction chemistry studies of uranium and thorium with quaternary ammonium salts; this was published in 2008 [77] and in detail in 2010/2011 [78]. A summary of these works is described here. The CARBEX process can be considered as an alternative water-chemical (aqueous) method of SNF reprocessing to the PUREX process. The CARBEX process is based on replacement of nitric acid media, that has high oxidising and corrosion activity, by carbonate aqueous solutions with addition of hydrogen peroxide as an oxidiser at the stage of fuel dissolution into the carbonate solution. It is argued that such replacement significantly improves the safety of aqueous reprocessing of SNF solutions and increases selectivity of fissionable materials, enabling good separation from fission products (FP). Moreover it simplifies SNF reprocessing with final fabrication of ceramic nuclear fuel from the separated materials. A block schematic diagram of the CARBEX-process is shown in Figure 2.70 and includes the following stages:

- high-temperature oxidation of fuel with air oxygen or voloxidation;
- oxidative dissolution of fuel into the carbonate solution using hydrogen peroxide or another suitable oxidiser;
- separation of insoluble FP from the carbonate solution;
- refining of U(VI) and Pu(VI) using quaternary ammonium carbonate as an extractant;
- solid-phase re-extraction of U(VI) and Pu(VI) carbonate compounds from the organic phase;
- production of $UO_2$ and $PuO_2$ powder from carbonate residues;
- fabrication of ceramic nuclear fuel from $UO_2$ and $PuO_2$ powders.

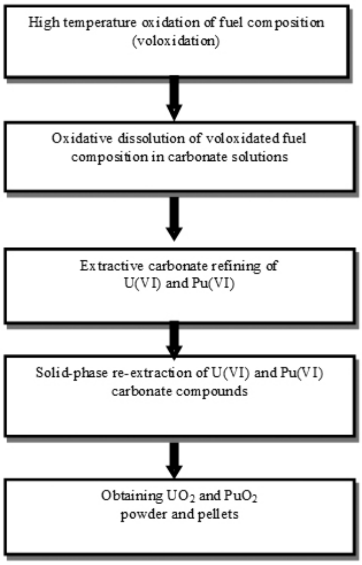
It should also be noted that extraction or sorption purification of carbonate solutions from highly soluble FP, such as cesium and molybdenum, is required with recycling of carbonate solution to the oxidative dissolution stage. Additionally, a variation to the standard scheme can be proposed that includes the separation of other species such as Np, Am, Cm and trivalent REE. The CARBEX processis distinctive from precipitation based methods of carbonate reprocessing, and uses extraction methods to separate uranium and plutonium from FP thus providing opportunities to achieve high decontamination factors of ~$10^5$-$10^6$. At present, laboratory scale research for each stage of the CARBEX process is being performed. The main results achieved in the current phase of works are briefly reviewed below.

- High-temperature oxidation of fuel composition

High-temperature oxidation of fuel with air oxygen is beneficial to downstream reprocessing operations; specifically, for dissolution in the carbonate solution and release of gaseous FP [79]. Voloxidation and similar methods are reviewed in Section 2.1 and so are not described again here.

One method to stabilise uranium in the hexavalent state during high-temperature oxidation is voloxidation in mixtures with alkali-metal carbonates or in melts with hydroxides. Uranium oxides interact with alkali-metal carbonates in air oxygen at elevated temperatures (300-900°C) to form alkali-metal mono-uranate and di-uranate compounds [80-84]. When voloxidation is carried out in melts of alkali-metal hydroxides at temperatures of 600-900°C, only formation of lithium, sodium and potassium di-uranates is observed; further treatment at 1 400°C for more than 1 hour does not result in mono-uranate formation. These alkali-metal uranates are easily dissolved in aqueous carbonate solutions to generate uranyl carbonate complexes, mainly lithium, sodium and potassium tricarbonateuranylates; these being a good base for subsequent reprocessing.

**Figure 2.70. Block schematic diagram of CARBEX-process**



- Oxidative dissolution stage

Under standard SNF voloxidation conditions, formation of $U_3O_8$ and other uranium oxides, including residual $UO_2$, requires further U(IV) oxidation to U(VI) to fully release uranium into the carbonate solution. Conditions for uranium oxidative dissolution in carbonate solutions by hydrogen peroxide have been established [86-89]. In carbonate-peroxide solutions, U(VI) forms carbonate complexes $Me_2[UO_2(CO_3)_2]$ and $Me_4[UO_2(CO_3)_3]$, and mixed peroxide carbonate complexes $Me_4[UO_2(O_2)(CO_3)_2]$ [82,87-89]. Formation of a polynuclear $Me_6[(UO_2)_2(O_2)(CO_3)_4]$ complex has also been demonstrated [91-93]. Kinetic curves of $U_3O_8$ oxidative dissolution in carbonate solutions are described well by the Yander equation [87]. The analysis performed made it possible to identify stages of purely oxidative dissolution of $U_3O_8$ as well as oxidative dissolution with hydrolysis of the generated U(VI) compounds, that has lower rate constants under the same process conditions. When the system moves into this area, a secondary precipitation occurs. According to pH, hydrolysis of U(VI) carbonate complexes may proceed by different routes in alkali medium (Equation 1); neutral medium (Equation 3) and in carbonate medium (Equations 2-4).

$$2[UO_2(CO_3)_3]^{4-} + 6OH^- \rightarrow [U_2O_7]^{2-} + 6CO_3^{2-} + 3H_2O \qquad (1)$$

$$2[UO_2(CO_3)_3]^{4-} + 3H_2O \rightarrow [U_2O_7]^{2-} + 6HCO_3^- \qquad (2)$$

$$UO_2^{2+} + H_2O + CO_2 \rightarrow UO_2CO_3 + 2H^+ \qquad (3)$$

$$3UO_2^{2+} + 4H_2O + CO_2 \rightarrow [(UO_2)_3(OH)_3CO_3]^+ + 5H^+ \qquad (4)$$

Hydrolysis significantly weakens $U_3O_8$ oxidative dissolution in carbonate solutions and has a negative influence on the next stage of extraction refining [87]. Ultrasound increases the rate constants, reduces the time for complete dissolution and gives higher uranium concentrations [88]; however, ultrasound accelerates not only dissolution but hydrolysis of soluble uranyl compounds as well.

Whereas U(IV) compounds are oxidised to U(VI) by hydrogen peroxide in carbonate solutions, hexavalent plutonium ions are quickly reduced to Pu(IV) by hydrogen peroxide [92]. Therefore, under oxidative dissolution in peroxide-carbonate solutions, plutonium will be in the tetravalent state. The carbonate complex $Na_6[Pu(CO_3)_5]$, which is formed under these conditions, has a limited solubility in aqueous carbonate solutions. With excess hydrogen peroxide, a mixed peroxide-carbonate $Na_8[Pu_2(O_2)_2(CO_3)_6]$ complex is generated and precipitates [94]. Stabilisation of Pu(VI) in carbonate solutions for subsequent extraction refining requires other oxidising agents such as $Cl_2$, $KBrO_3$ and $K_2S_2O_8$; of which potassium persulphate has the greatest oxidising capacity. Potassium persulphate has been shown to oxidise Pu(IV) and Pu(VI) hydroxides, generating $Me_4[PuO_2(CO_3)_3]$ complexes that are well soluble in the carbonate solution [87]. So, under oxidative dissolution in carbonate solutions, plutonium will be tetravalent in the case of hydrogen peroxide, and hexavalent after treatment by potassium persulphate. Generation of a mixed Pu(IV) peroxide-carbonate complex enables precipitation refining of plutonium from uranium and FP.

- FP solubility under oxidising dissolution conditions

FP release into carbonate solutions under conditions of oxidising dissolution of uranium oxides determines selectivity at this stage of the CARBEX process. Work on FP solubility performed with model samples (non-radioactive oxides of the corresponding elements) demonstrated high solubility for $MoO_3$ and CsOH under conditions of $U_3O_8$ oxidising dissolution in 0.9 mol/L $Na_2CO_3$ solutions with $H_2O_2$ at 70°C and with ultrasonic impact. After the whole sample dissolution, Mo(VI) concentration attained 37.5 g/L and Cs >150 g/L. REE oxides have low solubilities (in g/L): $Nd_2O_3 = 0.373$, $Sm_2O_3 = 0.317$, $Pr_6O_{11} = 0.119$ and $ZrO_2$, $CeO_2$ and SrO are all practically insoluble [95].

- Extraction refining in carbonate solutions in the CARBEX process

Development and justification of uranium carbonate extraction refining is described [96]. The most efficient extracting agents from carbonate solutions are quaternary ammonium salts, among which methyltrialkylammonium (MTAA) salts including Aliquat 336, Adogen 464, $N_{263}$, TAMAC, etc. are well-known examples [97]. To carry out extraction carbonate refining, carbonate or bicarbonate forms of MTAA are needed [95]. Extraction of U(VI) carbonate complexes from carbonate solutions by MTAA salts has been studied in detail unlike U(VI) peroxide-carbonate complexes. It can be supposed that formation of mixed peroxide-carbonate complexes under $U_3O_8$ oxidising dissolution will define the chemistry of U(VI) extraction from such solutions.

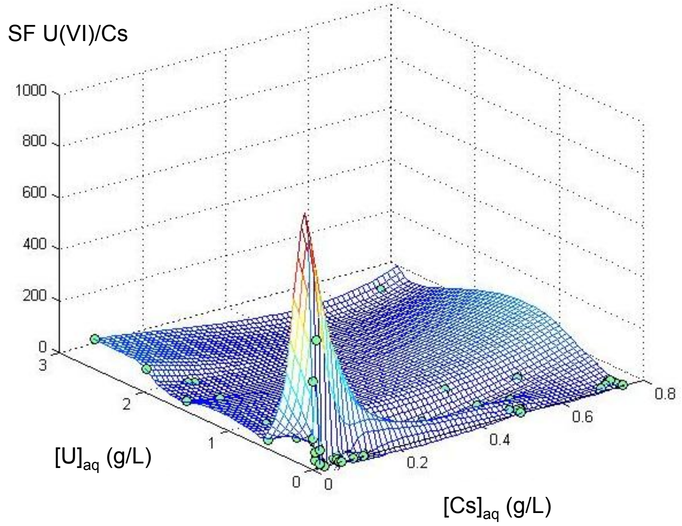
Investigations performed in reference [33] on the extraction chemistry of U(VI) peroxide-carbonate complexes, from carbonate solutions, identified extracted compounds that included mononuclear uranyl compounds $(R_4N)_4[UO_2(CO_3)_3]$, $(R_4N)_4[UO_2(O)_2(CO_3)_2]$ as well as polynuclear compounds $(R_4N)_6[(UO_2)_2(CO_3)_4]$, $(R_4N)_6[(UO_2)_3(O_2)_2(CO_3)_3]$, where $R_4N$ is a quaternary ammonium cation. In the case of extraction of uranyl polynuclear compounds the extractant is highly saturated with metal, >130 g/L for 0.5 mol/L of MTAA carbonate; this improves efficiency for FP decontamination.

Taking into account data on various FP solubilities in carbonate peroxide solutions, the main difficulties should be expected in uranium and plutonium purification from freely soluble FP: Tc, Re, Te, Mo, Cs. It is necessary to note that Tc(VII), Re(VII) and Mo(VI) oxo-anions are well extracted by quaternary ammonium salts. FP separation data are reported in reference [78]. Regarding the specific problem of molybdenum, it can be shown that extraction separation of U(VI) and Mo(VI) is rather effective if U(VI) in carbonate solutions is in the form of peroxide-carbonate complexes, and Mo(VI) is as sodium molybdate, and for uranyl carbonate complexes there should be a low concentration of sodium carbonate.

With regards to cesium, an experimentally obtained isotherm of $Cs_2CO_3$ extraction from aqueous solutions by 0.35 mol/L solution of MTAA carbonate in toluene at 25°C showed rather high distribution of cesium in the organic phase with distribution coefficients up to 0.46 measured. Extraction was attributed to a monosolvate complex

$(R_4N)_2CO_3{\cdot}Cs_2CO_3$. $Na_2CO_3$ addition to the solutions suppressed cesium extraction quite effectively. Cesium extraction was suppressed further by the presence of freely extractable uranyl peroxide carbonate complexes. Figure 2.71 illustrates the dependency of U(VI) and Cs on U(VI)/Cs separation factors under extraction from mixed 0.5 mol/L aqueous solutions of $Na_2CO_3$ by 0.5 mol/L solution of MTAA carbonate in toluene at 20±2 $^{0}$C. It is evident that there is an area of high U(VI)/Cs separation factors situated along the axis of U(VI) concentrations and at Cs concentrations close to 0. In this area the maximum U(VI)/Cs separation factors are achieved with values within the range of 50-490. The second interesting area is located within the concentration ranges of ~0-2 g/L U and ~0.5-0.7 g/L Cs. In this area, U(VI)/Cs separation factors reach 10-50. The first area is explained by low Cs content in the original solutions and the second area by a high content of U(VI) in the organic phase which suppresses Cs extraction. Experimental data thus proved the efficiency of extraction separation of U(VI) peroxide-carbonate complexes, while enabling conditions for decontamination of U(VI) from cesium in carbonate solutions to be determined.

**Figure 2.71. Dependency of U(VI)/Cs separation factors (SF) as a function of concentrations of U(VI) and Cs in extraction raffinates [95]**



Special attention was paid to extraction of plutonium as it can be tetra- or hexavalent in carbonate solutions after the oxidising dissolution stage. Investigations performed with U(VI) and Pu(IV) extraction from mixed carbonate solutions by MTAA carbonate demonstrated [95] that Pu(IV) practically is not extracted by MTAA carbonate; Pu(IV) distribution coefficients are <0.025 for volume ratios of organic and aqueous phases (O:A) from 1:10 to 10:1 while U(VI) distribution coefficients increase from 0.006 to 38 across this range. This leads to increasing U(VI)/Pu(IV) separation factors from 0.4 to 3167. These data indicate the possibility of U(VI) separation from Pu(IV) by extraction from carbonate solutions. With U(VI)-Pu(VI) mixed solutions, however, their joint extraction by MTAA carbonate is observed. These facts enable purification of uranium and plutonium from FP by varying means. At the first stage U(VI) can be separated from FP and Pu(IV) and after this Pu(IV) extraction separation from FP can be carried out. Alternatively, Pu(IV) is transformed into Pu(VI) and then separated from FP. If there are U(VI) and Pu(VI) in the original solution, it makes sense to conduct their joint extraction with separation from FP and a subsequent solid-phase re-extraction from the organic phase in the form of carbonate complexes.

At present, further investigations on extraction carbonate refining of uranium and plutonium are being carried out; they are directed towards optimisation of separation conditions for the freely extractable oxo-anions $TcO_4^-$, $ReO_4^-$ and soluble compounds of tellurium.

- Solid-phase re-extraction of uranium and plutonium

The next stage of the CARBEX process is solid-phase re-extraction of uranyl and plutonyl carbonate complexes from the organic phase MTAA carbonate. Solid-phase re-extraction of ammonium tricarbonate-uranylate is well known in the processing of uranium-containing raw materials. The process is based on reducing the solubility of uranyl carbonate complexes by increasing ammonium carbonate and bicarbonate concentrations in the aqueous phase together with control of precipitation temperatures. There is much less data regarding solid-phase re-extraction of Pu(VI) carbonate compounds and so this must be studied experimentally to optimise precipitation conditions. Further reprocessing of U(VI) and Pu(VI) compounds into $UO_2$ and $PuO_2$ dioxides is an established industrial operation.

- Conclusion

The various carbonate based methods of SNF reprocessing have not gone beyond laboratory research, but they are intensively developed and adapted to solve different problems of the closed nuclear fuel cycle, particularly for uranium and plutonium extraction; fractionation of transuranium elements and REE; cesium and strontium extraction. As an alternative to the established PUREX process, carbonate methods, once fully developed and optimised, can perhaps be considered as promising options for an alternative aqueous reprocessing technology. It has been shown that the recently proposed CARBEX process is a promising incarnation of an aqueous carbonate reprocessing scheme.

### *2.2.4. Cs, Sr separation*

The need for separation of $^{90}Sr$ and $^{137}Cs$ from other radionuclides lies in the fact that they are the main short-term heat generators in high-level waste (HLW). The heat generated causes higher temperatures that, in turn, can (1) accelerate chemical reactions, which then accelerate the degradation of waste packages (WPs); (2) cause water movement that may transport radioactivity to the open environment; and (3) create uncertainties in disposal facility performance. Heat can accelerate water movement in both unsaturated and saturated geological environments. As heat is a driver for groundwater movement, it is also a driver for radionuclide transport [1].

In order to limit repository temperature, the amount of HLW per waste package (WP) is limited and the WPs are spread over a large area. If the decay-heat-generating high-heat radionuclides (HHRs) are removed from HLW, resultant low-heat radionuclides (LHR) repository size (area, number of WPs, total tunnel length) may be reduced to < 20% of the size of a conventional repository. With a waste partitioning and transmutation process that includes removal of the minor actinides (americium and curium) from the LHR waste, significant further reductions in repository size are possible. The minor actinides are the next largest heat generators in LHR waste.

Separate management of HHRs requires separation of the HHRs from the HLW and a separate HHR disposal facility. The HHRs would be disposed of in a separate lower-cost facility made possible by the limited lifetimes (half-life ~30 years) of the HHRs. There are potentially significant gains in economics and repository performance for separate management of HHRs and LHRs in some types of fuel cycles. Furthermore, the selective separation of cesium and strontium from waste solutions allows the residuals to be solidified as medium- or low-active waste, for which the processing and final disposal regulations are much less rigorous.

These are the reasons why there is interest in developing methods for separating Cs and Sr present in nuclear waste.

*Overview of techniques for Cs and Sr removal*

Cesium and strontium create most of the radioactivity in waste solutions produced at both civil and military nuclear-fuel-reprocessing plants. In the fission process, they are produced in approximately the same yields, and in acidic reprocessing solutions, their activity concentrations are almost equal. In the neutralisation of these solutions with sodium hydroxide, cesium remains almost exclusively in solution, but strontium is partially coprecipitated with hydroxides of other metals and as a carbonate. Most other radionuclides are precipitated as hydroxides, leaving only traces of these nuclides behind in the solution phase. In high burn-up fuels processed after five or more years after reactor discharge, cesium is the greatest contributor to the total radioactivity of neutralised alkaline waste solutions, and strontium is the second greatest.

Existing technologies and current research for removing $^{137}$Cs and $^{90}$Sr from nuclear waste streams fall into the general categories of solvent extraction, precipitation, and ion exchange/adsorption.

- Solvent extraction

Solvent extraction methods for cesium and strontium are based on dicarbollide and macrocyclic polyethers [2]:

- extraction process with chlorinated cobalt dicarbollide (ChCoDiC)-CCD PEG

The fundamentals of the extraction process of chlorinated cobalt dicarbollide (ChCoDiC) (Figure 2.72) in a polar diluent were jointly developed by the specialists from Radium Institute and Institute of Nuclear Research (Czech Republic) [3]; thereafter, Radium Institute in collaboration with “Mayak” PA brought this development up to commercial use at the radiochemical plant.

The extraction of cesium, strontium and other elements into polar solvents by cobalt dicarbollide (anion with (-1) charge) proceeds as a result of the recovery of dissociated ion pair $Cs^+B^-$ (B:ChCoDiC anion) into the organic phase. The constants of extraction exchange of cesium cation for a proton of organic phase decrease considerably with increasing acidity of the aqueous phase, which provides the possibility for efficient stripping of cesium.

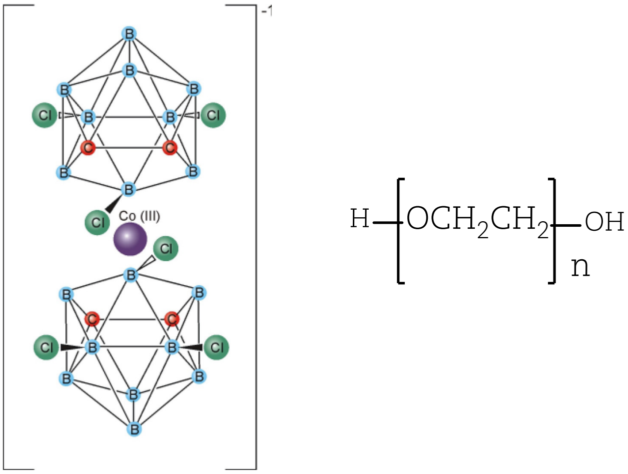
Strontium recovery efficiency from $HNO_3$ solutions is about 3 times less in comparison with cesium. This is due to the hydrophilic character of strontium cation. The recovery of strontium by ChCoDiC can be achieved by the introduction of polyethylene glycol (PEG) into extraction mixture and the PEG exerts a synergistic effect which increases the distribution coefficient of strontium by a factor of ~1 000, thus enablingstrontium to be extracted even from strongly acidic media. Cesium extraction by ChCoDiC – PEG mixtures is nearly to the same degree, as in the absence of PEG.

Among the substances investigated for suppressing strontium extraction, hydrazine is most efficient for strontium stripping; hydrazine can be easily removed during regeneration of the organic phase.Results from studies have revealed the feasibility of developing the flowsheet for cesium and strontium recovery by ChCoDiC and PEG (Figure 2.73); the advantages of this flowsheet are as follows:

- ChCoDiC (in the presence of PEG) allows the recovery of Cs and Sr directly from acidic HLW solutions; thus considerably simplifying the subsequent operations of preliminary preparation of LHR waste solutions for disposal;
- extraction selectivity is high;
- ChCoDiC losses with the aqueous phase are negligible;

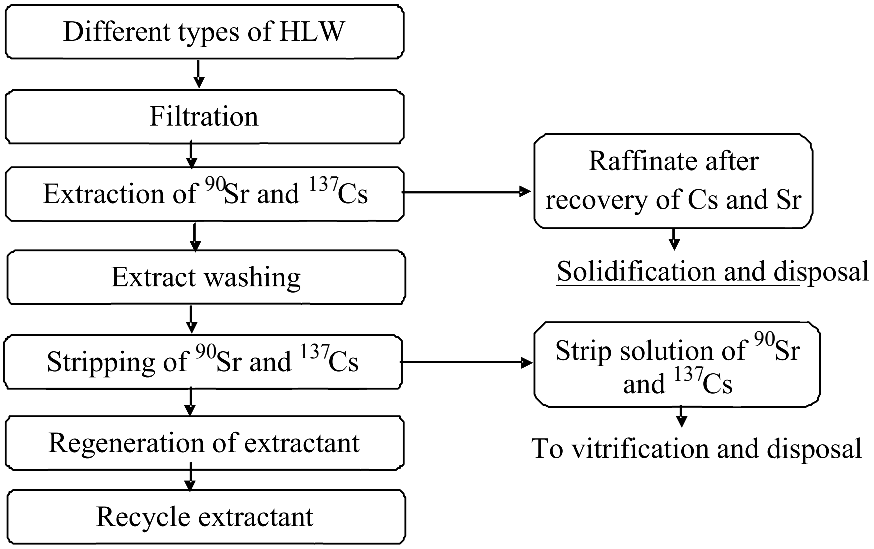
- chemical and radiation stability of ChCoDiC is high and enables prolonged contact of extractant with strongly acidic HLW and fissionproducts radionuclides without significant degradation;
- extraction process with crown ethers (CSSEX).

**Figure 2.72. Chlorinated cobalt dicarbollide, CCD (left), and polyethylene glycol, PEG (right)**



$$H\!-\!\left[OCH_2CH_2\right]_n\!-\!OH$$

**Figure 2.73. Extraction flowsheet for reprocessing of HLW with the use of ChCoDiC at industrial facility $^{35}$U in "Mayak"**



Sizable crown-ethers were first investigated in the 1990s at the CEA Cadarache as strontium and cesium carriers through supported liquid membranes [4,5].

Derivatives of 18C6 and 21C7 crown-ethers, respectively, were optimised for strontium and caesium selective extraction, and enhanced in the presence of cation exchanger synergists. However, the drawback of these processes, besides the use of high-polarity diluents in order to solubilise the extractants in the supported liquid membrane, was the lack of selectivity for strontium.

Search for more selective extractants led the European researcher community to develop functionalised calixarenes, respectively calix[6/8]arenes-(di-N-alkyl)amide for strontium extraction and calix[4]arenes-mono/bis-crown-6 for caesium extraction (Table 2.24) [6,7].

Very selective extracting mixtures, based on 1,3-(2,4-dialkyloxy)-2,4-calix[4]arene-crown-6, were optimised at the CEA Cadarache site for cesium extraction. Counter-current hot tests were successfully carried out in the shielded cells of the ATALANTE facility at the CEA Marcoule site (Figure 2.74) [8]. Nevertheless, due to the abandonment of the French strategy of recycling Cs and Sr in future nuclear reactors, the separation and recovery processes for Cs and Sr have no longer been developed at the CEA or in Europe since 1995.

**Table 2.24. Calix[6/8]arenes-(di-N-alkyl)amide investigated for strontium extraction and Calix [4] arenes-mono-crown-n and Calix [4] arenes bis-crown-n investigated for caesium extraction**

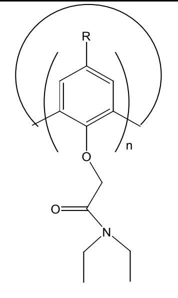
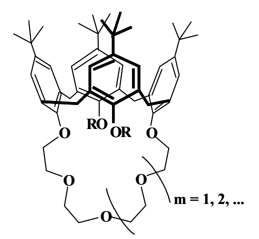
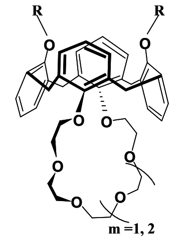
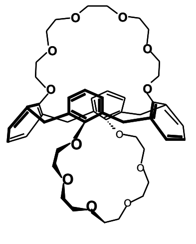
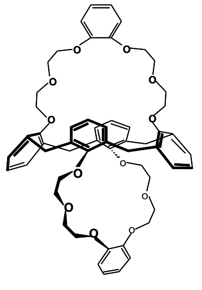
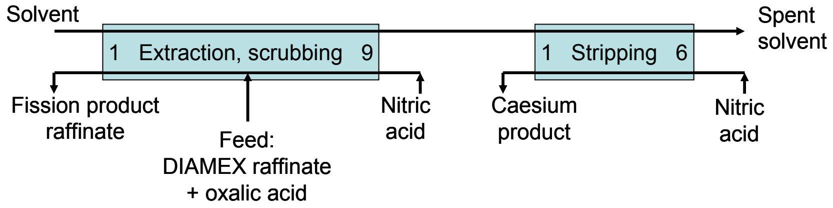
| | | | | |
|---|---|---|---|---|
|  |  |  |  |  |
| CA4: R = tert-butyl, n = 6 | R = -H, -alkyl, -ester, -amid, -acid, … | R = -H, -alkyl, -ester, -amid, -acid, … | Examples of biscrown-calix[4]arenes in the *1,3-alternate* conformation | |
| CA12:<br>R = -OCH$_3$,<br>n = 6 | | | | |
| CA16:<br>R = O(CH$_2$)$_7$CH$_3$,<br>n = 8 | *p*-tert-butylCalix[4]arenes-crown-n in the *cone* conformation | Calix[4]arenes-crown-n in the *1,3-alternate* conformation | | |

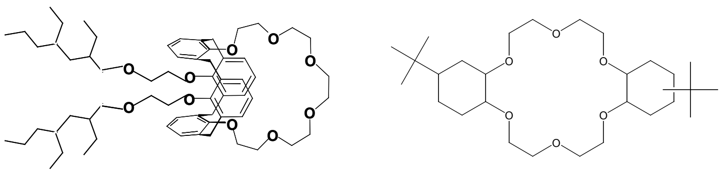
**Figure 2.74. Flowsheet of the CSSEX process implemented on a highly active DIAMEX raffinate solution at the CEA Marcoule**



- Cs-Sr separation by extraction chromatography developed in Japan

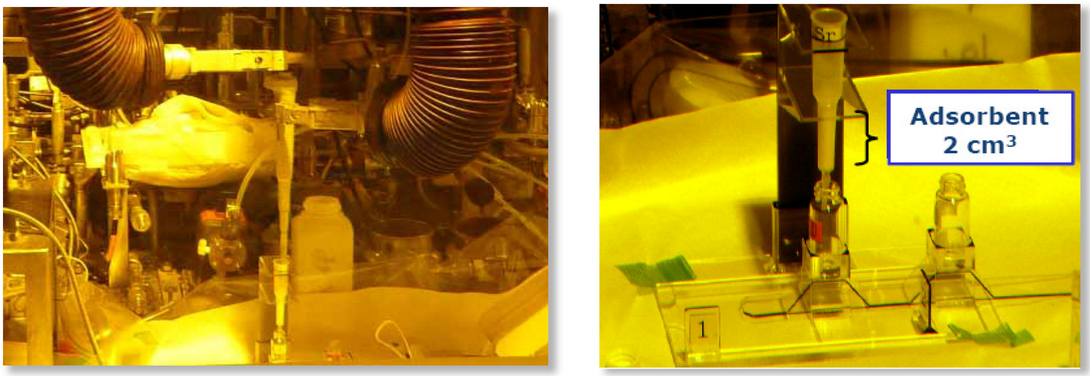
A new separation process for transuranium elements (TRU = Np, Pu,Am and Cm) and some fission products (Sr, Cs and Mo) has been developed by Japan Atomic Energy Agency, JAEA, using new innovative extractants and adsorbents [9]. Phosphorus-free compounds consisting of carbon, hydrogen, oxygen and nitrogen (CHON principle) were applied to the separation steps for TRU, Cs and Sr from acidic solution. In this process, reduction of the HNO3 concentration and potential precipitation of some of the fission product elements in the high-level liquid waste was avoided. Extractants for Cs and Sr, calix-crown derivatives for Cs, and crown ether derivatives for Sr, were applied to separate Cs and Sr from the acidic solution by extraction chromatography rather than solvent extraction. One of the most important advantages of extraction chromatography is that the use of diluents is not necessary. Figure 2.75 shows the extractants used for Cs and Sr, Calix-crown R14 (1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene) for Cs and DtBuCH18C6 (di-t-butylcyclohexano-18-crown-6) for Sr. The extractants were loaded on porous silica particles coated with an inert copolymer of formylstyrene and divinylbenzene [10] with modifier, hexadecanol. Some column adsorption experiments were performed using simulated solutions containing radioactive isotopes at nitric acid concentrations of 2 to 4 M [11]. In the separation by the DtBuCH18C6 adsorbent column, the Sr fraction was contaminated by Tc and Pu. On the other hand, in the separation by Calix-crown R14 adsorbent column, Cs was separated from other elements in an almost isolated fraction, and the first Sr effluent did not contain any Pu and less Tc. These experiments led to the conclusion that Cs should be separated first, while Sr is separated from Cs raffinate.

**Figure 2.75. Calix-crown R14 for Cs (left) and DtBuCH18C6 for Sr (right)**



Experiments with a genuine HLLW were also performed with a 2 $cm^3$ column in a hot cell at Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF), JAEA Tokai, as shown in Figure 2.76. The results showed that element behaviour in the Cs and Sr adsorption process was similar to those tests using simulants, even with a genuine HLLW [9,11].

**Figure 2.76. Small scale adsorption tests for Cs and Sr separation with a genuine HLLW [9]**



Generally speaking, however, the techniques based on solvent extraction have several shortcomings that leave them less desirable than other technologies. Solvent extraction plants typically require more extensive process equipment, resulting in a larger footprint and capital investment. Moreover, solvent extraction distribution coefficients for Cs are typically small, resulting in more separation stages and the use of extracting solvents and stripping agentsthat are often undesirable from environmental and safety perspectives.

- Cs-Sr separation developed in the United States

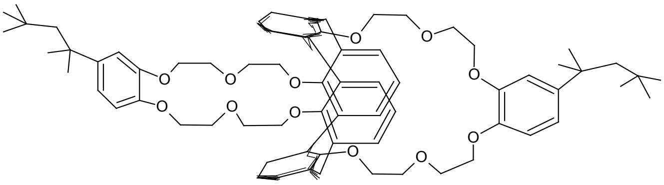
The current research and development approach in the United States as related to advanced processes for the recycling of used nuclear fuel does not include Cs and Sr separation. The approach is decay storage to reduce the activity of Cs and Sr in the high-level waste (HLW). However, prior to this decision considerable progress was made towards developing and demonstrating a solvent extraction process for the separation of Cs and Sr from acidic dissolved used nuclear fuel. Initial work resulted in development, and laboratory-scale demonstration with actual used fuel, of the CCD-PEG process [12]. More recently the Fission Product Extraction (FPEX) process was developed and demonstrated and an improved process, FPEX II was developed.

  - Fission Product Extraction (FPEX) process

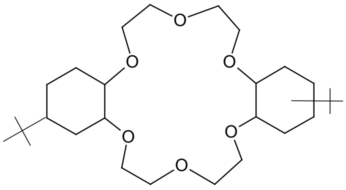
In previous work, cesium and strontium have been removed from acidic nuclear waste solutions and related alkaline waste using separate solvent extraction processes designed specifically for these elements. In general, crown ethers have been selected for the removal of strontium [13], and calixarenes [14], have been selected for separations of cesium. A novel process was developed at the Idaho National Laboratory (INL) which combines these two types of extractants to create a solvent that will extract both cesium and strontium, simultaneously from acidic media. This technology, the Fission Product Extraction (FPEX) Process [15], utilises 4,4',(5')-di-(t-butyldicyclohexano)-18-crown-6 ($DtBuCH_{18}C_6$) for the extraction of Sr, and calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) for the extraction of Cs, plus 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) as a solvent modifier, TOA (trioctylamine) and Isopar® L diluent (Figure 2.77). The flowsheet developed for the FPEX process is presented in Figure 2.78.

**Figure 2.77. Molecular structures of the cesium and strontium extractants and the Cs-7SB modifier used in the FPEX process solvent [15]**

**BOBCalixC6**
calix[4]arene-bis-(tert-octylbenzo-crown-6)



**DtBuCH18C6**
4,4’,(5’)-di-
(t-butyldicyclohexano)-18-crown-6



**Cs-7SB modifier**
1-(2,2,3,3-tetrafluorpropoxy)-3-(4-sec-butylphenoxy)-2-propanol

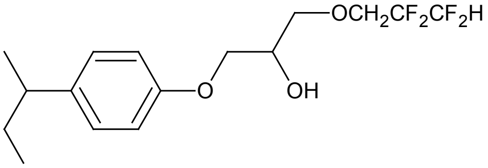
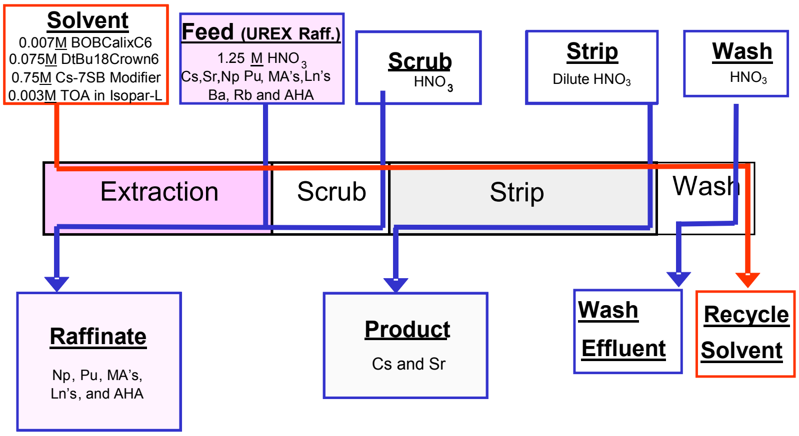


**Figure 2.78. Flowsheet of the FPEX process**



Development of the FPEX process culminated in two demonstrations tests with actual spent fuel. The first demonstration test was carried out at ANL using 2-cm centrifugal contactors and the second at ORNL using laboratory-scale mixer-settlers. Forthe ANL test, the feed solution was the raffinate from testing of the UREX process (1.25M $HNO_3$ feed), after destruction of the AHA, Greater than 99.99% of the Cs and 99.8% of the Sr were recovered with this test and>99% of the Ba and Rb, 21% of the Zr, 77% of the Mo and 9% of the Tc were co-extracted with Cs and Sr. For the demonstration testi at ORNL, the feed solution was the raffinate from the UREX+ co-decontamination and TRUEX process tests (1.4 M $HNO_3$ feed), and resulted in removal efficiencies of 99.94% and 99.99% for Cs and Sr, respectively. Additionally, the FPEX process solvent was evaluated with regards to radiolytic stability at INL, and results indicated high resistance to degradation [16].

– FPEX II Process

Laboratory testing indicates that the FPEX process can effectively separate Cs and Sr from acidic solutions containing large quantities of actinides and lanthanides, such as used LWR fuel. However, there are issues relative to the solubility of the BOBCalixC6 in the Isopar L diluent and with stability of the BOBCalixC6. The maximum BOBCalixC6 concentration in the FPEX solvent is limited by solubility to 0.007 M. As a result, loading of the BOBCalixC6 with Cs reduces distribution coefficients for Cs. Due to the alkyl substituent on the benzyl moiety of the BOBCalixC6, the benzyl ring is activated towards nitration. While nitration of the BOBCalixC6 does not severely impact the measured Cs distribution ratios, the products of the nitration of BOBCalixC6 are less soluble in the organic solvent. This further exacerbates the limited BOBCalixC6 solubility in the process solvent. Therefore, in collaboration with ORNL and Texas Tech University, INL developed the FPEX II process to address these concerns [17,18].

The subsequently developed process consists of an optimum composition for the FPEX II solvent of 0.020 M 1,3-Alternate-25,27-Di(2,7-dimethyl-1-octyl)calix[4]arene-benzocrown-6 (MaxCalix), 0.090 M di-tert-butyl-dicyclohexano-18-crown-6, and 1.5 M Exxal-8 dissolved in Isopar L. Proof-of-principle experiments with the FPEX II process were completed using simulated feed streams spiked with radiotracers. These tests have demonstrated feasibility of the process including increased solubility and stability of the Cs extractant as compared to the FPEX process. No research is currently ongoing relative to Cs/Sr separation.

- Precipitation

Precipitation has been used successfully in some cases. Phosphotungstic acid has been used to recover Cs from PUREX process waste at the Hanford DOE site. However, the higher alkanility typically associated with precipitation methods often results in the precipitation of macro quantities of metals, thus necessitating further separation or decontamination process steps.

Ferrocyanide solids have important applications for the removal of radioactive cesium from nuclear waste solutions [19]. These materials are prepared by mixing soluble ferrocyanides and salts of divalent transition metals or other divalent cations. The simple precipitations most commonly give very fine particles or slimes of variable compositions. Special preparation procedures have been developed to control the compositions or to prepare granular solids suitable for column operation. The removal of cesium from solutions has been measured for many different ferrocyanide solids. Some of these solids show an exchange of $K^+$, $Na^+$, or $NH_4^+$ for cesium, but many show sorptions of cesium without a true ion exchange.

Strontium is usually removed from waste solutions by precipitation, aided by calcium phosphate, calcium carbonate, or barium sulphate, or by flocculation with iron(III). For example, at the La Hague reprocessing plant in France, strontium is removed from low-active waste streams by iron flocculation at pH 10.5 and from medium-active waste streams with barium sulphate at pH 8.5. Decontamination factors of 100 and above for strontium have been obtained in these processes.

Ferric hydroxide flocs, in particular, proved successful in removing radioactive fission product strontium from aqueous solutions in contrast to cesium, which is poorly removed (less than 5%). The process was improved (1) by raising pH to a maximum of 10.5, (2) increasing the iron/strontium ratio, or (3) by adding phosphate ion, provided the phosphate/iron mole ratio did not exceed 0.33. The mechanism of removal has been identified as an ion-exchange reaction at the surface of the ferric hydroxide particles; consequently, when considering the process for the removal of $^{90}Sr$ from process waters, competitive effects from the larger concentrations of calcium and magnesium present in the water would become important.

Other methods that have been proposed for removing strontium from aqueous solutions generated by processing radioactive waste solutions have included, adsorption onto activated carbon which was successfully studied [20].

Packed column operations utilising ion exchange or extraction chromatography provide several advantages over other techniques. Column separations usually require less process equipment and capital investment and have lower operating costs. They can be operated in-line for a given process stream and typically do not require additional reagents or pH adjustment. Several inorganic compounds exist which have high cesium capacity. Because of this, $^{137}Cs$ removal can be accomplished with smaller beds and acceptable pressure drop in process streams.

**Table 2.25. Main properties of the most used inorganic exchangers**

| Inorganic exchanger | Physical status | pH conditions |
|---|---|---|
| Sodium titanosilicate (CST) | Granular form | the selectivity for $Cs^+$ decreases significantly in highly alkaline solutions of high sodium concentration |
| Sodium titanate (Sr Treat) | Poorly crystalline | very efficient for strontium removal in basic solutions, but, because it is weekly acidic exchanger, it performs poorly even in slightly acidic conditions |
| Potassium cobalt hexacyanoferrate, KCoFC<br>(Cs Treat) | KCoFC, produced by precipitation is in the form of a fine powder, unsuitable for column operations. One way to overcome this shortcoming is to prepare a $SiO_2$.KCoFC composite ion exchanger in the form of porous beads | very selective for the removal of cesium from aqueous waste<br>No adsorption competition is observed between $Cs^+$ and $H^+$ in the concentration range 0.001-3M HCl. However, in the case of $HNO_3$, $K_d$ of Cs decreases when concentration exceeds 0.1 M |
| Ammonium molybdophosphate (AMP) | Requires immobilisation in polyacrylonitrile (AMP-PAN) to be a cesium selective sorbent material | AMP-PAN exchanger has high selectivity and capacity for removing $^{137}Cs$ from acidic raffinate and acidic waste streams resulting from nuclear fuel reprocessing |
| Zeolites | Synthetic zeolites can be prepared as microcrystalline powders, pellets or beads, and can be engineered with a wide variety of chemical properties and pore sizes, and are very stable at high temperatures. However, they have relatively high costs, an ion specificity susceptible to interference from similar sized ions, and a poor mechanical stability, due to their brittleness. | limited chemical stability at extreme pH ranges (either high or low) |

- Ion exchange/adsorption

Various inorganic exchange materials for selective cesium and strontium removal have been developed. Some of them show high selectivity, but mechanically stable forms have not been available for process applications. Moreover, their use is limited by pH. Apart from sodium titanosilicate (CST), which can remove cesium from high salt waste solutions over a broad pH range, the other exchangers require specific conditions for their application (Table 2.25). If such conditions are not satisfied, the solutions must to be pre-treated. The following paragraph illustrates a typical procedure for concentration and neutralisation of acidic solutions.

*Concentration and neutralisation of acidic solutions containing nitric acid*

Liquid wastes are pretreated by evaporation/distillation to:

- minimise the volume of liquid waste and, consequently, the volume of final waste forms;
- minimise the content of radioactivity in liquid condensate effluents released to the environment, in line with modern concepts of nuclear installations with virtually no release of radioactive materials (ALARA);
- allow the recycle of $HNO_3$ for the preparation of solutions used to wash the primary liquid waste storage tanks.

The system includes two sections:

- an evaporation section, which consists of an evaporator and a condenser, where the radioactivity contained in the secondary liquid waste (concentrate) contained in a very small fraction of liquid, while the condensate is a mixture of water and nitric acid;
- a distillation section, which consists of a distillation column, a reboiler, a capacitor and a series of storage tanks, where the condensate produced in the evaporation section is treated, to separate water from nitric acid;

The acidic concentrate solutions are neutralised by adding 50 wt.% (19M) sodium hydroxideuing, an excess of 5% compared to the stoichiometric value to maintain alkalinity. The high concentration of 19 M aims at minimising the volume of the solution to be treated and, consequently, the volume of final waste form.

A series of neutralisation reactions take place according to the general scheme:

$$HNO_3 + NaOH \longleftrightarrow NaNO_3 + H_2O$$

$$H_2SO_4 + 2NaOH \longleftrightarrow Na_2SO_4 + 2H_2O$$

$$Fe(NO_3)_3 + 3NaOH \longleftrightarrow Fe(OH)_3 + 3NaNO_3$$

$$Hg(NO_3)_2 + 2NaOH \longleftrightarrow Hg(OH)_2 + 2NaNO_3$$

$$Al(NO_3)_3 + 3NaOH \longleftrightarrow Al(OH)_3 + 3NaNO_3$$

$$UO_2(NO_3)_2 + 3NaOH \longleftrightarrow 0.5Na_2U_2O_7 + 2NaNO_3 + 1.5H_2O$$

In the latter reaction, uranium precipitates as sodium diuranate in a powder slurry form, whith consistency such that it is easily maintained in suspension and does not pose any problems for transfer or handling. Aluminum precipitates in the form of hydroxide. This method is successfully applied at the Dounreay plant for the neutralisation of streams having high aluminum content.

An alternative process is to leave aluminum in solution. In this case, due to its amphoteric properties, aluminum would remain as $AlO_2^-$ in the strongly alkaline environment. In such a case, the resulting liquid would present many difficulties for conditioning, especially if cement is chosen as the final matrix. Moreover, the formation of metastable equilibria can occur due to the presence of the $AlO_2^-$ formed by addition of sodium hydroxide. The following equilibrium would occur:

$$Al(OH)_3 + NaOH \longleftrightarrow NaAlO_2 + 2H_2O$$

Any lowering of the pH, caused by the presence of side equilibria which could consume hydroxide ions, could shift the above reaction to the left, with formation of aluminum hydroxide and consequent volume increase.

The most significant increase in volume, caused by the neutralisation process, is approximately 30% for the primary waste solution. For other waste steams the volume increase is about 10%.

Moreover, an increase in temperature, determined by considering the exotherm neutralisation reactions, is estimated less than 8-10°C.

*Inorganic ion exchangers for Cs and Sr*

Several inorganic ion exchangers are presently in use at nuclear power plants and reprocessing plants to treat the large amounts of nuclear waste around the world. In particular, various exchangers such as zeolites, sodium titanates, titanosilicates and hexacyanoferrates are used to remove Cs and Sr. A short review of these molecules, together with their properties and application, is presented below.

- Crystalline silicotitanates, CST (sodium titanosilicate)

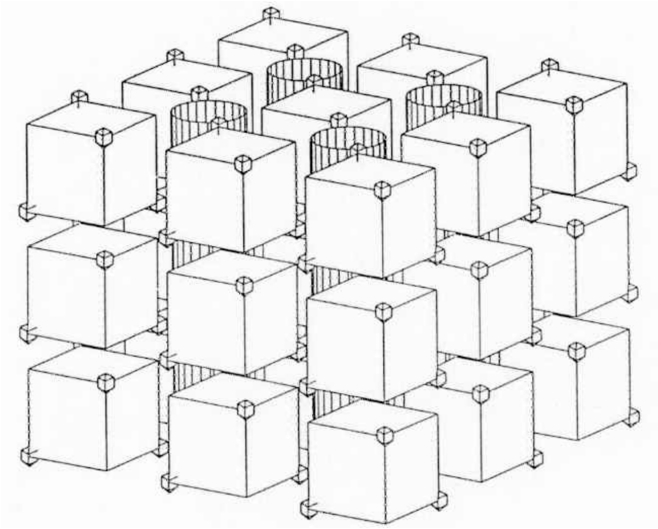
Presently, sodium titanosilicate is the most promising material for the removal of radioactive cesium from high salt waste solutions over a broad pH range.

The current version of crystalline silicotitanate (TAM5) is commercially available from Union Oil Products, UOP, under the trade name IONSIV® IE-911 [21]. TAM5 was synthesised by hydrothermal synthesis using sodium hydroxide and the alkoxides of titanium and silicon (Figures 2.79 and 2.80). It is structurally related to a rare Russian mineral, Sitinakite, from Kibinskii alkaline massif. The idealised formula for the mineral is $Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2K(H_2O)_{1.7}$. Similarly the formula for TAM5 is $Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2Na(H_2O)_{1.7}$. The presence of potassium is the major distinction between Sitinakite and TAM5. The Sitinakite also contains about 5 wt% of niobium, as well as small amounts of other elements.

Replacing about 25% of the titanium atoms with niobium atoms will modify TAM5. The resulting product was tested extensively to enable its use as an inorganic ion exchanger for the removal of radioisotopes, especially $^{137}Cs$, from highly alkaline nuclear waste solutions. IONSIV® IE-911 is such a granular form of modified TAM5 (MTAM5) that is commercially available from Union Oil Products, UOP.

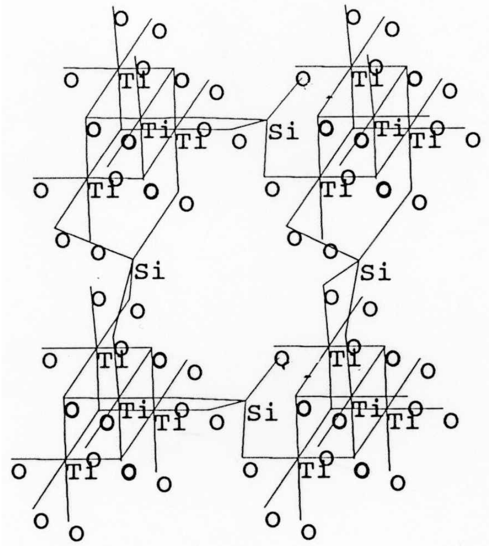
TAM5 has straight uniform channels with 3.5 Å diameter and belongs to a new class of materials similar to Molecular Sieves. Typical crystal sizes are in the range of 0.1 – 0.4 µm. Sodium ions are ion exchangeable with protons and also with other alkali-metal ions without affecting the crystal structure. Since the channel size of TAM5 and the diameter of Cs ions are very similar, ion exchange with Cs ions is almost irreversible. However, the selectivity for $Cs^+$, decreases significantly in highly alkaline solutions of high sodium concentration. Also, the presence of macro component potassium is a strong interfering factor both in cesium and strontium uptake for this material.

**Figure 2.79. Structure of sodium silicotitanate (TAM5) showing the parallel channels [21]**



In the cube, corners with circles represent Ti and corners without circles represent O. Si are in-between a pair of cubes and Na is between two pairs of Si, which are not shown.

**Figure 2.80. A section of TAM5 structure showing the $Ti_4$ clusters linked with tetrahedral silicates**



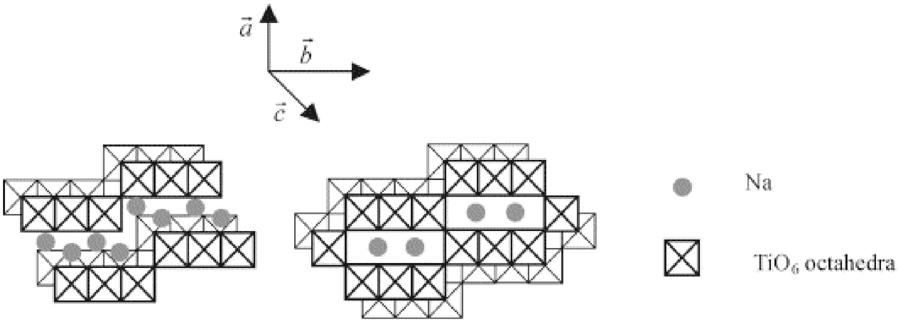
The hole in centre represents the cross-section of the channel [21,53].

- Sodium titanate (SrTreat)

SrTreat is a layered material, which has been found to be highly selective for strontium in basic conditions in the presence of high concentrations of sodium. It is prepared by refluxing titanium dioxide in a solution of concentrated sodium hydroxide, but the product is typically poorly crystalline [22]. Therefore, its exact crystal structure has not yet been determined. Generally, sodium titanates are built from three $TiO_6$ octahedra sharing edges, which are joined together through corners to other similar chains of octahedra, thus forming layers (Figure 2.81). The sodium ions are located in between the layers. As the ion exchange properties strongly depend on the crystallinity of the material, the strontium selectivity of sodium titanate also varies, depending on the synthesis conditions of the material.

Typically, the ion exchange properties of crystalline layered materials may be controlled by the interplanar distance. Since layered structures are generally more elastic than rigid three-dimensional frameworks, changes in the structure can be achieved by intercalation, or simply by changing the interstitial cations of the two-dimensional system. The interlayer distance, which usually is between 3-15 Å in titanates, is about 9.7 Å for $Na_4Ti_9O_{20}.nH_2O$ in the hydrated form. This is large enough to allow the diffusion of cations in their hydrated forms into the structure and thus strontium may also be sorbed as $Sr(OH)^+$, explaining the high selectivity. Titanates may possess ion exchange capacities as high as 9 meq $g^{-1}$. A Finnish company, Fortum Ltd., manufactures sodium titanate (SrTreat®) in large scale for industrial applications.

**Figure 2.81. Structure of sodium titanate [23]***



$Na_2Ti_3O_7$ $Na_2Ti_6O_{13}$

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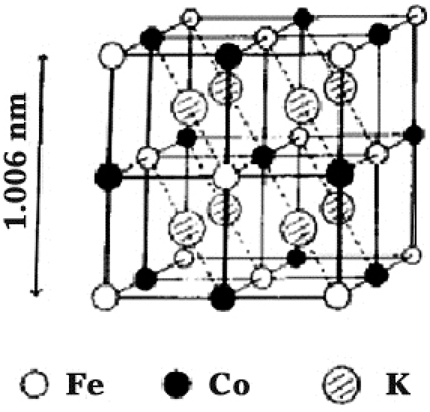
The influence of pH on Sr absorption has been studied [24]. In particular, when strontium is absorbed on $Na_4Ti_9O_{20}.xH_2O$ from neutral solutions, the formation of $Sr_2Ti_9O_{20}.xH_2O$ occurs. This compound decomposes to $SrTiO_3$ and $TiO_2$ when heated to 870°C. From alkaline solutions strontium is absorbed both as $Sr(OH)^+$ and $Sr^{2+}$ with the proportion of the former species increasing with pH. At pH 12.8- only exchange of $Sr(OH)^+$ has been observed and the exchanged form is $Na_2/SrOH/_2Ti_9O_{20}.xH_2O$. This compound decomposed to $Na_2Ti_6O_{13}$ and an unidentified strontium titanate when heated to 870°C. Distribution coefficients have been determined for alkali and alkaline earth metal ions as a function of pH. The selectivity sequence for alkaline earth metal ions was Ba>SrCa>Mg, and that for alkali-metal ions was Cs>K>Li /pH 2–6/ and Li>Cs>K/pH 7/.

In conclusion, SrTreat® is very efficient for strontium removal in basic solutions, but, being a weekly acidic exchanger, performs poorly even in slightly acidic conditions.

- Potassium cobalt hexacyanoferrate, $K_2CoFe(CN)_6$ (CsTreat)

Potassium cobalt hexacyanoferrate (Figure 2.82), abbreviated to KCoFC, is very selective for the removal of cesium from aqueous waste. KCoFC produced by precipitation is in the form of a fine powder, which is unsuitable for column operations [25,26]. One way to overcome this shortcoming is to prepare a $SiO_2$.KCoFC composite ion exchanger in the form of porous beads [27]. A formulation, B8/p4 was obtained with the highest KCoFC loading of 1.36 g-KCoFC/g-$SiO_2$.

**Figure 2.82. Cubic crystal structure of potassium cobalt hexacyanoferrate ($K_2CoFe(CN)_6$)***



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*CN groups are located between Fe and Co in the framework [28,53].

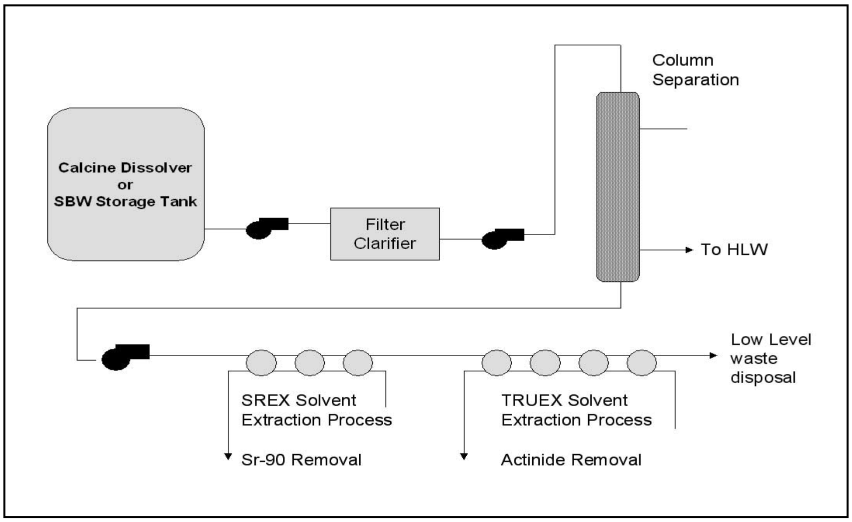
The Cs uptake capacity was determined to be 0.6 meq Cs/g-KCoFC, about 1.6 times higher than that of pure KCoFC. No adsorption competition was observed between $Cs^+$ and $H^+$ in the concentration range 0.001-3 M HCl. However, in the case of $HNO_3$, the $K_d$ of Cs decreases when the concentration exceeds 0.1 M. The distribution coefficient of Cs for KCl in the concentration range 0.001-0.01 M lies between 2-3 x $10^5$ ml/g-composite. Adsorption competition is observed between $Cs^+$ and $K^+$ when the KCl concentration exceeds 0.03 M.

- Ammonium molybdophosphate, AMP

Ammonium molybdophosphate (AMP), especially if immobilised in polyacrylonitrile (PAN), is an engineered form of cesium selective sorbent material developed at Czech Technical University in Prague. It was evaluated with simulated sodium bearing waste (SBW) and dissolved pilot plant calcine at the Idaho Nuclear Technology and Engineering Centre (INTEC) [29].

The AMP-PAN exchanger has high selectivity and capacity for removing $^{137}$Cs from acidic raffinate and acidic waste streams resulting from nuclear fuel reprocessing. The material has been shown to maintain this high Cs capacity with high flow rates of heavily salted feed solutions and also has the unique advantage over other inorganic exchangers in that feed adjustment is not required. Cs removal in a fixed-bed system is a very promising technology and merits further engineering study (Figure 2.83).

**Figure 2.83. Conceptual flow diagram of separation facility at INTEC *[29]**



(*Reprinted from in Tranter T. J, R. S. Herbst, T. A. Todd, A. L. Olson and H. B. Eldredge (2002), *Advances in Environmental Research*, 6(2), 107-121, with permission from Elsevier)

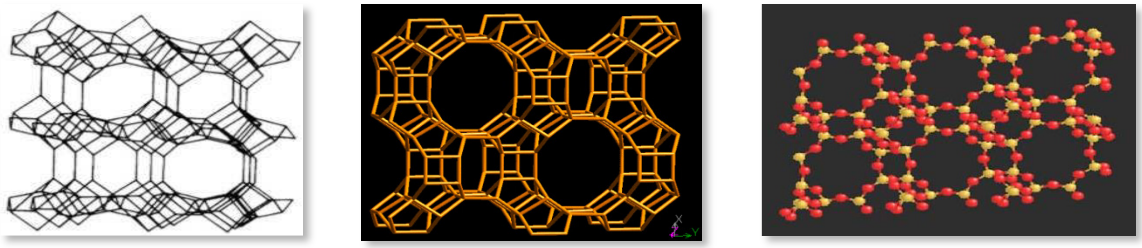
Interesting studies about selective adsorbents for Cs, like potassium nickel hexacyanoferrate(II) (KNiFC), ammonium molybdophosphate (AMP), and ammonium tungstophosphate (AWP) have been conducted in Japan. These adsorbents by themselves are difficult to be granulated to a size large enough to use in an adsorption column, but attempts were made to overcome this problem by two different methods; one is to impregnate the adsorbent into porous media such as zeolite and silica gels [30-32] and the other is to encapsulate the adsorbent in a biopolymer consisting of calcium alginate (CaALG) gels [33-36]. Column experiments with these granulated adsorbents were successfully performed and demonstrated very high selectivity towards Cs. More recently, a new system was studied, where the AMP adsorbents were impregnated into porous media (mordenite) using the biopolymer, CaALG [37]. The microcapsule of CaALG gels can also contain organic extractants; for example, d Sr adsorption was tested by a microcapsule containing the crown ether compound, decyl-18-crown-6 (D18C6) [38]. These adsorption experiments were performed using simulated HLLW, with or without radioactive tracers, and even if the systems were not verified by real HLLW, the separation methods could be easily scaled-up.

- Zeolites

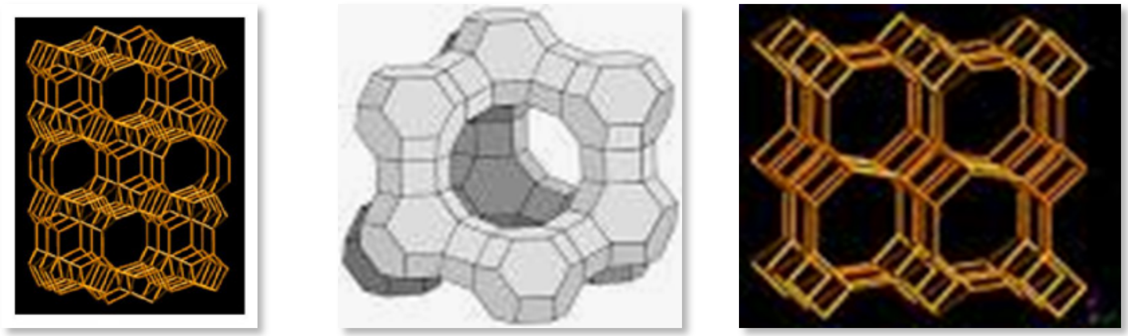
Naturally occurring zeolites were the first inorganic materials to be used for the large scale removal of radionuclides from nuclear waste effluents [28]. They are crystalline alumino-silicate-based materials, built from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral connected by oxygen bridges. The rigid three-dimensional structure, with cavities and tunnels of 4-7 Å in size, often acts as an “ion-sieve” and it structurally separates ions according to size (Figure 2.84). The main properties of the most important zeolites are outlined in Table 2.26 [39].

**Figure 2.84. Structures of naturally occurring zeolites**

(a) clinoptilolite (b) mordenite (c) chabazite*



(d) ferrierite** (e) faujasite (f) phillipsite**



*Source: www.mta.gov.tr/v2.0/eng/daire-baskanliklari/metut/index.php.

**Source: Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures, www.iza-structure.org/databases/.

Synthetic zeolites can be prepared as microcrystalline powders, pellets, or beads; they can be engineered with a wide variety of chemical properties and pore sizes, and are very stable at high temperatures. The main limitations in their use are that they have relatively high costs, a limited chemical stability at extreme pH ranges (either high or low), an ion specificity susceptible to interference from similar sized ions, and a poor mechanical stability, due to their brittleness.

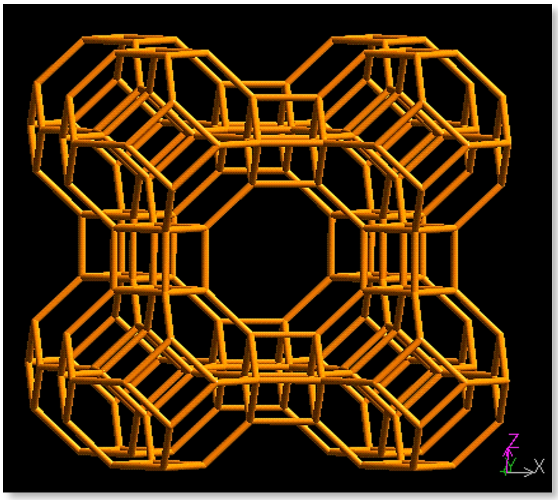
The selectivity and capacity of zeolites can provide a satisfactory processing of low strength salt solutions, while in high salt solutions, such as evaporator concentrates and fuel reprocessing effluents, the processing capacities are very low. As the waste streams usually contain other ions that will occupy some of the exchange sites, the processing capacity is reduced. In particular, potassium interferes strongly with the exchange of cesium.

Research demonstrated that Type A zeolite (Figure 2.85) is the most selective to remove strontium from aqueous waste containing high concentration of sodium salts, and that more than a simple reversible exchange reaction was responsible for this selectivity [40].

**Table 2.26. Selected physical properties of important zeolites [39]**

| Zeolite | Void volume, % | Channel dimensions, Å | Thermal stability | Ion-exchange capacity, meq/g |
|---|---|---|---|---|
| Analcime | 18 | 2.6 | High | 4.54 |
| Chabazite | 47 | 3.7 x 4.2 | High | 3.81 |
| Clinoptilolite | 397 | 3.9 x 5.4 | High | 2.54 |
| Erionite | 35 | 3.6 x 5.2 | High | 3.12 |
| Faujasite | 47 | 7.4 | High | 3.39 |
| Ferrierite |  | 4.3 x 5.5<br>3.4 x 4.8 | High | 2.33 |
| Heulandite | 39 | 4.0 x 5.5<br>4.4 x 7.2<br>4.1 x 4.7 | Low | 2.91 |
| Laumontite |  | 4.6 x 6.3 | Low | 4.25 |
| Mordenite | 28 | 2.9 x 5.7<br>6.7 x 7.0 | High | 2.29 |
| Phillipsite | 31 | 4.2 x 4.4<br>2.8 x 4.8<br>3.3 | Low | 3.87 |
| Linde A | 47 | 4.2 | High | 5.48 |
| Linde X | 50 | 7.4 | High | 4.73 |

**Figure 2.85. Structure of Type A zeolite**



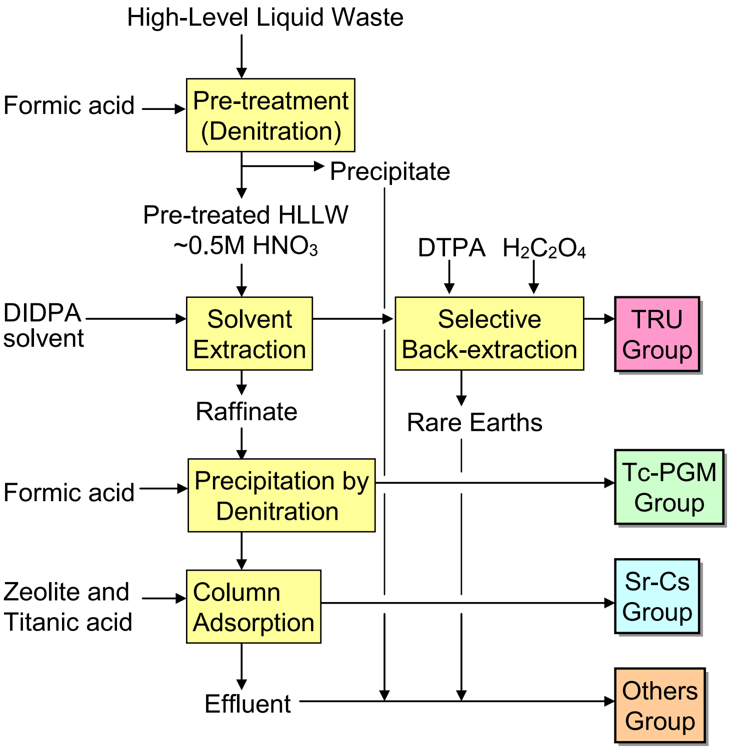
Source: Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures, www.iza-structure.org/databases.

The instability of most zeolites in acid environments considerably limits their application. No acid-resistant, natural zeolites are known with the exception of the two high-silica species, mordenite and clinoptilolite. Their cation selectivity and pH stability range allow them to compete successfully with the more used organic exchange resins. The latter, on their own, are characterised by poor radiation and thermal stabilities, and inability to selectively remove radioisotopes from macro-concentrations of non-radioactive salts.

From the early 1980s, separation by adsorption with inorganic ion exchangers has been developed by Japan Atomic Energy Agency, JAEA [41]. Zeolite (natural mordenite) and titanic acid was applied for the adsorption of Cs and Sr, respectively. Natural mordenite used for Cs separation is available at a small cost, shows almost the same adsorption performance as synthetic mordenite and can be used at about 0.5 M $HNO_3$ solution as the maximum acid concentration [42].

On the other hand, titanic acid requires neutralisation of the solution, which would be the only drawback of this adsorption method. In the 4-Group Partitioning Process developed in Japan,a neutralisation step is used before the adsorption step for Cs and Sr works also for a separation step for Tc and platinum group metals which are precipitated by denitration with formic acid, as shown in Figure 2.86 [43]. The performance of the 4-Group Partitioning Process was confirmed by performing tests with real concentrated HLLW, and decontamination factors for Cs and Sr at the adsorption step were more than $10^6$ and $10^4$, respectively, in all effluent samples [44].

**Figure 2.86. Flowsheet of 4-group partitioning process developed by JAEA**



- Management of spent ion-exchange materials

Loaded ion-exchangers must be immobilised as high-activity waste. Immobilisation is the process of incorporating waste (in this case inorganic ion exchange materials) into a matrix material for solidification and subsequent disposal. In particular, the technique of immobilising radioactive waste in cement has been used in the nuclear industry and at nuclear power centres for many years. Cement has many characteristics in its favour: it is readily available and widely used in civil engineering, the raw materials are inexpensive, and the processing equipment can be based on conventional technology. The resulting waste forms are strong, non-combustible and radiation resistant, have a high density (providing radiation shielding), have a reasonable chemical stability, and have a moderate resistance to the release of radionuclides. The high pH conditions typical for cement results in a low solubility for many radionuclides by the formation of hydrolysed species, carbonates, etc., which provide a good resistance to leaching. The main disadvantage of the process is that the final waste volume is high, compared with the initial volume, owing to the low waste loadings which results are achievable.

In previous studies, inorganic absorbers have been immobilised in cement [45]. These investigations examined the encapsulation of the oxides of titanium and manganese, the phosphates of titanium and zirconium, polyantimonic acid and copper hexacyanoferrate. It was found that, with each of these absorbers, a 33 wt% loading in the waste could be reached, which provides a good quality solidified product.

Also, the immobilisation of a composite absorber in cement has also been examined [46]. Loadings of 5 to 9 wt% of absorber produced acceptable waste forms.

An interesting study made by ENEA [47] took into account the stabilisation of zeolite pellets in type 325 Italian pozzolanic cement. In order to establish the maximum waste loading that was compatible with acceptable characteristics of the final waste form (Figure 2.87), several formulations were tested (Figure 2.88).

**Figure 2.87. Density (*left*) and crush strength (*right*) of zeolite-cement composites [40]**

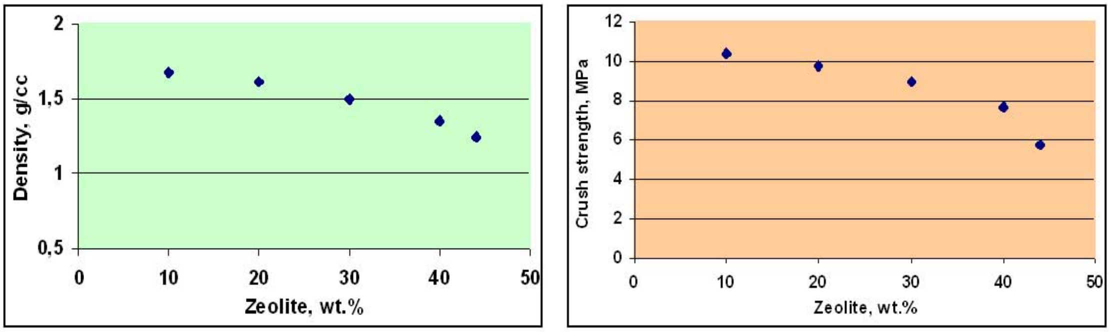
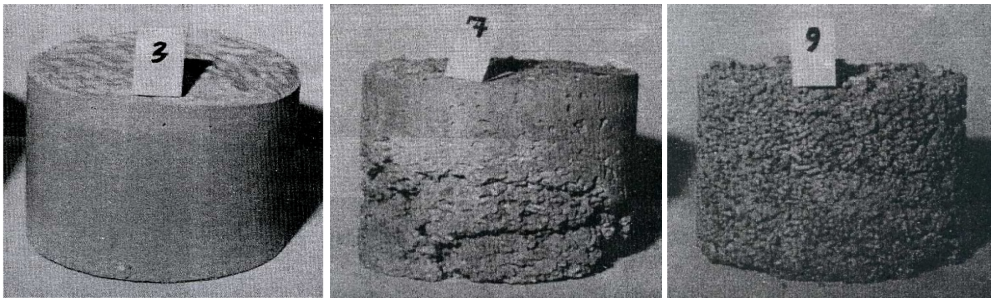


**Figure 2.88. Zeolite-cement composites with increasing waste loadings [47]**



Based on the results obtained, the incorporation of about 30 wt% of dry zeolites into pozzolanic cement can be proposed.

Recent studies demonstrate that the content of saturated zeolites containing $Zn^{2+}$ ions affect the hydration and solidification processes, but do not affect the mechanisms of hydration [48]. Further investigations showed that chabazite and clinoptilolite are suited to cement encapsulation and that the leach resistance is entirely compatible with long-term storage [49]. Solidification of the adsorbents containing Cs and Sr was also performed by cold isostatic pressing and subsequent calcination in Japan [50]. Characterisation of the solid form and leaching tests showed stability enough for waste forms [50,51].

*Plants in operation*

The most important sites where nuclear power plants and reprocessing plants use ion-exchangers are shown in Table 2.27 [28]. A few notes about some well-known plants are reported herein.

**Table 2.27. Ion exchangers tested or in use at nuclear power plants and reprocessing plants [28]**

| Site | Type of waste | Media/Ion exchanger | Radionuclides removed | Starting year of application |
|---|---|---|---|---|
| Loviisa NPP, Finland | Evaporator concentrates | CsTreat® | $^{137}Cs$ | 1991 |
| Olkiluoto NPP, Finland | Floor drains | CsTreat® | $^{137}Cs$ | 1997 |
| Callaway NPP, USA | Floor drains | CsTreat® | $^{137}Cs$ | 1996 |
| Paldiskij, Estonia | Various waste | CsTreat® | $^{137}Cs$ | 1996 |
| Murmansk, Russia | Waste from icebreakers | CsTreat®<br>SrTreat® | $^{137}Cs$<br>$^{90}Sr$<br>($^{60}Co$, $^{125}Sb$) | 1996-1997 |
| JAERI, Japan | Reprocessing waste waters | CsTreat®<br>SrTreat® | $^{137}Cs$<br>$^{90}Sr$ | 1992-2000 |
| Savannah River Site, United States | Contaminated pool disassembly water | CsTreat®<br>SrTreat® | $^{137}Cs$<br>$^{90}Sr$ | 2000 |
| EARP Sellafield, United Kingdom | Reprocessing plant | CsTreat® as precipitant | $^{137}Cs$ | 1994 |
| Paks, Hungary | Evaporator concentrates | CsTreat® | $^{137}Cs$ | 2001 |
| Oak Ridge, United States | Highly alkaline tank waste | CST (IONSIV IE-911®) | $^{137}Cs$<br>$^{90}Sr$ | |
| Hanford, United States | Highly alkaline tank waste | CST (IONSIV IE-911®) | $^{137}Cs$<br>$^{90}Sr$ | |
| Idaho, United States | Acid waste | AMP-PAN | $^{137}Cs$ | |
| Mayak, Russia | Acidic HLW solutions | CCD | $^{137}Cs$, $^{90}Sr$ | 1995 |

Zeolites have been applied to the separation of cesium for years. The naturally occurring clinoptilolite $(Na,K,Ca)_2Al_6Si_{40}O_{72}.24H_2O$, has been used for the removal of $^{137}Cs$, $^{90}Sr$ and corrosion products at the Sellafield SIXEP (Site Ion Exchange Effluent Plant) since 1985. A simplified process flow diagram is shown in Figure 2.89.

The main processes in the plant at Sellafield include:

- the removal of suspended solids in the feed by sand filtration;
- pH adjustment from pH 11.5 down to pH 8.1, by means of carbon dioxide;
- the absorption of caesium and strontium by ion exchange;
- the interim storage of sludges from filter backwashes, etc., and spent ion exchangers.

**Figure 2.89. Simplified process diagram for SIXEP, Sellafield, UK [52]**

(Reproduced with the permission of IAEA)

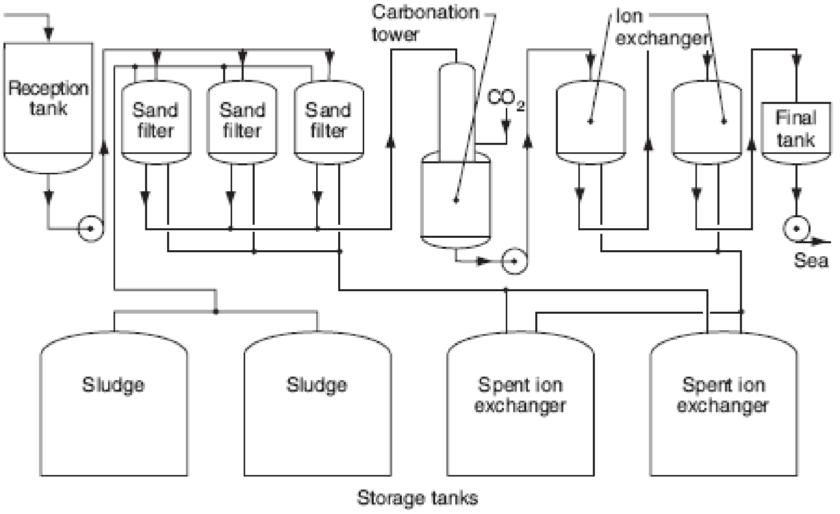
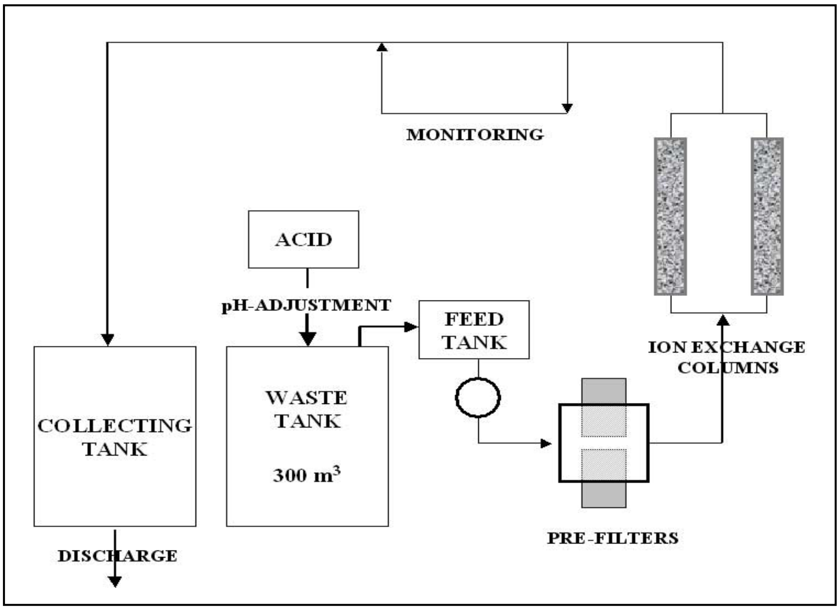


**Figure 2.90. Simplified flow sheet of the IVO-CsTreat System [26]**



In order to minimise the volume of spent ion exchanger arisings, work was done to optimise a system of column reversal such that each charge of material is used first in the trailing position followed by use in the leading column. It has been demonstrated that a few percent of spent ion exchanger remaining in a column after transfer has a marked effect on the decontamination factor obtained from the next charge of ion exchanger in the vessel.

The ion exchanger is discharged hydraulically from the column when it reaches the end of its useful life and is stored in a 1 000 $m^3$ tank similar to those used for sludge.

Trials with the ion exchange material (naturally occurring clinoptilolite) have shown that it can be satisfactorily encapsulated into a high strength concrete.

Potassium cobalthexacyanoferrate (CsTreat) has been successfully used at Loviisa NPP, Finland, since 1991 to remove cesium from a high-salt evaporator concentrate (3 M $NaNO_3$ and 0.3 M $KNO_3$) in column operations (Figure 2.90). It has also been used at Olkiluoto NPP and Callaway NPP, US, in low-salt floor drain waters for the separation of $^{137}$Cs.

At the Enhanced Actinide Removal Plant (EARP), Sellafield, United Kingdom, CsTreat was applied in batch precipitation experiments to remove cesium from both low and intermediate level radioactive waste streams. A schematic diagram of the process is shown in Figure 2.91. The EARP is one of the facilities serving the reprocessing of fuel at Sellafield site. This system is designed to handle in excess of 60.000 m$^3$/y of liquid effluents containing a total of about 2 TBq of alpha activity. Development work demonstrated that it is possible also to improve beta activity removal, particularly in the case of concentrates, by the addition of small amounts of specific inorganic ion exchangers.

**Figure 2.91. Low active effluent treament at the EARP, Sellafield, UK [52]**

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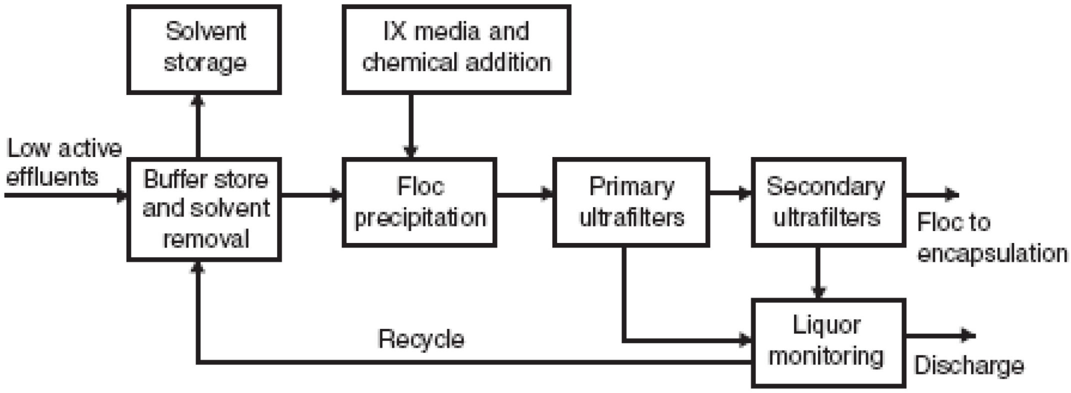


SrTreat was used for the first time in an industrial-scale separation process in Murmansk, Russia, in 1996. During that operation, 2 500 bed volumes of low-active (22 kBq/L) waste solution with moderate salt concentration was decontaminated from $^{90}$Sr with an average decontamination factor of 7 400. The exchanger is especially suited for the decontamination of alkaline concentrated sodium nitrate solutions that are characteristic of neutralised stored waste from some nuclear-fuel-reprocessing plants. It was also applied at Loviisa.

A pilot-industrial facility for HLW partitioning (UE-35) using chlorinated cobalt dicarbollide (ChCoDiC) was built at "Mayak" PA in 1995. The extraction section of the facility was specifically adjusted to the existing and perspective extraction systems. Main units of the facility are four contactors of the mixer-settler type with pulse- phase mixing. The contactors are arranged in blocks, each consisting of two stages in one casing. The total working volume of the contactors is 2.88 m$^3$. The flowrate for the total streams that are processed is around 700 ℓ/h.

The flowsheet involves a unit for filtration of initial HLW and recycle extractant. Furthermore, the UE-35 facility is equipped with a three-stage system of gas-cleaning, an alarm system, a remote system of fire-extinguishing, a system for sampling through stationary boxes with a sample conveyer, a unit for preparation and dosage of reagents, temperature and level control instruments and blocking valve system.Along with assembling and mounting efforts in 1992-1995, a complex of scientific research was carried out. The ChCoDiC-based extraction system was adapted for the combined recovery of Sr and Cs radionuclides from $HNO_3$-solutions of HLW with very high salt content. The operating life of the extraction system was determined in the course of reprocessing of aged defence HLW; it was estimated that as high as 1 900 full cycles of the extractant were used. To assure the operational safety, regarding the stability of hydrazine nitrate in process products, the character of its decomposition, and the distribution of the decomposition product,hydrazoic acid between aqueous solutions and the gaseous phase were studied as applied to HLW partitioning conditions.

In August 1996, the world's first pilot-industrial facility for HLW partitioning was put into operation with the use of actual solutions. In the framework of the stated problem on the combined recovery of long-lived strontium and cesium radionuclides, three contactor units were operating: 8 extraction stages, 2 extract scrubbing stages, 14 stripping stages and 2 entrained recycle extractant removal (diluent washing) stages.

At the beginning of the facility operation, the optimal phase flowrates were established, and the composition of extractant and stripping solution was adjusted. When bringing the facility to stable operating conditions, the total flowrates were about 370 ℓ/h, i.e. somewhat more than 50% of the highest possible value. The extractant composition was consistent with that determined earlier. A 9M $HNO_3$ solution in the presence of 25 g/ℓ hydrazine nitrate was used as stripping agent.

The practically unsalted concentrate of $^{90}$Sr and $^{137}$Cs was added to solutions directed to vitrification. Volume activity of the prepared charge was about 32 Ci/ℓ, compared to 16-20 Ci/ℓ which is obtained in conventional facility. This made it possible to produce glass of two-fold specific activity (up to 550 Ci/kg). As a result, the 5% increase in cost of the partitioning facility has led to the reduction of production costs of high-level glass by 60%. Results of the UE-35 operation at the close of 2001 are presented in Table 2.28. Thus, the operating experience of UE-35 facility enables one to draw a conclusion that it is possible to dispose of the most hazardous waste with concurrent emptying of tanks over several years.

**Table 2.28. Industrial operation results of separation facility UE-35 on PA "Mayak"**

| Operation year | Duration operation, months | Characteristics of reprocessed HLW | |
|---|---|---|---|
| | | *Volume, m$^3$* | *Total activity, kCi* |
| 1996 | 3 | 210 | 11886 |
| 1998 | 2.5 | 95 | 6539 |
| 1999 | ~1 | 62 | 1498 |
| 2000 | ~3 | 254 | 6156 |
| 2001 | 11 | 558 | 23436 |
| Total | 20.5 | 1179 | 49515 |

Finally, silicotitanates, which have a high selectivity for both $^{137}$Cs and $^{90}$Sr, have been tested in the purification of Hanford-site tank waste. However, no industrial processes utilising silicotitanates have been reported.

### *2.2.5. Curium separation technology*

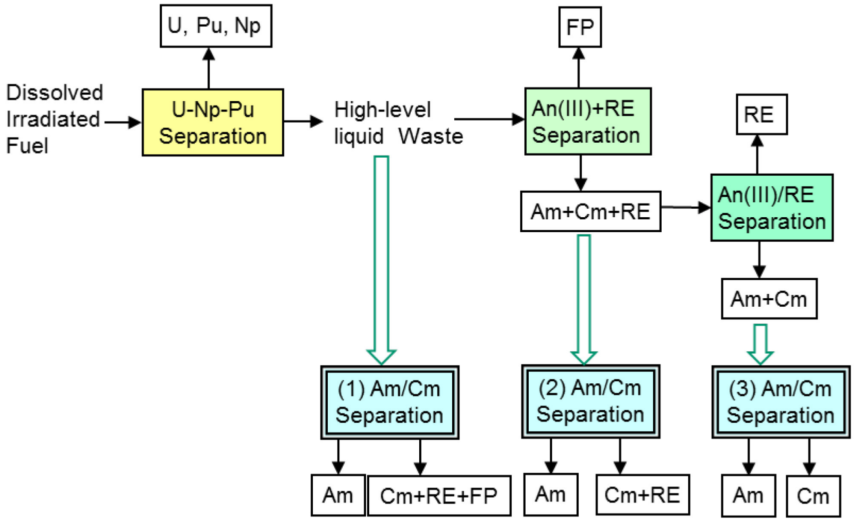
*Introduction*

The most dominant isotope of Cm in the irradiated nuclear fuel of light water reactor is $^{244}$Cm, of which the half-life is 18.1 y. Even though the mass of Cm produced in the nuclear fuel is small, the $^{244}$Cm is the major source of spontaneous fission neutrons and a significant contributor to decay heat emission for several decades after irradiation. For these reason, if Cm is separated from Am which is produced in greater mass in the irradiated nuclear fuel, the treatment of the separated Am becomes easier in the transmutation system. Since Cm and Am show very similar chemical behaviour, separation of Cm from Am is very challenging.

*Separation scheme for Cm*

The separation of Cm from Am can be approached as the separation of Am from other elements including Cm, in high-level liquid waste. Three strategies would be possible as is shown in Figure 2.92. In general, the separation processes become more complicated and difficult when more elements are of concern. Therefore, most studies on Am/Cm separation were carried out to develop the third strategy, which is the separation from the mixture of Am and Cm.

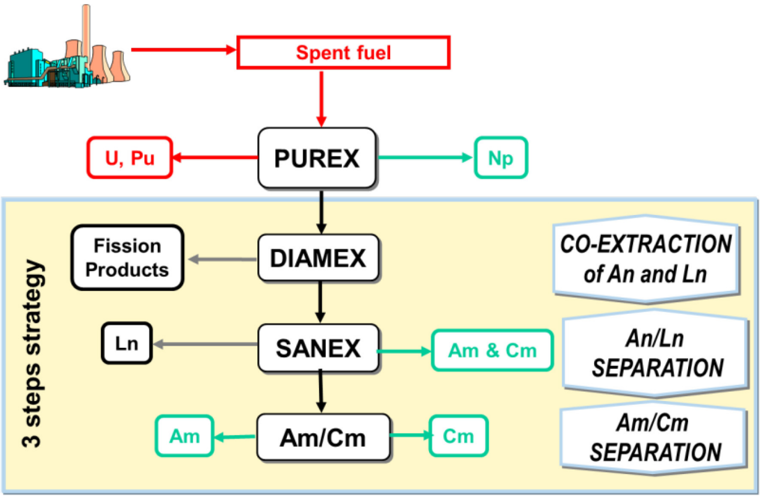
**Figure 2.92. Three possible strategies for Am/Cm separation**



*Process development in France*

Within the framework of the 1991 French Act on High-Activity Waste, a three-step process, which takes the third strategy in Am/Cm separation, was conceived [1-3] (see Figure 2.93).

**Figure 2.93. Three-step strategy for minor actinide separation**



For the third step, Am(III) separation from Cm(III), two options were investigated. The first one, the SESAME process is based on the aptitude of Am to be oxidised to oxidation state VI which is not the case for curium. The second option is based on a solvent separation of Am and Cm in the oxidation state +III.

- a) SESAME process

SESAME (partitioning by selective extraction of americium by electrochemical methods) is based on the selective oxidation of Am(III), previously oxidised to the oxidation state (IV) and then (VI) by electrolysis; a lacunar heteropolyanion is used to stabilise the intermediate state by complexation. The Am(VI) is then easily extracted by the TBP.

After acquiring the basic data relating to the electrochemical oxidation phenomena of Am, as well as its extraction by solvents, validating, by four high-level trials, the different unitary operations of the process and selecting the reagents, the implementation of a scientific feasibility trial was performed in 2001 in shielded cells at ATALANTE under real conditions. The main results of this test are the following:

- a 78% recovery rate of the initial americium, with a purity of 99.5%;
- a loss of 13% of the americium in the catholyte during electrolysis of the incoming flow; this fraction would still be potentially recyclable;
- a leakage of 7 to 8% of the americium in the extraction phase due to limited oxidation into Am (VI) in the incoming flow, which is no doubt attributable to the presence of impurities.

For curium, the recovery rate is 88% in the solution arising from the second extraction and the loss of 14% in the catholyte of the first oxidation. Thus, the SESAME process did not demonstrate its efficiency for reprocessing true high-level effluents.

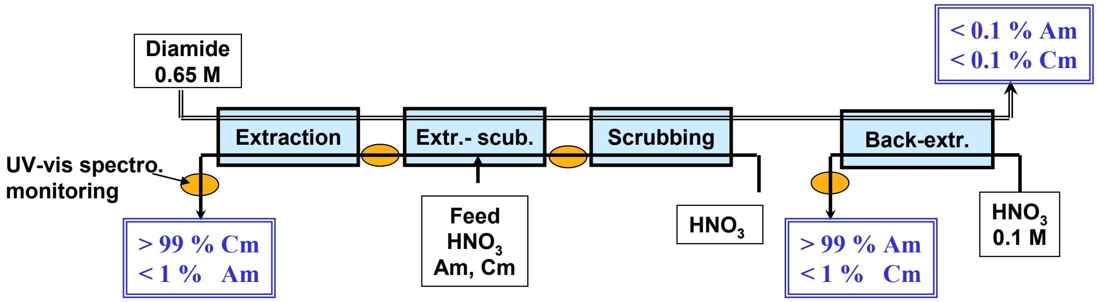
- b) alternative process based on DIAMEX

The inadequate performance shown by the above SESAME experiment has led to the development of an alternative process by liquid-liquid extraction based on the slight selectivity of the DIAMEX solvent for Am(III) versus Cm(III) (separation factor equal to 1.6).

A trial of this alternative process was performed in December 2002 on a representative solution using mixer-settler banks of forty-eight stages for the extraction-scrubbing step. The main results were (Figure 2.94) [4]:

- 99.9% of the two actinides were recovered;
- the recovery rate of americium reached 99.4% with only 0.7 % of the curium from the feed.

**Figure 2.94. Am-Cm partitioning hot test performed on surrogate solution in ATALANTE facility**



- innovative single step process: ExAm

More recently, in the frame of The 2006 Act, the objective was to develop a single step process to recover the sole Am(III). The corresponding process was called ExAm (Extraction of Americium). This ambitious objective appeared achievable partly thanks to the progress accomplished during GANEX process developments [5-6].

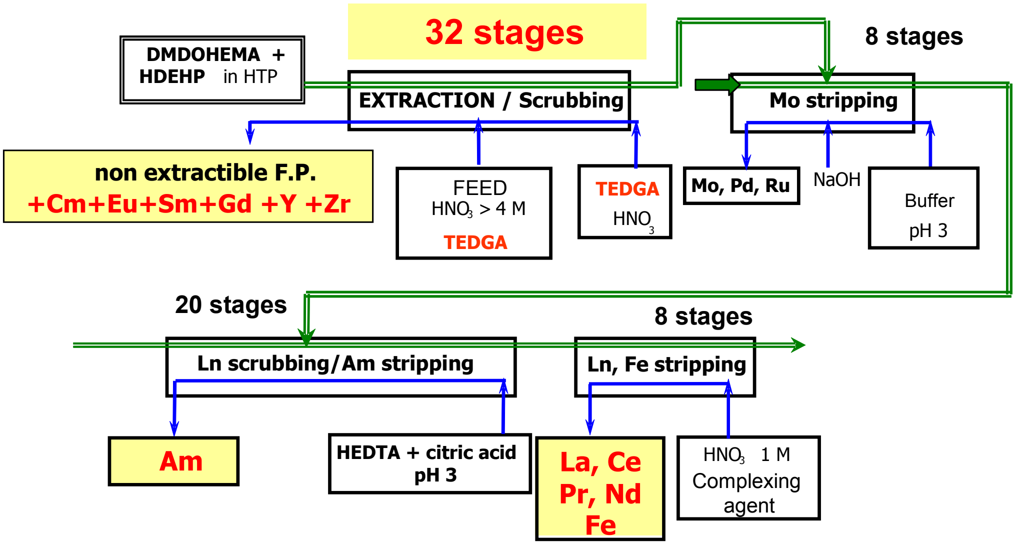
The principle of the ExAm process is also based based on the slight selectivity of the DIAMEX solvent for Am(III) versus Cm(III). Therefore it is possible to extract americium together with some light lanthanides having close values of distribution coefficients in high nitric acidity, while curium and other lanthanides remain in the aqueous phase. The TetraEthylDiGlycolAmide (TEDGA) is added in the aqueous phase, as a hydrophilic ligand, in order to increase the selectivities Am/Cm and Am/heavy Lns, because of the preferential complexation of curium and heavy lanthanides by this amide: global efficiency of the process is largely improved, with a corresponding decrease of the number of the necessary separation stages. Then, Am is selectively stripped from the light lanthanidesas in the DIAMEX-SANEX/HDEHP process [7].

Numerous experimental data have been acquired mainly for the key step (Am+light Lns extraction and scrubbing): distribution coefficients versus [$HNO_3$], [TEDGA], $[\text{cations}]_{org}$; identification and stoichiometry of complexes, both in the organic and aqueous phases;and determination of stability constants between Ln and TEDGA. The data were used to implement a phenomenological model in the PAREX process code.

Spiked counter-current testing, involving mainly the innovative extraction-scrubbing step, was performed in 2009 in the gloveboxes of the ATALANTE facility on a surrogate feed spiked with lanthanides, $^{241}$Am and $^{244}$Cm, to assess the Am/Cm and Am/heavy Lns separation efficiency in comparison with the modelling. Satisfactory results were obtained: more than 97% of the americium was recovered, with a decontamination factor higher than 1 000. The concentrations of the radioelements measured during the test were in good agreement with the values calculated using the PAREX code.

Finally, a complete hot test, using a genuine PUREX raffinate was carried out in April 2010, in order to confirm these promising results (see Figure 2.95). This counter-current hot test lasted about 60 hours. It consisted of 68 mixer-settler stages to enable selective extraction-scrubbing-stripping of americium. Good agreement between experimental and simulated performances was obtained: more than 99% of americium initially in the raffinate was extracted and the decontamination factor of americium versus curium was more than 500.

**Figure 2.95. ExAm process flowsheet tested in 2010 to recover the sole Am(III) from genuine PUREX raffinate**

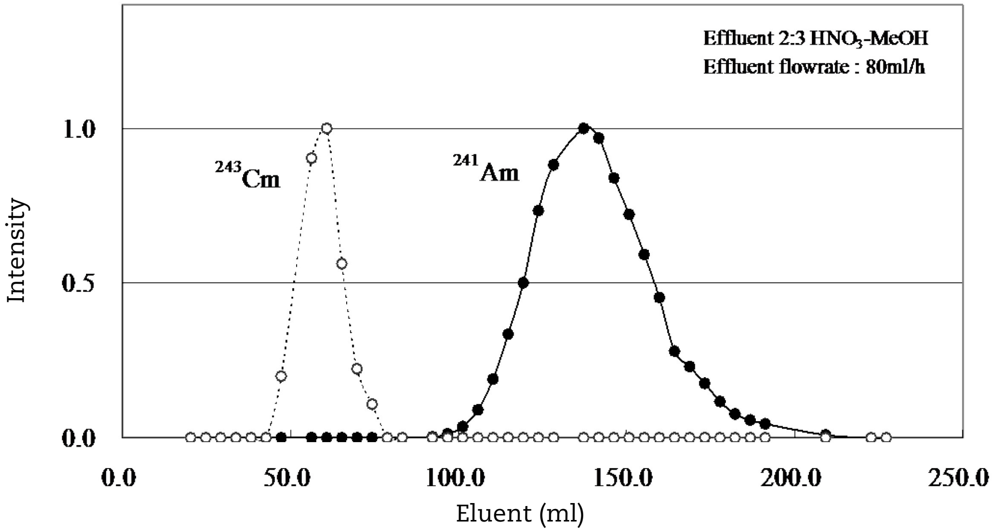


*Study on Cm separation in Japan*

A recent study on Cm separation from Am in Japan was carried out in the framework of the research and development of reprocessing based on ion exchange method by using tertiary pyridine resin [8,9]. The resin was synthesised by polymerisation of 4-vinylpyridine (80 wt%) and m/p-divinylbenzene (20 wt%) on the surface of high porous silica beads[10,11] By using the silica-supported resin, the pressure loss in chromatography operation is considerably suppressed, and ions can easily diffuse into the resin because of the high porous structure. The resin was confirmed to have rather good stability against gamma-irradiation in nitric acid media and a much better stability in hydrochloric acid media [12]. The tertiary pyridine resin has two functions; one is a function of a weakly basic anion exchanger, and the other is a function of the soft donor ligand [9], which can be used both for the separation of trivalent actinides (Am and Cm) from lanthanides [13] and for the separation between Am and Cm [8,9].

The separation of Cm from Am was achieved by chromatography in nitric acid and methanol medium. The methanol promoted the interaction between the actinide cations and pyridine, due to its dehydration effect [14,15]. Similar methods were used in former studies for the separation of actinides elements. These were small-scale applications developed for the purpose of actinide analysis [16]. After, large-scale experiments with Am and Cm tracer were performed, the separation method was tested with a small amount of real dissolved fuel from the test fast reactor “JOYO” [1]. Feed solution for the separation of Cm from Am was prepared by first removing actinides other than Am-Cm and fission products by ion exchange, the drying the Am-Cm residue, and finally redissolving the dried residue with a 2:3 (in volume) mixture of 8M nitric acid and methanol. The Am was separated from Cm using the chromatographic separation from the pyridine resin and the eluent composition was the same as above. Figure 2.96 shows the results of the chromatographic separation test [8]. Cm was almost perfectly separated from Am. The decontamination factor (DF) against Am in the Cm fraction was 8.7×$10^4$ and the DF against Cm in the Am fraction was 2.2×$10^3$. This separation method would be very attractive for the separation of Am from Cm if the use of methanol could be accepted in industrial plants.

**Figure 2.96. Chromatogram of Am and Cm separation by ion exchange using tertiary pyridine-type resin [8]**



Fundamental studies on separation by solvent extraction were also performed to find higher separation factor (SF) between Am and Cm by the combination of an extractant in the organic phase and a complexing agent in the aqueous phase. Sasaki et al. [17] showed a SF of 2.44 in the system of 0.3M DOODA(C12) in the organic phase and 0.01M TEDGA in the aqueous phase. He also showed increased SF of 3.26 in the system of 0.1M TDdDGA – 0.2M DOODA(C2). Here, DOODA(C12), DOODA(C2), TDdDGA and TEDGA is N,N,N',N'-tetradodecyl-3,6-dioxaoctanediamide, N,N,N',N'-tetraethyl-3,6-dioxaoctanediamide, N,N,N',N'-tetradodecyl-diglycolamide and N,N,N',N'-tetraethyl-diglycolamide, respectively.

## 2.3. Pyrochemical processess

### 2.3.1. Introduction

The new reactor concepts under development in the framework of the Gen IV International Forum (GIF) [1] may be able to recycle most of the fertile and fissile uranium and plutonium as well as other long-lived actinides produced in the nuclear fuel. The consequences are that, on one hand, recycle fuel or targets fabrication could be more challenging, but on the other hand the long-term waste radiotoxicity could be considerably reduced. This might be achieved while maintaining or even improving the safety, the economical competitiveness and minimising risks of proliferation.

Two types of processes can be applied to the separation of long-lived radionuclides: hydrochemical (wet) and pyrochemical (dry) processes, or combinatiosn of the two. These have advantages and disadvantages and should be applied in a complementary way. If a so-called double strata concept (e.g. proposed in the OMEGA project [2]) was adapted, the well-established industrial reprocessing of commercial LWR fuel with a recycling of U, Pu, and Np based on PUREX extraction, should logically be combined, with an advanced aqueous partitioning scheme also based on liquid-liquid extraction to separate the long-lived radionuclides along with applicable pyrochemical process steps. In the second stratum of new generation reactors systems, different combinations of wet and dry processe steps may be more applicable because shorter decays periods prior to reprocessing are probable tp maximise recovery of fissile plutonium, and the spent fuel will contain more of the short-lived fission products (higher radioactivity).

Therefore the decision on the partitioning process to be applied should depend on the boundary conditions, such as the most efficient method for accomplishinh the process steps needed. Aqueous- and pyro-partitioning are not to be seen as competitive options to achieve the partitioning of long-lived MAs and fission products from used nuclear fuel. In any case, whatever the reprocessing approach is, an efficient and selective recovery of the key elements from the spent nuclear waste is absolutely essential for a successful sustainable fuel cycle concept. Advanced reprocessing requires the selective separation of Am and Cm from lanthanide fission products which is, a new and challenging task due to the very similar chemical behaviour of trivalent elements. The two major reasons to separate actinides from lanthanides are:

- neutron poisoning: lanthanides (especially. Sm, Gd, Eu) have very high neutron capture cross-sections, e.g. > 250 000 barn for $^{157}$Gd;
- material burden: in used LWR fuels, the lanthanide content is up to 50 times that of Am/Cm.

*Known pyrochemical processes*

Pyrochemical molten salt processes rely on refining techniques at high temperature (500°C-900°C) depending on the melting point of the molten salt eutectic mixture used. Typically chloride salt systems operate at a lower temperature compared to fluoride salt systems. In spent fuel reprocessing technology, some processes are based on electrorefining and others on extraction from the molten salt phase into liquid metal.

For more than 50 years, pyrometallurgy 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, developed at RIAR in (Dimitrovgrad, Russia), was developed for oxide fuels [3], and the second is being developed formetallic fuel in the US as part of the Integral Fast Reactor (IFR) process [4]. 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 the treatment of transplutonium elements and that aspect will therefore be discussed in more details.

The pyro-electrometallurgical process was applied for the first time as part of the IFR system separation process steps for the recovery of uranium and, to some extent, for plutonium. These types of processes have been investigated for decades [5] as the core process in the present EBR-II Spent Fuel Treatment Programme. The fuel is recycled using an pyro-electrochemical process based on molten chloride salts and liquid metals. The fuel is electrochemically dissolved using an appropriate potential between the fuel holding basket, which is used as the anode and a stainless steel electrode in the salt phase, used as cathode. As the fuel starts to dissolve, uranium and a small part of the transuranium (TRU) elements are collected at the cathode. Once the fuel is completely dissolved and most of the uranium is deposited on the solid steel, the cathode rod is replaced by a liquid-cadmium cathode, and the remaining TRUs can be co-deposited with the remaining uranium. The liquid-cadmium cathode is a ceramic crucible, containing molten cadmium and can be lowered into the salt bath. The cadmium in the crucible is put at cathodic potential. Because of the chemical activities of the TRU elements in cadmium, the TRUs can be more easily deposited 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, which are remotely fabricated into recycle fuel.

The alkali, alkaline earth, rare earth and other 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 conditioned into a ceramic high-level waste disposal. More than 90% of the noble metal fission products, fuel alloy material, and chopped fuel cladding segments are retained in the anode baskets. This residue can be stabilised into a metallic high-level waste form for disposal.

Adaptations of the IFR technology for the treatment of both oxide and nitride fuels are being developed in Japan [6]. The flow sheet for the treatment of nitride fuels is similar to that of the metal fuel. Nitride fuels are also fed directly into the electrorefiner, where the actinides are dissolved from the fuel cladding and collected electrochemically in liquid cadmium or bismuth cathodes. A characteristic of this process is an evolution of nitrogen gas. If the formation of $^{14}C$ from $^{14}N$ should be avoided during the fuel irradiation the recycle nitride fuel should be enriched in $^{15}N$. For obvious economic reasons nitrogen should be recycled back into the liquid cathodes where actinide nitrides are formed. This process and the fuel refabrication are challenging. After distillation of the cadmium, the recovered metal nitrides are separated and then fabricated into recycle fuel using a vibro-packing step.

The treatment of nitride fuel is also being investigated in Russia. For fuels from the Russian BREST Lead-Coolant Fast Reactor, the use of natural non-enriched nitrogen is planned [67-70] for the following reasons:

- $^{14}C$, which is accumulated in spent nitride fuel, will not transfer into the gaseous phase as $CO_2$ during the pyroprocessing because of the pure inert atmosphere;
- all of the $^{14}C$ from the spent fuel will stay in the molten salt in the elementary form of a carbon black collected on a melt surface from where this deposited carbon powder may be removed compactly and easily;
- as for economic efficiency of the closed fuel cycle based on nitride fuel, the additional cost of treatment of $^{14}C$ containing waste will be less than the cost of nitrogen enrichment and its subsequent recycling.

*Programmes and strategies*

- European pyroprocessing projects

During the last 20 years, several collaboration projects dealing with separation technology were carried out within the 5th to 7th framework programmes of the European Union. Most of those included the development of pyroprocessing technologies [7-9].

The main objectives of the European pyroprocessing projects were:

- to obtain basic data to allow conceptual design and assessment of reprocessing processes suitable for many different types of fuels and targets;
- to assess the feasibility of separating uranium, plutonium and minor actinides from fission products using pyrometallurgy in a molten chloride or fluoride system;
- to identify and characterise solid matrices for the conditioning of the waste resulting from the pyroprocesses;
- to carry out system studies for comparing some selected reprocessing methods for used fuels from advanced nuclear reactors including the accelerator-driven system (ADS);
- to revive and consolidate European expertise in pyroprocessing.

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

A very important work was the thermodynamic data acquisition in molten chloride media, with a comprehensive study of actinides, lanthanides and other important fission products. In comparison to molten chloride salts, studies in molten fluoridesalts are much less developed. Even if many experiments are carried out in various salts, it appears to be more difficult to get relevant thermodynamic data, mainly due to the lack of a reliable reference electrode. Particularly for Cm, the data available are very scarce.

Two efficient processes for the separation of An from Ln have been selected as promising core processes: (1) electrorefining process on a solid reactive cathode in molten chloride, and (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.

These results were used to optimise the two reference core processes. Moreover, several new experimental installations for process tests have been designed and constructed. In the United Kingdom, NNL has built a new facility in an alpha-active glovebox. In Italy, ENEA has commissioned the Pyrel II facility for process scale-up and modelling. 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.

Another key issue, similar to aqueous-based technology, is the waste issue. Successful recycling should have similar goals for the acceptable loss of uranium and TRUs, and this should be applied to all methods of reprocessing. A realistic value for losses is below 0.1% for all actinides. In particular, pyroprocesses should produce the lowest possible volume of waste salts, and those waste salts that are produced must be converted into an acceptable form for storage and disposal. Real progress has been made in the decontamination of used chloride salts coming from electrorefining. Both of the techniques of zeolite ion-exchange filtration and phosphate precipitation were selected for the ability to efficiently treat used salt waste. A number of specific matrix materials for salt confinement were identified (sodalite, pollucite); however, further work is still needed.

The system studies which were performed in the course of the European Research Programmes for development of the fuel cycles included: (1) double-strata concept for ADS, (2) IFR, and (3) molten salt reactor. In a first step, the general principles used for the assessment of pyrochemical separation processes were defined and a common methodology for technical and economical comparisons and the selected flowsheets was set up. During the second step, the work focused on detailed flowsheet studies and mass balance calculations. The major interest of these studies was the validation of the "process approach", a very useful tool to identify key issues and eventually re-orient R&D programmes. A large variety of basic properties of An nd some FPS in molten salts (chlorides and fluorides) and in liquid metal solvents were studied [10-12]. Since the flow sheets addressed different scenarios and fuels, it was very difficult to make a direct inter-comparison in terms of advantages and disadvantages.

In molten chloride media, significant efforts were made in basic data acquisition, mainly at ITU with a comprehensive study of actinides (U, Pu, Np, Am, Cm), lanthanides and important fission products. Thermochemical properties were derived from the electrochemical measurements and from basic thermodynamic data, for example, in the case of Np for $NpCl_3$ and $NpCl_4$ in the crystal state [13,14]. It was demonstrated, that $NpCl_3$ has a strong non-ideal behaviour in molten LiCl–KCl eutectic. For these experiments a double glovebox was constructed, where the outer glovebox was operated under nitrogen and the inner box under a purified argon atmosphere at over pressure condition. This allowed maintaining a very pure Ar atmosphere and provides excellent conditions for a precise determination of the required data. Auxiliary equipment was devoted to chlorination, material processing and electrochemistry in room temperature ionic liquids, a potential alternative to the high temperature molten salt systems [15].

- Pyroprocessing strategy in Japan

Despite not be industrially deployed, intensive efforts of R&D on pyroprocessing have been lcarried out in several countries, includinh the US [16,17] and Japan [18,19] since 1980s, and followed more recently by Korea [20] and India [21]. The process includes the transportation of actinides from the anode to a cathode through a LiCl-KCl eutectic salt at around 500°C. Spent fuel in the metal form is loaded in an anode basket, and a separated actinide metal (usually uranium) is collected at the cathode. The recovered actinide metal can be a source material of recycle fuel for fast spectrum reators. The advantage of the process is that it does not require additional processes to recover minor actinides, because a similar electrochemical process step collects actinides, U, Np, Pu, Am and Cm, together [22]. This leads to a crucial level of radiation [23]. Pyrometallurgical processing with metal electrorefining was initially proposed for recycling technology of metal fuel from a fast reactor collocated to a processing facility, such as the integral fast reactor, IFR [24]. It currently, expands to treat oxide fuels, in which oxides should be reduced to metals [25,26] prior to recovery of actinides by electrorefining. Meanwhile, uranium recovery prior to the oxide reduction was also proposed to reduce the volume to be treated with electrorefining. The waste salt used in a main stream is purified by removing remaining actinides and fission products and recycled them to minimise the volume of waste.

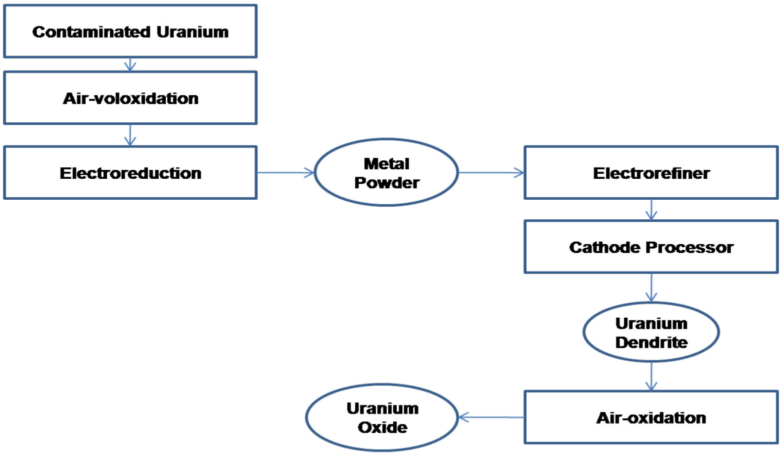
### *2.3.2. Uranium recovery*

A lot of reusable uranium (DU, NU, LEU) in the form of metal, such as $UO_2$, $UO_3$ and $UF_4$ is stored worldwide [27] and some member states have developed pyroprocessing techniques in order to allow the recovery of pure uranium before its conversion to uranium oxide in air.

*Uranium recovery process developed at KAERI (Korea)*

A flow diagram for the pyroprocessing of $UO_2$ is illustrated in Figure 2.97. In order to recover relatively pure uranium oxide from contaminated uranium sources, the off-specification uranium is first converted and pulverised into $U_3O_8$ powder by air-voloxidation in order to reduce it easily into a metal form. The $U_3O_8$ powder is introduced into a LiCl molten salt bath for a conversion of the oxide powder into a metal form. During the electrochemical reduction step, the oxide powder is reduced into a metal form which normally contains most of the transition elements, uranium and rare earth elements, thus just leaving group I and II elements in the molten LiCl salt phase. The metal mixture is then transferred to the electrorefiner with LiCl-KCl eutectic salt in order to recover the pure uranium on the solid cathode. The uranium is continuously collected at a solid cathode and spontaneously falls from the surface of the solid cathode to the bottom of the electrorefiner, and then the deposit containing the salt is sent to a cathode processor to distill the salt to make pure uranium dendrite. After the cathode process, the pure uranium dendrite is oxidised to a uranium oxide powder.

**Figure 2.97. A schematic block diagram for the treatment of contaminated uranium**

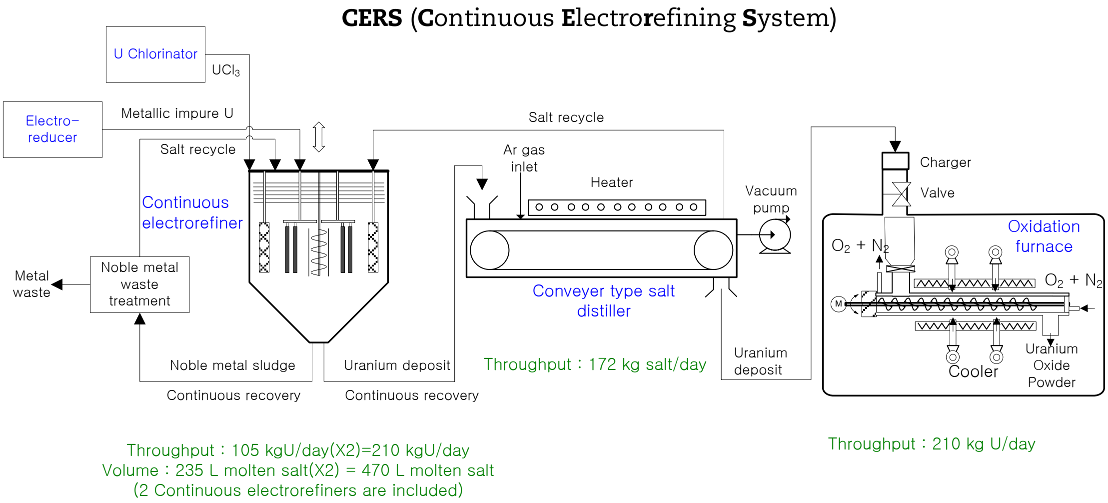


- Electroreduction

The contaminated uranium in the form of chips or particles is first oxidised in ambient or dry air in order to remove some species such as carbon in the form of gases. Under oxidising conditions, stable $UO_2$ forms $U_3O_8$. The reaction temperature should be higher than 500°C to obtain a sufficient reaction rate under an excess air blowing condition. The resulting oxide is sintered to granules and fed to an electroreducer where the oxide is reduced to metal. The electrolytic reduction occurs in a molten LiCl-1wt% Li2O electrolyte at 650°C [28]. The Li metal is formed by electrolysis of Li2O on the cathode surface. The electrochemically produced Li metal proceeds with a chemical reaction with $U_3O_8$ to form a metallic uranium and $Li_2O$. The resultant $Li_2O$ is ionised and the $O_2$- ion is eventually evolved as $O_2$ gas on the anode surface.

The reduced metal is further treated in a subsequent salt removal process to separate the salt residue from the recovered metal. The salt is evaporated at around 700°C under a vacuum. More than 99% of the salt contained in the metal product is removed by this process. The treated uranium metal granules are transported to an electrorefining step where the metal is used as an anode.

**Figure 2.98. Schematic process diagram for electrorefining**



- Electrorefining for the recovery of pure uranium

The role of the electrorefiner is to separate the uranium from the impure uranium mixture which is the product material of the electroreduction system. The uranium metal from the electroreduction system is fed into an anode basket, which is placed at the periphery of the reactor. They rotate to enhance the solution mass transfer. The cathodes are where the uranium dendrites are deposited in the core part of the reactor. The salt is a LiCl-KCl eutectic solution. It also contains $UCl_3$ for the uranium ion. The deposited uranium at the cathodes is separated spontaneously at 500°C. It is continuously collected at the bottom of the reactor and conveyed to the salt distiller [29].

The remaining materials after a depletion of the uranium from the feed material at the anode basket are noble metals such as Fe and Mo in this system. Silicon which is reduced by the electrolytic reducer is thermodynamically more noble than Zr and U, so it does not dissolve in the electrorefiner under the usual electrorefining conditions. Hence, silicon is retained in the anode basket and recovered with the noble metals. They are ultimately collected at the bottom of the reactor and separated from the uranium product. A part of rare earth elements are introduced into the electrorefiner as an oxide form. This rare earth oxide reacts with $UCl_3$ during the electrorefining step. In this step, a small portion of $UCl_3$ transforms into uranium oxide, and is recovered with noble metal particles. The U recovery depends on how much impurities are included in the feed material. The recovery of uranium using pure depleted U as a feed material is usually more than 99%.

Uranium deposits from the electrorefiner contain about 30~40 wt% salts. In order to recover pure uranium and transform it into an oxide form, the salts have to be removed from the uranium deposits. A certain amount of the uranium deposits containing salts conveyed from the electrorefiner is fed into the salt distiller. Then, a batch operation for the removal of salt is carried out by heating and vacuum evaporation. It is operated at 700 ~ 900$^0$C and less than 1 Torr. Thereafter, the salt-removed uranium dendrites are transferred to the uranium oxidation system, which transforms the pure uranium metal into an oxide form. The removal efficiency of the salts is more than 99% for manufacturing pure uranium metals.

The role of a U chlorinator is to supply the initial U in the LiCl-KCl eutectic salt to an electrorefining reactor. The process for a uranium chloride salt product includes two steps: reaction of gaseous chlorine with liquid cadmium to form $CdCl_2$ which occurs in the Cd layer, then $UCl_3$ is produced by the reaction of U in the LiCl-KCl eutectic salt and $CdCl_2$. The apparatus for producing $UCl_3$ consists of a chlorine gas supply, a chlorinator and an off-gas wet scrubber.

- Conversion of uranium metal to oxide powder

The oxidation furnace can fully oxidise the distilled uranium power fed from the distiller by heating with $O_2$ + $N_2$ gas. The oxidation furnace consists of a hopper, a chamber, and a screw with a motor, a heater and a cooler, and a gas injector.

A certain amount of distilled dendrite is fed into the oxidation furnace chamber and heated at 200 ~ 500$^0$C with $O_2$ + $N_2$ gas. The heated dendrite powder is oxidised and produces heat due to its exothermic reaction. The oxidation reaction is carried out properly by controlling the amount of $O_2$ and $N_2$ and the cooling rate.

- Off-gas treatment

The off-gases generated in this process consist of $O_2$, $CO_2$, air and $Cl_2$. Especially, $Cl_2$ off-gas is issued from the $UCl_3$ chlorinator. Since the $UCl_3$ is required as an initial material for a uranium deposition, an additional treatment process has not been considered.

- Waste salt treatment and management

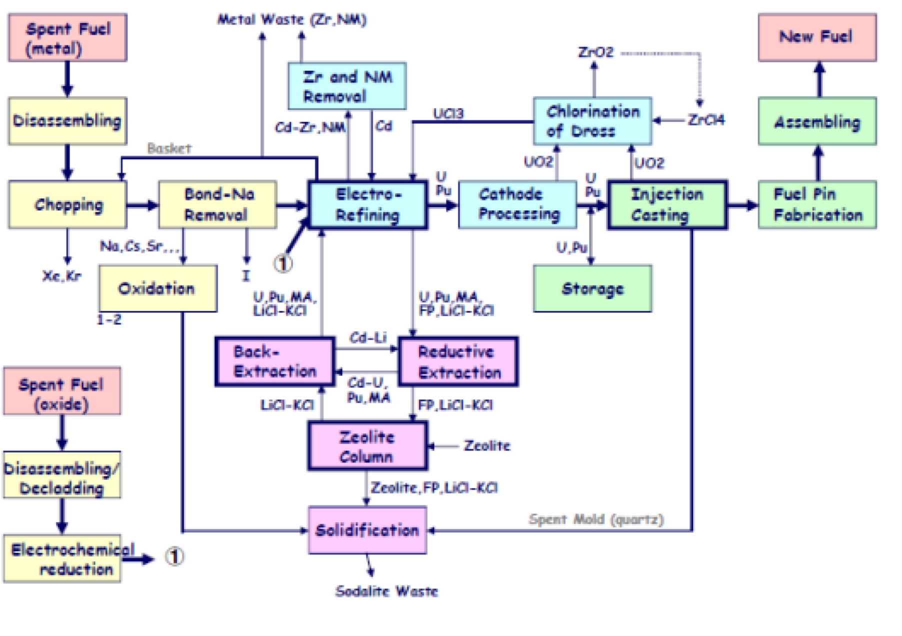
The waste salts are LiCl and eutectic LiCl-KCl salt. It is expected that the contamination of LiCl would be negligible; however, some rare earth elements might be accumulated in the eutectic LiCl-KCl during electrorefining and thus change the physical properties of the electrolyte. Hence, a waste salt treatment and management process should be considered according to the initial content of rare earth elements in the contaminated uranium oxide.

*Pyrometallurgy with $UO_2$-electrowinning developed in Japan*

- Basic process description

Figure 2.99 shows the process diagram for a metal fuel cycle and for oxide fuel treatment. The upper stream is the main process to recover uranium and transuranium elements by electrorefining, and to make new fresh fuel by injection casting after distillation of salt. The lower stream with extraction is the salt waste treatment process where refined salt that has been passed through a zeolite column is recycled into the main process. Absorbed salt form the zeolite column contains radioactive fission products and is heat-treated to make a stable sodalite form, which then could be disposed of into a geologic repository. To minimise the waste volume, most of the solvents, i.e. salt and liquid metal, are recycled after refining or re-used after distillation. The treatment of spent oxide fuels is also depicted in this figure. Most elements in oxides form after conversion to metals are transferred to the electrorefining. Some elements, such as alkali and alkaline earth elements, resolve into salt and accumulate. As an option, uranium dioxide consisting for most part of spent fuel can be electrowinned prior to the electrochemical reduction in order to minimise the volume to be treated in the following processes. The actinide metals separated by electrorefining and distillation of salt/cadmium are conveyed to a fuel fabrication process with injection casting after adjusting a composition.

**Figure 2.99. Process diagram for metal fuel cycle and for oxide fuel treatment**



- Uranium recovery (as necessary)

Spent fuel from LWRs contains more uranium than plutonium and minor actinides. The ratio of U/Pu is much higher than the ratio which satisfies the composition of fresh fuel for FRs, in which plutonium ratio of is 15-25% depending on the requirements for the core design of FRs.

In the case where the pyrometallurgical process is applied on spent fuels of LWRs, the additional option with $UO_2$-electrowinning prior to reduction of the oxides helps to significantly reduce the volume to be treated in the following steps and to adjust the fuel composition for FRs. The electrowinning occurs according to the following equations:

$$\text{Anode:}\quad UO_2 \longrightarrow UO_2^{2+} + 2e^-$$
$$\text{Cathode:}\quad UO_2^{2+} + 2e^- \longrightarrow UO_2$$

Spent $UO_2$ or MOX from LWRs loaded in an anode basket re electrolysed to collect a pure-$UO_2$ on a cathode in a LiCl or LiCl-KCl bath at 550°C or higher temperature so as to achieve a high electric conductivity. Alkali and alkaline earth elements dissolve into a salt to make cations of those elements and produce $O^{2-}$.

The issue foreseen in this process is a contamination of salt at the subsequent reduction process. $UO_2^{2+}$ ions adhered on the oxides at the anode are conveyed into a salt of LiCl, and precipitate as $UO_2$ by reduction in a bottom of the reduction furnace. Pyrographite is the most appropriate candidate for crucible components, vase, anode basket and cathode. Contrary, pyrographite is not usable in the subsequent reduction process, because lithium metal as a reductant easily penetrates into and reacts with pyrographite.

- Reduction

Oxides from spent fuels or after $UO_2$-electrowinning are required to be reduced to metals by chemical reduction or electrochemical reduction. The chemical reduction with Li as a reductant reagent has been verified by use of sim-fuel contained fission product elements [30].

The chemical reduction occurs as following equation:

$$MO_2 + 4Li \longrightarrow M + 2Li_2O$$

Currently, many efforts are devoted to the electrochemical reduction, aiming for the minimising of a secondary waste. The oxides on a cathode electrochemically are reduced to metal using an inert anode in a LiCl bath, based on the following reaction.

$$\text{Cathode:}\quad MO_2 + 4e^- \longrightarrow M + 2O^{2-}\ \text{(salts phase)}$$
$$\text{Anode:}\quad 2O^{2-}\ \text{(salt phase)} \longrightarrow O_2 + 4e^-$$

where M denotes actinides, such as uranium and plutonium.

- Electrorefining

The metals used in rectors are electrorefined to recover actinides in a LiCl-KCl bath at 500°C. The solid cathode is used to recover uranium metal and the liquid cathode for plutonium and minor actinides. Similar electrochemical potentials of actinides due to low activity coefficients in liquid cadmium make it possible to recover plutonium, neptunium, americium and curium together. The following reaction occurs:

$$\text{Anode:}\quad M \longrightarrow M^{x+} + xe^-$$
$$\text{Cathode:}\quad M^{x+} + xe^- \longrightarrow M\ \text{(on solid cathode)}$$
$$M^{x+} + xe^- \longrightarrow M\ \text{in Cd (in liquid cathode)}$$

Uranium metal deposits on a solid cathode with dendrite formation. Uranium and plutonium collected into the liquid cadmium cathode form inter-metallic compounds, such as $UCd_6$, $UCd_{12}$, $PuCd_6$ and $PuCd_{12}$ when exceeding low solubility limits.

Candidate is stainless steel for constituent material including anode and cathode baskets.

- Achievement

- Electrochemical reduction

Figure 2.100 shows the process for treatment of spent oxide fuels. The $UO_2$ pellets with low theoretical density of 60 – 70% were prepared prior to the reduction [31]. The pellets are loaded in a cathode basket (a) where they are electrolytically reduced in a LiCl salt with 1wt% Li2O at $650^0$C.

Figure 2.100. Pyrochemical reprocessing flow for spent oxide fuels

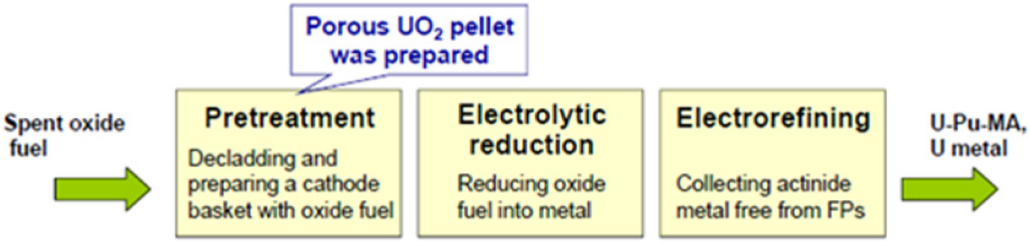
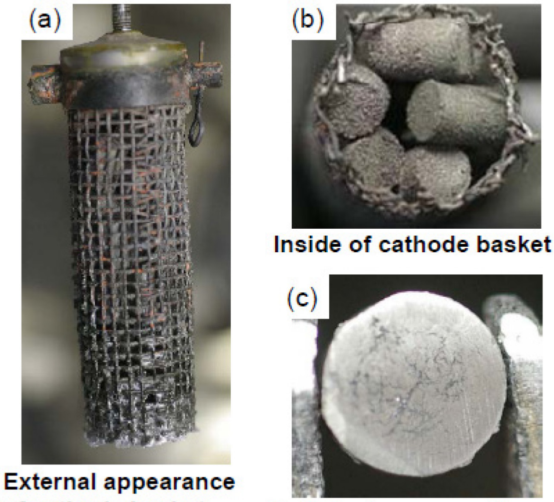


Figure 2.101 exhibits the cathode basket and uranium metals reduced in the basket. Ca.100g of $UO_2$ were completely reduced within 10 hours at the current density of 62-64%. The metals covered with salt (b) are conveyed to the electrorefining process to recover uranium on a solid cathode. The metal phase appears entirely in the cross-section of the pellet after reduction (c).

Figure 2.101. Cathode basket and uranium metals reduced



Inside of cathode basket

External appearance of cathode basket

Polished cross section of reduced $UO_2$ sinter

- Electrorefining

The engineering scale model of the electrorefiner was installed in a uranium facility to achieve high collection efficiency. Figure 1.3.6 depicts each device of an electrorefiner.

Ca. 10kg of U metal was loaded in two pairs of anode baskets and electrochemically transferred to a solid cathode located by the encompassing anode baskets. The electrolyte is a LiCl-KCl eutectic salt operated at 500°C. The morphology of uranium metals accumulated in the bottom collector by scraping uranium deposited on a cathode wall are also shown in Figure 2.102 [32].

**Figure 2.102. Engineering-scale electrorefining test**

- Melt transfer rig

In order to achieve a high throughput and improve operational capability, the transferring rig of the melt has been developed. The large scale of argon-atmosphere glovebox was installed, in which an engineering scale of electrorefiner and distillation furnace were located. The system is equipped with a transferring rig of salt and liquid cadmium with a pumping system operating at high temperature [33]. The exploiration of a pumping system has started in order to examine the transferring rate depending on a pumping capability.

- Salt waste treatment

The waste salt treatment has to be effectively designed in order to minimise radioactive waste. The salt which contains a small amount of actinides conveyed from the refining process contacts with cadmium with some amount of lithium as a reductant by a multistage counter-current extraction. The actinides reduced into cadmium are again oxidised in a LiCl-KCl salt, and then re-used in the electrorefining (see Figure 2.104). Laboratory scale experiments with simulated and genuine material prepared by reprocessing of spent fuels have verified the recovery more than 99.5% of each actinide, i.e. Np, Pu, Am and Cm, into liquid cadmium [34,35]. The salt, from which actinides are removed, still contain a large amount of fission products. Zeolite is the potential material to absorb most of the fission products. Figure 2.106 shows the schematic diagram of a scrubbing system of waste salt as well as the engineering scale test equipment. The zeolite with fission products is transformed to sodalite when treated above 1 500°C. Sodalite, which is stable artificial mineral with low leachability, should be disposed into a geological repository.

**Figure 2.103. Molten salt transport test**

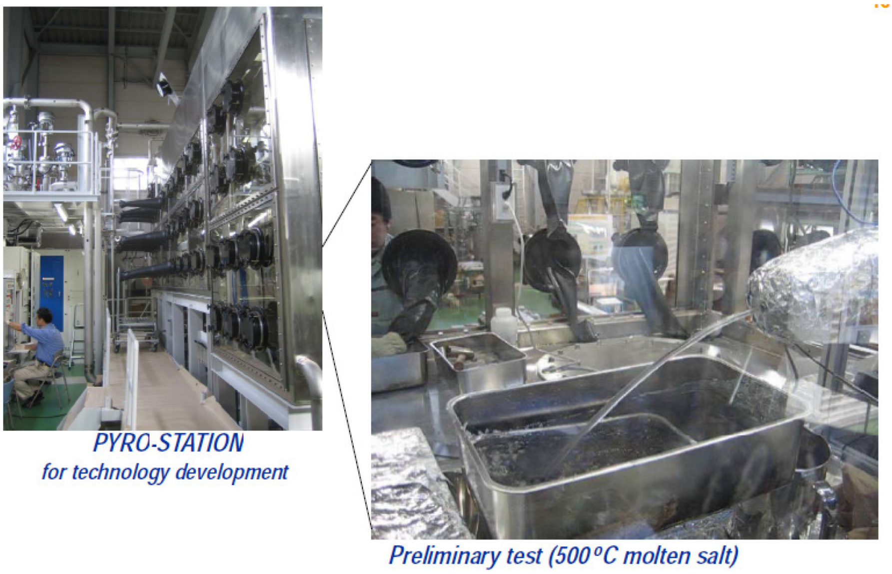
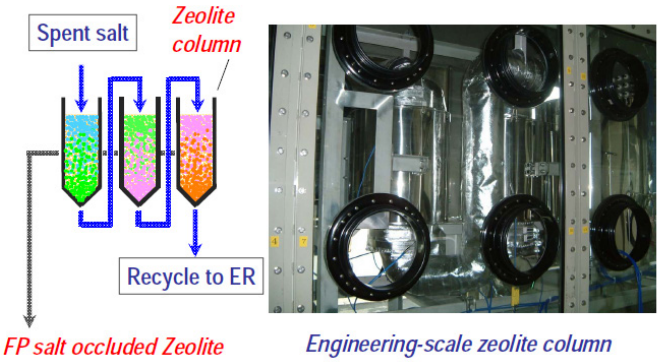


**Figure 2.104. Schematic diagram of scrubbing system of waste salt and the engineering scale test equipment**



- Future activities

Main programmes consist of the process verification with irradiated materials and the development of an engineering scale device. The pyroprocessing verification for an oxide including material balance is under investigation by use of commercially irradiated MOX fuels through the co-operation of the Institute of Transuranium Elements in Karlsruhe. The irradiated metal fuels containing minor actinides are investigated to verify the integral system metal fuel cycle. Irradiation of those fuels were completed without any failure up to ca.10 at% burn-up in the Phenix reactor in France and most of the fuels have been transported in a hot cell at ITU. The development of an engineering scale device will be used to explore a throughput capacity of each unit more than 10t/y. This programme is proceeding in a uranium facility and in an inactive facility described previously. In addition to two large programmes, a design study of accounting measures of fissile material for safeguard systems should also be explored.

### *Development of the US electrochemical process for processing used nuclear fuels*

The pyrolytic electrochemical (EC) process for separation of used nuclear fuels (UNF) has been under development at US national laboratories, primarily Argonne National Laboratory and Idaho National Laboratory, since the 1980s. Flowsheets have been developed to process oxide fuels from Light Water Reactors or Fast Reactors and metal fuels from Fast Reactors. Current development work is aimed at improved online monitoring of the fissile plutonium by means of cyclic voltammetry or optical spectrophotometry to enable efficient process control as well as for safeguarding the process.

- Online monitoring – Cylic voltammetry

Online monitoring of the actinide concentrations in the electrochemical systems is necessary for process control/monitoring as well as for safeguarding the process. For the past several years, electroanalytical methods such as cyclic voltammetry (CV) have been shown to provide high-precision (i.e., relative errors are <1%) online measurements of U and Pu concentrations in a molten salt when standard area addition is combined with proper electrode pretreatment protocols.

Studies have examined U, Np, and Pu concentrations ranging from 0.5 wt% up to 2 wt% and U concentrations as high as 10 wt%. The higher concentrations are more typical of actual processing conditions and proved to be more challenging than the lower concentration measurements in three respects. First, the higher concentrations required a more extensive electrode pretreatment protocol as well as a larger electrode diameter to achieve reliable measurements using the standard area addition method. Second, the higher concentration tests indicated that the $U^{3+}$ diffusion coefficient decreases slightly after the concentration exceeds 2 wt%. This result raised the possibility that fission product cations (e.g. $Cs^{+}$, $Ba^{2+}$, $Sr^{2+}$, and lanthanides) may also alter the U and Pu diffusion coefficients requiring solution-specific calibration cures to correlate the voltammetry data with concentration. These calibration curves can be developed whether using a range of simulated salt compositions or using ex situ samples of electrorefiner salt with standard additions of U and Pu. Third, voltammetric measurements of multicomponent systems at higher concentrations required a refinement of the data analysis method to prevent interference effects. Specifically, the extended tail of the $U^{3+}/U$ voltammetric peak makes it difficult to accurately determine the baseline for the adjacent $Pu^{3+}/Pu$ voltammetric peak. Fortunately, the difficulty can be resolved by using semi-differentiation, a mathematical manipulation of the voltammetric data.

Applying a semi-differential treatment of the current vs. time data improves the baseline resolution between the U and Pu deposition peaks as well as giving an additional reduction in relative error. After semi-differentiation, baseline determination is straightforward and the resolution between peaks is improved as well. Concentrations were determined with a relative error of less than 1%.

Collectively, these refinements in experimental technique and data analysis continue to demonstrate the viability of using CV for online measurements of U and TRU in the electrorefiner salt over the range of concentrations that will be encountered in processing systems.

- Online monitoring – Optical spectrophotometry

The objective has been to obtain fundamental information needed for online, real-time, process spectroscopic instrumentation to be designed for use in monitoring and controlling fuel reprocessing flow sheets. The goal of this work was to establish quantitative optical detection of U, Pu, and Np in molten salt media to support electrochemical process monitoring under pyroprocessing conditions (LiCl/KCl eutectic, 500°C). Initial experiments were designed to demonstrate this ability using vis-NIR and fluorescence spectroscopy on molten salt/non-aqueous systems. While the goal was to measure actinides in LiCl/KCl molten salt media, initial work was focused on moderate-temperature molten salt systems and using lanthanides as non-radioactive surrogates for the actinides.

Recent work performed vis-NIR and electrochemical measurements under pyroprocessing (molten salt) conditions. Both optical and electrochemical researches under pyroprocessing (molten salt) conditions have been accomplished. Vis-NIR measurements of a series of lanthanide salts (simulants for actinides Pu, U, Np) in LiCl/CsCl and LiCl/KCI molten salt media were performed, and Beer's law observance was demonstrated. Quantitative PLS models were demonstrated on multicomponent mixtures of lanthanides within the molten salt media. Electrochemical measurements of Us, Tm, and Sm in molten salt and ionic liquid (IL) media were performed using various electrochemical and spectroelectrochemical techniques.

### *2.3.3. Options for co-processing of actinides*

*Introduction*

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 a possible option to selectively separate transuranium elements (TRU). However the success of this process is not very encouraging, the decontamination factors that can be obtained are always very 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 a on solid aluminum cathode in molten chloride and the one based on liquid-liquid reductive extraction in a molten fluoride/liquid aluminum were extensively studied in both European and Japanese (electrochemical route only) programmes. 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.

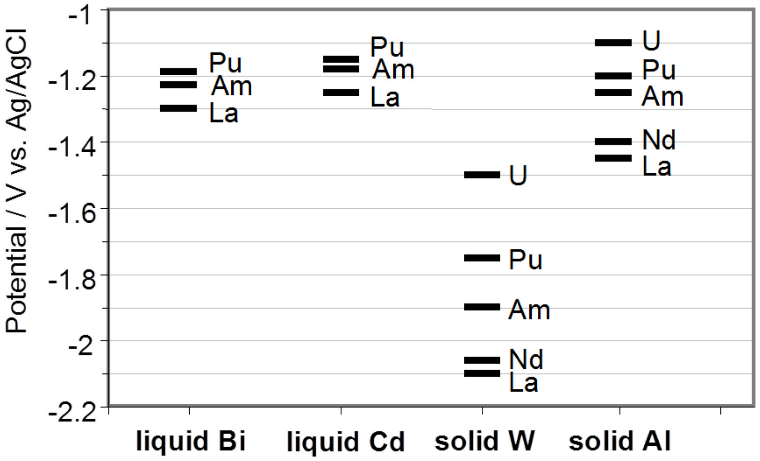
*Pyroprocessing assessment in molten chloride salts (European investigation programmes)*

- Electrorefining on solid aluminum cathode in molten chloride media

To comply with the sustainability goals defined for innovative reactor systems, a major objective is the development of a grouped actinide recycling process based on 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 transuranium actinides on a liquid Cd cathode [36], 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 [37]. In contrast to stainless steel or tungsten, aluminum is a reactive electrode material, i.e. it forms stable alloys with the actinides, thereby avoiding the re-dissolution of trivalent actinides. Also the redox potentials on solid cathodes show a much larger difference in the reduction potential between actinides and lanthanides. Figure 2.105 shows the reduction potentials for $U^{3+}$, $Pu^{3+}$, $Am^{3+}$, $La^{3+}$ and $Nd^{3+}$ determined by transient electrochemical techniques (mainly cyclic voltametry and chronopotentiometry) on different cathode materials. On Bi and Cd, the selectivity of the minor actinide recovery seems to be limited due to the small difference in reduction potentials between actinides and lanthanides.

**Figure 2.105. Reduction potentials of some actinides and lanthanides on different cathodic materials**



Solid Al has therefore been selected for two main reasons:

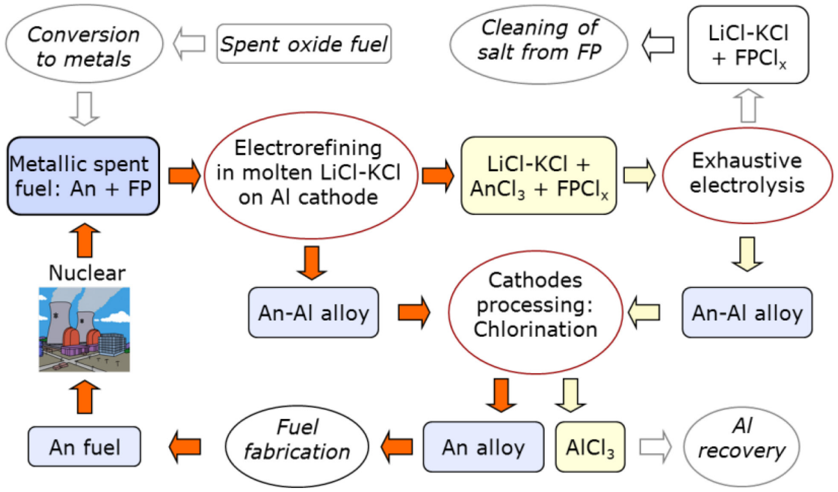
- Stable actinide deposits (alloys) are formed and are consequently very adherent to the cathode; at the same time a re-dissolution of the trivalent An by comproportionation with the trivalent actinides in the salt to form divalent Ans can be avoided (cf equation below according to: Am(III) + Am(0) = 3 Am(II))
- The difference in the reduction potentials compared to lanthanides is sufficiently high to avoid their co-deposition.

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 An from Ln. 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 aluminum cathodes, the process scheme is being proposed as shown in Figure 2.106.

The electrorefining process as presented here is operated in a batch mode. After multiple use of the eutectic salt bath, an exhaustive An electrolysis is required to avoid losses > 0.1% to the waste, before cleaning of the salt bath takes place. It is evident that the Ln content in the electrodeposited An- Al alloy in the exhaustive electrolysis contains more Ln than in the runs were metallic fuel is deposited and must eventually 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 to the fuel fabrication.

**Figure 2.106. Process scheme for the electrorefining of metallic fuels An - actinides, FP - fission products, Al - aluminum**

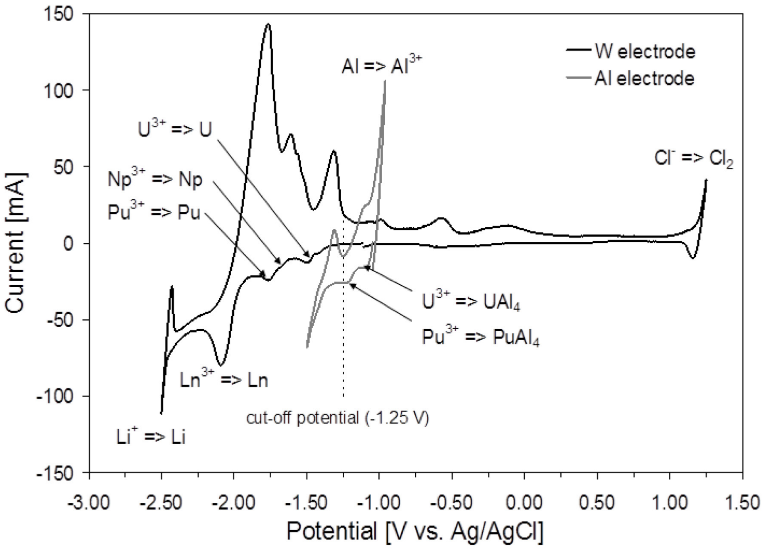


Laboratory experiments have shown that 3.72 g of actinides were deposited in 4.17 g Al, corresponding to 44.6 wt% An in Al or 68 wt% of the maximal loading, considering that $AnAl_4$ alloys are formed [38]. A successful demonstration of the Am/Nd separation was carried out using a mixture of 255 mg Am, 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 integral 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 stabilise the fuel during reactor irradiation. The same type of fuel is used for transmutation studies initiated by CRIEPI, Japan in collaboration with ITU and was irradiated in the METAPHIX experiment in the Phenix reactor in France [39]. This fuel containing 2% of Am and lanthanides ($U_{61}Pu_{22}Zr_{10}Am_2Ln_5$) was fabricated at ITU and the remnants of the fuel fabrication campaign were used for separation studies.

In the pyroprocessing, the metallic alloy is anodically dissolved in a LiCl-KCl eutectic [40] and the actinides are collected together into Al cathodes as alloys, leaving lanthanides in the salt phase. A large-scale pyroprocessing using molten salt electrorefining will very likely 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 5g of $U_{61}Pu_{22}Zr_{10}Am_2Ln_5$ fuel was treated in this experiment and various process parameters were studied. Figure 2.107 shows the cyclovoltamogram of the alloy on Al and W electrodes.

**Figure 2.107. Cyclic voltamogram 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.

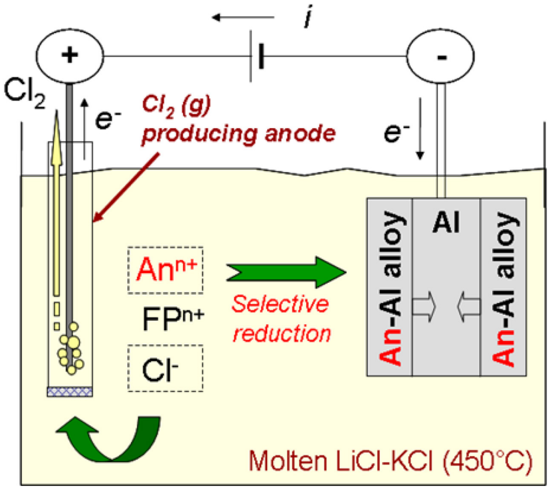
The goal of this 25-run test was to find optimal conditions for the recovery of Am. The recovery rate of actinides was difficult to evaluate because new fuel was added in each run. Nevertheless, a stable recovery rate, better than 99.9%, was achieved throughout the whole experiment. Uranium, the main constituent of the fuel with a less electronegative electrodeposition 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 (mAm/mLn) increases despite an increasing content of not-electro-deposited lanthanides in the salt. This means that the target of 99.9% recovery can be reached for this process.

The results of this 25-run electrorefining experiment for which genuine fuel materials were used and for which the salt bath has not been changed, are very promising in view of a large-scale development of pyroprocessing in advanced nuclear fuel cycles.

- 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 prevents a selective deposition of actinides on the cathode. An exhaustive electrolysis is proposed for the first purification step, a complete grouped recovery of the remaining actinides without further fuel dissolution on a solid aluminum cathode (see Figure 2.108). 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 Figure 2.108.

**Figure 2.108. Principle of the exhaustive electrolysis process**



In order to prove feasibility of the method, two galvanostatic electrolyses were carried out using a mixture of $UCl_3$-$NdCl_3$ [41]. The potentials of both electrodes were constantly followed and a decrease of the uranium concentration from 1.7 to 0.1 wt.% with no co-deposition of neodymium was recovered observed. Although the maximum applicable current densities were relatively low, the results are promising and showing high current efficiency and selectivity of the proposed method.

- Head-end conversion processes

Today, all commercial reactors operate with oxide fuels and advanced reactor systems selected in the Gen IV roadmap rely also on oxides as one of the major fuel options. As mentioned above, the pyrometallurgical process based on oxides developed in Russia, RIAR (Dimitrovgrad) does not allow the recycle of MA's. Pyroprocessing 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 lithium dissolved in LiCl at 650°C. The recovered metal can directly be subjected to electrorefining and the $Li_2O$ converted back to lithium metal by electrowinning. A more elegant method is the so-called direct electroreduction [42]. 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 being carried out to study this conversion process. Lithium reduction process using lithium metal as a reductant is performed in molten lithium chloride. The reduction of $UO_2$ and simulated used LWR fuel [43] was studied mainly by CRIEPI in Japan in collaboration with AEA Technology in the United Kingdom. The optimised thermodynamic conditions for the reduction of transuranium elements and the behaviour of major fission product elements were determined. Li is converted into $Li_2O$ 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 $Li_2O$ and recycled to the 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 $Li_2O$ 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 electrorefing to separate actinides as described in the previous paragraph can be carried out in the same device [44].

An electrochemical process is being developed at present mainly in the US (INL) and again in Japan (CRIEPI) in collaboration with the EC (JRC Karlsruhe). 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% $Li_2O$ 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 oxidised to oxygen gas. The corresponding reactions are:

$$\begin{array}{ll} \text{Cathode:} & MxOy + 2y\,e^- \longrightarrow xM + yO^{2-} \\ \text{Anode:} & yO^{2-} \longrightarrow y/2\ O^2\,(g) + 2y\,e^- \end{array}$$

where M = metal fuel constituent.

The $Li_2O$ present in the salt is reduced to Li together with U and reduces chemically the fuel oxide. Consequently the INL process is a combined chemical/electrochemical process.

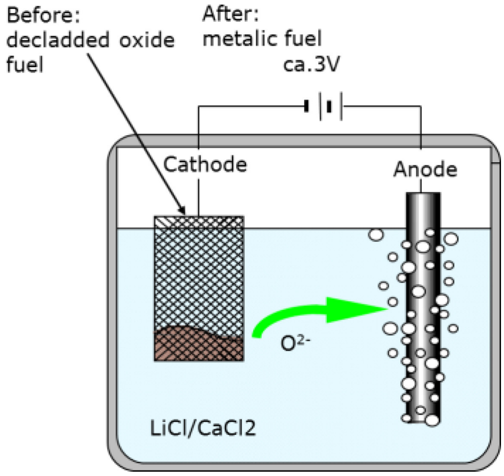
The molten salt can be either LiCl or $CaCl_2$. In $CaCl_2$ the higher temperature of 1 123 K in comparison to 923 K for LiCl induces a faster diffusion of oxygen ions to the anode. At the same time an increased initial reaction rate leads to the formation of a thin dense metal layer at the fuel surface hampering the diffusion of oxygen ions into the salt.

For the CRIEPI/ITU 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:

$$\begin{array}{lll} \text{Cathode:} & MxOy + 2y\,e^- & \longrightarrow xM + yO^{2-} \\ \text{Anode:} & yO^{2-} + y/2C & \longrightarrow CO_2\,(g) + 2y\,e^- \text{ or} \\ & yO^{2-} + yC & \longrightarrow CO\,(g) + 2y\,e^- \end{array}$$

The electroreduction process is shown in Figure 2.109.

**Figure 2.109. Schematic layout of an electroreduction process developed by CRIEPI/ITU**



The CRIEPI/ITU process was tested on various non-irradiated MOX (Pu content 5-45%) fuels which were reduced. It could be shown that U and Pu were efficiently co-reduced, but complete reduction requires very long reaction times. The reduction of irradiated fuel particles was considerably faster and a complete reduction of all fuel constituents including fission products and MAs was achieved. Figure 2.110 shows the reduced fuel particles of irradiated MOX fuel particles (43 GWd/tHM) in the cathode basket cut in the middle.

**Figure 2.110. Reduced fuel particles of irradiated MOX fuel particles (43 GWd/tHM); section of cut 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 establishing a mass balance of the electroreduction process. Results show that the fuel is completely reduced at least as far as actinides are concerned (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 similarly 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.

The pellet remained in its original shape, it became porous and shiny metallic colour 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 RE 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 RE oxide phase rather than in the reduced U-Pu alloy. This represents of course a major issue for a grouped actinide recovery. Also the handling of highly reactive Li and problems in developing the corresponding equipment especially for the lithium recovery are major drawbacks of this process.

*Pyroprocessing assessment in fluoride melts*

Although hydrometallurgical processes have been considered as the reference route for P&T strategies and for studies on Gen IV spent fuel reprocessing by the Nuclear Energy Division of the Commissariat à l'Energie Atomique et aux Energies Alternatives (hereafter

CEA/DEN), other motivations drove the launch of a R&D programme for the assessment of pyroprocesses.

One motivation was to assess the presumed inherent advantages of such processes: compactness, more favourable criticality constraints, and the fact that the non-aqueous solvents working at high temperature are less subject to radiation influence. Another important motivation is to evaluate these technologies as a potential route for two specific applications: (1) reprocessing of irradiated targets or dedicated fuels used for the minor actinides transmutation, (2) reprocessing of Gen IV spent nuclear fuels (e.g. carbide fuel proposed for gas cooled fast reactor, metallic or oxide fuel proposed for fast neutron reactors and molten fuels for molten salt reactors).

Launched at CEA Marcoule in the late 1990s, the R&D programme on pyrochemistry must provide sufficient experimental results to answer the following question: Is there a combination – media & techniques – which allows grouped management of actinides with sufficient fission products decontamination? An alpha laboratory was therefore equipped in the ATALANTE facility. Nevertheless, even if the technology is working well, any pyroprocess cannot be viable without treating and confining its waste; that is the reason why R&D is also devoted to this field. Ideally a pyroprocess should not generate more waste and should be at least as safe and cost effective as the hydrometallurgical processes currently implemented at industrial scale. Therefore, along with experimental research, it is necessary to conduct system studies to devise potential processes and to assess their capability to achieve the assigned objectives. These are: (1) to recover and recycle all the actinides (>99.9%) present in the feed, (2) to ensure sufficient decontamination of actinides towards fission products, (3) to generate the minimum of ultimate waste flows, and (4) to have suitable confinement of process waste. Preliminary experimental studies showed that fluoride medium is very attractive in terms of confinement: direct fluoride immobilisation into glass matrix up to 15 wt% was successfully proved at lab-scale [45].

- Chemical liquid/liquid extraction in fluoride melt

Two technologies were investigated for actinides/fission product separation. The first one, considered at present time as the reference route, consists of a two-step liquid/liquid extraction:

The first step of the process route is a chemical reductive extraction performed in molten fluoride medium by liquid aluminum (Figure 2.111) [46]. The occurring reaction can be described by the following equilibrium (1):

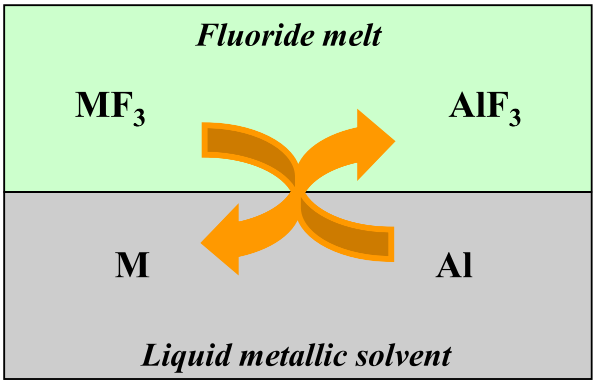
$$MF_3(\text{salt}) + Al(\text{metallic solvent}) \longrightarrow AlF_3(\text{salt}) + M(\text{metallic solvent}) \qquad (1)$$

For a given element M and temperature, the distribution coefficient DM ($D_M=X_M/X_{MF3}$) is (2):

$$D_M = K^{\circ}_M(T)\frac{a_{Al}}{x_{AlF_3}\gamma_{AlF_3}}\frac{\gamma_{MF_3}}{\gamma_M} \qquad (2)$$

where $K^{\circ}_M(T)$ is the thermodynamic constant of the reaction calculated from the free enthalpies of formation of the pure species involved (reference state being the pure compound in the liquid state, except for $AlF_3$ for which the reference state is the pure solid), $x_i$ is the ratio of the molar fractions of M in the metallic solvent and in the salt at equilibrium, and $\gamma = a/x$ is the activity coefficient.

**Figure 2.111. Chemical reductive extraction diagram**



The distribution coefficients of actinides and rare earths have been measured in different LiF–$AlF_3$ mixtures corresponding to the first eutectic (E1: 85–15 mol%), the cryolitic (C: 75–25 mol%) and the second eutectic composition (E2: 65–35 mol%), contacted with AlX (X = Cu or Al) metallic phase at 830°C. Table 2.29 summarises the obtained results in LiF–$AlF_3$ (85–15 mol%). According to Table 2.29, actinides and rare earths (Ce, Nd, Sm and La) are distributed in two separated groups. Firstly, plutonium, americium and curium, having similar distribution coefficients, could be co-extracted. Secondly, their separation from rare earths should be easily reached thanks to the high separation factors ($SF_{An/Ln}$ > 1 000). The difference between the distribution coefficients obtained by using Al-Cu and pure Al is mainly due to the variation of the Al mole fraction in the metallic solvent; besides a probable and slight variation of $\gamma$ Al should also be taken into account to explain that difference (copper being not totally inert). A grouped actinide recovery can be expected because the distribution coefficients for actinides are very close.

**Table 2.29. Weight distribution coefficient (DM) and separation factor (SAm/M) in LiF–$AlF_3$ (85–15 mol%)/AlX (X = Cu or Al) at 830°C [47,48]**

| Element | Al-Cu (72-22 mol%) | | Pure Al | |
|---|---|---|---|---|
| | $D_M$ | $SF_{Am/M}$ | $D_M$ | $SF_{Am/M}$ |
| U | 489±49 | 0.29±0.1 | Not measured | – |
| Pu | 197±30 | 0.73±0.21 | 273±126 | 0.78±0.47 |
| Am | 144±20 | 1 | 213±30 | 1 |
| Cm | – | – | 185±31 | 1.15±0.35 |
| Ce | 0.142±0.01 | 1014±213 | 0.162±0.02 | 1315±289 |
| Sm | 0.062±0.006 | 2323±488 | 0.044±0.004 | 4954±1139 |
| Eu | <0.013 | >11000 | <0.03 | >7100 |
| La | <0.06 | >2400 | 0.03 | 7100 |

The second step of the process consists of the actinide back-extraction from the Al matrix (coming from the reductive extraction step). It is also based on a liquid/liquid extraction method. This extraction is provided by a chloride melt containing an oxidising agent, i.e. $AlCl_3$. The occurring reaction is described by the following equilibrium:

$$\text{An(metallic solvent)} + \text{AlCl}_3\text{(salt)} \longrightarrow \text{Al(metallic solvent)} + \text{AnCl}_3\text{(salt)} \quad (3)$$

Feasibility experiments were carried out on the back-extraction of U since it is known from thermodynamic studies that U is the most difficult actinide to be recovered from the Al matrix [49]. Because $AlCl_3$ is highly volatile, particularly in chloride acidic melts, several experiments were performed using different salt mixtures in order to define optimal conditions regarding the U back-extraction efficiency and the $AlCl_3$ volatilisation. Several concentrations of the oxidising agent were also investigated. These experiments led to an U back-extraction efficiency of 96% in a single stage (at 700°C), using a LiCl-$CaCl_2$ (70-30 mol%) mixture, an $AlCl_3$/U ratio equal to 6 and a tightened container (preventing $AlCl_3$ volatilisation).

The grouped An back-extraction feasibility study was carried out on three metal ingots containing U, Pu, Am and some Nd, coming from reductive extraction step (one for each LiF-$AlF_3$ composition, i.e. E1, C and E2). Table 2.30 summarises the extraction efficiencies of different elements after contacting the three metal ingots with $CaCl_2$-LiCl + $AlCl_3$ ($AlCl_3$/An ratio was set equals to ~7).

**Table 2.30. Back-extraction efficiency of the different studied An and the Nd**

| Run | Back-extraction efficiency (%) | | | |
|---|---|---|---|---|
| | U | Pu | Am | Nd |
| E1 | 87.4 | 99.1 | 99.9 | 92.2 |
| C | 94.7 | 99.0 | 99.8 | 92.4 |
| E2 | 94.2 | 98.9 | 99.98 | 86.2 |

These experiments successfully confirmed the feasibility of the back-extraction of An using $CaCl_2$-LiCl + $AlCl_3$ (such as $AlCl_3$/An = 6 – 7). Pu and Am were quantitatively back-extracted (>99%) in a single stage while the back-extraction efficiency of U was lower (87 to ~95%), confirming that U is the most difficult actinide to be back-extracted. As Nd back-extraction is also important, no selectivity between An and Ln can be expected during this step of the process. It demonstrates the importance to reach a high An/Ln separation at the reductive extraction step.

Investigations were also carried out on the conversion of the purified actinides into oxides. The investigated way of conversion is precipitation using wet argon sparging in the chloride salt (at 700°C). $O^{2-}$ ions (needed to convert the $An^{3+}$ into oxides) are provided by the decomposition of water in the salt:

$$H_2O(g) + Cl\text{-(salt)} \longrightarrow O^{2-}\text{(salt)} + 2HCl(g) \quad (4)$$

The use of a gaseous reagent for the precipitation is interesting from a process point of view because it does not increase the salt volume and does not change the solvent composition. First experiments were performed on cerium and neodymium as actinides surrogates [50]. Then, the method was applied on uranium and plutonium precipitation.

Co-precipitation of uranium (III) and plutonium (III) (several U/Pu ratios were studied, i.e. 25/75, 50/50 and 75/25) using wet argon sparging formed mixtures of $UO_2$ and $PuO_2$. Therefore, this way of actinides conversion is oxidative enough to obtain $PuO_2$ and moderated enough not to oxidise uranium oxide beyond $UO_2$. This process directly leads to the oxide form in the case of uranium and plutonium which is a positive point for new fuel fabrication. No U-Pu solid solution formation could be observed mainly because of the uranium high sensitivity to precipitation (uranium reacts first before plutonium).

Despite a reaction of precipitation in the salt over 99%, a part of uranium is lost by volatilisation. This is caused by $UCl_3$ partial oxidation to $UCl_4$ occurring during the precipitation reaction, which is volatile at the working temperature ($T_{vap}(UCl_4)$ = 689°C). The precipitation of Pu was almost quantitative (>99% yield) and no volatility was observed.

A similar technology of liquid/liquid extraction for the molten fluoride salt/liquid bismuth reductive extraction system is described in Section 2.3.7 related to the processes connected with the MSR technology.

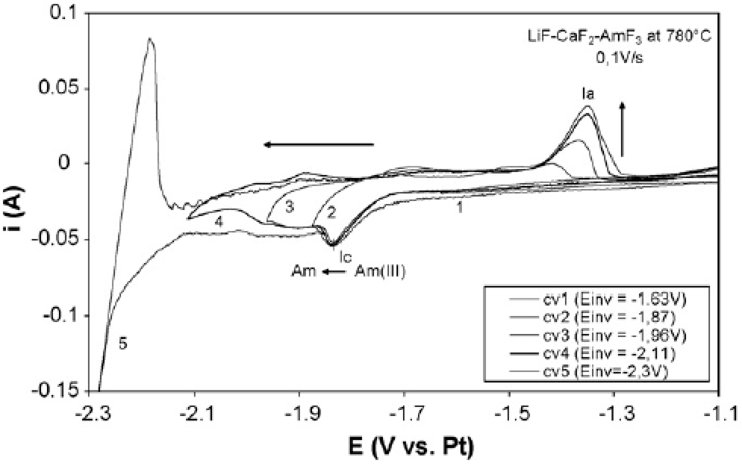
- Electrolytic separation

An alternative route (without aluminum) could be necessary if troubles occur in the subsequent step of the process where the actinides have to be recovered from the liquid aluminum. One possible route, investigated by CEA, is based on an electrolytic separation. Preliminary basic research showed that LiF-$CaF_2$ (77-23 mol %) melt appears to be a potential electrolyte for (U, Pu)/lanthanides separation [51].

A brand-new study on americium by cyclic voltammetry (Figure 1.3.16) proves that Am(III) reduction occurs in a single reduction wave (peak Ic is associated to the Am(III)/Am(0) reduction) at a potential approximately equal to +0.5V vs Li+/Li at 780°C. Thus, the +II oxidation state of americium is not stable in fluoride medium contrary to the chloride one (already observed in eutectic LiCl-KCl at 504°C) [52,53]. Consequently, the fluoride melt shifts the equilibrium (5) to the left, which avoids a possible corrosion of americium deposit in the case of electrolytic recovery.

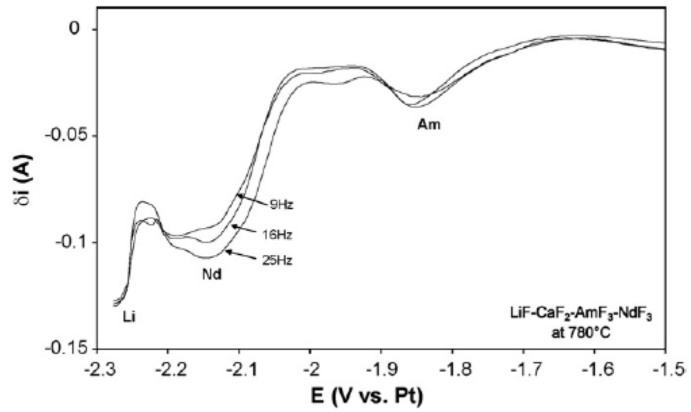
$$2\ \mathrm{Am(III)} + \mathrm{Am(0)} \longrightarrow 3\mathrm{Am(II)} \qquad (5)$$

**Figure 2.112. Cyclic Voltammetry on W electrode (SWE=0.16 cm²) in LiF-$CaF_2$-$AmF_3$ ([$AmF_3$] = 1.5510$^{-2}$ mol/kg) at 780°C; v=0,1V/s; Pt reference electrode; CE: graphite**



Square wave voltammetries at various frequencies (9, 16 and 25Hz) on a solution containing Am(III) and Nd(III) ions (Figure 2.113) give an estimation of the apparent standard potential E'° for Am(III)/Am(0) and Nd(III)/Nd(0) couples.

**Figure 2.113. Square Wave Voltammetry on W electrode (SWE=0.16 cm$^2$) in LiF-CaF$_2$-AmF$_3$-NdF$_3$ ([AmF$_3$] = 1.5510$^{-2}$ mol/kg, [NdF$_3$] = 5.710$^{-2}$ mol/kg) at 780°C; Pt reference electrode; CE: graphite**



The peaks observed were, respectively, attributed to the Am(III)/Am, Nd(III)/Nd and Li(I)/Li redox couples (potentials were measured vs. Pt and then referred to the Li$^+$/Li couple Table 2.31).

The estimation of the difference E'°[Am(III)/Am(0)]– E'°[Nd(III)/Nd(0)] is an essential parameter for assessing the easiness of the Am/Ln separation. Calculations give: E'°[Am(III)/Am(0)]=+0.43V vs Li$^+$/Li and E'°[Nd(III)/Nd(0)]=+0.14V vs Li$^+$/Li, hence a difference of about 290 mV, theoretically wide enough for achieving Am/Nd quantitative electrolytic separation.

**Table 2.31. Estimated (by sqw) apparent standard potential in LiF-CaF$_2$ (77–23 mol%) at 780°C**

| Redox couple | Li(I)/Li | Nd(III)/Nd | Am(III)/Am |
|---|---|---|---|
| E'°(V vs.Pt) | -2.28 | -2.14 | -1.85 |
| E'°(V vs.Li) | 0 | +0.14 | +0.43 |

The R&D programme launched by CEA on pyrochemistry proves that fluoride melts are very promising for the selective An group separation and the confinement of the ultimate process waste, compared to the chloride melts.

Firstly, high An/Ln separation factors could be obtained during the reductive liquid-liquid extraction in LiF-AlF$_3$/Al and the feasibility of a grouped An back-extraction was successfully demonstrated. Wet argon sparging in molten chloride appears to be a promising way for U and Pu conversion to oxides in order to fabricate new nuclear fuels and leads to the desired oxides forms UO$_2$ and PuO$_2$ formation in a single step. However, the partial volatilisation of uranium needs to be reduced by optimisation of the experimental conditions.

Secondly, Am/Nd electrolytic separation efficiency is increased by using LiF-CaF$_2$ melt instead of the conventional LiCl-KCl electrolyte. All the experimental results encourage us to pursue the evaluation, notably on irradiated materials at laboratory scale and possibly higher scale.

*Technical uncertainties of the pyroprocessing*

In the Spent Fuel Treatment Programme at INL many parts of the pyroprocess 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 transuranics. Large-scale equipment designed and constructed was never tested beyond laboratory scale, because of the termination of the IFR programme.

The remote fabrication of IFR fuel was not part of the Spent Fuel Treatment Programme, but this technology was used to fabricate cold fuel for EBR-II and a demonstration of another pyroprocess (melt refining) for recycling EBR-II in the 1960s employed remote fabrication for 34.500 fuel elements [5].

Another key challenge for a pyroprocessing 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 pyroprocessing seems quite similar to 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 pyroprocessing 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 used fuel have started at a laboratory scale. In addition to nitride fuels, a demonstration of the above mentioned recycling of nitrogen (15N) is essential for the economic considerations.

### 2.3.4. Nitride fuel treatment

*Introduction*

The experience gained in the investigations on pyroprocessing technology for oxide and metal fuels has considerably helped in developing a pyrochemical method for nitride fuel. Research on nitride fuel reprocessing is mainly being carried out in Japan and in Russia. Pyroprocessing steps offer several advantages such as compactness of facility, and large margin to criticality. Another advantage lies in the ease of recovery of $^{15}$N-enriched nitrogen used for nitride fuel.

*Treatment of nitride fuel for MA transmutation developed at JAEA (Japan)*

A nitride fuel cycle for the transmutation of the minor actinides (MA: Np, Am, Cm) has been developed by JAEA under the double-strata fuel cycle concept [54]. Reprocessing of spent nitride fuel is performed by using a pyro-electrochemical process which is similar to the process used for processing metallic spent uel from fast reactors but with minor modifications [23]. The process developed at JAEA (dedicated to ADS fuels) involves molten salt electrorefining followed by re-nitridation of the recovered actinides.

Spent nitride fuel from dedicated systems, such as an accelerator-driven system (ADS), is dissolved at the anode, and actinides are recovered at the liquid metal cathode. The recovered actinides are then reconverted to nitride using nitrogen gas.

The double-strata fuel cycle concept employs ADS as a transmutation system, in which MA are fed from first-strata commercial fuel cycle to a second-strata, dedicated transmutation fuel cycle (Figure 2.114). An ADS with 800 MWth can transmute MA at the rate of 250 kg/year, which corresponds to the MA amount produced by 10 PWR plants per year [55]. Spent fuels from ADS are reprocessed to separate FPs from MA and plutonium in order to refabricate nitride fuel.

Figure 2.115 shows the schematic of molten salt electrorefining. This section summarises the status of development of a pyro-electrochemical process for spent nitride fuel from an ADS.

**Figure 2.114. Combination of nitride fuel and pyro-electrochemical process based on double-strata fuel cycle concept**

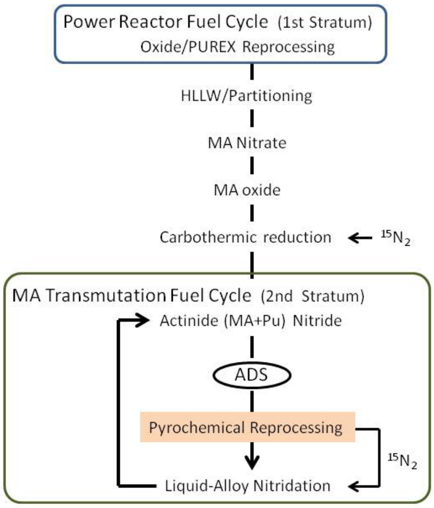
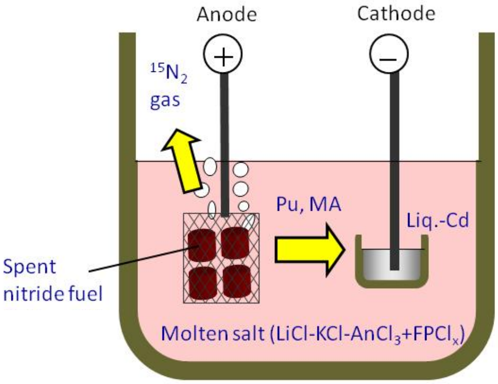


**Figure 2.115. Schematic of molten salt electrorefining of spent nitride fuel for ADS**



Anode : $AnN = An^{3+} + 3e^- + 0.5\ N_2$

Cathode : $An^{3+} + 3e^- = An_{(in\ Cd)}$

- Anodic dissolution of nitride spent fuel

The anodic dissolution behaviour of actinide nitrides has been investigated mainly through laboratory-scale electrochemical measurements using unirradiated samples. Table 2.32 summarises the equilibrium potential of AnN (An= U, Np, Pu, Am) against a $Cl_2/Cl^-$ reference electrode. The potentials were derived from EMF values measured in the molten salt. The potentials in Table 2.32 have similar values, which suggest that their anodic dissolution behaviour is also similar.

**Table 2.32. Equilibrium potential of AnN, E($An^{3+}$/AnN), vs. $Cl_2/Cl^-$ reference electrode**

| | UN [56] | NpN [57] | PuN [58] | AmN [59] |
|---|---|---|---|---|
| E($An^{3+}$/AnN) vs. $Cl_2/Cl^-$ (v) | -1.944 | -2.007 | -2.114 | -2.195 |

The potentials in Table 2.32 correspond to the equilibrium between the actinide nitride and the trivalent actinide in the molten salt as shown in Equation (6):

$$AnN \longrightarrow An^{3+} + 3e^- + 0.5N_2 \qquad (6)$$

According to the cyclic voltammograms of AnN measured with a Mo electrode, the anodic current is much larger than the cathodic one. The reason is that $N_2$ gas generated by Equation (6) readily escapes from the molten salt. Thermodynamically, the equilibrium potential of AnN is expressed as follows:

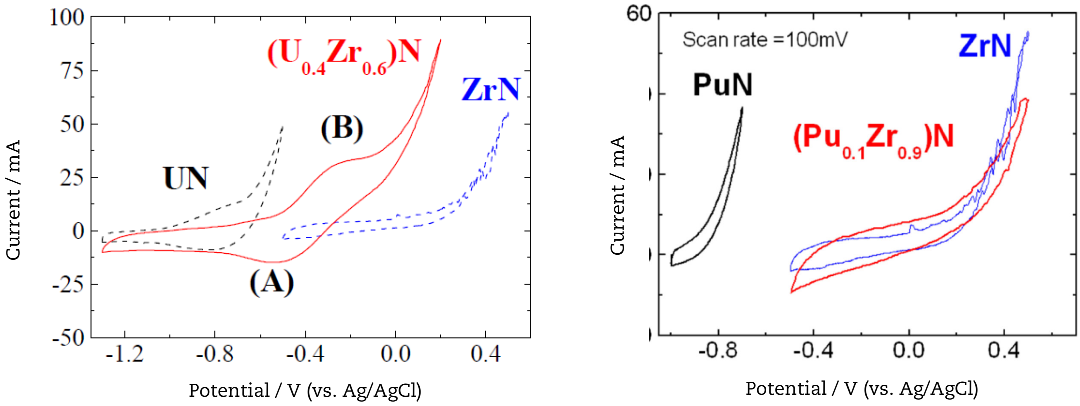
$$E(An^{3+}/AnN) = E^{0'}(An^{3+}/An) + (RT/3F)\cdot \ln X(An^{3+}) - \Delta G_f(AnN)/3F + (RT/6F)\cdot \ln(p(N_2)) \qquad (7)$$

where, $E^{0'}(An^{3+}/An)$is the formal standard potential of An metal in the molten salt; $X(An^{3+})$ is the molar ratio of $AnCl_3$ in the molten salt; $\Delta G_f(AnN)$ isthe Gibbs free energy of formation of AnN; R is the ideal gas constant (J/mol K); T is the absolute temperature (K); F is the Faraday constant (C/mol) and $p(N_2)$is the partial pressure of nitrogen in the AnN sample. The value of $p(N_2)$ is estimated to be approximately between 0.001 and 0.2 atom in Equation (7).

The nitride fuel for an ADS contains no U, but is an inert matrix fiel in which the inert matrix material is used in place of U) as the diluting materials for the MA and Pu. ZrN was used as the first candidate diluting material. ZrN forms a solid solution with actinide nitrides (MA, Pu, Zr)N. It is therefore important to examine the effect of the addition of ZrN on the anodic dissolution behaviour. In general the addition of ZrN leads to thermodynamic stabilisation by the formation of a solid solution, but the anodic dissolution of actinides becomes difficult in the molten salt. The cyclic voltammogrammes of $(U_{0.4}Zr_{0.6})N$ and $(Pu_{0.1}Zr_{0.9})N$ solid solutions, measured with a Mo electrode, are compared to those of UN and PuN, respectively, in Figure 2.116 [60]. The positive shift of dissolution potential by the adition of ZrN is clearly seenin Figure 2.116. However, if the dissolution potential is applied, ZrN will dissolve at the anode and contaminate the molten salt.

In addition, UN-based simulated nitride fuels were subjected to anodic dissolution tests. The fabricated UN pellets contained Mo (as asurrogate of Tc), Pd (as a surrogate of all PGM elements) and Nd (as a surrogate of all RE elements). Chemical forms of Mo, Pd and Nd were assumed to be Mo metal, $UPd_3$ and (U,Nd)N, respectively. The anodic dissolution behaviour with UN was similar to that of iUN+Mo and UN+$UPd_3$ samples. The formation of stable $UPd_3$ type of intermetallic compound probably resulted in the increase of anode residue containing non-negligible actinides. In comparison, Nd in (U,Nd)N sample easily dissolved in the molten salt because of the similar dissolution potential of UN and NdN. Since the accumulation of RE elements in the molten salt can affect the separation efficiency between actinides and lanthanides in the electrorefining process, part of the molten salt in the electrorefiner should be continuously removed and treated by the Zeolite process for purification as done with the pyrochemical process for metallic fuel [61].

**Figure 2.116. Cyclic voltammograms of $(U_{0.4}Zr_{0.6})N$ and $(Pu_{0.1}Zr_{0.9})N$ in comparison with UN, PuN and ZrN [60]**



- Recovery of actinides into a liquid Cd cathode

Laboratory-scale experiments on the recovery of actinides have also been carried out. Cd is the primary candidate for the liquid metal cathode material in the electrorefining process of spent nitride for ADS, because all actinides can be recovered simultaneously, and Cd is easily separated by distillation, later in the process. Indeed, the observed formal standard potentials in liquid Cd, $E^{0'}(An^{3+}/An\text{-}Cd)$ against a $Cl_2/Cl^-$ reference electrode, show similar values for U, Np, Pu and Am, as shown in Table 2.33.

**Table 2.33. Formal standard potential of An in liquid Cd, $E^{0'}(An^{3+}/An\text{-}Cd)$, vs. $Cl^2/Cl^-$ reference electrode**

| | U [62] | Np [62] | Pu [62] | Am [63] |
|---|---|---|---|---|
| $E^{0'}(An^{3+}/An\text{-}Cd)$ vs. $Cl_2/Cl^-$ (v) | -2.544 | -2.579 | -2.610 | -2.56 |

As described before, a significant amount of Zr in (An,Zr)N solid solutions will dissolve in the molten salt at the potential applied to the anode. In the electrorefining of (U,Zr)N and (Pu,Zr)N with liquid Cd cathode, some Zr is recovered into liquid Cd cathode as well as actinides [64]. Further study on the behaviour of Zr is necessary for demonstrating the feasibility of pyrochemical process of spent nitride fuel for ADS.

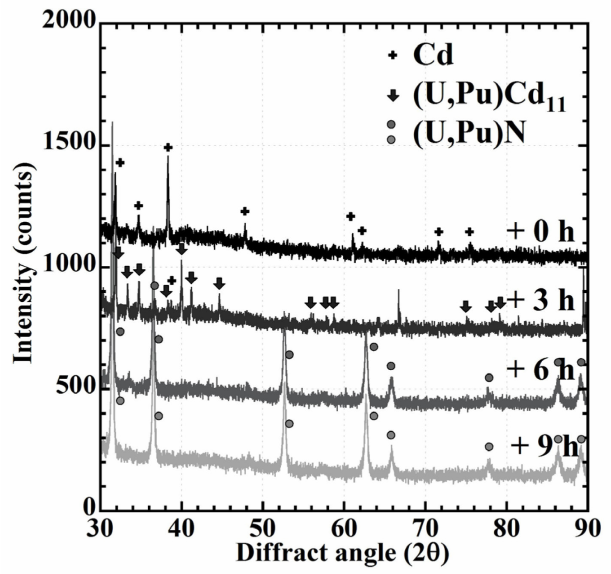
- Nitridation of actinides in Cd alloy

Actinides recovered into the liquid Cd cathode must be converted back to nitride for use as recycled fuel. The nitridation-distillation combined process was developed in which nitridation of actinides and distillation of Cd, occur simultaneously when heating An-Cd alloy at 973 K in a nitrogen gas stream. It has been demonstrated that gram-scale powders of PuN, (U,Pu)N and AmN can be prepared from Pu-Cd [65], U-Pu-Cd [67] and Am-Cd [59] alloys, respectively. Figure 2.117 shows the change of X-ray diffraction pattern of the sample during the nitridation-distillation combined process for U-Pu-Cd alloy.

It is inevitable that part of the RE elements in the molten salt will accompany the actinides into the liquid Cd cathode, because the reduction potentials of the RE elements are similar to those of the actinides. However, further decontamination of the actinides from the RE elements can achieved, if necessary, during the combined nitridation-distillation process, since the RE elements in liquid Cd are more stable than the actinides [68].

Unfortunately, the behaviour of Zr recovered into the liquid Cd cathode is not yet clear; therefore, and further investigations will be undertaken.

**Figure 2.117. X-ray diffraction pattern of (U,Pu)N powder prepared by the nitridation-distillation combined process [66]**



Source: OECD/NEA Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, 25-29 September 2006, Nîmes, France, p.117.

- Summary

The combination of nitride fuel and the pyro-electrochemical process is proposed using on a double-strata fuel cycle concept. The status of laboratory-scale experimental studies made on the pyro-electrochemical process, including anodic dissolution of spent nitride fuel, recovery of actinides into liquid Cd cathode, and nitridation of actinides in Cd alloy, was summarised. Besides the experimental study, process-flow preparation and mass-balance evaluation in a dedicated MA transmutation fuel cycle is underway. In this case, a few supplementary processes, such as the anode-residue treatment process and the zeolite process for purification of molten salt were included.

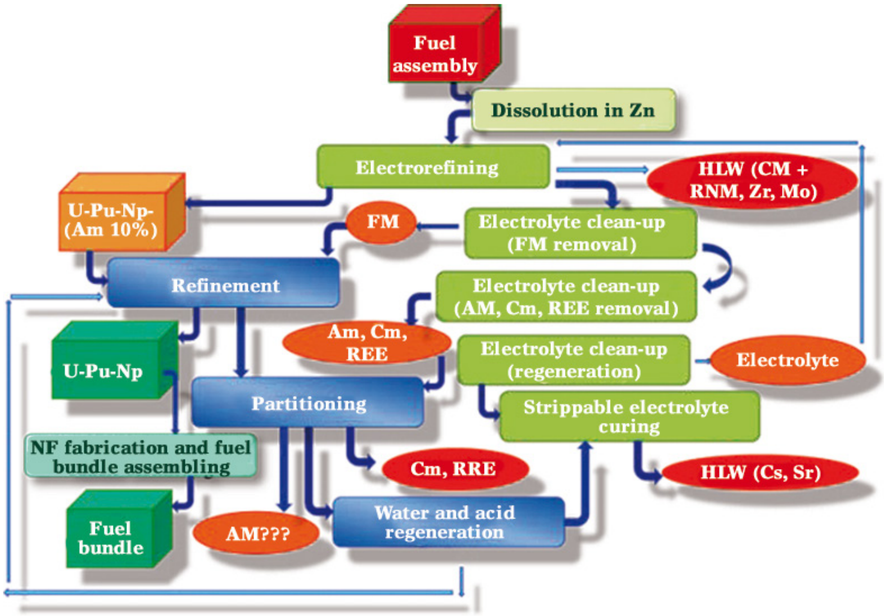
The basic feasibility of the process has been demonstrated by the laboratory-scale experiments which were carried out using unirradiated samples. For the demonstration of technological feasibility, however, further development is necessary, both in quality and quantity of the samples and apparatus. Recent progress in several countries, of the pyro-electrochemical process for the metallic fuel cycle will also be useful for the development of nitride spent fuel for ADS.

*Nitride fuel reprocessing in Russia*

Since 2010, R&D on pyro-electrochemical processing has focused on nitride fuel for a closed fuel cycle [69-72] to be carried out at the fast reactor site. Currently, a combined process (hydro+pyro) is applied (Figure 2.118). This combined technology uses pyro-electrochemical operations to separate the bulk of the highly radioactive fission products from uranium, plutonium and neptunium. Another approach using only a pyroprocessing scheme is planned for 2030 (Figure 2.119). Mixed U-Pu nitrides from spent fuels are dissolved at the anode and U, Np, Pu, Am and Cm are recovered at the cathodes. The different steps of the pyrochemical process for reprocessing nitride fast reactor spent fuel include:

- disassembly of the fuel rod array and the formation of fuel element shipment with nitride SNF;
- chemical de-cladding of the fuel elements in molten zinc;
- regeneration of zinc;
- reprocessing of SNF with depositing of U-Pu-Np-Am at the anode;
- local off-gas cleaning of the volatile fission products separated in various operations in the gas phase Cs, Sb, Te, Se, radioactive noble gases, tritium;
- recovery of salt and cadmium from various products;
- cleaning of salt from plutonium, producing $PuO_2$;
- cleaning of salt of REE , Am, Cm, U with the production of Am, Cm, U, REE oxides;
- cleaning of salt with production of salt ingot for HLW solidification and recycling of purified salt.

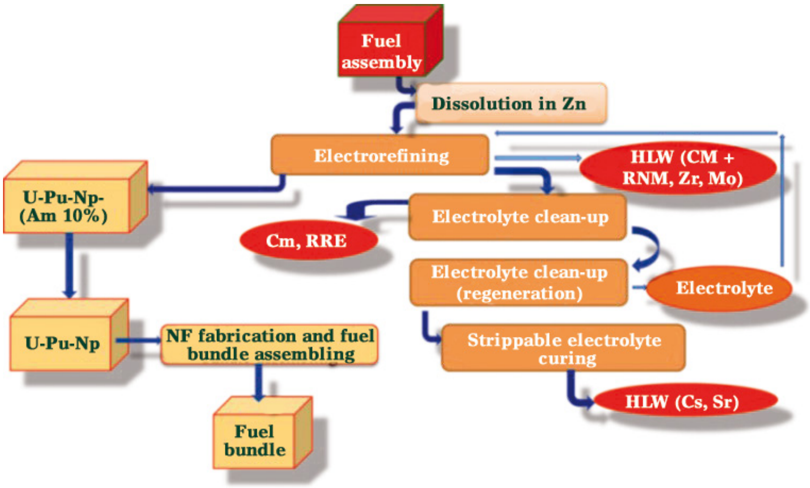
**Figure 2.118. Combined hydro and pyro scheme**



Pyrochemical methods have been studied for the production ofrecycle fuel composition since the end of the 20th century:

- uranium-plutonium fuel with high plutonium content (30-50% of Pu);
- LWR-type fuel containing 2-8 % of Pu;
- oxide fuel containing 3-9 % of Np;
- oxide fuel with americium additions;
- mixed uranium-thorium oxide fuel;
- $PuO_2$ for pellet MOX-fuel production.

**Figure 2.119. Full pyrochemical scheme**



To date, there is still a lack of remote technology for shielded recycle fuel pellet production. Thus, highly efficient decontamination is needed prior to recycle fuel production. Table 2.34 summarises the different technologies for spent fuel reprocessing being considered.

**Table 2.34. Technology comparison**

| | Purification coefficient, U-Pu (Np) from FP | | Actinides recovery Pu (Am) | | Cooling time | |
|---|---|---|---|---|---|---|
| | Achieved | Potential | Achieved | Potential | Achieved | Potential |
| Pyro | $10^3$ | $10^6$ | 98% | 99.9% | 1 year | 6 months |
| Fluoride volatility | $10^4$-$10^6$ | $10^7$ | ~95% | 99.9% | 1 year | 6 months |
| Hydro | $10^7$ | $10^7$ | 99.9% | 99.9% | 4 years | 3 years |
| Pyro + Hydro | - | $10^7$ | - | 99.9% | - | 6 months |

Pyrochemical reprocessing of FBR spent fuel was performed for the first time in 2010. It consisted of reprocessing ~0.6 kg of SNF from four different fuel pins: U-Pu nitride, U-Pu metal, U-Zr metal and U-Pu-Zr metal. The different SNF types were reprocessed using the same salt andThe same electrorefiner. Features of the main technological operations tested can be seen in Figures 2.120 to 2.124.

The experimental equipment is currently being improved and additional tests such as Zn decladding, electrorefiner (bothbatchor semi-continuous mode), Zn/Cd and salt distillation, will be conducted.

**Figure 2.120. Empty cladding after anodic dissolution of nitride SNF in chloride melt**

**Figure 2.121. Zn Decladding unit in hot cell during experiment**

**Figure 2.122. Zn distillation unit for clad material separation**

**Figure 2.123. Electrorefiner up to 2000 A on cold test facility**

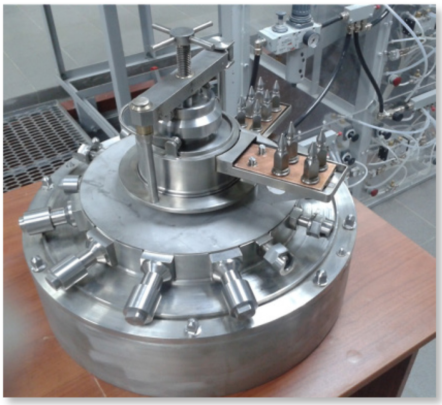
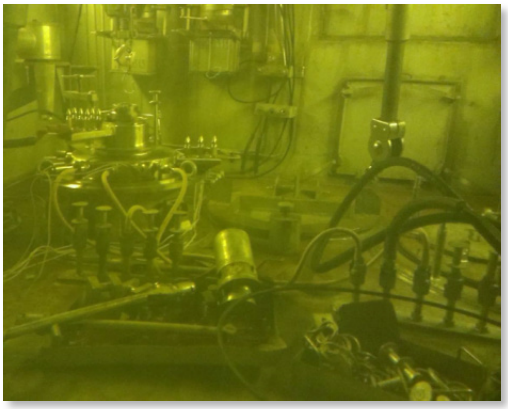
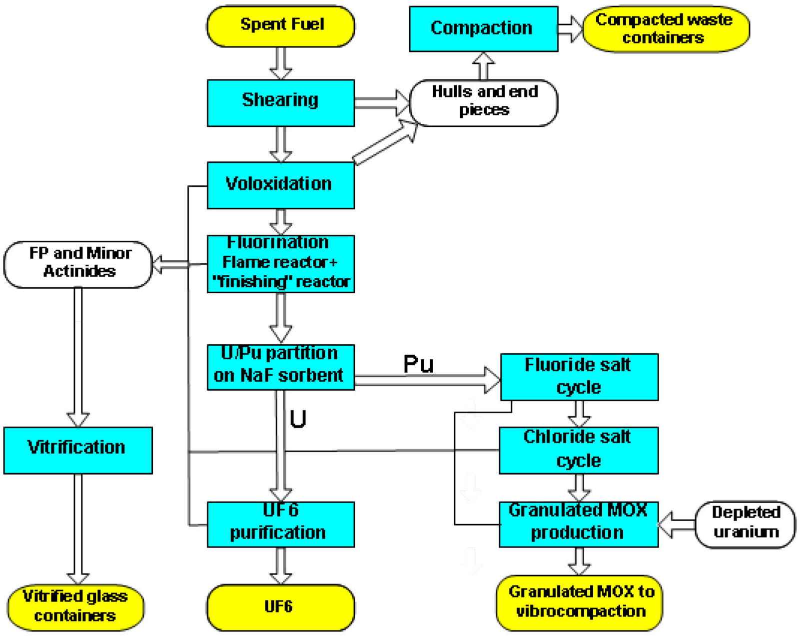


**Figure 2.124. Electrorefiner in hot cell during test with real SNF**



Finally, an LWR reprocessing scheme based on pyrochemistry has been initiated and is under development (see Figure 2.125).

**Figure 2.125. LWR SNF reprocessing scheme (full pyro)**



### 2.3.5. *Separation of Cs and Sr from LiCl salt waste by a melt crystallisation process*

*Introduction*

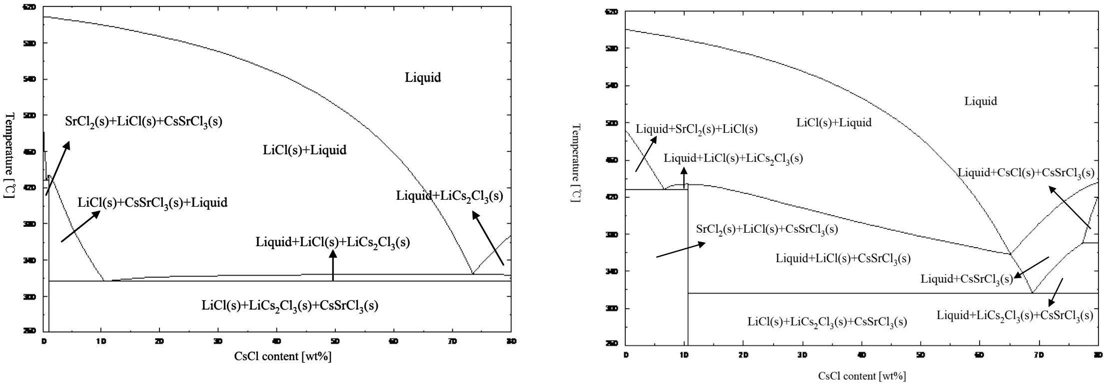
Attempts have been carried out to separate Group I and II fission products such as Cs and Sr, from LiCl salt waste, using various chemical agent addition methods [1] or ion-exchange methods [2]. The separation of both Cs and Sr from LiCl salt waste is nearly impossible using a chemical agent addition method since this method has resulted in a low conversion efficiency tp separated chemical forms, especially Cs. In addition, the separation of Cs and Sr products from LiCl molten salt by reaction with chemical agents is very difficult since the Cs and Sr products have good solubility in the molten salt. Furthermore, due to the residual added chemical agents in the LiCl molten salt, the re-use of the LiCl in an electrolytic reduction process is very difficult. Group I and II fission products could be separated from the LiCl-KCl eutectic salt with a high separation efficiency by ion-exchange using zeolite-A. But in the case of LiCl, its melting temperature is about 610$^0$C, and therefore the working temperature of the zeolite process has to be higher than 610$^0$C. At this temperature, the structure of the zeolite-A is broken, and the zeolite-A loses its ion-exchange capability. Consequently, the separation of cesium and strontium from a LiCl salt by the zeolite process is nearly impossible.

Due to these difficulties for the separation of both Cs and Sr, a melt crystallisation process was investigated at KAERI (Korea). Melt crystallisation relies on the partial crystallisation of multi-component liquid (or melt) mixtures and uses the solubility difference of impurities between a solid (that is, crystal) and a melt phase. The impurities prefer to remain in the melt phase rather than in the crystal phase [3,4]. Of the many possible melt crystallisation processes, focuswas placed on a layer crystallisation process.

*Possibility of Cs and Sr separation by melt crystallisation process*

The possible separation of Cs and Sr from LiCl molten salt by melt crystallisation can be determined from the phase diagram. Figure.2.126 shows the solid-liquid phase diagram for the LiCl-CsCl-$SrCl_2$ system, drawn using the FactSage software [5]. As shown, under the condition of constant composition, with decreasing temperature, the phase and type of components are changed. If LiCl molten salts containing CsCl and $SrCl_2$ are cooled, i.e. crystallised at a temperature above over about 430$^0$C, only LiCl is present as a solid, and CsCl and $SrCl_2$ exist as a liquid phase. Consequently, it is possible to purify LiCl waste salt by using the melt crystallisation process; i.e. cesium and strontium can be concentrated in a small part of the LiCl waste salts.

**Figure 2.126. Solid-liquid phase diagram for the LiCl-CsCl-$SrCl_2$ system**



(A) $SrCl_2$ content = 2wt%

(B) $SrCl_2$ content = 10wt%

*Separation of Cs and Sr by the layer melt crystallisation process*

A layer crystallisation process has been commercially used for the separation and purification of a number of chemical products. Layer crystallisation is a very simple process. It uses cooled plates immersed in a melt for crystal formation andgrowth as a compact crystalline layer on the cooling surface. In this process impurities are concentrated in the melt phase and not in the crystal layer. In the layer crystallisation process, the crystal growth rate is the governing factor determining the structure of the crystal layer and the impurity concentration in the crystal layer.

Preliminary experiments using layer crystallisation were carried out in a small scale apparatus as illustrated in Figure 2.127. Compressed dry air was used as the cooling agent; the cooling rate, and therefore the crystal growth rate were controlled by varying the air flow rate. The initial cooling air temperature was fixed at 28°C, and the cooling air flow rate, the initial molten salt temperature and concentration of Cs and Sr were chosen as experimental variables.

Since the layer crystallisation process is based on the growth of a solid layer on a cooled surface, the crystal growth rate affects the formed crystal structure and the inclusion of impurities in the crystal. At a high cooling air flow rate, the crystals showed a bed crystal structure: that is, no directional growth causes the entrapment of many impurities. In this case, all the LiCl, cesium and strontium chlorides are cooled together and therefore no separation (or concentration) occurs (Figure 2.128(b)). By contrast, in the high impurity separation case, the crystal shows good directional growth shape (Figure 2.128(a)).

**Figure 2.127. Schematic diagram of the experimental set-up**

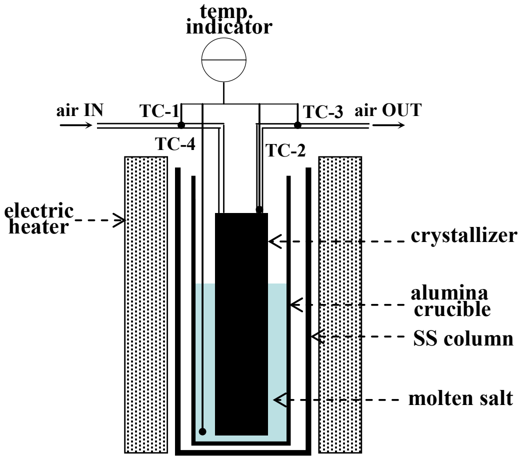
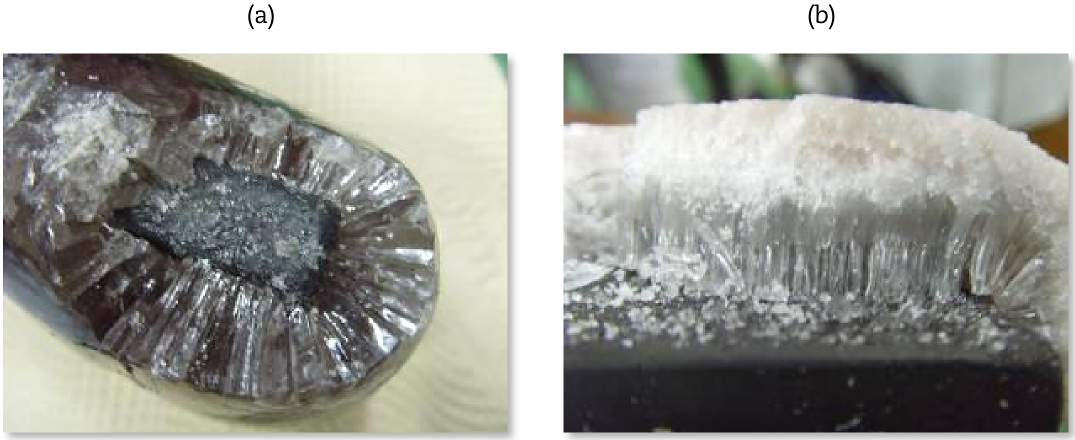


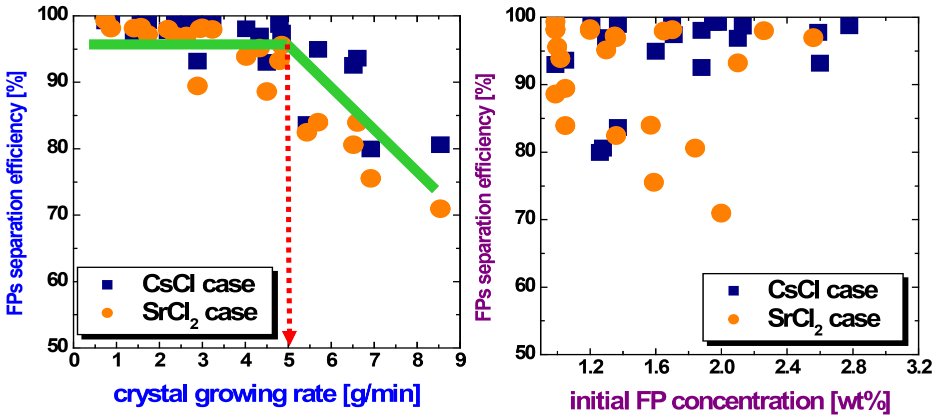
**Figure 2.128. A crystal formed at the surface of the crystalliser**


(a)

(b)

The effects of the crystal growth rate and the initial Cs and Sr concentration on the separation efficiency can be seen in Figure 2.129, in which a 90% LiCl re-use rate (or 90% LiCl crystal formation) was assumed. The separation efficiency decreased with increasing crystal growth rate. This is because, at a high crystal growth rate, many impurities are entrapped in the crystal layer. The effect of the initial Cs and Sr concentration in LiCl molten salts was nearly negligible within the experimental range [6].

**Figure 2.129. Effect of crystal growth rate and initial Cs and Sr concentration on the separation efficiency in the layer crystallisation process**



### 2.3.6. *Fluoride volatilisation processes*

The separation techniques known as “volatilisation” or “fluoride volatility” are typical “dry” processes based on the specific chemical property of uranium to form volatile uranium hexafluoride. The main techniques involve fluorination of spent fuel with fluorine gas or with some strong fluorination agents and subsequent separation of resultant volatile compounds, (mainly uranium hexafluoride) from non-volatile fluorides, in the first instance from $PuF_4$. There are two main volatilisation techniques: (1) the reaction between fluorine gas and a fused salt, and (2) the reaction between fluorine gas or a fluorinating agent, and solid powdered material [1-3].

The volatilisation technique was studied at Oak Ridge National Laboratory (ORNL) mainly during the Molten Salt Reactor Experiment (MSRE) program in the 1960s and 1970s. This technique was based on bubbling fluorine gas into a fused fluoride salt, containing elements that formed volatile fluorides species. The main objective of the program was the development and verification of a process to remove uranium (in the form of volatile $UF_6$) from the molten fluoride salt carrier (based on $LiF$-$BeF_2$ or $LiF$-$BeF_2$-$ZrF_4$ mixtures). The processes were successfully verified in 1968, with complete separation of uranium from the MSRE salt [3].

The volatilisation technique which is based on a heterogeneous reaction between fluorine gas and powdered spent fuel oxides, is known as the “Fluoride Volatility Method”. This process, originally designed for fast neutron reactor fuel reprocessing, had been mainly studied in the United States, Russia, France, the Czech Republic, Belgium and Japan. The fluorination process was performed either in a fluidised bed reactor (United States, France, Belgium and Japan) or in a flame fluorinator (former Soviet Union and Czechoslovakia) [4-10]. In recent times the process has been under further development, only in the Czech Republic, Russia and Japan [11,12]. All fluoride volatilisation studies have confirmed high efficiency of uranium recovery, and promising possibilities for plutonium recovery; however; the efficiencies of individual minor actinide recovery have not been fully verified yet.

*Fluoride volatility method*

The fluoride volatility method (FVM) is regarded as a promising advanced pyrochemical reprocessing technology, which can be used for reprocessing mainly oxide spent fuels from future light water reactors (LWRs) or Gen IV fast reactors (FR), especially fast neutron reactors. The technology could be chiefly suitable for reprocessing advanced oxide fuel types, e.g. fuels with inert matrices, and/or fuelswith high burn-up and high content of plutonium and short cooling time, which might be more difficult to be reprocessed by hydrometallurgical technologies, due to the higher radioactivity.

The fluoride volatility method is a separation process, based on the specific properties of uranium, neptunium and plutonium for forming volatile fluoride species whereas most of the fission products (lanthanides) and transplutonium elements that present in irradiated fuel form non-volatile trifluorides. Variations of the fluoride volatility process have been developed for fluorination of irradiated fuel, either by strong fluorinating agents like $BrF_3$, $BrF_5$, $ClF_3$ or even by pure fluorine gas. Development activities were carried out in the 1950s and 1960s in the United States at the Brookhaven, Argonne and Oak Ridge laboratories [3] in the 1970s, in France, Fontenay-aux-Roses [5,6] and in Belgium at Mol [2]; in 1970s and 1980s in the former Soviet Union, at Dimitrovgrad [9] and in former Czechoslovakia, at Rez [10].

Original intentions of the development of this dry pyrochemical method of reprocessing spent fuel were motivated in the past by the planned commercial utilisation of fast neutron reactors (FNRs). Introduction of FBRs in the power industry can be economically efficient only in the case of a closed fuel cycle. However, reprocessing of fast reactor spent fuel brings about a number of specific difficulties in comparison to the reprocessing of spent fuel from thermal reactors. They are caused, for example, by higher burn-up and shorter cooling time resulting in a higher amount of energy released by the fuel, higher concentration and amount of plutonium, different cladding material, presence of metallic sodium, different fission products composition, etc. Therefore, the countries that were planning to introducte fast reactors, were attempting to develop suitable methods for reprocessing, because the industrial hydrometallurgical PUREX process, employing organic extractants and solvents, was not believed to be well-suited for processing fast reactor spent fuel. Hence, the most intensive effort in the development of the fluoride volatility processes was in the 1960s and 1970s, together with the development of FNRs.

Currently, renewed interest in the dry – pyrochemical reprocessing methods is motivated by requirements on the development of advanced fuel cycle technologies devoted to the planned Gen IV nuclear reactor systems.

The reprocessing technology based on the fluoride volatility method consists of the following main operations:

- removal of the cladding material from spent fuel elements;
- transformation of the fuel into a powder with granulometric properties, allowing the fluorination reaction;
- fluorination of the powdered fuel (the purpose of this operation is the separation of most of the uranium component from plutonium, minor actinides and most fission products). (A second fluorination step may be used to separate the U-Pu-Np for fission products and trivalent Am-Cm.);
- purification of the products obtained.

The first two steps represent preparatory stages prior to the fluoride volatility process step. One suitable technology for the cladding material removal is melting in a high temperature furnace. The cladding material of oxide fuel is zircalloy or stainless steel, and either can be fully removed. Transformation of the fuel pellets into a powder is possible either mechanically by grinding or by oxidation of $UO_2$ into $U_3O_8$. This latter process is called by a variety of names, such as voloxidation, but all are dry pyrochemical oxidation processes. Either flowing air or oxygen at 450°C to 600°C is used as oxidising agent. The original voloxidation process was developed in ORNL in US and then further developed in several countries. However, to prepare a uniform powder of required granulometry by the voloxidation technique, for subsequent fluorination is rather difficult [15].

The early fluorination techniques of the FVM were fluidised bed processes; however, the direct flame fluorination of powdered fuel is currently considered as the most promising unit operation for future industrial application.

*Description of the fluoride volatility process*

Significant development of the fluoride volatility process has been done in Russia or in the former Soviet Union since the 1950s. The original studies were initiated by RRC – Kurchatov Institute and VNIIKHT (Leading Research Institute of Chemical Technology) in Moscow. Both institutes used large scale equipment for the production of elemental fluorine and developed the volatility processes for the production of uranium hexafluoride, initially for the purposes of uranium isotopic enrichment. In the early 1960s the the Research Institute for Atomic RReactors (RIAR,Dimitrovgrad) performed R&D, and designed and constructed the experimental installation, called FREGAT, for fluoride volatility reprocessing of SNF from the BOR-60 fast reactor [9].

Though the physical and chemical principles of the fluoride volatility process are simple, technical problems connected with the properties of fluorine, such as its exceptional chemical reactivity and the high thermal output of the fluorination reactions, were encountered. Although the industrial production of uranium hexafluoride had been done previously, extensive R&D was required to optimise the process of spent fuel fluorination, an extensive R&D was required to achieve efficient heat removal at sufficiently small (criticality safe) size, and with adequate filtration of the gaseous flow at the outlet of the apparatus.

The problem of control over $U_3O_8$ fluorination in the fluidised bed was studied at the Kurchatov Institute [14] where the throughput rate reached by the experimental fluorinator, which had a diameter of 100 mm, was 790 kg of uranium/hr per square meter of fluorination zone cross-section. Also, the process conditions under which the fluidised bed does not cake were calculated and experimentally confirmed. Elutriation of $U_3O_8$ fines from the fluidised bed wasprevented by using a high-efficiency filter bed formed of the same material as in the fluidised bed reactor and returning the filter bed to the lower section in the reaction zone. A criticality-safe fluorinator with a cross-section of 0.1 x 0.4 m, was designed to process 100 t/y of irradiated fuel in the experimental plant.

During fluorination of a uranium-plutonium mixture, uranium hexafluoride is formed much more rapidly than plutonium hexafluoride; thus making it possible to separate the majority of the uranium from the plutonium. The equilibrium constant for the reaction, $PuF_4 + F_2 = PuF_6$, at 500°C, is only 0.01 [15], which gives a low rate of $PuF_6$ formation, even with a large flow of fluorine. Atomic fluorine is produced in a high frequency discharge, and can be used to increase the concentration of plutonium hexafluoride in the gas stream [16]. In this case, heating is not required. In experiments with uranium, the average rate of $UF_6$ formation from $UF_4$ was 20-57 kg U per $m^2$ per hour, which is. 2.5-4 times higher than that attained for formation of $PuF_6$ with molecular fluorine. Corrosion of structural materials is not a problem in fluorination at 500°C. In any case, it is reasonable to fluorinate both plutonium and uranium in a cold fluidised bed using atomic fluorine. This makes it possible to avoid engineering problems associated with heating the apparatus to 500°C, as well as increasing the degree of purification of both U and Pu from fission products at the fluorination stage.

Another method of fluorination of irradiated fuel, using a flame-type cold-wall apparatus, was also developed in Russia. At a flame temperature over 1 300 K, uranium and plutonium are fluorinated at a high rate. In bench-scale experiments on fluorination of spent fuel, yields of uranium and plutonium above 99% and 89-91% respectively were obtained [9]. This type of apparatus would be useful, for example, in the initial fluorination of the bulk of the fuel, followed by fluorination of the plutonium-bearing residue by atomic fluorine in a separate facility. Purification of uranium hexafluoride from volatile fluorides, including fission products fluorides, has been successfully demonstrated on industrial scale. Small bathes of $UF_6$ (up to hundreds of kilograms) can be purified conveniently by a sorption method using NaF, while distillation of liquid $UF_6$ does best of all for large-scale production [17-19].

The primary advantage of the fluoride volatility process is the possibility of producing non-volatile fission products in a compact form; this has been experimentally demonstrated during the 1970s at the FREGAT facility at RIAR by t reprocessing just over 4 kg of irradiated uranium dioxide, with an average burn-up of about 10%, from an initial enrichment of 90% of $^{235}U$, and cooling of 6 months. About 85% of the total fission product radioactivity was concentrated in the residues, which did not exceed 15% of the fuel mass [9]. Thus, the volume of the solid media containing the fission products extracted from a unit mass of irradiated fuel at a fluoride facility would be tens of times less than from a solvent extraction plant process, prior to evaporation and conversion to a solid fission product waste. This is explained by the absence of buffer tanks for dissolved fuel and for the raffinate and concentrate. In an accident, the solid materials produced in the fluoride process could not escape far from the container (with the exception of aerosols), while the liquids produced in the solvent extraction could be carried for large distances.

As discussed above, the latest development of the fluorination process within the FVM has been focused on direct flame fluorination by pure fluorine gas. This method of flame fluorination reaction of a spent oxide fuel is very hopeful for industrial process. The reaction between the fuel powder and pure fluorine gas is spontaneous and highly exothermic. The temperature of ignition is over 250°C. Subsequently the temperature in the flame can reach the range of 1 300°C to 1 700°C and therefore, the walls of the reactor chamber and the reactor body have to be immediately and intensively cooled.

The principal fluorination reactions of the main fuel components are described below:

- uranium

$UO_2\ (s) + 3F_2\ (g) \rightarrow UF_6\ (g) + O_2\ (g)$ $\quad \Delta_r H^0_{298.15} = -1062.4$ kJ/mol U (1)

or $U_3O_8\ (s) + 9F_2\ (g) \rightarrow 3UF_6\ (g) + 4O_2\ (g)$ $\quad \Delta_r H^0_{298.15} = -955.8$ kJ/mol U (2)

- plutonium

$PuO_2\ (s) + 2F_2\ (g) \rightarrow PuF_4\ (s) + O_2\ (g)$ $\quad \Delta_r H^0_{298.15} = -722.4$ kJ/mol Pu (3)

$PuO_2\ (s) + 3F_2\ (g) \rightarrow PuF_6\ (g) + O_2\ (g)$ $\quad \Delta_r H^0_{298.15} = -693.1$ kJ/mol Pu (4)

$PuF_4\ (s) + F_2\ (g) \leftrightarrow PuF_6\ (g)$ $\quad K_p = [PuF_6] / [F_2]$ (5)

  - lanthanides

$2Ln_2O_3\ (s) + 6F_2\ (g) \rightarrow 4LnF_3\ (s) + 3O_2\ (g)$ (6)

- minor actinides
- neptunium

$NpO_2\ (s) + 3F_2\ (g) \rightarrow NpF_6\ (g) + O_2\ (g)$ $\quad \Delta_r H^0_{298.15} = -907.9$ kJ/mol Np (7)

$NpO_2\ (s) + 2F_2\ (g) \rightarrow NpF_4\ (s) + O_2\ (g)$ $\quad \Delta_r H^0_{298.15} = -844.7$ kJ/mol Np (8)

$NpF_4\ (s) + F_2\ (g) \leftrightarrow NpF_6\ (g)$ $\quad K_p = [NpF_6] / [F_2]$ (9)

- americium and curium

$2Am_2O_3\ (s) + 6F_2\ (g) \rightarrow 4AmF_3\ (s) + 3O_2\ (g)$ (10)

$2Cm_2O_3\ (s) + 6F_2\ (g) \rightarrow 4CmF_3\ (s) + 3O_2\ (g)$ (11)

The reaction enthalpies were determined from the thermochemical data of pure substances [20-22].

Based on these reactions, the main partitioning of spent fuel is realised directly in the fluorination reactor. Whereas the volatile products of the fluorination reaction leave the apparatus in the off-gas, the non-volatile fluorides remain catched in the fluorinator bottom in the form of ash. The distribution of the spent fuel fluorination products according to their volatility is listed in Table 2.35. The further separation of most of individual components forming volatile fluorides is generally possible by sorption, condensation or distillation processes. However the separation of some volatile components is questionable, owing to their chemical similarity.

**Table 2.35. Distribution of fluorinated spent fuel according to the volatility [23]**

| Group I (highly volatile) | | | Group II (volatile) | | | Group III (non-volatile) | | |
|---|---|---|---|---|---|---|---|---|
| Agent | m.p. °C | b.p. °C | Agent | m.p. °C | b.p. °C | Agent | m.p. °C | b.p. °C |
| Kr | –157,2 | –153.4 | $IF_7$ | 5 | 4 | $AmF_4$ | subl. | 513 |
| $CF_4$ | –184 | –129 | $MoF_6$ | 17.6 | 33.88 | $RhF_3$ | subl. | 600 |
| Xe | –111.8 | –108.1 | $NpF_6$ | 54.8 | 55.18 | $SnF_4$ | subl. | 705 |
| $TeF_6$ | subl. | –38.6 | $TcF_6$ | 37.9 | 55.2 | $ZrF_4$ | 912 | 918 |
| $SeF_6$ | subl. | –34.5 | $UF_6$ | 64 | 56.5 | $PuF_4$ | 1 037 | 927 |
| | | | $PuF_6$ | 51.9 | 62.2 | CsF | 703 | 1 231 |
| | | | $IF_5$ | 9.4 | 98 | RbF | 760 | 1 410 |
| | | | $SbF_5$ | 6 | 142.7 | $UF_4$ | 1 036 | 1 450 |
| | | | $NbF_5$ | 80 | 235 | $AmF_3$ | 1 427 | 2 067 |
| | | | $RuF_5$ | 101 | 280 | $CmF_3$ | 1 406 | 2 330 |
| | | | $RuF_6$ | 51 | 70 | $YF_3$ | 1 136 | 2 230 |
| | | | $RhF_5$ | 95.5 | n/a | $BaF_2$ | 1 353 | 2 260 |
| | | | $RhF_6$ | 70 | 73.5 | $EuF_3$ | 1 276 | 2 280 |
| | | | | | | $GdF_3$ | 1 380 | 2 280 |
| | | | | | | $CeF_4$ | 838 | decomp. |
| | | | | | | $CeF_3$ | 1 430 | 2 330 |
| | | | | | | $PmF_3$ | 1 410 | 2 330 |
| | | | | | | $SmF_3$ | 1 306 | 2 330 |
| | | | | | | $SrF_2$ | 1 400 | 2 460 |

While the fluorination of uranium to the volatile hexavalent form is spontaneous, plutonium hexafluoride is thermally unstable and can be obtained only with a considerable oversupply of fluorine gas. The behaviour of neptunium varies between uranium and plutonium based on the amount of surplus fluorine gas. However, the thermal stability of neptunium hexafluoride is substantially higher than plutonium hexafluoride, so the thermal decomposition of $NpF_6$ is significantly less. Other chemical properties of neptunium, such as the reaction of $NpF_6$ with NaF, and the physical-chemical properties of $NpF_6$, could cause both uranium and plutonium product streams to be contaminated by neptunium. Conditions of satisfactory separation of neptunium have not been found yet; however, current R&D efforts offer a chance to solve this problem.

Uranium, plutonium and neptunium hexafluorides do not form a liquid phase at atmospheric pressure, and their sublimation points are similar: 56.5°C for $UF_6$, 55.2°C for $NpF_6$ and 62.2°C for $PuF_6$. A mathod to separate neptunium from uranium and plutonium from the fluorinator off-gas steam is by using sorption – desorption traps on sodium and magnesium fluorides [10]. Sodium fluoride is commonly used for the decontamination of $UF_6$. Uranium, neptunium, and plutonium hexafluorides are completely sorbed on NaF at 100°C. Uranium and neptunium hexafluorides can be completely desorbed at 400°C while passing fluorine gas through the bed, but desorption of plutonium hexafluoride is impossible because it forms the complex $PuF_4.3NaF$, which is thermally stable even in the fluorine gas flow. Partial separation of neptunium from uranium is possible only via irreversible sorption of $NpF_6$ on a$MgF_2$ trap at 100°C. Under these conditions, $UF_6$ is not sorbed on the $MgF_2$, but the sorption of $NpF_6$ on the trap proceeds with the efficiency of 60 -70%.

Final purification of uranium hexafluoride from $MoF_6$, $TcF_6$, $IF_5$ and $SbF_5$, all of which tends to accompany $UF_6$ in the fluorinator off-gas stream, could be done with a rectification process. Distillation of $UF_6$ can be performed within a temperature range from 75°C to 90°C, at a pressure of about 2 atm., in order to have uranium hexafluorides in liquid form. This technology was studied in the 1980s with partial success, but the rectification process still needs further intensive development [10].

Suitable structural materials for FVM equipment are pure nickel and nickel alloys. The rates of corrosion of nickel by fluorine gas, anhydrous HF and volatile fluorides are sufficiently low at up to 600-650°C [2]. Although pure nickel exhibits very good corrosion resistance, the use of high-nickel-content alloys could be more appropriate for manufacture of the fluoride volatility equipment and piping, due to difficulties by welding of pure nickel material. [24].

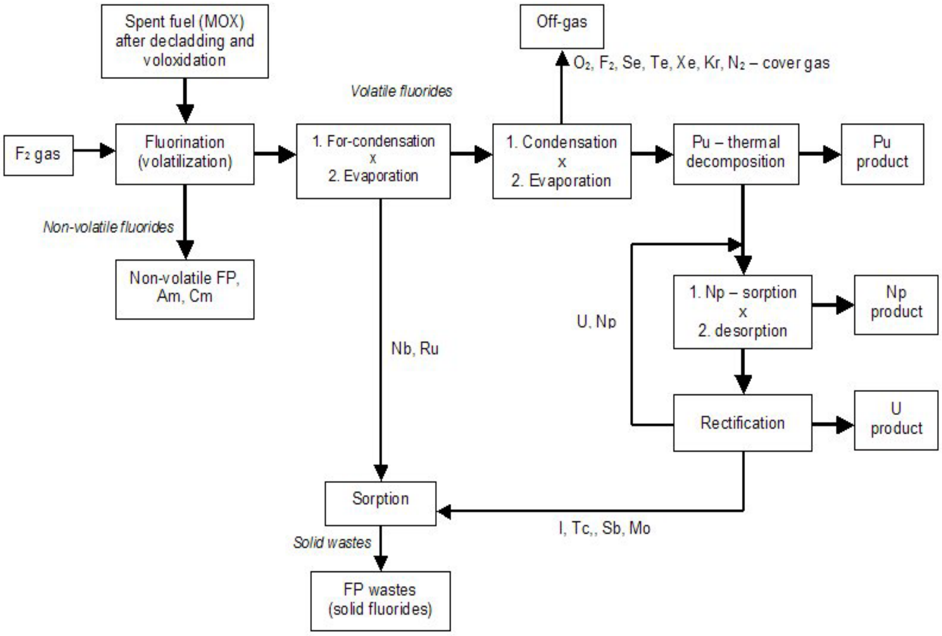
*Current status of R&D on fluoride volatility method*

Currently, the only laboratory where the FVM is under technological R&D is UJV Rez (former Nuclear Research Institute) co-operating in this field with Research Centre Rez. There, the current R&D represents the follow-up of the former long-lasting R&D activities in FNR fuel reprocessing as part of the GREGAT-2 programme [10] which occurred during the 1980s. The FREGAT-2 equipment, which was located in RIAR Dimitrovgrad, was used in an attempt to reprocess the spent fuel from BOR-60 experimental fast reactor. Unfortunately, the FREGAT-2 programme was interrupted before the development of the process and equipment could be completed due a change of priorities after the Chernobyl accident. However, because the main equipment components ib the FREGAT-2 line were made by Czech companies and owned by UJV Rez, these components were returned to to UJV Rez after the interruption of the FREGAT-2 programme. Now, after substantial reconstruction they comprise the basic part of the new FERDA line, which is devoted to the present technological development of the FVM.

The current experimental R&D programme on the development of the pyrochemical reprocessing of current and advanced oxide fuel type, was launched by the UJV Rez in 2004. The aim the current activities is to develop a suitable pyrochemical technology, which could be used, either for reprocessing of LWR spent mixed-oxide fuels (MOX,) or for reprocessing of advanced types of fast reactor spent fuel.

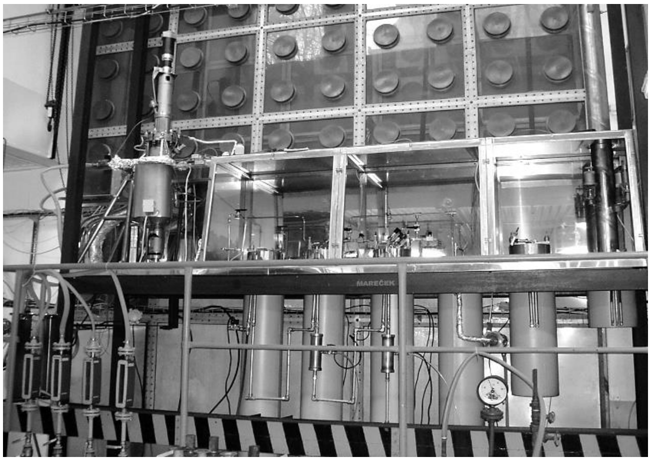
The process flowsheet for the investigated FVM technology, which has been investigated, is based on the direct fluorination of powdered spent fuel by fluorine gas and on the subsequent purification of volatile products by condensation, sorption, thermal decomposition and distillation; the flowsheet is shown in Figure 2.130. The main partitioning process step for spent fuel components is performed in a flame fluorinator, where during the fluorination reaction, the volatile fluorides of uranium, neptunium, plutonium and some fission products are successively transferred into the reactor off-gas stream from which The U, Pu, and Np are trapped in a series of condensers or sorption columns. The group of non-volatile fluorides (most of the fission products (FP) and americium and curium) are collected in the ashpan beneath the reactor. In the initial fluorination, most of ruthenium and niobium are separated from the U, Np and Pu. After subsequent evaporation of uranium, neptunium and plutonium hexafluorides from a second condenser, the plutonium is separated from uranium and neptunium by thermal decomposition of volatile $PuF_6$ according to the inverse of Equation (5). Neptunium is then separated from the uranium by sorption of $NpF_6$ on a $MgF_2$ trap. Finally, the purification of uranium from the remaining volatile fission product fluorides ($IF_5$, $TcF_6$, $MoF_6$, $SbF_5$) is done by using multiple distillations and rectification of $UF_6$. The main desired products of the reprocessing technology, which are uranium and plutonium, are obtained in the form of volatile $UF_6$ and solid $PuF_4$.

**Figure 2.130. Process flowsheet of fluoride volatility method**



The current experimental R&D programme focuses mainly on the development of individual unit operations, equipement design, process contro and material research [25, 26]. The experimental semi-technological equipment line called FERDA, shown in Figure 2.131, was manufactured and placed in the alpha-radiochemical laboratory of the UJV Rez. The technology consists of a flame fluorinator, a series of condensers, sorption columns and a distillation column. The short-term capacity of the flame fluorination reactor is 1-3 kg of fuel per hour, but the process has a batch character and the maximum quantity of material processed during an experiment is about 7 kg. The pressure of pure fluorine gas leaving the cylinder is reduced by a regulator to about 1 atmosphere before entering the fluorination reactor, and the flow of process gases through the line is controlled by the vacuum system.

**Figure 2.131. Experimental line FERDA for R&D of fluoride volatility method**



From the left: flame fluorination reactor, series of three condensers, sorption columns and distillation column.

Current experimental efforts are focused on mastering the fluorination process and on the elimination of some bottlenecks of the technology. After tests performed with pure uranium fuel ($UO_2$ or $U_3O_8$) were completed, the present experimental work is aimed at the development of the process using simulated spent oxide fuel constiting of a mixture of uranium oxides and non-radioactive oxides that represent selected fission products (lanthanides, Cs, Sr etc.). The objective of this work is to demonstrate partitioning of volatile from non-volatile products of the fluorination reaction. The next phase will be done to verify the suitability of the technology for reprocessing of advanced types of oxide fuels, especially those containing selected inert matrices ($ZrO_2$, MgO). Expected resulting separation efficiencies of the FVM are shown in Table. 2.36. The anticipated differences in separation efficiency of uranium are dependent on the allowable content of neptunium in the product.

The final demonstration using the FERDA line will be done using actual irradiated fuel and is planed to be carried out in the in new hot cell complex of the Research Centre Rez (a subsidiary of UJV Rez).

**Table 2.36. Demonstrated separation efficiencies of selected spent fuel components using the of fluoride volatility method**

| Chemical elements | Separation efficiency (%) |
|---|---|
| U | 95 – 99.5 |
| Pu | ~98 – 99.5 |
| Np | ~60 - 70 |
| Nb, Ru | ~95 – 99 |
| Am,Cm | individually inseparable<br>(in non-volatile fluoride stream) |
| FP forming solid fluorides | individually inseparable<br>(in non-volatile fluoride stream) |

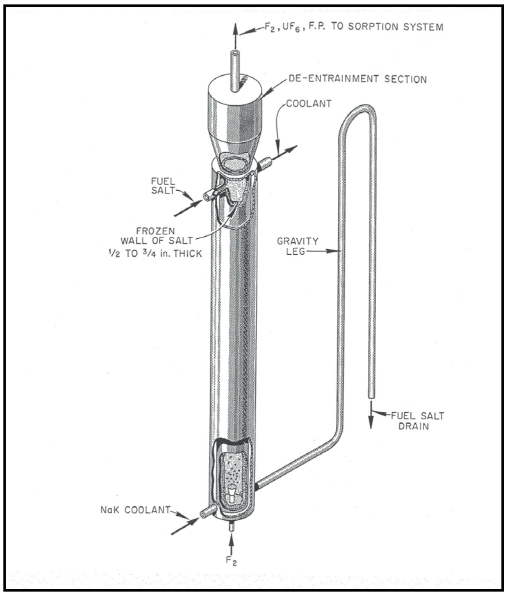
The fluoride volatility method has good potential to be used for reprocessing spent fuels from several current or advanced reactor types and current or future advanced oxide fuel types. A primary attractiveness of the technology would be for reprocessing fast neutron reactor spent fuel, owing to the extreme high radiation resistance of the used chemical agents (fluorine gas, inorganic fluorides). Use of FVM to prepare recycled fuel for molten salt transmutation reactors is highly attractive due to the capability to convert oxide form of original spent fuel into fluorides – the chemical form used in molten salt reactors. Another attractiveness of the process is the capability to process oxide fuel types that are insufficiently soluble in nitric acidsuch as oxide fuels with inert matrices containing $ZrO_2$ or fuels with high content of plutonium. Further advantages of the technology come from the compactness of the process equipment and from the exclusion of any moderating agent, which allows higher amount of fissile material to be processed in smaller volume. However, despite the attractive features of the FVM, the separation efficiencies similar are low in comparison to those achieved by current industrial hydrometallurgical processes; therefore further intensive research and development will be required to improve the capability.

*Fused salt volatilisation method*

Fluoride volatilisation of fused fluoride salt was a technique for uranium extraction from the fuel salt of the Molten Salt Reactor Experiment (MSRE) [3], a project carried out in the United States in 1968 at Oak Ridge National Laboratory (ORNL) and in which this technology was demonstrated. The FVM was used in the MSRE to remove the original original $^{235}U$ and replace it with $^{233}U$. In the MSRE, the carrier molten fluoride salt, in which uranium was dissolved, was a LiF – $BeF_2$ melt. Uranium-235 was removed from the carrier salt as uranium hexafluoride, by sparging the salt with fluorine gas. Fluorine gas was bubbled through the salt, which contained uranium in the form of dissolved $UF_4$ to produce of $UF_6$ at the gas-liquid phase interface. The rate of the fluorination reaction was sufficiently high in the temperature range of 500-600°C. Therefore, the mass transfer of uranium compounds in the liquid phase was likely the limiting stage of the process.

Special equipment for continual fluorination of the salt was designed by ORNL in 1960s [27]. The crucial part of the equipment was the continuous fluorination reactor with a frozen wall for corrosion protection (Figure 2.132). The main structural material of the fluorinator was pure nickel.

**Figure 2.132. Fused salt fluorination reactor (Courtesy of ORNL)**



The carrier molten salt containing dissolved $UF_4$ flowed into the top of the fluorination reactor and was contacted by a counter-current stream of fluorine gas, which stripped out the uranium in the form of volatile $UF_6$ according to the following reaction:

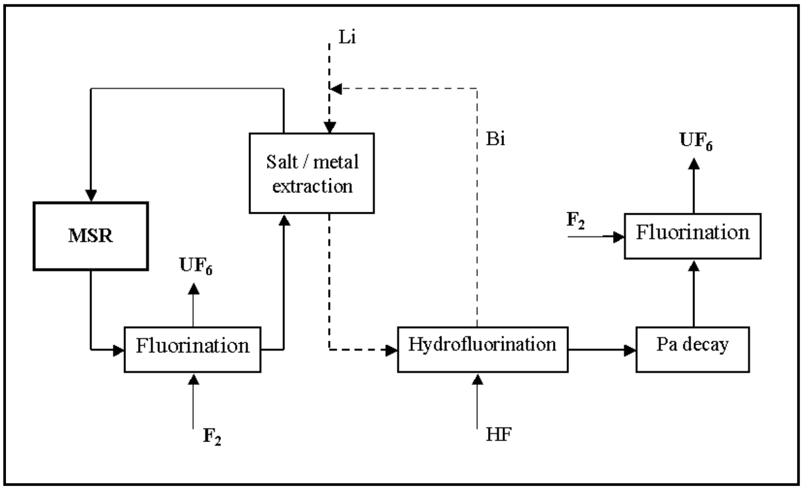
$$UF_4 + F_2 \longrightarrow UF_6 \qquad (12)$$

The working temperatures were in the range of 500-550°C; the reactor wall coolant was NaK. The off-gas containing uranium hexafluoride, fluorine gas, and volatile fluorides of some fission products (mainly $CrF_4$ and $CrF_5$) passed through a sorption column filled with NaF pellets and heated to 400°C for removal of chromium fluorides. $UF_6$ was then trapped in a secong NaF trap at 100°C. Similar technology was under development in ORNL during the ensuing MSBR programme during the early 1970s, and was aimed mainly to design an online reprocessing scheme for molten salt reactors using $^{232}Th$ – $^{233}U$ fuel cycle [28].

This method of uranium removal was also studied in the RRC Kurchatov Institute in the 1980s and 1990s. Both static and dynamic conditions of the fused salt fluorination method were investigated [29,30].

The technology of uranium removal by fused salt volatilisation is now a widely recognised method as one possible technique for use within the online fuel reprocessing of future MSRs with Th-fuel. The removal of uranium from the fuel salt of MSRs is a part of the protactinium removal process. Protactinium ($^{233}Pa$) is produced in the reactor core from thorium $^{232}$Thby nuclear reactions. The half-live of radioactive decay of $^{232}Pa$ is 27 days and its only daughter product is $^{233}U$. However, the arising protactinium, which is also a neutron poison, has to be immediately removed from the circulating fuel salt in the reactor to prevent loss of criticality. A suitable technology for protactinium removal from the fluoride molten salt carrier is the “molten salt/liquid metal reductive extraction process”, occasionally referred to as a “metal transfer process”. Because the fuel salt of a MSR contains several percent of uranium in the form of uranium tetrafluoride ($UF_4$), it has been shown, that uranium removal by fluoride volatilisation of the fused salt can save the amount of the reducing agent, $^{7}Li$, used for subsequent protactinium isolation. The simplified scheme for the protactinium isolation process, according to the ORNL proposal [3], is shown in Figure 2.133.

**Figure 2.133. Simplified scheme of protactinium isolation from MSR fuel**



### *FLUOREX technology*

A hybrid reprocessing technology, based on initial fluoride volatility and subsequent solvent extraction, was investigated in Japan by Hitachi and TEPCO, in co-operation with the RRC Kurchatov Institute during the first decade of this century. The investigation was motivated by the wish to develop an efficient reprocessing technology for the gradual transition from the current LWR fuel cycle to future FBR deployment. During the transition period, the reprocessing plant would treat spent fuels from LWRs and FBRs and supply recycle fuel materials to LWRs and FBRs.

A flexible reprocessing method named FLUOREX was investigated to meet the requirements for the transition period fuel cycle [12,31-37]. This method is a combination of fluorination and removal of the amount of uranium from the spent fuels to leave an almost constant U/Pu ratio for feed to the subsequent solvent extraction process in which U/Pu would be recovered from the fluorination residue that contains U/Pu, fission products (FP) and minor actinides (MA). The method, named FLUOREX, was designed for reprocessing of $UO_2$ and MOX spent fuels from LWRs from and FBRs.

The schematic outline of the FLUOREX process is shown in Figure 2.134. After dry decladding, pulverised spent fuel is fed into a compact flame reactor for rapid separation of U in the form of gaseous $UF_6$ which is then purified in adsorption columns. Some amount of Pu ($PuF_6$) in the gaseous phase is trapped by $UO_2F_2$ adsorbent and re-mixed with the fluorination residue. The residue, a mixture of U, Pu, MA and FP fluorides, is converted to oxide and dissolved in nitric acid solution to recover U/Pu (and MA) by the normal or advanced solvent extraction methods.

Fundamental experiments were conducted to learn the effectiveness of the FLUOREX process. Fluorination was studied for important nuclides, such as U, Pu, Np, Tc, in simulated spent fuel and actual BWR spent fuel with ~58 GWd/t burn-up. An experimental flame reactor with a capacity of 500 gU/h was designed (Figure 2.135). Also, the $UF_6$ purification, Pu trapping, fluoride conversion to oxide, oxide dissolution and analytical studies were carried out. These investigations showed that (1) the flame reactor can rapidly separate more than 90% of the U from the spent fuel, (2) $UO_2F_2$ can trap almost all of the $PuF_6$ from gaseous $UF_6$ stream and (3) the converted fluorides residue can be easily dissolved in nitric acid. Thus, it was basically proven that the FLUOREX technology can be applied successfully to spent fuel reprocessing.

### *2.3.7. Separation processes connected with MSR technology*

A molten salt reactor (MSR) is a non-classical nuclear reactor type, which exhibits some very specific features due to its use of a liquid molten salt fuel, which is circulated between the reactor core and heat exchangers. Moreover, the fuel circuit would include online fuel reprocessing unit, which os necessary to keep the reactor in operation for a long period of time. A MSR can be very effectively operated with either the uranium-plutonium or thorium-uranium-233 fuel cycle as was demonstrated in the MSRE. All these aspects of the MSR system significantly affect the chemical separation processes and technologies applicable within the MSR system [1].

Figure 2.134. Outline of the FLUOREX process

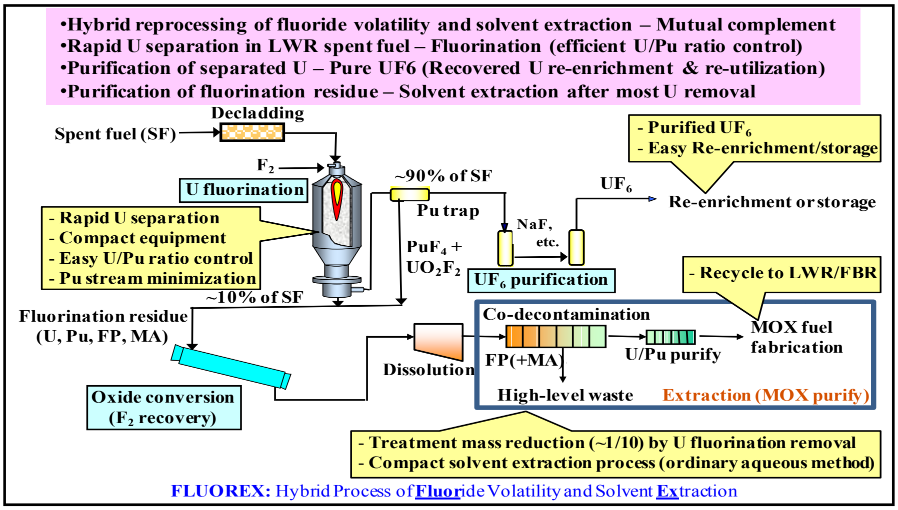
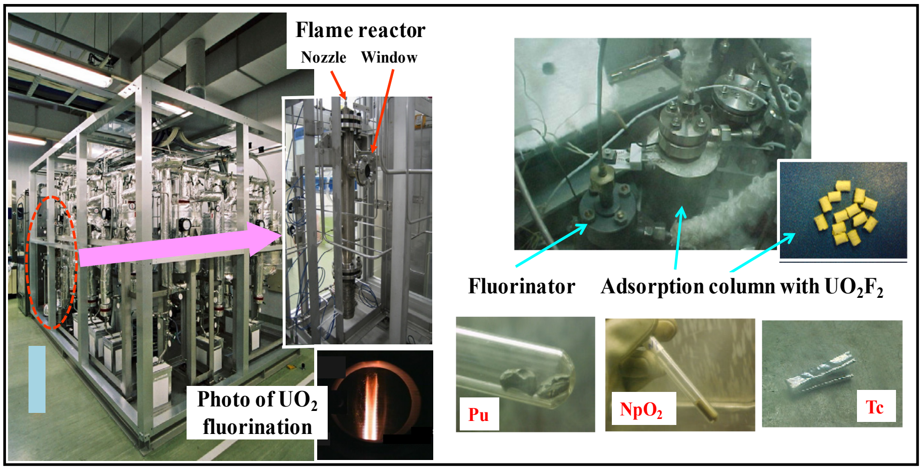


Figure 2.135. $UO_2$ flame reactor of 500 gU/h (left) and small apparatus for fluorination of Pu, Np and Tc (right)



The chemical separation processes applicable within the MSR fuel cycle technology have to be compatible with the chemical nature of the molten fluoride fuel and with the requirement for virtually immediate fuel processing after leaving the reactor core. Moreover, the separation processes must often be effective at temperatures over 500°C and must be highly radiation resistant. Only a few pyrochemical separation systems meet these requirements [2,3].

The original investigation and experimental development of separation processes devoted to the MSR fuel cycle were developed in the 1950s, 1960s early 1970s. The objective was to develop a fuel reprocessing technology devoted to the concept of a 1000 MWe molten salt neutron reactor using in the thorium – uranium fuel cycle. After the Gen IV International Forum was chartered in 2001, efforts to continue the investigation and development of the separation processes devoted to the MSR fuel cycle, were restored. The existing and proposed technological development comes extensively from the original investigations.

The main separation processes which are applicable within the reprocessing technology of the liquid molten salt fuel are:

- gas extraction process known also as helium bubbling;
- fused salt volatilisation;
- molten salt/liquid metal reductive extraction;
- electrochemical separation techniques from molten fluoride salt;
- vacuum distillation of molten salt;
- oxide co-precipitation.

These processes can enable removal of the actinides from the liquid molten salt fuel and clean-up the carrier salt from fission products (neutron poisons). Although early MSR experiments showed the system would work for either the uranium-plutonium or the thorium – uranium-233 fuel cycle (molten salt neutron reactor – MSNR programme developed by Oak Ridge National Laboratory), current MSR designs that are proposed by the French Centre National de la Recherche Scientifique (CNRS) and Russian National Research Centre "Kurchatov Institute" usethe fast spectrum MSR (molten salt fast reactor – MSFR and molten salt actinide recycler and transmuter – MOSART) [4-6].

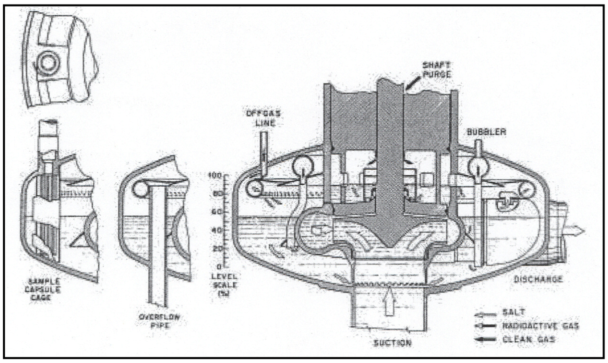
*Gas extraction process (Helium bubbling method)*

The principle of the helium bubbling method is based on–sparging the molten salt with inert gas (He) and on application of the scientific principle of Henry's Law. The solubility of dissolved gas (Xe, Kr) in a molten salt is proportional to the partial pressure of that gas in the atmosphere. If new inert gas (He) is introduced in the molten salt, the difference in partial pressure causes the dissolved gas (Xe, Kr) to leave the molten salt. The efficiency of sparging is influenced by many factors such as bubble size, temperature, gas pressure etc. Sparging is also a method to remove low-boiling components from a solution. In this case, it is an alternative method to distillation.

The Helium bubbling method was successfully used and verified in 1965-1969,during the MSREproject.The MSRE project used experimental 8 MWt MSR with the liquid fuel constiting of fluoride molten salt $^{7}LiF – BeF_2 – ZrF_4 – UF_4$, and later on $^{7}LiF – BeF_2 – UF_4$ and $LiF – BeF_2 – UF_4 – PuF_3$ molten salts. As the MSRE was operated only as an experimental reactor without the breeding of new fissile material, the complete reprocessing of its fuel salt was not necessary, except for the removal of main neutron poisons – xenon $^{135}Xe$ and to a lesser extent also krypton $^{85}Kr$. The gas extraction process (helium bubbling) emerged to be a suitable and effective method [5].

Among the fission products, noble gases (mainly $^{135}Xe$) are some of the most neutron poisoning elements in the fuel salt. Therefore, the removal of noble gases from the fuel salt had to be provided when the reactor was in operation. Noble gases have very low solubility in the fuel salt ($LiF – BeF_2 – UF_4$), enables to strip them from the fuel salt to reduce the poisoning effect of $^{13}5X$ by sparging the fuel salt with helium, which was then passed through charcoal traps in an off-gas clean-up system. The contact for noble gases (xenon and krypton) removal was produced by spraying of salt through the cover gas (helium) and into the pool of salt in the fuel primary pump bowl. The schematic view of the pump with helium sparging system is shown in Figure 2.136.

**Figure 2.136. Vertical section of fuel salt pump with helium sparging system**

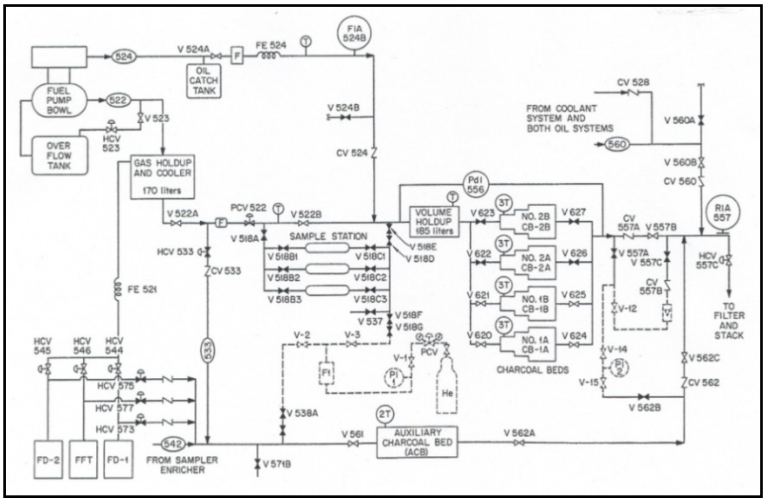


Source: ORNL.

At the end of the MSRE programme, helium was temporarily replaced by argon, which has a very much lower solubility in the fuel salt. Experiments at lower power showed substantial differences in the amounts of gas left in the core when using argon instead of helium. At low pump speeds, the small amount of helium drawn into the pump suction could almost completely dissolve in the salt before reaching the core. A similar amount of argon at the pump suction meant more bubbles in the salt going through the core because less dissolved. When the reactor was operated at t power with argon cover gas, the xenon poisoning at high void fractions was about the same as it was with helium, but the xenon poisoning was higher with argon when only small amounts of gas circulated with the salt. The difference between argon and helium is due almost entirely to the difference in solubility of these gases.

Xenon and krypton accompanied the purge stream (helium or argon) to the charcoal beds, where adsorption delayed their passage long enough for practically all the radionuclides except $^{85}$Kr to decay. The daughters of Xe and Kr were deposited on surfaces in contact with the gas stream, in quantities readily detectable by gamma-spectrometry and heat production. During the entire MSRE operation, temperatures in charcoal showed no evidence of any decrease in adsorptive capacity due to accumulation of these daughters [5,7]. The flowsheet of the MSRE fuel off-gas system is shown in Figure 2.137.

**Figure 2.137. Flowsheet of MSRE fuel off-gas system**



Source: ORNL.

Current investigation of the “gas extraction” process is being performed at the CNRS laboratory in Grenoble, France, where the experimental molten salt loop containing the helium bubbling equipment is under furthertechnological development. This effort is a part of the existing CNRS programme devoted to MSFR technology development [8].

Demonstration of the “3 gas extraction” process during the MSRE project was generally successful. Xenon gas, the main neutron poisoning element, was continuously removed from the fuel salt circuit during the reactor operation. The extraction capacity was designed to enable average xenon sorption time of about 20 seconds. A similar xenon processing time was designed for MSBR system.

However, xenon and krypton are not the only fission products which can be removed by gas extraction from the MSR fuel salt. As the MSR working temperatures are in the range of 650-750°C, there are some other elements which tend to leave the salt. It has been shown that, in addition to noble gases, some other fission product elements niobium, molybdenum, ruthenium, antimony and tellurium, which did not form stable fluorides in normal environment in the MSRE, tend to leave the MSRE fuel salt. However, the bulk of the fission product elements (lanthanides) does form stable and soluble fluorides and remained with the fuel salt.

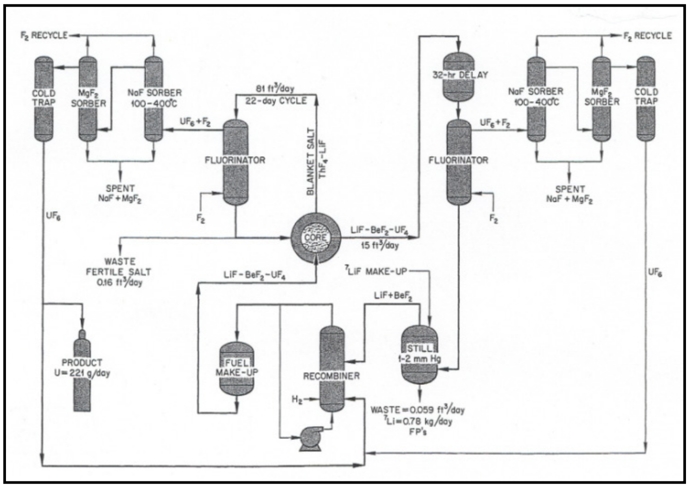
In the MSRE, the noble metals that accompanied the noble gases to the striping system settled as radioactive dust everywhere on the surface of pipes, filters and other parts of the off-gas system. The remaining the noble metals, which did not leave the primary circuit deposited on the surface of the primary circuit structural materials – Hastelloy N and graphite. The typical noble metals sorption” time designed for MSBR was similar as for xenon, of about 20-50 seconds [5].

*Fused salt volatilisation*

The method called “fused salt volatilisation” is based on the chemical reaction of fluorine gas with elements dissolved in molten fluoride salt carrier. Some elements form volatile fluorides, which evolve from the salt. Fused salt volatilisation was successfully applied applied for uranium removal from the fuel circuit (LiF – $BeF_2$ was the carrier salt) during the MSRE project. Uranium was removed from the fuel salt as uranium hexafluorides ($UF_6$) by sparging the salt with fluorine gas. A detailed description of the technology and description of the main equipment (continuous fluorinator) can be found in Section 2.3. 6 (“Fluoride volatilisation processes”).

Initial development of the fused salt volatilisation process occured during the first period of preparation for MSBR project at ORNL. A close-coupled facility for processing/ reprocessing the fuel and fertile streams of the MSBR was to be an integral part of the reactor system. (Initially, the MSBR was designed as a system with two separate circuits: fuel-stream and fertile stream.) The preliminary design of the MSBR fuel and fertile stream processing is shown in Figure 2.138.

**Figure 2.138. Initial design of MSBR fuel and fertile stream processing**



Source: ORNL.

As indicated in Figure 2.138, only four major operations were proposed to accomplish the fuel-stream processing: fluorination, sorption of $UF_6$, vacuum distillation and salt reconstitution. After 36 hours of cooling time, the fuel processing began by molten salt fluorination. Some fission products (Ru, Tc, Nb, Cs, Mo and Te) also form volatile fluorides and accompany the $UF_6$. Therefore, the gas stream leaving the fluorinator passes through a sorption system composed of temperature-controlled beds of NaF and $MgF_2$ pellets. The first section of the NaF bed is held at about 400°C and sorbs most of the fission products. The second section of the bed, which is held at about 100°C, sorbs technetium and part of the molybdenum, and allows the remaining fission products to pass through. Upon heating from 100°C to 400°C, the second section of the sorber releases volatile molybdenum, technetium and uranium fluorides$_6$. This vapor passes through a $MgF_2$ trap for retention of technetium while allowing uranium hexafluorides to pass through and then be frozen in cold traps and retained for recycle in the reactor [5].

There is currently no operational experimental development programme of the fused salt volatilisation technique, but nearly all existing flowsheets of the MSR fuel cycle proposed by several institutions under the frame of the Gen IV programme include this method. The fused salt volatilisation is often proposed to be used not only for uranium removal, but also for extraction of plutonium (in the form of $PuF_6$) and neptunium (in the form of $NpF_6$) [9]. However, it is necessary to take into account that, even though the formation of volatile $UF_6$ occurs relatively easyly and quantitatively,because the stable form of uranium is hexavalent, the formation of $PuF_6$ is more difficult and plutonium hexafluoride because it tends to decompose to $PuF_4$ and $F_2$ since the stable form of plutonium is tetravalent [10].

For an MSR processing plant, the continuous removal of protactinium from LiF -$BeF_2$ – $ThF_4$– $UF_4$ fuel salt is required in some cases. In the MSBR design protactinium removal from fuel salt was expected to be performed using reductive extraction in liquid bismuth with lithium addition. This method, however, has a number of disadvantages, such as, low protactinium recovery and processing rate, eventual contamination of the main reactor circuit with bismuth, etc. For these reasons, development of a more efficient method of protactinium removal is needed.

The fluoride volatilisation method of protactinium removal from LiF – $BeF_2$ carrier melt appears promising for this purpose [11]. In order to increase protactinium recovery and the process rate, bubbling fluorine gas through the melt at 700-750$^0$C has been proposed. Under the conditions of fluorine bubbling, protactinium tetrafluoride is oxidised to volatile $PaF_5$ and removed from the salt as a vapor along with the flow of unreacted fluorine. Experiments were performed at the Kurchatov Institute as follows: (1) thorium tetrafluoride was irradiated in a test nuclear reactor to produce $^{233}$Pa, (2) the irradiated $ThF_4$, containing protactinium was introduced into a fluorinator and dissolved in $LiF\text{-}BeF_2$ molten salt mixture and (3) heated to a temperature of 750°C under a fluorine pressure of 50 kPa. The normalised rate of $PaF_5$ removal from the salt surface into "cold" zone of the fluorinator, which had the wall temperature of 400°C was $\Delta m/m/\tau \approx 5 \cdot 10^{-2}\,hr^{-1}$. In this case, the $^{233}$Pa recovery from the salt reached 98% [12]. Thus, using fluorine bubbling, the process of protactinium removal can be intensified by an order of magnitude, as compared to the static fluorination method.

The method described for the removal of protactinium r from the fuel salt may be considered as very efficient, because it performs the protactinium removal in less than 10 hours providing a. very quick preparation of the fuel salt. By this means, it is possible to remove protactinium from the fuel to a level of a few parts per million, which is of importance, for implementing the two-zone, two-fluid design.

*Molten salt/liquid metal extraction*

The molten salt/liquid metal reductive extraction method of separation is proposed for the MSR fuel salt clean-up. This technique was investigated by ORNL both for protactinium removal from the fuel salt, and for the extraction of lanthanides fission products (which are the main group of fission products. The process is also proposed for removal of transuranium elements (Pu, Am, Cm). The main principles of the technology were based on selective molten salt/liquid bismuth metal reductive extraction in a multistage counter-current extraction system [5]. The theoretical principles of the molten salt/liquid metal extraction are described in Section 2.3.2 for the system molten fluoride salt/liquid aluminum.

The use of bismuth was selected because it is a low-melting (271°C) metal essentially immiscible with molten halide salt solutions, which include fluorides, chlorides and bromides. Bismuth has a negligible vapor pressure in the temperature range of interest, 500 to 700°C and the solubilities of metals, such as lithium, thorium, uranium, protactinium and the rare earths are adequate for processing application.

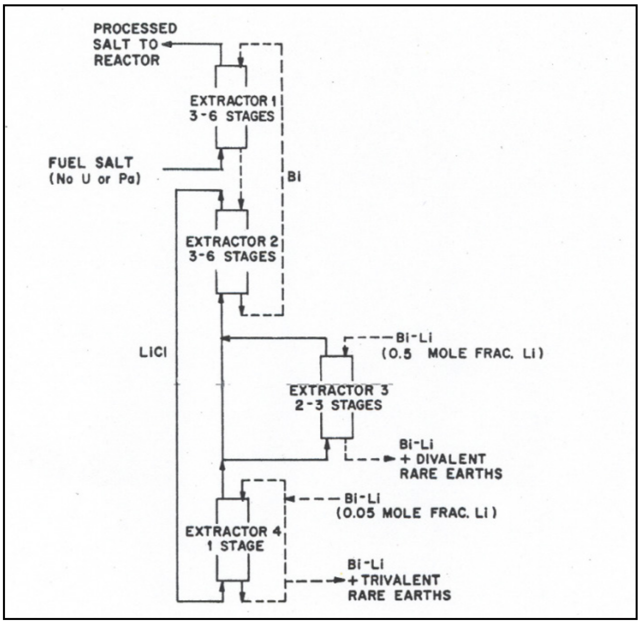
Reductive extraction reactions between materials in molten salt and liquid metal phases can be represented by the general reaction:

$$MXn + nLi\ (Bi) \longleftrightarrow M\ (Bi) + nLiX \qquad (1)$$

in which a metal halide $MX_n$ in the salt reacts with lithium in the bismuth phase to produce the metal, M, in the bismuth phase and the respective lithium halide in the salt phase. The oxidation state of M in the salt is n+, and X represents fluorine, chlorine or bromine.

Distribution data were obtained by ORNL for a number of materials between bismuth and MSBR fuel salt (72% LiF, 16% $BeF_2$, 12% $ThF_4$) at 640°C [13]. These data indicate that protactinium, as well as uranium and zirconium can be easily extracted from a salt stream containing $ThF_4$. However, the separation factors of rare earth elements/thorium are close to unity (from 1.2 to 3.5), which indicates that selective extraction of the rare earth elements (lanthanides) from a molten fluoride salt containing thorium tetrafluoride is either difficult or nearly impossible. Therefore, a chloride extraction system between liquid bismuth and molten lithium chloride was chosen as the most promising. In this system, the separation of both divalent and trivalent lanthanides elements from thorium is possible. The distribution coefficients for these materials are strongly affected by the concentration of lithium in the bismuth phase, and the best method for removing these materials from the LiCl appears to be by extraction into bismuth containing lithium at a concentration of 0.05 to 0.5 mole fraction. A simplified flowsheet for the lanthanides removal system is shown in Figure 2.139.

**Figure 2.139. Flowsheet of the lanthanide removal system for MSBR**

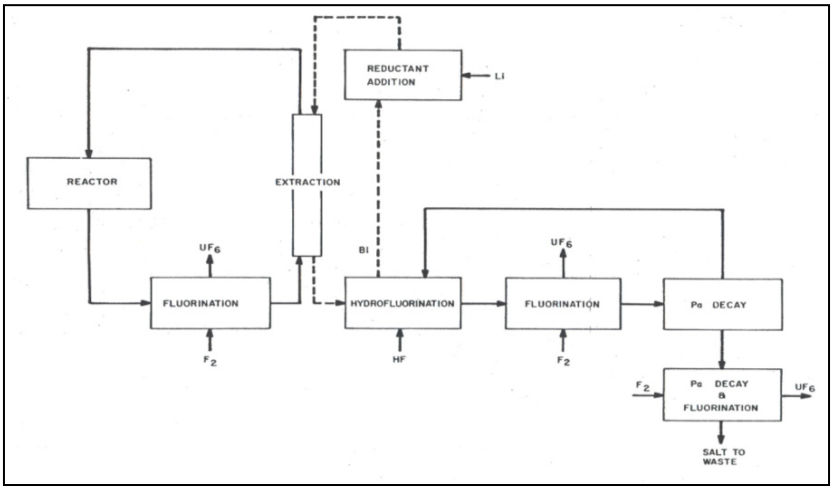


Source: ORNL.

As described above, the molten salt/liquid metal reductive extraction separation method was proposed by ORNL also for the protactinium removal [5]. Protactinium, which exists in the fuel salt as $PaF_4$, can be relatively easily reduced by lithium and extracted into liquid bismuth. In order to avoid the use of large quantities of reductant, prior removal of uranium from the salt by fluoride volatilisation was required.

After removal of uranium by conversion of $UF_4$ to volatile $UF_6$, protactinium is extracted into liquid bismuth and subsesequently converted by hydrofluorination to fluoride salt, from which the $^{233}$Pa decay daughter is extracted by fluorination to $^{233}UF_6$ after the protactinium decay. (The radioactive half-live of $^{233}$Pa is about 27 days.) A schematic flowsheet of protactinium isolation is shown in Figure 2.140.

**Figure 2.140. Flowsheet for protactinium separation from MSBR by fluorination and reductive extraction**



Source: ORNL.

At present, with the exception of limited French and Russian activities [14,15], there is no intensive experimental development programme on molten salt/liquid metal reductive extraction for the uranium, protactinium, thorium and fission products separation into liquid bismuth from fission products from molten LiF – $BeF_2$ salt mixture. At the Russian Kurchatov Institute, the extraction of lanthanum, neodymium and thorium from beryllium containing fluoride salts was experimentally investigated for application to the MSFR and MOSART design. Equilibrium values of the distribution coefficients were measured and compared with original ORNL data [15].

Other R&D has been devoted to the investigation of actinide/fission products separation in the system of molten fluoride salt/liquid aluminum. The studies were performed by CEA in the ATALANTE laboratories in Marcoule, France, for uranium, plutonium, americium and curium separation from selected fission products (lanthanides) [16]. Detailed description of the technology and achieved results are reported in Section 2.3.3. ("Pyroprocessing assessment in fluoride melts").

*Electrochemical separation processes devoted to MSR fuel reprocessing*

Efforts to use electrochemical separation processes for reprocessing MSR fuel containing thorium, is relatively new, associated with the MSR development under the Gen IV International Forum. The main reasons for these efforts was the facts that (1) the development of electro-separation processes has made remarkable progress since the 1960s, when MSR reprocessing experiments were carried out at ORNL and (2) that the molten salt/liquid metal reductive extraction studied in the frame of MSBR project showed some difficulties (described above) in the separation of thorium from the lanthanide elements. Since the electrochemical processes in molten salts were described in Section 2.3.2, only specific processes and techniques devoted to MSR fuel salt containing thorium are discussed in this section.

The theoretical as well as experimental investigation of the electrochemical separation processes that are applicable for the MSR thorium fuel reprocessing have been studied predominantly by the Nuclear Research Institute Rez - UJV in the Czech Republic and at the Université Paul Sabatier ,Toulouse, France. [17,18] The main objective of experimental R&D activities on electrochemical separation technology has been to determine the separation possibilities of selected actinides (uranium, thorium) and fission products (lanthanides) in various fluoride melt carriers.

Although the reference MSR fuel salt composition ($^7LiF$ – $BeF_2$ – $ThF_4$ – $UF_4$) was already selectedby reactor physicists, it is clear that the LiF – $BeF_2$ melts will not be applicable for all electrochemical separation steps because of the limited electrochemical stability of $BeF_2$. Therefore, the first step was to determine the type of fluoride melts that are suitable for electrochemical separations.

The selected melts should meet some basic characteristics, such as low-melting point, high solubility for pertinent compounds, high electrochemical stability and appropriate physical properties (electrical conductivity, viscosity etc.). Unfortunately, no melt that fulfilled all the requirements was found. Therefore, three candidate eutectic melts that have most of the needed characteristics were selected for further electrochemical separation studies: (1) the eutectic mixture of LiF-NaF-KF (acronym FLINAK, m.p. 454°C, however with limited electrochemical stability), (2) a mixture of LiF-$BeF_2$ (acronym FLIBE, m.p. of chosen composition 456°C, however with limited electrochemical stability) and (3) the eutectic mixture of LiF-$CaF_2$ (m.p. 766°C, good electrochemical stability). (Electrochemical stability of the carrier melt is defined by the electrochemical window. It is a voltage range in which the carrier melt is neither oxidised nor reduced.).

The cyclic voltammetry (CV) method was used for studying the basic electrochemical properties of actinides and fission products dissolved in the selected fluoride melt media. A special reference electrode, based on the $Ni/Ni^{2+}$ redox couple was developed to provide reproducible electrochemical measurements in molten fluoride salts [19,20].

Results obtained from the measurements can be interpreted in follows:

- In the FLIBE melt, there is a good possibility for electrochemical separation and removal of uranium can eventually be substituted for the fused salt volatilisation method. Although electrochemical studies of protactinium has not been done yet, there is a presumption that protactinium could be separated from this melt, based on the thermo-dynamical properties of $PaF_4$.
- In the FLINAK melt, only uranium can be directly separated.
- In the $LiF\text{-}CaF_2$ melt, uranium, thorium and most of fission products (lanthanides) can be electrochemically separated.

The redox potentials evaluated by UJV for uranium, thorium and selected fission products in the three individual carrier molten salts being evaluated are listed in Table 2.37 [17].

**Table 2.37. Evaluated redox potentials**

| Redox couple | LiF-NaF-KF | $LiF\text{-}CaF_2$ | $LiF\text{-}BeF_2$ |
|---|---|---|---|
| | Ref. $Ni/Ni^{2+}$ In FLINAK | Ref. $Ni/Ni^{2+}$ in $LiF\text{-}CaF_2$ | Ref. $Ni/Ni^{2+}$ in $LiF\text{-}BeF_2$ |
| $U^{3+}/U^0$ | -1.75 | -1.90 | -1.4 |
| $U^{4+}/U^{3+}$ | -1.20 | -1.40 | |
| $U^{5+}/U^{4+}$ | +0.40 | – | |
| $U^{6+}/U^{5+}$ | +1.40 | – | |
| $Th^{x+}/Th^0$ | ~ -2.00 | -1.70 | out of window |
| $Th^{4+}/Th^{x+}$ | -0.70 | – | |
| $Nd^{2+}/Nd^0$ | < -2.05 | -2.00 | out of window |
| $Nd^{3+}/Nd^{2+}$ | ~ -1.00 | not-detected | |
| $Gd^{2+}/Gd^0$ | < -2.05 | -2.10 | out of window |
| $Gd^{3+}/Gd^{2+}$ | ~ -1.00 | not-detected | |
| $Eu^{3+}/Eu^{x+}$ | ~ -0.75 | not-detected | |
| $Eu^{x+}/Eu^0$ | -1.95 | < -2.30 | |
| $Zr^{4+}/Zr^{x+}$ | -1.50 | – | |
| $Zr^{x+}/Zr^0$ | -1.80 | – | |
| $Sr^{2+}/Sr^0$ | < -2.05 | – | |
| $La^{3+}/La^0$ | < -2.05 | – | out of window |
| $Pr^{3+}/Pr^0$ | < -2.05 | – | out of window |
| $Sm^{2+}/Sm^0$ | -0.8 | – | – |
| $Sm^{3+}/Sm^{2+}$ | out of window | – | – |

*Molten fluoride salt clean-up by vacuum distillation*

The technology of vacuum distillation was also tested by ORNL for clean-up of the MSR fuel carrier salt (LiF – $BeF_2$) containing fission products. Originally this process, operated at 1 200°C was also proposed for removal of the lanthanide elements; and later for the separation of those elements that, cannot be extracted from salt by reductive extraction due to their high thermodynamic stability, typically for alkaline fluorides and alkaline earth fluorides, such as CsF, RbF, $SrF_2$ and $BaF_2$. However, the high cost, length of time requied and the need to process a large volume of fuel salt caused this technology to be nearly abandoned [21,22].

*Oxide precipitation*

Fluorine-oxygen ion-exchange reactions were proposed as a method for the MSR fuel in the early 1960s [23]. It was shown that both uranium and thorium can be precipitated from fluoride melts and separated from the lanthanide elements and the solubilities of various metal oxides in the LiF-NaF eutectic melt at 800°C were studied [24-26]. The oxides were deliberately introduced in excess with respect to the stoichiometry fluorine-oxygen exchange reaction, for instance:

$$UF_4 + 2CaO \longrightarrow UO_2 + 2CaF_2 \qquad (2)$$

This was determined using the isothermal melt saturation technique at the temperature of 800°C, under argon atmosphere, in nickel crucibles with periodic intermixing of the melt, followed by settling the melt and taking samples for analysis. The results are presented in Table 2.38.

**Table 2.38. The solubility of oxides in LiF-NaF solvent system at 800$^0$C**

| Oxide | Solubility, in mass.% |
|---|---|
| BeO | 0,003 |
| MgO | < 0,1 |
| CaO | < 0,1 |
| $Al_2O_3$ | 0,58 ± 0,2 |
| $Ln_2O_3$ | 0,07 ± 0,03 |
| $CeO_2$ | 0,035 ± 0,015 |
| $ZrO_2$ | < 0,27 |
| $ThO_2$ | < 0,1 |
| $UO_2$ | 0,05 |
| $PuO_2$ | 0,05 |
| NiO2 | 0,12 |
| $Fe_2O_3$ | 0,025 |
| $Cr_2O_3$ | 0,01 |

As seen in Table 2.38, the solubility of oxides in the LiF-NaF melt is rather low, and this fact can be considered as evidence of the absence of any reactions between the system components, i.e. the LiF-NaF melt is a sufficiently inert medium for uranium tetrafluoride reactions with the oxides. The saturation of the LiF-NaF melt with oxides is attained rather quickly, essentially during the first 30-minute period of the intermixing with the melt. The only exception is magnesium oxide, forming a relatively stable suspension, which does not flake off in 5 hours of settling.

The obvious possibility of lanthanide precipitation on addition of by lanthanide oxides was confirmed in experiments with lanthanum and cerium compounds:

$$LnF_3 + Ln_2O_3 \longrightarrow 3LnOF \qquad (3)$$

Addition of lanthanide oxide in excess of the reaction stoichiometry leads to a decrease of LnOF solubility in the melt, due to formation of $LnOF$-$Ln_2O_3$ solid solutions in the sediment. It was also shown that lanthanum and neodymium are not precipitated by aluminum and beryllium oxides even when the amount added was in significant excess over the stoichiometry of the corresponding exchange reactions.

Comparison of the experimental results, showed that one definite succession of precipitation of the investigated metal oxides from the salt melts occurs and can be presented as the sequence:

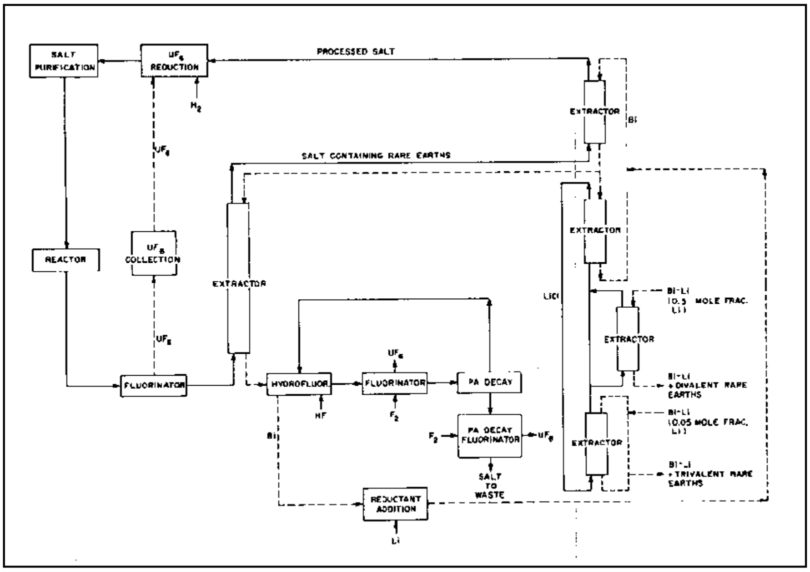
U, Zr, Th, Pu(+4) - Be - Al - Rare earth elements. (4)

In this sequence, the preceding elements are precipitated by oxides of succeeding ones, and this is the main factor of fractionating components of nuclear fuel while it is reprocessed in fluoride melts. “Semi-noble” metals (such as iron and nickel), as well as zirconium, co-precipitate in the form of oxides with actinide oxides. Evidently, these elements should be removed from salt melts prior to starting the process of fluorine-oxygen exchange. This could be done by reduction and recovery in the form of metals, as is implicated by the electromotive series in the molten fluorides solvent system [27].

*MSR fuel reprocessing flowsheets*

The separation techniques discussed above were used to design several schemes of online reprocessing for MSR fuels. The original conceptual flowsheets were proposed by ORNL for the MSBR system with $LiF – BeF_2 – ThF_4 – UF_4$ composition. A flowsheet intended for a single-fluid MSR design is shown in Figure 2.141 [5].

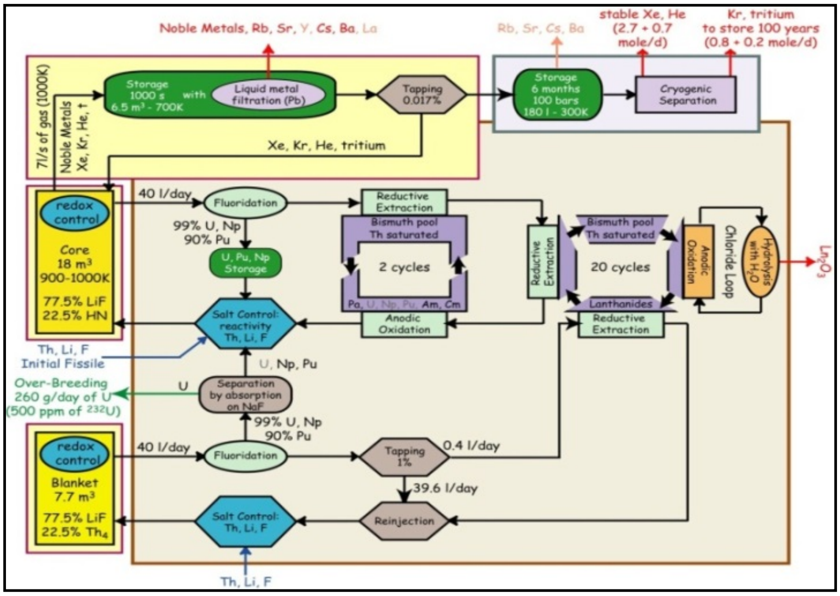
**Figure 2.141. Th breeder flowsheet proposed by ORNL for MSBR**



Source: ORNL.

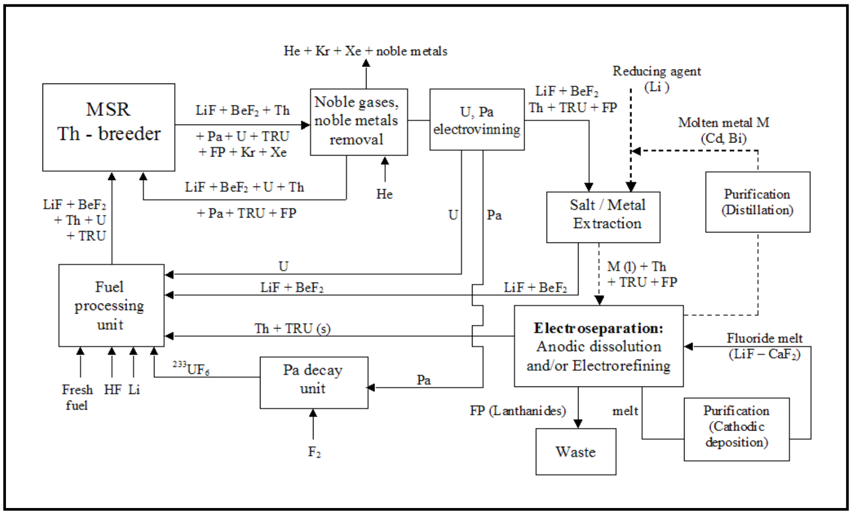
Current flowsheets proposed under the Gen IV activities were derived from the original MSBR scheme, but include some changes in MSR fuel salt composition and some due to progress in electrochemical separation techniques. The conceptual reprocessing flowsheet of an MSFR iso-breeder reprocessing proposed by CNRS is shown in Figure 2.142 [28,29] and the MSR online reprocessing flowsheet based on a broader use of electrochemical separation processes proposed by the Nuclear Research Institute Rez – UJV is illustrated in Figure 2.143 [17].

### Figure 2.142. Detailed flowsheet of two-fluid MSFR fissile and fertile salt reprocessing



Source: CNRS.

### Figure 2.143. Conceptual flowsheet of the single-fluid MSR online reprocessing technology



TRU – transuranium elements, FP – fission products (Source UJV).

Acquisition of fundamental data for the extraction processes is still needed especially for the actinide-lanthanide fission products separation. The extraction of lanthanide has to be done because of the low solubility of these trifluoride elements and their high neutron capture cross-sections that decrease the reactivity balance. This critical step for the pyro-electrochemical process has to be examined from both a thermodynamic and kinetic point of view. The different steps involved in the reprocessing of the molten liquid fuel have not yet been studied from the technological and engineering points of view and will have to be implemented as the system is developed from the lab-scale to the industrial scale. Non-proliferation issues related to the fuel salt processing scheme must also be addressed more deeply.

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# 3. Process criteria

## 3.1. Introduction

The preceding Chapter 2 has described many of the proposed approaches for major (U, Pu) and minor (Np, Am, Cm) actinide separations. The next chapter, Chapter 4, attempts to make some comparisons between these processes, primarily regarding their technical maturity using the well-known technology readiness level (TRL) approach. This chapter will provide a link between these chapters by briefly considering how some of the fuel cycle scenarios and criteria placed upon fuel recycling processes will impact on process development and ultimately the down-selection of options to industrially deployable technologies.

## 3.2. Feeds to the recycling plant(s)

The nature of the spent fuel from reactors will have a major impact on the recycling plant design. Different fuel types are under consideration internationally:

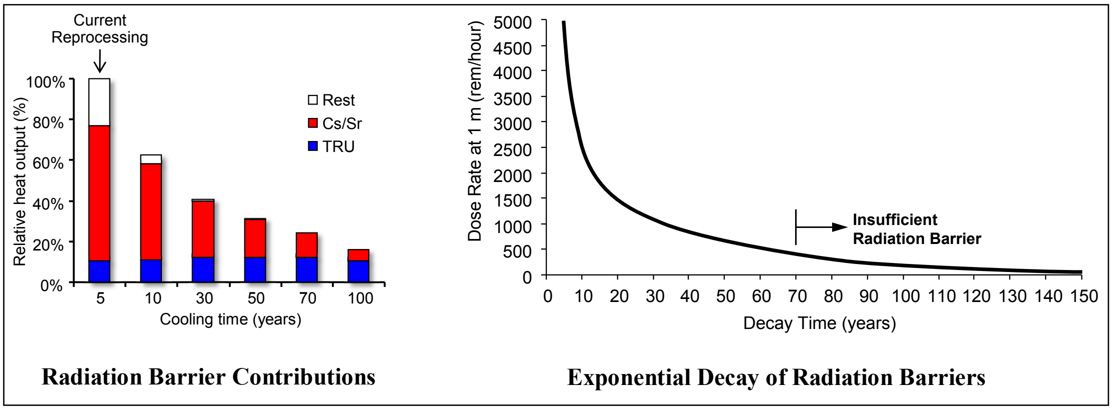
- thermal uranium oxide – standard fuel from thermal reactors, with increasing burn-up;
- thermal (U,Pu) mixed oxide fuel – up to 10% plutonium content;
- fast reactor oxide;
- fast reactor nitride;
- fast reactor carbide;
- fast reactor metal alloys;
- inert matrix fuels;
- high-temperature reactor TRISO-type fuels;
- molten salt in the molten salt reactor (MSR).

Fast reactor fuels will contain elevated levels of plutonium, up to perhaps ~20-30 wt%. Also, there may be elevated levels of minor actinide bearing fuels from multiple recycling of fuels and targets.

Many of these fuels, particularly the fast reactor fuels, will contain substantially larger quantities of plutonium compared to thermal UOx fuels. While a future closed fuel cycle with fast reactors almost certainly implies recycling plutonium through the reactor several times ("plutonium multi-recycling"), it may also be necessary to separate minor actinides (Np, Am, Cm) out of the fuel for transmutation (partitioning and transmutation or "P&T" scenario). In this instance, there may be a need to multi-recycle fuels or targets with high levels of minor actinides.

As well as reactor type and the fuel matrix, burn-up and cooling are important parameters to define the feed envelope of the recycling plant. While trends are towards higher burn-ups of UOx fuel (up to 60 GW/te and perhaps higher) compared to past operations, much higher burn-ups can be expected for fast reactor fuels (up to ca. 200 GWd/te). Depending on the fuel cycle scenario, the recycle plant may be designed to process long cooled fuels from countries' stockpiles of historic fuels (reprocessing oldest fuels first approach) or to reprocess short cooled fuels from fast neutron reactors (<1 year cooling). This wide range of challenging scenarios can be compared against current reprocessing experience: for instance, against the reference fuels which the La Hague (France) or Thorp (United Kingdom) plants were designed of 33-45 GWd/te, 3 to 5 year minimum cooled PWR UOx fuel; respective extensions up to 60 and 48 GWd/te were made during operations. Figure 3.1 illustrates the implications of cooling time on the heat output and radiation from typical spent LWR fuel.

**Figure 3.1. Relationship between heat output and radiation dose with cooling period for typical LWR spent fuel**



**Radiation Barrier Contributions**

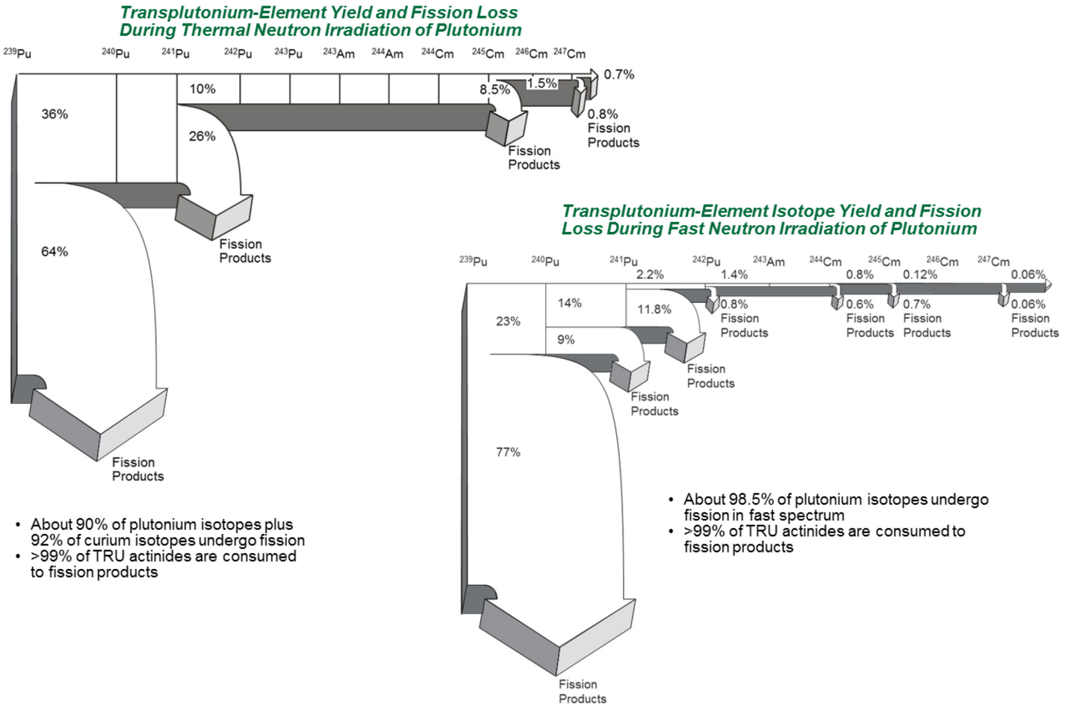
**Exponential Decay of Radiation Barriers**

The effects of higher burn-up or transmutation on plutonium isotopes are that yields of fission products and higher minor actinides are increased due to the sequence of progressive neutron captures and beta decay reactions, as illustrated in Figure 3.2. The products vary depending on whether plutonium burning uses thermal or fast neutron spectrum reactors.

Many of the problems in dealing with different feed materials will need to be dealt with in the head-end area of a reprocessing plant where fuel is disassembled, declad, chopped and dissolved. Reduction-oxidation processes such as VOLOX and AIROX can be used to oxidise fuels (carbides, nitrides, metals), remove volatile and semi-volatile species into off gases ($^{3}$T, $^{14}$C, $^{15}$N, I, Cs, Ru, etc.), and pulverise fuel by oxidation of $UO_2$ to $U_3O_8$. The fuel matrix will determine solubility of fuels in nitric acid (for an aqueous process) but this is also influenced by the fuel manufacturing process. For instance, some MOX production routes give a more homogeneous product that is easier to dissolve than a MOX fuel that contains plutonium-rich particles. How easily fuels can be dissolved into nitric acid is one factor that will influence the choice of separation process (e.g. aqueous vs. non-aqueous).

In aqueous reprocessing, after the head-end plant, the feed to the separation process will be a quite standard product. As in the conventional PUREX process it will be uranium, plutonium, minor actinides and fission products in a clarified solution of nitric acid of specified molarity. Volatile species and (most) solids will have been removed and (probably) plutonium oxidation state adjusted to Pu(IV) by a conditioning step. The (U+Pu) heavy metal content and U:Pu ratio may differ from conventional PUREX reprocessing of thermal UOx fuel but it will still be within a specified range, dependent on the fuel to be processed and the constraints of the solvent extraction process flowsheet (accounting for safe operating conditions such as avoiding a 3rd phase formation).

**Figure 3.2. Transplutonium-element yield and fission loss during irradiation of plutonium [1]**



- About 90% of plutonium isotopes plus 92% of curium isotopes undergo fission
- >99% of TRU actinides are consumed to fission products

- About 98.5% of plutonium isotopes undergo fission in fast spectrum
- >99% of TRU actinides are consumed to fission products

The discussion above has assumed a (U,Pu) fuel cycle. However, there is a renewed interest in the thorium fuel cycle [2]. Thorium oxide requires hydrofluoric acid-catalysed nitric acid for dissolution and the added requirement for processing the decay daughters of $^{232}$U. So inclusion of thorium fuels will add additional dimensions of complexity to recycle R&D programmes.

Clearly, at some point in the design and selection of the separation process the feed envelope needs to be bounded by definition of a reference feed material in order for detailed design to progress. However, most advanced nuclear energy R&D programmes at this time have not reached this level of maturity and are focused on developing options for evaluations and demonstrations. This means that separation processes for recycling plants will need to be developed to cover a broad range of potential feed materials depending on the closed fuel cycle strategies under consideration by a particular national or international programme.

## 3.3. Products required from the recycling plant(s)

### *3.3.1. Introduction*

In the current partially closed nuclear fuel cycle, when spent fuel is separated, solid uranium oxide (either $UO_3$ or $U_3O_8$) and plutonium dioxide products are formed. These need to meet product specifications that have been defined to facilitate (U,Pu) recycle into fuel manufacturing plants. The end point of the current reprocessing plants is that the uranium and plutonium oxide products are stored in drums or welded cans and placed in interim stores. Whether recycling as new fuel is prompt or delayed by a period of interim storage depends on various factors, such as government policy, economics, MOX fuel fabrication plant availability, etc. The fuel fabrication plants and reprocessing plants have not been necessarily integrated. For example, while the Sellafield MOX Plant

(United Kingdom) was adjacent to the Thorp reprocessing plant at Sellafield, MELOX in France is at Marcoule while reprocessing is carried out at La Hague.

Future fuel recycle plants will need to contain integrated spent fuel separations and recycle fuel manufacturing, particularly for the recycle of plutonium and minor actinides. This will be required for non-proliferation and security reasons as well as efficiency and economic reasons.

In a similar way as to how the feeds affect the choice of the downstream separation process(es), also the form of the recycled fuel(s) may have a major impact on the recycle plant design. For instance, coated particle spent fuel will require a different disassembly and separation process to remove the carbon-silicon chloride coatings than the disassembly process used for the more prevalent metal-clad spent fuel.

### 3.3.2. Aqueous processes

Based on our current understanding, it is reasonable to assume that any future fuel recycle plant (for bulk thermal or fast reactor) fuels will produce a uranium product and that this will need to meet similar specifications to current reprocessed uranium products. For an aqueous process, finishing to the oxide by a denitration process remains the most likely route for industrial scale uranium "alone" conversion.

As regards the finishing of the transuranic (TRU) products, R&D is required to link conversion to solid products at the back end of the separations process to fabrication of recycle fuels and targets in order to optimise efficiencies. Preparing products in isolation with large facilities for interim storage will no longer be acceptable.

A range of forms of TRU products can be produced, depending on the separation processes selected, including: (U,Pu), (U,Np,Pu), (Pu,Np), (Np), (U,Am), (Am,Cm), (Am), (Pu,Np,Am,Cm), (U,Np,Pu,Am,Cm). Pure plutonium products will probably need to be avoided for non-proliferation reasons. Am-Cm containing products will require remote fuel or target fabrication rather than hands-on glovebox operations. Whether neptunium-containing fuels will require remote fabrication facilities is unclear. Tolerable levels of fission products in these TRU products will need to be assessed. This will be some "trade-off" between "dirty" products providing more proliferation resistance and "pure" products being easier to work with in fuel fabrication. The effects of residual fission products in downstream plants would also need to be assessed, e.g. what is the permissible level of lanthanides in fast reactor fuels? Aqueous processes in the past have been used to produce high purity plutonium products but this is a legacy of weapons production and flowsheets with low decontamination factors for specific components (such as uranium) can be designed if this is a desirable feature to lower the "attractiveness level" of fissile material in the recycled TRU. It will need to be recognised that relaxation of specifications in one part of the fuel cycle can have benefits and disadvantages in other parts of the fuel cycle. Means of assessing the overall optimum configuration of the fuel cycle that then define the requirements at each stage will, therefore, be needed.

Various process options are available to convert liquid products to solids, with microwave heating denitration, modified direct denitration, oxalate co-conversion, and gelation methods probably being the leading technologies. Presently, there is an assumption that oxide products are preferred forms, but this may change.

Physicochemical properties of finished products such as specific surface area (SSA) and particle size, need to align with the requirements of the fuel manufacturing processes.

As with the feed materials, at some point in the design of a fuel recycle plant, the product specifications need to be defined in order for detailed design to progress. However, most advanced nuclear energy R&D programmes at this time have not reached this level of maturity and are focused on developing options for evaluations and demonstrations. This means that separation processes for recycling plants need to be developed that lead to a broad range of potential products, depending on the closed fuel cycle strategies under consideration by a particular national or international programme. Integration of product finishing with TRU fuel or target manufacturing will be essential in optimising the advanced fuel cycle.

### 3.4. Performance criteria required from the recycling plant(s)

If the feeds and products are defined then the performance criteria that the fuel recycle plant must meet are easy to calculate. It is then simply a matter of developing and demonstrating flowsheets that meet these criteria. However, as noted above neither the feeds to nor products from future recycle plants can be definitively identified. Therefore, a baseline scenario or a range of likely scenarios must be identified and a range of separation processes developed that meet the different scenarios.

### 3.5. Constraints placed on the recycling plant(s)

As well as meeting the performance criteria defined by the feeds and product specifications, which must be demonstrated at appropriate scales, future recycling plant designs will be influenced by a broad range of other requirements. Firstly, any plant will need to meet ever-more stringent requirements for ensuring process safety, including safe by design engineering. Other factors related to safeguards and security, proliferation resistance, environmental impact, sustainability and waste management will also need to be addressed while ensuring that plant sizes and costs are reduced so that the economics of future recycling are viable. Regarding how these factors affect the core separation process, some trends are becoming established, although specific requirements are yet to be established. Table 3.1 gives examples of how some of the requirements put on advanced fuel cycles with regards to sustainability, waste and non-proliferation etc. may affect design and engineering of the separation processes.

**Table 3.1. Requirements for advanced reprocessing**

| Strategic objective | Fuel cycle requirement | Potential implications for reprocessing plant flowsheets |
|---|---|---|
| Process safety | o Geometrically safe<br>o Safer processes | o Engineering design<br>o Continuous vs. batch processes<br>o Non-aqueous processes<br>o Low temperature & pressure processes<br>o Avoid specific reagents, e.g. hydrazine<br>o Fundamental understanding of process chemistry<br>o Modelling and simulation |
| Sustainability | Plutonium multi-recycling | o Dissolution of high Pu content fuels<br>o High Pu recovery yield<br>o High Pu concentrations in plant<br>o High solvent loading, risk of 3rd phase<br>o Increased solvent degradation and radiolysis<br>o Ruthenium decontamination in short cooled fuels |

| | | |
|---|---|---|
| Waste management & environmental impact | o Minor actinides multi-recycled for transmutation (P&T) and Plutonium multi-recycling<br>o Reduced impact of fuel cycle on GDF (geological disposal facility) footprint (radiotoxicity and heat loading)<br>o Reduced waste generation and lower environmental impact | o >99% recovery of Np from flowsheet<br>o Options needed for >99% recovery of Am+Cm and Am alone from HLW<br>o Cs, Sr separations or decay storage<br>o Reduced number and volumes of aqueous waste streams<br>o Ideally CHON reagents (e.g. salt free solvent washing) and solvents or, if not, compatibility with wasteforms.<br>o Target "near-zero" emissions<br>o Capture of volatile species ($^{3}H$, $^{14}C$, $^{85}Kr$, $^{129}I$)<br>o New wasteforms |
| Non-proliferation | o Increased physical safeguards and monitoring<br>o Integrated SNF storage, separations, and recycle fuel/targets fabrication | o (U+Pu) or (U+Np+Pu) co-processing in Advanced PUREX flowsheets<br>o Increased fission and/or minor-actinide product contamination of Pu product<br>o Near real time accountancy, online process monitoring<br>o Sampling and analysis<br>o Proliferation resistance assessment methodology |
| Economic | o Reduced capital costs through smaller plant footprint<br>o Greater flexibility of processes | o Intensified processing<br>o Fit-for-purpose equipment for solvent extraction<br>o Single cycle reprocessing<br>o Fewer waste streams<br>o Integrate with waste and fuel fabrication plants<br>o Process LWR, MOX and fast reactor fuels<br>o Feed variations (carbide, nitride and metal fuels as well as oxides)<br>o Higher burn-ups<br>o Short cooled fast reactor or very long cooled LWR fuels – depends on scenario |

These issues are too large and complex to discuss comprehensively in this report. However, the proliferation resistance of future fuel recycling plants is perhaps different to the other factors in that it is open to a greater degree of interpretation, with some disagreement between technical and political analyses about the effects of various risk reduction measures; whereas, with regards to the safety, environmental impact, economic and waste management issues, it is mainly a matter of optimising processes to meet requirements (often set by regulatory authorities) where it is easier to quantify success. Therefore, a short discussion is included on some aspects of non-proliferation in advanced recycling processes below. However, it should be noted that this is a contentious and complex issue, and this is by no means a comprehensive review of this subject.

## 3.6. Nonproliferation requirements for recycling components of spent nuclear fuel (SNF)

### *3.6.1. Introduction*

This section is dedicated to a brief consideration of recent activities undertaken internationally to address some of the non-proliferation requirements of future fuel cycles. Firstly, non-proliferation aspects of two example separation processes are included:

- The separation of $^{233}$U in the molten salt reactor system for thorium based spent fuel– a specific and distinctive case study.
- A proliferation resistance assessment of pyroprocessing. Advocates of pyroprocessing indicate that there are prospective benefits in addressing non-proliferation requirements when compared to aqueous separation processes. Understanding the advantages of pyroprocessing as regards to non-proliferation is, therefore, a key part of assessing the suitability of pyroprocessing as a separation process for future spent fuel management.

The scope of this section then covers some basic issues without regard to specific separation methods:

- an overview of systems studies and isotopics;
- a consideration of the impact of plutonium separation;
- use of engineered safeguards and safeguards by design to address non-proliferation needs;
- a summary of uncertainties in non-proliferation assessments.

### *3.6.2. Example 1: Separation of uranium ($^{233}$U) from thorium based SNF within MSR online reprocessing*

Separation of uranium from thorium based SNF can be effectively done by the hydrometallurgical THOREX process. The process is based on solvent extraction and is very similar to PUREX technology, but due to lower solubility of thorium in nitric acid, THOREX technology is considered to be more difficult. Bred uranium from SNF is never pure $^{233}$U, it is always a mixture of isotopes $^{233}$U, $^{234}$U, $^{235}$U and $^{232}$U. The presence of $^{234}$U and chiefly $^{232}$U causes significant radioactivity in reprocessed $^{233}$U due to high radioactivity of their daughter products (this applies especially to daughter products of $^{232}$U). This means higher levels of radioactive $^{232}$U decay daughters (namely $^{208}$Tl) in reprocessed $^{233}$U are present and, therefore, the intrinsic proliferation resistance is increased.

Separation of bred uranium within the molten salt reactor technology represents a very specific pyrochemical technology, different to other Gen IV options. One of the basic differences is that the separation technology must be directly connected to the reactor. It follows that, in addition to the uranium separation, protactinium can also be separated from the liquid fuel. Consequently, after protactinium decay, relatively pure $^{233}$U can be obtained in the form of $UF_6$. The main barrier against diversion is the extreme difficulties inherent in MSR online reprocessing technology and the fact that all separation steps must be carried out in hot cell facilities [6].

### *3.6.3. Example 2: Korean proliferation resistance assessment of pyroprocessing*

*Introduction*

In 2002, world experts gathered and defined the term of “proliferation resistance” as “the characteristic of a nuclear energy system that impedes the diversion or undeclared production of nuclear material, or misuse of technology, by a State in order to acquire nuclear weapons or other nuclear explosive devices" [11]. The same report also defines the following terms:

- *Intrinsic barriers (technical features) of proliferation resistance* are those features that result from the technical design of nuclear energy systems, including those that facilitate the implementation of the extrinsic measures.
- *Extrinsic barriers (institutional measures) of proliferation resistance* are those features that result from the decisions and undertakings of states related to a nuclear energy system.

The intrinsic barriers are further divided into *material barriers*, which are the "intrinsic, or inherent, qualities of materials that reduce the inherent desirability or attractiveness of the material as an explosive," and *technical barriers*, which are the "intrinsic technical elements of the fuel cycle, its facilities, processes, and equipment that serve to make it difficult to gain access to materials and/or to use or misuse facilities to obtain weapons-usable materials" [8]. The material barriers include isotopic, chemical, radiological, mass, bulk or ease of detection, while the technical barriers include facility unattractiveness, accessibility, available fissile mass, ease of detection and time required for diversion, as well as skills, expertise and knowledge.

*Pyroprocessing – Korean analysis*

The proliferation resistance of pyroprocessing is often challenged on the grounds of the "attractiveness" of the nuclear materials that are subject to diversion. How attractive to proliferators these materials would be may vary. The kernel, however, is a characteristic called "self-protection". Both the US Department of Energy (DOE) and the International Atomic Energy Agency (IAEA) use a radiation dose of one Sievert (100 rems) per hour measured at a distance of one metre to be the level that provides a measure of self-protection [9,10].

According to calculations performed by the Korea Atomic Energy Research Institute (KAERI), TRU metal, which contains 16% of rare earth (RE) with $^{154}$Eu, meets the IAEA standard, although the self-protection of the materials produced by pyroprocessing is lower than that of the spent fuel itself. In the case of TRU metal without $^{154}$Eu, however, the dose rate falls short of the IAEA threshold for self-protection. The calculation was performed using the details of the products given in Table 3.2, and the results are mainly on account of the dose rates compared in Figure 3.3, where it can be observed that it is the incomplete separation of $^{154}$Eu ($t_{½}$ = 8.8 y) that produces the radiation barrier. Undoubtedly, though, the results are subject to change depending on the material balance of the process as it further develops.

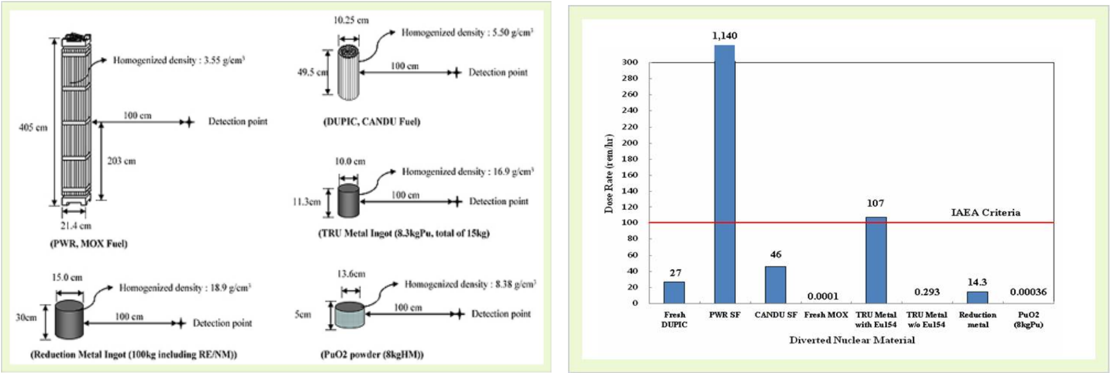
According to a NPIA report which qualitatively compared and assessed proliferation resistances of advanced processing technologies such as UREX, COEX and pyroprocessing with that of PUREX, pyroprocessing (grouped, in the study, with other processes which do not separate Pu) was assessed to have a better proliferation resistance [12]. This is mainly due to the fact that the final product of pyroprocessing contains plutonium that has not been separated from uranium, americium, neptunium, and curium, and the pyroprocessing option, therefore, secures some level of "intrinsic barriers" (pyroprocessing scores high on "chemical barriers"). However, none of the separation methods were judged to be sufficient without physical safeguards because the fissile plutonium is still present and could be diverted and subsequently isolated if not physically protected. In addition, materials processed and recovered by pyroprocessing give off substantial radiation and heat, such that they cannot be handled manually and, accordingly, must be processed remotely in a hot cell facility. This makes for easier implementation of "containment and surveillance (C/S)", one of the key measures of IAEA safeguards.

Especially for the state attempting covert proliferation and for diversion by non-state actors, the material barriers (isotopic, chemical, radiological, mass, bulk, ease of detection etc.) and the technical barriers (facility unattractiveness, accessibility, available fissile mass, ease of detection, time required for diversion, and skills, expertise and knowledge etc.) can be effective, as indicated in the above-referenced NPIA report.

**Table 3.2. Comparing spent fuels and $PuO_2$ with TRU metal products from pyroprocessing**

| Category | Type | Features |
|---|---|---|
| PWR SF | Assembly | - Initial enrichment : 4.3%<br>- Burn-up: 50 GWd/tU, 10-year cooling time |
| CANDU SF | Bundle | - Initial enrichment: 0.71%<br>- Burn-up: 7.5 GWd/tU, 10-year cooling time |
| MOX fuel | Assembly | - Contains 7% Pu, 427 kgHM |
| TRU metal (with $^{154}$Eu) | Metal ingot | - Total weight: 15 kg<br>- U 20%, TRU 64%, RE 16% |
| TRU metal (without $^{154}$Eu) | Metal ingot | - Total weight: 15 kg<br>- U 20%, TRU 64%, RE 16% |
| $PuO_2$ | Oxide | - Contains 8 kg Pu |

**Figure 3.3. Dose rate relative to IAEA self-protection standard**



### 3.6.4. Systems studies

Systems studies have been made to determine non-proliferation requirements and uncertainties that have arisen related to closing the back end of the nuclear fuel cycle. The approach taken was to identify what components of spent nuclear fuel (SNF) are proliferation concerns. Most of the mass (~ 94 – 97 wt%) is residual uranium, cladding, and hardware. The plutonium content ranges from ~ 0.6–1.0 wt%, and the remainder is composed of minor actinides and fission products ranging from ~2.5 – 5.0 wt%.

Four fissile isotopes are of concern to proliferation: $^{235}$U, $^{239}$Pu, $^{241}$Pu within the (U, Pu) fuel cycle and $^{233}$U within the (Th, U) fuel cycle. Even though the mass of $^{235}$U is about the same as the sum of $^{239}$Pu and $^{241}$Pu, the $^{235}$U concentration in the uranium element is sufficiently low that it would require isotopic enrichment to become a proliferation and safeguards concern. However, the fissile plutonium isotopes are in the range of 50 – 80% of the plutonium element, depending on burn-up, making the plutonium element a proliferation safeguards concern because chemical separation processes, which are relatively less difficult to undertake than isotopic enrichment processes, can be used to produce separated plutonium [3].

The actinides and fission products in the spent fuel lower the "attractiveness level" to proliferation (radiation barrier). Figure 3.1 illustrates how the radiation barrier of spent fuel decreases with storage time. This radiation barrier is provided by the presence of short-lived and intermediate-lived radioactive fission products but the barrier decays at an exponential rate, making used fuel older than several decades (>70 years in the example in Figure 3.1) more vulnerable to diversion and theft. Vulnerability can be eliminated if fuel recycle is begun before the intrinsic radiation barrier has decreased to a susceptible level – re-irradiation will then restore the effective radiation barrier to the spent fuel as well as burning part of the actinide inventory. (This is discussed further below).

### *3.6.5. Separation of plutonium from SNF components*

A variety of well-known separation methods used by the chemical and hydrometallurgical industries could be used to separate plutonium. These separation methods include fluoride volatility, pyro-electrochemical, solvent extraction, ion exchange, and precipitation processes, or combinations of these. Furthermore, the technologies used for large-scale commercial SNF reprocessing operations may not be attractive for small-scale operations, and it is these alternative small-scale separation processes that could and should be of greater concern for undeclared weapons production activities. In any case, the conclusion is that plutonium has no intrinsic safeguards. Even though unseparated or partially separated plutonium in SNF may have a lower "attractiveness level" than purified plutonium, the plutonium remains capable of being separated [4]. Therefore, a further conclusion is that physical protection and other proliferation resistance methods are as necessary for unseparated SNF or partially separated plutonium as they are for separated plutonium. Continued storage or direct disposal locations containing SNF must be protected because recovery and separation of the plutonium will always be possible.

### *3.6.6. Engineered safeguards – the "radiation barrier"*

The radiation emanating from SNF is widely considered to be the primary safeguard for the once-through fuel cycle with direct disposal of SNF. However, the so-called "radiation barrier" decays at an exponential rate, thus making used fuel older than several decades more vulnerable to diversion and theft. For up to 5–10 years after reactor discharge, radiation barrier contributors are short-lived fission products, intermediate-lived Cs–Sr (half-lives of ~30 years), and long-lived transuranium actinide elements (TRU). From about 5–70 years, the major contributor to the radiation barrier is the gamma radiation from cesium. After about 70–100 years and beyond, the long-lived TRU elements are predominant, but they do not provide a sufficient radiation barrier [5]. The vulnerability of an insufficient radiation barrier can be eliminated if fuel recycle is begun before the radiation barrier has decreased to a susceptible level, because re-irradiation of the recycled plutonium will restore the effective radiation barrier. Similar principles are valid for separated $^{233}$U from thorium based SNF.

### *3.6.7. Safeguards-by-design*

Other engineered safeguards and physical protection requirements can be obtained by using the "safeguards-by-design" concept to co-locate and integrate the used fuel treatment facilities within the same "Recycle Plant". This method can ensure that (1) the used fuel storage, component separation (reprocessing), and recycle fuel fabrication facilities are co-located within the physically protected recycle plant; (2) the fissile material (i.e. plutonium) enters and leaves the recycle plant only in the form of large, heavy, easily accountable fuel assemblies; (3) effective continuous monitoring and surveillance of waste shipments and personnel exiting the plant are maintained; and (4) use of "near-real-time" monitoring and accounting of the plutonium location and movement are utilised to the extent technologically possible. (This is for "standard" reprocessing plants, in the case of MSR online reprocessing technology the process design is expected to be the main safeguarding method).

### *3.6.8. Summary-clarification of non-proliferation uncertainties*

Recognition of the following points is necessary to clarify non-proliferation uncertainties:

- The selection of a specific reprocessing separation technology over others can provide only insignificant effects on safeguards arrangements that will be placed on recycle plants to meet non-proliferation requirements as:
    - Plutonium is a chemically separable component of SNF, regardless of the processes selected for reprocessing separations and recycle fuel production.
    - A variety of well-known methods can be used to produce separated plutonium, especially for a small-scale, non-commercial operation, which could still be large enough to conduct an undeclared operation of proliferation concern.
- Separated plutonium, partially separated plutonium, and unseparated SNF must be protected by physical and other engineered safeguards, including safeguards-by-design. This is essential, whether the plutonium is stored, disposed of in a repository, or separated to enable recycling.
- The self-protecting radiation barrier decays exponentially with time. With indecision and continued storage for several decades, stored SNF becomes more vulnerable. This vulnerability can be eliminated by recycling and re-irradiation of the plutonium.
- Continued production of plutonium in nuclear fuels and storage of SNF for multiple decades of time, together with the exponential decay of the self-protecting radiation barrier, are genuine reasons for international and national proliferation concern.
- Safeguards-by-design co-location and integration of SNF storage, reprocessing separations, and recycle fuel production, together with application of multiple engineered safeguards, can provide the "defence-in-depth" necessary to prevent diversion and permit secure recycle of SNF.
- Materials from thorium based spent fuels in molten salt reactors can be separated to give $^{233}U$ in MSR online reprocessing but this process contains useful barriers against diversion due to the extreme difficulties inherent in MSR online reprocessing technology and the fact that all separation steps must be within hot cell facilities.
- Experience in non-proliferation analyses of several possible methods of separation of SNF components has shown that the various separations technologies that have been proposed for a closed back end of the nuclear fuel cycle do not offer significant non-proliferation differences. Therefore, the technologies to be used can be chosen for reasons such as process efficiency, maturity, and cost-effectiveness.

### *3.6.9. Conclusions*

Any facility dealing with nuclear materials has a certain level of risk of proliferation, even though the level differs for each facility and fissile material. The important question here, therefore, would be how to enhance the proliferation resistance of the given process. Undoubtedly, such enhancements of proliferation resistance should be achieved through the application of measures appropriately combined to strengthen the material, technological and institutional barriers to proliferation ("defence in depth"). The development of a "risk reduction methodology" and the implementation of a "safeguards-by-design" approach are also necessary in that regard.

As a final point, it is here emphasised that the selection of a specific separation process over others should be made as a part of the choices made on the overall nuclear fuel cycle. Since proliferation resistance only serves as one of various criteria to make such a choice, the final decision really depends on which criterion the policymakers consider more important (resource utilisation, waste management, economics, technical maturity, non-proliferation, etc.).

### 3.7. Choice of separation process

It is clear that global comparisons between different separation processes are, at the present time, of limited value. This is because the various separation processes have been designed for different fuel cycle scenarios by various agencies influenced by differing national priorities and also the technical maturities of the various options are at different stages. Further, while demonstration of technical feasibility is essential, many other factors must be evaluated and compared before choices can be made regarding the optimum separation process to use in any particular scenario. These factors include:

- safety – chemical, nuclear, radiological;
- proliferation resistance;
- environmental impact;
- economics;
- waste management;
- nuclear energy policy;
- public and political acceptability.

Even once these factors have been studied and can be evaluated, how they are compared in a fuel cycle model and what weightings are given to specific factors is a very difficult question requiring detailed analysis. Also such evaluations are likely to change between different countries as national priorities will vary. Further, variations with time will occur within the same country as technical, social, political and economic influences change. In the specific case of non-proliferation it is even difficult to find criteria for assessment that have a technical basis with broad agreement on the methodology. So although options can be assessed by individual nations making baseline assumptions concerning their nuclear energy strategies, it remains difficult to see how international comparisons can be made.

### 3.8. Conclusions

It is not yet possible to define clear criteria that separation processes must meet as there are a range of options for future nuclear systems. Nevertheless, some key questions can be addressed to help refine the process development; these include:

What are the bounding feeds to a recycle plant expected to be for the most relevant fuel cycle scenarios and what products will be required for recycle fuel and target fabrication?

What methodologies are available for comparing the various factors that influence separation process design and how are these weighted?

What fuel cycle scenarios cause pyrochemical processes to become more favourable than the dominant, industrially established, aqueous-based processes?

How do we down-select separation processes for technology demonstration and can the international community collaborate on the design and build of technology demonstrators for advanced fuel cycle plants?

The separation process(es), that lie at the heart of nuclear fuel recycling, are key components in any analysis of the benefits/barriers of closing the nuclear fuel cycle. Therefore, there is a clear need to (1) develop methodologies to compare fuel cycle options against the different pathways for nuclear energy; (2) prove technical feasibility of leading options for a range of likely fuel cycle scenarios (up to TRL 6) and (3) demonstrate selected technologies at engineering scales with spent fuels (TRL 7-8).

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# 4. Comparison of chemical processes

## 4.1. Introduction

The objective of this chapter is to compare the technical maturity and state of R&D of the major aqueous and pyrochemical separation processes that were described in Chapter 2. When making such comparisons it is beneficial to employ a consistent methodology. While this may not fully eliminate subjective judgement it should at least ensure that the assessments are internally consistent and inter-comparisons are at least valid on a relative scale. These assessments of the technical status of the various processes will be assisted by the adoption of the well-established technology readiness level (TRL) methodology, which is widely used and recognised internationally. Clearly, this is just one tool available and a full assessment must also draw on other measures and judgements. It is also noted that TRL evaluations and technical risk are not necessarily linked – a low TRL does not immediately imply high technical risk. Technical risk should be evaluated separately. The proposed approach to assessing TRL is described in Section 4.1.1 below, but it should be understood that in this review only the technology readiness of the separation process is assessed, not the TRL of the full process plant.

### *4.1.1. Technology readiness levels (TRL) for comparing separation processes*

An approach similar to that used by the NEA transmutation fuel development community (Expert Group on Innovative Fuels)[1] is proposed in which a matrix approach is used to indicate at what scale development or testing has been completed against specific feeds from non-active simulants to high-activity feeds such as spent fuel. TRLs from 1-9 are customised for separation process development and defined in Table 4.1 below. However, these TRLs are a relatively coarse measure of the maturity of advanced separation processes, which themselves have many individual components. In particular they combine judgements on the readiness levels of the process chemistry (flowsheet) and the plant equipment/engineering. The focus of this report is on the separations process chemistry. Most of the separation processes described are in the R&D phase and would be operable in established engineering technology. So engineering is not expected to be a limiting factor in assessing the TRLs of these processes. If, in the future, some of these advanced processes proceed towards deployment then detailed and specific assessments of engineering and plant equipment will be needed during the concept and detailed design stages. Hence, a matrix has been developed and the TRLs mapped onto the matrix to try and assess TRL as a function of both the scale of development and the feeds used in testing (Table 4.2). It should be noted that a TRL is not reached by completion of just one square of the matrix; this simply indicates the working level and is only a guide to the final judgement on the TRL, which must also take into account other factors. Process development should therefore progress up and across the matrix with the TRL consequently rising.

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[1] *NEA State-of-the-art report on Innovative Fuels for Advanced Nuclear Systems*, NEA No. 6895, 2014.

**Table 4.1. Summary of TRL definition for separation processes**

| TRL | Function | Definition |
|---|---|---|
| 9 | Proof of performance | Multiple years of operational experience established at industrial scale. Processing and recycle of minor actinide fuels/targets. |
| 8 | | Full scale process demonstrated in a limited operational environment. |
| 7 | | Prototype system demonstrated under conditions fully representative of operations. |
| 6 | Proof-of-principle | Engineering or pilot scale testing of technology component or process step. Process flowsheets proven through hot tests using spent fuel. Process models validated. |
| 5 | | Technology component or process step validated at bench scale under relevant conditions. Process models developed. Proof-of-principle hot tests using spent fuel. |
| 4 | | Technology component or process step validated under laboratory conditions. Tests performed using active materials in simulated feeds. Fundamental properties measured. |
| 3 | Proof of concept | Lab scale tests to prove concepts, fundamental data obtained. |
| 2 | | Technology application developed and options investigated. |
| 1 | | Initial concepts are proposed and basic principles established. |

**Table 4.2. TRL assignments for separation process maturity**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

An additional analytical tool that is of relevance to the current exercise in comparing progress in separation chemistry of prospective processes is an adaptation of the TRLs developed by NNL (United Kingdom) and termed scientific readiness levels (SRL™). SRLs described in Table 4.3 are potentially better suited to the assessment of the state of the underlying science behind a process or plant. Hence, these are applicable to our assessment of the state of knowledge of the separations chemistry and R&D progress for each individual process.

**Table 4.3. Definition of scientific readiness levels**

| Level | Label | Scientific readiness level |
|---|---|---|
| 6 | Established<br>(Investment primarily driven by needs of maintaining expertise) | Some deficiencies such that, although understanding is well developed, there are still minor judgements required to make predictions to regions not covered by the underlying data. Timely to consider funding for training successors. |
| 5 | Mature but needs some support | Good understanding of the controlling physical and chemical processes but some elements require further support to demonstrate their validity. |
| 4 | Mature but needs underpinning | Good understanding of the controlling physical and chemical processes but major elements require support to demonstrate their complete validity. |
| 3 | Judgemental<br>(Investment primarily to fund a doable R&D programme) | Controlling physical and chemical processes have been identified but major assumptions required to make predictions for parameter space of interest. However, the research required to justify such assumptions can be specified and it is possible to detail a R&D programme to move up SRLs. In addition, there may be only a limited number of individuals capable of developing the required arguments. |
| 2 | Exploratory<br>(Investment for speculative R&D programme) | The potential physical and chemical processes have been assessed, but exploratory research is required to confirm the controlling processes. Predictions require assumptions of both the controlling processes and detailed parameters. |
| 1 | Emerging issue<br>(Investment required to move up SRLs) | Little or no confidence in making predictions but possible to identify physical and chemical processes that need to be understood and where expertise has to be established. |

## 4.2. Head-end processes

Head-end processes are being developed for advanced reprocessing operations to capture the gaseous, volatile, and semi-volatile fission products and activation products, T, $^{129}$I, $^{86}$Kr, and $^{14}$C, from off-gas streams of the various advanced head-end processes being developed. These efforts are aimed primarily at dry sorbent adsorption materials that will become solid waste that can be properly disposed. Some of the potential adsorbents have been tested at the bench and engineering-scale. Therefore, most TRLs are 5-6 and the SRLs are 3-4.

### *4.2.1. Disassembly, fuel exposure and dissolution*

*Disassembly and dissolution*

Because used nuclear fuel is enclosed in a chemically resistant metal cladding, the fuel must be exposed for subsequent chemical treatment. The spent nuclear fuel (SNF) disassembly process for full fuel-assembly shearing is a well-established, industrial-scale process used in reprocessing plants for multiple years in several countries. Therefore, the processes have technology readiness level (TRL) of 9 (Table 4.4). Scientific readiness level (SRL) is 6.

**Table 4.4. TRL and SRL assignments for head-end processing maturity – Current practices – Disassembly and fuel exposure**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Dissolution*

At present, all reprocessing plants dissolve the oxide fuel in hot nitric acid. Although the dissolver design differs from plant to plant, the process is a well-established industrial practice both in batch and continuously operated equipment. The technology readiness level (TRL) is 9 (Table 4.5) and the scientific readiness level (SRL) is 6.

**Table 4.5. TRL and SRL assignments for head-end processing maturity – Current practices – Dissolution**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Korea processes for disassembly, decladding and dissolution*

Newer methods for disassembly of spent fuel assemblies and decladding of fuel rods are being developed. The Korean process developed specifically for PWR fuel assemblies starts with the extraction of the individual rods from the fuel assemblies and is followed by the cutting of the approximately 4 m long fuel rods into shorter sections of 15 to 25 cm long. The decladding process is done by slitting of the sectioned rods and can be combined with the oxidation of the fuel to produce a fine powder at temperatures between 450 and 750°C while releasing tritium. Further processing at temperatures above

1 000°C and under different gas atmospheres can be used to remove a large fraction of several additional volatile and semivolatile fission products that are trapped by a specialised off-gas system. The pre-treated fuel is then dissolved in a molten salt and fed into an electrochemical separative process. The technology readiness level (TRL) is 5-6. The scientific readiness level (SRL) is 4.

**Table 4.6. TRL and SRL assignments for head-end processing maturity – New processes – Korean processes for disassembly, decladding and dissolution**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Russian process for decladding, fuel oxidation and release of tritium*

The Russian decladding process is based on the high temperature reaction of nitrogen on zirconium cladding; as a result, the cladding becomes very brittle and easily breaks down.

After separation from the broken cladding, the uranium dioxide-based fuel is transformed into a fine $U_3O_8$ powder by oxidation in air or oxygen. This reaction is accompanied by tritium evolution. The technology readiness level (TRL) is 7. The scientific readiness level (SRL) is 5.

**Table 4.7. TRL and SRL assignments for head-end processing maturity – New processes – Russian process for decladding, fuel oxidation and release of tritium**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### *4.2.3. US Process for recovery and purification of zirconium from SNF cladding*

The US process for recovery and purification of zirconium from spent nuclear fuel (SNF) cladding is being developed to convert the irradiated cladding to low-level waste, or for recycle and re-use. The chlorination process has been tested for feasibility using actual SNF cladding and the purification of the product salt ($ZrCl_4$) has been tested with unirradiated zirconium alloy cladding tubes. The process can be applied to the cladding hulls resulting from present industrial practices, or integrated into an advanced head-end process following voloxidation, or as the first step for chemical decladding of the fuel assemblies. The technology readiness level (TRL) is 6-7. The scientific readiness level (SRL) is 4.

**Table 4.8. TRL and SRL assignments for head-end processing maturity – New processes – US process for recovery and purification of zirconium from SNF cladding**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### *4.2.4. US process for dry pre-treatment for tritium management and continuous fuel dissolution*

The US process for dry pre-treatment using air and or oxygen is being developed for release of volatile tritium, conversion of ceramic $UO_2$ pellets finely divide $U_3O_8$ powder, followed by continuously-operated dissolution in either hot nitric acid or molten salt solution. The technology readiness level (TRL) is 6-7. The scientific readiness level (SRL) is 5.

**Table 4.9. TRL and SRL assignments for head-end processing – New processes – US process for dry pre-treatment for tritium management and continuous fuel dissolution**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### *4.2.5. US Process for dry pre-treatment for tritium management and continuous fuel dissolution or extraction based on $NO_2$*

The US process for dry pre-treatment using $NO_2$ is being developed for the release of volatile tritium, and iodine; while selectively converting the $UO_2$ –based fuel into finely divided $U_3O_8$, $UO_3$, or nitrate powder. The process can be followed by continuously-operated dissolution in nitric acid, or directly interfaced with the organic solvent extraction (e.g. 30%TBP in dodecane) or dissolution into a molten salt solution. The technology readiness level (TRL) is 5-6. The scientific readiness level (SRL) is 4.

**Table 4.10. TRL and SRL assignments for head-end processing – New processes – US process for dry pre-treatment for tritium management and continuous fuel dissolution or extraction based on $NO_2$**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

The technology readiness level (TRL) and the scientific readiness level (SRL) of each of the various head-end processes described in Chapter 2, Section 2.1 has been estimated to compare the status of the process development and demonstration, or industrial-scale experience. A summary of the results of the analyses is shown in Table 4.11 below.

**Table 4.11. Summary of TRLs/SRLs for head-end processing**

| Current Practices | TRL | SRL |
|---|---|---|
| Disassembly and fuel exposure | 9 | 6 |
| Dissolutions | 9 | 6 |
| Potential additional process steps for future reprocessing plants | | |
| Korean process for disassembly | 5 | 4-5 |
| Korean process for decladding | 6 | 4-5 |
| Russian process for decladding and fuel oxidation | 7 | 5 |
| US process for recovery and recycle of zirconium | 5 | 4 |
| Removal of volatile and activation fission products | | |
| US process for dry pretreatment removal of tritium | 5 | 4 |
| Korean process for dry high temperature pretreatment | 5-6 | 4 |
| Off-gas treatment | 5-6 | 3-4 |
| Korean process for off-gas pretreatment | 5-6 | 3-4 |
| Advanced aqueous dissolution | 5 | 4 |

## 4.3. Aqueous processes

### 4.3.1. *Uranium recovery*

*GANEX 1st cycle (see Chapter 2, Section 2.2.1)*

The 1st cycle of the GANEX process has been demonstrated through a pilot scale hot test using spent fuel (3 kg) using laboratory scale mixer-settlers. So the process flowsheets performances are proven through hot tests. A process model has been developed and validated for the steady state. Therefore the TRL for the 1st cycle of the GANEX process is higher than 5 (hot test on spent fuel) and could be estimated at 6 except that it has not been demonstrated using the representative technology of industrial contactors.

The scientific readiness level for this process is 5 as attested by the very good agreement between model predictions and test results.

**Table 4.12. TRL assignments for separation process maturity – GANEX 1$^{st}$ cycle process: Analysis supports TRL = 5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | TRL 4 | TRL 6 | TRL 7 | |
| Fuel simulants | TRL 3 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*U recovery by crystallisation in the NEXT Process (see Chapter 2, Section 2.2.1)*

The process of U recovery by crystallisation has been developed in Japan as the first separation step in the NEXT process for reprocessing fast reactor spent fuel, where about 70% of U is to be separated from the dissolved spent fuel. As described in Section 2.2.1 the process including sweating and melting-filtration after crystallisation was tested with irradiated MOX fuel (from JOYO) in a flowsheet test (The process requires further improvement to obtain higher decontamination factors for Pu and Cs). Engineering scale tests were also performed by cylindrical annular type crystalliser using U solution. evaluated technology readiness level (TRL) for separation process maturity is shown in Table 4.13. Overall TRL of this U crystallisation process would be 4-6.

The scientific readiness level for U recovery by crystallisation in the NEXT Process is 5.

**Table 4.13. TRL assignments for separation process maturity – U recovery by crystallisation in the NEXT process: Analysis supports TRL = 4-6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### *4.3.2. Co-processing of actinides (U, Pu, Np) (see Chapter 2, Section 2.2.2)*

*The Thorp PUREX process (see Chapter 2, Section 2.2.2.)*

Thorp is a conventional PUREX process designed in the 1970-1980s, commissioned in 1994. The chemical separation process uses 3 cycles of solvent extraction with an early split of U from Pu followed by separate uranium and purification cycles. U(IV) with hydrazine is used to reductively strip Pu from the solvent in the U/Pu split. Pulsed columns are used for Pu-containing process streams, mixer-settlers for U streams. $UO_3$ and $PuO_2$ products are manufactured in the finishing plant areas. Table 4.14 supports an overall TRL of 9 as would be expected for a commercial operating plant.

Given the industrial experience and huge amount of scientific studies related to the PUREX process over ~60 years, the SRL is clearly 6.

The conventional, industrialised PUREX process, as used at Thorp and also elsewhere, thus provides a benchmark against which the advanced processes can be compared.

**Table 4.14. TRL assignments for separation process chemistry maturity – Thorp PUREX process: Analysis supports TRL = 9**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*COEX$^{TM}$ (see Chapter 2, Section 2.2.2)*

For the COEX$^{TM}$ process, as it is in fact is basically an evolution of the PUREX process, by modifying it to produce a U + Pu mixture (U/Pu > 20%), rather than pure plutonium without any new reagent introduced in the process and for the major part of this process only some flowsheet "tuning" in comparison to the PUREX process. So the TRL of this process can be evaluated to 8 or 9.

The main difference between the PUREX process and the COEX$^{TM}$ in term of process chemistry is at the last step of this process where the oxalic conversion of plutonium (IV) is replaced by the oxalic co-conversion of uranium (IV) and plutonium (III) (neptunium (IV)). Therefore the analysis supports TRL 8 for COEX$^{TM}$ for the extraction steps part of the process (Table 4.15). For the co-conversion, the TRL is 4-5 since flowsheet tests have been done only at lab scale.

Given the industrial experience and huge amount of scientific studies related to the PUREX process over ~60 years, and the small differences between the COEX$^{TM}$ and the PUREX, the SRL for COEX$^{TM}$ is also 6.

**Table 4.15. TRL assignments for separation process maturity – COEX$^{\text{TM}}$ process: Analysis supports TRL = 8**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Advanced PUREX process (see Chapter 2, Section 2.2.2)*

This is described in Section 2.2.2 and is basically a simplified and modified PUREX process in which neptunium is extracted in the primary contactor and routed with the Pu product. A small proportion of the U is also routed with the Pu product (*ca.* 1:1 U:Pu ratio) while the bulk U is maintained in a separate stream. The objective of the development is to achieve decontamination factors that enable a single solvent extraction cycle to be operated. Options obviously exist to route the Np into a separate stream or with the HA raffinate; to vary the U:Pu ratio in the Pu product and to add on purification cycles if required. The contacting equipment to be used is expected to be centrifugal contactors. The major innovation is the proposed use of a hydroxamic acid complexant to separate Pu from U by complexation rather than reduction, eliminating the need for a stabilising agent, and to selectively reduce Np to Np(V), so it is routed with the Pu stream, rather than Np(IV), which is co-extracted with U in current plants using a U(IV) reductant. While this single cycle configuration has not been tested with spent fuel, hot tests of similar PUREX-based flowsheets with acetohydroxamic acid (AHA) have been reported. Table 4.16 suggests an overall TRL of 4-5. The SRL is relatively high since much of the underlying science is PUREX. Furthermore, flowsheet tests and process chemistry studies have proven the feasibility of some of the more innovative aspects. However, there are major elements of this Advanced PUREX process that still require demonstration. An SRL of 3-4 is estimated.

**Table 4.16. TRL assignments for separation process maturity – (NNL) Advanced PUREX: Analysis supports TRL = 4-5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*The UREX Co decontamination process (see Chapter 2, Section 2.2.2)*

The UREX decontamination solvent extraction process simultaneously separates a uranium product, a plutonium-neptunium product, and a technetium product from the minor actinides and fission products [high-level waste (HLW)] contained in LWR spent fuel. The process utilises tributyl phosphate as the extractant and normal paraffin hydrocarbon as the diluent. The experimental tests were made at Oak Ridge National Laboratory in the solvent extraction test facility (SETF), located in the high-level cells of the Radiochemical Engineering Development Centre (REDC).

This process has been demonstrated successfully for light water reactor (LWR) used fuels having a wide range of burn-up (20-65 GWd/te) and decay storage prior to separations treatment (4-32 years). Moreover, the process has been operated with and without the “Tc Strip” operation and with the partial partition process varied to produce a U-Pu-Np product containing either ~10% Pu-Np for potential recycle to LWRs or ~30% Pu-Np for potential recycle to fast reactors.

The process has been tested at engineering scale through hot test using spent fuels. In addition the SEPHIS process model has been validated for the U, PU and nitric acid components of the process. Therefore, overall TRL for this process is 6.

### Table 4.17. TRL assignments for separation process maturity – UREX co-decontamination: Analysis supports TRL = 6

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants orrepresentative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

The process is established and demonstrated although some deficiencies need minor judgements. Investment is primarily driven by needs of maintaining expertise. The overall SRL is estimated at 5.

*U-Pu-Np co-recovery by TBP extraction in the NEXT process (see Chapter 2, Section 2.2.2)*

The process of U-Pu-Np co-recovery by extraction with TBP has been developed in Japan as the second separation step after the U crystallisation step in the NEXT process. It was tested with irradiated JOYO MOX fuel using miniature centrifugal contactors. Simultaneously, engineering scale centrifugal contactors have been developed for this process. Overall TRL of this U-Pu-Np co-recovery process would be 5-6, as shown in Table 4.18.

The scientific readiness level for U-Pu-Np co-recovery by TBP extraction in the NEXT Process is 6.

### Table 4.18. TRL assignments for separation process maturity – U-Pu-Np co-recovery by TBP extraction in the NEXT process: Analysis supports TRL = 5-6

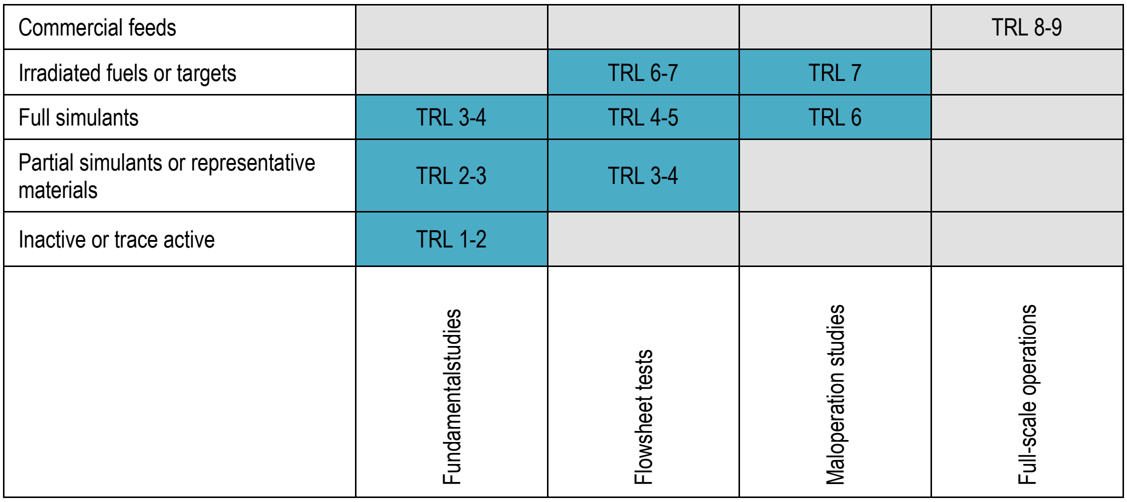
| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants orrepresentative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Russian "Simplified PUREX" process (see Chapter 2, Section 2.2.2)*

To process spent nuclear fuel (SNF) from VVER-1000 reactors in the Test Demonstration Centre of the Mining and Chemical Combine (FSOE "MCC"), a version of the PUREX process was developed by the "NPO V. G. Khlopin Radium Institute" in St. Petersburg, Russia; this has been termed "Simplified PUREX". This process was selected as the baseline process for the Experimental Test Centre being constructed at the site of the Mining and Chemical Combine (FSOE "MCC"), Zheleznogorsk, Krasnoyarsk region. Solving the first goal allows the elimination of pure plutonium recovery thus increasing the resistance of a recycling process to nuclear materials propagation. Solving the second goal provides an opportunity not only to recycle water within a single technology, but also to reduce sufficiently the costs for liquid radioactive waste processing in comparison with those experienced in the Russian RT-1 plant and RT-2 project.

Overall TRL of this process would be 7, as shown in Table 4.19. Scientific readiness levels for the "simplified PUREX"process are 6.

**Table 4.19. TRL assignments for separation process maturity – Russian "Simplified PUREX" process analysis supports TRL = 8**



| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamentalstudies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Russian REPA process (see Chapter 2, Section 2.2.2)*

The efficiencies of the REPA process are defined by the stage of UNH crystallisation, extraction of the U+Pu fraction and fractionation processes for the actinides, REE and other FPs. To optimise a separation process for UNH crystals, some research works were performed on UNH solubility in nitric-acid solutions, which became a base to obtain calculated nomographs to define the uranium output in crystals at different temperatures. Nitric acid concentrations were found to increase the rate of UNH conversion into solids and to optimise crystal flushing from impurities.The overall TRL of this process would be 5 and the scientific readiness levels for REPA process are 4.

**Table 4.20. TRL assignments for separation process maturity – Russian REPA process**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Russian (U,Pu) co-crystallisation process (see Chapter 2, Section 2.2.2)*

The co-crystallisation of uranium and plutonium nitrate hexahydrate in the process of mixture undivided refining crystallisation is under investigation at the Bochvar Institute (VNIINM), Moscow, Russia. Production of mixed uranium-plutonium fuel includes steps of obtaining a master mix $(U,Pu)O_2$ with a ratio of $Pu/U \geq 0.25$ and subsequent "dry" adjustments of this ratio by adding the required amount of $UO_2$. The important issue in manufacturing the master mixture is achievement of maximum homogenisation of $UO_2$ and $PuO_2$ (at a level of a solid-solution). Use of precursor compounds is a prerequisite for such homogenisation. Uranium and plutonium nitrates (UN, PuN) are such compounds. Co-crystallisation of hexahydrates $UO_2(NO_3)_2.6H_2O$ and $PuO_2(NO_3).6H_2O$ is both a refining operation for obtaining an undivided mixture of uranium and plutonium and the method to achieve the desired chemical form for subsequent conversion into $(U,Pu)O_2$. The TRL for this process is estimated at 4. The scientific readiness levels are 4.

**Table 4.21. TRL assignments for separation process maturity –**
**Russian (U,Pu) co-crystallisation process: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### 4.3.3. *TRU actinide extractions using new solvent systems*

*DIAMEX (see Chapter 2, Section 2.2.3)*

The DIAMEX process has been demonstrated through a pilot scale hot test using spent fuel (20 kg) and using same technology component (pulsed column) as the envisaged technology for industrial application of this process. So the process flowsheets are proven through hot tests and a process model has been validated for steady state and transient behaviour. So TRL is 6 and could be evaluated also to 7. Scientific readiness levels for DIAMEX are 6 as attested by the very good agreement between model predictions and test results.

**Table 4.22. TRL assignments for separation process maturity – DIAMEX process: Analysis supports TRL = 6-7**

| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Fuel simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |

*SANEX BTBP (see Chapter 2, Section 2.2.3)*

The Institute for Transuranium Elements of the European Commission Joint Research Centre, through the European supported programs in actinide reprocessing and recycling, has been a part of the development of several processes, e.g. the DIAMEX, SANEX and EURO–GANEX processes. In the hot cell facility of ITU demonstration tests involving irradiated fuel as feed material are often carried out for these projects.

- The r-SANEX process

The process is described in detail in Chapter 2, Section 2.2.3 and is a part of the European strategy for heterogeneous recycling of actinides where the trivalent actinides are separated from the lanthanides. The r-SANEX process (r = regular) is the original process developed for the selective extraction of actinides from a DIAMEX raffinate containing both the trivalent lanthanides and the minor actinides. Later developments and improvements have included the 1c-SANEX (1-cycle) and the i-SANEX (innovative) processes. The regular SANEX process has been extensively investigated in fundamental studies and is well understood. The process chemistry and corresponding separation schemes has been tested in flow-sheet tests with tracers, fuel simulants and with genuine fuel materials. Due to the high dose rate to the solvent from the minor actinides, centrifugal contactors are the equipment of choice. The two main drawbacks of the process are slow extraction kinetics and the limited solvent extractant concentration, forcing low flow-rates to be used. The process has so far been developed and tested only at lab scale. The overall technology readiness level is evaluated to a TRL of 4-5 and a scientific readiness level of SRL 4 has been estimated.

**Table 4.23. TRL assignments for separation process maturity – r-SANEX process: Analysis supports TRL = 4-5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 5-6 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

- The iPr-BTP-SANEX

The iPr-BTP-SANEX process has been tested through a pilot scale hot test using DIAMEX product coming from spent fuel dissolution solution and treatment using laboratory scale mixer-settlers. During this high-activity trial, iPr-BTP was shown to be efficient in terms of An(III) retrieval (99.9%) and purification as concerns Ln(III), but it degraded during the trial under the effect of radiolysis. So TRL for iPr-BTP-SANEX is limited to 3 as its radiolytic stability target was not reached. The formulation studies of this molecule family have been pursued in the scope of European framework projects. Scientific readiness levels for iPr-BTP-SANEX is 3-4 as even if the results of the hot test was well simulated by the model, the degradation mechanism remains insufficiently understood.

**Table 4.24. TRL assignments for separation process maturity – iPr-BTP-SANEX process: Analysis supports TRL = 3**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | TRL 4 | TRL 6 | TRL 7 | |
| Fuel simulants | TRL 3 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*DIAMEX-SANEX-DMDOHEMA/HDEHP (see Chapter 2, Section 2.2.3)*

The DIAMEX-SANEX process has been demonstrated through a pilot scale hot test using spent fuel (3 kg) using laboratory scale mixer-settlers. So the process flowsheets are proven through hot tests. A process model has been developed and validated for the main steps of this process but this does not cover all the steps (i.e. molybdenum scrubbing step). For the An/Ln co-extraction step and An selective stripping step the model has been validated for steady state and transient behaviour. So TRL for DIAMEX-SANEX is higher than 5 (hot test on spent fuel) and could be 6 except that it has not been demonstrated using the representative technology of industrial contactors.

Scientific readiness levels for DIAMEX-SANEX are 5 as attested by the very good agreement between model predictions and test results for the steps covered by the model but some steps need further model development.

**Table 4.25. TRL assignments for separation process maturity – DIAMEX-SANEX process: Analysis supports TRL = 5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | TRL 4 | TRL 6 | TRL 7 | |
| Fuel simulants | TRL 3 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*An(III) separation process by diglycolamide (DGA) in Japan (see Chapter 2, Section 2.2.3)*

A new extractant of diglycolamide (DGA), TODGA (*N,N,N',N'*-tetraoctyldiglycolamide), has been developed in Japan for separation of trivalent actinides (An(III)). A modified DGA extractant, TDdDGA (*N,N,N',N'*-tetradodecyldiglycolamide), which has higher extraction capacity, was applied to develop a separation process for An(III). The process was tested with a simulated high-level liquid waste containing Am using a small scale mixer-settler and the separation performance was confirmed. There would be no difficulty in scale-up of this process because it is a normal extraction process which has no particular problems such as crud or third phase formation. Overall TRL of the An(III) separation process by extraction with TDdDGA would be 3-5, as shown in Table 4.26. Scientific readiness levels for An(III) separation process by extraction with TDdDGA are 4.

**Table 4.26. TRL assignments for separation process maturity – An(III) separation process by extraction with TDdDGA in Japan: Analysis supports TRL = 3-5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Russian studies: Influences of diluent on DGA extractions (see Chapter 2, Section 2.2.3)*

One of the most known and well-studied extractants for co-recovery of actinides and lanthanides is N,N,N',N'-tetraoctyl diglycolamide (TODGA). TODGA contains three oxygen atoms and acts as a tridentate ligand. It is well-soluble in aliphatic n-dodecane and shows very high distribution ratios for extraction of An(III) and An(IV) from concentrated nitric acid into n-dodecane. Many studies on TODGA extraction chemistry have been reported and several processes have been developed and tested.

Most of the studies on the metal extraction by TODGA have been performed in dodecane. The extraction of Am and Eu by TODGA from nitric acid into diluents with different dielectric constants were studied at the Khlopin Radium Institute in St Petersburg, Russia. The TRL is estimated at 4 and SRL at 3.

**Table 4.27. TRL assignments for separation process maturity – influences of diluent on DGA extractions: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3 | TRL 4 | TRL 6 | |
| Partial simulants or representative materials | TRL 2 | TRL 3 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Minor actinide/lanthanide separation using the Actinide-Lanthanide Separation (ALSEP) Concept (see Chapter 2, Section 2.2.3)*

To date, proof-of-principle experiments on the ALSEP concept have been completed using simulated feed streams spiked with radiotracers. These tests have demonstrated separation factors of minor actinides from the lanthanides ranging from 20 to 40. Research and development of the ALSEP concept continues with the near-term goal of laboratory-scale flowsheet testing in centrifugal contactor or mixer-settler equipment using radiotracer spiked simulant followed by similar testing with actual dissolved spent nuclear fuel. The level of maturity supports a TRL of 4 for the ALSEP process. Fundamental properties have been measured but process models have not been developed to date. Technology readiness level and scientific readiness levels for ALSEP are both 4.

**Table 4.28. TRL assignments for separation process maturity – ALSEP process: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*New diamides of 2,2 ′-dipyridyl-6,6 ′-dicarboxylic acid for actinide-lanthanide separation (see Chapter 2, Section 2.2.3)*

The extraction of americium and lanthanides by diamides of 2,2 -dipyridyl-6,6 -dicarboxilic acid solutions in polar diluents was studied at the Khlopin Radium Institute. The highest extraction was found for the compounds with the ethyl-group and the alkyl-substituted aryl-group on the amidic nitrogen. Am/Ln separation factors higher than 10 were achieved for extraction from high acidity media. Tests were performed using active materials in simulated feeds. Therefore, the level of maturity supports a TRL of 4. Technology readiness level and scientific readiness levels for this process are respectively 4 and 3.

**Table 4.29. TRL assignments for separation process maturity – New diamides: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Minor actinide separation using TRUEX/TALSPEAK and TRUEX/advanced TALSPEAK (see Chapter 2, Section 2.2.3)*

- TRUEX-TALSPEAK (see Chapter 2, Section 2.2.3)

The TRUEX/TALSPEAK process has been demonstrated in centrifugal contactor and mixer-settler equipment used actual dissolved spent fuel. While the results of these tests were very good, the pH range of acceptable operation is small and there is a lack of a complete understanding of the process chemistry in the TALSPEAK portion of the flowsheet. This lack of flexibility in the pH range could become important under maloperations. The level of maturity supports a TRL of 6 for the TRUEX/TALSPEAK process. A steady-state process model (AMUSE Code) has been developed for this process. The TRUEX portion of the flowsheet is well understood and modelling results have been validated. The scientific readiness level for TRUEX/TALSPEAK is 5.

**Table 4.30. TRL assignments for separation process maturity – TRUEX/TALSPEAK process: Analysis supports TRL = 6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

- TRUEX-Advanced TALKSEAK (see Chapter 2, Section 2.2.3)

The TRUEX/Advanced TALSPEAK process seeks to improve upon the TRUEX/TALSPEAK process by reducing the dependence of the process performance on the aqueous solution pH, obtaining more predictable extraction behaviour, and having more rapid extraction kinetics. Development of the Advanced TALSPEAK portion of the flowsheet has progressed to the level of the use of active components in full simulants under laboratory conditions. Additionally, single stage testing in centrifugal contactors has been performed using active simulants. The level of maturity supports a TRL of 4 for the TRUEX/Advanced TALSPEAK process. Process models have not been developed to date for the Advanced TALSPEAK portion of the flowsheet. Scientific readiness levels for TRUEX/Advanced TALSPEAK are 4.

**Table 4.31. TRL assignments for separation process maturity – TRUEX/advanced TALSPEAK process: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*CEA GANEX and EURO-GANEX processes (see Chapter 2, Section 2.2.3)*

As described in Chapter 2, the GANEX process involves an initial U extraction cycle followed by a TRU extraction cycle. In the TRU cycle, Pu, Np, Am and Cm are co-extracted with the lanthanide elements from the bulk of the fission and corrosion products. The actinides are then selectively stripped away from the lanthanides. Two versions of the GANEX TRU cycle have been so far developed to the point of having an underpinned flowsheet – (1) CEA-GANEX and (2) EURO-GANEX. As both processes have reached a similar level of R&D, basic chemistry followed by flowsheet design and a single hot test, the assessments are similar. The EURO-GANEX process is characterised by an actinide-lanthanide co-extraction followed by selective actinide strip using a sulphonated bistriazinylpyridine ligand and acetohydroxamic acid whereas, in the CEA-GANEX, the selective actinide strip is done using HEDTA, hydroxyurea and citric acid. The contacting equipment to be used could be centrifugal contactors. Table 4.32 suggests an overall TRL of 4-5 for the separation process chemistry. The SRL is assessed at 3 since basic chemistry and flowsheeting studies have been performed but within a limited parameter space. However, understanding is at the point where a developmental forward R&D programme can be defined.

### Table 4.32. TRL assignments for separation process maturity – EURO-GANEX process: Analysis supports TRL = 4-5

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*HLW reprocessing with zirconium salt of dibutyl phosphoric acid (see Chapter 2, Section 2.2.3)*

The zirconium salt of dibutylphosphoric acid (ZS of HDBP) is an effective extractant for liquid high-level waste (HLW) and medium active level waste processing. Zirconium forms adducts with HDBP that are insoluble in water solutions and, among them, the most interesting is the adduct in which one molecule of zirconium interacts with eight molecules of HDBP. ZS of HDBP represents a complicated adduct with general formula $ZrA_4(HA)_4$, where HA – is an HDBP molecule and A is an HDBP anion. ZS of HDBP allows recovery of transplutonium elements (TPE), residual U, Pu, Np and also Sr, rare earths and other elements from nitric acid solutions with subsequent separation into individual fractions. The level of maturity supports a TRL of 6. The scientific readiness level is 5.

### Table 4.33. TRL assignments for separation process maturity – HLW reprocessing with zirconium salt of dibutyl phosphoric acid: Analysis supports TRL = 6

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### *An(III) separation process by extraction chromatography in the NEXT process (see Chapter 2, Section 2.2.3)*

A separation process for trivalent actinides (An(III)) by extraction chromatography has been developed in Japan as a part of the NEXT process, which utilises the adsorbents where the extractants for An(III) are loaded on porous silica particles coated with an inert copolymer. The process is composed of two steps. In the first step An(III) and lanthanides (Ln) are co-recovered using TODGA or CMPO and in the second step An(III) is separated from Ln using HDEHP, i-Hex-BTP or TOPEN. Both steps were tested with a genuine high-level liquid waste and the optimum extractants were selected. Simultaneously, engineering scale tests of column adsorption and elution have been performed including slurry transfer and column bed establishment. Overall TRL of this MA separation by extraction chromatography would be 4-6, as shown in Table 4.34. Scientific readiness levels for An(III) separation process by extraction chromatography in the NEXT process are 5.

**Table 4.34. TRL assignments for separation process chemistry maturity – An(III) separation process by extraction chromatography in the NEXT process: Analysis supports TRL = 4-6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### *CARBEX process (see Chapter 2, Section 2.2.3)*

In laboratory scale tests were carried out of the reprocessing process using the simulator of uranium-containing SNF but not containing plutonium and minor actinides (americium, neptunium, and curium). The tests included the cycle of operations for the oxidative dissolution of $UO_2$ in carbonate solutions; the 1st extraction cycle of U(VI) from carbonate solution using methyltrioctylammonium carbonate as an extractant for separating U(VI) from the bulk of the soluble fission products; a solid-phase re-extraction of uranyl-carbonate compounds; dissolution of carbonate compounds of U(VI) in ammonium carbonate solution and extraction-refining of U(VI) (second cycle of extraction in CARBEX process), followed by solid-phase re-extraction of carbonate compounds of U(VI) and obtaining high purity $U_3O_8$. The value of purification coefficients of U(VI) from the soluble fission products reached $10^5$-$10^6$. The level of maturity supports a TRL of 4. The scientific readiness level is 3.

**Table 4.35. TRL assignments for separation process chemistry maturity CARBEX process: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### 4.3.4. *Cs, Sr separation*

*CCD PEG (for HLW) (see Chapter 2, Section 2.2.4)*

A pilot-industrial facility for HLW partitioning (UE-35) using chlorinated cobalt dicarbollide (ChCoDiC) was created at "Mayak" PA in 1995. The ChCoDiC-based extraction system was adapted to the combined recovery of Sr and Cs radionuclides from $HNO_3$-solutions of HLW with very high salt content. In the period 1996-2001, 1 179 $m^3$ (49 515 kCi) of HLW have been processed. The overall TRL is estimated at 8. Scientific readiness levels for CCD process are 6.

**Table 4.36. TRL assignments for separation process chemistry maturity – CCD process: Analysis supports TRL = 8**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 7-8 |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive solutions | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Cs-Sr separation by extraction chromatography developed in Japan (see Chapter 2, Section 2.2.4)*

A separation process for Cs and Sr by extraction chromatography has been developed in Japan using the adsorbents where the extractants for Cs and Sr are loaded on porous silica particles coated with an inert copolymer. The extractants used for Cs and Sr are

Calix-crown R14 (1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene) for Cs and DtBuCH18C6 (di-t-butylcyclohexano-18-crown-6) for Sr. Some column adsorption experiments were performed using simulated solutions containing radioactive isotopes and it was concluded that Cs should be separated at the first step. Then both steps were tested in a very small scale with a genuine high-level liquid waste. Overall TRL of the Cs-Sr separation process by extraction chromatography would be 5-6, as shown in Table 4.37. Scientific readiness levels for Cs-Sr separation by extraction chromatography are 4.

**Table 4.37. TRL assignments for separation process maturity – Cs-Sr separation by extraction chromatography developed in Japan: Analysis supports TRL = 5-6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Fission Product Extraction (FPEX) process (see Chapter 2, Section 2.2.4)*

The FPEX process for the separation of Cs and Sr from spent fuel has been demonstrated in centrifugal contactor and mixer-settler equipment used actual dissolved spent fuel. Results of the testing were very good and there is a good understanding of the controlling physical processes. This level of maturity supports a TRL of 6 for the FPEX process. Limited process modelling work has been performed but data needed to support model development are available. Scientific readiness levels for FPEX are 5.

**Table 4.38. TRL assignments for separation process chemistry maturity – FPEX process: Analysis supports TRL = 6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*FPEX II process (see Chapter 2, Section 2.2.4)*

The FPEX II process for the separation of Cs and Sr from spent fuel has been developed to improve the extractant solubility in the Isopar L diluent and the radiolytic/hydrolytic stability. The FPEX II process has been demonstrated with good results in 5-cm centrifugal contactors using inactive surrogate feeds. This level of maturity supports a TRL of 4 for the FPEX II process. Limited process modelling work has been performed but data needed to support model development are available. Scientific readiness levels for FPEX II are 5.

**Table 4.39. TRL assignments for separation process maturity – FPEX II process: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*CST (see Chapter 2, Section 2.2.4)*

CST process, based on crystalline sodium silicotitanate, has extensively been tested to enable its use as an inorganic ion exchanger for the removal of radioisotopes, especially $^{137}$Cs, from highly alkaline nuclear waste solutions. Since the channel size of CST and the diameter of Cs ions are very close, ion exchange with Cs ions is almost irreversible. However, the selectivity for $Cs^+$, decreases significantly in highly alkaline solutions of high sodium concentration. Also, the presence of macro component potassium is a strong interfering factor both in cesium and strontium uptake for this material. The technology readiness level and scientific readiness levels for CST process are both 4.

**Table 4.40. TRL assignments for separation process maturity – CST process: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*AMP-PAN (see Chapter 2, Section 2.2.4)*

Ammonium molybdophosphate (AMP), especially if immobilised in polyacrylonitrile (PAN), is an engineered form of cesium selective sorbent material developed at Czech Technical University in Prague. It was evaluated with simulated sodium bearing waste (SBW) and dissolved pilot plant calcine at the Idaho Nuclear Technology and Engineering Centre (INTEC). AMP-PAN exchanger has high selectivity and capacity for removing $^{137}$Cs from acidic raffinate and acidic waste streams resulting from nuclear fuel reprocessing. The material has been shown to maintain this high Cs capacity with high flow rates of heavily salted feed solutions and also has the unique advantage over other inorganic exchangers in that feed adjustment is not required. Cs removal in a fixed bed system is a very promising technology and merits further engineering study. Scientific readiness levels for AMP-PAN process are 5.

**Table 4.41. TRL assignments for separation process maturity – AMP-PAN process: Analysis supports TRL = 5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Cs-Sr separation process by adsorption with inorganic ion exchangers in 4-group partitioning process developed in Japan (see Chapter 2, Section 2.2.4)*

A separation method for Cs and Sr applied to the 4-group partitioning process which was developed for the treatment of high-level liquid waste (HLLW) in Japan Atomic Energy Research Institute (JAERI, presently Japan Atomic Energy Agency, JAEA) is the adsorption method with inorganic ion exchangers, zeolite (natural mordenite) for Cs and titanic acid for Sr. These inorganic ion exchangers after adsorption of Cs and Sr can be converted directly into stable materials by calcination. Before the Cs-Sr separation, actinides are separated by solvent extraction and Tc-platinum group elements were separated by precipitation where the solution is neutralised by denitration in the 4-group partitioning process. The whole process was tested with a genuine concentrated HLLW, but no scale-up tests were performed for the Cs-Sr separation. Overall TRL of the Cs-Sr separation process by adsorption with the inorganic ion exchangers would be 6, as shown in Table 4.42. Scientific readiness levels for Cs-Sr separation process by adsorption with inorganic ion exchangers in 4-group process are 5.

**Table 4.42. TRL assignments for separation process maturity – Cs-Sr separation process by adsorption with inorganic ion exchangers: Analysis supports TRL = 6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### 4.3.5. *Curium separation technology (see Chapter 2, Section 2.2.5)*

*SESAME*

The SESAME process has been demonstrated using partial simulant (Am, Cm some Ln) solutions. The next step has been realised using iPr-BTP-SANEX product coming from spent fuel dissolution solution and treatment using laboratory scale centrifugal contactors. The performances in terms of recovery yield was limited to 78% and 88% for Am and Cm respectively. So the understanding of the impact of impurities on the oxidation mechanism of Am needs to be deepened.

Scientific readiness levels for SESAME are 3 due to partial comprehension of the chemical mechanism involved.

**Table 4.43. TRL assignments for separation process maturity – SESAME process: Analysis supports TRL = 3-4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | TRL 4 | TRL 6 | TRL 7 | |
| Fuel simulants | TRL 3 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*ExAm*

The EXAM process has been demonstrated through a pilot scale hot test using a genuine PUREX raffinate, and treatment using laboratory scale mixer-settlers. The process flowsheets are proven through hot tests. In conclusion, TRL for EXAM is higher than 5 due to the realisation of a hot test on spent fuel. To reach a TRL of 6, the EXAM process still needs to be demonstrated using representative industrial contactors technology. The first tests of the extraction step have been performed on non-radioactive surrogates using pulsed columns were a good behaviour of the extracting system in such an extracting device was observed.

Scientific readiness level for EXAM is 4-5 as indicated by the agreement between model predictions and test results for the steps covered by the model. Further model development remains outstanding in order to fully cover the EXAM process performance.

**Table 4.44. TRL assignments for separation process maturity – EXAM process: Analysis supports TRL = 4-5**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | TRL 4 | TRL 6 | TRL 7 | |
| Fuel simulants | TRL 3 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Cm separation from Am by ion exchange using tertiary pyridine-type resin studied in Japan (see Chapter 2, Section 2.2.5)*

The process of Cm separation from Am by ion exchange using tertiary pyridine-type resin has been studied in Japan in the framework of the research and development of reprocessing based on ion exchange method. The process was tested with a small amount of real dissolved fuel and the separation performance was demonstrated. In this test, element concentration is low and therefore the evaluated technology readiness level (TRL) for separation process chemistry maturity would be low, 2-3, as shown in Table 4.45. Scientific readiness levels for Cm separation by ion exchange using tertiary pyridine-type resin are 3.

**Table 4.45. TRL assignments for separation process maturity – Cm separation by ion exchange using tertiary pyridine-type resin: Analysis supports TRL = 2-3**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

## 4.4. Pyrochemical processes

### 4.4.1. *Uranium recovery*

*Pyroprocessing in Korea (see Chapter 2, Section 2.3.2)*

In the 1960s, the early version of pyroprocessing, called melt refining, was proposed and tested with Experimental Neutron Reactor II spent fuel in the United Sates. This early version was improved in the Integral Fast Reactor programme in the mid-1980s with the development of group recovery mechanism for uranium and transuranic elements from fission products. KAERI has developed pyroprocessing since 1997, and it has performed core concept development, bench-scale tests, and lab-scale demonstration since 2006. From 2007 to 2011, it conducted the design and construction of engineering-scale integrated system, named Pyroprocess integrated inactive demonstration facility (PRIDE) with an annual capacity of 10 tonnes using inactive simulants with depleted uranium. Pyroprocessing being developed at the KAERI consists of head-end processes (i.e. decladding, voloxidation, oxide feed preparation), electrochemical processes (i.e. electrolytic reduction, electrorefining, electrowinning), and waste treatment processes.

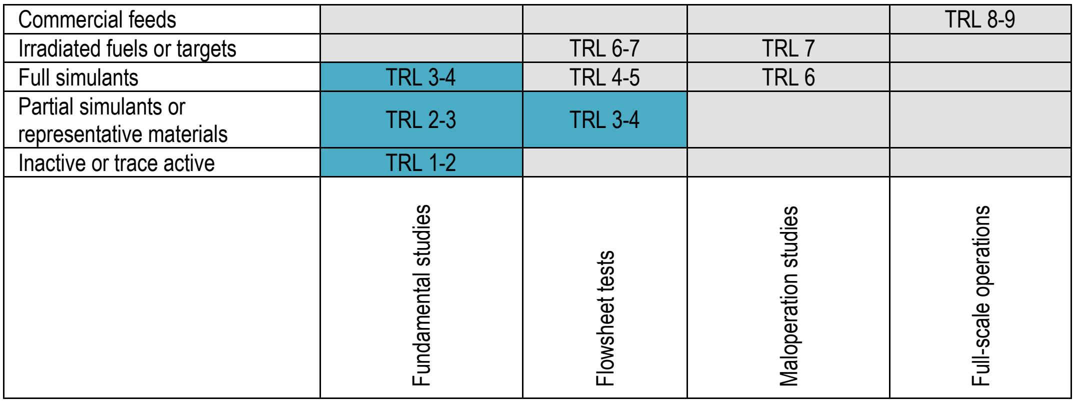
The head-end process converts spent fuel assembly into a suitable feed material for the electrolytic reduction. The metal products produced by the electrolytic reduction can be directly transferred to the electrorefining by reducing oxide to metal. Electrorefining recovers pure uranium from the metal feed, and electrowinning simultaneously recovers uranium and transuranic elements the remaining salt.

Table 4.46 shows that the overall TRL of pyroprocessing in Korea is 3-4 for separation process chemistry maturity.

TRL can be improved to 4-5, if PRIDE, 10 ton/year, successfully demonstrates an overall process flow with simulants including depleted uranium. In combination with this engineering-scale test, the bilateral co-operation with the United States can improve TRL up to 6-7 with a lab-scale flowsheet test using irradiated spent fuel.

The underlining mechanism of pyroprocessing is revealed from the 1980s Integral Fast Reactor programme. In addition, KAERI proposed and tested several innovative concepts for unit processes to achieve high efficiency and reliable safety. Given this long global wide history and its almost 20-year long lab-scale experience, the SRL of pyroprocessing in Korea is 4.

**Table 4.46. TRL assignments for separation process maturity – Korean pyroprocessing: Analysis supports TRL = 3-4**

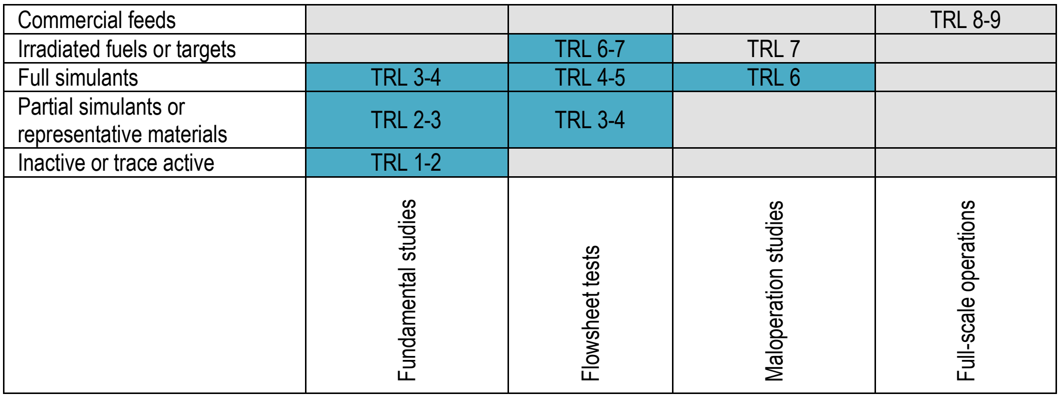


| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Pyrometallurgical process for metal fuel reprocessing developed in Japan (see Chapter 2, Section 2.3.2)*

Pyrometallurgical process with electrorefining has been developed in Central Research Institute of Electric Power Industry (CRIEPI), Japan for metal fuel reprocessing. Uranium recovery by electrochemical reduction from oxide fuel was also studied for the treatment of spent $UO_2$ fuel from LWRs. Engineering scale tests of electrochemical reduction, electrorefining and salt waste treatment including pumping system at high temperature were performed and the process feasibility was demonstrated. The process verification with irradiated materials is under investigation with the co-operation of the Institute of Transuranium Elements in Germany. Overall TRL of the pyrometallurgical process for metal fuel reprocessing developed in Japan would be 5-6, as shown in Table 4.47. Scientific readiness levels for pyrometallurgical process for metal fuel reprocessing are 5.

**Table 4.47. TRL assignments for separation process maturity – Pyrometallurgical process for metal fuel reprocessing developed in Japan: Analysis supports TRL = 5-6**



| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*US electrochemical process (see Chapter 2, Section 2.3.2)*

The main unit operation in the US electrochemical process flowsheet is the uranium electrorefiner, which separates a purified uranium product from the used nuclear fuel dissolved into a LiCl/KCl molten salt eutectic. Recovery of a purified uranium product in the electrorefiner has been the focus of process development to the point that it is the most mature of the electrochemical technologies. Pilot-scale operation of a uranium electrorefiner in a remote environment has been demonstrated at the Idaho National Laboratory in the stabilisation of spent fuel from the Experimental Neutron Reactor II. Operations data from these electrorefiners were used to design a commercial prototype module that was constructed and performance tested at Argonne National Laboratory. Experimental evaluation of the prototype module led to the development of a scalable, semi-continuous system for uranium electrorefining. Electrochemical reprocessing concept designs and mass balances have been developed to provide waste form information for consideration. The Overall TRL of the US electrochemical process for uranium recovery from metal fuel would be 7, as shown in Table 4.48. Note that the online monitoring development research as described in Chapter 2 for the US electrochemistry separations programme is at a much lower TRL (3-4). Scientific readiness levels for the electrochemical process for uranium recovery from metal fuel are 6.

**Table 4.48. TRL assignments for separation process chemistry maturity – US electrochemical process for uranium recovery from metal fuel: Analysis supports TRL = 7**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### 4.4.2. *Co-processing of actinides*

*Pyroprocessing in molten salt chloride (see Chapter 2, Section 2.3.3)*

The pyroprocess developed essentially in the frame of European research programmes is based on the CRIEPI concept described in Section 4.3.1. For the electrodeposition either molten metal (e.g. Cd) or reactive solid cathodes (Al) were used. Both options have been demonstrated at a pilot scale using g amounts of lanthanide (RE) and minor actinide (MA) containing metallic fuels with a general composition U-19Pu-10Zr, U-19Pu-10Zr-2MA-2RE. As well fresh and irradiated fuels were and in the case of the Al cathode a fully efficient grouped actinide recovery of all actinides could be demonstrated. A full process flowsheet was established and tested including material recycling and waste treatment. Therefore, the TRL is between 5 and 6. Scientific readiness levels of the pyroprocess for full actinide recovery are 5.

**Table 4.49. TRL assignments for separation process maturity – Pyroprocessing in molten salt: Analysis supports TRL = 5-6**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants orrepresentative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Liquid/liquid reductive extraction in molten LiF-AlF$_3$ (see Chapter 2, Section 2.3.3)*

The core of the liquid/liquid reductive extraction pyrochemical process has been demonstrated at the laboratory scale on mixtures of An and Ln. The behaviour of some other FP of interest, i.e. Zr, Mo, has also been investigated. Some head-end steps have been assessed on representative material. The experimental work has been completed with flowsheets studies in order to evaluate the sustainability of the complete process. Thus, TRL for liquid/liquid reductive extraction pyrochemical route is in between 3 and 4. Scientific readiness levels for liquid/liquid reductive extraction are 4.

**Table 4.50. TRL assignments for separation process maturity – Liquid/liquid reductive extraction pyrochemical process: Analysis supports TRL = 3-4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### 4.4.3. *Nitride fuel treatment*

Nitride fuel treatment by molten salt electrorefining studied in Japan (see Chapter 2, Section 2.3.4)

The combination of nitride fuel and pyrochemical process is proposed and studied in Japan for transmutation of minor actinides (MA; Np, Am, Cm) based on the double-strata fuel cycle concept. Laboratory-scale experiments on the pyrochemical process including anodic dissolution of spent nitride fuel, recovery of actinides into liquid Cd cathode by molten salt electrorefining and nitridation of actinides in Cd alloy was performed using unirradiated samples and basic feasibility of the process was demonstrated. Overall TRL of the nitride fuel treatment by molten salt electrorefining studied in Japan would be 3-4, as shown in Table 4.51. The scientific readiness level is 4.

**Table 4.51. TRL assignments for separation process maturity – Nitride fuel treatment by molten salt electrorefining studied in Japan: Analysis supports TRL = 3-4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

*Combined (pyro+hydro) reprocessing of nitride fuel in Russia (see Chapter 2, Section 2.3.4)*

The new flowsheet for the spent nitride fuel reprocessing based on a combination of pyrochemical and hydrometallurgical processes is under development in Russia at the RIAR and Bochvar Institutes since 2010. According to this approach the pyroprocesses were applied to head-end stages of reprocessing for "hot" spent nitride fuel with the cooling time less than one year. The hydro-processes will be applied to final technological stages for partitioning and purification of the reprocessing products such as U, Pu, MA; so achieving decontamination factors more than $10^6$. All technological stages were tested on the pilot equipment with real spent nitride fuel on the level up to several kilos. Currently the pilot industrial facility for on-site reprocessing of BREST reactor spent nitride fuel is under the design stage.

Overall TRL of the nitride fuel treatment studied in Russia would be 7, as shown in Table 4.52. The scientific readiness level is 5.

**Table 4.52. TRL assignments for separation process maturity – Combined (pyro + hydro) reprocessing of nitride fuel maturity: Analysis supports TRL = 7**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants orrepresentative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

### 4.4.4. *Fluoride volatility (see Chapter 2, Section 2.3.6)*

Fluoride volatility method (FVM) (described in Section 2.3.6) is a pyrochemical reprocessing technology originally proposed for the reprocessing of FBR oxide fuels. Reprocessing by FVM was completely demonstrated in the 1970s in USSR and in France, but only at lab scale. Later on the further development was limited and the present effort reached the semi-pilot scale, but proceeds outside of hot conditions and is focused mainly on the mastering of selected steps of the technology. The technology readiness level and scientific readiness level are both 4.

**Table 4.53. TRL assignments for separation process maturity – Fluoride volatility method: Analysis supports TRL = 4**

| | | | | |
|---|---|---|---|---|
| Commercial feeds | | | | TRL 8-9 |
| Irradiated fuels or targets | | TRL 6-7 | TRL 7 | |
| Full simulants | TRL 3-4 | TRL 4-5 | TRL 6 | |
| Partial simulants or representative materials | TRL 2-3 | TRL 3-4 | | |
| Inactive or trace active | TRL 1-2 | | | |
| | Fundamental studies | Flowsheet tests | Maloperation studies | Full-scale operations |

## 4.5. Conclusions

The objective of Chapter 4 was to evaluate the technological maturity of the various separation processes described in Chapter 2 using the well-known technology readiness level (TRL) scale. Consistent with other studies by NEA expert groups, a matrix-style approach was adopted to account for how research and development of separation processes typically proceeds from fundamental studies through small or bench scale low-active inventory experiments to demonstration tests using small quantities of spent fuel before scale up and industrialisation until eventually full commercial operations. It should be noted that, in some cases, the R&D path may be different for engineering or equipment development than it is for establishing the process chemistry. However, in this report, given the futuristic nature of the separation processes reviewed, the readiness levels have been assessed primarily from the standpoint of the maturity of the process chemistry. By adopting the matrix approach, the overall TRL could be more reliably estimated and any gaps in the underpinning of the TRL identified. An additional tool, “scientific readiness levels” explained in the text above, was also used to evaluate how well the processes are underpinned by scientific understanding as opposed to empirically based process testing. Some general observations are now made to conclude this chapter.

- Head-end stage

Conventional head-end processes for disassembly of fuel and dissolution in nitric acid are established at the industrial scale and are TRL 9, SRL 6.

A range of novel, dry, pre-treatment processes were assessed; these generally aim to powderise spent fuel by oxidation of $UO_2$ to $U_3O_8$ and release volatile (and sometimes semi-volatile) fission products for off-gas capture. TRLs for these processes are generally in the range 5-6 as substantial work has been done; SRL is typically 4. These dry pre-treatment processes can be followed by either aqueous or pyrochemical separations steps.

A side process for treating zirconium hulls to enable recycle and reduce waste is being developed in the US. This is also a dry process, based on chlorination, and TRL is estimated as ~6 with SRL ~4.

In summary, the head-end processes evaluated are generally at a quite mature R&D stage (TRL 5-6 and SRL ~4), particularly when considering UOx fuel recycling. Nevertheless, substantial further work will be needed to take these processes from R&D to readiness for commercial operations and also to develop suitable head-end plants for fast reactor and non-oxide based fuels. In particular, as head-end involves mechanical operations on spent fuel assemblies, efficiencies leading to cost reduction are needed and also improved capture of volatile species from off gases generated in pre-treatment oxidation and dissolution stages.

- Aqueous separations

Conventional PUREX reprocessing is of course TRL 9 and SRL 6 as this is well established industrially with past or current commercial operations in a few countries (France, United Kingdom, Russia, etc.).

Evolutions of PUREX such as COEX™, UREX (U extraction cycle), NEXT and Simplified PUREX have been proposed based on varying degrees of underpinning R&D and demonstration. In general, these options are considered to have rather high technological maturity since only parts of the overall flowsheet or equipment are changed from conventional PUREX reprocessing. TRLs in the range 5-8 and SRL 5-6 are proposed while recognising that small parts of the process may be at lower TRL (4-5) and require greater underpinning.

More radical variations on the PUREX process such as an advanced PUREX process have lower TRL (4-5) and SRL (3-4). While process chemistry is generally well established, insufficient testing under realistic conditions (hot tests) leaves questions as to the attainable levels of performance and operability of such innovations.

A few processes (NEXT; Russian REPA and Co-crystallisation processes) propose a crystallisation stage to reduce the dependence on and performance required of liquid-liquid extraction cycles. These are less well developed with TRL in the range 4-6 and SRL 4-5, although the Japanese NEXT process has been subjected to several hot tests and is at quite an advanced stage of R&D.

There are many variations of minor actinide recovery processes (DIAMEX; SANEX; TRUEX; TALSPEAK etc.). The most mature are those that use two processes for actinide-lanthanide co-recovery before actinide-lanthanide separation (DIAMEX; TRUEX-TALSPEAK) where TRL ~6 or even 7 and SRL 5-6 can be claimed. The combined DIAMEX-SANEX process from CEA is also close to this level of development with TRL 5 and SRL 5. Of the minor actinide separations, there are many options but the trend is towards single cycle processes that recover minor actinides directly from PUREX high active raffinates. These are much further from industrialisation. European SANEX processes, of which there are several varieties, have TRLs probably ~4 and SRL 3-4. The same is true for similar international options such as US ALSEP, Japanese TddDGA, Russian DGA or diamide based processes.

The GANEX process represents a special case, being a process designed to recover all actinides. The second stage of the GANEX process (TRU recovery) is recognised as being the most challenging part of the process. Two options exist currently, CEA-GANEX and EURO-GANEX, both of which are at a similar stage of development having been demonstrated by hot tests but with significant issues still to be addressed before industrialisation would be considered (hence TRL 4-5 and SRL ~3).

There are a range of Cs and Sr separation processes, some of which are at a high level of technological maturity (TRL >6). However, for direct application to extraction from high-level waste streams (as opposed to clean up of more dilute secondary liquid effluents from processes) the CCD-PEG, FPEX and extraction chromatography are evaluated to be closest to application (TRL 6-8; SRL 5-6).

Of the described processes for curium removal or recovery, only the EXAm process has been developed to the proof-of-principle stage (TRL 4-6).

- Pyrochemical separations

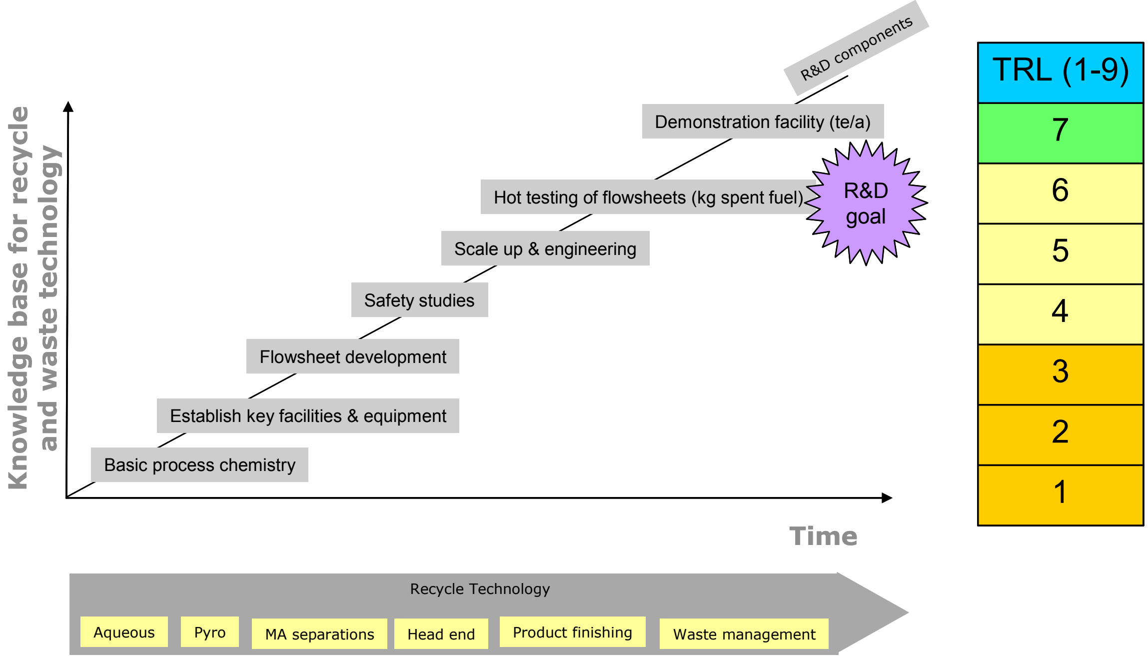
Uranium recovery is clearly the most well developed aspect of pyrochemical processing of spent fuel. Of the processes evaluated, the US electrochemical process is TRL 7 and SRL 6 due to the experience gained processing EBR-II fuels at the Idaho National Laboratory. Japanese and Korean versions are still in the proof-of-principle stage (TRL 4-6) but Korea, in particular, has clear plans to raise TRLs using their PRIDE facility and joint programme with the United States.

The actinide co-recovery processes are much less well proven; the exception being the Russian pyrochemical process developed at RIAR (TRL 7, SRL 5). Other proposed approaches are generally TRL 3-4 and SRL ~4.

Advanced recycle technology development requires a broad range of R&D activities from experimental work to modelling, simulation and engineering design. Experimental and engineering development work requires facilities at different scales. Some facilities must be capable of accommodating radioactive materials up to spent fuels needed as feeds for ultimate process demonstrations. Initial research on simulants and trace quantities of radioactive isotopes must be transferred to lab-scale testing using active facilities licensed for nuclear materials, including plutonium (proof of concept TRL 1-3). Once the chemistry is established and process flowsheets defined, demonstration tests using kilogram quantities of used fuel (hot tests) are required to prove the flowsheet (proof-of-principle: TRL 4-6). Process safety studies, engineering design and process optimisation are used to refine the laboratory flowsheet to a process suitable for industrial deployment. In parallel, engineering scale up using non-active simulants or uranium-active simulants are needed to develop the engineering and plant design. Active experiments can be minimised and focused by use of computer based modelling and simulation. Beyond these R&D stages, there are decisions on whether an active pilot or demonstration plant (few tonnes per year throughput) is needed to fully test the technology in a realistic environment prior to the design and build of the full scale facility (the pilot plant would be proof of performance: TRL 7). One advantage of the demonstration plant is that it can also be used to treat small quantities of legacy or orphan fuels from historic nuclear industry activities, as is occurring in the pyroprocessing facility at the Idaho National Laboratory. Figure 4.1 illustrates this progression of R&D activities and the approximate relation to the TRL scale.

The evaluations made in this chapter provide an indication of the technological maturity of a broad range of separation processes being developed internationally in NEA countries. The evaluation will help identify the leading contenders for industrial applications and also gaps in the technical and scientific underpinning of the various options that must be filled by further focused R&D.

**Figure 4.1. Development ladder for development of advanced separation processes; showing links with technology readiness levels**



Adapted from Advanced Reprocessing: Research and development needs, NNL Position Paper, National Nuclear Laboratory, www.nnl.co.uk.

# 5. Perspectives for future R&D

## 5.1. France

In France, the development of an ambitious nuclear power programme was driven by the political will to achieve a substantial level of energy independence in a country poorly endowed in fossil fuels and having domestic uranium resources available in limited amounts. France chose the closed fuel cycle at the very beginning of this nuclear programme, and since the 1980s, reprocessing and mixed oxide (MOX) fuel fabrication have been implemented on an industrial and commercial basis both for domestic and export markets, with the opening of the Areva reprocessing plants at La Hague and the Melox MOX fuel fabrication plant in Marcoule. The French strategy in support of the closed fuel is based on the principles that the closed fuel cycle increases the nuclear power programme's sustainability as it allows the recovery of U and Pu fissile materials to fuel present and future generations of power reactors; it also provides a safe and more secure management of vitrified waste forms (containing almost no U and Pu) specifically adapted to long-term geological disposal, significantly reducing their volume and radiotoxicity and minimising the burden left to future generations. In France, the issue of recycling has been settled based not only on economics, but on larger national policy matters.

All along the development of the nuclear programme, reactor and fuel cycle technologies have been continuously improved through a large R&D effort mainly carried out by the French Alternative Energies and Atomic Energy Commission (CEA). All major advances have been implemented at industrial scales in a consistent and evolutionary approach. The Areva reprocessing and recycling facilities currently in operation are using industrially mature technologies, based on the PUREX process developed in the 1950s. At La Hague, the uranium and plutonium separations factor has now reached 99.88%, leaving in the vitrified matrix only about one gram of plutonium for each kilogram recovered. At Marcoule, the Melox plant is able to market 195 t/year of pressurised water reactor (PWR) MOX fuel for French and foreign customers. The CEA and Areva have also developed a future evolutionary advancement of PUREX that goes a step further with the COEX process. This technology modifies the PUREX process by co-extracting plutonium and uranium together, such that plutonium is never separated alone, and the combined plutonium-uranium product stream is then converted more directly to MOX. It is likely that, when the current reprocessing units at La Hague reach the end of their operating lives in the 2040 time frame, new units based on COEX technology will replace them. In this context, for the coming years, a large research and development (R&D) effort will be devoted in France to support the existing La Hague industrial plant to achieve good operating conditions with some important improvements such as the implementation of COEX in specific workshops, and to develop new process concepts to be implemented in the "2040 plant".

For the future, plutonium management options are key challenges for the development of future sustainable nuclear fission systems: the deployment of Gen IV fast neutron reactors in the French fleet could allow a complete and recurrent recycle of both uranium and plutonium, drastically extending (about two orders of magnitude) the natural uranium use, and possibly eradicating any transuranic (TRU) content in the final waste. For MOX fuels, industrial reprocessing could be implemented in order to produce the necessary plutonium for starting the Gen IV fast reactors. Such options have been and still are currently investigated in the framework of the "French Waste Management Act" voted in 1991, with R&D organised for fifteen years, then by the 2005 Energy Policy Act and the 2006 Act on the "Sustainable management of radioactive materials and waste". Different scenarios have been drafted and will be assessed (taking into account the diverse criteria and appropriate attributes), as a joint work embedding research and industrial bodies.

Concerning waste management, the aim of further reducing the radiotoxic inventory has been pursued. This 2006 Act specifies a step by step R&D programme based on three routes which complement each other, and a central point is the creation of a national management plan defining the solutions, the goals to achieve and the research actions to be launched to reach these goals. This plan is updated every three years and published (according to the law on nuclear transparency and security; the law insists on transparency and democratic control). Based on this plan, the objectives of the fuel cycle research for the coming years are:

- to continue the studies for the optimisation of the concepts of Pu multi-recycling in sodium-cooled Gen IV fast reactors;
- to confirm the concepts of separation for the MA recovery, mainly by a hydrothermal process;
- to pursue the development of fabrication processes for MA bearing fuels, and to implement irradiation tests of these fuels;
- to develop technical and economic system studies for a step by step SFR deployment starting around 2050.

A dedicated research programme, the ASTRID programme, has been launched by the CEA: it aims at designing a Gen IV sodium-cooled demonstrator (both reactor and related fuel cycle facilities), which could be operated before 2030 and would allow the demonstration on an industrial scale of the recycling of plutonium and of minor actinides, mainly americium. Fuel cycle technologies will continue to focus on important issues, concerning both fuel fabrication and used fuel processing: the main goals will be, keeping a progressive step-by-step approach, to improve current technologies (to simplify, to increase compactness, to improve safety and safeguardability), to adapt them to the specific features of fast neutron reactor future fuels (higher Pu content, higher burn-up, etc.), and, in a longer perspective, to complete them to allow in addition TRU recycle (Am recovery in used fuel and Am-bearing fuels manufacturing).

## 5.2. Japan

In Japan, the new Strategic Energy Plan was issued in April 2014, which includes the following descriptions concerning nuclear power and the nuclear fuel cycle [6,7]:

- Nuclear power is an important base-load power source as a low-carbon and quasi-domestic energy source, contributing to stability of the energy supply-demand structure (with the major premise of ensuring its safety).
- The Government of Japan will make efforts to reduce the volume and harmfulness of radioactive waste and create a nuclear fuel cycle that contributes to effective utilisation of resources and will promote reprocessing and plutonium use in LWRs.
- The Government of Japan will promote technology development on volume reduction and mitigation of degree of harmfulness of radioactive waste. Specifically, development of technologies for decreasing the radiation dose remaining in radioactive waste over a long period of time and enhancing the safety of processing and disposal of radioactive waste, including nuclear transmutation technology using fast reactors and accelerators, will be promoted by utilising global networks for co-operation.

In spite of the drastic change of domestic and international circumstances regarding energy (the largest change caused by the accident of the Fukushima Daiichi Nuclear Power Plant), the plan defines nuclear energy as an important base-load power source. The plan puts emphasis on the importance of activities to resolve the challenge of how to manage and dispose of spent fuel, as well as Fukushima restoration, safe operation of nuclear plants and public acceptance.

The reprocessing of spent nuclear fuel and the partitioning and transmutation (P&T) technology for high-level waste should be promoted to contribute to the above mentioned "volume reduction and mitigation of degree of harmfulness of radioactive waste". The Rokkasho Reprocessing Plant is preparing for operations by adaptation to the new regulations developed after the accident at the Fukushima Daiichi Nuclear Power Plant. As for P&T technology, a working party launched by the Ministry of Education, Culture, Sports, Science and Technology issued an Interim Report in November 2013, which said:

"The evaluation of technological readiness levels of the technical fields (partitioning, ADS, fuel cycle, and fuel) showed that we are approximately on the stage to move up R&D from 'conceptual study' to 'principle demonstration', and it is appropriate to shift the R&D to the next stage of engineering scale".

Various R&D activities related to P&T technology have to be promoted more intensely than before, aiming at engineering scale tests. For the partitioning of minor actinides (MA) and some fission products, repeated tests with real waste solutions at bench scale should be performed to establish the separation process. Simultaneously, cold tests with simulated solution at the engineering scale should be performed. For transmutation of MA, there is a plan to construct the Transmutation Experimental Facility (TEF), which consists of two facilities: the ADS Target Test Facility (TEF-T) and the Transmutation Physics Experimental Facility (TEF-P) [8,9]. Even in these situations, both large scale tests to put the technology into practice and the fundamental studies to support the technology development should be conducted in an appropriate balance, considering also the development of young researchers and engineers.

## 5.3. Korea

Although the Korean government is still maintaining a "Wait and See" policy on the management of spent nuclear fuel, there has been a strong and increasing demand for the establishment of a long-term spent fuel management programme or policy to resolve the spent fuel accumulation issues. The public and stakeholder engagement programme by the Public Engagement Commission on Spent nuclear fuel management (PECOS) was launched in September 2013. The main mission of the PECOS was to propose basic directions for spent fuel management including interim storage to the Ministry of Trade, Industry and Energy (MOTIE) by the end of June 2015. Based on these recommendations, a national spent fuel management policy will be established.

The draft recommendations were announced at a press briefing on 11 June 2015 after nearly 20 months of public debate that included international seminars and town hall meetings on how the country should dispose of its spent nuclear fuel. The commission said that the government should take full responsability for managing nuclear waste by putting its citizens' safety at the top of its priorities and immediately start looking for a geologically stable region for underground storage of spent nuclear fuel. The commission said that the government should find the site and start excavating by 2020, and added that the underground research laboratory with trial burials should start in 2030. The construction of a permanent storage facility should be completed by 2051. The commission also highlighted the need to build interim storage facilities for spent nuclear fuel, noting the country's existing facilities are expected to reach full capacity from as early as 2024. As for the long-term R&D programmes, the commission pointed out that the spent nuclear fuel treatment technologies and the relevant regulation guides need to be developed along with spent fuel storage and disposal technologies. A final report of the commission will be submitted before the end 2015 to the MOTIE, with possible changes to the reported recommendations, according to the commission.

To provide technical information for the government's decision making on whether to select direct disposal or treatment (recycling) of spent fuel, KAERI has been conducting a systematic and consistent R&D programme on advanced nuclear fuel cycles for a long time, such as transportation and storage of spent fuel including high-level waste, pyroprocessing technology development with waste treatment and PR/PP, sodium-cooled fast reactor system development linking to pyroprocessing, and disposal of high-level waste. The benefit of pyro-SFR fuel cycle (future nuclear energy system) is expected to be that the amount of high-level waste can be reduced remarkably by recovering useful uranium which takes major part of spent fuel. The repository area also can be reduced by the removal of heat generating elements such as TRUs, Cs and Sr. Burning of long-lived elements in a fast reactor also decreases the period for radioactive waste to reach the natural level of radiotoxicity. These are very attractive factors to a small land country like Korea. The long-term R&D Plan for future nuclear energy systems was set up at the 255th Atomic Energy Commission on November 2008 and revised at the 1st Atomic Energy Promotion Commission on January 2011. This long-term closed fuel cycle development plan will be carried out with the long-term vision of the construction of the pyroprocessing demonstration facility by 2025 in association with an advanced prototype SFR plant by 2028.

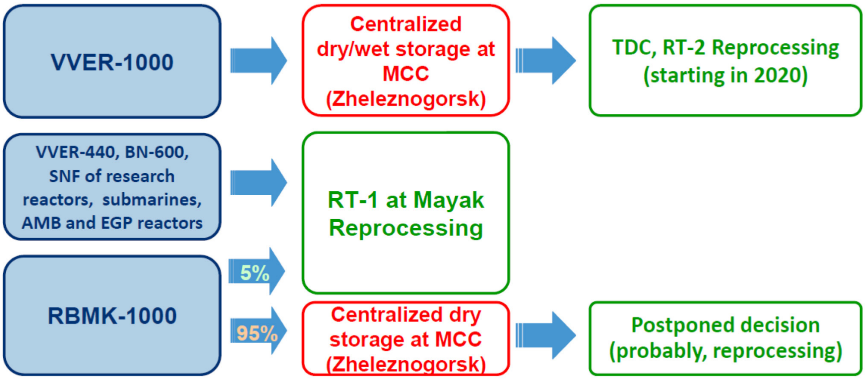
On 13 April 2011, Korea and the United States entered into a new era of bilateral nuclear energy partnership. The Joint Fuel Cycle Studies (JFCS) was launched and includes three working groups: Electrochemical Recycling, Safeguards and Security, and Fuel Cycle Alternatives. The 10-year JFCS is divided into three phases. All phases include joint safeguards development and evaluations of technologies. After completion of Phase I in 2012, both sides jointly confirmed that the pyroprocessing is technically feasible at the lab-scale. During Phase II, the integral recycling test equipment (several kilograms per batch scale) will be installed in HFEF at INL, and then recovery of actinides will be performed. In Phase III, the TRU fuels fabricated with recovered uranium and TRU will undergo irradiation and post-irradiation tests at ATR. The final purpose of this JFCS is to jointly evaluate the technical and economic feasibility and non-proliferation acceptability of pyroprocessing technology.

### 5.4. Russia

The basis of the Russian policy in the area of SNF management is based on SNF reprocessing in order to ensure ecologically acceptable management of nuclear fission products and return of the regenerated nuclear materials into the nuclear fuel cycle.

The strategic areas in SNF management are the establishment of a reliable system for long-term controllable SNF storage, development of SNF reprocessing technologies, balanced involvement of the SNF regeneration products into the nuclear fuel cycle and final isolation (disposal) of radioactive waste generated after the reprocessing. According to this provision and considering the peculiarities of management approaches for different types of SNF, Figure 5.1 demonstrates the general pattern of SNF management in Russia.

**Figure 5.1. Technological patterns of SNF management: Temporary storage and reprocessing**



The RT-1 plant is today the only commercial SNF reprocessing plant in operation in Russia since 1977.

More than 5 000 tonnes of SNF have been reprocessed. The designed capacity is 400 tonnes per year. This plant annually reprocesses approximately 100-120 tonnes of spent nuclear fuel from VVER-440, BN-600, research reactors, icebreakers and submarines. The infrastructure for diversifying the type of SNF suitable for reprocessing is being developed (damaged spent fuel from RBMKs, SNF from AMB, EGP and all the types of research reactors). Reprocessing technology is based on the PUREX process (recovery of regenerated uranium, plutonium and neptunium as the reprocessing products).

The reprocessing process ("modified PUREX") includes dissolution of spent fuel with subsequent separation of plutonium, uranium and neptunium from fissile products and minor actinides. RT-1 deals with a wide range of spent fuel compositions producing both highly enriched reprocessed uranium and low enriched reprocessed uranium that are further used to manufacture fresh nuclear fuel. The end products from SNF reprocessing are:

- melt of uranyl nitrate hexahydrate (enriched for RBMK-1000 fuel fabrication). Re-enrichment is achieved by blending the purified uranyl nitrate solutions resulting from reprocessing of different spent fuel types with different uranium enrichment levels (BN, RRs, propulsion reactors fuels and VVER fuel);
- uranium oxides with $^{235}$U enrichment up to 17%;
- neptunium dioxide (for production of $^{238}$Pu isotope);
- plutonium dioxide (for fast reactor fuel).

The first semi-industrial facility for partitioning of high-level waste was put in operation at RT-1 in August 1996. SNF reprocessing is accompanied with a production of RadWastes which are subjected to treatment. Current practice for ILW and HLW management from SNF reprocessing at RT-1 plant involves HLW vitrification in EP-500 ceramic melter with a design capacity of 500 litres of concentrated HLW per hour. Alumophosphate matrix of the radioactive glass is produced using direct evaporation-calcination-vitrification technology. Vitrified waste are placed in steel canister and are stored in a dry vault-type storage facility.

A Pilot Demonstration Centre (PDC) in Mining and Chemical Combine (Krasnoyarsk area) is under construction to reprocess VVER-1000 SNF.

The key goal of the PDC is to develop economically efficient reprocessing technology for SNF from power reactors to enable regenerated components to be routed back into the

Russian NFC. Negative impacts on the environment must be minimised and all nuclear and radiation safety requirements are to be met.

The PDC will be constructed in two stages. The first stage namely the research hot cells with capacity about 5 tonnes of SNF per year and the entire infrastructure required are planned to be commissioned by the end of 2015. The goal is scientific research in the area of new technologies for SNF reprocessing from thermal neutron and fast neutron reactors as well as the nuclear fuel cycle closure.

The PDC will be constructed in two stages. The first stage, namely the research hot cells (RHC), and the entire infrastructure required are planned to be commissioned by the end of 2015. The goal is scientific research in the area of new technologies for handling SNF from thermal neutron and fast neutron reactors as well as for the closure of the nuclear fuel cycle. The PDC will address the following challenges:

- improvement of new technologies for reprocessing of SNF from fast and thermal neutron reactors;
- development of HLW partitioning technologies for further radioisotope recovering for commercial purposes and reducing the radiotoxicity of ultimate disposal waste.

The PDC second stage is to meet the extent of full capacity operation equal to 250 tonnes of SNF per year. This is planned to be commissioned in 2020 and will represent a complete complex of operations from the SFA destruction to final product output along with conditioned radioactive waste vitrified for subsequent disposal.

A comprehensive programme for transition to a closed fuel cycle is implemented with the development of two technologies for fast reactors with sodium and heavy metal coolant. In 2014, the fast reactor with sodium coolant BN-800 at Beloyarsk NPP and the MOX (uranium-plutonium oxide) fuel fabrication plant at the Mining and Chemical combine (Krasnoyarsk area, Siberia region) were put into operation. In 2014 the production plant of dense uranium-plutonium nitride fuel for fast neutron reactors with lead cooled was started to construction in Seversk, in Siberian Chemical Combine (Tomsk region). The creation of a pilot energy complex with one reactor on fast neutrons with lead cooled BREST-300 megawatts and fuel fabrication and reprocessing modules is planned.

Simultaneously, the problem of spent fuel accumulation could be solved using reprocessed uranium and plutonium in thermal reactors. The concept of REMIX (REgenerated MIXture of U, Pu oxides) has been developed in Russia. REMIX fuel is fabricated from an unseparated mixture of uranium and plutonium obtained from SNF reprocessing, that is further adjusted with enriched natural uranium in order to give the required content of fissile nuclides in the recycled fuel. Calculations have shown that the composition of REMIX fuel (1.0-1.5% Pu + 2.5% $^{235}$U) allows multiple recycling of the total amount of uranium and plutonium reprocessed from spent nuclear fuel with 100% loading in the WWER-1000 core. State Corporation "Rosatom" initiated a programme for fabrication of three experimental fuel assemblies (FAs) with REMIX fuel with further download of REMIX- FAs to unit 3 of Balakovo NPP (VVER-1000) planned in the second half of 2016.

## 5.5. United Kingdom

In the United Kingdom, the last decade or so has seen the focus placed on clean-up of the nuclear legacy left over from ~60 years of civil and military nuclear activities [13] with the UK Nuclear Decommissioning Authority (www.nda.gov.uk/) created to deliver this mission. However, there has also been growing government interest in the role of new nuclear power in delivering future UK energy needs as part of a diversified and secure supply, while meeting carbon dioxide emissions targets [14,15]. Current policy, which now has cross-party support in the United Kingdom, is a "replacement" scenario in which new capacity up to 16 GW will replace existing reactors as they reach the end of their lifetimes. These reactors will be light water reactors (LWRs) built and operated by international vendors and utilities that are licensed in the United Kingdom by the Office for Nuclear Regulation (ONR; www.onr.org.uk/). To date, the majority of used or spent nuclear fuel from the UK reactor fleet has been reprocessed but, with contracted reprocessing programmes in the United Kingdom now close to completion, both Thorp and Magnox reprocessing plants at Sellafield are scheduled to stop operations between 2018 and 2020 [16]. Post-reprocessing, the United Kingdom will still have ~7.700 tonnes of used fuel from its Advanced Gas cooled Reactors, Sizewell B PWR (pressurised water reactor) and legacy "exotic" fuels that are planned to be disposed directly in a geological disposal facility (GDF). Given that the preferred Government policy for the UK's plutonium stockpile is to recycle as new fuel, there may also be ~1 500 tonnes of used MOX fuels. The new build of nuclear reactors up to 16 GW capacity will lead to a further ~23.500 tonnes of used LWR fuel [17]. The policy is that these used fuels will be stored prior to disposal in the United Kingdom GDF around 2075; that is, the United Kingdom is moving to an open fuel cycle.

In addition, the government has recently published a series of reports looking at the longer term future for nuclear energy in the United Kingdom including a roadmap [18] that describes three potential pathways for nuclear energy in the United Kingdom: (1) essentially clean-up of the legacy and phase out of nuclear power; (2) the replacement scenario that is current policy and (3) expansion scenarios, even up to 75 GW, to meet expected energy demands and targets for carbon dioxide emissions.

The management of UK spent fuel in an expansion scenario would become very difficult under an open fuel cycle and, as described in the roadmap, would most likely require reinstatement of a closed fuel cycle with reprocessing and actinide recycling due to concerns about both the security of supply of uranium for a large domestic programme and the capacity for the GDF to manage the volumes of arising spent fuels. The assumption being that this would be a fully closed fuel cycle with the introduction of fast reactors and recycle of at least uranium and plutonium from LWRs to fuel the first fast reactors before fast reactor recycling was established [18]. The expansion scenario with a fully closed fuel cycle clearly represents the most challenging scenario and would require the most evaluation and underpinning through research and development (R&D). Additional options for directions of nuclear energy in the United Kingdom are also "on the table" including small modular reactors (SMR) [19] or novel systems, including thorium based systems [20], and potential use of GE Hitachi's PRISM reactor for disposition of the UK's plutonium stocks accumulated through historic reprocessing activities [21]. The overarching UK Nuclear Industrial Strategy (NIS) summarises the ambitions of Government, industry and academia and, for the reasons outlined above, calls for options for fuel cycles to be kept open through a nationally funded R&D programme [22].

Internationally, a number of countries are engaged in similar discussions around their future nuclear energy and associated fuel cycle needs although, as seen in this Chapter, generally their R&D programmes are more advanced than those in the United Kingdom. Therefore, a number of recent reports have highlighted the need for a UK national R&D programme in advanced nuclear energy to maintain skills and underpin policy development, which would include spent fuel management and actinide recycling [23-26]. To address these issues the Government have created the Nuclear Innovation and Research Advisory Board (NIRAB; www.nirab.org.uk/) with the objective of developing proposals for national level R&D programmes in nuclear energy; NIRAB recently issued its first annual report, re-iterating the need for R&D in order to meet the objectives of the NIS [27].

In order to implement an expansion of nuclear energy ca. 2050, as described in the Roadmap, including start up of commercial fast reactors, LWR reprocessing would need to re-commence ~2040 to generate sufficient plutonium for fast reactor fuels [18]. This suggests that decisions on the future of the UK nuclear fuel cycle will probably be needed by around 2030 and, therefore, there is perhaps only 10-15 years for R&D to develop innovations to commercial scale LWR recycling technology. Such innovations are needed to deliver step changes in competitiveness, performance and acceptability over conventional PUREX technology that will undoubtedly be needed for recycling to become a viable future option in the United Kingdom [17]. It is becoming apparent that this "window" for R&D coincides with the rundown of current plants and potential loss of the skill base; this is a matter of increasing concern to the industry.

It is clear that to evaluate the potential benefits and dis-benefits of closing the nuclear fuel cycle in the United Kingdom in the timeframe of 2030-2070 and to meet the aims of the NIS that R&D in reprocessing and actinide recycling, and hence separation chemistry, will be required as an integral part of any national level nuclear energy R&D programme. The objective of R&D should be to develop technologies, demonstrating the technical feasibility and making advanced recycling a competitive option compared with the open fuel cycle. This will avoid foreclosing the option to deploy closed fuel cycles in the United Kingdom later this century. To do this, potential barriers related to safety, proliferation resistance, costs and waste need to be addressed by R&D. Engagement with the public to explore options in an open and transparent dialogue is also needed. Programmatic objectives for recycle R&D, currently being developed under the auspices of NIRAB, would be to raise the technology readiness levels of candidate processes to TRL 5-6 for LWR and fast reactor fuels recycling, using primarily aqueous separations. Demonstration should culminate in "end-to-end" hot tests (i.e. taking kilogram quantities of spent fuels through the full process: dissolution, separations (major and minor actinides), conversion to oxides, waste management). A complementary but secondary track in pyrochemical separations for metal alloy fast reactor fuels (molten salt electrorefining, salt waste treatment) is also being proposed as pyroprocessing is seen as the most likely alternative to aqueous reprocessing under specific fuel cycle scenarios. A pyroprocessing programme would culminate with active demonstration of unit stages to underpin the feasibility of industrialisation. Such programmes also require specialist facilities and the facility and equipment needs to deliver an advanced recycling R&D programme are also under evaluation with the aim to network existing and new facilities in academia and the National Nuclear Laboratory. It is expected that such an R&D programme and facility base would also deliver a means to grow technologies and opportunities for future business across the UK nuclear industry, provide a sound science and technology basis to underpin future policy options, a platform for international co-operation with opportunities for leverage and influence and maintain core skills with development of the next generation of subject matter experts.

Over the next five years, therefore, the roadmap for nuclear energy in the United Kingdom will become clearer as new nuclear build gets underway and fuel cycle plants at Sellafield move into decommissioning. The needs and directions for national level R&D that underpins the longer term roadmap and addresses the skills agenda will also be clarified through proposals made to government by NIRAB. It is expected that this will include advanced reprocessing and development of separation processes for LWR and fast reactor recycling with a strong emphasis on international co-operation through both bilateral and multilateral collaborative programmes.

### 5.6. United States

The current fuel cycle policy in the United States is based on the "once-through" technology under which used fuel is stored until a permanent geologic repository is available for its disposal. However, that policy is augmented by research and development on advanced Generation-IV reactors, including fast reactors, as well as on advanced used fuel recycle technologies. Many of those advanced fuel recycle studies were described earlier in this publication. Maintaining a vigorous fuel cycle research and development programme provides three advantages: first, it maintains a technical capability to respond to future fuel cycle requirements that may include extensive used fuel recycle, second, through the involvement of American universities in advanced fuel cycle R&D (the DOE Office of Nuclear Energy devotes 20% of its research budget to support university research), it strengthens the capabilities of the next generation technical leadership and third, it provides a basis for international cooperative programmes and thus broadens the opportunities for innovation.

Fuel cycle chemistry R&D continues into the future with the stated goal of informing future decisions on new technologies that may contribute to meeting future energy demands, non-proliferation requirements, waste reduction, waste form development and efficient waste disposal improvements. Current projects include both evolutionary improvement technologies and revolutionary processing methods, with the latter primarily supporting recycle of future Gen IV reactor used nuclear fuels. Fundamental chemistry studies in minor actinide/lanthanide separation processes and off-gas treatment methods and materials are currently sponsored. The latter are needed for sufficient retention of volatile fission and activation product radionuclides to enable discharged off-gas to meet environmental regulations. Fuel cycle chemistry R&D also includes the head-end treatment of used fuel by means of dry, pyrochemical oxidation to release tritium and other volatile radionuclides, prior to fuel dissolution in aqueous nitric acid or molten salts, from which tritium recovery and waste management could be significantly more difficult. The R&D project for recovery, decontamination and potential recycle of zirconium from used nuclear fuel cladding has a great potential for reducing the mass and volume of radioactive waste that currently requires emplacement in a geologic repository, and may enable the economic recycle of the relatively expensive, hafnium-free zirconium in new cladding manufacture. All of these projects have been described in this report, as well as in numerous publications.

If a future decision is made to recycle used nuclear fuel in the United States, R&D on further development of processes for co-conversion of uranium and selected actinides to mixed oxide (MOX) recycle fuels could be resumed, such as the relatively simplified and efficient "modified direct denitration (MDD)" process. If fast neutron reactors are deployed in the future, the MDD process, together with the pyro-electrochemical process could be used to prepare mixed metal recycle fuels. Reduced-scale studies on the electrochemical process development continue today, and could be enhanced, along with volatility process development, if molten salt reactors are deployed.

If other Gen IV reactors, such as gas or salt-cooled high temperature reactors are deployed in the future and utilise new fuel forms, such as carbon and silicon carbide-coated fuel elements, R&D on used fuel disassembly, dissolution, and waste form development will need to be resumed from previous studies. Similarly, if the thorium-$^{233}$U fuel cycle needs to be deployed, R&D on the used fuels containing thorium-uranium and fission products will need to be resumed.

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# 6. Conclusions

This report reviews progress on separation chemistry processes, focusing in particular on the technologies associated with the separation and recovery of minor actinides for recycling so as to help move towards the implementation of advanced fuel cycles.

The status of current technologies is detailed according to the fuel components to be separated. Technological readiness of the various reprocessing techniques is also assessed and perspectives for future R&D are provided.

As of today, numerous processes have been developed to answer specific needs in a particular situation. Chapter 1 described processes that address the separation of specific elements using different types of technology:

- head-end processes to prepare the used nuclear fuel (UNF) for chemical separation;
- aqueous reprocessing (hydrometallurgy) for U recovery, co-processing of actinides (U,Pu,Np), group actinide separation, Cs, Sr separation and americium and/or curium separation;
- pyroprocessing through electrochemical or liquid metal extraction processes for U recovery, co-processing of actinides, and treatment of nitrides fuels, fluoride volatilisation processes and technologies for molten salt reactors.

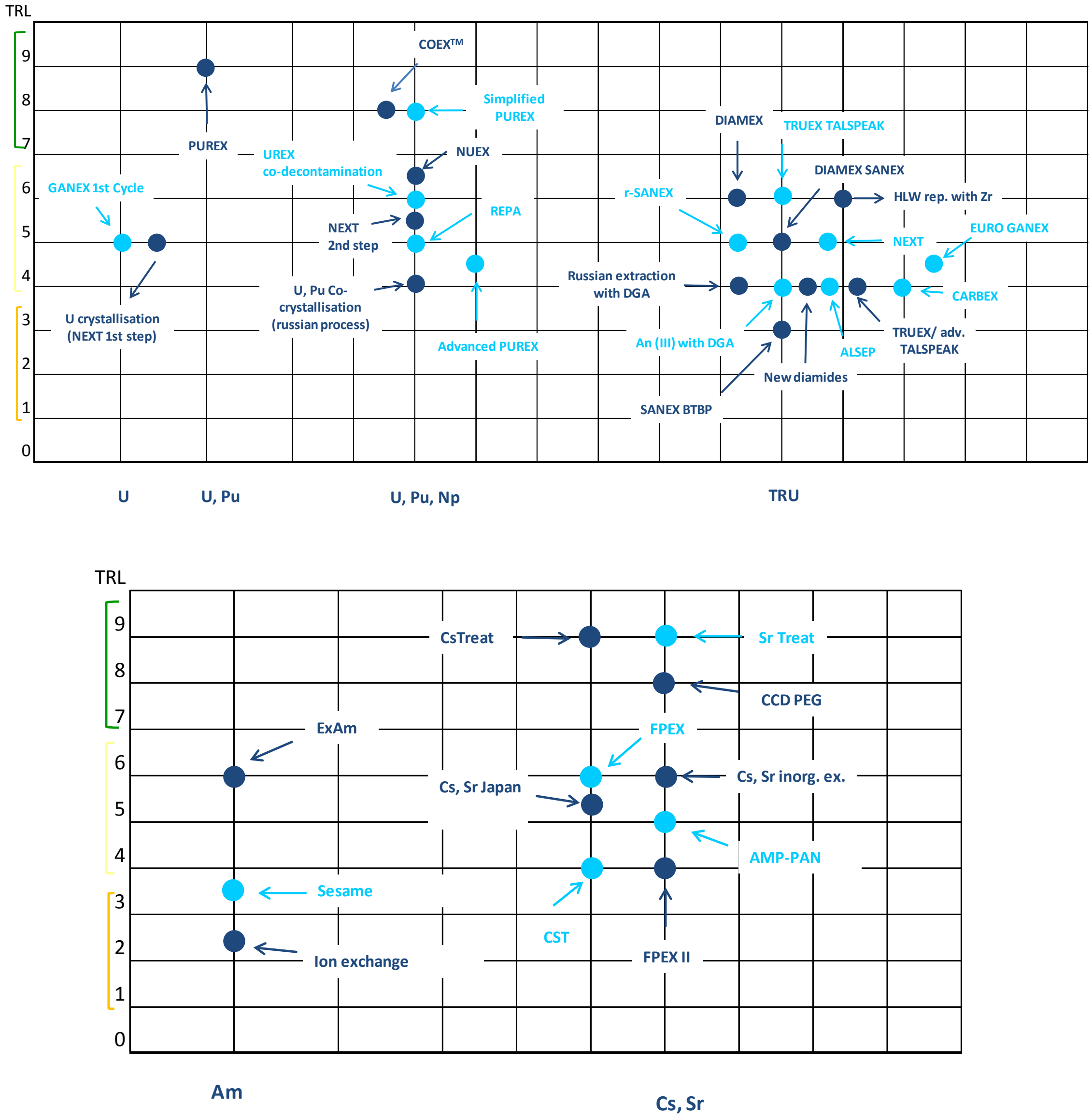
The development of all these separation processes addresses the anticipated needs of future fuel cycles. Enough scientific knowledge has now been gained to allow partitioning of most elements, such as the separation of Am. As shown in Figures 6.1 and 6.2, respectively, for hydrometallurgy and pyroprocessing, the technology readiness level (TRL) was estimated for most processes at between 4 and 6 (proof-of-principle) where process steps have been validated through hot tests or by using spent fuel. These values show that a good understanding of the physical and chemical processes has been reached, but further support is needed to demonstrate the validity of the process.

Although the different processes have not reached the same level of maturity, it must be noted that, as of today, no "showstopper" has been detected that could jeopardise their development at industrial scale. Further development will clearly be required to bring these separation processes to the point at which they can be industrialised.

Therefore, the down-selection of options to industrial deployable technologies will be mainly based on the fuel cycle scenario: type of reactor fleet (thermal or fast reactors), type of fuels (oxide, nitride, carbide, metal alloys, molten salt), recycling strategy deployment (for example, in France the strategy is to recover U-Pu and then U-Pu-Am, and finally all actinides). For instance, if metallic fuels are required for fast reactors, then pyroprocessing may be a more suitable process choice. Other factors will also influence the choice of options such as cost, safety and environmental impact. Non-proliferation requirements may also impact this down-selection of processes; such as the processes UREX, NUEX, COEX$^{TM}$, simplified PUREX, that have been developed as alternatives to the PUREX process without the presence of pure plutonium in the process.

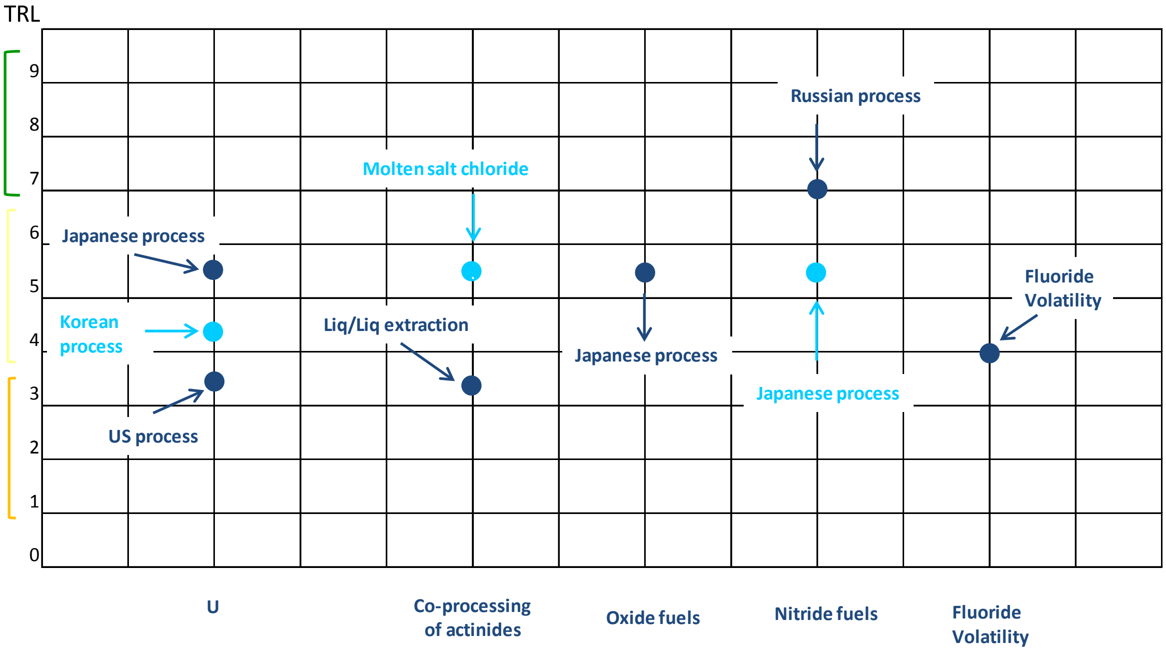
As discussed in Chapter 4 ("Perspectives of future R&D"), even in countries that do not support nuclear fuel recycling in the near-term (such as in the United States), R&D programmes are being pursued in order to be able to reopen the closed cycle option in the future. The implementation of processes at a commercial scale, in particular the less advanced processes, could benefit from international collaboration between countries wishing to develop similar processes.

**Figure 6.1. Summary of TRL assessments for hydrometallurgy processes***



*The tables summarise the TRLs assessment from Chapter 4, according to the target element as done in Chapter 2.

# Figure 6.2. Summary of TRL assessments for pyroprocessing



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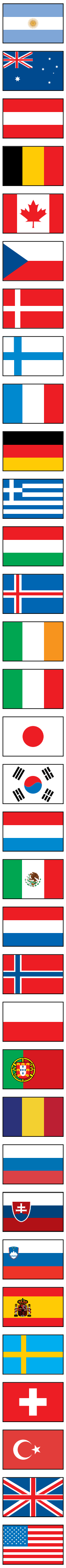

# State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry

The implementation of advanced nuclear systems requires that new technologies associated with the back end of the fuel cycle are developed. The separation of minor actinides from other fuel components is one of the advanced concepts being studied to help close the nuclear fuel cycle and to improve the long-term effects on the performance of geological repositories. Separating spent fuel elements and subsequently converting them through transmutation into short-lived nuclides should considerably reduce the long-term risks associated with nuclear power generation.

R&D programmes worldwide are attempting to address such challenges, and many processes for advanced reprocessing and partitioning minor actinides are being developed. This report provides a comprehensive overview of progress on separation chemistry processes, and in particular on the technologies associated with the separation and recovery of minor actinides for recycling so as to help move towards the implementation of advanced fuel cycles. The report examines both aqueous and pyro processes, as well as the status of current and proposed technologies described according to the hierarchy of separations targeting different fuel components. The process criteria that will affect technology down-selection are also reviewed, as are non-proliferation requirements. The maturity of different reprocessing techniques are assessed using a scale based on the technology readiness level, and perspectives for future R&D are reviewed.

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