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National Programmes in Chemical Partitioning

A Status Report

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NUCLEAR ENERGY AGENCY
Organisation for Economic Co-operation and Development

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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NUCLEAR ENERGY AGENCY

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Foreword

Under the auspices of the NEA Nuclear Science Committee (NSC), the Working Party on Scientific Issues of the Fuel Cycle (WPFC) was established to co-ordinate scientific activities regarding various existing and advanced nuclear fuel cycles, including advanced reactor systems, associated chemistry and flow sheets, development and performance of fuel and materials, and accelerators and spallation targets. The WPFC has established several expert groups to address these issues.

The Expert Group on Chemical Partitioning was created in 2001 to: *i)* perform a thorough technical assessment of separation processes as applied to a broad set of partitioning and transmutation (P&T) operating scenarios; *ii)* identify important research, development and demonstrations necessary to bring preferred technologies to a deployable stage; and *iii)* recommend collaborative international efforts for further technology development.

This report describes ongoing and planned national research programmes related to chemical partitioning in the Czech Republic, France, Italy, Japan, Korea, the Russian Federation, Spain, the United Kingdom and the United States. European Commission research programmes are also included. The programmes continue to evolve so as to take national strategies into account.

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Executive summary

This section comprises a series of summaries that describe the individual national programmes for development of hydrometallurgical and pyrochemical partitioning processes for nuclear fuel treatment.

The chemical partitioning programme in the Czech Republic is closely linked to the development of the fuel cycle technology of molten salt reactor systems. The principal partitioning processes under development are pyrochemical. The main effort is devoted to the technological development of the Fluoride Volatility Method designated for reprocessing of advanced oxide and metal fuel types and for initial processing of fluoride transuranium fuel for a molten salt transmutation reactor. Additional R&D is aimed at the development of electrochemical separation methods from fluoride molten salt media, which could be applied within the on-line reprocessing of molten salt reactor fuel. Here also the development of thorium fuel reprocessing is the focus of interest. A limited effort is devoted to the R&D of selected hydrometallurgical separation processes focused mainly toward the utilisation of dicarbollides and calixarenes.

The French research programme in partitioning had been carried out under the terms of the French Radioactive Waste Management Act of 30 December 1991 and will be pursued in the framework of the new Waste Management Act voted in June 2006. The objective is to investigate separation processes for subsequent transmutation of long-lived radionuclides to significantly reduce the radiotoxicity of the ultimate waste forms produced by the nuclear industry. Most studies are primarily dedicated to the minor actinides (Am, Cm, Np) and, to a lesser extent, to selected fission products (I, Cs, Tc). Hydrometallurgical techniques are investigated as the first reference. The technological feasibility of the Am and Cm processes as well as Np separation was demonstrated through the treatment of 13 kg of genuine spent nuclear fuel in the ATALANTE facility. Several hydrometallurgical processes are now available to meet one of the requirements of the 1991 French Act. As specified by the latest Waste Management Act, the P&T programme is connected to Gen-IV reactors. Partitioning processes developed during the first waste management act (1991-2006) are connected to heterogeneous minor actinide recycling, while Grouped Actinide by Extraction (GANEX) processes are concerned with homogeneous recycling. A pyrochemical technique is also investigated as a second alternative route. The Nuclear Energy Division (DEN) of the French Commissariat à l'énergie atomique (CEA) has identified two possible future applications of pyrochemistry in the civil nuclear industry: *i)* the reprocessing of irradiated targets or dedicated fuels arising from minor actinide transmutation (if multiple recycling is considered); *ii)* the reprocessing of Generation IV metallic fuels.

In Italy, in spite of the fact that nuclear power plants are no longer in operation, research activities have been under way during the past few years with the aim of comparing the two main treatment processes for spent nuclear fuel: hydrometallurgy and pyrometallurgy. These activities are performed as part of collaborative projects, with both European and international institutions.

In Japan the LWR spent fuel (SF) reprocessing technology and the FBR-SF reprocessing technology have been developed. A wide range of advanced technical options for the FBR fuel cycle system (reprocessing and fuel fabrication) was evaluated to select promising concepts as candidates for commercialisation. The study concluded that the advanced aqueous reprocessing system with oxide fuel was the most promising concept and that the alternative was the pyrochemical reprocessing system with metal fuel. For the advanced aqueous reprocessing system, the New Extraction System for TRU Recovery (NEXT) process has been developed, and pyrochemical reprocessing based on electrorefining technology has also been studied. Along with the development of these systems, basic and fundamental research and development of partitioning technologies are promoted, which are expected to produce innovative scientific knowledge and technologies.

Since 1997, the Republic of Korea has been focusing on the development of a non-proliferation nuclear fuel cycle based on pyroprocessing and transmutation technologies with the goal of long-term spent fuel management. In 2005, KAERI proposed the "Korean Innovative, Environmentally-friendly Proliferation-resistant Programme for the 21st Century" (KIEP-21) to the Korean government. This programme includes several different elements: *i)* Direct Use of PWR Spent Fuel in CANDU reactors (DUPIC); *ii)* Advanced Spent Fuel Conditioning Process (ACP); *iii)* pyrometallurigical partitioning and transmutation. At the moment, research is being performed on a reduction of oxide to metal (20 kg batch scale) and an electrorefinning for recovery of uranium (1 kg batch scale). On the basis of these results, KAERI will develop an engineering scale process with higher uranium throughput as well as a salt waste treatment process for waste salt minimisation.

In the Russian Federation, the Khlopin Research Institute (KRI) has developed an advanced aqueous reprocessing process for LWR SNF – "Simplified PUREX". Based on this concept the Russian state corporation "Rosatom" initiated the creation of the new Russian Experimental-Demonstration Centre (EDC) for LWR SNF reprocessing development, which will be constructed in Krasnoyarsk (Zhelesnogorsk) in about 2015. The main initial characteristics of EDC are: *i)* capacity of up to 100 t of SNF per year; *ii)* new generation approaches for RAW management [exclusion of any liquid RAW, immobilisation of tritium, Cs, Sr, separation of minor actinides (MA) and long-lived fission products (LLFP) for future transmutation]; *iii)* new generation processes of decladding and preparation of SNF for dissolution; *iv)* improved PUREX process. For advanced fuel cycles the recycling of all MA are proposed within the framework of pyrochemical technologies. RIAR proposed the new generation DOVITA-2 concept to close the FR fuel cycle, including recycling of MA based on pyrochemical processes adopted for different kinds of fuel (oxide, nitride, metallic, IMF). In 2008, in the context of the so-called "nuclear renaissance", the Russian Federal Task Programme "New Generation Nuclear Energy Technologies" was initiated; it is dedicated to government support of innovative technologies during the period 2010-2020. The pyrochemical non-aqueous technologies, including both molten salt and fluoride volatility processes, are considered by this federal programme to be key technologies for the future advanced fuel cycle.

The Spanish contribution describes the ongoing research programme related to the separation of actinides for their transmutation with the aim of reducing the volume and radiotoxicity of high-level waste. Separation R&D activities, that include both hydro- and pyrometallurgical processes, will help the Spanish governments to make a definitive decision concerning nuclear waste management.

Although P&T is not presently viewed as a promising long-term nuclear waste management strategy by the government of the United Kingdom, the topic presents technical challenges of significant scientific interest. The UK National Nuclear Laboratory (and its predecessor organisations) has undertaken development of advanced reprocessing techniques over the past two decades. Many of these techniques are applicable to meeting the challenges of partitioning for advanced fuel cycles. This account describes UK developments in both aqueous and pyrochemical technologies for reprocessing with a view towards partitioning for transmutation. For aqueous processing this account covers concept flow sheet definition, head-end and solvent extraction development (including process chemistry and process modelling), and engineering scale development, *e.g.* centrifugal contactors for an intensified solvent extraction process. For pyrochemical processes the focus has been placed on examining technical factors which impact industrialisation and commercial viability. A description of recent UK pyrochemical programmes including details of fundamental studies, pilot plant facilities and engineering development is provided.

In the United States of America, the programme for partitioning is based on developing processes to separate and recover the components of used nuclear fuels. Such processes allow recycle and reuse of the contained fuel by enabling effective management of wastes and recovery of energy resources. The primary criteria are to perform the separations, recovery, recycle and reuse in the most cost-effective manner while ensuring safety to people and the environment, and providing sufficient use of safeguards to ensure non-proliferation of weapons uses. Cost and waste management require a focus on simplification of the entire partitioning, recovery and recycle process. Flexibility of the partitioning flow sheet requires the capability to process used fuels from different types of reactors. The current scope of the partitioning programme includes emphasis on: *i)* advanced aqueous-based separations; *ii)* advanced dry head-end separations; *iii)* advanced electrochemical separations; *iv)* process equipment scale-up; *v)* applications of process control and monitoring; *vi)* process modelling and simulation; *vii)* regulatory and safety considerations; *viii)* demonstration of the comprehensive coupled processes.

European research on nuclear energy is carried out mainly on the basis of Article 7 of the EURATOM Treaty, and since the early 1980s as part of the so-called Framework Programme (FP) of the

European Commission. Activity is focused on nuclear safety and security aiming at the creation of a true European Research Area (ERA). Research is organised through co-funded research programmes carried out by consortia of national research organisations, universities and industrial organisations. In the field of partitioning significant scientific and technical progress has been made in the projects NEWPART, PARTNEW, EUROPART, CALIXPART, PYROREP and in the presently running ACSEPT programme in the FP7 (2007-2011). The major research subjects are the measurement of basic data underpinning the process development, demonstration of core processes and also research related to their head- and back-end. A second type of research in the European Commission is directly funded and carried out in the Joint Research Centre (JRC). Nuclear activities are mainly concentrated in the Institute for Transuranium Elements (ITU) at Karlsruhe, Germany. Regarding the fuel cycle the programmes address research activities relative to the development of sustainable concepts with an integrated waste minimisation through partitioning and transmutation (P&T). In the partitioning field, the JRC participates in networks in the EU (mentioned above) and world wide. Major partners include: CEA and EDF in France, CRIEPI in Japan, Chalmers University in Sweden, CIEMAT in Spain, SCK•CEN in Belgium, FZK and FZJ in Germany, Reading University in the UK, NRI/REZ in the Czech Republic and KAERI in Korea.

Introduction

Background

The development of peaceful utilisation of nuclear energy to the level of ~15% of total world electricity generation has been ascribed to an effective and safe performance of not only nuclear power plants but also to all fuel cycle facilities. Growing concerns about the deterioration of the global environment and the risk of nuclear proliferation has led to the evolution of additional requirements for the future sustainable utilisation of nuclear energy:

- to maximise the utilisation of nuclear energy from uranium (U) by recycling valuable fissile U remaining in spent fuels, and the recovery/reuse of the plutonium (Pu) generated in a reactor, *i.e.* as MOX fuels, and hence minimising consumption of U resources;
- to minimise the cost of long-term storage/disposal of high-level waste (HLW) in a geological repository by reducing the volume and the heat load of the HLW;
- to reduce the potential impact of radioactive wastes on the environment, *i.e.* the long-term radiotoxicity of the HLW.
- to improve safety and security (proliferation-resistance).

Responding to these contemporary requirements, partitioning and transmutation (P&T) is a radioactive waste management option complementary to geological repositories being investigated among OECD and non-OECD countries. The P&T strategy consists of a partitioning process and a transmutation cycle. In a partitioning process most of the transuranics (TRU: Np, Pu, Am, Cm), and in some cases, long-lived fission products (LLFP: ^{99}Tc, ^{129}I and ^{135}Cs) and heat-generating fission products (^{90}Sr and ^{137}Cs), are partitioned by chemical separation in addition to U. During the first 150 years after discharge of spent uranium oxide fuel from a reactor, the thermal burden of the HLW on the repository principally resides with the ^{90}Sr and ^{137}Cs and this restricts the design conditions of the repository. After about ~150 years the HLW radiotoxicity is dominated by the minor actinides (MA: Np, Am, Cm), while after more than 200 000 years it reaches the uranium ore radiotoxicity threshold and this is regarded as having no additional impact on the environment. Thus the removal of all the MA from HLW would markedly reduce the long-term radiotoxicity of the waste and make it below that of the original uranium ore after less than 3 000 years. In the transmutation cycle, the transuranium actinides are transmuted in either a thermal or a fast spectrum irradiation.

In the P&T strategy, separation of the transuranium actinides from fission products is required. Partitioning of Am-Cm is a much more difficult task than separation of Pu and Np since it necessitates discrimination of Am-Cm from lanthanides (Ln), whose chemical properties are very similar to those of Am-Cm but which occur in amounts more than 20 times larger. Extensive research has been undertaken on the separation methods which use both hydrometallurgical and pyrochemical processes.

Over the last couple of decades, considerable scientific and technical effort has been devoted to developing partitioning processes through domestic and international projects: SPIN (France), OMEGA (Japan), GNEP (AFCI: USA), bilateral co-operation and EURATOM Framework Programmes (NEWPART, PARTNEW, EUROPART, CALIXPART, PYROREP, etc.). Significant scientific and technical progress has been made. In Europe, the newest R&D programme, relating to partitioning studies, ACSEPT, has just started under the 7th EU Framework Programme (FP7).

Hydrometallurgical partitioning processes

A conventional PUREX process based on the solvent extraction of U and Pu with TBP is currently practiced in France, Japan, Russia and the United Kingdom. Extension of the process to include partitioning of MA and LLFP is a goal of the advanced fuel cycle. Among the elements in the MA, Np can be partitioned within a modified PUREX process, *i.e.* by controlling the process conditions. The redox properties and distribution behaviours of Np in a TBP extraction process have been well demonstrated in experiments and analysed by a simulation model. Finely controlled separation of Np has recently been demonstrated on a laboratory scale at the ATALANTE facility (CEA-Marcoule) using genuine spent fuel. The modified PUREX process can also separate Tc.

Several partitioning processes for Am-Cm are based on solvent extraction processes and are being developed and tested in "hot" laboratories, *e.g.* the DIAMEX process by DMDOHEMA (France), TRUEX by CMPO (USA), 4-Group by DIDPA and ARTIST by TODGA (Japan) and Total-P by TRPO (China). The NEXT process (Japan) separates TRU after crystallisation of bulk U as uranyl nitrate hexahydrate. As these processes separate the trivalent Am-Cm and the lanthanides (Ln) together from the rest of the fission products, an additional step is necessary to isolate the Am-Cm from the Ln. Several techniques have been proposed and tested on highly active process streams, *e.g.* extraction with new extractant molecules [$(ClPh)_2PS_2H$, BTP, C5-BTBP] and the Talspeak methods using HDEHP and complexing agents (DTPA, HEDTA). An important factor is the stability of the ligand molecules against radiolysis and hydrolysis.

Pyrochemical partitioning processes

From the 1950s to the 1970s, pyrochemical processes were studied largely for separation of U and Pu from MA and fission products. These pyrochemical processes, however, could not always achieve the individual element separation or the level of product decontamination required. The research almost completely stopped when the PUREX process and light water reactors were adopted world wide. The former Soviet Union, current Russian Federation and the United States, however, pursued the development of pyrochemical technologies for dealing with oxide and metallic fast reactor fuels, respectively.

In the latter half of the 1980s, certain programmes concerning pyrometallurgical/pyrochemical processes have vitalised. Argonne National Laboratory (ANL, USA) started the IFR programme, which integrated pyrometallurgical reprocessing with metal electrorefining and metal fuel fast reactor. CRIEPI (Japan) was also exploring this subject. Today, pyrometallurgical processes attract strong interest, as they offer advantages for compact facilities and proliferation resistance. Several programmes with metal electrorefining have been launched for metal fuel [INL (USA), CRIEPI (Japan), KAERI (Korea)] and for nitride fuel of dedicated transmutation system (JAEA, Japan). This process provides the separation of minor actinides together with uranium and plutonium without any additional process. JRC-ITU explored the technological feasibility of using a liquid aluminium cathode instead of a cadmium cathode. The pyrochemical process with electrorefining and precipitation of oxide in chloride bath initiated from MOX fuel production has been applied for reprocessing of spent oxide fuel (Russia, RIAR Dimitrovgrad Dry Process), in which the DOVITA process to recover minor actinides from this salt has been proposed. A fluoride bath has also been applied to investigate electrorefining and liquid metal extraction [CEA (France)]. Liquid metal extraction from chloride salt is examined to recover actinides from high-level waste after converting chlorides by use of genuine material. Fluoride volatility has another interest as a means of treatment of molten salt reactor fuel [NRI (Czech Republic)].

The OECD/NEA had organised a Pyrochemistry Working Group to review the various applications of pyrochemical technology and issued a status report on "Pyrochemical Separations in Nuclear Applications" in 2004.

Current study

The present report comprises a series of contributions that describe the individual national programmes for development and improvement of processes for nuclear fuel treatment. The national programmes are described in alphabetical order as follows: Czech Republic, France, Italy, Japan, Republic of Korea, Russian Federation, Spain, United Kingdom and the United States of America. A subsequent chapter is devoted to the European Commission (EC). (NB For the present purposes, the EC is counted as a national entity, though it is recognised that some of its member countries have their own research and development programmes as well as contributing to EC programmes.)

Chapter 1: Czech Republic

Sustainable development of nuclear energy is one of the key points of the National Energy Policy for the next 30-year period adopted by the government of the Czech Republic in 2004. Development of technologies which are able to minimise the ecological impact of nuclear power utilisation is therefore a focus of interest of responsible state institutions and authorities. The gradual closing of the nuclear fuel cycle in connection with the deployment of new nuclear reactors of the Gen-III+ generation is considered inevitable. Subsequently chemical partitioning and nuclear transmutation of long-lived radioactive isotopes present in spent fuel are considered to be prospective technologies allied with the deployment of Gen-IV nuclear reactors. The present-day development of these technologies is in good agreement with the national concept of radioactive waste and spent fuel management adopted by the Czech government in 2002. The support of a national P&T programme is considered as the development of an alternative to replace the earlier concept based primarily on the disposal of spent fuel into an underground repository without reprocessing.

The Czech research and development programme in the field of partitioning and transmutation is based on the Molten Salt Transmutation Reactor system concept with fluoride salt-based liquid fuel. Fuel processing is based on pyrochemical and/or pyrometallurgical fluoride partitioning of spent fuel. The choice of Molten Salt Reactors, within the Gen-IV nuclear reactor family, arises from the attractiveness of this type of reactor for transmutation of actinides from spent nuclear fuel and the possibility of using the ^{232}Th-^{233}U fuel cycle with minimised production of nuclear waste. Both features can also render MSR attractive for electricity-generating companies, which must now pay a fee corresponding to the production of radioactive wastes. The last – but not least – reason for the MSR choice has been the historical experience of several Czech institutes and companies in the development of nuclear fluoride technologies.

The only Czech company presently generating electricity in nuclear power plants is the Czech Power Company CEZ, which operates two nuclear power plants (NPP) with six PWR (VVER) units. At present, the spent fuel from Czech NPP, after discharge from reactors, spends from five to six years cooling at reactor pools and is then stored in a spent fuel storage facility. According to the Czech Atomic Act, the State guarantees the safe disposal of all radioactive wastes including spent nuclear fuel. The disposal of non-reprocessed spent fuel in an underground repository is described as a solution, feasible by current accumulated scientific and technical knowledge and expresses the certainty of a safe solution to fuel cycle back-end issues. Therefore, preliminary planning of an underground repository exists with the possibility that the first spent fuel will be accepted after 2065. Because of this, the decision on how to dispose of spent fuel will have to be made in tens of years; the chance to develop a technically, economically and socially more attractive solution than underground disposal of spent fuel is thus in the foreground of professional interest at the present time and for the decades to come.

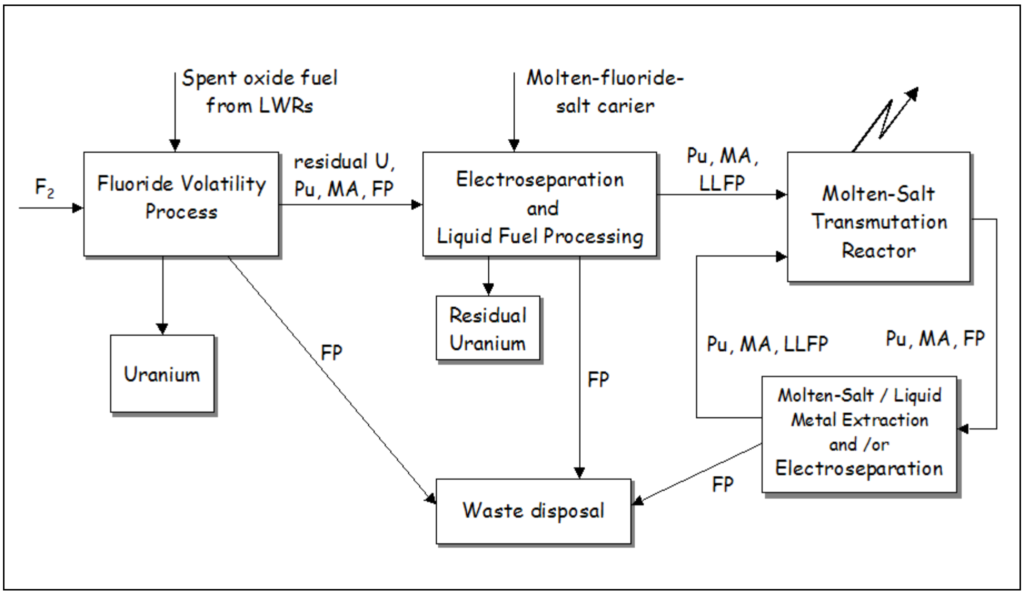
1.1 Pyrometallurgical technologies for MSTR fuel cycle

The fundamental advantage of Molten Salt Transmutation Reactors (MSTR) demonstrates itself above all in connection with a continuous or at least quasi-continuous on-line chemical separation process.

For such a compact coupling of MSTR with chemical reprocessing it is eminently appropriate to maintain the fuel, as far as possible, in one chemical form throughout the entire fuel cycle. Accordingly, if the MSTR fuel is based on fluoride melt then the separation processes should also be based on separation techniques from fluoride melt media. Pyrochemical and pyrometallurgical technologies generally comply with this requirement.

The Czech research and development programme in the field of pyrochemical and pyrometallurgical partitioning technologies is based first of all on the experience acquired in the past in the development and realisation of a pilot-plant fluoride technology process for the reprocessing of spent fuel from the Russian BOR-60 fast reactor. At present, this experience is utilised for the development of suitable separation processes and technologies for the fluoride-based MSTR fuel cycle.

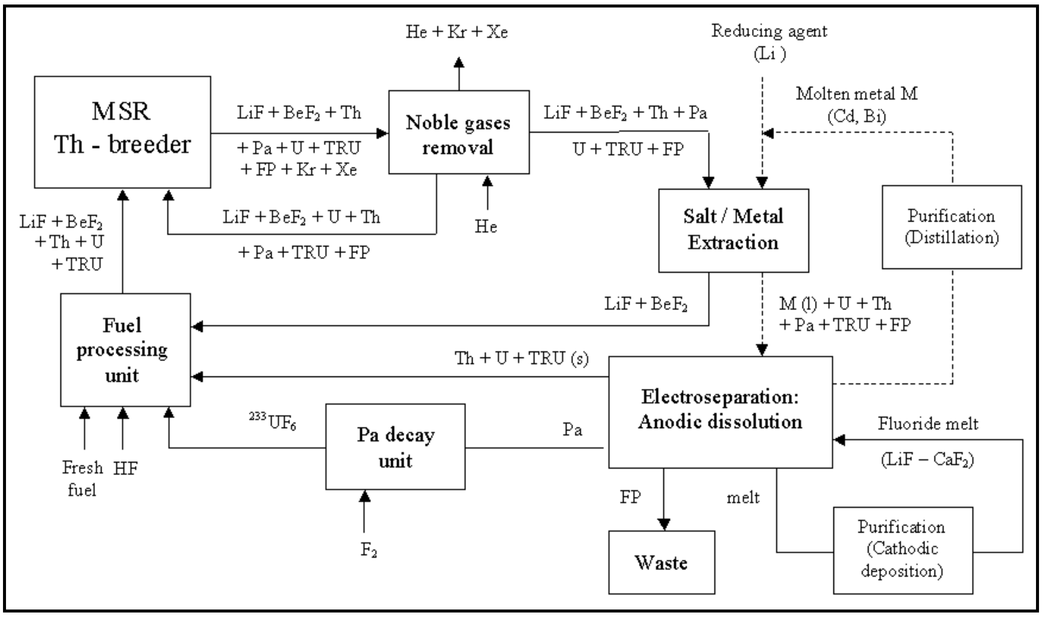
Figure 1.1: Simplified scheme of MSTR fuel cycle



Experimental and theoretical studies in the field of pyrochemical technology development for the MSTR fuel cycle are oriented in particular toward the following areas:

- Technological research in the field of the "fluoride volatility method" directed at the suitability verification of a technology for PWR spent fuel reprocessing, which may result in a product the form and composition of which might be applicable as a starting material for the production of liquid fluoride fuel for MSTR. Consequently, the objective is a separation of a maximum fraction of uranium components from Pu, minor actinides and fission products. The technology under development is based on the fluorination of the spent fuel by fluorine gas in the flame fluorination reactor, where the volatile fluorides are separated from non-volatile ones, and on the subsequent purification of the components using technological operations of condensation, rectification and sorption. The "fluoride volatility method" can be ranked at the "front end" area within the Molten Salt Transmutation Reactor fuel cycle. At present, the greatest attention is aimed to the realisation of the pilot-plant technology for the separation of the uranium component from other spent fuel components by the fluoride volatility method. The problems of wastes arising from the fluoride volatility method are studied as well; of these the main part is represented by several solid sorbent materials (such as pelletised NaF, MgF_2, Al_2O_3, etc.) contaminated by fission products. The fixation technology, currently under development, is based on their vitrification into ceramics.
- Laboratory research on electroseparation methods in fluoride melts media in relation to the study of their properties. The effort in this field is aimed at the development of separation processes suitable for the final processing of fresh TRU fuel of MSTR following application of the fluoride volatility process and chiefly for the MSTR "on-line" reprocessing technology. The research programme in this area is further directed to the determination and study of selected physicochemical properties of fluoride melts.
- The flow sheeting research of Molten Salt Reactor fuel cycles is aimed at the design of an "on-line" reprocessing of fuel salt of the MSR. The solution of the MSR on-line reprocessing is considered to be a crucial point of the whole MSR technology and efforts to resolve this question are consistently monitored.

Figure 1.2: Conceptual flow sheet of MSR on-line reprocessing designed by NRI Rez plc



Experimental research work related to the development of pyrochemical and pyrometallurgical partitioning technologies is concentrated mainly in the Nuclear Research Institute Rez plc, which represents the main research and development base for the Czech Power Company CEZ. The research work in the field of pyrochemical partitioning technologies development is carried out as a component of the national P&T programme within the framework of the "Transmutation" consortium whose members include both research institutions and companies in the Czech nuclear industry. The principal project of the Czech national P&T programme, covering also R&D of MSTR pyrochemical technologies, is named SPHINX (Spent Hot Fuel Incineration by Neutron Flux). The project is directed and financially supported by the Ministry of Industry and Trade of the Czech Republic.

Figure 1.3: Equipment of the fluoride volatility technology in the NRI Rez plc

1.2 International R&D co-operation

An important part of the research activities in the field of pyrochemical partitioning has been performed in the framework of international R&D projects, *e.g.* the PYROREP and MOST projects of the 5th Framework Programme EC/EURATOM and the subsequent EUROPART and ACTINET projects of the 6th Framework Programme. The participation in the EC projects complements very well the research activities of the national programme framework.

Although the nuclear reactors operated in the Czech Republic to date use only uranium fuel, the future use of MOX fuel cannot be ruled out, notably in Temelin NPP, which operates the two newest PWR units in Europe and where new LWR reactor units are planned for operation in about 2020. Therefore interest in the development of selected hydrometallurgical partitioning technologies, connected to the PUREX process, is also appropriate. The research and development activities in the field of hydrometallurgical partitioning methods have been performed as a component of international P&T programmes of EC/EURATOM projects, *e.g.* the previous CALIXPART and EUROPART projects of the 5th and 6th Framework Programmes, respectively. The principal effort has been devoted to the research and development of selected fission product separations. The extractions of caesium, strontium and europium by cobalt dicarbollides and calixarens have been developed in the laboratories of the Nuclear Research Institute Rez plc in collaboration with the Institute of Inorganic Chemistry of the Czech Academy of Sciences and KATCHEM Ltd. Another separation technique using solid extractants based on the malonamide reagent family has been developed in the Center for Radiochemistry and Radiation Chemistry of the Faculty of Nuclear Sciences and Physical Engineering of the Czech Technical University in Prague. The proposed extraction methods are aimed at partitioning fission products from high active raffinate containing trivalent actinides and lanthanides after reprocessing of spent fuel by an improved PUREX process.

The Czech partitioning programme responds to the intentions of the Czech Republic and also of the Czech Power Company CEZ to participate in the international co-operation and joint development of future nuclear technologies. These will have wide public acceptance as well as high efficiency, reliability and safety.

Chapter 2: France

The research programme described in this document has been carried out under the terms of the French radioactive waste management act of 30 December 1991 and will be pursued in the framework of the new waste management act voted in June 2006, with the objective of investigating separation processes for subsequent transmutation of long-lived radionuclides to significantly reduce the radiotoxicity of the ultimate waste forms produced by the nuclear industry.

Most of the studies involve the following radionuclides:

- primarily the minor actinides (americium, curium, neptunium) which, after plutonium, account for the bulk of the long-term radiotoxic inventory of spent fuel;
- various fission products (iodine, caesium, technetium) selected for their abundance in spent fuel, the existence of a long-lived isotope, and their potential long-term mobility in a geological repository.

For the separation and recovery of these elements, two techniques are investigated:

- the first, designated as the reference route, is based on hydrometallurgy processes, which have attained a certain maturity level, related to the PUREX process;
- the second, more prospective, designated as the alternative route, is based on pyrochemical processes.

2.1 Hydrometallurgy programme

2.1.1 Strategy

The reference separation process involves modifying the PUREX process to recover neptunium, technetium and iodine, as well as developing additional solvent extraction processes to separate the americium, curium and caesium contained in the high-level liquid effluent after spent fuel reprocessing.

In compliance with the 2006 deadline specified by the first waste management act, the research work involves two phases with the objective of demonstrating scientific feasibility (validation of the basic separation concepts) by the end of 2001, and technical feasibility (overall validation of the processes) in 2005.

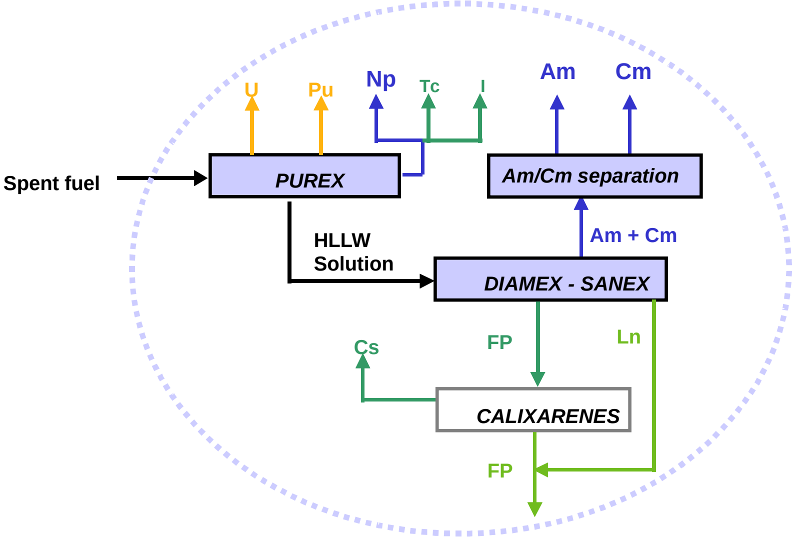
The progress obtained on the first issue over a decade of work led to the conclusion in 2001 that selective extraction of these minor actinides (Np, Am and Cm) and fission products (I, Tc, Cs) from high-level spent fuel reprocessing solutions is a viable concept [1,2].

This conclusion was based on the following results:

- Nearly 97% of the iodine is recovered today by the PUREX process implemented at La Hague.
- Neptunium and the soluble technetium fraction can also be recovered by modifying the operating conditions in the same process.
- The separation of americium, curium and caesium is possible by supplementing the PUREX process with additional extraction steps using new extractant molecules. The required element recovery and purification yield has been demonstrated by laboratory-scale tests on genuine fuel reprocessing solutions.

Following the first phase of the study, the most promising processes were selected for the second “technical feasibility” phase (Figure 2.1).

Figure 2.1: Processes selected for technical feasibility demonstration



The objective of the second phase is comprehensive validation of the processes for future industrial implementation. For the processes based on new extractant systems, this implies:

- experimental testing of all the process steps including, for example, solvent recycling;
- demonstration of the representativeness of the experimental conditions, *e.g.* demonstrations at suitable scale of sufficient duration for critical aspects (primarily the process endurance);
- a preliminary assessment of the conditions under which they could be implemented at industrial scale.

2.1.2 Methodology: General objectives

The scientific feasibility of recovering neptunium, americium, curium and caesium was demonstrated at laboratory scale by validating the main steps (extraction-scrubbing, stripping) of the liquid-liquid extraction processes.

It is important to continue testing the processes in the perspective of deploying enhanced separation in the future. The technical feasibility demonstration phase therefore addresses the following objectives:

- extend validation to all the process steps, and in particular those concerning solvent recycling;
- demonstrate that the laboratory performance can be obtained at larger scale (considering the effects of time and dimensions);
- define the ancillary functions of the separation processes, in particular those concerning reagent and effluent management, and the coupling between processes;
- estimate the cost of a facility implementing these processes.

The safety-related aspects (chemical, criticality and radiation hazards) were taken into account in this phase of the study in a preliminary risk analysis.

The separation processes investigated are implemented either directly within the PUREX spent fuel reprocessing line or through subsequent extended processing. The study assumed reprocessing of an annual spent fuel volume corresponding to an electrical production of 400 TWhe as an order of magnitude of the required capacity of industrial enhanced separation processes.

The objective of these studies was to provide:

- process flow sheets for the enhanced separation operations, validated by experimental results of representative scale and/or duration;
- a summary analysis of the process sensitivity to the operating conditions;
- an overview of the integration of enhanced separation processes in a spent fuel reprocessing plant (preliminary equipment design criteria);
- a cost assessment for the facilities in the configuration defined for this study.

On completion of this phase, the process will have been validated at a sufficient scale to consider industrial deployment with the aid of suitable modelling.

These are indispensable steps on the way to process industrialisation. However, prior to industrial implementation, further research will be necessary in addition to the engineering design work:

- examination in greater detail of some aspects of the technical feasibility demonstration that require further consolidation (*e.g.* the endurance of solvent recycling operations);
- validation of the processes at near-industrial scale by testing in a demonstration pilot unit;
- specification of the process equipment items and their operating ranges;
- examination of degraded operating modes and development of the process control system;
- continuation of the risk analysis in greater detail.

2.1.3 R&D topics

The enhanced separation technical feasibility demonstration studies and tests were defined by a working group in which most of the participants had prior experience in the development of facilities recently commissioned at La Hague.

The research activities are described below from the standpoint of developing liquid-liquid extraction processes, as these techniques are the basis for the main separation concepts investigated. The research topics have been itemised for structural clarity, although of course they are generally inter-related. The work was undertaken concurrently and coherently in each area of investigation.

2.1.3.1 Establishing the process flow sheets

A comprehensive flow sheet must be developed for each process to achieve the performance objectives (recovery yield and purity) while preserving operating margins compatible with industrial operation.

Development of extraction flow sheets for the core process

Flow sheets are devised and optimised through the use of calculation codes to simulate the extraction performance of a flow sheet and thereby minimise the number of experimental tests required for process development. To ensure reliable calculations, the behaviour or the species involved and the type of contactors used in the experiment must be taken into account as realistically as possible.

The calculation codes devised for the development of the PUREX process were adapted to handle enhanced separation processes. The chemical data characterising the new extractant systems were taken into account mainly for DIAMEX from the scientific feasibility phase. Development work has continued on these models to extend their applicability (for example, extending DIAMEX to Am/Cm separation) and to allow flow sheet optimisation and perturbation calculations. Additional data on the partitioning of species and on the kinetics of interphase transfers have also been obtained and integrated into the models, to simulate the behaviour of the species over a wide range of operating conditions.

The process flow sheet calculation models were also modified to predict the performance of liquid-liquid contactors of the same type as those used for the PUREX process at La Hague. For example, the characteristics of small-diameter pulsed columns (like the ones in the CBP hot-cell line at ATALANTE) are taken into account by means of various parameters, some of which had to be determined for this purpose: transfer coefficients, exchange surface area between phases, dispersed phase hold-up (volume fraction) and axial dispersion coefficients (diffusion characteristic of the flowing species). One of the purposes of the process implementation studies (see Section 2.1.3.2) is to obtain the characteristics of industrial extraction equipment for use in flow sheet calculations.

Partial experimental validation may be necessary to optimise the flow sheet parameters (reactant flow rates and concentrations). In this case, the calculated results are compared with test data obtained on surrogate solutions (containing inactive surrogates), on synthetic solutions (doped with low-irradiating elements), or on genuine solutions. Tests of the complete process flow sheet on genuine solutions are also used for overall validation (see Section 2.1.3.3).

A laboratory extractor design group has been maintained to support experimental activities. Examples include:

- nuclearisation of Couette-Taylor columns to provide small, single-compartment contactors suitable for experiments on genuine solutions, allowing extended testing while generating only limited effluent volumes;
- development of contactors for experimental diamide solvent treatment in which phase separation problems have been observed in conventional contactors.

Development of extractant system recycling steps

In solvent extraction operations, the extractant system is degraded by hydrolysis and radiolysis, leading to the formation of compounds that can limit process performance. Loop operation of the extractant system therefore assumes prior investigation of solvent stability and the development of regeneration treatments to eliminate any degradation products.

The first step is to identify the degradation products and assess their effect on process performance. This implies evaluating the nature and quantities of these compounds depending on the chemical and radiolytic conditions of the medium, through specific experiments implementing, for example, irradiator tests to quantify the effects of hydrolysis and radiolysis.

Techniques are then developed specifically to eliminate the major degradation products. Chemical treatments are developed with an increasingly representative approach to cover the potential degradation products.

Chemical treatments defined by experiments with surrogate solutions are then submitted to extended testing in an irradiation loop to simulate actual degradation conditions. An irradiation loop known as MARCEL (from the French acronym for “advanced radiolysis module for extraction-scrubbing cycles”) was developed and implemented for this purpose in the G1 building. The loop is used for tests of extended duration: a few hundred hours in MARCEL are equivalent to a year of plant operation. The effectiveness of these treatments must be confirmed by comparison with the demonstration tests on genuine solution (see Section 2.1.3.3), in which the solvent will be recycled about ten times. The solvent endurance under realistic conditions can then be estimated, and the representativeness of tests in the irradiation loop can be evaluated by comparing the degree of solvent degradation obtained in the two types of experiments.

2.1.3.2 Process implementation

Three types of extractor can be used at industrial scale: mixer-settlers, centrifugal contactors and pulsed columns. The latter have many advantages (including compatibility with solid suspensions, ease of maintenance) and appear best suited for use with high-activity media. Pulsed columns were therefore selected for extraction operations in enhanced separation processes.

Process implementation studies are performed to demonstrate that the separation operations can be carried out in an industrial-scale device, not only to guarantee satisfactory hydrodynamic operation but also to ensure that mass transfer meets the separation performance requirements of the process flow sheet.

Extractor models have not yet reached a stage at which their hydrodynamic behaviour and extraction performance can be predicted directly from the contactor dimensions and the physical and chemical characteristics of the phase system used. Tests in a small inactive mock-up with the different phase systems implemented appear sufficient at this time to verify the hydrodynamic operation of the device.

A model based on the characteristic flow and mass transfer parameters for a given phase system is used to calculate the extraction performance of the contactors. This simplified chemical operating description proved its effectiveness during the development of the extractors used for industrial implementation of the PUREX process. It is an integral part of the calculation codes used for process flow sheets.

For the technical feasibility demonstration phase, the contactor description is thus limited to providing a realistic set of characteristic operating parameters (with the relevant phase system); this level of description is considered sufficient to determine the overall dimensions of the industrial unit and estimate its cost.

The model operating parameters (axial dispersion, transfer coefficient) will be determined from the data obtained with a small-scale mock-up (mainly under inactive conditions) for the selected phase systems, and from the characterisation of currently available industrial contactors.

Innovative dedicated devices were also developed to meet the solvent treatment requirements. The work to date has been limited to the development of laboratory contactors for validation testing with genuine solution or in the irradiation loop.

2.1.3.3 Overall validation

Validation of the complete process flow sheet requires demonstration testing with genuine solution over extended time periods.

The tested flow sheets will therefore include the extractant system recycling steps (solvent treatment) and will be implemented in equipment representative of the units suitable for use at industrial scale. Although modelling allows transposition between different types of contactors, it is preferable from a validation standpoint to approximate the actual operating conditions. The experiments will therefore be carried out in devices with operating characteristics (continuous or compartmented exchange, contact surface area between phases, residence time) comparable to those specified for industrial-scale equipment.

The overall validation experiments are intended to provide preliminary data on the stability of the process flow sheets over time. To test the endurance of two-phase systems, the duration of the experiments far exceeds the time necessary to reach steady-state operating conditions; the test duration is sufficient for the extractant system to be recycled about ten times.

The experiments are carried out with equipment optimised to limit the effluent management constraints in active facilities. This includes miniaturising continuous contactors to allow for experimentation in a small diameter extraction column (with flow rates about four orders of magnitude lower than in an industrial pulsed column). The development and nuclearisation work on Couette-Taylor columns was carried out in this context.

With regard to neptunium separation, however, pulsed column experiments (with a flow ratio of about 1:1 000) were necessary to ensure representative conditions.

About 13 kg of spent fuel were dissolved for these tests, producing about fifty litres of solution requiring treatment.

2.1.3.4 Transposition to industrial scale

This activity should provide a preliminary “image” of an industrial enhanced separation facility based on analysis of existing data. The main objective is to identify technological obstacles at the earliest possible stage, and to take industrial requirements (safety, cost, etc.) into account.

2.1.3.5 Cost assessment of an industrial facility

The preliminary capital cost assessment for an enhanced separation facility is based on the main equipment schedule and layout diagram.

2.1.4 Separation of Np, Tc and I by modified PUREX process

2.1.4.1 Neptunium separation

In the first-cycle extraction/scrubbing operation of the La Hague plants, although most of the Np inventory is co-extracted with uranium and plutonium [3], a significant fraction of the Np inventory remains in the high-active raffinate. In the uranium/plutonium splitting operation, nearly all the co-extracted neptunium follows the uranium into the solvent and is then separated from uranium in the "uranium purification cycle" [3]. The objective of the studies was to increase the Np extraction yield to above 99% by modifying the extraction/scrubbing flow sheet as little as possible. In this operation, neptunium is present in two oxidation states: Np(V), for which TBP exhibits a very low affinity, and Np(VI), which can be extracted by TBP with nearly the same affinity as for U(VI). The ratio between these two oxidation states of neptunium results from the following reaction (1):

$$\begin{array}{l} NpO_2^{+} + 3/2H^{+} + 1/2\,NO_3^{-} \leftrightarrow NpO_2^{2+} + 1/2\,HNO_2 + 1/2\,H_2O \\ (\text{catalysed by}\,HNO_2) \end{array} \tag{1}$$

Neptunium is present in spent fuel dissolution liquors mainly (80-90%) as Np(V). The observed behaviour of neptunium during the extraction/scrubbing operation is thus attributable to the shift of Eq. (1) to the right due to the extraction of Np(VI) and nitrous acid by TBP. It should be noted that the oxidation of Np(V) to Np(VI) by nitric acid [Eq. (1)] must be catalysed by nitrous acid, HNO_2. In the first cycle, nitrous acid is always present to a certain extent due to the radiolysis of the medium.

Using the PAREX code to simulate the PUREX process, it has been shown that an increase in the nitric acid concentration in the PUREX feed solution should lead to a high neptunium extraction yield (> 99%), due to enhanced Np(V) oxidation kinetics [Eq. (1)]. This positive effect of the nitric acid concentration on the neptunium extraction yield has been verified in an alpha active test in a small pilot facility equipped with pulsed columns 25 mm in diameter and 4 m high.

To demonstrate the technological feasibility of this new PUREX flow sheet, an experiment based on these extraction conditions was carried out in April 2005 in the new CBP shielded cell facility of ATALANTE using 13 kg of spent LWR fuel. The shielded cell is equipped with three pulsed columns 15 mm in diameter and 4 m high, as well as mixer-settlers. In this flow sheet, two pulsed columns were devoted to the extraction operation in order to be representative of the residence time in the corresponding industrial extraction pulsed column, which is 8 m high. The results issued from this experiment showed that neptunium extraction was quantitative (extraction yield > 99.6%) and in agreement with calculation [4].

Thus, such a PUREX adaptation would be possible in an industrial shop, with limited equipping required.

2.1.4.2 Iodine separation

During the fuel dissolution step (Figure 2.2), most of the iodine is oxidised into molecular iodine, I_2, which is trapped (as a mixture of I^- and IO_3^- ions) from the dissolver off-gases by washing with an aqueous soda solution. The recovered iodine (~97%) is currently discharged into the sea. During various steps in the PUREX process, some iodine is trapped on "iodine filters" loaded with silver nitrate, so very small fractions of the iodine inventory are released into the atmosphere. In order to increase the overall iodine recovery yield to 99%, a process has been developed to strip I from the solid filters.

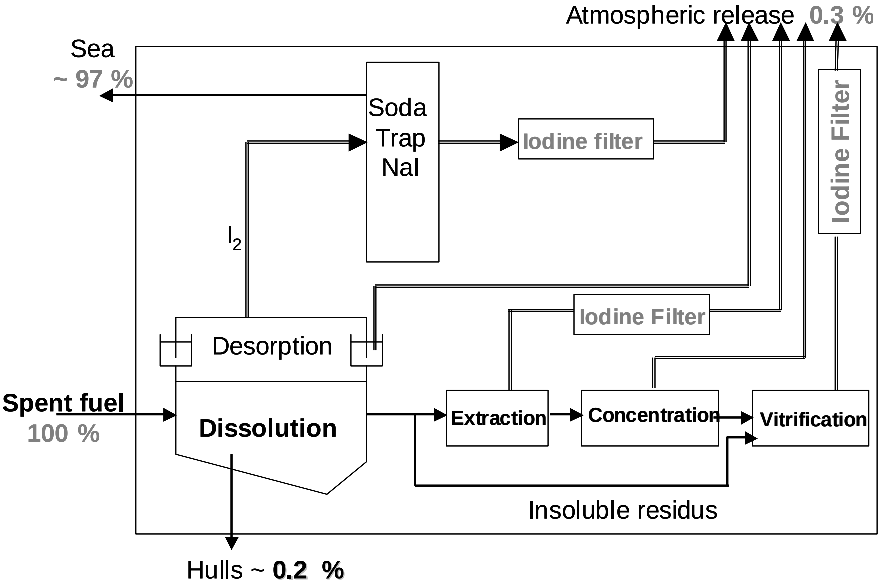
This process [5] is based on reductive scrubbing of the solid filters using sodium ascorbate in soda medium:

$$AgI(s) + Red(aq) \rightarrow Ag(s) + I^-(aq) \tag{2}$$

Decontamination factors better than 100 were obtained on simulated filters. After optimisation, this "one-step" process was validated on samples of iodine filters from the La Hague plants.

A selective process has also been designed to recover and purify molecular iodine desorbed during the fuel dissolution step. This process is based on reductive acid scrubbing of the dissolver off-gases with hydroxylammonium nitrate followed by oxidation with hydrogen peroxide to obtain selective desorption. The technological feasibility of this process was demonstrated in 2001 by a test performed in a small pilot facility with an iodine recovery yield of 99% from the dissolver off-gases [6].

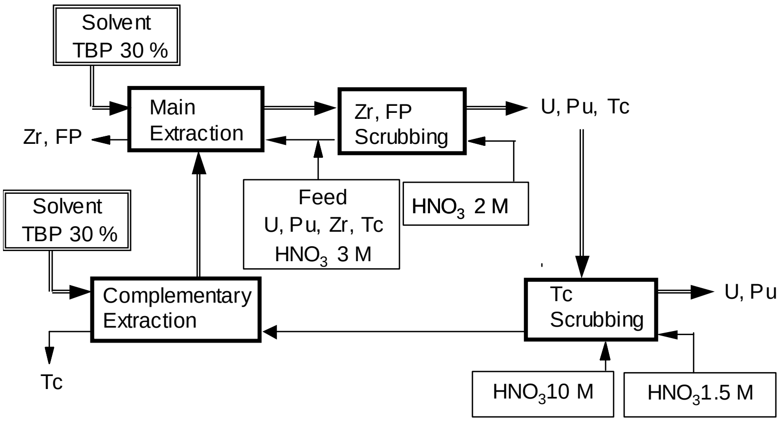
Figure 2.2: Iodine behaviour in industrial operations at AREVA La Hague



2.1.4.3 Technetium separation

The technetium dissolution yield varies from 50 to 90% of the Tc inventory, depending on the fuel burn-up and dissolution conditions. Technetium exists within the spent fuel dissolution liquors as Tc(VII), in the form of TcO_4^-(aq), and can be co-extracted with zirconium, uranium and plutonium by TBP. As technetium catalyses the destruction of hydrazine by nitric acid, it can cause major dysfunctions in the uranium/plutonium splitting operation, where hydrazine is used as a Pu(III)-U(IV) stabiliser. The flow sheet of the extraction-scrubbing operation of the first PUREX cycle used in the AREVA La Hague plants has therefore been optimised [3] to minimise technetium co-extraction with uranium and plutonium (Figure 2.3).

Figure 2.3. Flow sheet of the first PUREX extraction cycle at AREVA La Hague



Following the “complementary extraction” step (Figure 2.3), more than 95% of the soluble Tc fraction is purified. The research done in this field by the CEA aims at validating the process flow sheet, which should insure a Tc recovery yield corresponding to 99% of its soluble fraction.

The PUREX experiment carried out in CBP shielded cell in April 2005 (see Section 2.1.4.1) showed that, under these conditions, Tc yield extraction was increased: more than 99% of technetium soluble fraction was extracted.

2.1.5 Separation of Am, Cm and Cs by new solvent extraction processes

2.1.5.1 Americium and curium separation

Owing to the complexity of the separation of americium and curium from the fission products – and notably from lanthanides – in the acidic high-active raffinates, three variants of the DIAMEX-SANEX process were studied until 2001 for the scientific feasibility demonstration step [2].

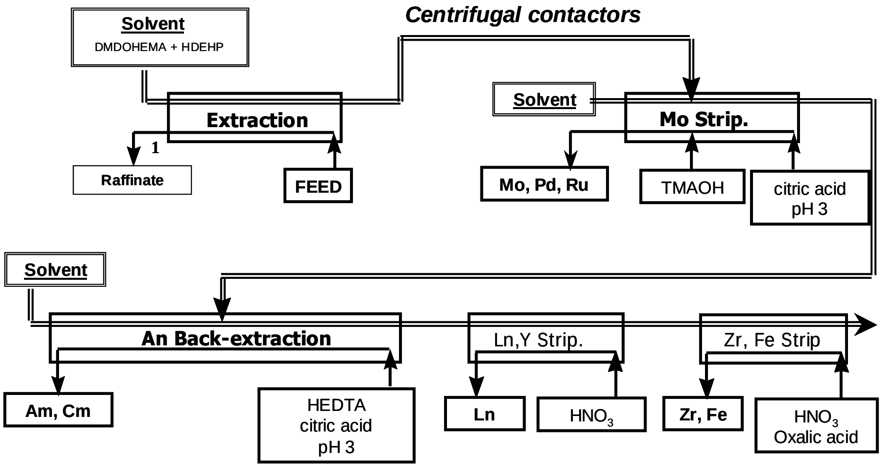
The process selected for the technological feasibility demonstration is based on:

- co-extraction of actinides and lanthanides with DMDOHEMA (DiMethyl-DiOctyl-HexylEthoxy MalonAmide), as in the extraction step of the DIAMEX process;
- followed by selective stripping of the trivalent actinides from loaded diamide solvent using an aqueous selective complexing agent;
- and finally stripping of the lanthanides.

This process allows the trivalent actinides and lanthanides to be co-extracted and separated in a single liquid-liquid extraction cycle.

The scientific feasibility of this process has been demonstrated (~99.9% An recovery yield with less than 0.3 wt.% Ln in An) by testing a flow sheet (Figure 2.4) in which the DIAMEX solvent was supplemented by an acidic extractant, diethylhexylphosphoric acid (HDEHP), to ensure effective extraction at pH > 2. A mixture of HEDTA (actinide-selective polyamino-carboxylate complexing agent) and citric acid (pH 3 buffer) was selected for selective stripping of the trivalent actinides [2].

Figure 2.4: Flow sheet of the DIAMEX-SANEX process tested on genuine solution in 2000

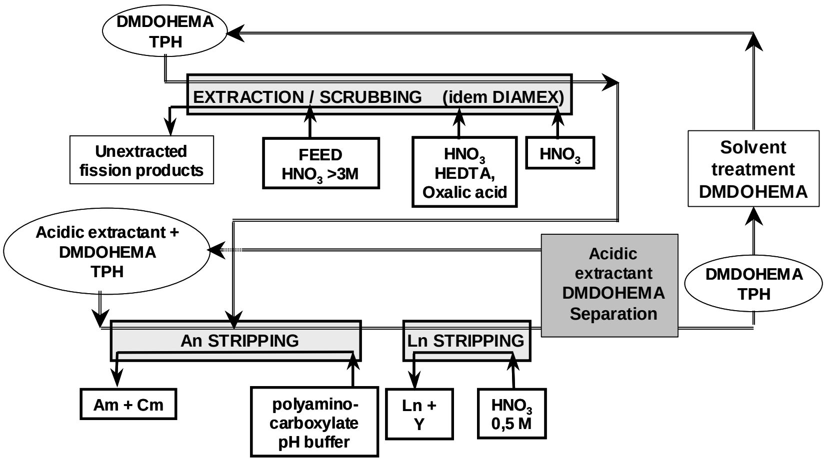


The main drawback of this flow sheet is the presence of the acidic extractant in the extraction step, and the need for additional steps (Figure 2.4) for back-extracting molybdenum, palladium and ruthenium before selectively stripping the actinides, and for back-extracting zirconium and iron after lanthanide stripping.

The process has recently been improved in order to remove these additional steps which result in large effluent volumes. This was achieved by splitting the solvent into two parts (acidic extractant and diamide in diluent) after stripping the lanthanides. The improved flow sheet is the following (Figure 2.5):

- selective co-extraction-scrubbing of actinides and lanthanides using only the diamide in an aliphatic diluent (first extraction-scrubbing step of the “classical” DIAMEX process [2]);
- selective stripping of the actinides with introduction of the acidic extractant in this step;
- stripping of the lanthanides;
- splitting of the two extractants, the diamide being recycled in the first step and the acidic extractant in the second step.

Figure 2.5: Principle of the improved DIAMEX-SANEX process flow sheet



The feasibility of this process and in particular of the two extractants separation has been demonstrated through an inactive run on simulated solution. The acidic extractant used for this test belongs to the family of dialkyl-phosphoric acids.

Nevertheless, the maturity of this new concept was insufficient to assure the success of its implementation in a large integration test planned in 2005. So, for the runs implemented in the CBP facility in the frame of technological feasibility demonstration, the separation of Am and Cm from the PUREX raffinate was performed in two steps:

- co-decontamination of actinides and lanthanides from other fission products using the well demonstrated [2,7] DIAMEX process, but now including the solvent clean-up operation (Figure 2.6);
- followed by a second step based on a simplified version (Figure 2.7) of the DIAMEX-SANEX process tested in 2000 and selected for the technological feasibility demonstration.

With regard to the DIAMEX-SANEX process (Figure 2.5), as there is no more Zr, Mo and Pd in the feed (An-Ln product solution issuing the DIAMEX process), the operations devoted to their stripping have been suppressed in this simplified version. Even more, in comparison to the original flow sheet, two new functions are added:

- acid scrubbing section at low acidity has been added to limit the acidity of the solvent at the input of the selective actinide back-extraction;
- the solvent clean-up step before recycling.

This two cycle route, although less optimised, allowed the validation of the main steps of the “improved” DIAMEX-SANEX process under development except of course the two extractants splitting step.

Figure 2.6. Flow sheet of the DIAMEX process implemented in CBP

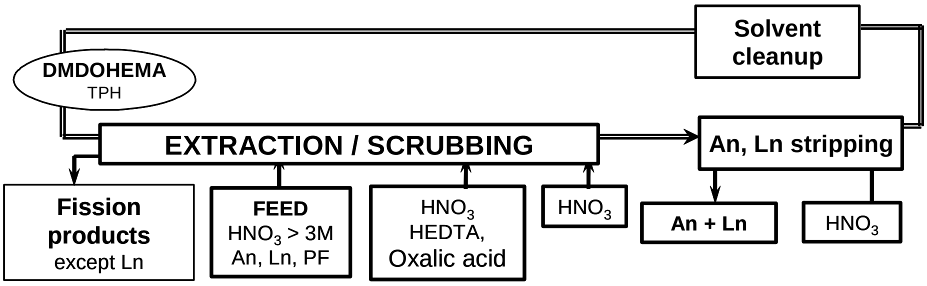
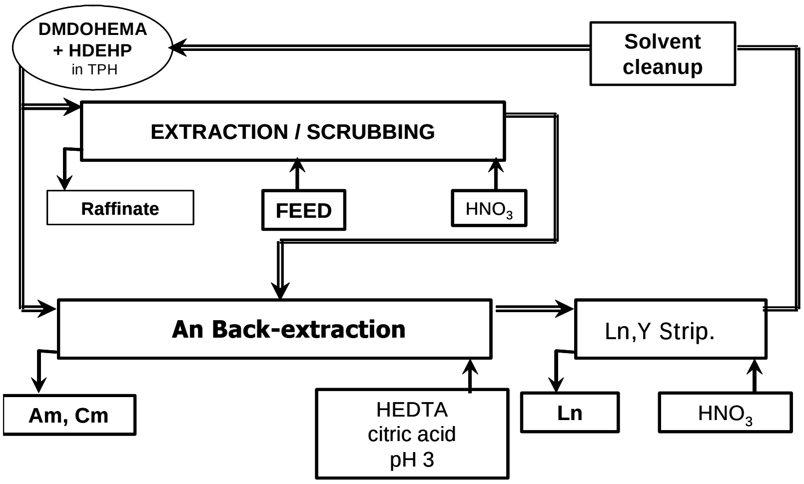


Figure 2.7. Flow sheet of the DIAMEX-SANEX process implemented



The technological demonstration test of these two flow sheets was performed for the end of 2005 (November and December respectively for DIAMEX and SANEX) in the ATALANTE facility on genuine solution issuing from the PUREX test for neptunium separation. Experimental recovery yields of americium and curium were consistent with the objectives (> 99.9%) and confirmed the results obtained in 2001 [8].

2.1.5.2 Americium-curium splitting

The process chosen for this separation is based on the difference in the affinity of the DIAMEX solvent (DMDOHEMA) for americium and curium (Am/Cm separation factor ~1.6). As this difference is relatively small, the process requires a large number of stages and the performance is sensitive to flow sheet parameters. Nevertheless, a flow sheet of this type was successfully tested in 2002 using surrogate solution without major difficulties. The test performance was consistent with the calculated values:

- 0.6% Am in the Cm product solution;
- 0.7% Cm in the Am product solution;
- 0.02% Am and 0.01% Cm in the stripped solvent.

Taking DIAMEX knowledge into account, the technological demonstration test of this process in the CBP facility on genuine solution from the DIAMEX-SANEX test, was not considered as necessary.

2.1.5.3 Caesium separation

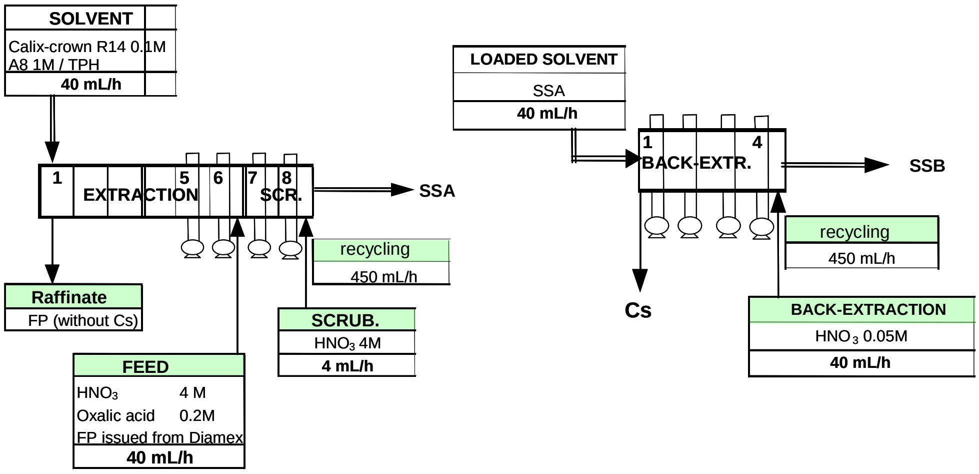
The selective separation of caesium by a solvent extraction process (CCCEX) based on the use of calyx-crown molecules has been studied at CEA Cadarache. Two tests using a genuine HA raffinate have been carried out in the ATALANTE facility on the following systems:

- 1,3 [di-octyloxy]-2,4-crown-6-calix[4]arene = 0.062 mol/L, TBP = 1.5 mol/L in TPH;
- 1,3 [(2-4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene = 0.1 mol/L, methyloctyl-2-dimethyl-butanamide = 1 mol/L in TPH.

The flow sheet tested for the second system is shown in Figure 2.8.

Excellent results were obtained with both systems (Cs extraction yield > 99%), demonstrating the scientific feasibility of the CCCEX process. Solvent degradation studies showed great stability towards radiolysis. In addition, hydrodynamic tests in a pulsed column were satisfying. So no redhibitory defect which could question the technological feasibility of this process was revealed.

Figure 2.8: Flow sheet for system 2: 1,3 [(2-4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene 0.062 M, methyloctyl-2-dimethyl-butanamide 1 M in TPH



2.1.6 Conclusion – perspectives

Several effective partitioning processes are now available to meet one of the requirements of the 1991 French high-level radioactive waste management act. The technological feasibility of the americium and curium processes (DIAMEX and SANEX in two steps) was demonstrated through the treatment of 13 kg of genuine spent nuclear fuel in the ATALANTE facility.

On 28 June 2006, a new waste management act was voted. Concerning partitioning and transmutation, the programme is now connected to fourth0generation reactors, in which transmutation of minor actinides could be operated. In this frame, the next important milestone is the evaluation of the possible transmutation roads, which are:

- minor actinide homogeneous recycling, in the whole reactor park, with a low content of MA (~3%) in the whole fuel assemblies;
- minor actinide heterogeneous recycling, in about one-third of the reactor park, with a higher content of MA (~30%) in dedicated targets put in the periphery of the reactor.

In this framework, partitioning processes developed during the first waste management act (1991-2006) are connected to heterogeneous recycling, while GANEX processes (grouped actinide separation by extraction) are connected to homogeneous recycling.

Thus, concerning DIAMEX and SANEX processes already demonstrated up to 2009, possible simplifications will be assessed. In parallel, a demonstration of the GANEX process is planned before 2009; for that, the experience gained in the course of the minor actinide partitioning can be put to use.

The next step will involve the studies necessary prior to industrial implementation of these processes.

Another additional step could be the building of a small partitioning shop (micro-pilot) dedicated to the production of fuel assemblies containing minor actinides which would be recycled in the fourth-generation prototype reactor planned in 2020.

2.2 Pyrochemical applications foreseen in France

At the outset of studies into spent nuclear fuel reprocessing, the CEA considered the non-aqueous techniques as a possible alternative to the hydrometallurgical ones, particularly in respect to cost reduction (due to their presumed compactness: limited number of conversion steps, small apparatus size). A separation process based on the fluoride volatilisation was studied up to pilot scale. When France selected in the 1970s the UOX fuel cycle coupled with a park of PWR reactors, the volatility process was abandoned for two reasons: *i)* the level of development was considered insufficient for the treatment of large quantities of spent nuclear fuels (plant capacity of ~800 T/year); *ii)* that such a process could not achieve the performance required for the separation and the decontamination of the uranium and plutonium.

Later, research and development activity in pyrotechnology has been renewed from scenarios of the French Legislative Act (30 December 1991) on Nuclear Waste Management. First, the potential of pyrochemistry to extract the minor actinides present in a PUREX raffinate had to be assessed. The inability of the non-aqueous techniques to partition minor actinides from one another (particularly americium from curium), the positive results quickly obtained in hydrometallurgy and the industrial background of the La Hague plant meant that the hydrometallurgy option was chosen as the benchmark in view of an industrial application in the medium-term.

The potential of pyrochemistry processes is now being assessed in case of transmutation scenarios involving multiple recycling of minor actinides either in homogeneous (dedicated fuels) or heterogeneous (targets) ways. Here the interest consists in the use of non-aqueous media, especially high-temperature molten salts or liquid metals; they are largely less sensitive to the influence of radiation than are organic solvents and do not act as neutron moderators. Both factors should allow the chemists to operate with a high concentration of minor actinides and with irradiated nuclear materials (targets or fuels) cooled for shorter times. Ultimately, molten salts are also of interest, finding application in the most innovative options such as the transmutation of long-lived radionuclides in molten salt reactors.

Today the interest of pyrochemistry has been strengthened with the new international initiatives on Generation IV nuclear systems, for which all the actinides should be recycled together and where cycles for treating hot and refractory fuels are expected [9].

2.2.2 Research programme

Whatever the foreseen application, a lot of questions concerning the pyrochemistry performances remain open, including: the selective access to the fissile compound, the feasibility of a quantitative grouped actinide recovery (higher than 99%) with sufficient decontamination from fission products, the development of (semi-)continuous devices (dissolution and separation) for the treatment of large capacity, the waste treatment and confinement. R&D studies are conducted at laboratory scale for answering these open questions/uncertainties. The programme originally proposed in 1999 and developed at Marcoule (ATALANTE facility) is now supported by French collaborations within the PRACTIS and GEDEPEON research groups, within the network of excellence ACTINET, by the 5th and 6th European Framework Programmes (PYROREP, EUROPART) and by international bilateral collaborations (Russia, United States and Japan).

The investigations are carried out for a better understanding of the actinide chemistry in molten salt and liquid metal media, for testing new, promising separation techniques and for comparing existing techniques with regard to the new separation and recovery constraints.

2.2.3 Main experimental results

The key question is: is there a combination – media and techniques – which allows a quantitative recovery of all (> 99%) the actinides present with sufficient fission product decontamination? With regard to chemical and physical properties (electrochemical window, chemical stability, melting point, viscosity, electrical conductivity…), the molten halides (especially chlorides and fluorides) are the most promising media and are being assessed. Among the partitioning techniques which can be considered, the electrolysis and salt/metal extraction present better selectivity than fractional precipitations.

2.2.3.1 Actinide electro-recovery assessment

Actinide partitioning from fission products and recovery using electrolysis on an inert solid cathode in LiCl-KCl at 500°C is being assessed within a collaboration with Argonne National Laboratory and the first experiments involve studies on the dependence of operating conditions (potential, current density) and system configuration (anode-cathode distance) on U and Pu recovery yields.

Alternatively, the potential of using a liquid cathode is also being assessed. Such a cathode could offer some advantages over an inert solid cathode:

- stabilisation in the deposit of actinides having a stable oxidation state (II) like americium;
- grouped extraction of actinides (curium's behaviour being unknown at present);
- scavenging of salt in the deposits not occurring;
- design of (semi-) continuous electrolysers.

Researchers from ANL proposed cadmium as a cathodic material; this allows the actinides to be recovered in the form of an ingot after the cathodic deposit has been distilled under vacuum. The feasibility of plutonium recovery on liquid cadmium was thus shown by numerous institutes [10]. A similar test on americium was done at the start of 2003 in ATALANTE [11]. This exploratory test, performed with an electrolyser implemented in a shielded cell, proved that the apparatus was well suited to studying electrodeposition mechanisms but that it was not suitable for quantitative recovery of americium; the main reasons being low current density, insufficient renewal of the salt/cadmium interface and a spread of americium electrodeposited on the various liquid cathode materials (crucible, pounder, electrical wires). The electrolyser's design must therefore be reviewed before starting new experiments for the recovery of actinides either alone or in a mixture.

An actinide/lanthanide electrolytic partitioning test (simulated by a mixture of plutonium and neodymium) on a liquid cadmium cathode was also done at the end of 2003. Its aim was to recover the plutonium in the cadmium and to assess the quantity of neodymium scavenged with the plutonium (neodymium being the most troublesome lanthanide fission product). Performed in a glove box with a LiCl-KCl-$PuCl_3$ (1.55 wt.%)-$NdCl_3$ (0.98 wt.%) solution and with a controlled potential, this test revealed that only 79% of the plutonium is recovered in the cadmium, which also contains around a quarter of the neodymium initially present in the salt. This separation performance is unsatisfactory with regard to the separation constraints required for fuel re-fabrication and recycling.

The performance of actinide (III)/lanthanide (III) partitioning on such a liquid cathode mainly depends on the affinity of the metallic solvent for actinides and lanthanides. Among metals with a low melting point, the ability to partition actinides from lanthanides would be in the following order: aluminium and gallium > bismuth > zinc > cadmium [12,13]. Of aluminium and gallium, aluminium appears promising, despite the fact that its melting point is quite high (660°C) [14]. Studies continue at ATALANTE to assess the potential of gallium (currently performed by measuring the activity coefficient of Pu and Ce in liquid Ga).

2.2.3.2 Actinide recovery by salt/metal extraction

Here the elements are selectively distributed between two immiscible phases (in general between molten salt and liquid metal). Fluoride salts were first identified as a promising salt medium (in terms of An/FP separation, from calculations on energies of formation of pure compounds). Later, in collaboration with LPTCM (Grenoble), aluminium was identified as both the most promising reducing agent and metallic solvent [15]. Since then, further investigations have been carried on in ATALANTE and the feasibility of (Pu, Am) separation from lanthanides (Ce, Sm) has been successfully demonstrated in LiF-AlF_3/AlCu system at 830°C [16]. This process offers the potential for a grouped actinide recovery and sufficient separation from fission products.

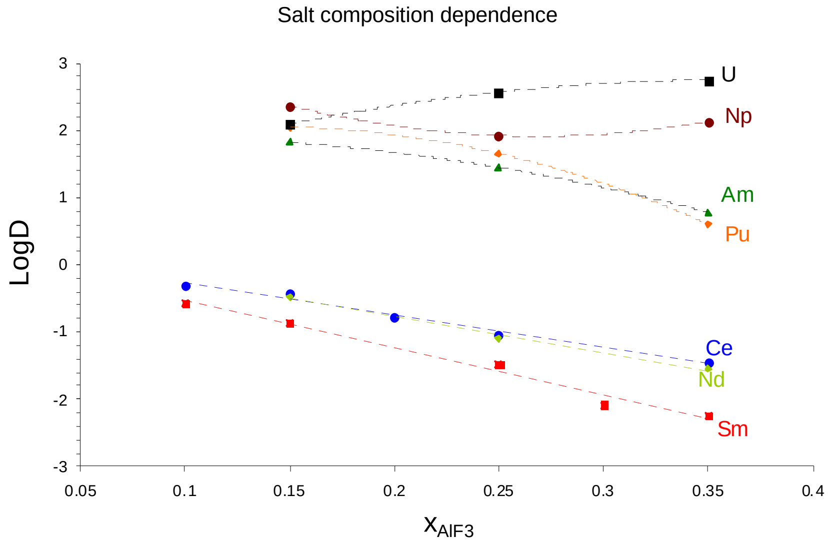
2.2.3.3 Integration studies

A preliminary process flow sheet based on fluoride salt/metal extraction has been proposed for the treatment of oxide nuclear material (fuel or target). It could then be adapted to carbide material by adding an oxidation step for converting carbide into oxide. The process involves the following main steps: mechanical treatment of spent nuclear material for cladding and matrix removal, thermal treatment for volatile fission product removal, dissolution in LiF-AlF_3 salt by hydro-fluorination, platinum group metal fission product digestion, actinide/lanthanide separation using liquid Al-based alloys, recovery of actinides as oxides, recycling of both salt and metallic phases and fission product fluoride immobilisation (in glass).

2.2.3.4 Actinide recovery

Experiments related to the measurement of distribution coefficients of U and Np in LiF-AlF_3/AlCu system at 830°C have also been performed. The results for all the actinides (U to Am) are shown in Figure 2.9.

Figure 2.9: Actinide and lanthanide partitioning in LiF-AlF_3/AlCu (78-22 mol%) system at 830°C



Two remarks can be drawn from this graph: *i)* two separate groups are clearly identified, the actinide group (U to Am) and the lanthanide group; *ii)* the distribution value of the first group is significantly higher than that of the second one. This proves the scientific feasibility of the co-extraction of actinides.

The results have been confirmed by one demonstration experiment performed in the ATALANTE facility. In this, a molten AnF_3-LnF_3-LiF-AlF_3 mixture wherein the {AnF_3+LnF_3} loading was 15 wt.% was contacted with fresh Al-Cu alloy. After mixing of both phases (initial melt/alloy weight ratio ~1, Pu/Ln ~3), the results were:

- Distribution coefficients (DM) for Pu and Am are 197±30 and 144±20 respectively.
- The recovery yields for both Pu and Am are about 98.5 wt.% in one contact.
- Separation factors: SPu/Ce = 1 307±308, SPu/Sm = 3 177±760, SPu/Eu > 15 000 and SPu/La > 3 000.

The high An/Ln separation factors (for U to Am) clearly demonstrate the interest of pursuing investigations on Cm/Ln separation assessment. A high-temperature salt/metal contactor suitable for tele-manipulators has been constructed and will be used for tests in a shielded cell on all actinides (U to Cm). The study of the removal of platinum group metal fission products in a front-head salt/metal extraction is also underway.

2.2.3.5 Apparatus development and waste confinement studies

The main salt properties pertinent to molten salt apparatus development are the density, viscosity and surface and interfacial tensions. Some measurements of surface and interfacial tensions are currently being performed by methods based on drop detachment; the drop volume depends on surface tension for gas-liquid system, and on interfacial tension for liquid-liquid system. Experiments have begun with room temperature systems and will be adapted for 800-900°C. Investigations on LiF-AlF_3 salt recycling could be under consideration in the near future. Finally, direct fluoride immobilisation into glass at up to 15 wt.% has been proven at laboratory scale [17].

2.2.4 Conclusions and prospects

The Nuclear Energy Division (DEN) of the French Atomic Energy has identified two possible future applications of pyrochemistry in the civil nuclear industry: *i)* the reprocessing of irradiated targets or dedicated fuels arising from minor actinide transmutation (if multiple recycling is considered); *ii)* the reprocessing of Generation IV fuels (all actinide recycling). Consequently, CEA/DEN launched an R&D programme in 1999 to provide a general overview of the potential of these processes with regard to various assessment criteria (separation performance, chemical engineering, operating conditions, waste treatment).

For An/FP separation, the CEA first assessed the electrolytic recovery on liquid cadmium in molten LiCl-KCl at 500°C. As U and Pu electro-recovery on liquid Cd had already been studied, CEA focused its attention on americium electro-recovery. Several runs of Am electro-depositions on liquid cadmium have been performed in LiCl-KCl eutectic. Cadmium was shown to be inappropriate with regard to the separation constraints required for fuel re-fabrication and recycling. Other metallic solvents (like gallium) are considered to be potential liquid cathode materials.

In parallel, the CEA proposes salt/metal extraction as a possible main An/FP separation step. Fluoride salts have been identified as promising salts (in terms of An/FP separation). The biphasic system LiF-AlF_3/AlCu seems to be an interesting route for operating a grouped actinide recovery with sufficient decontamination from the more troublesome fission products (lanthanides). Pu-Am co-extraction has been demonstrated at laboratory scale with promising results: actinide recovery yield of more than 98% in one stage, An/Ln separation factors higher than 1 000. A preliminary process flow sheet based on fluoride salt/metal extraction has been proposed for the treatment of oxide nuclear material (fuel or target). This could be adapted to carbide material (Gen-IV fuel candidate for gas-cooled fast reactor) by adding an oxidation step for converting carbide into oxide.

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Chapter 3: Italy

In the framework of the management of nuclear wastes, treatment methods have received particular attention and research efforts have been addressed to both consolidated methods and "new" systems for separation and recycle of the very-long-lived radioactive transuranic elements. Actually high-level waste volume from the pyroprocesses is lower than that from either the direct disposal of spent fuel or from conventional PUREX-type reprocessing. So, together with traditional hydrometallurgical processes, electrorefining of spent fuel has been under consideration in recent years. Such activities are performed as part of collaborative projects, with both European and international institutions.

3.1 Hydrometallurgy

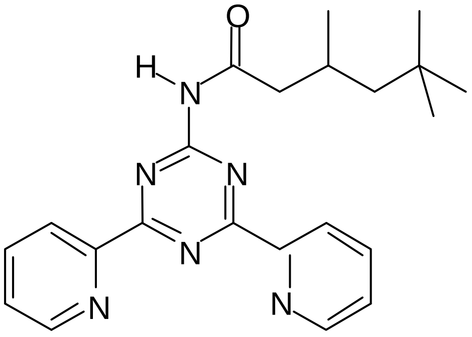
Reprocessing of spent nuclear fuels produces a noticeable quantity of high-level liquid waste (HLLW). Nowadays, the common strategy employed to minimise the radiological risk for the environment is the vitrification of the HLLW. The glass is then stored indefinitely in a deep underground repository. It is well known that the most important contributors to the long-term radiotoxicity of the vitrified HLLW are the so-called minor actinides (MA), which are neptunium, americium and curium. Therefore, a strategy which takes into consideration the selective removal of these MA from the HLLW before the vitrification process seems to be a huge improvement upon the current strategy. In fact, it is well known that the long-lived minor actinides could be transmuted in order to produce stable and short-lived fission products.

The aqueous waste which results from the PUREX process is used to extract uranium, plutonium and neptunium from the liquor obtained by dissolving the spent fuel in a concentrated solution of nitric acid. The waste has a very complex composition: americium and curium are the minor elements, and fission product and lanthanide content is quite high. Then, the separation procedure must be very selective for the elements of interest. The strategy uses a liquid-liquid extraction process to selectively remove the trivalent MA. Some organic extractant mixtures containing diamide molecules have already been successfully tested. This so-called DIAMEX process (DIAMide EXtraction) can generate a mixture of trivalent MA (Am and Cm) and lanthanides [Ln(III)], separated from the other fission products. The extraction process employs a tri-synergistic organic extractant mixture and a centrifugal contactor battery of eight stages.

The principle of hard and soft nucleophiles and electrophiles states that hard (soft) molecules react preferentially with hard (soft) ions. A hard nucleophile is characterised by a low-energy High Occupied Molecular Orbital (HOMO) and usually by a negative charge; on the other hand a soft nucleophile has a high-energy HOMO but does not necessarily have a negative charge. Hard and soft electrophiles are defined on the basis of the energy of the Lowest Unoccupied Molecular Orbital (LUMO), which is a high-energy orbital for the hard ones, and for the presence or absence of any positive charge.

Based on this principle, the partitioning of actinides from lanthanides can be accomplished if extractant molecules containing soft centres, as N atoms instead of O atoms, are used. Then, a molecule with many soft centres is a good molecule for the selective partitioning of actinides in an aqueous waste issued from the PUREX and DIAMEX processes. The triazine BADPTZ (Figure 3.1) was used as N-polydentate ligand chosen to achieve the An(III)/Ln(III) separation, while alpha-cyanodecanoic acid (α-CNC_{10}, Figure 3.2) was used as a "carrier" molecule from the aqueous phase of the elements of interest and the diamide C_{14} (Figure 3.3) was added into the organic phase to avoid third phase formation. This process is called SANEX (Selective ActiNides EXtraction). The three organic molecules were dissolved in an aliphatic solvent, the TPH (a ligroin-like solvent), in order to obtain the desired concentration, and then contacted counter currently with the aqueous waste in a centrifugal contactor battery of eight stages.

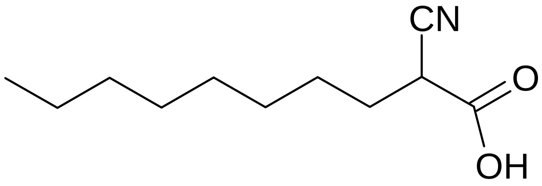
Figure 3.1: Molecular structure of the triazine BADPTZ



4,6-Di-(pyridin-2-yl)-2-(3,5,5-trimethyl-hexanoylamino)-1,3,5-triazine

BADPTZ

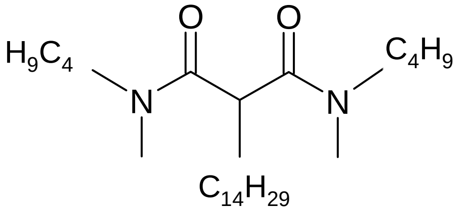
Figure 3.2: Molecular structure of the α-CNC_{10} acid



α-cyano-decanoic acid

$\alpha - CNC_{10}$

Figure 3.3: Molecular structure of the diamide C_{14}

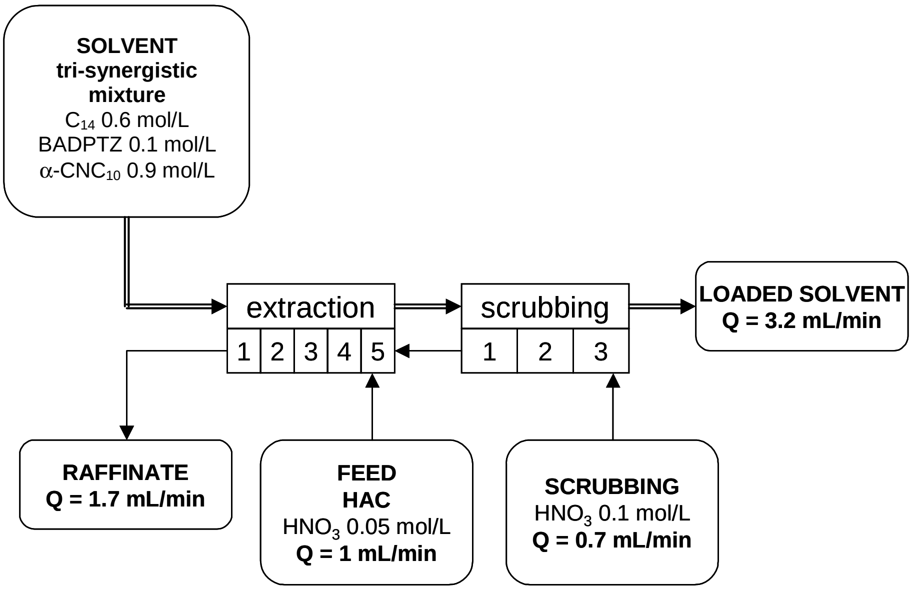


N,N'-dimethyl-N,N'-dibutyl-tetradecyl-malonamide

C14

The composition of the solvent of this tri-synergistic SANEX process was: 0.1 M BADPTZ, 0.9 M α-CNC_{10}, and 0.6 M C_{14}, in TPH. A bank of eight CCs was installed in a glove box at ENEA Saluggia laboratories for testing the process using synthetic spiked solutions. As only eight CCs were available, a simplified flow sheet was designed at Politecnico of Milan, including five stages dedicated to the extraction phase and the remaining three to the scrubbing phase. The flow sheet of the SANEX tri-synergistic process tested is presented in Figure 3.4.

Figure 3.4: SANEX tri-synergistic process flow sheet



The decontamination factors for "cold" lanthanides are determined in a similar way by ICP-OES, by comparing the initial concentrations with those found at the final stage of the battery after an exactly measured elapsed time. More tests have been carried out and each test was performed on the basis of the results obtained with batch simulations, which gave the optimal values for the acidity of the aqueous solution and for the concentration of the organic molecules, supporting them with a computer code simulation in order to optimise the most suitable general flow sheet. The computer program utilised to simulate the operation of the centrifugal contactor battery is FORTRAN based and uses, as input data, the measured values of the trivalent metal ions distribution ratios to calculate the best operating conditions (flow rates, acidity and composition of the ingoing phases) as a function of the desired decontamination factors.

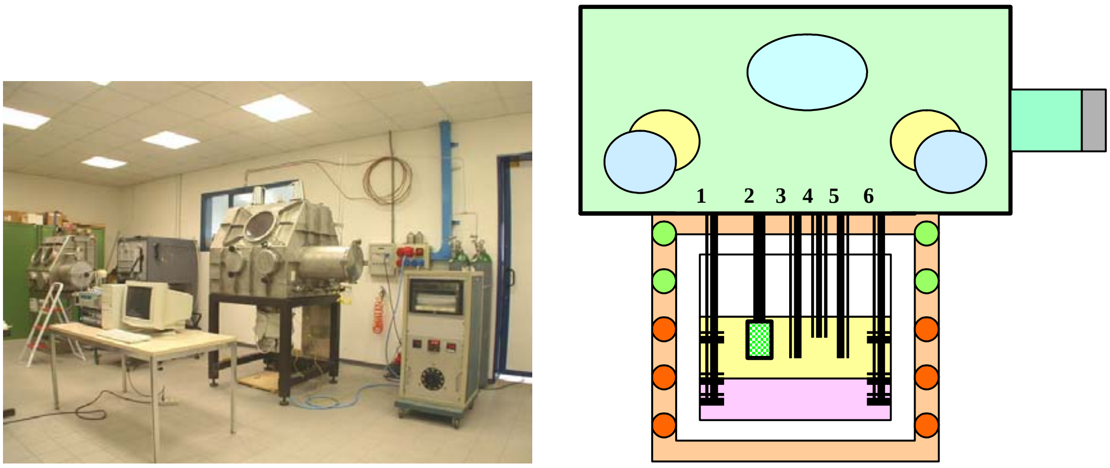
The results obtained clearly show the possibility to achieve good partitioning of the MA even if they are only minor elements in the liquid waste issuing from the reprocessing of spent fuel elements. Moreover, the centrifugal contactor battery is a fully automatic extraction system which can be considered suitable for future industrial application. Eight stages for a centrifugal contactor battery seem insufficient to determine a suitable decontamination factor. The same can be said for the tri-synergistic extractant mixture; more studies must be done so as to obtain a better chemical stability.

3.2 Pyrometallurgy

Concerning partitioning, main efforts are presently devoted to pyrometallurgy. Electrorefining is the key step in the pyroprocess, which is the process for recovery of actinides (uranium and transuranic elements) by using electrochemical differences among elements in molten LiCl-KCl salt and liquid cadmium (or bismuth) under a high-purity argon atmosphere at 773 K [1]. Chopped spent fuel segments are placed in a perforated steel anode basket and lowered into the electrolyte salt. Noble metals are left in the anode basket in metal form. The other elements are dissolved into the salt in the form of their chlorides. Actinides are recovered at two different cathodes: a solid steel cathode, at which almost pure uranium is collected; a liquid-cadmium (or bismuth) cathode, at which plutonium chloride is reduced and collected with uranium, other transuranic elements, and a small amount of rare-earth fission products. Chemically more active elements (alkali-metal, alkaline-earth, and rare-earth elements) remain in the salt.

A pilot plant known as Pyrel II (Figure 3.5) has been installed at ENEA Brasimone laboratories for pyrochemical process studies under inactive conditions. The general aim of the work with this facility is to obtain experimental data for the characterisation of process parameters and for the comprehension of the process itself, in order to improve the performance of industrial scale electrorefiners. This

Figure 3.5: General view of the Pyrel II plant (left); schematic of the electrorefiner (right) equipped with two paddle-shaped stirrers (1, 6), fuel dissolution basket (2), solid steel cathode (3), reference electrode (4), and thermocouple guiding tube (5)



target should be achieved through a modelling program, which will allow obtaining data suitable to both understand the phenomena which take place and to make previsions about the behaviour of an ER under different experimental conditions, namely different fuel compositions, accumulation of fission products, and so on.

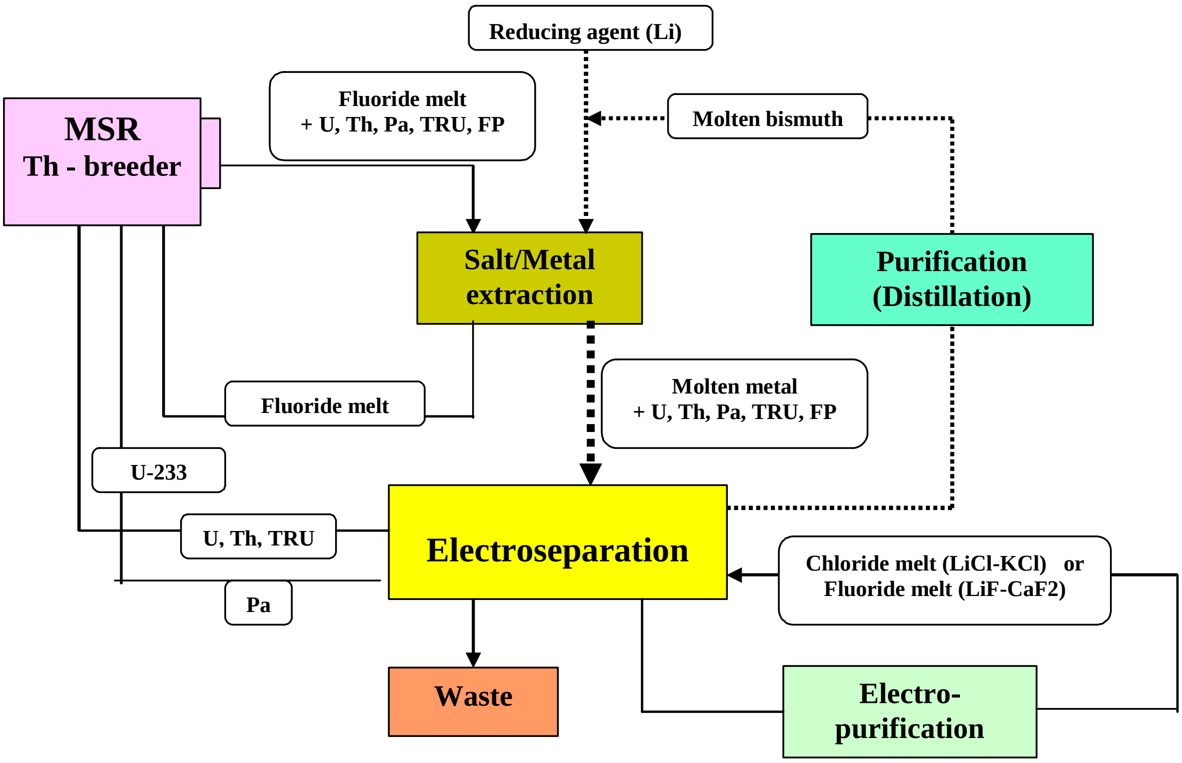
The tests performed up to now confirm the reliability of the Pyrel II plant in terms of conducting experimental campaigns aimed at understanding the kinetics of the processes involved, as well as at evaluating the performance of the electrorefiner according to the different operating modes: direct transport, anodic dissolution, direct dissolution, deposition at both solid and liquid metal cathodes and salt clean-up.

Another plant, termed Pyrel III, for experiments with radionuclides is being commissioned and will be installed and operated at ENEA Casaccia laboratories presumably within 2008. In particular, the activities with the new plant – related to the molten salt reactor technology – will be conducted in an electrorefiner with uranium, thorium and fission products dissolved in liquid bismuth and separated by electrodeposition at a cathode, through an electrolyte made of a chloride salt (LiCl-KCl eutectic mixture, Figure 3.6.).

Within the realm of pyroprocess studies, experimental activities are also under way concerning the conditioning of chloride salt wastes through synthesis and characterisation of suitable matrices. Presently the research efforts are focused on sodalite, a naturally occurring mineral which contains chlorides. Studies about exchange reactions of sodalite with both alkaline and alkaline-earth metal ions, as well as synthesis of a pure sodalite mineral with microwaves are under way. Pollucite, a naturally occurring mineral which contains caesium, is also being studied and characterised as a matrix for containment of caesium ions.

An experimental programme for decontamination of fluoride salts (LiF-CaF_2 eutectic) containing fission products in the frame of studies on molten salt reactors, is also envisaged.

Figure 3.6: Block diagram related to the on-line reprocessing of fuel from a molten salt reactor (MSR-Th breeder)



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Chapter 4: Japan

In Japan the LWR spent fuel (SF) reprocessing technology and the FBR-SF reprocessing technology have been developed. At the Tokai Reprocessing Plant (TRP: 0.7 t-HM/d), approximately 1 023 t-HM of LWR-SF have been reprocessed. Original Japanese technologies have been developed through a wide experience of this operation, which have been transferred to the Rokkasho Reprocessing Plant (RRP: 800 t-HM/y). At RRP, the final confirmation test (the so-called Active Test) is being carried out.

The Japan Atomic Energy Agency (JAEA) initiated the "Feasibility Study on Commercialised Fast Reactor (FR) Cycle Systems" (FS) with related companies and institutes in Japan in July 1999, in order to establish the future FR cycle systems that can achieve the targets of economic competitiveness, reduction of environmental burden, enhancement of nuclear non-proliferation, etc. A wide range of advanced technical options for the FR fuel cycle system (reprocessing and fuel fabrication) was evaluated to select several promising concepts as candidates for commercialisation. In March 2006, the outcomes of the Phase II study of the FS concluded that the advanced aqueous reprocessing system with oxide fuel was the most promising concept for the fuel cycle system. The alternative was determined to be the pyrochemical reprocessing system with metal fuel.

Along with the development of these systems, basic and fundamental research and development of partitioning technologies are promoted, which are expected to produce innovative scientific knowledge and technologies. Innovative partitioning technologies are also studied within the framework of partitioning and transmutation (P&T) technologies.

4.1 Aqueous processes

For the advanced aqueous reprocessing system for the FBR-SF reprocessing, the New Extraction System for TRU Recovery (NEXT) process is being developed. Along with the development of the NEXT process, JAEA also proposes alternative partitioning technologies that are expected to be the options for the NEXT process, considering reduction of the risks for development and future improvement of performance.

4.1.1 NEXT process

The NEXT process consists of partial recovery of U by a crystallisation of uranium nitrate hexahydrate from dissolver solution, U-Pu-Np co-recovery by a solvent extraction with single cycle flow sheet 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 4.1.

4.1.1.1 Crystallisation of U

The crystallisation process is the first treatment for the spent fuel dissolver solution in the NEXT process. The selective crystallisation of U in the spent fuel dissolver solution is theoretically possible due to the temperature dependence of the solubility of uranyl nitrate hexahydrate (UNH) crystal into HNO_3. More than 70% of U in the solution can be recovered prior to the following solvent extraction process; further, this process can reduce the solution and solvent. Figure 4.2 shows a continuous crystallisation apparatus (2 kg/h) and obtained UNH crystals.

Figure 4.1: Schematic flow of the NEXT process

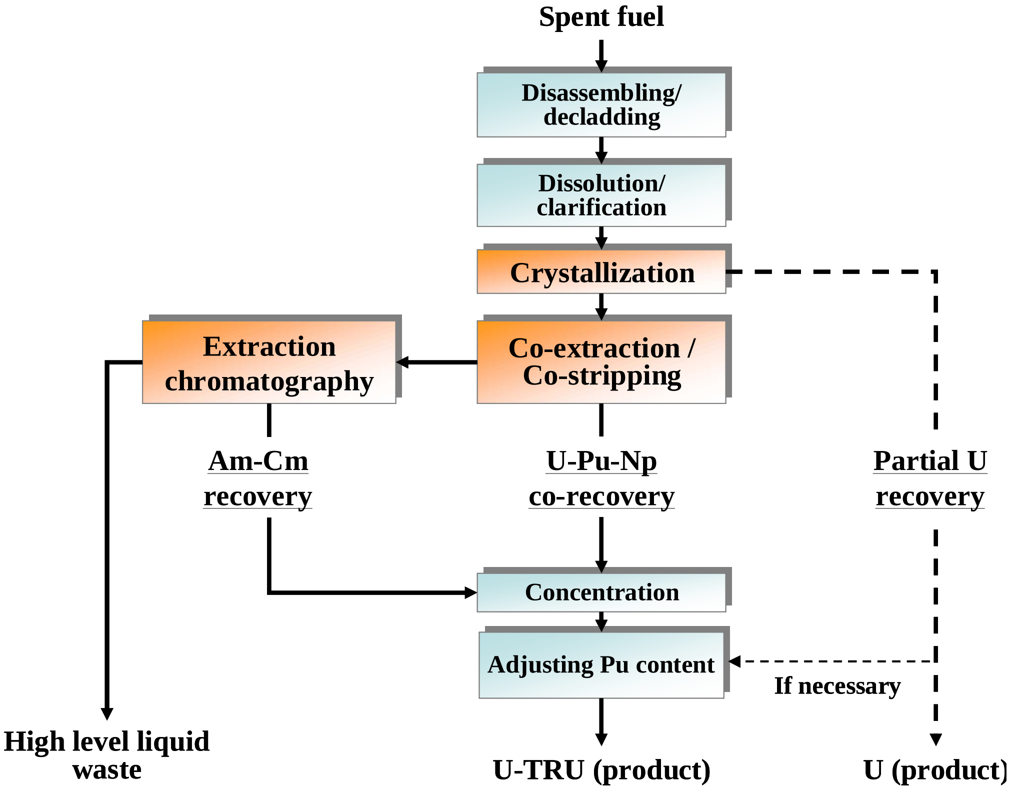


Figure 4.2: Continuous crystallisation apparatus and obtained UNH crystals

One of the main obstacles to the ideal crystallisation is the co-crystallisation of Pu and FP with U which leads to low decontamination factor (DF). The crystallisation experiment using a dissolver solution of FBR MOX fuel showed that the crystallisation behaviour of Pu was dependent on the valence of Pu in the dissolver solution; Pu(VI) is co-crystallised with U whereas Pu(IV) remains in the dissolver solution. The adjustment of the Pu valence to Pu(IV), therefore, is an important means of preventing the co-crystallisation of Pu with U [1,2].

Recent studies suggest that some fission products have the possibility of making double nitrate with Pu(IV), which can be crystallised under certain conditions. The elucidation of such a mechanism of some FP and development of the purification process for UNH crystal contaminated with FP are in progress.

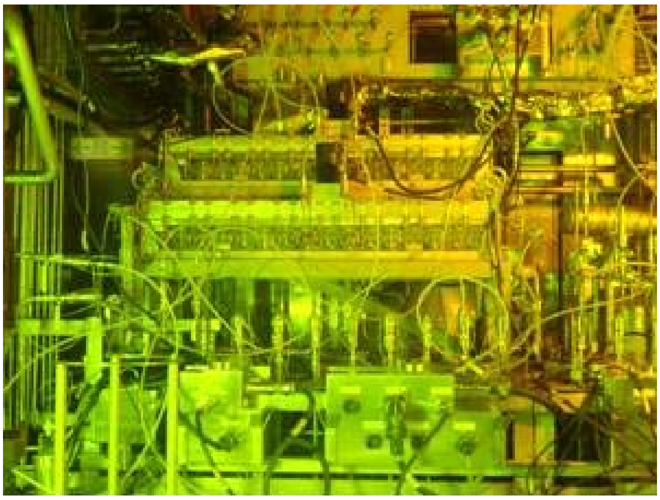
4.1.1.2 Co-recovery of U-Np-Pu

The solvent extraction with single cycle flow sheet using TBP is applied to the dissolver solution (mother solution) from the crystallisation process to recover (extract and strip) U, Pu and Np simultaneously. In the extraction section of the U-Np-Pu co-extraction, it is very important to control the valence of Np for its effective extraction. The formation of UNH crystal in the crystallisation process brings comparatively higher nitric acid concentration in the mother solution (feed solution) than the conventional PUREX process. This condition is quite favourable for the oxidation of Np to extractable Np(VI) [3].

Uranium, Np and Pu loaded into the solvent are co-stripped in the stripping section by diluted nitric acid solution without any reductants. This process requires that the temperature be carefully controlled and the flow rate be optimised in the stripping section to prevent the leakage of these elements to the used solvent and to decrease the liquid volume (waste volume) in the process to control [4].

Taking account of these characteristics of the process, several counter-current experiments were carried out using the dissolver solution of FBR MOX fuel as the feed solution. These experiments showed that co-recovery of U-Np-Pu with sufficient DF can be achieved under appropriate conditions. Figure 4.3 shows the centrifugal contactor bank for U-Np-Pu co-recovery experiment in a hot cell at the Chemical Process Facility (CPF), JAEA.

Figure 4.3: Centrifugal contactor bank for U-Np-Pu co-recovery experiment



4.1.1.3 Recovery of Am and Cm

In the last decade, JAEA has developed a solvent extraction process called Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO-complexant System (SETFICS) for the recovery of Am and Cm, which utilises CMPO for MA/Ln extraction and DTPA for MA/Ln separation. Although MA elements were successfully recovered by the SETFICS process, several drawbacks, such as low efficiency, must be overcome to elaborate a commercially available flow sheet.

As an alternative to SETFICS, the extraction chromatography technique was proposed; this process uses silica-based extraction resin in which various extractants can be embedded and immobilised [5,6]. Extraction chromatography is superior to SETFICS with respect to the amount of waste and economical load. Separation experiments using CMPO-embedded resin demonstrated the excellent ability of the extraction chromatography, and various extractants have been developed and proposed for the MA/Ln separation process.

The leading tasks of the extraction chromatography are completion of the flow sheet, design study, manufacturing and operation of the engineering-scale apparatus and safety managements considering heat and gas generations in separation columns. Research and development for those subjects are under way.

4.1.2 Development of innovative extractants and adsorbents

New extractants called branched-alkyl monoamide (BAMA) and N,N,N′,N′-tetraoctyl-diglycolamide (TODGA) have been developed for uranium separation and all TRU separation, respectively. One of the advantages of the process is to use phosphorus-free compounds consisting of carbon, hydrogen, oxygen and nitrogen (CHON principle) to reduce the waste from the process [7]. Basic experimental data for these extractants have been accumulated thus far. Basic study is also under way to separate Am and Cm from the rare earths and to separate Sr-Cs from the solution.

The research and development effort on partitioning is presently concentrated on development and improvement of innovative extractants and adsorbents as the elemental technologies. Molecular modelling, quantum chemistry, radiation chemistry and structural studies on extractants and f-element complexes have also been investigated for the research and development of new extracting molecules for separation of actinides and long-lived fission products.

4.1.2.1 Selective extraction of U

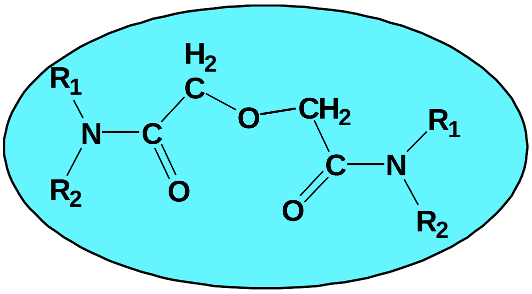
N,N-dialkylamides have some advantages, *e.g.* their complete incinerability (CHON principle) and high stability for hydrolysis and radiolysis. Furthermore, N,N-dialkylamides are beneficial to control its reaction nature, *i.e.* extractability and selectivity by modifying its alkyl groups attached to carbonyl carbon and/or amidic nitrogen atoms. For exclusive separation of uranium, which is the major element of spent nuclear fuel, some of BAMA were originally designed and synthesised to discriminate actinide(VI) ions from the other valence state ions, especially the actinide(IV) ion. The BAMA extractants having bulky alkyl group attached to carbonyl carbon have large steric hindrance on the co-ordination with actinide ions, which results in a higher distribution coefficient for U(VI) than that of Pu(IV) [8].

It was found through the experiments that N,N-di-(2-ethyl)hexyl-2,2-dimethylpropanamide (D2EHDMPA), N,N-di-(2-ethyl)hexyl-2-methylpropanamide (D2EHMPA) and N,N-di-(2-ethyl)hexyl-(2-ethyl)hexanamide (D2EH2EHA) as the BAMA extractants can separate U(VI) effectively from Pu(IV) in 3 M nitric acid solution, with large separation factors. Fission products (Sr, Zr, Ru, Rh, Pd, Ba, Nd, Mo, Ce and Tc) and minor actinides (Am and Cm) were not extracted under the same experimental conditions. From extraction behaviour of Np, D2EHDMPA can extract and separate U(VI) from Np(VI) without reduction of Np(VI) to Np(V) or Np(IV).

4.1.2.2 Total recovery of TRU

During the course of the studies on the modification of a bidentate malonamide, JAEA proposed TODGA for the recovery of long-lived actinide ions. TODGA has several advantages, *i.e.* high distribution coefficients for actinide(III) and actinide(IV) ions from concentrated nitric acid to n-dodecane, high stability in aliphatic diluents, CHON compounds and easy synthesis. Moreover, the lipophilic and hydrophilic properties of diglycolamide (DGA) compounds can be changed by modifying its alkyl groups attached to amidic nitrogen atoms. The molecular structure of DGA is shown in Figure 4.4.

Figure 4.4: Molecular structure of DGA



The extraction of various metal ions by TODGA from nitric acid to n-dodecane was studied. The distribution coefficients measured show that Ca(II) (ionic radius, 100 pm), trivalent and tetravalent ions with ionic radii of 87-113 pm and 83-94 pm are highly extractable by TODGA [9].

In order to evaluate the extraction capacity in extraction solvent using DGA compounds, the limits of metal concentration (LOC) were measured for Ca(II), Nd(III) and Zr(IV) but their LOC values were lower than the stoichiometric values. DGA compounds with longer alkyl groups, *i.e.* N,N,N′,N′-tetradecyl-diglycolamide (TDDGA) and N,N,N′,N′-tetradodecyl-diglycolamide (TDdDGA), and the modifier of solvent, N,N-dihexyl-octanamide (DHOA), were examined to improve the LOC value. LOC increased with the length of alkyl chain attached to nitrogen atoms of DGA and with DHOA concentration.

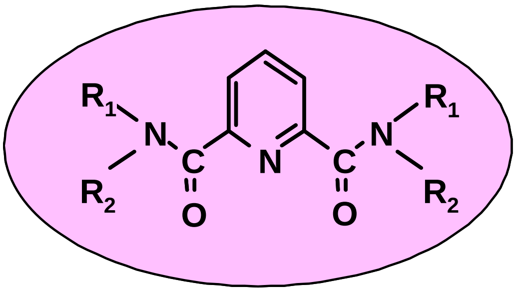
4.1.2.3 Separation of MA and rare earths

Separating trivalent actinides [An(III)] from rare earths or lanthanides [Ln(III)] has been one of the most challenging issues because of their similarity in terms of chemical properties. One promising approach for separating An(III) from Ln(III) is to use soft-donor ligand based on its preferable co-ordination to softer An(III). Nitrogen-containing heterocycle-based multidentate ligands have been presently attracted by their combustibility.

It was found that some separation systems which employ N,N,N′,N′-tetrakis(2-methylpyridyl)-ethylenediamine (TPEN) have high separation factors of An(III)/Ln(III), $SF_{(An/Ln)}$ [10]. Furthermore, two new ligand systems were designed, which are expected to efficiently separate An(III) from Ln(III). The one is an “oligo-pyridine” ligand containing multiple pyridines and the other is a “chirality-controlled” ligand containing chiral centres in the ligand. More than thirty ligands were synthesised, among which twelve ligands were found to have the ability to separate An(III) from Ln(III) with $SF_{(Am/Eu)} > 10$.

Work is under way to develop new ligands which have sufficiently high stability for hydrolysis and radiolysis, high lipophilicity, and sufficient extractability and selectivity in nitric acid. As an example, on the basis of the results concerning the extraction of An(III) and Ln(III) by N,N′-dimethyl-N,N′-diphenylpyridine-2,6-dicarboxyamide (DMDPhPDA) which extracts An(III) more selectively than Ln(III) from HNO_3 solution [11], an investigation is being made on some pyridine dicarboxyamide (PDA) compounds by modifying its alkyl groups attached to amidic nitrogen atoms. The molecular structure of DGA is shown in Figure 4.5.

Figure 4.5: Molecular structure of PDA



4.1.2.4 Separation of Sr-Cs

On the basis of the development of a four-group partitioning process, a column-adsorptive separation of Sr-Cs is studied, as a simple and economical technology. The development of selective adsorbents, which can adsorb Sr and/or Cs under high nitric acid concentration, is quite important in this study.

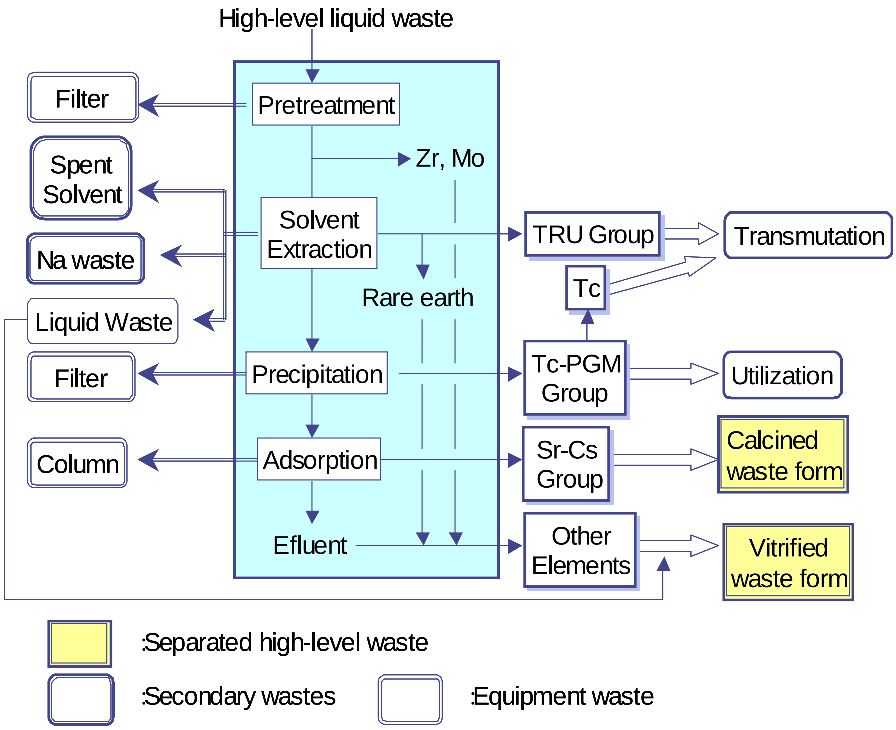
It was found that novel tantalum-based inorganic adsorbents, sodium-tantalum-silicon and sodium-tantalum-titanium mixed-oxides prepared by hydro-thermal synthesis, are highly Cs-selective against proton and stable in a nitric acid solution [12].

It is also anticipated that novel selective adsorbents can be prepared by impregnating selective extractants onto supporting materials. Thus, the study of innovative adsorbents was started, using porous silica-based material (composite with macro reticular-type polymer) as a non-conventional support (lower content of organics compared to conventional polymer supports), crown-ether for Sr (di-t-butylcyclohexano-18-crown-6, for example) and calix-crown for Cs separation (1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene, for example) as selective extractants [13].

4.1.2.5 Four-group partitioning process

As the partitioning part of the P&T technology based on the double-strata fuel cycle concept is described below, we address here the four-group partitioning process which has been established over the past decade [14]. In this concept, HLW exhausted from reprocessing plants is partitioned into four groups: TRU, Sr-Cs, Tc-platinum group (PGM) and the other elements. A schematic of the four-group partitioning process is shown in Figure 4.6.

Figure 4.6: Schematic of the four-group partitioning process



TRU is transmuted in ADS. Sr-Cs is contained in calcined waste forms and is to be disposed of in a compact manner after a certain period of cooling and/or utilisation as a heat source. Tc-PGM can be utilised as catalysts or disposed of. The other elements can be disposed of as glass waste forms which no longer have intense heat sources or strong long-term radiological toxicity.

To demonstrate the feasibility of the process, process tests using real liquid waste were conducted for the pre-treatment step, the extraction step by diisodecylphosphoric acid (DIDPA) for TRU separation, the precipitation step through denitration for Tc and PGM separation, and the adsorption step with inorganic ion exchangers for Sr and Cs separation. It was shown that targeted performance was achievable and no major problem arose during the process operation [15].

4.2 Pyrochemical processes

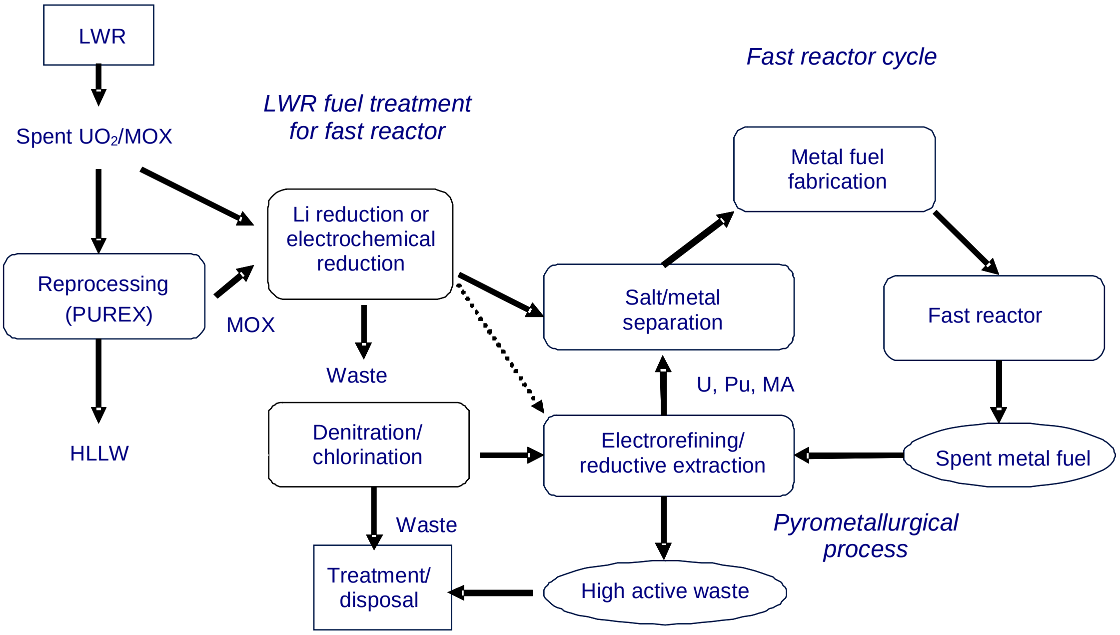
Development of pyrochemical technologies for irradiated fuel processing in Japan is being pursued by the Central Research Institute of Electric Power Industry (CRIEPI) and the Japan Atomic Energy Agency (JAEA).

4.2.1 CRIEPI

In Japan, CRIEPI is taking part in the feasibility study (FS) for the development of a fast reactor and fuel cycle system and in the OMEGA programme, which involves long-term research and development on partitioning and transmutation (P&T) technology. Under these programmes, CRIEPI's work is focused on the research and development of pyrometallurgical process technology for the metal-fuelled fast breeder reactor (FBR) cycle and on the pyrochemical partitioning of transuranium elements from high-level liquid waste (HLLW) resulting from PUREX-type reprocessing, which could contribute to reducing long-term radiotoxicity of transuranium elements. The chemical reduction or electrochemical reduction of oxide fuels is introduced to treat irradiated oxide fuels from LWR for subsequent treatment by pyrometallurgy.

The system proposed by CRIEPI is shown in Figure 4.7 [16]. The objective is to establish an advanced nuclear fuel cycle featuring environmental safety and strong non-proliferation attributes, as well as an economic advantage. Near full recycle of actinides is achieved and no complete separation of plutonium from other actinides takes place. For application of pyrometallurgy to HLLW, the nitrate solution or slurry must be converted to oxides and then chlorides. For chemical reduction of oxides, lithium is a possible reagent. The electrochemical reduction should be another potential device for reduction.

Figure 4.7: CRIEPI pyrochemical process for the recycle of actinides



Collaboration with JAEA, Kyoto University and overseas institutes (DOE/Argonne National Laboratory, University of Missouri, AEA Technology and the Institute for TransUranium Elements) is exploited to accumulate experimental data with actinides.

4.2.1.1 *Thermodynamic properties*

The study of pyrometallurgy at CRIEPI was undertaken in 1980. Following the measurement of thermodynamic properties of lanthanides in a LiCl-KCl/Cd system, the electrochemical potentials of U, Pu, Np and Am were measured in a cell of M/MCl_n,LiCl-Cl//AgCl,LiCl-KCl/Ag as a function of the molar fraction of MCl_n in LiCl-KCl [17]. Applying the Nernst equation to measured data gave the standard potentials of actinides and lanthanides. Knowledge of these potentials is necessary for precise prediction of the separation of actinides from lanthanides, which are chemically very similar.

4.2.1.2 *Separation of actinides from lanthanides*

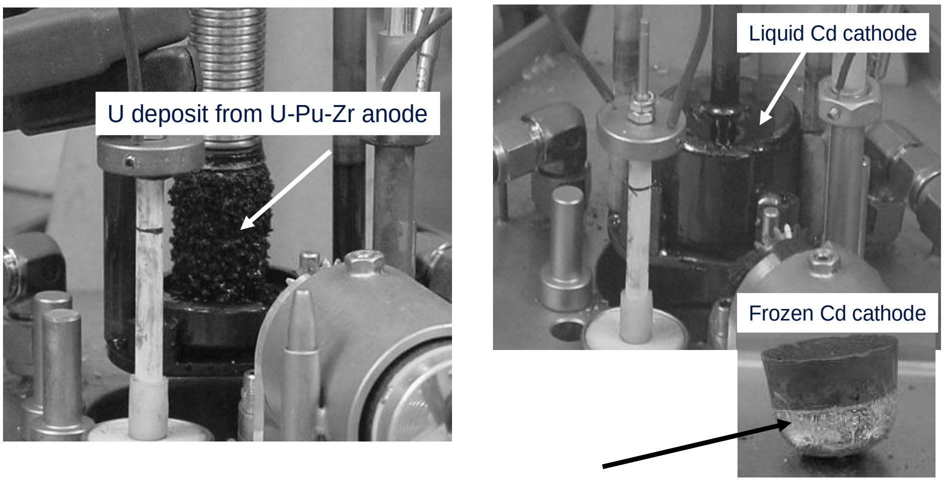
Separate experimental devices for electrorefining and reductive extraction were examined for separation of actinides from lanthanides [18,19]. An electrorefining evaluation used a single actinide element and two lanthanide elements in LiCl-KCl and showed a low separation factor between americium and gadolinium, due to the small difference of electrochemical potentials. In seeking high separation efficiency between actinides and lanthanides through reductive extraction, the distribution coefficient of each element was measured in LiCl-KCl/Cd and LiCl-KCl/Bi systems at 450°C, from which the separation factor between actinides and lanthanides was obtained. Following measurements of electrochemical potentials and distribution coefficients, separation tests of actinides have been carried out using electrorefining and reductive extraction.

4.2.1.3 U and Pu electrorefining process

CRIEPI aims to optimise operating conditions for the use of electrorefining methods. Uranium tests at a scale of 1 kg have been successfully conducted by Argonne National Laboratory (ANL) scientists, following their development of electrorefining technology. Engineering scale demonstration of electrorefining with irradiated fuel was attained for uranium recovery. Before the Global Nuclear Energy Partnership (GNEP) was launched in February 2006, no engineering scale demonstration of transuranic recovery by pyroprocessing had been realised by ANL due to the US policy prohibiting the utilisation of plutonium.

CRIEPI is proceeding to develop and demonstrate the electrorefining of U, Pu and Np with solid and liquid cathodes in a joint study with JAEA [20]. In a collaboration study with ITU, CRIEPI has succeeded in collecting uranium onto a solid cathode and plutonium onto a liquid cathode by electrochemically transferring actinides from the anode. Figure 4.8 shows uranium on the solid cathode and plutonium on the liquid cadmium cathode. Currently, more than 10% of plutonium concentration in cadmium has been achieved [21].

Figure 4.8: Overview of uranium and plutonium collected on a solid cathode and in a cadmium cathode, respectively, by electrorefining



3.18 wt.% – Pu, 0.06 wt.% – U, 0.008 wt.% –Am in Cd at 3 600 C (h = 92%)

4.2.1.4 Reduction process for oxide fuel

Experiments on the reduction of UO_2 carried out in co-operation with Kyoto University have confirmed that more than 99% of the UO_2 was converted into metallic form. Further experiments using single elements of PuO_2, Am_2O_3 and NpO_2, as well as MOX pellets, showed the feasibility of conversion to metals. These studies were jointly conducted by CRIEPI and AEA Technology [22]. Process feasibility using simulated MOX irradiated fuel has been achieved. Currently, electrochemical reduction is another effective method that should be explored for process flow studies and engineering installations. Feasibility has been confirmed using uranium oxide and mixed-oxide fuels such as $(U\text{-}10Pu)O_2$, $(U\text{-}40Pu\text{-}5Np)O_2$ [23].

4.2.1.5 Chlorination process of high-level liquid waste

Feasibility studies using simulated HLLW indicate that most of the lanthanides, noble metals and actinides are de-nitrated by calcination at 500°C, with some alkali nitrates remaining. The oxides formed are converted to chlorides by passing chlorine gas with carbon reductant through a LiCl-KCl bath at over 700°C. The demonstration using genuine HLLW is in progress in a hot cell in ITU.

4.2.1.6 Reductive extraction process for recovering transuranic elements

Multi-stage extraction using counter current flow is being examined as a means to lower lanthanide concentration in the actinide product salt stream arising from the electrorefining of chlorinated HLLW. Separation studies of transuranics from waste salts with simulated HLLW components were carried out.

4.2.1.7 Waste treatment process development for pyroprocess wastes

Two kinds of waste treatment process had been developed. Firstly, sodalite, in which waste chlorides are immobilised in a mineral matrix, is synthesised by heating $NaAlO_2$ and SiO_2 with waste salts at high temperature. The second process forms a borosilicate glass waste. Salt waste is converted to oxides through electroreduction in liquid lead followed by vitrification with B_2O_3 and SiO_2 in an air atmosphere. In addition to these developments, formation of glass-bonded sodalite from ion-exchanged zeolite was tested. Low leachability was measured for the products.

4.2.1.8 Process flow diagram and design study

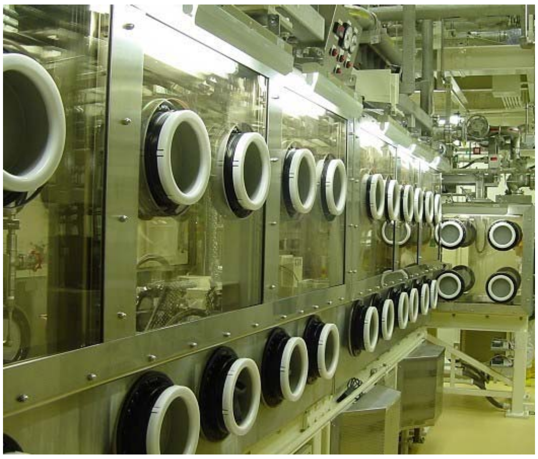
Optimised process diagrams with material balances for the reprocessing of metal fuel and for separation of TRU from HLLW have been established based on experimental data. This makes it possible to perform a design study of each installation and facility. Preliminary cost has been evaluated for a facility of 50 t/y throughput in the framework of the feasibility study at JAEA.

4.2.1.9 Integrated process developments

Equipment for electrorefining and reductive extraction, to separate actinides from actual fuel and wastes, has been installed in a hot cell facility at ITU. Recycling tests with the fuels of U-Pu-Zr contained minor actinides (Np, Am, Cm) and rare earths (Ce, Nd, Y, Gd) irradiated in Phénix are planned to be carried out after PIE.

A glove box facility shown in Figure 4.9 for the integrated experiment of Li reduction of oxide fuel, electrorefining and distillation has been installed in the Chemical Process Facility (CPF), JAEA. One continuous operation of the whole process using UO_2 was demonstrated with good mass balance. A test with PuO_2 was also successfully completed. An integrated test with MOX fuel is under way. These tests have been carried out within the CRIEPI-JAEA collaboration [24].

Figure 4.9: Glove box facility at JAEA for the demonstration of metal electrorefining of simulant oxide fuel



4.2.2 JAEA

JAEA is leading the feasibility study (FS) in Japan concerning the development of a commercialised fast reactor and its associated fuel cycle system. In the framework of the FS, JAEA has developed the pyrochemical processes for oxide and metal fuels. JAEA has also developed the pyrochemical process for nitride fuel in the framework of the research and development of partitioning and transmutation (P&T) technology.

4.2.2.1 Pyrochemical process for oxide fuel

For the oxide fuel, oxide electrowinning of a modified RIAR process was developed. At the small-scale experimental level with uranium (~10 g) and simulated fission products, work has been performed on the chlorination and anodic dissolution of UO_2, Rh, Zr and CeO_2 in molten alkali salts, and the electrowinning of noble metals and UO_2 decontaminated from noble metals. Noble metal (Rh) separation was effective at small voltage corresponding to low current density (~0.02 A/cm^2).

A design study concerning small-scale uranium and plutonium laboratory equipment for oxide fuel electrowinning tests has been undertaken. In addition, an assessment has been performed of oxide fuel electrowinning at the industrial scale, together with flow sheet and process description for mixed-oxide fuel electro-co-deposition, including off-gas processing and chlorine recycle.

A test equipment is being commissioned for electrodissolution and electrodeposition tests (~100 g simulant scale) using a molten salt/Cl_2 apparatus mounted in a vacuum glove box. Material studies, including corrosion rates of ~1 g samples in 50 g molten salt/Cl_2, are also being performed. Molten salt handling, safety trials and remote operation tests of a 20-litre graphite vessel suitable for oxide electrowinning are under way. Detailed design work is also under way for an integrated U-Pu active process test for the oxide fuel cycle, with a view to possible installation of the equipment in CPF.

4.2.2.2 Pyrochemical process for metal fuel

For the integrated experiment of Li-reduction of oxide fuel, electrorefining and distillation, installation of a glove box facility has been completed in the Chemical Process Facility (CPF), JAEA, within the CRIEPI-JAEA collaboration. Licensing of equipment was complete for electrorefining of plutonium and uranium metals and oxides. Tests with UO_2 and PuO_2 were successfully completed and the test with MOX fuel is under way within the context of the CRIEPI-JAEA collaboration.

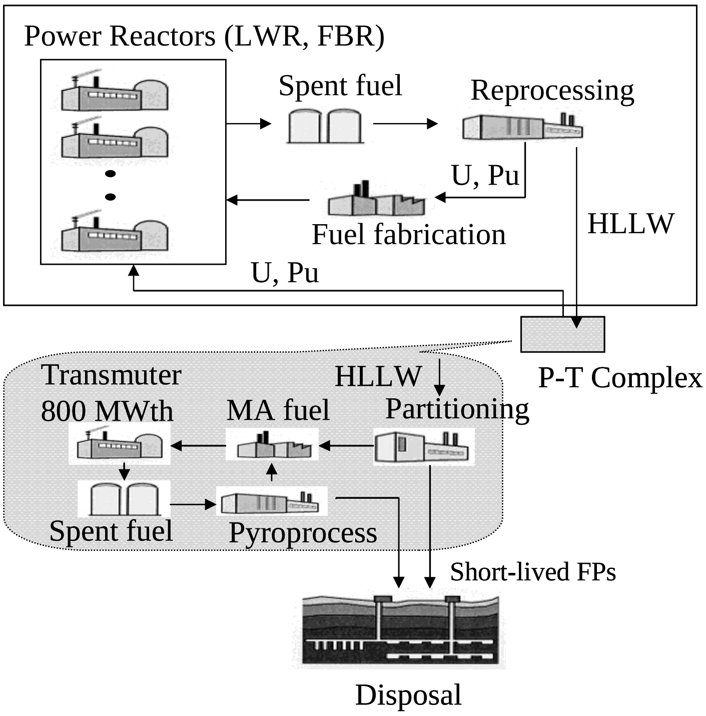
4.2.2.3 Pyrochemical process for nitride fuel

JAEA has proposed a double-strata fuel cycle for P&T, comprised of a commercial U/Pu fuel cycle (first stratum) followed by a P&T cycle for partitioning of HLLW and transmutation of long-lived minor actinides (MA) (second stratum). For the transmutation of MA, JAEA is considering a nitride-fuelled accelerator-driven system (ADS) as a reference, in which irradiated fuel is treated by pyrochemical processes. The schematic of the double-strata fuel cycle, as proposed by JAEA, is shown in Figure 4.10 [25].

Electrorefining of nitride fuel in LiCl-KCl molten salt was started in the mid-1990s in collaboration with CRIEPI [26]. High-purity argon gas-atmosphere glove boxes for pyrochemical studies were manufactured; two electrorefiners and one cathode processor were installed in the glove boxes. Experiments with 10 g material inventories are under way using U, Np and Pu. To date, the following experiments have been carried out [27-34]:

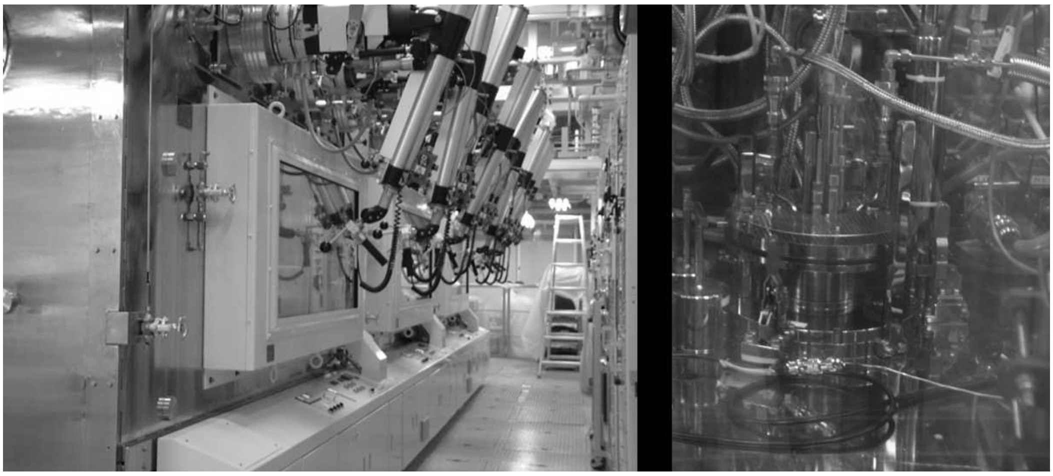
- direct electrolysis of UN, NpN, PuN and (U,Pu)N including determination of the redox potentials of the nitrides in the chloride molten salt;
- electrochemical investigation of the electrode reaction of the actinides and demonstration of the recovery of actinides at solid and liquid cathodes;
- nitrogen evolving behaviour at an anode and the feasibility of recovery of expensive ^{15}N;
- study of the characteristics of actinide nitrogen chlorides that are insoluble in the chloride molten salt;
- investigation of actinide nitride formation behaviour in liquid Cd by bubbling N_2 gas.

Figure 4.10: Double-strata fuel cycle proposed by JAEA



JAEA must vigorously pursue the above studies to demonstrate the feasibility of the pyrochemical process, which is one of the key technologies for P&T. It includes co-deposition of several actinides at a liquid cathode, electrorefining of simulated irradiated nitride fuel and so on. Moreover, data on Am and Cm are extremely limited compared with those on the lighter actinides. So JAEA constructed a modular facility for TRU high-temperature chemistry, called "TRU-HITEC", composed of three hot cells shielded by steel and polyethylene with one glove box, having a high-purity argon atmosphere and equipped with several experimental apparatus, where experiments at the 10-g scale of Am and 10-mg scale of Cm can be made. TRU-HITEC was completed in the NUCEF facility at JAEA in 2003 (see Figure 4.11), and the experiments with Am are under way [35].

Figure 4.11. Appearance of TRU-HITEC for pyrochemical study of MA



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Chapter 5: Korea (Republic of)

The nuclear power industry in Korea has grown dramatically since the first commercial nuclear power plant, Kori #1, started operation in 1978. Twenty nuclear power plants (16 PWR and 4 PHWR) are currently in operation, supplying about 40% of the total electricity demand. As of December 2005, the accumulated spent fuels amounted to 7 962 te including 4 286 te of CANDU spent fuel, and they are stored at four reactor sites. The cumulative amount is expected to reach 19 324 te by 2020. Even if the cumulated amount of spent fuel continues to increase, Korea has no fixed policy for the ultimate management of this spent fuel as of yet. However, in December 2004, the Korea Atomic Energy committee decided to store the of spent fuels at nuclear power plant sites until 2016, by expanding the interim storage capacity and as well as continuously implementing R&D studies on spent fuel management technologies for a future determination of a appropriate direction regarding the spent fuels. Korea is presently focusing on the development of a non-proliferation nuclear fuel cycle based on pyroprocessing and transmutation technology in view of long-term spent fuel management. In 2005, KAERI proposed the “Korean Nuclear Fuel Cycle” to the Korean government as a long-term plan for Korea. It has been designated the Korean Innovative Environmentally-friendly Proliferation-resistant for 21st Century (KIEP-21). This plan includes the Direct Use of PWR Spent Fuel in CANDU Reactors (DUPIC) programme, the Advanced Spent Fuel Conditioning Process (ACP) programme, pyrometallurgical partitioning and transmutation programme in order to reduce the spent fuel inventory on the whole, and a high-level waste disposal programme.

5.1 Current status of pyroprocessing R&D in Korea

The basic premises for the development of fuel cycle technologies are to secure and strengthen the sustainability, proliferation safety, environmental safety and economic competitiveness of current nuclear energy systems. The Korean approach for fuel cycle technology developments are shown in Figure 5.1. The DUPIC fuel cycle is an intermediate measure to recycle the PWR spent fuel directly into the CANDU reactors by using the OREOX and fuel refabrication processes [1]. The DUPIC concept provides advantages as per the elimination of PWR spent fuel inventories, savings of natural uranium resources for the CANDU fuel and a reduction of the spent fuel arising from the CANDU reactors. As the medium- and long-term plan of Korea, the main efforts on the development of a pyroprocess are directed to the electrolytic reduction of oxide fuel and an electrorefining, targeting the reduction of the volume, heat load and toxicity of the spent fuel and application to the Gen-IV reactor systems as the recycling and transmutation methods for closing the fuel cycle. Figure 5.2 shows a schematic diagram of the pyroprocess being developed by KAERI.

5.1.1 DUPIC

DUPIC fuel cycle technology is to directly fabricate the CANDU fuel from the spent PWR fuel through a dry thermal/mechanical process without separation of the stable fission products and transuranic materials. The basic concept of the DUPIC process is illustrated in Figure 5.3. The existence of residual fission products in the fresh DUPIC fuel is a distinctive feature of the DUPIC fuel. Due to the high radioactivity of the fuel material, all the manufacturing processes should be performed remotely in a highly shielded facility. Even if the remote fabrication and handling of the DUPIC fuel presents technical challenges, this is an advantage for enhancing proliferation resistance in terms of: *i)* no purposeful separation of the fissile isotopes and fission products during the dry thermal and mechanical fabrication processes; *ii)* difficulties concerning physical access and diversion of materials; *iii)* a self-contained processing facility.

Figure 5.1: A long-term plan for partitioning and transmutation of long-lived nuclides

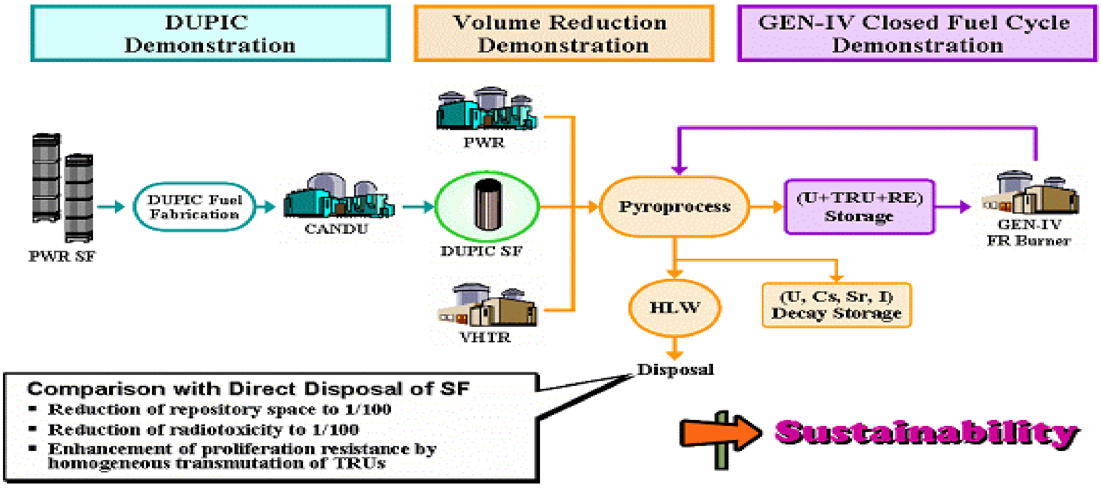


Figure 5.2: A strategy of a partitioning and a transmutation to be developed at KAERI

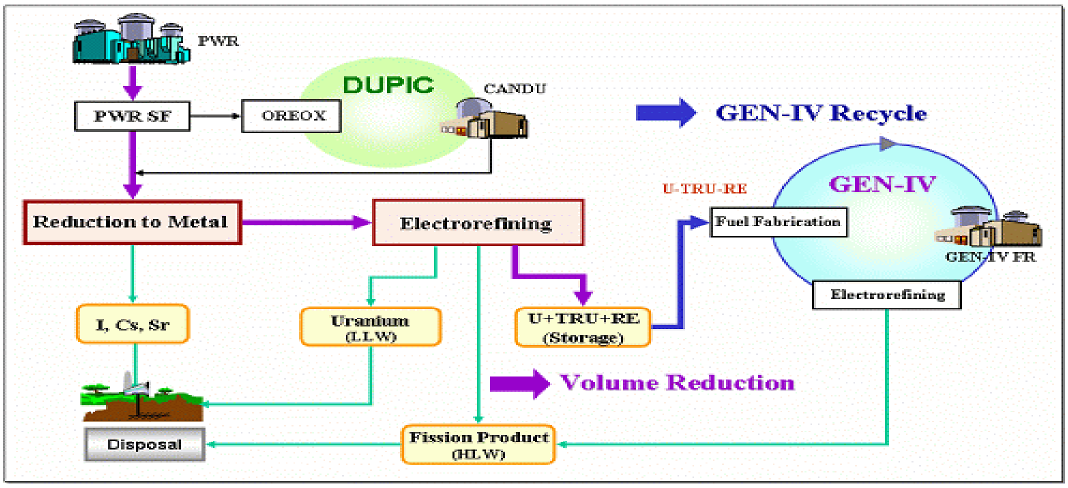
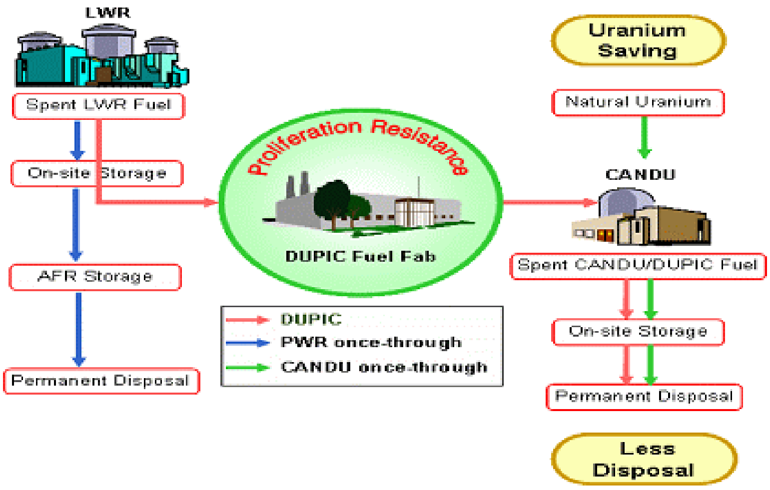
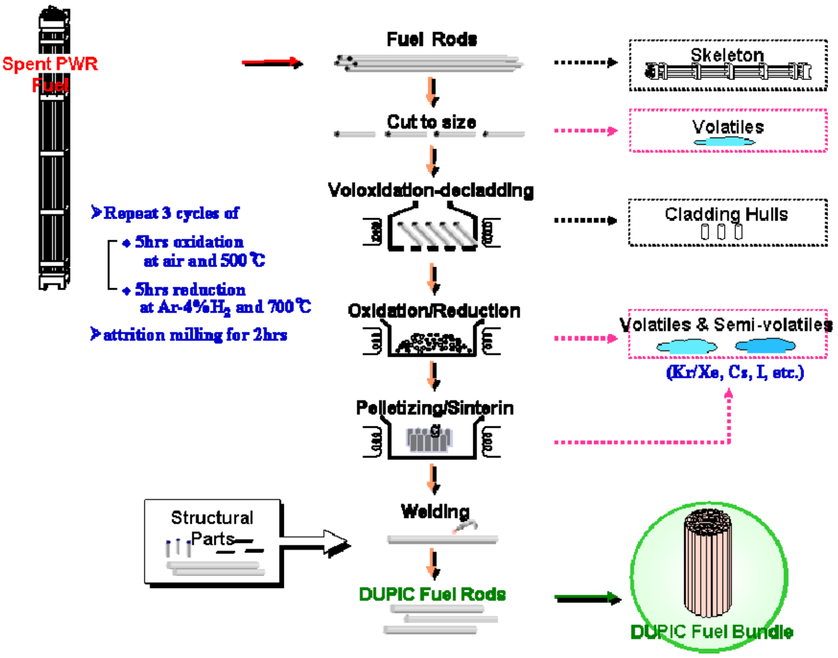


Figure 5.3: The basic concept of the DUPIC fuel cycle



As for the fuel fabrication process, the spent PWR fuel is first disassembled and then decladded to retrieve the irradiated fuel material. This fuel material is treated by repeated cycles of an oxidation and a reduction, named the Oxidation and Reduction of Oxide fuel (OREOX) process, to make it re-sinterable. Once the re-sinterable powder feedstock is prepared, the remaining fabrication steps are similar to the conventional CANDU fuel fabrication process, *i.e.* powder treatment, compaction, sintering, end cap welding and bundle assembly. A detailed flow sheet of the process is shown in Figure 5.4.

Figure 5.4. Flow sheet for the fabrication of DUPIC fuel



Since all the fabrication processes should be performed in a shielded facility, a designated remote fabrication laboratory, the DUPIC Fuel Development Facility (DFDF), was established in 2000 by refurbishing an existing hot cell at KAERI.

The DUPIC programme was launched in 1991 as an international collaboration programme jointly with Canada (AECL) and the USA (led by the US Department of State with the participation of the Los Alamos National Laboratory). DUPIC fuel development is being carried out in a phased approach. Phase I (1991-1993) was a feasibility study, the goal of which was to conceptually evaluate various DUPIC fabrication processes and their safeguardability. Phase II (1994-2001) focused on demonstrating that DUPIC fuel can be fabricated by using the OREOX process on a laboratory scale, and its fuel performance was assessed by using a research reactor. KAERI and AECL initiated collaboration in the area of the fabrication technology, reactor physics calculation and mechanical fuel performance assessment, while KAERI developed the safeguards methods with the participation of the USA and the IAEA. Based on the results of the Phase I and Phase II studies, verification of the DUPIC fuel performance was carried out during Phase III (2002-2007). Phase III includes such activities as an improvement of the DUPIC fuel element fabrication technology, development of remote bundle fabrication technology, and irradiation tests of the DUPIC fuel by using the research reactor, etc. The maximum linear power was 36 kw/m with 68 FPD (full power day) and the discharge burn-up was 6 700 Mwd/tHM. Table 5.1 shows the chemical analysis results of the composition before and after an irradiation test.

Recently, DUPIC fuel from a spent PWR fuel with a burn-up of 27.3 GWd/tU and 15 years cooling was irradiated in the HANARO research reactor for a performance evaluation. According to the results obtained up to now, the performance of the DUPIC fuel is thought to be quite similar to that of conventional CANDU fuel.

Table 5.1: DUPIC fuel composition before and after an irradiation test

	Nuclides	Units	Fresh DUPIC fuel		Irradiated DUPIC fuel
			OREOX powder	Sintered pellet	
Fissile material	Total U	g/g sample	0.8422±0.002	0.8421±0.001	0.8391
	Total Pu	g/g sample	0.0075	0.00761	0.00391
	^{234}U	Atomic %	0.01556 (61%*)	0.01556 (16.0%*)	0.0168
	^{235}U	Atomic %	1.0841 (0.54%)	1.0842 (0.22%)	0.4190
	^{236}U	Atomic %	0.3978 (1.7%)	0.3978 (0.64%)	0.4973
	^{238}U	Atomic %	98.4326	98.4443	99.0670
	^{238}Pu	Atomic %	1.4874 (5.3%)	1.4717 (0.11%)	5.6733
	^{239}Pu	Atomic %	63.8778	68.2063	43.5667
	^{240}Pu	Atomic %	24.4356 (0.073%)	24.1787 (0.01%)	32.4959
	^{241}Pu	Atomic %	6.5471 (1.5%)	6.4783 (0.03%)	7.9882
	^{242}Pu	Atomic %	4.6746 (0.4%)	4.6255 (0.02%)	10.2759
Fission products	^{134}Cs	MBq/g-U	$1.96 \times 10^{+1}$ (2.11%)	< N.D. (2.19%)	$3.169 \times 10^{+3}$ (2.08%)
	^{137}Cs	MBq/g-U	$1.976 \times 10^{+3}$ (1.92%)	$1.834 \times 10^{+1}$ (2.00%)	$4.568 \times 10^{+4}$ (0.53%)
	^{154}Eu	MBq/g-U	$5.569 \times 10^{+1}$ (2.2%)	$5.478 \times 10^{+1}$ (2.00%)	$1.133 \times 10^{+4}$ (2.50%)
	^{155}Eu	MBq/g-U	$1.174 \times 10^{+1}$ (2.82%)	$1.158 \times 10^{+1}$ (2.03%)	$6.635 \times 10^{+3}$ (2.01%)
	^{125}Sb	MBq/g-U	4.738 (9.87%)	1.151 (9.10%)	$3.075 \times 10^{+3}$ (5.35%)
Rare earth elements	Gd	g/MTU (ppm)	92 (0.63%)	105 (3.81%)	100
	Eu	g/MTU (ppm)	112 (1.36%)	123 (0.00%)	100
	Sm	g/MTU (ppm)	700 (0.92%)	770 (0.65%)	730
	Nd	g/MTU (ppm)	3.420 (0.69%)	3 770 (0.41%)	3 580
	Pr	g/MTU (ppm)	933 (0.63%)	1 030 (0.41%)	940
	Ce	g/MTU (ppm)	1 830 (0.69%)	2 030 (0.26%)	1 900
	La	g/MTU (ppm)	1 110 (0.72%)	1 220 (0.56%)	1 130
	Y	g/MTU (ppm)	373 (0.94%)	410 (0.42%)	380
	Zr	g/MTU (ppm)	3 110 (1.00%)	3 560 (1.41%)	3 390

* Relative standard deviation (RSD)

5.1.2 Pyrometallurgical process

5.1.2.1 Electroreduction of oxide into metal

The Advanced Spent Fuel Conditioning Process (ACP) has been under development at KAERI since 1997. The main concept is to reduce spent oxide fuel into a metallic form in a high-temperature molten salt, as an intermediate step for the conditioning of a spent fuel for an eventual disposal and for a recycling and transmutation of the spent fuel in a Gen-IV fast reactor. It includes several process steps such as an air voloxidation of the oxide fuel pellets, an electrolytic reduction of the oxide fuel powder in a $LiCl-Li_2O$ molten salt bath [2], and a smelting of the reduced metal powder.

The first step of the ACP is an air voloxidation of UO_2 pellets to produce U_3O_8 powder. This step is adopted to increase the reaction rate at the subsequent reduction step by serving as a substantial surface area for the metal oxides to be reduced and to remove volatile fission products from the spent fuel. The produced U_3O_8 powder is introduced into a molten salt bath for conversion of the spent fuel oxides to base metals. Early development activities for the reduction process focused on a conventional Li-reduction process in which a highly reactive lithium metal was used as a reducing agent. However, since 2001 a new electrolytic reduction technology has evolved as an innovative approach and it has replaced the Li-reduction process. In this process, the spent oxide fuel serves as a cathode of a cell in which the metal oxides are reduced to base metals, and the oxygen anions are oxidised at an inert anode to produce oxygen gas, which is then vented from the cell. The new concept has advantages over the Li-reduction process such as simplicity of the process systems, reduction of the molten salt waste and an increase of the reduction yield. Over the period 2002-2005, the following results were obtained from the inactive electrolytic reduction tests of a 10 gU / batch to a 20 kgU/batch:

- From the viewpoint of a reduction yield, more than 99% of the uranium oxides could be reduced to uranium metal powders in the bench-scale (10 gU/batch) to lab-scale (20 kgU/batch) tests by using a LiCl-Li_2O molten salt at 650°C.
- The alkali and alkali earth oxides were changed chemically to their corresponding chlorides during the electroreduction and they were consequently removed from the reduced U metal. Most of the rare earth elements accompanied the reduced U metal due to their low solubility in a LiCl molten salt.
- A uranium metal ingot could be obtained under a reduced pressure of 10^{-2} torr and at a temperature of 1 300°C at the smelter.

Recently, laboratory scale mock-up tests have been carried out for an electroreduction using a 20 kgHM/batch scale.

The containment/surveillance technology of the ACP facility has also been developed to enhance reliability and transparency for the nuclear R&D activities internationally through implementing IAEA safeguards. A non-destructive nuclear material assay and accounting system, which was developed through performance analysis and a modification of the existing neutron accounting system, has been devised for a material control and accountancy (MC&A) of the spent fuel to be conditioned. On the basis of these results, in 2006, the laboratory scale demonstration equipment (20 kg HM/batch) was installed in a hot cell (Advanced Spent Fuel Conditioning Process Facility, ACPF) as shown in Figure 5.5. The hot experiments in the ACPF are not yet scheduled. However, the process units installed in the ACPF will be used to verify the ACP on a laboratory scale using the inactive material and will produce data for designing an engineering scale facility in the coming years.

Figure 5.5: Overview of the Advanced Conditioning Process Facility (ACPF)

5.1.2.2 Pyropartitioning using an electrorefining process

Since 1997, KAERI has been conducting an R&D project on pyropartitioning for the recovery of long-lived radionuclides. The study for partitioning is focused on the development of pyroprocessing based on the electrorefining of actinides, where all the transuranic metals are separated together as a mixture. In order to achieve the above objective, the study on pyropartitioning is being carried out in three phases. Phase I (1997-2000) was mainly focused on the concept of a fluoride molten salt reactor proposed by LANL. Accordingly, the target of the research was to review and obtain basic technologies on pyroprocessing such as electrowinning and reductive extraction, using a fluoride molten salt (FLiNaK and FLiBe). However, in Phase II (2001-2003), the concept of pyroprocessing was changed from a fluoride-based molten salt reactor to a chloride-based metallic fuel proposed by ANL, with the purpose of using a metal ingot produced from the ACP process. During Phase II, the goal of the research was to obtain the key technologies of pyroprocessing such as uranium electrorefining and a cathode process.

Electrorefining was performed at the temperature of 500°C by loading the metal ingot into a molten LiCl-KCl electrolyte for dissolution and electrotransporting of the uranium as a cathode product. The uranium deposit containing the salt was then treated under a vacuum at the cathode processor in order to remove the salt from the uranium.

In Phase III (2004-2006), R&D activities such as a scale-up (1 kgU/batch) of the electrorefining equipment and a cathode processing were carried out based on the results of Phase II. This scale-up electrorefining system was successfully operated through two demonstration tests to obtain a uranium deposit and a metal ingot (see Figure 5.6). Recently, KAERI began developing a new electrolysis system with a high throughput of uranium. KAERI's approach to the high throughput electrorefining is to remove the scraping process which causes a sticking problem during harvesting of the uranium deposit. In order to realise this goal, the conventional steel cathode was replaced with a graphite one. The graphite cathode exhibited a self-scraping behaviour in which the electro-deposited uranium dendrite falls from the cathode surface by itself without any kind of mechanical operation such as a scraping or a rotation of the electrode. This self-scraping phenomenon of the graphite cathode was interpreted by the formation of a uranium graphite intercalation compound [3].

Figure 5.6: Electrorefiner system (left) and the received uranium dendrite (middle) and uranium ingot (right)

In this self-scraping mechanism, uranium atoms elongate the graphite's outermost layer by an intercalation reaction, so the uranium dendrite deposited falls off spontaneously as the gravitational force their exceeds the bonding strength of the layers. Based on preliminary work, this self-scraping should increase the efficiency of the electrorefinning due to an elimination of a scraping as well as the stripping steps of the cathode.

The main activities performed during Phase II and III are as follows:

- examination of the experimental conditions such as the optimum current density applicable to an operation, initial uranium concentration, separation factor of the uranium from rare earth, and salt distillation behaviour, etc.;
- scale-up of the electrorefinning system (throughput: 1 kgU/batch) and an operation;
- development of a new concept of an electrolysis system with a high throughput of uranium.

5.1.2.3 Treatment of waste salts

In relation to a treatment of waste salts, KAERI is developing technologies, which can reduce the disposal load through recycling the waste salt in a pyrorpocessing system. The aim is to provide a new way to minimise the amount of waste salt to be discharged to a repository, while removing the high decay heat fission products from the waste salts generated during the pyroprocessing procedure. KAERI is presently performing a study on the removal of the Cs, Sr and rare-earth elements arising from the pyroprocessing units. Figure 5.7 shows a schematic diagram for removal of fission products from the waste salts [4]. First, Cs could be removed in the form of an oxide gas from the voloxidation process at an elevated temperature. Then, Sr could be completely recovered by a carbonate precipitation using Li_2CO_3 chemicals from the waste LiCl salt. Finally, rare-earth elements including Y in the spent LiCl-KCl waste generated during the course of an electrorefining are removed in the form of an oxide precipitate using air oxidation. KAERI is focusing on a total recycling of the waste salts to the pyroprocessing units after removing these fission products resulting from each process unit, by not releasing them to a permanent repository. The experimental results showed that the removal yields of each element were approximately 95% for Cs at around 1 500°C, higher than 99% for Sr at a molar ratio of [$Li_2CO_3/SrCl_2$ = 3] and about 99% for the rare earth elements including Y, respectively.

Figure 5.7: A schematic diagram for removal of fission products

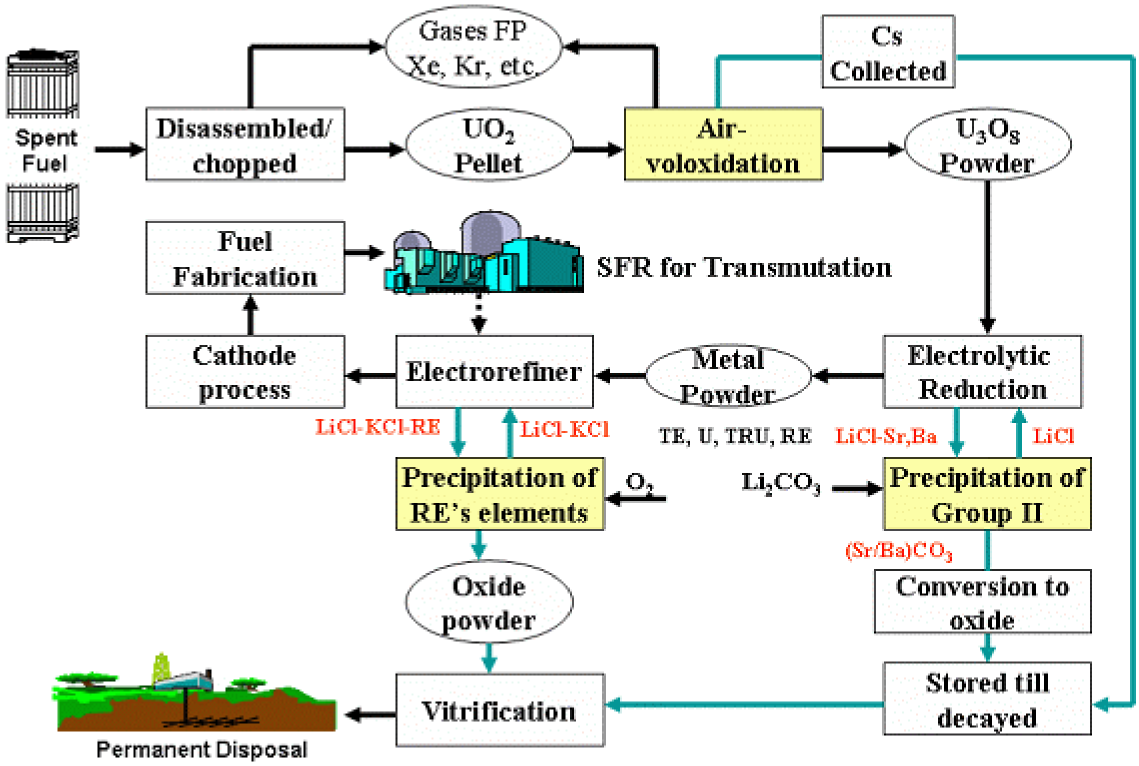
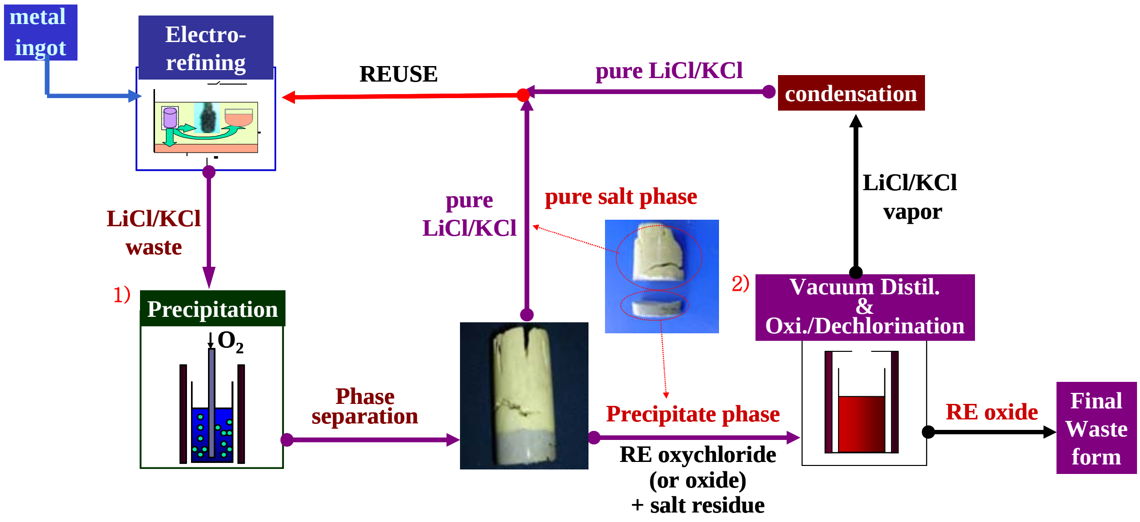


Figure 5.8 shows an example of a salt recycling for the electrorefiner after removal of the rare-earth elements as precipitates from the waste LiCl-KCl eutectic molten salt. Precipitates in the salt mixture (LiCl-KCl-RE) are produced by a reaction of the rare-earth elements with oxygen and then precipitated on the bottom of the waste treatment reactor. After sedimentation of the precipitates, a phase separation occurs in the salt, leaving a pure salt at the upper part of the reactor. The cooled-down salt is then cut around an interface between the pure salt occupying a 75% vol. and the precipitated part of a 25% vol. Then, the pure salt is directly recycled to the electrorefiner for reuse and the precipitated part is transferred to a vacuum distiller to vaporise the LiCl-KCl salt mixed with precipitates (at temperatures less than 1 000°C and reduced pressure of 0.5 torr). The vaporised salt is also recycled in the electrorefiner and then a small amount of the oxide powder is vitrified to be disposed of in a repository. Through this procedure, it is possible that all most of all the salt could be recycled and hence we can minimise the amount of the waste salt to be disposed of. Further R&D is focused on the establishment of an integral system for realising these waste salt recycles. As with the separation of the rare-earth elements, this method is applicable to the separation of Sr from LiCl salt.

Figure 5.8: Treatment system for a waste salt minimisation



1) $RECl_3 + 0.5O_2 \rightarrow REOCl + Cl_2$ (or $RECl_3 + O_2 \rightarrow REO_2 + 1.5Cl_2$) ; Precipitation reaction

2) $REOCl + 0.25O_2 \rightarrow 0.5RE_2O_3 + 0.5Cl_2$; Oxidation and Dechlorination reaction

5.2 Future R&D activities

KAERI has been preparing the next ten-year plan for the development of P&T on the basis of the aforementioned research experiences. The aims of the plan are to establish an engineering-scale mock-up by 2011 and then to develop utilisable technologies related with the pyroprocess by 2016. In this long-term plan, core pyroprocessing technologies and concepts developed by KAERI up to now are to be further improved as viable technologies. It is currently recognised that the challenges in the pyroprocessing technologies prior to their commercialisation are classified into two categories. The first is a low throughput, because most processes such as an electrolytic reduction, electrorefining and cathode process are composed of batch-wise processes. Hence, efforts will be concentrated on the development of a continuous or at least a semi-continuous process for throughput enhancement. The second category is the generation of a substantial amount of high-level ceramic waste during the salt waste treatment process, because presently the waste salt is considered as a material to be loaded into zeolite without cleaning the fission product. As KAERI proved the possibility of a complete recycling of a waste salt by precipitating and separating $SrCl_2$ and rare-earth elements from a waste salt which is generated during an electrolytic reduction and an electrorefining process, respectively, an integrated salt waste treatment process will be established within this time frame. Especially, international co-operative research should be performed to validate the developed processes with regard to the behaviour of the actinide elements during pyroprocessing.

5.3 Conclusion

Since the introduction of the first nuclear power plant in 1978, nuclear energy has become an essential source for meeting a sustainable electricity supply in Korea. However, an effective disposition of the accumulating spent fuel has evolved as one of the most pressing issues for the continued growth of nuclear energy.

Recently, Korea has been focusing its efforts on the development of a pyroprocess, by targeting a reduction of the volume, heat load and toxicity of the spent fuel and its application to the Gen-IV reactor systems through recycling and transmutation methods to close the fuel cycle. The pyroprocess development plan will be harmonised with the Gen-IV reactor system development schedule.

In particular, KAERI's P&T research has been performed as the second long-term nuclear power R&D programme funded by the Korean government since 1997. It will end in 2006 and the third stage of this programme will start in 2007 and continue until 2016.

During this period, KAERI will develop an engineering-scale process to make the pyroprocess practicable. Also, international collaborative research is gaining more importance than ever for an effective development of innovative fuel cycle technologies.

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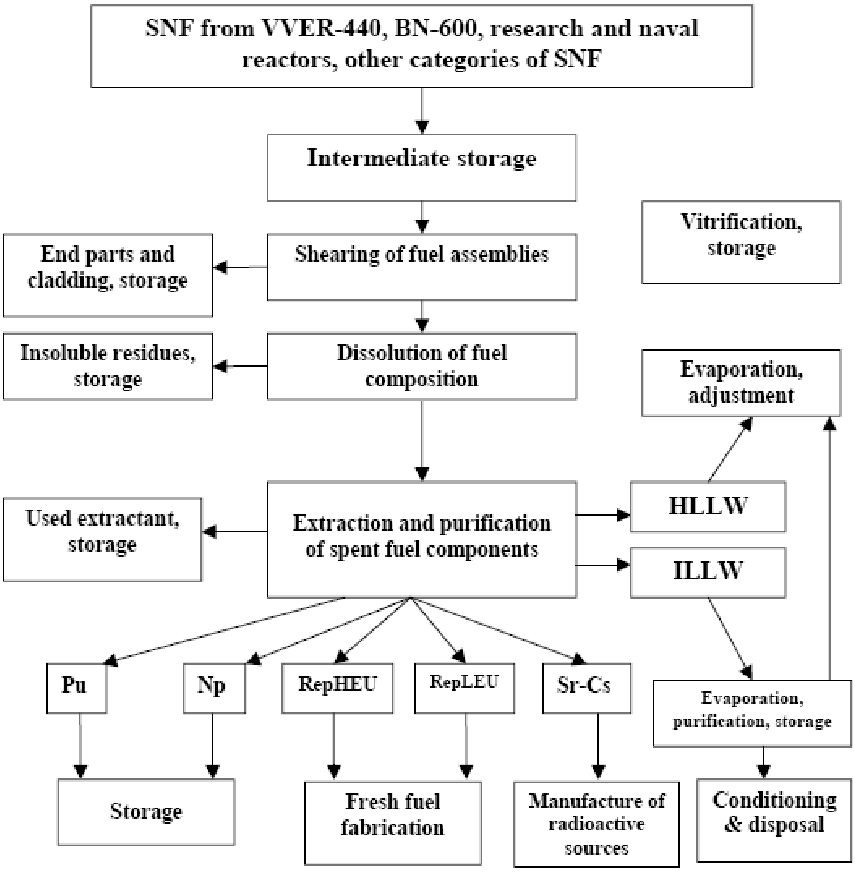
Chapter 6: Russian Federation

Concerning development of the aqueous partitioning process in Russia, the efforts by Khlopin Radium Institute (KRI) to establish processes for simultaneous separation of ^{90}Sr and ^{137}Cs for large-scale applications should be mentioned. Chlorinated cobalt dicarbollide (CCD) is used as a Cs extractant, and CCD-polyethylene glycol (PEG) as a Sr extractant at the Mayak-RT1 reprocessing plant. The process was modified on the basis of the PUREX process so as to incorporate actinide extraction, and was thus renamed the PUREX-TRUEX process. It has been successfully demonstrated at laboratory scale. For advanced fuel cycles the recycling of all minor actinides is proposed in the framework of pyrochemical treatment of fuel for recycling. RIAR proposed the DOVITA closed fuel cycle, which is designed for MA transmutation by fast reactor, and has been developing pyrochemical processes since 1992.

6.1 Review of Russian national programmes in partitioning

The partitioning of flows during reprocessing of spent fuel was introduced as part of the technology of the RT-1 plant (Mayak Plant, Russia) in the 1980s. The technological flow sheet of reprocessing includes the process of full extraction of the Np and Cs-Sr fractions (see Figure 6.1) [1].

Figure 6.1: Principal flow sheet of the RT-1 reprocessing plant at the Mayak plant [1]



Russian activity in the partitioning field is mainly related to the modification of the PUREX process for the direct extraction of long-living components' fractions, or the development of new extracting processes for partitioning of necessary fractions from HLLW streams formed by the PUREX process without updating the basic technology.

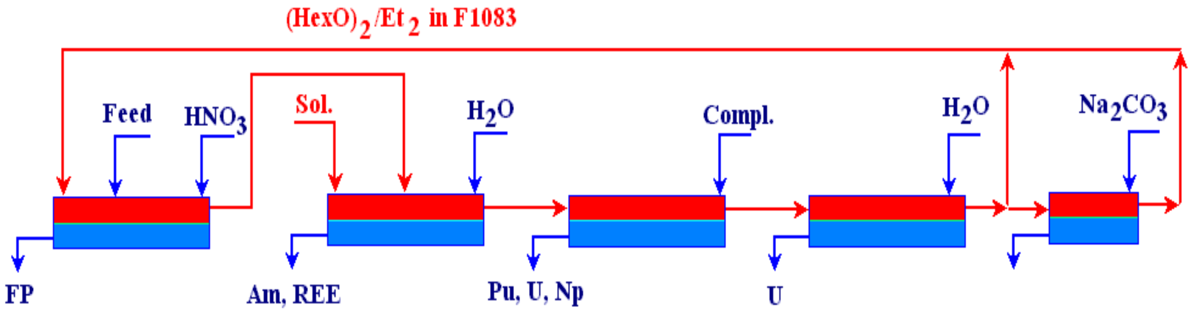
Some studies were carried out at the Khlopin Radium Institute, Bochvar Institute and Mayak Plant laboratory on development of the improved flow sheet for RT-1 plant modernisation [2]. The task to be solved is complex, and in addition to partitioning, studies concerning waste volume reduction are also carried out. Among waste processes allowing Cs, Sr and TPE extraction from highly saline acid HLW, three groups are of the most interest for implementation in the RT-1 technological flow sheet:

- processes based on application of macrocyclic compounds, primarily crown-ethers;
- processes using liquid cation exchangers – mainly chlorinated cobalt dicarbolite (CCD);
- processes using diphenyl-N,N-dibutylcarbamoylmethylenephosphineoxide solutions in a heavy nitroaromatic diluent - metanitrobenzotrifluoride.

The possibility of commercial application of HLW partitioning technologies at the Mayak Plant was demonstrated at the end of the 80s, at which time experimental and industrial verification of TPE and REE extraction was performed using actual solution. An amount of 40 m^3 of solution was processed, and 10 m^3 of TPE re-extract and 10 m^3 REE re-extract were received. Radionuclide extraction into extract came to 97%. On the second stage of work TPE re-extract was concentrated to 2.4 m^3; the concentrate contained 240 g of ^{241}Am and 20 g of Cm. This is the only process which passed large scale tests on acute solutions in Russia [2].

Other examples of modified systems on the basis of PUREX are flow sheets such as SUPERPUREX or united technology of reprocessing and partitioning (PUREX-TRUEX) [3]. PUREX-TRUEX is a promising technology which provided reprocessing and partitioning in the framework of a single extraction cycle using dihexyldiethylcarbamoyl phosponate – $(HexO)_2/Et_2$ (see Figure.6.2).

Figure 6.2: Flow sheet for the combined PUREX-TRUEX process



Complex studies for separation of Am and Cm from spent fuel or irradiated targets were undertaken at RIAR and the Kurchatov Institute during the period 1960-1980. An overview of this experience is available in the form of a monograph [4].

The partitioning of radionuclides was established in the flow sheet of the RT-2 reprocessing plant, which was never completely constructed under the USSR.

During 1993-2001 the Minatom Programme "RECYCLE" was under development. This programme was headed by the Khlopin Institute (Professor R.I. Lubtsev) and was related to improving the RT-2 flow sheet. The main tasks of this programme were: *i)* separation and collecting of I, Tc, Am; *ii)* development of reactor conceptions of FP and MA incineration (transmutation). Participating organisations include the Mayak Reprocessing Plant, Bochvar Institute, Kurchatov Institute, RIAR, IPPE and the Moscow Institute of Physical Chemistry of the RAS.

The main results of this programme were the following [5]:

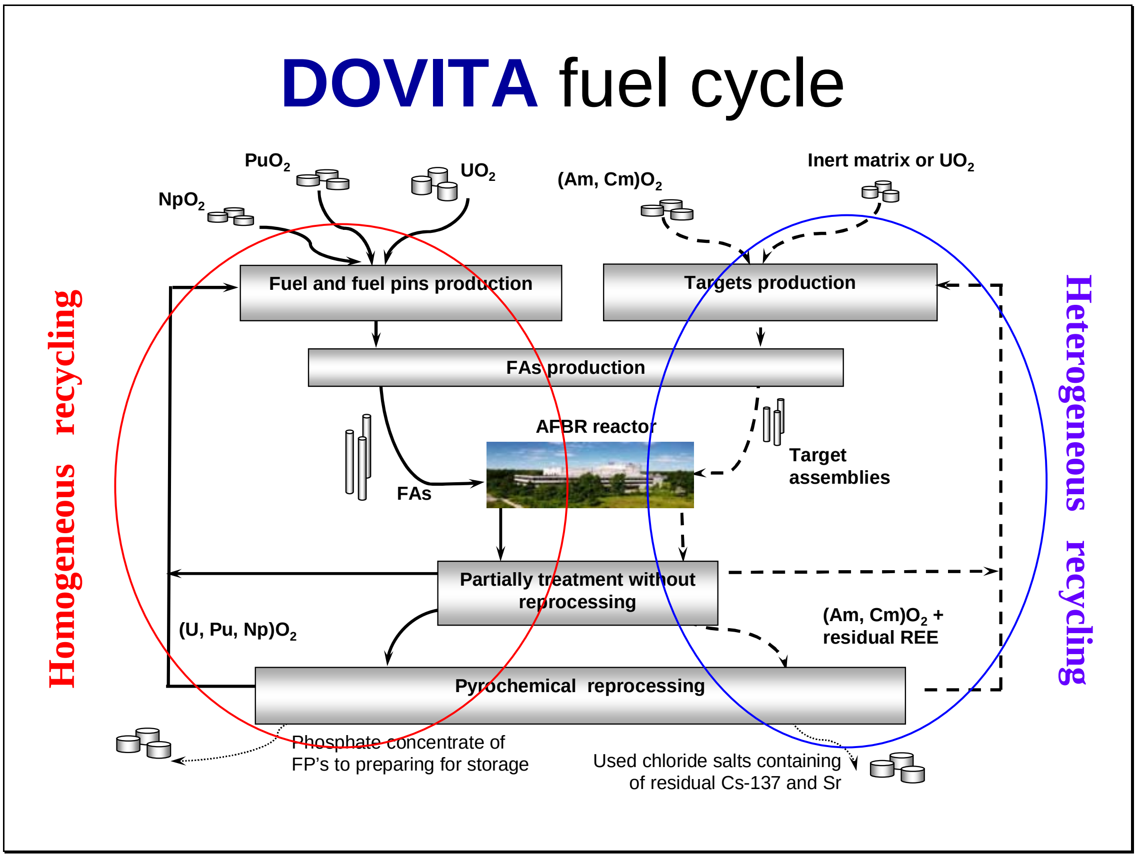
- A Russian version of an advanced PUREX process was developed: *i)* separation and obtaining of Tc in metallic form; *ii)* separation of Am from REE in a solution with a high content of REE; *iii)* separation and collecting of iodine.
- RIAR initiated R&D on separation of Am and REE in chloride melts and some studies were completed.

The Russian Federation does not have a programme devoted to partitioning at this time.

RIAR proposed a concept related to a closed fuel cycle for a fast reactor initially designated for MA transmutation: the DOVITA programme [6]. This concept was based on fairly simple ideas: dry technologies for MA oxide fuel reprocessing and preparation, vibropacking automated technology for fuel pin production. The fuel recycle is carried out according to the flow sheet shown in Figure 6.3. The basic (driven) MOX fuel, after 15-20% burn-up, goes through a series of steps: decladding, crushing, vacuum reprocessing and repeated vibropacking. After two cycles of irradiation, the basic fuel is reprocessed by pyroelectrochemical methods. U, Pu and Np (and a portion of Am) come back to irradiation. The materials of targets with Am, Cm and REE are irradiated for three to four cycles with periodic decladding and treatment, and then directed to a pyrochemical process. The pyrochemical process of Am and Cm separation from REE will be carried out in a molten salt system with a liquid metal electrode, thus only the REE portion is dumped. The bulk of the experimental studies has been accomplished over the last 13 years.

Of course initially this system was developed especially for a fast reactor burner, but the main part of developments could be realised for a closed fuel cycle of the BN-800 reactor which is currently under construction in Russia.

Figure 6.3: DOVITA fuel cycle [6]



Partitioning processes are now being considered for advanced fuel cycles of fast reactors – BN-800 and BREST. For advanced fuel cycles the recycling of all minor actinides is proposed in the framework of pyrochemical treatment of fuel for recycling. This idea was established in the Russian Strategy of Nuclear Power Development for the First Half of the XXI Century [7].

Russian institutes have actively participated in other research programmes related to partitioning in collaboration with organisations of the EU (particularly France), Japan and the Republic of Korea.

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Chapter 7: Spain

High-level radioactive waste in Spain consists of spent nuclear fuel from nuclear power plants, and the vitrified waste arising from reprocessing of fuel from the "Vandellós I" nuclear plant at La Hague, France.

The capacity of fuel storage in the pools of the different nuclear plants has been increased, substituting the old racks for new ones with higher neutronic absorption capacity that allows an increase in the packing density of the fuel elements. This is only a temporary solution as the capacity of some of the storage pools will soon be reached.

This situation leads to the consideration of two phases in the management of nuclear wastes, the first one up to 2010 with the acute capacity problem of one of the nuclear plants, and the second one from 2010 with additional issues arising from decommissioning of old plants receiving vitrified waste from La Hague. For this second stage it is envisaged that the construction of a long-term centralised temporary storage facility (ATC) will solve these problems, at least temporarily. A possible alternative could be to reprocess these fuels abroad, but in any case it would be necessary to construct the ATC.

Taking into account the generalised delay in the R&D programmes in other countries, the uncertainties with respect to definitive solutions and the availability of temporary solutions, it has been decided to postpone any final decision to the end of 2010. Meanwhile, and to help guide this decision, Spain is considering and investigating the following three main options [1,2]:

- Centralised interim repository (ATC) for a long term (100-300 years). Construction by 2010 is planned.
- Disposal in a deep geological repository without reprocessing.
- Partitioning and transmutation (P&T) followed by disposal in a deep geological repository.

In 1997 the National Nuclear Waste Management Enterprise (Spanish acronym: ENRESA), which is responsible for managing nuclear wastes in Spain, began financing several P&T research projects. The partitioning and transmutation option, considered a challenging technology, is conceived in the framework of an international collaboration, with the participation of the most developed countries in this field. To carry out this investigation ENRESA signed a scientific and technical agreement with CIEMAT that also included national universities and research centres to participate in projects financed both by ENRESA and by the European Commission within the Framework Programmes of R&D related to chemical partitioning and transmutation [2].

The objective of this research is to investigate the separation processes for later transmutation of long-lived radionuclides with the aim of reducing the volume and radiotoxicity of the final nuclear wastes generated in the nuclear industry and to produce electricity.

Chemical partitioning research concerning both hydrometallurgical and pyrometallurgical methods started in CIEMAT in 1998 with the main purpose of firstly, evaluating the feasibility of the different stages of the processes, mainly related to actinide and long-lived fission products. Then, to design a possible flow sheet of the separation process, identifying the type, forms and volume of the final and secondary wastes produced; to determine the partitioning efficiency, and to assess the scaling-up of the processes, from laboratory to pre-industrial scale. The combined results of these studies will allow the evaluation of the economic and technological impact of these technologies for nuclear waste management.

At present, the development of these techniques is still in its very early stages for both hydro- and pyroprocesses, working in batch laboratory scale and under low activity conditions.

7.1 Hydrometallurgical separation

The objective of this project is to define an advanced hydrometallurgical process that could be applied at pre-industrial scale to selectively separate the minor actinides contained in the high-level liquid waste (HLLW) arising from the PUREX process and for advanced nuclear fuel cycles.

The main activities performed at CIEMAT during the period 2000-2003 were developed within three projects, two of them included in the 5th Framework Programme of the EU, PARTNEW and CALIXPART, and another national project that studied the behaviour of some organometallic compounds known as "cobalt sandwich anions" (COSAN). In 2004, these activities were included in the Integrated Project EUROPART, and the programme was financed by ENRESA. The EUROPART project ended in June 2007.

Within PARTNEW the main activities were related to the development of new organic molecules to be applied in the DIAMEX process for the co-extraction of actinides (An)(III), and lanthanides (Ln)(III), and in the SANEX process for the selective extraction of An(III). These new molecules based on malonamides (DIAMEX) and thiomalonamides (SANEX) were synthesised by the *Universidad Autónoma de Madrid* (UAM) and tested at CIEMAT with aqueous solutions containing ^{241}Am and ^{152}Eu at the characteristic nitric acid concentrations of high active raffinate (HAR) from the PUREX process. Among all the compounds tested, one malonamide ligand synthesised by UAM gave interesting extraction results, having a higher extraction capacity than DMDOHEMA, used in the DIAMEX process [3]. The selectivity of this compound was also studied with synthetic solutions prepared at FZK-Jülich; these solutions simulated high active raffinates coming from the PUREX process treatment of a UO_2 fuel having a 3.5% initial ^{235}U enrichment, a burn-up of 33 GWd/t and three years' cooling time. Initial tests indicated a quantitative co-extraction of major fission products such as Zr, Fe, Mo and Pd, the addition of some commercial complexing agents avoided the extraction of Zr, Fe, Mo and significantly reduced the extraction of Pd. This new ligand is quite stable against radiolysis and hydrolysis when chlorinated solvents are avoided. For the applicability of this compound at pre-industrial scale the main problem is its low solubility in industrial solvents.

Therefore, during EUROPART project some modifications of this molecule were proposed and tested to increase its lipophilicity [4]. As a consequence, a new bis-MA soluble in aliphatic solvents was found and its properties for An(III)/Ln(III) co-extraction were studied [4]. These molecules displayed higher distribution coefficients than the single malonamide DMDOHEMA, suggesting that bis-MA could pre-organise the binding groups around the cation more efficiently than the single monomalonamide. This bis-MA showed good hydrolytic and radiolytic stability. Aside from these malonamide ligands, a new family of compounds based on two diglycolamide moieties linked to a suitable spacer were synthesised and tested. As a result of the EUROPART project, two new bis-DGA compounds with aromatic or alkyl chain as a linker of the functional groups were selected for process development and hot counter-current tests with genuine solutions. A joint European patent with application n° 06380268.0 (November 2006) has been registered [5]. The institutions involved in the patent are CIEMAT, UAM, ICIQ and FZJ. These new compounds showed important advantages over TODGA [6] such as lower fission product extraction, meaning fewer steps during the extraction process. In the near future more studies will be carried out with the two new bis-DGA selected to develop a suitable process for An(III)/Ln(III) co-extraction and hot tests will be performed in the framework of the European partitioning project. A new line was launched to study the selective extraction of An for advanced fuel cycles related to accelerator-driven systems. For this, it is necessary to develop organic systems for the entire group of actinides (III-VI) to be extracted [7].

The second project, CALIXPART, was related to the development of extractants for the selective extraction of An(III) and the co-extraction of An(III)/Ln(III). The strategy was to link ligands with sufficient affinity to pre-structured molecules such as calixarenes, dendrimeres or cavitants that are able to complex the An(III) and Ln(III) cations in the raffinates from the PUREX process. These compounds were synthesised by the UAM, and their chemical structures are based on calix[4,6]arenes with ligands such as malonamides and diglycolamides. The corresponding extraction and stability studies of these compounds and others synthesised by other partners of the CALIXPART project were also performed. Results indicated that calix[4,6]diglycolamides showed high extractive properties at high acid concentration for Ln(III) and good selectivity versus An(III). The compound calix[4]CMPO presents good radiolytic and hydrolytic stability but poor selectivity, however, this could be increased by using synergic mixtures with calix[6]picolinamides or diglycolamides. Nevertheless, the solubility of all these compounds must be improved [8]. During the EUROPART project, the use of several synergic mixtures was tested in order to check their selectivity.

The third hydrometallurgical project was initially a national project that started in 2002, which involved the use of compounds containing the anion bis(1,2-dicarbollyl) cobalt(III)ate, COSAN and its derivatives which belong to the metallacarbonaranes group, to be used for the separation of An(III)/Ln(III). These compounds were synthesised by the *Instituto de Ciencia de Materiales de Barcelona* (ICMB) and tested at CIEMAT using solutions containing ^{241}Am and ^{152}Eu. Initial results indicate a low extraction, but the use of synergic mixtures with CMPO seems to give good extraction yields for both Ln and An. The main drawbacks of these compounds were the need to use nitrobenzene as a solvent to obtain good extraction results [9]. During the EUROPART project some new COSAN molecules were synthesised in order to increase both solubility and extraction capacity. These products were also tested in combination with CMPO and bipyridines in order to increase the selectivity.

7.2 Pyrochemical separation

As for the hydrometallurgical process, the main objective of this research is to assess the feasibility of the different stages of the processes, to design a possible flow sheet of the separation process, identifying nuclear wastes and to assess the scaling-up of the process in order to evaluate the economical and technological impact on nuclear waste management. It should be noted that this type of process is only being considered for the reprocessing of advanced transmutation fuels.

The pyrochemical separation project started in 1998 with a project financed by ENRESA and continued in 2000 with the European PYROREP project. CIEMAT participated in this project in collaboration with the molten salt group of the *Universidad de Valladolid* (UVA). CIEMAT continued research in this field from 2004 through its participation in the EU project EUROPART.

In both projects the CIEMAT investigation was performed using the molten salt mixture LiCl-KCl eutectic taking as reference material an oxide-type fuel. Activities performed were mainly focused on the study of the dissolution kinetics of the oxides by chemicals (HCl, Cl_2 and Cl_2+C). The oxides tested include UO_2, UO_2 Simulated Fuel (SIMFUEL), several lanthanide oxides and PuO_2; the work was performed at Marcoule-CEA (France) within the framework of a scientific agreement. The dissolution of NpO_2 was also performed at Marcoule during 2004-2005.

During the PYROREP project the determination of basic thermodynamic and kinetic properties by electrochemical techniques in molten salts started with the study of some lanthanides, U and Pu (CEA-CIEMAT agreement) [10]. In EUROPART this work continued with the determination of the basic properties of other lanthanides, noble metals, transition metals and Np (CEA-CIEMAT agreement) [11].

The basic thermodynamic properties of some lanthanides in liquid metals Cd and Bi, and solid Al cathodes were obtained by the UVA during the PYROREP project [12]. This work continued during EUROPART in CIEMAT; based on results obtained during PYROREP the work was focused only on Al cathodes [13,14].

At the same time some An/FP separation tests were performed using this Al cathode at the JRC-ITU (JRC-ITU-CIEMAT agreement). The objective of these tests was to determine the recovery yields for the residual actinides contained in the molten salt after the electrorefining step, and the separation factor from lanthanides in an exhaustive electrolysis step.

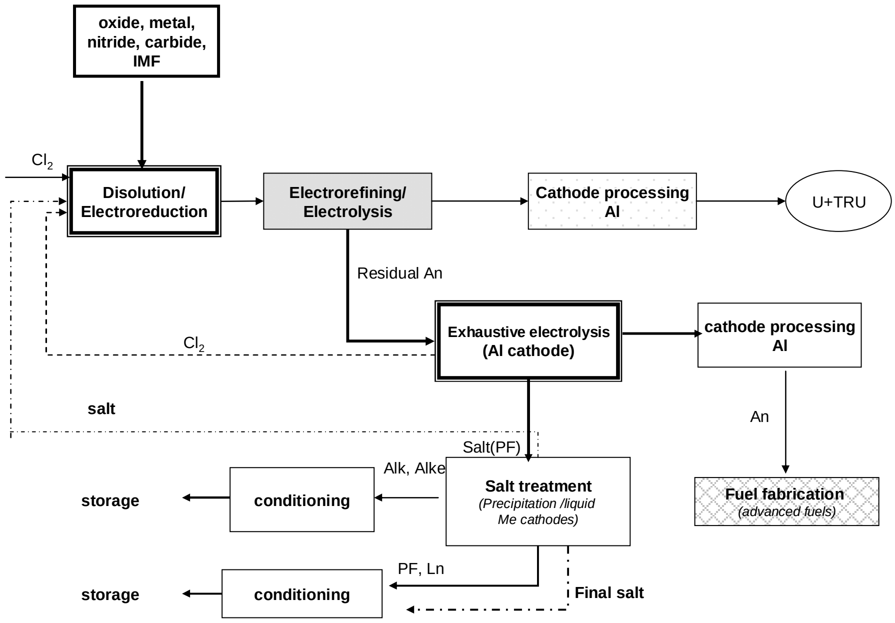
During PYROREP work related to the salt decontamination from lanthanide fission products was performed by precipitation to obtain the corresponding oxides or oxychlorides. Results indicated a quantitative precipitation of these elements in tests performed with individual lanthanides. The decontamination from residual actinides, U, Pu and Np, was also studied by precipitating them as oxides.

The research on salt decontamination by precipitation continued during EUROPART. The previous results showed that lanthanides tend to form oxychlorides instead of oxides when carbonates or oxides precursors were used; however, this type of compound has to be transformed into oxides in order to be compatible with a conventional vitrification process. To avoid this additional step, the possibility of precipitating the lanthanides as phosphates was also studied. Among other fission products, the noble metals (Ru), transition metals (Mo) and Sr, Ba and Cs were also investigated.

The study also focused on the selective removal of Sr, Ba and Cs with the aim of recycling the molten salt to the separation process and to obtain waste forms suitable for the final disposal of these fission products. Results obtained show that the removal of alkaline and alkaline-earth metals by precipitation in this molten media was not possible, neither as oxides nor as phosphates. For this reason, the study of their removal by electrolysis using liquid metal cathodes such as Pb was started at the end of EUROPART project. Preliminary results show that selective recovery of these elements is not feasible and they will be co-electrodeposited with the Li and K constituting the electrolyte.

The general flow sheet that is being considered is shown in Figure 7.1, and is similar to those proposed by other European countries. One of the advantages of this process would its versatility; that is, it could be applied to different fuel types with only limited modifications.

Figure 7.1: Schematic flow sheet for the pyrochemical processes



7.3 Conclusion

Studies of several steps of the separation process are ongoing but all are at early stages. The main results are summarised here.

With respect to the hydrometallurgical separation process, a bis-malonamide ligand, synthesised by UAM, exhibits very promising behaviour for the co-extraction of actinides (III) and lanthanides (III), compared with the monomalonamide DMDOHEMA. A new family of ligands based on bis-diglycolamides has been developed. These compounds showed good solubility in aliphatic solvents, extraction capability for An(III)/Ln(III) and hydrolytic and radiolytic stability. A European patent (n° 06380268.0, November 2006) has been registered under CIEMAT, UAM, ICIQ and FZJ.

The use of synergic mixtures calix[4,6]arenes and COSAN derivatives with CMPO reagent is also very promising.

Much work remains in order to be able to design and test cold and hot continuous laboratory scale separation processes, and even more so for the scaling-up of such processes. A similar conclusion applies to the pyrochemical process, for which the main finding is that the dissolution of an oxide-type fuel is feasible, although it has been only tested at milligram scale.

Based on the standard potential data obtained during PYROREP and EUROPART, the separation of actinides, all together, seems feasible using aluminium cathodes, in a batch process. Salt (LiCl-KCl) decontamination from Ln and residual An by precipitation techniques appears to be relatively straightforward, however, this is not the case for Sr, Ba and Cs. For the removal of these elements, the use of liquid lead cathodes is under investigation.

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Chapter 8: United Kingdom

Although the adoption of partitioning and transmutation (P&T) is not seen by the UK government as the most promising way forward for addressing nuclear waste management issues, it may be more important in the longer term following a renaissance of the nuclear industry.

Set against this background, the concept of P&T is viewed by the scientific nuclear community within the UK as being both technically challenging and scientifically interesting and to offer some potential benefits to the long-term management of long-lived radioactive wastes and in particular the management of irradiated fuel. Indeed, some overlap between the technologies to be developed within P&T and those required within the UK for managing the nuclear legacy are apparent. The role that collaborative international programmes play in both leveraging national programmes and maintaining nuclear skills is also recognised within the UK nuclear science community and funding agencies.

The UK government has recently agreed to the formation of the UK National Nuclear Laboratory (NNL), bringing together capabilities previously held within Nexia Solutions (the R&D subsidiary of British Nuclear Fuels plc) and research facilities (Figure 8.1) owned by the Nuclear Decommissioning Authority (NDA) with a mission that includes undertaking strategic nuclear R&D and safeguarding skills. The NNL, therefore, continues to develop techniques applicable to reprocessing and hence to partitioning. This work consists of both extensions to and refinements of the current reprocessing techniques, *i.e.* the PUREX process, and the development of more novel technologies using non-aqueous media, including pyrochemical studies. A key element of current programmes is the participation in international programmes.

Sections 8.1 and 8.2 of this chapter set out the broad scope of both aqueous and non-aqueous separations programmes being pursued in the United Kingdom and report some of the developments that have been made in the last five or so years.

Figure 8.1: External view of Central Laboratory, Sellafield

8.1 Aqueous-based separations studies

In the UK and world wide, substantial experience exists at the industrial scale of using aqueous-based processes for treating spent nuclear fuel, separating and purifying the valuable components (U, Pu) for recycle as new fuels and conditioning the residual fission products and minor actinides in suitable waste forms for interim storage and ultimate disposal. Extension of these technologies to enable the partitioning of minor actinides (MA = Np, Pu, Am, Cm) and problematic fission products is a rational goal. Over the last 15+ years the UK has investigated advanced reprocessing that includes extending the PUREX process to recover Np and Tc and to avoid separated Pu within the process. More recently, the UK has participated in collaborative international efforts to separate the trivalent MA, particularly through the European 6th and 7th Framework Programmes (FP6, FP7). This section gives a brief overview of this history.

8.1.1 Advanced PUREX development

The advanced PUREX development programme used current reprocessing plants such as THORP as its starting point with the aim of reducing the costs and environmental impacts of the process, whilst enhancing proliferation resistance. A common development strategy has been adopted in all areas, the main elements of which are:

- development of concepts;
- fundamental laboratory studies;
- production of computer models using advanced simulation tools;
- design and construction of targeted rigs at various scales to test concepts and prove models;
- concurrent research and engineering design.

Each stage involves close interactions between experimentalists, engineers and modellers with feedback loops, *e.g.* fundamental data is required to develop models, the models then identify where uncertainties in the fundamental data exist and new experimental work is generated that then refines models. Process improvements have been investigated in all aspects of the PUREX process from fuel dissolution and other head-end processes through the solvent extraction separations and into product finishing. As the scope of this review is limited to separations, we therefore concentrate on developments in the field of fuel dissolution, as the necessary precursor to any aqueous-based separation process, and solvent extraction, which is key to performing the required separations. However, the technical challenges to be faced in finishing or converting transuranic (TRU) nitrate liquors to advanced mixed-oxide (MOX) products in any future process should not be underestimated.

8.1.2 Head-end process development

The primary purpose of a head-end process is to convert irradiated nuclear fuel into a form suitable for the separation of fission products from fissile and fertile elements remaining in the fuel. This involves the exposure of the fuel from within its cladding to a suitable solvent, conventionally nitric acid. Some drivers to be considered when developing alternative dissolution processes are:

- minimisation of the number of individual operations;
- avoidance of mechanical plant wherever possible;
- simplification of the diversity of waste streams;
- increase of flexibility towards different feeds;
- avoidance of the production of metallic fines;
- use of fuel cladding to form matrix for encapsulation of fission product wastes;
- improved fuel dissolution performance;
- minimisation of insoluble fission products.

Development of a range of head-end equipment and processes has been conducted by NNL (and its predecessor organisations) in recent years. These studies have included:

- continuous dissolver design [1];
- electrochemical dissolution of fuel and cladding [2];
- chemical dissolution of fuel and cladding [3];
- effects of dissolver chemistry on extent of insoluble fission product formation [4];

- enhanced dissolution processes to assist with dissolution of insoluble plutonium [5];
- colloidal and insoluble iodine behaviour during fuel dissolution.

Of particular relevance to separations required for partitioning and transmutation are the studies associated with iodine behaviour during dissolution and methods of increasing the solubility of plutonium which is particularly important when considering the recycling of plutonium from fuels with high plutonium contents such as LWR MOX and Generation IV fuels.

Studies investigating iodine behaviour have shown that whilst greater than 95% of iodine is volatilised during the dissolution of spent fuel small traces may remain present in the dissolver liquor in reduced forms. Encouraging results have been achieved in laboratory studies in which an oxidised form of iodine (iodic acid) has been added in order to oxidise iodides to volatile iodine whilst being itself reduced to iodine.

Fast reactor fuels, which are under serious consideration for Generation IV (Gen-IV) nuclear fuel cycles, often contain an appreciable plutonium content which may lead to solubility issues during reprocessing. The most promising technology for dissolution of insoluble plutonium dioxide is based on the use of electrochemically generated divalent silver, Ag(II) [6], however, this work has been almost entirely restricted to the dissolution of plutonium dioxide in the absence of potentially interfering compounds that may be present following the dissolution of spent nuclear fuel. We have therefore conducted fundamental studies into the kinetics of Ag(II) with plutonium dioxide and a range of fission product element compounds.

Further investigations of the Ag(II) process and advanced dissolution options for Gen-IV fuels (*e.g.* mixed actinide oxides, carbides and nitrides) are currently being undertaken by NNL within the context of the European Framework Programme (FP) VII project ACSEPT.

8.1.3 Solvent extraction development

As noted previously, aqueous separations for advanced fuel cycles will undoubtedly continue to rely on solvent extraction (SX) based technologies. Advanced solvent extraction development projects have, therefore, formed a major part of NNL's Advanced Reprocessing and Advanced PUREX programmes. The SX component has traditionally been divided into four task areas, *viz.*:

- process chemistry;
- flow sheet development including modelling and simulation;
- flow sheet testing;
- equipment development.

A principal goal of the Advanced PUREX programme is to reduce the number of solvent extraction cycles to one from the current multi-cycle process. The THORP plant at Sellafield, for instance, requires three SX cycles to purify separate UO_3 and PuO_2 products, suitable for storage and re-use (see Figure 8.2). The products required from a future process have not yet been defined and so the development programme has aimed to support a range of options. The most restrictive option is a notional "high specification" single cycle flow sheet, as shown in Figure 8.3 (designed to produce products of similar purity to those produced by existing reprocessing plants); other options under development produce a plutonium product of reduced purity due to the co-routing of neptunium and a small portion of the uranium with the Pu product whilst retaining a pure uranium product (*i.e.* co-processing) and separation of a Tc product. A more conservative version of these single cycle concepts has recently been proposed in partnership with Energy*Solutions* under the US-led Global Nuclear Energy Partnership (GNEP) initiatives and termed NUEX™ [7]. Generically, these modified PUREX processes combine some or all of the following unit stages:

- primary extract/scrub (fission product removal) (termed HA/HS conventionally);
- Tc rejection;
- U/Pu partition, including options for Pu/Np or Pu/Np/U co-processed products;
- Np rejection (if Np not routed with Pu product);

- U backwash;
- additional purification cycles (uranium and/or transuranic purification cycles);
- diluent washing of aqueous streams, solvent washing/recovery, etc.

Figure 8.2: Outline THORP flow sheet

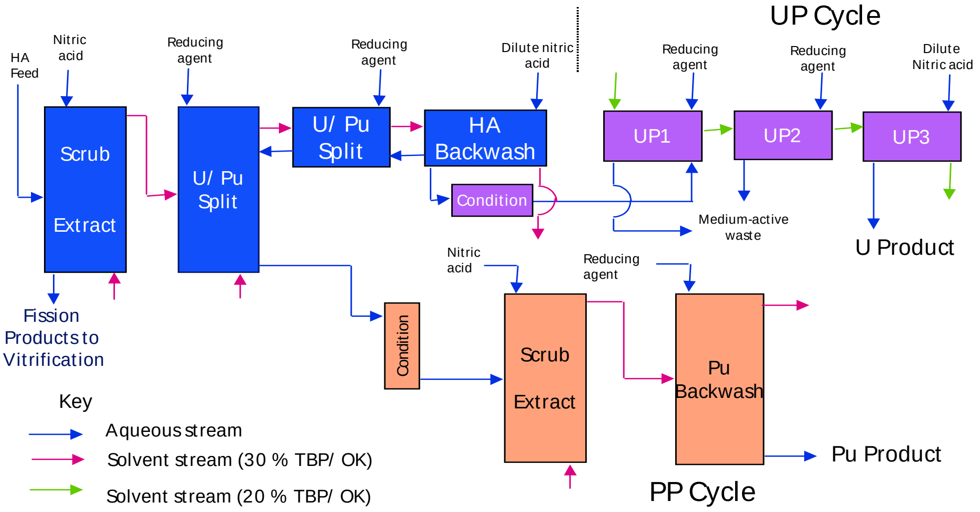
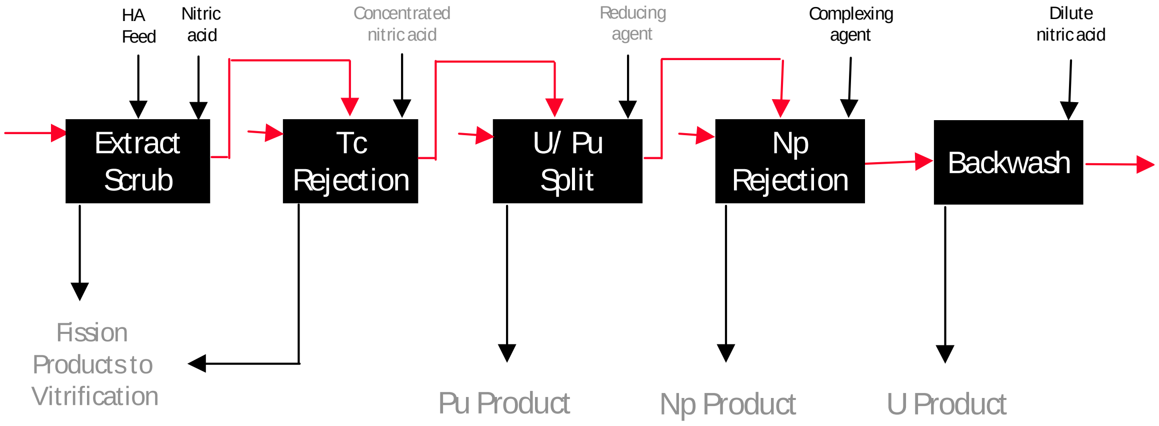


Figure 8.3: Conceptual "high specification" flow sheet, aimed at emulation of THORP-type performance within a single cycle



8.1.3.1 *Process chemistry*

The target of moving from three- to two- or single-cycle processes raises a number of challenges with respect to control of particular elements, notably: plutonium, neptunium and, to a lesser extent, technetium. Indeed, much of the process chemistry based R&D within the Advanced PUREX project has focused on underpinning the control of these key elements.

The use of a high concentration acid scrub for technetium rejection has become widely adopted in recent years although there are subtle issues which we continue to study such as the mass transfer characteristics of the various pertechnetate-metal cation-TBP complexes. Additionally, interactions between technetium and promising reductant/complexants should be understood [8].

The issues associated with controlling neptunium and plutonium within rationalised flow sheets are rather more complex and much effort has been expended on developing alternative reductants and complexants for use within Advanced PUREX processes as Np and Pu stripping agents. Much detailed work [8-13] led to the choice of hydroxamic acids as a promising class of stripping agents for achieving improved actinide separations in PUREX-based reprocessing flow sheets.

The major flow sheet change introduced by using hydroxamic acids is to change the U/TRU separations from reductive stripping, as used in conventional reprocessing flow sheets to stripping based on complexants [14]. Hydroxamic acids also serve a dual purpose in that they are suitable both for strongly complexing tetravalent actinides in a hydrophilic complex and for reducing extractable, hexavalent neptunium to the inextractable pentavalent state at very fast rates [15]. A further advantage is that although the Pu(IV)-hydroxamate complex is slowly reduced to Pu(III) [16], the rate is very low and the flow sheet, therefore, does not rely on Pu(III) reduction, indeed it is undesirable and suppressed. Hence a stabilising agent such as hydrazine or sulphamic acid is not required in hydroxamic acid based flow sheets to prevent redox cycling of Pu in the contactor.

In common with workers in Japan, France and the USA, studies have also been made in the UK relating to the control of neptunium by variation in nitric acid strength and solvent extraction contactor residence time, in order to ensure quantitative extraction of Np in the primary extract/scrub contactor. Np redox kinetics in aqueous and TBP phases are key to this flow sheet step [17].

8.1.3.2 Flow sheet development/modelling and simulation

Mathematical modelling is a powerful tool that can be used to develop successful flow sheets without excessive recourse to full experimental testing and is used extensively within NNL for simulating prospective flow sheets [18]. The strategy adopted to produce a reliable flow sheet modelling capability has included the following steps:

- identification of required thermodynamic and kinetic parameters such as distribution data, reaction kinetics, mass transfer rates, etc.;
- obtaining the necessary data through literature sources or by experiment;
- model development;
- model validation through experimental testing;
- model application.

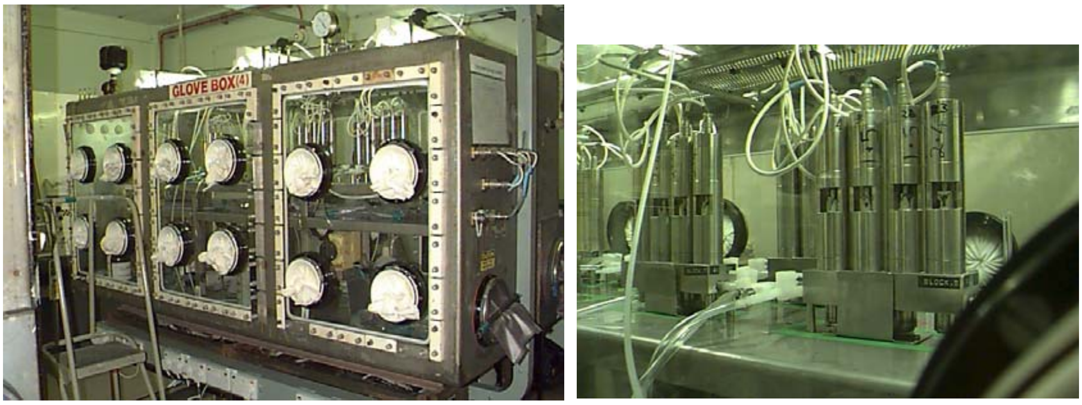
Key fundamental information required for the models includes:

- contactor-specific data such as mixer volumes, settler volumes and heat capacities;
- distribution data for species of interest, *e.g.* nitric and nitrous acids, U(IV,VI), Pu(III, IV, VI), Np(IV,V,VI), Zr(IV), Tc, Cs, Sr, Ce(III) and water, etc;
- mass transfer kinetics for extraction and back-washing: fundamental and more empirical approaches, including contactor-specific stage efficiencies, have been considered and data experimentally determined in some cases;
- chemical kinetics of reactions in both aqueous and solvent phases;
- radiolysis and hydrolysis effects (primarily dibutyl phosphate production);
- solvent dilation effects caused by extraction;
- extraction enthalpies;
- entrainment of one phase in another.

Where information has not been available from literature or previous experiments, the necessary experimental programmes have been put in place to fill gaps leading to further refinements in the models. Mass transfer data have been collected using single-stage or small banks of contactors (Figure 8.4) and data from flow sheet trials utilising larger cascades of contactors (Figure 8.5) are used to validate models.

Figure 8.4: Centrifugal contactors used for solvent extraction experiments

Figure 8.5: Glove box centrifugal contactor cascade



8.1.3.3 *Flow sheet testing*

In order to demonstrate the suitability of specific reagents and flow sheets, counter-current extraction trials using multiple contactors are performed. Dependent upon flow sheet complexity, up to 36, Chinese-design INET 1 cm rotor diameter (RD) extraction stages are included in such tests. Glove box facilities as shown in Figure 8.5 have been used to permit the use of appropriate quantities of plutonium as well as uranium, neptunium, technetium, zirconium and other inactive fission product simulants.

In-line and at-line analysis has been developed to maximise the amount of data collected and to improve experimental efficiencies. The use of UV-vis and UV-vis-NIR absorption spectroscopies to monitor U loading and Pu oxidation state/complexation on-line is a key feature of NNL cascades.

A range of experimental flow sheets have been tested for simulated LWR, LWR-MOX, fast reactor MOX and UK exotic legacy fuel, including:

- technetium rejection;
- neptunium rejection from a U product stream [19];
- complexant based co-stripping of neptunium/plutonium using hydroxamic acids (7-40 wt.% Pu feeds) [20];
- reductive co-stripping of neptunium/plutonium using HAN (7 wt.% Pu in feed) [20];

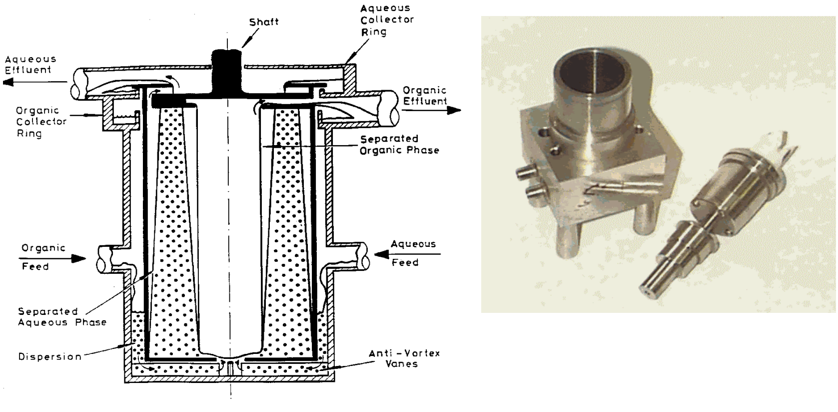
Additionally, trials based on current UK reprocessing plant flow sheets are tested to underpin or enhance Sellafield operations and safety cases [21].

8.1.3.4 Equipment development

In the past, NNL's Advanced PUREX programme has included the investigation of intensified solvent extraction contactors, in particular fluidic and centrifugal. The programme now assumes that centrifugal contactors, see Figure 8.6, will be used in a future reprocessing plant. The main areas for development of these contactors are:

- contactor design and capacity (throughput) issues;
- scale-up, this largely involves mass transfer issues.

Figure 8.6: Diagram and photograph of single stage centrifugal contactor



Much of the flow sheet testing is undertaken using small contactors of 1 or 2 cm RD. These have the advantage of requiring relatively small volumes of process liquors and thus minimise the inventory of nuclear materials required within a laboratory environment and also the radioactive wastes generated. Fine control over the contactors and associated equipment is required for the stable operation of such small contactors and a good understanding of their mass transfer and hold-up characteristics is required for simulation. However, the chemical engineering aspects of the contactors are also studied at a larger scale in order to determine hydrodynamic properties of the contactors such as maximum and minimum flow rates, acceptable solvent-aqueous ratios and mass transfer characteristics. Past studies have used modularised four-block 5.5 cm rotor or at still larger scale, single stage 10 cm RD contactors, as shown in Figure 8.7.

Figure 8.7: 10 cm rotor diameter centrifugal contactor

The hydrodynamic characteristics determined by experiment are compared with model predictions based on the use of computational fluid dynamics techniques (CFD). Improved CFD models are then used to predict mass transfer characteristics and throughput rates for different size contactors and thus to scale equipment for particular duties.

Over the last few years, engineering development of industrial scale centrifugal contactors has been suspended within the NNL, with a focus placed on flow sheet testing and modelling development, using commercially available ("off-the-shelf") small scale contactors, reflective of the more immediate needs in advanced reprocessing and partitioning process development. We would expect that as P&T technologies move towards a state of maturity, requiring pilot-scale demonstration, engineering programmes to industrialise centrifugal contactors for nuclear process plants will again be required.

8.1.4 Future PUREX development

Future recycle strategies place much more of an emphasis on total actinide recycle. That is, recovery of uranium and all the transuranics (Np, Pu, Am, Cm…) and their subsequent fabrication into fuel or targets suitable for actinide incineration by fast neutrons. Practically all strategies assume that the PUREX process (*i.e.* SX using diluted tri-butyl phosphate (TBP) as the sole extractant) will continue to be used, albeit in modified form, for controlling U, Pu, Np, I and Tc. As seen from the preceding sections, NNL has a strong track record in developing modified PUREX processes for advanced fuel cycles and will continue such R&D. Some likely areas for future development include:

- continuing the development of complexant-based processes that utilise simple hydroxamic acids to achieve improved Np and Pu control within process flow sheets;
- achieving quantitative Np extraction from the first (HA/HS) contactor within advanced flow sheets, especially at short residence times;
- better approaches to dealing with mass transfer kinetics in process models;
- proliferation-resistant flow sheets;
- MOX and Gen-IV fuel processing;
- definition and validation of design reference flow sheets, including hot tests within the NNL Central Laboratory (when HA cells are available).

8.1.5 Other aqueous (non-PUREX) separation processes

A range of alternative, non-PUREX based, aqueous separation processes were examined by NNL (as its predecessor organisations) during the early 1990s including the use of carbonate media and crystallisation processes. After initial study it was concluded that none of these alternative processes showed sufficient potential to warrant further investment in the form of additional development. This conclusion was reached after assessments of the degree of separation that the alternative processes might realistically be expected to achieve and their degree of developmental maturity. AEA-T, the privatised arm of the United Kingdom Atomic Energy Authority (UKAEA) have, however, been active in the field of uranium separation by crystallisation through contractual research arrangements with Japanese workers [22].[1] Whilst progress has been made internationally in these fields, for the foreseeable future it is expected that NNL resources will continue to be focused on SX-based separation processes, which remain most highly relevant to current and next generation fuel cycles.

8.1.6 Trivalent actinide separations

8.1.6.1 Selective ligand development for DIAMEX/SANEX processes

Complementary to the work performed by NNL to refine the separations performed in the PUREX process is the work of the University of Reading in the field of selective actinide (III)/lanthanide (III) complexants for DIAMEX and SANEX processes. Through participation in a number of European FP

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[1] Reflecting the ongoing rationalisation of the UK nuclear industry, in 2005, the nuclear sciences business within AEA-T was sold to BNFL (Nexia Solutions) and has since been amalgamated into the NNL.

projects, NEWPART, PARTNEW, EUROPART, ACSEPT, the University of Reading has been involved with the synthesis, characterisation and analysis of a range of potential complexants including particularly the malonamides and heterocyclic nitrogen ligands [23-27].

A wide range of malonamides and heterocyclic nitrogen ligands, *e.g.* ter- and higher oligo-pyridines, bis-triazine pyridines and other polynitrogen ligands, have been synthesised and crystal structures determined for a large number of complexes [27]. Significant improvements to the synthetic procedures in terms of increased yields and decreased number of steps in the routes have been made. This is particularly important as it has allowed the production of larger amounts of a wider number of compounds than would otherwise have been possible.

NNL have also modelled the performance of DIAMEX flow sheets using DMDOHEMA (dimethyldioctylhexylethoxy-malonamide) and DMDBTDMA (dimethyldibutyltetradecyl-malonamide) extractants and SANEX flow sheets with n-PrBTP (n-propyl-2,6-di(1,2,4-triazin-3-yl) pyridine) and $CyMe_4BTBP$ (6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2′] bipyridine), highlighting the importance of mass transfer effects in these actinide (III) partitioning processes [28].

8.1.6.2 GANEX process development

Recently, as the NNL contribution to the FP VII programme ACSEPT, studies into developing a workable Grouped Actinide Extraction (GANEX) process have been initiated. The approach mirrors our approach to Advanced PUREX development in combining initial studies of process chemistry (distribution data, third phase formation, etc.), model development and alpha-active flow sheet trials. It is currently anticipated that prototype GANEX flow sheets will be cold-tested at NNL laboratories during 2009-10. Initial efforts are focused on adapting mixed extractant-based flow sheets for GANEX.

8.1.7 Conclusions regarding aqueous separations

The UK has a long involvement with the development and practice of aqueous chemical separations in the processing of spent nuclear fuel. This continues through the operation of two reprocessing plants at Sellafield and the separation of tonne quantities of plutonium per year.

Within NNL and its predecessor organisations an active development programme seeking to further refine the PUREX process has led to significant process developments with regard to the control of key species such as technetium, plutonium and neptunium and this work continues through fundamental chemistry studies, modelling and flow sheet testing. A major component of this programme has been the development and application of simple hydroxamic acids in complexant-based flow sheets.

The increased interest shown by other parties with regard to the control of the higher actinides is recognised within the NNL and the NNL is actively involved with international programmes, primarily those under the European Frameworks and the Global Nuclear Energy Partnership (GNEP). Reflective of UK strengths, NNL generally seeks to focus on aspects of process development and industrialisation, complementary to expertise brought by other organisations within such projects.

Work in the UK university sector is highly complementary to that of the NNL, in particular in the fundamental development and characterisation of specific ligands suitable for the separation of actinides and lanthanides from both other metals and one from another.

8.2 Pyrochemical separations studies

8.2.1 Background to the UK pyrochemical separation programme

In the UK, there is interest in the treatment of legacy fuels, management of fuel residues and advanced reactor types and associated fuel cycles. Internationally, the advantages of pyrochemical or molten salt processes to deal with such issues have been advocated. Based on our experiences, the NNL believes that the greatest challenge facing pyrochemical technology along with the understanding of underpinning science is the transformation into one or more commercially viable industrial-scale processes against given needs.

In the 1990s, the Advanced Reprocessing Programme examined a number of technologies for future fuel treatment and recycle applications including pyrochemistry. This led to the founding of the Molten Salts Project that consequently developed a capability within the company and established links internationally. Small-scale experimental programmes were established along with a number of assessments and pre-conceptual design studies. Work, much of it now in the open literature, was performed on the dissolution of uranium dioxide in carbonate melts [29-30].

In more recent years, the NNL programme was geared towards understanding process possibilities against legacy fuel management needs and Generation IV fuel cycles and examining the technical factors, which impact on industrialisation and commercial viability [31].

In the UK, AEA Technology (AEA-T), the privatised commercial division of UKAEA, has provided contract research services for the pyrochemical separations area in recent years for a number of organisations including CRIEPI [32-33] and KAERI [34] and NNL (then as BNFL Research and Technology) as part the European Commission 5th Framework (FP5) PYROREP programme [35] (see footnote 1).

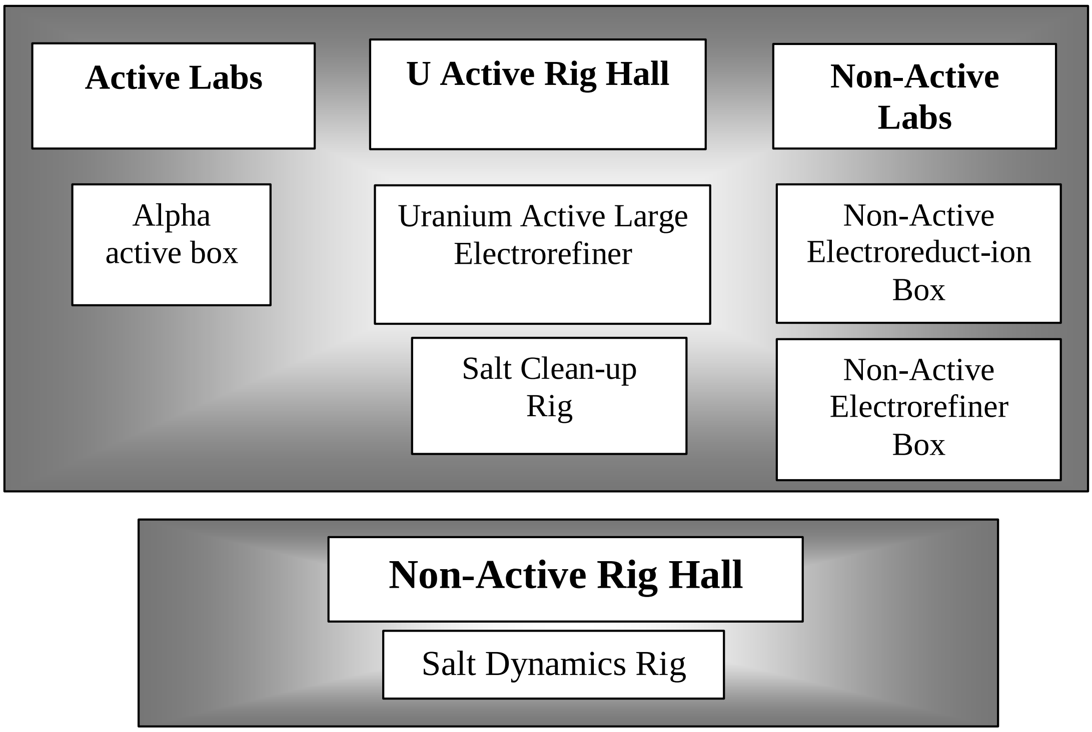
8.2.2 Current pyrochemical separations programme

Between 2001-07, a major molten salts project was completed within the NNL, including pyrochemical test work at bench scale in the Central Laboratory. The pyrochemical bench and pilot scale work planned within that programme is shown in Figure 8.8. NNL participated in the 6th and now the 7th Framework Programmes (notably the EUROPART and ACSEPT projects).

The aims of the NNL pyrochemical separations programme included:

- investigate and understand industrialisation of pyrochemical technology;
- construct experimental facilities to continue fundamental studies;
- construct pilot plant facilities to develop industrialised designs of equipment;
- maintain and develop technical and engineering expertise;
- establish a network of co-operation with international organisations.

Figure 8.8: Planned pyrochemical bench and pilot scale work in the Central Laboratory, Sellafield



Consequently, the main technical parts of the NNL Molten Salt Project were:

- laboratory scale U and U-Pu-Am-Nd-Ce electrorefining (FP5 and FP6);
- design and cost studies for industrialisation of pyrochemical separations;
- legacy fuels test case pyroprocess studies;
- conceptual and detail design for pilot-scale uranium electrorefiner;
- molten salts dynamics rig;
- alpha active laboratory scale electrorefiner;
- other rigs and laboratory tests – salt purification, direct electrochemical reduction of oxides, inactive electrorefiner visualisation, etc.;
- salt clean-up (FP7);
- international collaborative studies;
- university research projects.

8.2.3 NNL actinide electrorefining and partitioning study

A major part of the NNL Molten Salt programme in the period 2000-2003 was the design, construction and testing of a 1 L capacity, alpha active chloride salt electrorefiner and associated reductive extraction equipment. These have been used to measure various kinetic and thermodynamic data as well as to explore and develop further partitioning process features. Electro-transport to solid and liquid cathodes was used together with selective reductive extraction, using Cd-Li, etc., and molten salts. Determinations of distribution coefficients between different salt and metal phases were made. Tests included:

- electrorefining of uranium (electrodeposition of pure U at solid cathode);
- electrorecovery of plutonium alloy (electrodeposition of Pu-U-MA in liquid cadmium cathode);
- electropartitioning of minor actinides and simulated rare-earth fission products at low major actinide concentrations (selective electrodeposition at liquid cathodes);
- chemical partitioning of minor actinides and simulated rare-earth fission products in the presence of actinides (reductive extraction using molten salt transport).

Progress has been reported during the past several years and the following results have been obtained [36-37]:

- good separation of uranium from other solutes by electrolytic deposition at a solid cathode (electrorefining), effective separation factors of >1 000 and >500 for Pu and rare-earth elements respectively;
- electrorecovery of Pu-U-Am achieved using liquid cadmium cathodes (LCC);
- partitioning of Pu-U-Am by electroseparation from Nd, representative of rare-earth elements was, as expected, less effective than predicted from literature values of separation factors obtained from equilibrium measurements and declined with increasing LCC current density;
- separation of Pu from Am also declined with increasing LCC current density;
- reductive decontamination of LiCl-KCl electrorefiner salt from U, Pu, Am and Nd chlorides was rapid and quantitative using Li metal;
- salt decontamination by use of a Li/Cd anode and a solid cathode was performed but was not straightforward because of current limitations and chemical reaction between Li-Cd and U-TRU in the salt.

A simplified drawing and a picture of the BNFL electrorefiner are shown in Figures 8.9 and 8.10. The latter shows the electrorefiner mounted within a hot well and inside an argon atmosphere glove box. Photographs of electrorefined uranium metal of dendritic morphology at a steel cathode are shown in Figures 8.11 and 8.12.

Figure 8.9: Simplified drawing of NNL electrorefiner for Pu-U-Am electrorecovery and partitioning from Nd, and U electrorefining

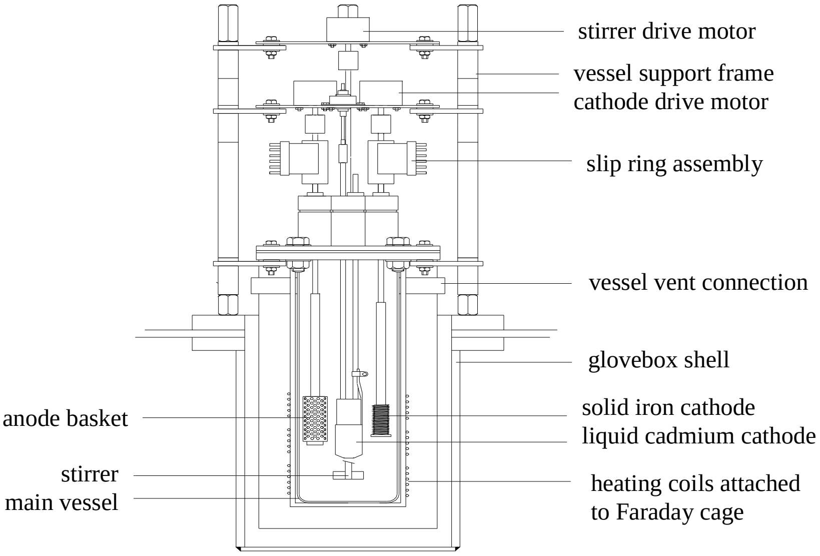


Figure 8.10: Photograph of NNL electrorefiner for Pu-U-Am electrorecovery and partitioning from Nd and U

Figure 8.11: Uranium electrodeposit on steel cathode – dendritic morphology

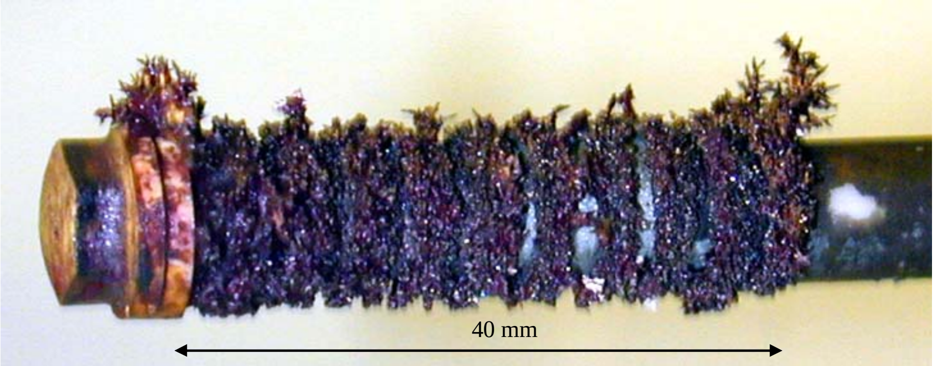
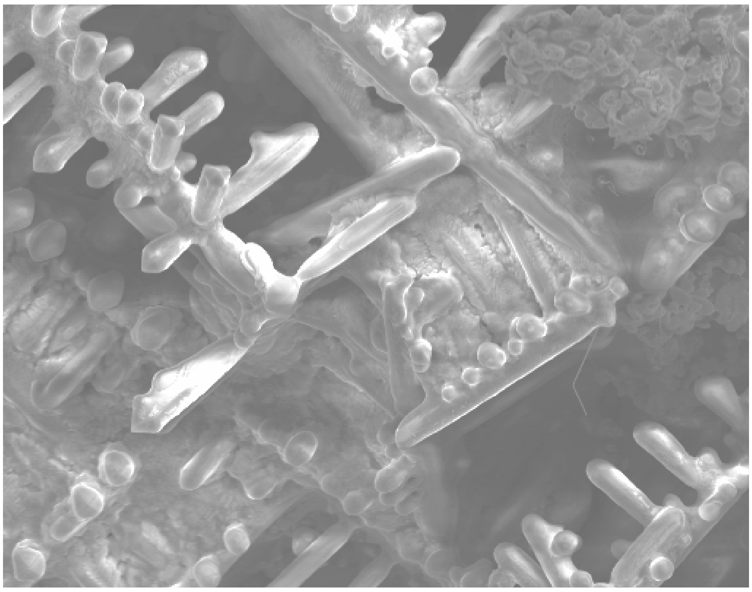


Figure 8.12: Dendritic morphology uranium electrodeposit on steel cathode

Image width of 625 μm



8.2.4 Design and cost studies

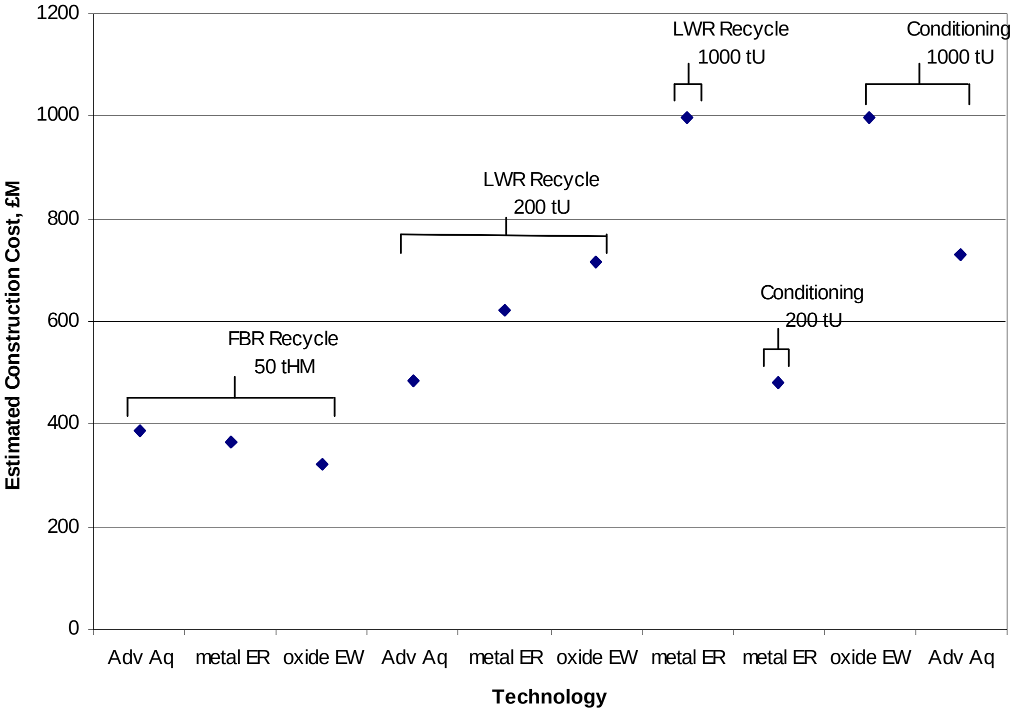
NNL has examined various options for pyrochemical-based flow sheets to process spent nuclear fuel. A number of engineering and modelling studies were performed to compare the suitability of these flow sheets against various treatment strategies. Within the flow sheet, consideration of the detailed operating parameters, such as electrorefining efficiencies and decontamination factors, needs to be taken to allow engineers to size the equipment. However, just as important is the consideration of secondary processes and their effect on the overall size and economics of the facility.

Estimated construction costs of reprocessing facilities using a variety of technologies and for various throughputs are shown in Figure 8.13. The following conclusions were drawn from the design and cost studies [38]:

- Pyrochemical technology could be the most economic option for small-scale recycle or partitioning applications where high burn up fuels or targets are likely.
- Large-scale spent LWR fuel treatment facilities are unlikely to be pyrochemical; aqueous technologies still offer the most economic option.

- Industrial nuclearisation of hardware is crucial, but must be supported by a strategic scientific programme with the primary aim of investigating issues relating to industrialisation.
- Electrorefining development will not deliver a complete process and the treatment of waste salt must be given sufficient priority if pyrochemical technology is to be applied at a commercial scale.
- Robust industrial designs of pyrochemical equipment will rely on successful nuclearisation of fluid and solid transfer systems, infrastructure and waste treatment systems.

Figure 8.13: Estimated construction costs for various spent fuel treatment facilities



8.2.5 *Design of pilot-scale uranium electrorefiner*

Uranium electrorefining and electrorecovery of TRU-U are central to the pyrochemical separation of spent nuclear fuel by the Idaho National Laboratory (INL) process [39] as demonstrated recently by treatment of fuels at INL [40]. NNL and JAEA have a technical co-operation agreement in the fuel cycle area which includes performing technical collaboration in the industrialisation of pyrochemical separations. Scale-up, capacity factor and safety are considered key to the application of electrorefiner (ER) technology at commercial scale. Existing and alternative ER design concepts have been identified and are being assessed for use as industrial units. The aim was to perform a transparent design procedure including peer review and recommendation of a small number of favoured candidates, later to be reduced to one. Design objectives have been based on the use of high fissile content fuel taking account of severe criticality safety constraints and with an initial facility throughput of 50 t(HM)/a with possible later deployment at 200 t(HM)/a. The selected industrial ER candidates in order of preference were [41]:

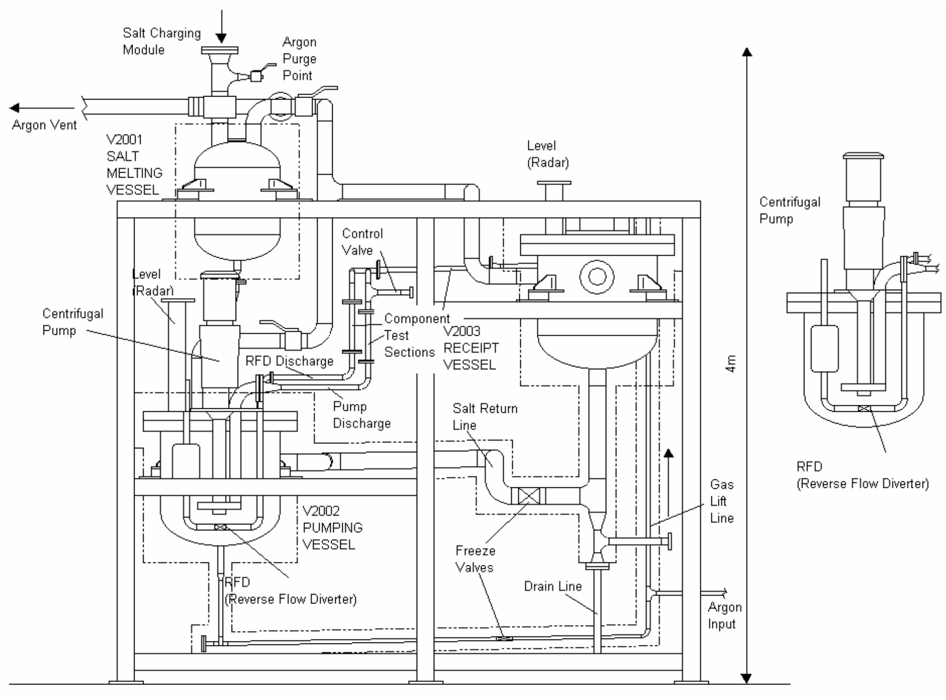
1) crusting liquid metal cathode with anode basket;
2) scraped vertical planar cathode with anode basket;
3) liquid U-alloy metal cathode with fluid ramp anode.

A 1/5th-scale pilot plant, using depleted U and alkali chlorides, was taken to the detailed design stage although construction and testing were not a part of this project phase.

8.2.6 Molten salts dynamics rig

A schematic of the NNL molten salt dynamics rig is given in Figure 8.14. The functions of the rig include: salt charging (melting, freezing), salt transfers [gas lift, centrifugal pump and reverse flow diverter (RFD)], atmosphere control, freeze valves, materials properties, components behaviour and instruments and controls. RFD are widely used in PUREX plant and in HLW storage tanks. Salt transport behaviour has been investigated during transfers and by flow between vessels. The salt inventory is around 60 litres.

Figure 8.14: Molten salts dynamics rig



8.2.7 Other experimental facilities for the NNL pyrochemistry programmes

Further molten salt tests and equipment developed during the Molten Salts Project included rigs for oxide reduction, U electrorefining, U and TRU electrorefining and partitioning, and waste processing. A general-purpose argon dry box with two hot wells, an alpha active argon glove box and dedicated rigs for electrorefining and waste management has been constructed although not yet actively commissioned.

A laboratory-scale test rig for direct electrochemical reduction of refractory metal oxides in calcium chloride electrolyte has been used in inactive simulant and zirconia reduction experiments with significant conversions to metal form established. Studies on electrolyte systems, electrodes, conversion and selectivity were carried out.

8.2.8 Recent international collaborative studies in pyrochemistry

International collaborative pyrochemical activities have taken place between Japan and the UK in recent years. In 2001, NNL and JAEA (then JNC) of Japan signed a Technical Co-operation agreement that includes pyrochemical studies. An NNL engineer was seconded for two years (2000-2002) to Tokai Works as a JNC International Fellow. The fellowship involved the investigation of pyrochemical processes applied to fast reactor fuel reprocessing. Work addressed the scale-up of pyrochemical equipment. Another NNL research scientist was seconded to JAERI during 1999 to 2001. Work concentrated on the measurement of fundamental thermodynamic properties and electrochemical studies.

NNL has performed a number of pyrochemical plant design and feasibility studies under contract with other Japanese organisations including JAPC and JNC. CRIEPI and NNL were involved with the PYROREP European Commission 5th Framework Programme (FP5). AEA Technology (AEA-T) has performed contract research for a number of organisations. Work was performed with CRIEPI, examining the reduction of actinide oxides using lithium metal. Uranium, plutonium, americium and neptunium oxides and un-irradiated mixed-oxide pellets were studied [32-33].

KAERI and AEA-T have collaboratively performed electrorefining studies at Harwell on the electrolysis of actinide and lanthanide fluorides in LiF-NaF-KF melt [34].

Links between NNL and US groups include secondments to ANL and participation in a cost study with Babcock and Wilcox and Burns and Roe Enterprises that examined the best publicly available information on electrometallurgical (EM) treatment technology for management of gas-cooled metallic irradiated fuel. There have also been research contracts with the Colorado School of Mines investigating the electro-metallurgical separation of magnesium from uranium.

NNL has also had a number of visits, collaborative projects and work packages with RIAR Dimitrovgrad, whereby NNL have sought information about the electrowinning process to determine its possible success and applicability to future UK requirements. NNL has also had some linkage under ISTC with RRC-Kurchatov Institute at Moscow concerning their molten salt reactor programme.

NNL has been involved with European Commission FP5 project PYROREP with collaborative participation of CEA Marcoule (France), CIEMAT (Spain), NRI Rez (Czech Republic), ENEA (Italy), ITU (Germany) and CRIEPI (Japan). The PYROREP programme was targeted at achieving a greater understanding of the application of pyrochemical technology to partitioning, in particular the separation of the minor actinides. NNL subsequently collaborated on pyrochemical separations within FP6 project EUROPART and the current FP7 project ACSEPT.

8.2.9 Pyrochemical separations R&D work at UK universities

NNL has collaborated with a number of staff within UK universities on pyrochemical or supporting electrochemical studies, including Bath, Belfast, Cambridge, Edinburgh, Leeds and Manchester universities.

Several of these institutes have subsequently published some of this research work in the open literature [29-30,42-45]. This includes the work at the University of Leeds which concentrated on the dissolution of uranium oxides in molten carbonates, and that at the University of Manchester which emphasised chlorinative dissolution of uranium and fission product simulants in alkali chloride melts including *in situ* spectroscopic studies. The Universities of Belfast, Cambridge and Edinburgh have all undertaken electrochemical studies, the former on room temperature ionic liquids.

8.2.10 Conclusions regarding pyrochemical separations

- Pyrochemical separations technology has many features that are well suited to partitioning of highly rated, robust and short-cooled fuels. These attributes are favourable to recent designs of fast neutron burner reactors and accelerator-driven subcritical systems.
- NNL has considerable experience with pyrochemical separations through major projects over a number of years. NNL particularly favours national and international level collaborations in the field, encourages technical publication and has ongoing interests in technology industrialisation.
- Highlights include:
  - actinide electrorefining experiments performed using LiCl-KCl giving good U purity – high DF from Pu, etc.;
  - TRU electrorecovery experiments using liquid cadmium cathodes and showing rare-earth (Nd, Ce) partitioning from U, Pu, and Am;
  - direct electrochemical reduction experiments of refractory oxides in molten salt;
  - Molten salt, LiCl-KCl, dynamics rig testing;

  - selection of concept plus detailed design of industrial U electrorefiner unit;
  - construction of new non-radioactive and alpha-active glove box facilities for a range of molten salt experiments;
  - pyroprocess plant test case development (legacy fuels and waste);
  - pyroprocessing plant design and cost studies (LWR and fast reactor);
  - wide range of pyrochemical fuel processing and partitioning studies.
- Finally, the NNL Molten Salts project reached its conclusion in 2007, having enabled NNL and UK to gain a sufficient capability base to investigate and assess the potential commercial applications of molten salt separation processes. Given the relatively lower technical maturity of pyrochemistry compared to alternatives such as aqueous-based processing or encapsulation, applications to legacy waste management in the UK are now considered unlikely. However, NNL believes that molten salts still has likely applications to Gen-IV fuel cycles, particularly scenarios where metal fuels, transmutation targets, very high burn-up fuels or "island sites" are being considered. It should, therefore, continue to be part of a balanced international approach to fuel cycle development.

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Chapter 9: United States of America

The concept of the programme for partitioning in the United States is based on developing processes necessary to separate and recover the components of used nuclear fuels. Such processes allow recycle and reuse and thereby enable effective management of wastes and recovery of energy resources. The primary criteria are to perform the separations, recovery, recycle and reuse in the most cost-effective manner while ensuring safety to people and the environment, and providing sufficient use of safeguards to ensure non-proliferation of weapons uses. The latter area includes a policy of the US government against separation of pure plutonium during the recycle process.

The US programme for partitioning is a key part of the Advanced Fuel Cycle Initiative (AFCI) programme, which has the mission to enable the safe, secure, economic and sustainable expansion of nuclear energy by conducting research, development and demonstration focused on nuclear fuel recycling and waste management to meet US needs.

Because of its environmental advantages and abundant fuel resource base, nuclear power is expected to be an important source of energy in the future. Projections for the growth of nuclear power in the US vary over a wide range, with generating capacity in 2050 predicted to be between 175 and 500 GWe (compared to about 100 GWe today), leading to significant increases in the inventory of spent fuel if nothing is done to reduce the inventory. The legislated capacity of the Yucca Mountain geologic repository (63 000 tonnes of commercial spent fuel) will be reached in 2010 as the spent fuel inventory grows from the operation of the current fleet of commercial power reactors. The AFCI programme is intended to provide an alternative approach to high-level nuclear waste disposal in the future, by providing a closed fuel cycle technology that can support the current fleet of commercial power reactors over their lifetime as well as those reactors that are deployed in the future.

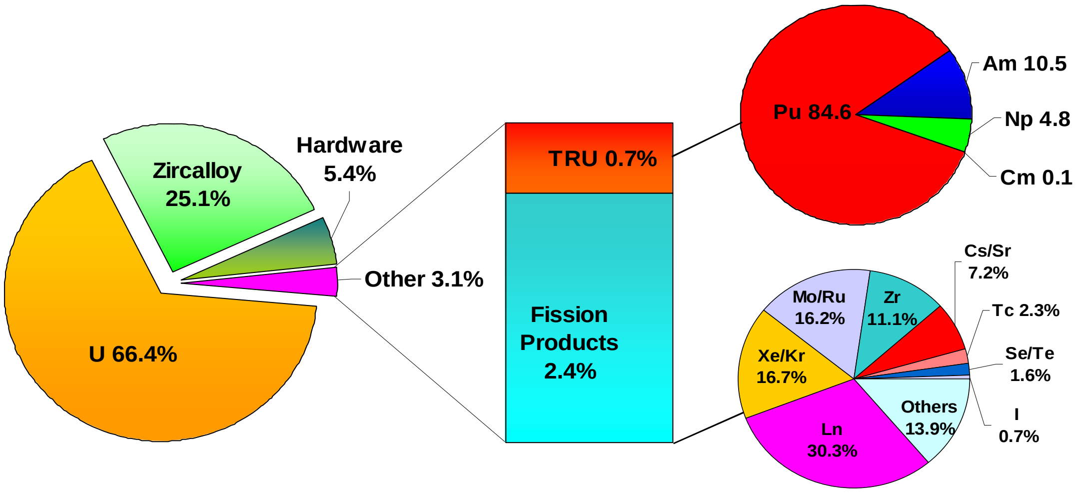
Projections of the long-range future of nuclear power in the United States are complicated by the existence of many unquantifiable variables. It has become clear, however, that nuclear power is receiving increasing public acceptance as an important element of the collection of electrical energy sources and that growth in nuclear power generation is required for both economic and environmental reasons. It can be concluded that light water reactors and advanced light water reactors will constitute the bulk of the US nuclear generating capacity for at least another 50 years, so the US programme may use a system in which components are recovered from light-water reactor (LWR) used fuel and recycled, first in LWR and subsequently in fast reactors. The constraint against the use of separations processes which produce a pure plutonium stream has had a significant effect on the development of used fuel processing technologies.

An evolutionary strategy is considered to be consistent with the realities of a transition to advanced nuclear power systems. Utilities in the US are likely to place new orders for advanced LWR in the near term, capitalising on the great strides made in increased operational efficiency and productivity with the current fleet of commercial reactors. If there are to be no new orders of any reactor type, then the need for an advanced fuel cycle technology is greatly diminished; but even if the future nuclear electricity generating capacity were only to remain constant at the current level of about 100 GWe through 2050, there is still likely to be a benefit to nuclear waste management from used fuel treatment.

9.1 Separable components of used nuclear fuels

As illustrated in Figure 9.1, the largest mass components of used nuclear fuels are uranium and the zirconium in the zircaloy cladding. Methods for uranium partitioning, recovery and recycle have been demonstrated in commercial operations. Zirconium partitioning, based on commercial methods used for natural zirconium, is potentially deployable, even though the recycled zirconium will contain a long-lived, beta radiation emitting isotope, ^{93}Zr. Of the transuranic (TRU) actinides, commercial recovery

Figure 9.1: Mass proportions of the chemical elements in used nuclear fuel



of the plutonium, which represents ~85% of the TRU actinides, is currently practiced with much of the recovered plutonium reused at least once in the form of mixed-oxide (MOX) fuels for LWR application. Current process development activities in the US are aimed at partitioning, recovery and possible recycle of the minor TRU actinides, neptunium, americium and curium. Concurrently, process development efforts are directed toward improving the management of the fission product wastes and developing improved waste forms for storage and disposal.

9.2 Partitioning requirements and strategy

Partitioning flow sheet development currently requires the use of a combination of mechanical and chemical processes and equipment, deployable at the industrial scale, to perform the needed disassembly, dissolution and separation of recyclable components of commercial used nuclear fuels. Cost and waste minimisation require a focus on simplification of the entire partitioning, recovery and recycle process. Much of the process simplification depends on systems analysis studies. For example, studies have showed that many process simplifications can be gained without incurring significant disadvantages, by waiting for 30 or more years after reactor discharge to process the used nuclear fuels.

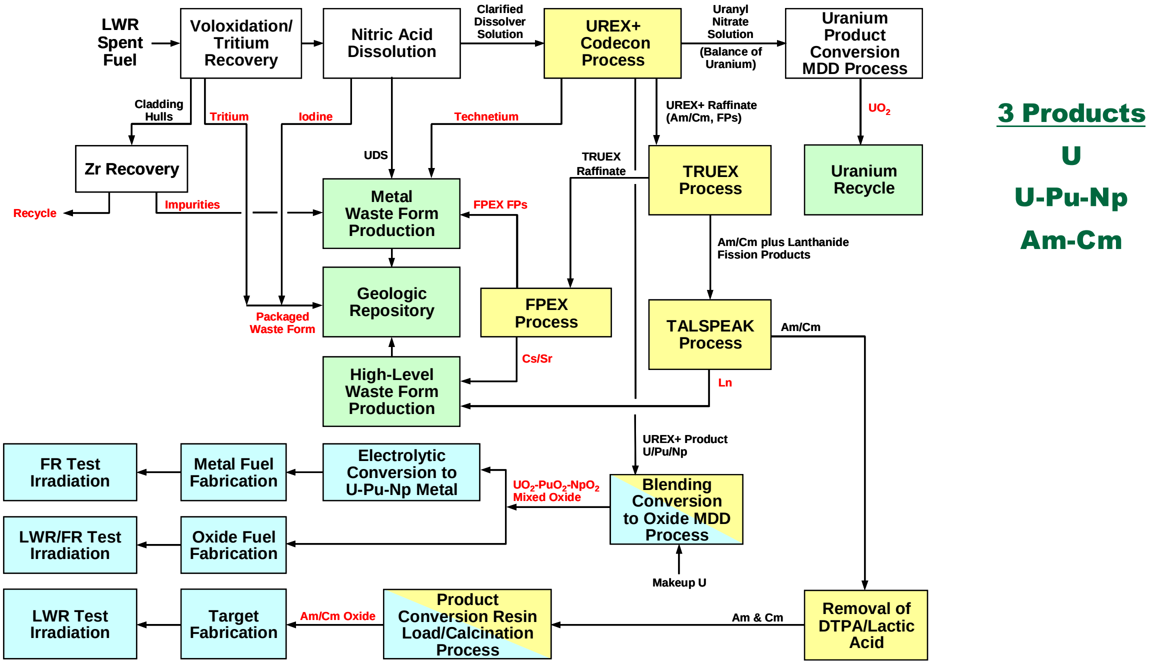
Flexibility of the partitioning flow sheet requires the capability to process used fuels from different types of reactors. For example, used fuels from low-enriched uranium (LEU), MOX fuels and minor actinide targets will have similar configurations such that the same process equipment can be used for the disassembly, cladding removal and dissolution steps. Used fuels from fast reactors will have a different configuration and cladding material and will require different disassembly and dissolution equipment. However, after dissolution, the used fuel components will require similar partitioning separations processes and can be blended to utilise the same equipment. The separations equipment will need to have the capability to provide recycle fuels with different fissile contents to enable recycle to either thermal or fast spectrum reactors.

The current scope of the partitioning programme places emphasis on: *i)* advanced aqueous-based separations; *ii)* advanced dry head-end separations; *iii)* advanced electrochemical separations; *iv)* process equipment scale-up; *v)* applications of process control and monitoring; *vi)* process modelling and simulation; *vii)* regulatory and safety considerations; *viii)* demonstration of the comprehensive coupled processes.

9.3 Current flow sheet development

Many alternative flow sheets for partitioning the components of used nuclear fuel are under consideration. One such flow sheet [1] is illustrated in Figure 9.2. The process shown in Figure 9.2 produces three products, including: *i)* a uranium oxide recycle fuel for either LWR (after re-enrichment)

Figure 9.2: An alternative flow sheet under consideration



or heavy water reactors (without re-enrichment); *ii)* a uranium-plutonium-neptunium recycle fuel in the oxide form for recycle in LWR in the near-term and either oxide or metal form for recycle in FR when they are deployed; *iii)* a minor actinide (americium-curium) oxide recycle transmutation target, possibly in the form of "burnable poison" rods.

The flow sheet shown in Figure 9.2 could provide the flexibility required for initial recycle to existing and new LWR and accommodate a later transition for recycle in fast spectrum reactors which may occur several decades from now. The flow sheet does not yet have the simplicity needed to enable minimised costs. As shown, the flow sheet requires four different solvent extraction processes to produce the three products and to partition the fission product wastes; thus, four independent solvent clean-up, storage and recycle systems are required. Current research and development efforts and systems analysis studies are aimed at simplifying this and other alternative flow sheets.

9.3.1 Dry head-end treatment

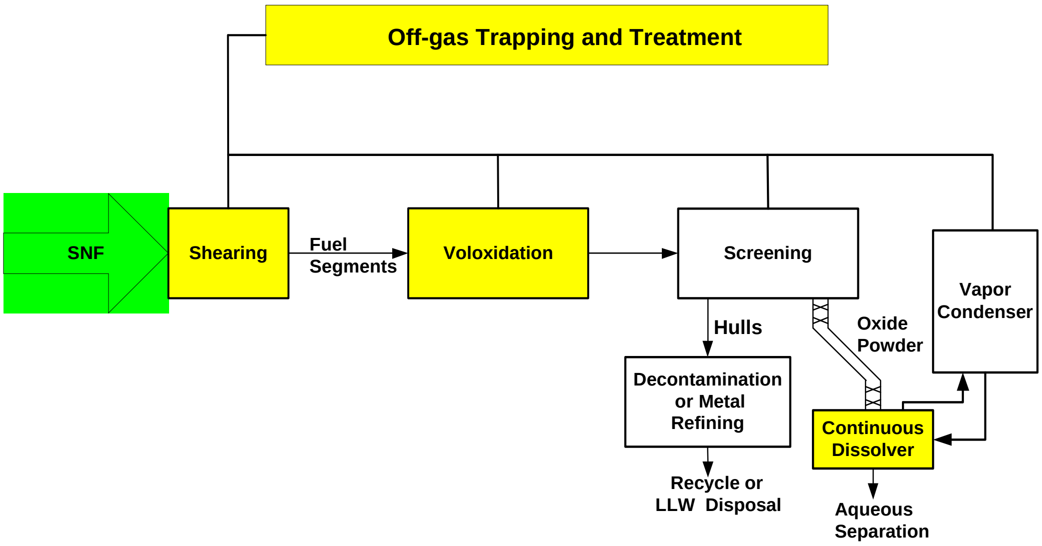
Figure 9.3 illustrates a process under consideration for dry head-end treatment and the subsequent oxide fuel powder dissolution. Standard mechanical disassembly and shearing of the fuel rods into 25-50-mm segments is the initial step which is followed by a "voloxidation" step to liberate volatile components from the fuel and enable their recovery in off-gas traps or scrubbers. The voloxidation process also converts the ceramic oxide pellets into a finely divided oxide powder that is amenable to rapid dissolution in nitric acid.

Voloxidation is a dry head-end method for removing tritium from used reactor fuel prior to aqueous processing. This avoids introducing the tritium into the aqueous systems where it would accumulate or might be released into the environment.

During voloxidation, partial release of volatiles and trace release of semi-volatiles occurs at conditions where the tritium is volatilised. Partial release of other volatiles is not expected to be a problem. 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, carbon-14 (as CO_2), and the radioactive noble gases (krypton, xenon) [2].

Recent studies include an advanced voloxidation process that utilises either higher temperatures or alternative reactants (*e.g.* ozone, steam) or a combination of both temperature control and alternative

Figure 9.3: Dry head-end treatment and oxide powder dissolutions



reactants to completely remove other volatile or semi-volatile 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.

During voloxidation, the UO_2 reacts with oxygen to form U_3O_8 which results in a restructuring of the crystallite accompanied by particle crumbing. 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 enterers the gas stream. The voloxidation process usually takes place at 480°C to 600°C. Higher temperatures increase the reaction rate. 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. In the standard process (about 4 h processing time), about half of the ^{14}C is volatilised, and minor fractions of fission products are volatilised including about 5 to 30% of krypton and xenon, 1% of iodine and bromine, and ~0.2% of the ruthenium, antimony and caesium. Iodine is chemically bonded with caesium and possibly other species, and is not completely released in standard voloxidation. The evolution of semi-volatiles at 480°C includes less than 0.2% of the ^{106}Ru, ^{125}Sb, $^{134\text{-}137}Cs$.

9.3.2 Oxide fuel powder dissolution

The reduction in particle size during voloxidation enables a greatly accelerated rate of dissolution. The higher oxidation state of the uranium reduces the nitric acid requirement, and reduces the amount of NO_x evolved (see Table 9.1). Because the rate of dissolution is rapid, a simplified continuous powder dissolver can be designed.

Table 9.1: Effect of uranium oxidation state on dissolution nitric acid requirements

Dissolution reaction(s)	HNO_3 (*M*)
UO_2	
$3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO + 4H_2O$	<10 [4]
$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$	>10 [4]
U_3O_8	
$U_3O_8 + 7.35HNO_3 \rightarrow 3UO_2(NO_3)_2 + NO_2 + 0.35NO + 3.65H_2O$	~8
UO_3	
$UO_3 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + H_2O$	*

* Theoretical; in actual practice a very small amount of NO_x is produced.

Standard voloxidation at 480°C generally increases the insoluble fraction of the fuel, more than doubling it (Table 9.2). The insoluble fraction consists primarily of ruthenium, rhodium, palladium, molybdenum and technetium, which also increase due to increasing quantities with increasing burn-up. The effect of voloxidation on the solubility of PuO_2 in LWR fuel is small as indicated in Table 9.2.

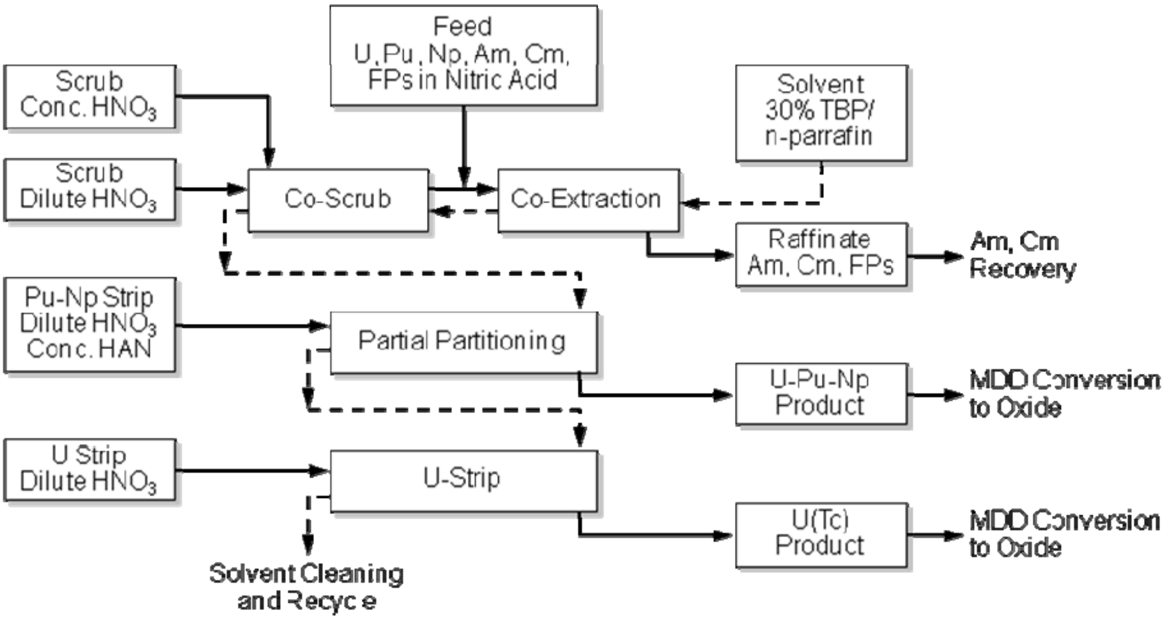
Table 9.2: Nitric acid-insoluble residue from the dissolution of typical LWR fuels [3]

	Dresden-3	Oconee-1	Robinson-2
Total residue			
Reactor burn-up, MWD/t	18 000	23 000	31 000
Oxidised, wt.% $(U,PuO)_2$			
Dissolved	0.280	0.370	0.590
Not oxidised, wt.% (U,Pu)O			
Dissolved	0.026	0.175	0.200
Insoluble plutonium			
Oxidised, % of total	0.025	0.024	0.019
Not oxidised, % of total	0.016	0.049	0.004

9.3.3 Recovery and purification of uranium, plutonium and neptunium

Uranium, plutonium and neptunium are recovered and purified from fission product elements by means of solvent extraction using 30% tri-n-butyl phosphate (TBP) in a normal paraffin hydrocarbon diluent as the solvent. The flow sheet, developed initially in 2003, is called the "UREX+ Co-decontamination Process" and is illustrated in Figure 9.4 [4]. In this process, the uranium plus the plutonium, neptunium and soluble technetium fission product are co-extracted into the solvent and the raffinate waste stream is subsequently processed further to recover americium and curium from the fission products (see Section 9.3.5). The solvent may be scrubbed in concentrated nitric acid to remove the technetium, or the technetium may be allowed to follow the uranium product from which the technetium can be removed by sorption in an anion exchange resin. The solvent extraction stream is treated initially to remove the plutonium, neptunium and part of the uranium in the partial partitioning process step, followed by complete stripping of the uranium product.

Figure 9.4: UREX+ Co-decontamination flow sheet



9.3.4 Co-conversion (denitration) of the U-Pu-Np product via the Modified Direct Denitration (MDD) process

The Modified Direct Denitration (MDD) process was initially developed in the 1980s for uranium denitration [5] and has been modified during the AFCI programme to enable co-conversion of the U-Pu-Np product obtained from the UREX+ Co-decontamination process. The MDD process is performed in simplified equipment using a rotary kiln denitration unit, as shown in schematic form in Figure 9.5. The experiment unit used to develop the co-conversion process is contained in a glove box as shown in Figure 9.6. The process is operated continuously using a counter-current flow of nitrate feed solution and air within the rotary kiln. The nitrogen gases leaving the furnace are scrubbed to recover nitric acid and small amounts of the mixed metal feed components, which are recycled.

Figure 9.5: Schematic diagram of the co-conversion of U-Pu-(Np) via the MDD process

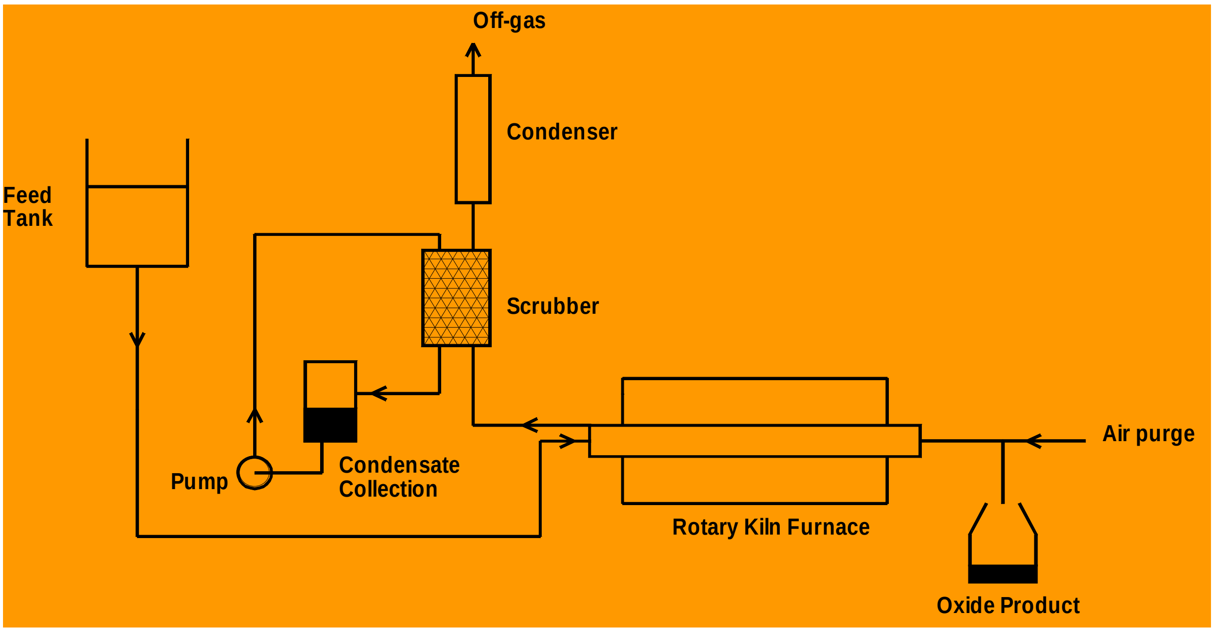
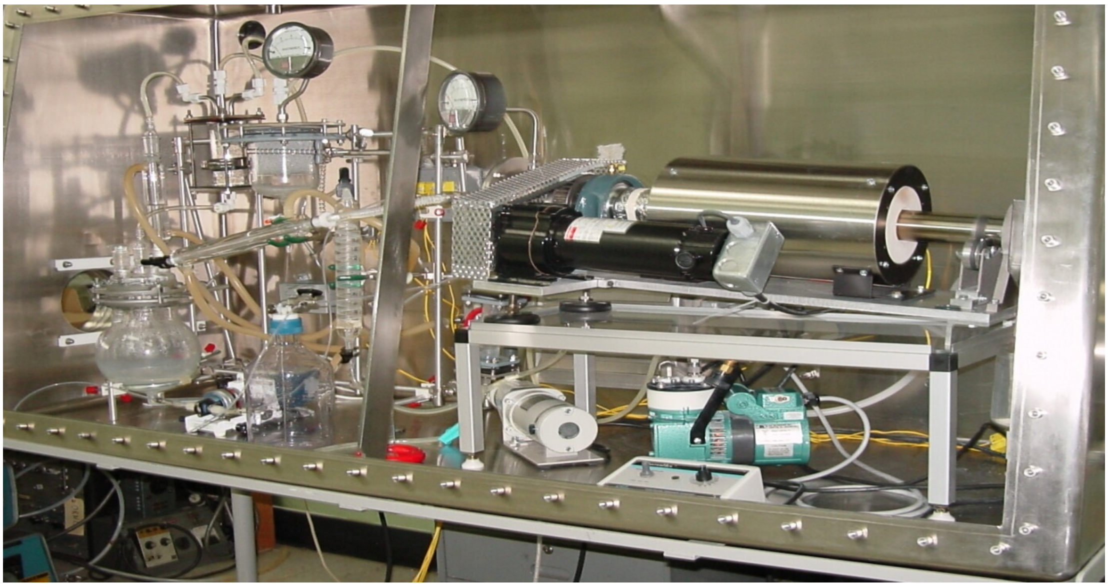


Figure 9.6: Experimental equipment for development of MDD co-conversion process



In the standard thermal decomposition process, the metal nitrate decomposition proceeds through dehydration and melting of the salt to form a sticky mastic phase. Further heating produces a denitrated oxide product that contains glossy chards which are not suitable for fuel fabrication. The overall direct denitration reaction of uranium is represented by the equation:

$$UO_2(NO_3)_2H_2O \rightarrow UO_3 + 2HNO_3$$

In the MDD process, excess NH_4^+ cations are added to enable formations of metal-ammonium nitrate double salts, which decompose without melting via the reactions (represented by uranium) such as:

$$2NH_4NO_3H_2O + UO_2(NO_3)_2H_2O \rightarrow (NH_4)_2UO_2(NO_3)_42H_2O \rightarrow UO_3 + 2NO_2 + 0.5O_2 + 6H_2O + 2N_2O$$

The co-converted U-Pu-Np oxide powder produced by the MDD process is a freely-flowing powder suitable for direct use in ceramic fuel fabrication without milling.

9.3.5 Americium-curium recovery

This process is not done in current industrial fuel cycle facilities. Development of a suitable process for the difficult separation of chemically similar transuranium actinides from lanthanide fission products, followed by recycle and transmutation of the recovered americium-curium, is a major challenge for advanced fuel cycles.

The most recently demonstrated flow sheet uses a sequence of: *i)* the TRUEX multi-stage solvent extraction process [6] to separate the trivalent americium, curium and lanthanide fission products as a group from the other fission product elements; followed by *ii)* the TALSPEAK multi-stage solvent extraction process [7] to separate the americium-curium product from the lanthanide fission products. The overall flow sheet sequence is shown in Figure 9.7.

A complexant solution (lactic acid + DTPA) is used to enable separation of the americium-curium product in the TALSPEAK process at closely controlled pH values. As illustrated in Figure 9.7, the complexant solution may be used to strip the Am-Cm-Ln product from the TRUEX solvent.

Following recovery of the Am-Cm in the TALSPEAK process, another solvent extraction or ion exchange step is necessary to remove the complexants from the Am-Cm product solution. Afterward, recycle or disposal of the complexant solution is required.

Because the reference TRUEX-TALSPEAK flow sheet is complicated, requiring several multi-stage solvent extraction steps, each with different solvent system requirements, other Am-Cm recovery processes are being considered in research and development studies. These include: *i)* more simple solvent extraction processes using new extractant molecules; *ii)* oxidation of americium to the elevated pentavalent or hexavalent state, followed by solvent extraction or precipitation/filtration separation processes; *iii)* chromatographic extraction chromatography or ion exchange separation processes.

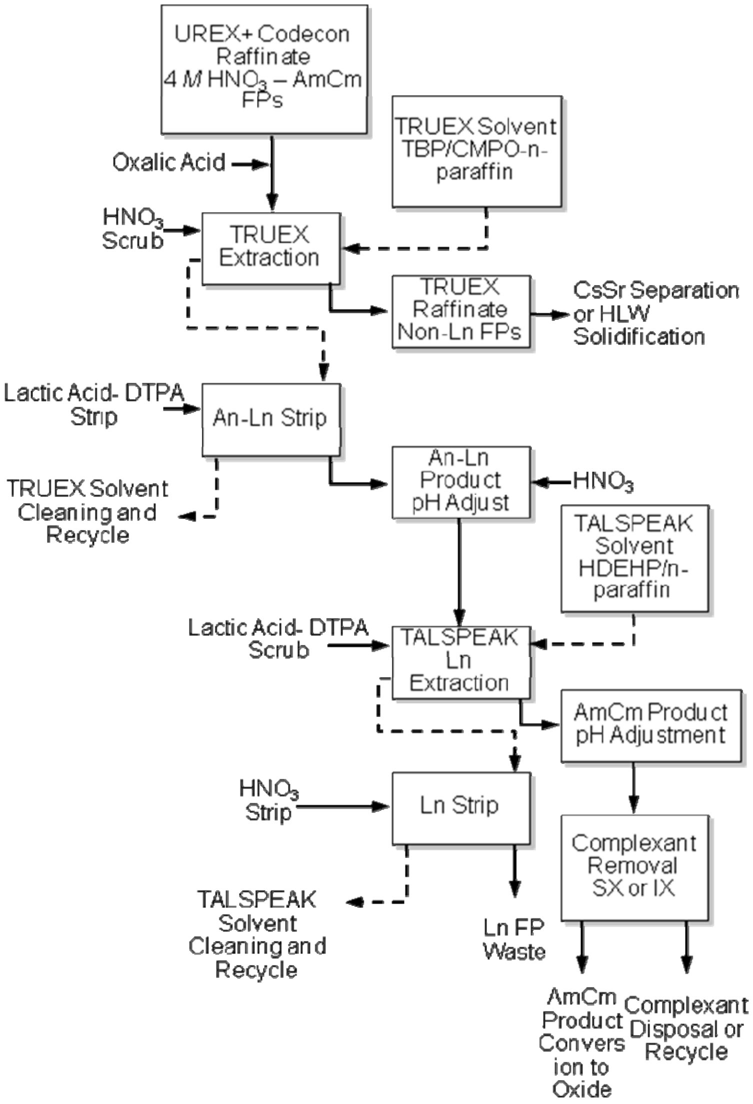
9.3.6 Electrochemical reduction of oxide recycle fuel

As indicated in the overall flow sheet development illustrated in Figure 9.2., the process is intended to have the flexibility to meet all recycle fuel requirements that will be needed, both in the near term for recycle to existing and new LWR, and in the longer term for recycles to Gen-IV reactors, especially fast spectrum reactors. The FR are expected to become economical in future years, especially as the supply of low-cost natural uranium becomes unavailable.

The partial partitioning step in the UREX+ Co-decontamination process (Figure 9.4) will have the capability to adjust the concentration of fissile isotopes in the recycle feed to low concentrations for recycle to LWR and to higher concentrations needed by FR. Thus, the oxide recycle fuel can be used in either type of reactor.

If metal form recycle fuel is needed for future FR, then the needed amount of oxide recycle fuel can be converted by dissolving in molten salt and electrochemically reducing the salt to the metal form. Conversion of the U-Pu-Np oxide recycle fuel can be done efficiently by means of electrolytic reduction, since the more difficultly reducible lanthanide fission products will have been removed previously.

Figure 9.7: Am-Cm recovery via TRUEX-TALSPEAK flow sheet

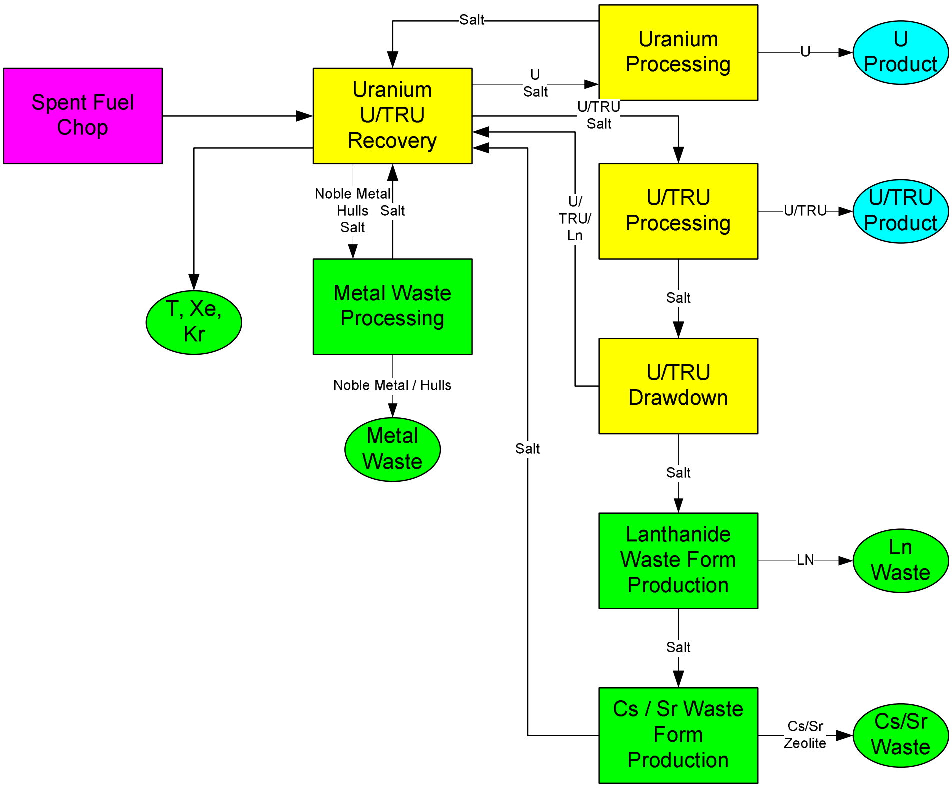


9.4 Development of non-aqueous alternative flow sheet for metallic fast reactor fuel

Another flow sheet is being developed for processing metallic fast reactor fuel without using aqueous processes [8] as an alternative that may be needed. This conceptual flow sheet is shown in Figure 9.8. The centrepiece of the flow sheet is the uranium electrorefining and U/TRU recovery process for separation of actinides and fission products. Products from the treatment process include uranium and a uranium-transuranium element alloy for recycle to metal-fuelled fast reactors. Waste streams include a ceramic destined for decay storage (the Cs-Sr waste) and two high-level forms, a lanthanide borosilicate glass and a metal alloy which contains technetium and other noble metal fission products.

Electrorefining has been used since 1996 for the conditioning of metallic spent fuel from the EBR-II reactor. In this process, the irradiated metallic fuel, typically an alloy of highly-enriched uranium with a small amount of zirconium, is chopped and anodically dissolved in molten LiCl-KCl salt. Uranium is electrotransported to a metallic cathode, and the transuranics are left in the salt together with the active metal fission products for eventual incorporation in a ceramic waste form. Noble metal fission products (including Tc) are melted together with the stainless steel cladding hulls to produce a metallic waste form.

Figure 9.8: The pyrochemical process for treatment of metallic fast reactor spent fuel



As seen from Figure 9.8, application of the pyroprocess to recycle of fast reactor metallic spent fuel requires the development of a transuranic recovery step to the process being used for EBR-II fuel conditioning. A process involving transuranic deposition in a liquid metal (cadmium) cathode has been demonstrated at engineering scale (1-2 kg TRU deposits), but the efficacy in achieving the necessary decontamination of lanthanide fission products has not been established. The current development programme schedule is consistent with the expected date, sometime in the 2025 period, at which there will be discharged fast reactor spent fuel available for processing.

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Chapter 10: European Commission

European research on nuclear energy is implemented mainly on the basis of Article 7 of the EURATOM Treaty and since the early 1980s as part of the so-called Framework Programme (FP). Activities are focused on nuclear safety and security aiming at the creation of a true European Research Area (ERA). The main body of the research is organised through co-funding of research programmes proposals submitted by consortia of national research organisations, universities, industrial organisations, etc., to the European Commission at the beginning of each FP. The main projects dealing with partitioning are EUROPART in FP6 and ACSEPT in the present FP7. In parallel, so-called Networks of Excellence for Actinide Sciences, called ACTINET6 in FP6 and ACTINETI3 in FP7 were set up as a consortium gathering more than 25 European research institutions, including a considerable number of universities. The objective of ACTINET is to take steps in order to bring both research infrastructures and human expertise in Europe to an adequate performance level, thereby contributing to the development of the European Research Area in the fields of physics and chemistry of actinides. Within the network one of the major scopes is on the back-end of the nuclear cycle including, of course, partitioning. The pooled facilities available in Europe are essential for a continued development of partitioning technologies in the framework of P&T strategies. Advanced research in actinide sciences is therefore recognised as one essential endeavour for continued development of a dynamic, competitive and sustainable knowledge-based nuclear industry, particularly in the partitioning field.

A second type of research in the European Commission is directly funded and carried out in the Joint Research Centre (JRC). Nuclear activities are mainly concentrated in the Institute for Transuranium Elements (ITU) in Karlsruhe, Germany. Regarding the fuel cycle, the programmes address research activities relative to nuclear fuel to reduce the amount and toxicity of radioactive waste through partitioning and transmutation (P&T). In the partitioning field, the JRC participates in networks in the EU and world wide, not least through the shared cost actions of the Euratom research framework programme described above. Major partners include: the Commissariat à l'énergie atomique and Electricité de France in France, Chalmers University in Sweden, CIEMAT in Spain, SCK•CEN in Belgium, Forschungszentrum Karlsruhe and Jülich in Germany, ENEA in Italy, Reading University and BNFL in the UK, NRI/REZ in the Czech Republic, CRIEPI in Japan, KAERI in Korea and CIAE in China.

10.1 European Framework Programme projects

10.1.1 EUROPART

Research in the field of the management of nuclear wastes issuing from the reprocessing of nuclear spent fuels is among the first priorities within the field of nuclear energy research in the European Union. For the management of nuclear spent fuels, several European countries choose the closed fuel cycle involving reprocessing. The nuclear wastes, *i.e.* the fission products and the minor actinides (Np, Am and Cm), issuing the reprocessing are vitrified. In the future, the vitrified nuclear wastes are supposed to be disposed of in deep geological repositories, but the selection of the sites for these repositories should consider the fact that these vitrified wastes contain long-lived radionuclides (LLR), essentially belonging to the family of the actinide elements (An), which induce important radiotoxicity for the long term. The elimination of these LLR from the vitrified wastes will induce a large decrease of the long-term radiotoxicity of these wastes and will simplify the selection of geological sites. After separation, the actinides will be either destroyed into short-lived or stable nuclides by irradiation (partitioning and transmutation, P&T) or conditioned into stable dedicated solid matrices (partitioning and conditioning, P&C). The European Union has supported research in this field since the beginning of the 1990s. Within FP5, three research projects were supported, two in the field of hydrometallurgy (CALIXPART and PARTNEW), and one in the field of pyrometallurgy (PYROREP). Thanks to these network collaborations, a large expertise has been created in this field in Europe. In the follow-up project EUROPART launched in FP6, the research addressed these subjects with a certain level of continuity, though with an increased emphasis on industrial implementation.

Within EUROPART, the field of applications of partitioning techniques for An have been extended and strongly consolidated. A large number of scientists (theoreticians, process development chemists, engineers, etc.) developed both the basic and the applied scientific and technological fields. Information and communication as well as training and education of young researchers in the field were other important issues within EUROPART.

Hot tests of the processes developed within EUROPART involved the treatment of wastes corresponding to hundred of grammes of spent fuels and leading to the separation of hundreds of mg of minor actinides. The goal was to define processes for the possible industrialisation of partitioning strategies.

The research within EUROPART had a major focus on the partitioning of the so-called minor actinides (MA), from Am through Cf, but in the case of the treatment of dedicated spent fuels or targets the actinides to be separated also included U, Pu and Np.

The separation techniques based on hydrometallurgy and pyrometallurgy were focused on the following main axes of research:

- partitioning of MA = Am-Cf from high burn-up UOX and multi-recycled MOX fuels;
- partitioning of all actinides together for recycling, for advanced dedicated fuel cycles, *i.e.* double strata concept, accelerator-driven system (ADS).

In hydrometallurgy, the main research was dedicated to the study of partitioning methods essentially using solvent extraction, though a minor activity was dedicated to the development of An co-conversion methods for fuel or target preparation.

The processes studied were based on a two-step scheme with first a joint partitioning of trivalent actinides contained in aqueous highly active raffinates (HAR) and/or highly active concentrates (HAC) issuing from the reprocessing of nuclear fuels, such as high burn-up UOX and MOX (multi-recycled), followed by a separation of the trivalent actinides from lanthanides in the product generated by the first processes.

The processes developed were aiming, of course, at very high recovery yields for An and in many cases values of >99.9% were achieved.

In pyrometallurgy the focus was on basic chemistry of transcurium elements in molten salts and on the development of An partitioning methods, including:

- determination of basic properties of An (including the transcurium elements) in molten halides (chlorides and fluorides), that are the media to be selected for the development of pyrometallurgical partitioning processes;
- definition of partitioning processes of An from high-level wastes issued from the reprocessing of UOX and/or MOX spent fuels by the PUREX process;
- definition of processes for advanced dedicated fuel cycles (such as those of ADS);
- definition of conditioning methods for the wastes to be generated by the partitioning processes;
- definition of the overall organisation of the methods to be implemented within pyrometallurgical partitioning processes.

Additional activities were related to the conditioning of the wastes and to system studies.

The studies carried out in EUROPART have led to significant progress, especially in the field of lanthanide-actinide separation, particularly by means of pyrometallurgy. Basic research has produced a considerable amount of relevant data and information in the field of hydrometallurgy, *e.g.* synthesis, characterisation, modelling, extraction properties and degradation assessment of new ligands from the families of bis-diamides (malonamides or DGA), CMPO-COSAN derivatives and tetradentate BTBPs.

Process development has made considerable progress as well for aqueous and pyrometallurgical systems, but additional hot tests are needed in view of an industrial implementation of both technologies, part of which are scheduled in the framework of the ACSEPT project.

10.1.2 ACSEPT

As a follow-up to the Integrated Project EUROPART, the Collaborative Project ACSEPT should provide a structured R&D framework to develop chemical separation processes compatible with fuel fabrication techniques, with a view to their future demonstration at the pilot level. Considering technically mature aqueous separation processes in ACSEPT, the most promising ones will be selected and optimised with a special emphasis on group separation. These developments will be appropriately balanced with an underpinning basic research focused on the design of new molecules.

In parallel, promising group actinide separation pyroprocesses will be developed beyond the current state of the art.

ACSEPT will also foster and promote the integration between partitioning and transmutation through fuel dissolution and actinide conversion studies. The interface between both fields is represented by the fuel. In various FP programmes, such as FUTURE, CONFIRM and EUROTRANS, a variety of inert matrix targets and fuels has been and is being studied with respect to their suitability within coherent partitioning and transmutation schemes in ADS and/or Gen-IV systems.

Concerning pyrochemical separation processes, ACSEPT will contribute to develop them beyond the current state of the art, as an alternative option for the longer term. In PYROREP and EUROPART, two reference routes were identified and proposed by the international community: the electrorefining of actinides onto solid aluminium cathode in molten chloride salts and the liquid-liquid reductive extraction in molten fluoride salts/liquid aluminium. In ACSEPT, the studies will first focus on the enhancement of these two cores of process by working on critical ancillary steps such as exhaustive electrolysis or actinide recovery from aluminium, common steps for the two processes. In parallel, an electrochemical core process in molten fluoride media will be developed as an alternative if some "show stoppers" are identified in the two previous processes.

All experimental results will be integrated by carrying out engineering and systems studies on aqueous and pyroprocesses to prepare for future demonstrations at the pilot level. A training and education programme will also be implemented to share the knowledge within the partitioning community and present and future generations of researchers. The challenging objectives of ACSEPT will be addressed by a multi-disciplinary consortium composed of European universities, nuclear research bodies and major industrial players. The consortium should generate fundamental improvements for a future design of an Advanced Processing Pilot Unit.

10.2 Partitioning research at the Joint Research Centre-Institute for Transuranium Elements (JRC-ITU)

EU-sponsored work in the partitioning field performed at the Joint Research Centre-Institute for Transuranium Elements (JRC-ITU), henceforth referred to as ITU, addresses two key issues:

- minimisation of the amount and long-term radiotoxicity of nuclear waste arising from commercial LWR, which may be accomplished by including suitable partitioning and transmutation (P&T) waste management strategies in the back-end of the fuel cycle;
- advanced reprocessing schemes for new reactor systems (*e.g.* Gen-IV).

At ITU both routes, *i.e.* the hydrometallurgical and the pyrometallurgical, are under investigation. Aqueous partitioning in particular has already been studied for a number of years, comparing the performance of various extractants proposed world wide for a selective extraction of MA from HLW coming from the PUREX process. Especially for the French DIAMEX process, good progress has been made in view of an industrial implementation. The fuels used in the new generation reactors will be significantly different from the commercial fuels of today. Because of the fuel type and the very high burn-ups reached, pyrometallurgical reprocessing could be the preferred method. The limited solubility of some of the fuel materials in acidic aqueous solutions, the possibility to have an integrated irradiation and reprocessing facility with improved economics and the higher radiation stability of the molten salt media are some additional arguments in favour of pyroreprocessing. Major drawbacks of the technique are of a far lower degree of development compared to hydrometallurgy: high operation temperature (450°C) and the need to work with highly pure Ar.

10.2.1 Aqueous reprocessing

In the ITU institutional research programmes dealing with aqueous reprocessing the combined PUREX–DIAMEX process has been successfully demonstrated at ITU using genuine HAR fuel solutions.

The main objective with respect to aqueous reprocessing is to demonstrate the viability of existing process schemes using real fuels and targets. As most of the actinide incineration strategies are based on a multi-cycle scenario, the elements to be transmuted have to be recovered several times from the fuel and recycled in order to close the fuel cycle. The feasibility of such recycling could, for example, be demonstrated for the so-called SUPERFACT irradiation experiment, jointly organised between the ITU and the CEA. The purpose of this experiment was to study the neutronic, material and chemical behaviour of oxide fast reactor fuels containing up to 45% minor actinides (MA).

A large number of extractants were tested using genuine irradiated nuclear fuels. In recent years the major focus was on the French DIAMEX process because it represents the best compromise between extraction and back-extraction properties. Of course most of these activities were carried out in the framework of the European research projects NEWPART, PARTNEW and the current EUROPART. At present a new solvent based on a TODGA/TBP mixture, an efficient mixture of ligands for the co-extraction of An(III, IV and VI), was successfully tested in several counter-current cold experiments using a spiked feed, in collaboration with the German Forschungszentrum Jülich (FZJ). Hot tests will be further implemented in centrifugal contactors and hollow fibre modules (HFM).

In view of a process industrialisation, the next step has been the development of a DIAMEX process for recovery of minor actinides from concentrated HAR, the so-called high active concentrate (HAC), which before vitrification represents today's industrial waste fraction after PUREX reprocessing of spent fuel. The main advantage is the volume reduction – up to 10-15 times is conceivable – which reduces waste volumes, making the industrial process more compact and thereby more economic.

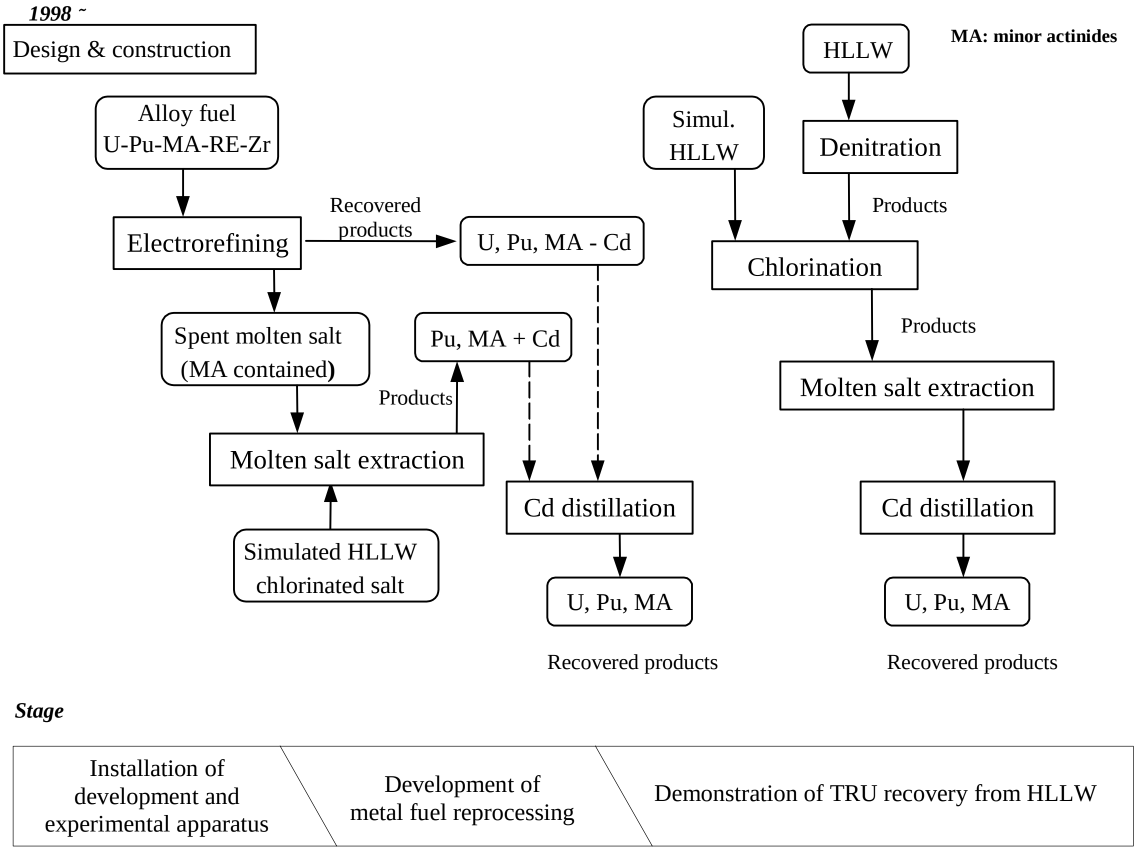
In the present work, for the first time, a DIAMEX process using high active concentrate has been carried out in a new 16-stage centrifugal extractor battery installed in a hot cell. The first step was the production of a genuine starting solution by small-scale PUREX reprocessing of MOX fuel. The obtained HAR solution was successfully subjected to a concentration process, where the volume was reduced by evaporation, and subsequently to a denitration process using formic acid in order to adjust the acidity for the following DIAMEX process. The high metal concentrations increase the risk of actinide(III) co-precipitation so the process of concentration and denitration was thus optimised to minimise their losses. The genuine HAC solution produced had a concentration factor of 10 and was 4 mol/L HNO_3 in acidity. In parallel, experimental conditions to carry out the hot DIAMEX-HAC test in centrifugal extractors were established based on results coming from batch extraction experiments, computer code calculations for the flow sheet development and a full centrifugal extractor test using a simulated HAC solution spiked with MA tracers. Finally, the DIAMEX experiment could successfully be carried out.

10.2.2 Pyroreprocessing

Pyrochemical separation processes for the recovery of uranium and to some extent for plutonium have been investigated for decades. The activities based on pyroreprocessing at ITU started with a joint collaboration with CRIEPI, the main focus being on investigating the transmutation of actinides in metallic fuels. The fuels containing minor actinides and lanthanides were fabricated and characterised at ITU as early as the late 1980s and irradiated in the Phénix reactor. A detailed plan of the project is given in Figure 10.1.

The metal electrorefining process for irradiated U, Pu, Zr, MA, Ln fuels is being studied. An argon atmosphere cell using a stainless steel container has been constructed to conduct these experiments. The argon atmosphere is continuously purified to keep levels of oxygen and water below 10 ppm. In this installation, a demonstration of the technical feasibility of electrorefining and reductive extraction concepts is being made. The stainless steel box has been equipped either with newly designed electrorefiner or multi-stage extraction equipment, fabricated and developed by CRIEPI as based on experience gained over a range of cold experiments, mainly in Japan. The electrorefiner consists of three electrodes and a liquid Cd pool covered by a molten LiCl-KCl eutectic mixture. Electrorefining tests on U and Pu using solid cathodes and a liquid Cd cathode have already proven the operational capabilities of the facility. Un-irradiated metal U-Pu-Zr based MA alloy fuel previously fabricated at ITU in a joint study with CRIEPI on transmutation of TRU targets has been processed. MA-Ln separation by multi-stage liquid metal-molten salt extraction has proven to be a promising alternative separation route. The stainless steel box is at present installed in a lead shielded hot cell and experiments on conversion of HLW into molten salt chlorides have started. In the coming years the reprocessing of the above mentioned fuels at present under irradiation in the PHENIX reactor in France are planned.

Figure 10.1: Experimental plan for the joint ITU/CRIEPI study



In the framework of the ITU institutional research programmes on pyrochemical separations, mainly electrorefining of metallic fuels are studied. The overall purpose is to investigate the separation of MA from lanthanides by selective electrodeposition onto solid and liquid cathodes. Furthermore, basic data (thermodynamic and electrochemical) for MA, especially Np, Am and Cm are determined. A double glove box has been constructed for these experiments. The outer glove box is operated under nitrogen and the inner box under a purified argon atmosphere. Other equipment is devoted to chlorination, material processing and electrochemistry in room temperature ionic liquids.

In the case of oxides a head-end reduction step is needed. It can be performed chemically, *e.g.* by reaction with lithium dissolved in LiCl at 650°C. The recovered metal can be directly subjected to electrorefining and the Li_2O converted back to lithium metal by electrowinning. A more elegant method is the so-called direct electroreduction. In this case, the heat-generating fission products are removed and the fissile materials are recovered as an alloy, which can again be directly reprocessed by electrorefining. These direct electroreduction processes using Pu-containing oxide fuels are under investigation at ITU.

Major emphasis is placed on the reprocessing of EBR-II type metallic alloy fuel with 2% of Am and 5% of lanthanides (U60Pu20-Zr10Am2Nd3.5Y0.5Ce0.5Gd0.5). An excellent grouped separation of actinides with an almost complete recovery (99.9%) was achieved on solid Al cathodes The major advantage of Al is its capability to form an alloy with trivalent actinides and thereby avoid a re-dissolution of the actinide by reaction with the trivalent species in the salt ($Am + 2Am^{3+} = 3Am^{2+}$). A good separation from lanthanides (An/Ln mass ratio = 2 400) – mandatory because of their high neutron capture and thereby detrimental effect on the neutron economy in the irradiation process and the efficiency of actinide fission – was obtained. The results are confirmed in conditions simulating the accumulation of Ln in the salt corresponding to a long time of electrorefining. These results represent the first demonstration of an efficient grouped actinide recovery from realistic metallic fuels and are therefore an important step in achieving the sustainability goals of future reactor systems (Gen-IV goals).

At present the focus of the electrofining on Al cathodes is directed towards the development of potential industrial processes. These activities also include the exhaustive electrodeposition of the actinides from a salt bath after multiple use. The goal is to minimise the losses of actinides to the waste. Another highly relevant issue is the recovery of actinides from the alloy with aluminium. Here the chlorination method of the cathode seems to be a very efficient and promising technique to recycle the actinides to the fuel fabrication.

New equipment is also being set up at ITU in the hot cell laboratory to analyse the special samples resulting from the various streams of the pyroprocess. The analysis of actinides in liquid metal (Bi, Cd) but also in molten salt is sometimes difficult, when using conventional techniques such as ICP-MS or ICP-OES due to a cumbersome and time demanding sample preparation.

Thus, a new NDA assay station with K-edge densitometry, XRF and gamma spectrometry along with neutron coincidence counting is now being installed in the hot cell laboratory for the analysis of the irradiated samples generated during pyroprocessing experiments.

Similar techniques and equipments have also been used for several years for the safeguarding of industrial reprocessing facilities in La Hague in France and Sellafield in the United Kingdom, as well as the plant in Rokasho, Japan recently put into operation. The facility now being installed at ITU could thus be used to conceive and develop an appropriate safeguarding scheme for pyroreprocessing. The control of fissile material is without any doubt mandatory if an industrial implementation of a pyroprocess is to be realised.

Conclusions and recommendations

The objective of this study is to summarise research programmes on partitioning and transmutation of OECD/NEA member countries. This report includes studies of eight OECD/NEA member countries (Czech Republic, France, Italy, Japan, Korea, Spain, the United Kingdom and the United States of America) and one international organisation (EC) as well as one non-OECD member country (Russian Federation). Two major chemical partitioning processes are considered: aqueous (hydrometallurgy) and pyro (pyrochemical) processes. Some countries are considering both types of processes and others only one process. This choice strongly depends on each country's interests and policy. The common goal of the programme, however, pursues maximising resource utilisation, minimising waste generation and enhancing proliferation resistance.

Aqueous processes have already been industrialised and currently provide commercial nuclear fuels, though scope exists to extend these processes particularly as regards the non-proliferation issue. Despite of its long history of development, pyroprocess still remains at the laboratory or pilot scale, but the current progressive trend toward increased international collaboration leads to believe that commercial implementation of the pyrochemical process will soon be possible. Combination of both aqueous and pyroprocesses are also proposed.

Because a great discrepancy in the interests and policies among the member countries was observed, it is important to maintain an open forum for communication. In the framework of the OECD/NEA, the biennial information exchange meeting on actinide and fission product partitioning and transmutation, which has been organised since 1990, is vital to unrestricted communication among the member countries. It is therefore recommended that such technical, multilateral and international meetings specialised in partitioning and transmutation should be continued.

Other ongoing activities of the OECD/NEA WPFC Expert Group on Chemical Partitioning – flow sheet studies and Cm management, as well as the newly undertaken study on progress of separation chemistry and minor actinide separation and prospective of future R&D – will also provide updated status reports concerning the technical maturity and readiness level of partitioning and transmutation.

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