

Nuclear Science

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# **Pyrochemical Separations in Nuclear Applications**

## **A Status Report**

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NUCLEAR ENERGY AGENCY  
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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## **FOREWORD**

The evolution of nuclear technology has involved the development of numerous methods for processing irradiated nuclear fuel. The first separation techniques were developed in the 1940s and were applied to the separation of plutonium for military purposes. Later, reprocessing of civilian irradiated nuclear fuel was introduced as a means of extending uranium resources, considered to be limited at the time. More recently, such reprocessing has also come to be regarded as a means to facilitate the disposal of the high-level nuclear waste arising from fuel irradiation. The introduction of more complex fuel cycle schemes, such as the dual-strata approach, originally conceived by the Japan Atomic Energy Research Institute (JAERI), has stimulated the development of reprocessing methods with the goal of minimising waste generation and reducing costs. This has resulted in renewed interest in dry reprocessing methods, the so-called "pyrochemical" processes. Such processes have been studied in the past, but have generally been found wanting because they could not achieve the individual element separation or the level of product decontamination required. In certain fuel cycle schemes presently under consideration, pyrochemical processes attract strong interest, as they offer the potential for more compact (and hence lower cost) facilities and the ability to operate with irradiated nuclear fuel cooled for shorter times.

At the June 1999 meeting of the OECD/NEA Nuclear Science Committee (NSC), it was proposed that the Agency sponsor an international workshop on pyrochemical separations. The workshop was held in Avignon, France on 14-15 March 2000 and was attended by more than 70 participants from 14 countries and 3 international organisations. At the end of the workshop participants agreed to propose the creation of an expert group whose task would be to prepare a state-of-the-art report on pyrochemical separations. The NSC endorsed the proposal and the first meeting of the Pyrochemistry Working Group was held on 30-31 October 2000. The members established a set of objectives that included reviewing the status of R&D and technology, assessing the feasibility and roles of future fuel cycles, and making recommendations for future R&D and international collaboration in the field of pyrochemical separation.

This report, a joint effort of the working group members listed in the Appendix, is published under the responsibility of the Secretary-General of the OECD. It does not necessarily represent official government opinions or those of the international organisations involved. The report is divided into four main sections:

- 1) national programmes on pyrochemical processing of nuclear fuel;
- 2) past and present international collaborative efforts in pyrochemical processing;
- 3) future research needed to advance pyrochemical processing technology;
- 4) possible future applications of the technology.



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## EXECUTIVE SUMMARY

This study revealed a surprising level of national interest in the development of pyrochemical technologies for the treatment of irradiated nuclear fuel. In addition to the very active and long-standing programmes in the Russian Federation and the United States of America, intensive efforts under way in France, Japan, Korea and the United Kingdom are beginning to show significant progress. Collaborative programmes sponsored by the European Commission have been proceeding for several years (first under the 5<sup>th</sup> Framework Programme and later under the 6<sup>th</sup> Framework Programme) and are making important contributions to the understanding of pyrochemical processes. The EC Joint Research Centre at Karlsruhe, Germany, in collaboration with a Japanese research organisation (CRIEPI), has performed significant experimental work with electrochemical processes.

Applications envisaged for pyrochemical processing of irradiated fuel vary from country to country. Some are directed towards the treatment of thermal reactor fuel for the purpose of recycling recovered actinides (primarily the transuranic elements) in fast spectrum reactors in order to provide sustainable national nuclear energy systems. Other applications include closure of the fast reactor fuel cycle, with processes being developed for treating metal, oxide and nitride fuels.

Pyrochemical processing is also being pursued for the purpose of nuclear waste management, as evidenced by the following examples:

- The French programme is focused on the extraction of minor actinides from the waste stream of aqueous reprocessing plants to permit inclusion of these highly radiotoxic elements in transmutation targets for irradiation in fast spectrum reactors or accelerator-driven systems.
- The development programme of the Republic of Korea is presently concentrating on the chemical/electrochemical reduction of LWR oxide fuel to the metallic state, in order to obtain a substantial reduction in the volume of waste requiring geological disposal.
- The Central Research Institute of the Electric Power Industry (CRIEPI, Japan) has demonstrated the use of pyrochemical methods in the treatment of high-level liquid waste arising from aqueous reprocessing for removal of residual actinide elements.

A somewhat different path is being followed in the Czech Republic, where national interest is directed towards the development of advanced-generation, molten-salt reactors (MSR). Workers at the Nuclear Research Institute (NRI), Rez, have been developing a fluoride volatility process for recovery of fuel materials from irradiated LWR fuel for the purpose of recycling these materials in a molten-salt reactor. Pyroelectrochemical methods would then be used for online processing of the MSR fuel to extract undesirable radionuclides. Processes initially developed in collaboration with the former Soviet Union in the 1980s are being further developed at the NRI.

It has become clear that there are significant mutual interests among the countries participating in this study, and that the many specialised experimental facilities could be used most effectively in concerted collaborative programmes. The pursuit of such programmes in the future is highly recommended.



## *Chapter 1*

### **INTRODUCTION**

The use of pyrochemical methods for the treatment of irradiated nuclear fuel has been stimulated in recent years by the development of technologies for dealing with oxide and metallic fuels in the former Soviet Union and the United States, respectively. Dedicated work at RIAR (Dimitrovgrad) and at Argonne National Laboratory led to the development of practical processes for the treatment of irradiated fuels for closure of the fast reactor fuel cycle. The Russian effort concentrated on oxide fast breeder reactor (FBR) fuels, and the American effort on metallic fuel for the Integral Fast Reactor (IFR). Both laboratories openly publicised their work, which included the recycle of recovered actinides to fast reactors (e.g. BOR-60 and EBR-II).

After several years of operation on a rather small scale in Russia and the US, other countries became interested in these technologies and began to develop their own indigenous technologies, sometimes in collaboration with the originators of the technology and sometimes independently. In addition, other pyrochemical technologies such as halide volatility processes, which had been initially investigated in the 1970s and later exploited on a demonstration scale in the 1980s, were given further consideration at the end of the 20<sup>th</sup> century as possible alternatives to aqueous processing of irradiated nuclear fuels.

Because the resources required for development of advanced nuclear fuel processing technologies are so large, it would be useful, for the benefit of future national interests, if such development could be performed on a collaborative basis with other countries having mutual concerns. It was the purpose of the OECD/NEA Pyrochemistry Working Group to characterise the level of national interest in various applications of pyrochemical technology, with the intention of identifying areas in which international collaboration could serve to eliminate costly duplication and accelerate the development of a technology that could conceivably be of considerable national importance. The OECD/NEA Pyrochemistry Working Group worked diligently to accomplish this task. The results follow.



## *Chapter 2*

### NATIONAL PROGRAMMES

#### **Introduction**

This section comprises a series of contributions that describe the individual national programmes for development of pyrochemical processes for nuclear fuel treatment. The national programmes are described in alphabetical order as follows: Belgium, Czech Republic, France, European Union (EU), Italy, Japan, Republic of Korea, Russian Federation, Spain, United Kingdom and United States of America. For the present purposes, the EU is counted as a national entity, while recognising that some of its member countries have their own research and development programmes as well as contributing to EU programmes.

#### **BELGIUM**

In the 1960s, a significant R&D effort was made on the pyrochemical reprocessing of fast reactor oxide fuel ( $\text{UO}_2\text{-PuO}_2$ ). The main emphasis was placed on fluoride volatility [1,2]. Projects were carried out at the Belgian Nuclear Research Centre (now SCK•CEN) over the period 1960-1968 and covered the following subjects:

- conversion of  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$ ,  $\text{UO}_2\text{F}_2$  into  $\text{UF}_4$  and  $\text{UF}_6$  by  $\text{HF}$ ,  $\text{F}_2$  and  $\text{ClF}_3$  and  $\text{ClF}$ ;
- zirconium volatilisation by  $\text{HCl}$  or  $\text{HF-O}_2$ ;
- fluidised bed chemistry and technology, mainly on  $\text{UO}_2\text{-UF}_6$ ;
- gas-phase purification of fluoride-containing compounds.

The concept was based on mechanical de-cladding followed by hydro-fluorination and fluorination with  $\text{HF}$ ,  $\text{F}_2$  or  $\text{ClF}_3$ .

#### **Fluoride volatility process**

Hydro-fluorination in the presence of oxygen transforms MOX fuel into a mixture of residual fresh MOX, solid  $\text{UO}_2\text{F}_2$ ,  $\text{PuF}_4$  and volatile  $\text{UF}_6$  with some  $\text{RuF}_x$  contamination. Fluorination by molecular fluorine ( $\text{F}_2$ ) results in a very exothermic reaction, which blocks further fluorination by *in situ* sintering of semi-liquid compounds. Therefore alternative fluorinating agents were investigated, specifically  $\text{ClF}_3$  and  $\text{ClF}$ . Fluorination of MOX with  $\text{ClF}_3$  has the merit that  $\text{UF}_6$  volatilises at temperatures below 300°C but “contamination” with  $\text{PuF}_6$  is difficult to avoid. Above 550°C, both  $\text{UF}_6$  and  $\text{PuF}_6$  volatilise, however some fission products, e.g. Zr, Ru, Tc and, of course, iodine are entrained with the gaseous fluoride stream. By using  $\text{ClF}$ , the formation of  $\text{PuF}_6$  is reduced and appropriate experimental conditions were found to eliminate the bulk of  $\text{UF}_6$  from a simulated “fissium” mixture. Under optimal conditions,  $\text{UF}_6$ , free of  $\text{PuF}_6$ , can be produced and absorbed in a  $\text{NaF}$  bed. The formation

of  $\text{UF}_6\text{-}2\text{NaF}$  is the “refined” fraction, which must be converted into  $\text{UO}_2$  for further use. As a result of these investigations, it appeared that the technological development of this process necessitated the use of fluidised bed techniques with an extremely well-functioning gas purification system. Much attention was paid to these items and a pilot-scale fluoride volatility facility was constructed and operated for several years with depleted uranium in order to investigate the technological parameters of the process.

Laboratory work continued to study the fluoride volatility technology of the residual non-volatile residue made up of  $\text{PuF}_4$ , fluorinated fission products and inert materials. The most important results of these laboratory studies with  $\text{ClF}_3$  showed that under the nominal volatilisation conditions of  $\text{UF}_6$ , a substantial fraction of Np and some fission products were vaporised. At 100°C, up to 45% of Ru and 93% of Tc is eliminated from the fuel. At somewhat higher temperatures, Np volatilises (46% at 300°C) and at 400°C Nb-Zr is about 60% removed from the fuel mixture. Due to these chemical interactions, studies were undertaken to separate  $\text{NpF}_6$ ,  $\text{RuF}_x$  and  $\text{TcF}_x$  by selective condensation at temperatures between 100°C and 400°C.

A conceptual design of an integrated fluoride volatility plant was developed in parallel. It consisted of a mechanical chopper feeding a fluidised bed reactor successively purged with gas streams of  $\text{HF-O}_2$  and  $\text{ClF}_3$ . Plutonium was assumed to be eliminated as  $\text{PuF}_6$  (though with some  $\text{UF}_6$  contamination) and transformed into  $\text{UO}_2\text{-PuO}_2$  for recycling. The bulk of the reclaimed  $\text{UF}_6$  was then to be purified by distillation. From a nuclear point of view the main design problem consisted of the formation of U, Pu and fission product fluoride mixtures, which required complex recycle flow sheets. The partial decomposition of  $\text{PuF}_6$  into  $\text{PuF}_4$  by contact with metallic surfaces was an issue that required further investigation.

Due to the partial transformation and depletion of  $\text{F}_2$ , HF, HCl,  $\text{ClF}$  and  $\text{ClF}_3$ , an integrated fluoride “regeneration” plant was needed to decrease the amount of chemical waste (solid fluorides from the scrubber) and toxic gaseous discharge at the stack. The gas purification plant attached to such a fluoride volatility complex is of the same magnitude as the core of the process itself. Severe corrosion problems occurred over the course of these investigations, and in 1972 the decision was taken to abandon the fluoride volatility route for the reprocessing of irradiated nuclear fuel.

In the meantime, the aqueous reprocessing route had been more successful for irradiated LWR fuel, leading to the construction of the EUROCHEMIC pilot PUREX reprocessing plant at Mol in Belgium. The plant was operated for several years and stopped its activities in 1974. The experience gathered with pulsed extraction columns at the EUROCHEMIC plant was transferred to the design team of the French reprocessing plants of Marcoule (UP1), and later on to that of La Hague (UP2).

## Fundamental studies on fluoride and chloride compounds

A specialised laboratory for handling trace amounts of TRUs was installed at the University of Liège in Belgium. The laboratory, supervised by the late Professor Duyckaerts, worked on the determination of thermodynamic data of fluorides, chlorides and molten-salt reactions. Professor Fuger carried out these studies. Later, he continued his work at the TransUranium Institute of Karlsruhe (ITU), which eventually became the EU Joint Research Centre specialising in TRU research.

## Current situation

The studies on fluoride volatility and on molten salts have been interrupted in Belgium and only “documented” knowledge exists [3]. The facilities that were developed and constructed were dismantled in the 1970s and no further work is planned.

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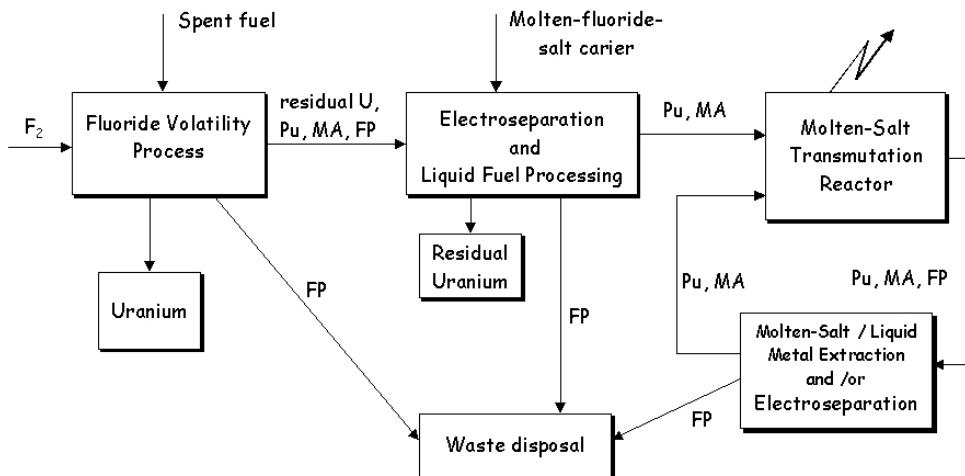
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## CZECH REPUBLIC

The development of pyrochemical methods and technologies in the Czech Republic is mainly linked to the Czech P&T programme. The development of partitioning and transmutation technologies in the Czech Republic stems from the belief that nuclear incineration of irradiated nuclear fuel represents a potential alternative concept to the currently adopted option based on the direct disposal of irradiated fuel in a deep geological repository.

The Czech research and development programme in the P&T area is founded on molten-salt transmutation reactor (MSTR) systems with liquid fuels using fluoride salts (see Figure 1). The fuel cycle is based on pyrochemical or pyrometallurgical fluoride reprocessing of irradiated liquid fuel. These MSTR systems, which should be directly connected with a continuous or quasi-continuous separation process, should ensure almost complete exploitation of the reactor transmutation power.

**Figure 1. Simplified scheme of the MSTR fuel cycle**



Currently, these systems may be conceived as critical assemblies and later, perhaps, as sub-critical accelerator-driven reactor assemblies. In addition to the nuclear burning of plutonium and minor actinides produced in the U-Pu cycle, these reactor systems might also, in the future, operate within the U-Th cycle. For such a compact coupling of a MSTR with an integrated chemical partitioning process, it will be advantageous to keep the fuel in a single chemical form, insofar as possible, throughout the course of the fuel cycle. If MSTR fuel can be based on fluoride melts, then the separation processes adopted should be effective with fluoride melt media. Pyrochemical and pyrometallurgical technologies comply generally with this requirement [1].

## Czech R&D programme

The Czech research and development programme regarding pyrochemical and pyrometallurgical separations is primarily based on experience acquired in the past in the development and realisation of experimental pilot-plant technology for the fluoride reprocessing of irradiated fuel from the Russian BOR-60 fast reactor [2]. At present, this experience is utilised for the development of suitable separation processes and technologies for the fluoride-based MSTR fuel cycle [3].

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

- technological research and development in the field of the “fluoride volatility method”;
- laboratory research on electro-separation methods in fluoride melt media;
- research on material and equipment for molten fluoride salt media.

Technological research for the “fluoride volatility method” can be categorised as the “front-end” area within the MSTR fuel cycle. The investigation is directed at the suitability and verification of a technology for thermal or fast reactor irradiated fuel reprocessing. This should result in a product with a form and composition applicable as a feed material for the production of liquid fluoride fuel for the MSTR. Consequently, the objective is a separation of a maximum fraction of uranium component from Pu, minor actinides and fission products.

The technology under development is based on irradiated fuel treatment with fluorine gas in a flame fluorination reactor, where the volatile fluorides are separated from the non-volatile ones (Figure 2). The technological operations of condensation, distillation and sorption are utilised for subsequent purification of the components. An integral part of this research is the creation of flow sheets for treating irradiated fuel into a form suited to the MSTR including the separation procedures before transmutation (front-end) and separation processes after irradiation of fuel in the transmutor (back-end) [4].

**Figure 2. View of upper part of  $\text{UF}_6\text{-NpF}_6$  condensers, instrumentation and piping system of the experimental fluoride volatility technology line in alpha-radiochemical laboratory of NRI Rez**



Laboratory research in the area of electro-separation methods is directed initially to the determination of optimal conditions for residual uranium and fission product separation from fluoride melts and further to the selection of a suitable composition of electrolyte based on fluoride salt mixtures. As the fluoride melt should be able to dissolve sufficient amounts of plutonium and minor actinide elements, mixtures of LiF-NaF and LiF-NaF-KF type are in the foreground of interest. The expected characteristic of sodium and potassium fluorides in forming co-ordination compounds with transuranium element fluorides and so significantly increasing their solubility in the melt was the reason for choosing the mixtures mentioned. The research programme in this area is further directed to the determination and study of selected physicochemical properties of fluoride melts [5].

The main objectives of research on material and equipment for fluoride salt media are: the verification of suitable construction materials, development of selected devices (firstly pumps) and achievement of melt handling and manipulation on a large scale. The Czech concept, in the area of P&T research, stems from the national power industry programme. This derives from the Czech Power Company's goal of extensive utilisation of nuclear power in the Czech Republic. Experimental research work related to the development of pyrochemical technologies is concentrated mainly in the Fluorine Chemistry Department of the Nuclear Research Institute plc, Rez. The Ministry of Industry and Trade mainly funds this programme and the Radioactive Waste Repository Authority also contributes. As the Czech Republic is a relatively small country, there is an understandable interest in its full integration within the international context for resolving issues associated with irradiated nuclear fuel. Wide international collaboration and good agreement of the national R&D programme with international R&D programmes in P&T is considered to be the only way for the Czech Republic to progress in this area.

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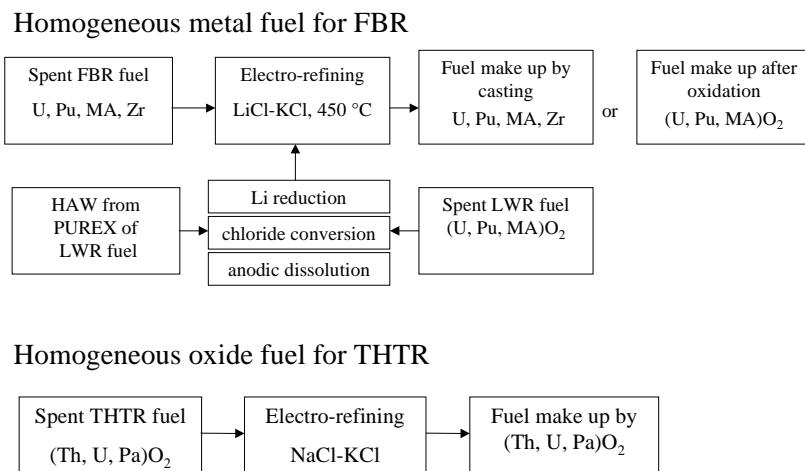
## **EUROPEAN UNION (EU)**

### **Introduction**

EU-sponsored work has been performed at the Joint Research Centre-Institute for TransUranium Elements (JRC-ITU), henceforth referred to as ITU, which is a part of the European Commission and is located in Karlsruhe, Germany. New reactor concepts and fuel strategies are being discussed world-wide to enable nuclear energy to be a major sustainable energy source in the future. One of the key issues addressed is minimisation of the amount and long-term radiotoxicity of nuclear waste arising, which may be accomplished by including suitable partitioning and transmutation (P&T) waste management strategies in the back-end of the fuel cycle. At ITU, advanced reprocessing schemes have been under investigation for several years. The main objective is to demonstrate the viability of existing process schemes using real fuels and targets. As most of the transmutation strategies are based on a multi-cycle scenario, the elements to be transmuted have to be recovered from the transmutation targets 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 Institute for TransUranium Elements (ITU) and 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). Reprocessing was, in this case, carried out using aqueous methods.

The study of metallic fuel targets has also recently been undertaken, which has led to a joint CRIEPI-ITU collaboration in pyrometallurgical partitioning of metallic fuels. At present, two fuel cycles involving pyrochemical reprocessing are mainly considered, as shown in Figure 3. The first is based on U-Pu-MA-Zr alloy fuels intended for transmutation and recycling in FBRs, and the second is based on ThO<sub>2</sub>, which avoids formation of additional minor actinides and is intended for dedicated accelerator-driven transmutation.

**Figure 3. Fuel cycles involving pyrochemical partitioning studied at ITU**

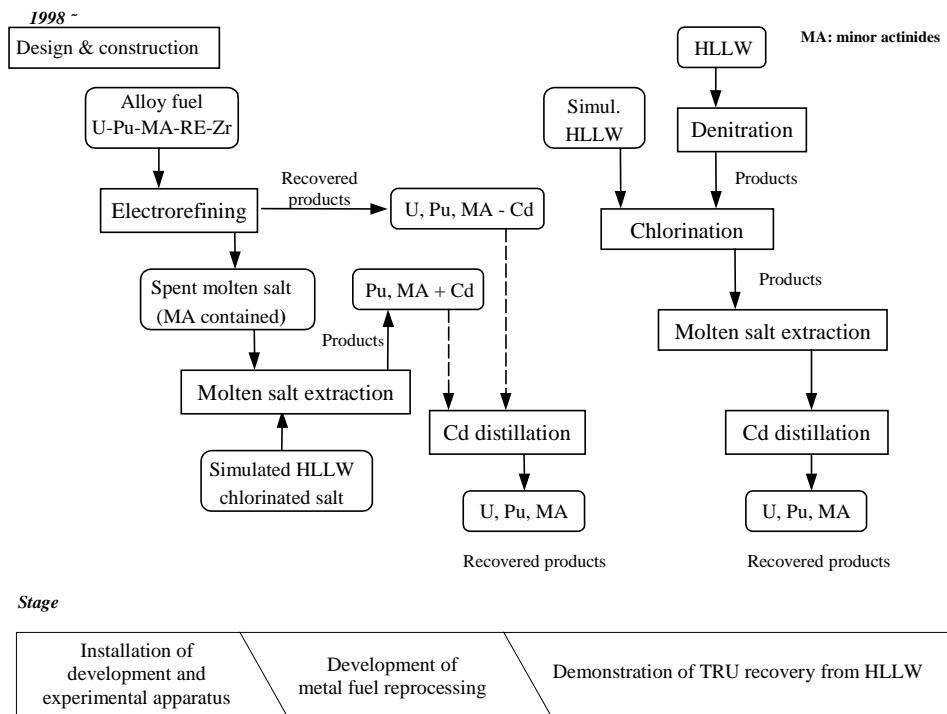


### **R&D programmes**

In the joint research programme between CRIEPI, Japan and ITU, the metal electrorefining process for irradiated U, Pu, Ma, Zr fuels is being studied. An argon atmosphere cell using a stainless steel container has been constructed to facilitate these experiments. This box operates with an argon atmosphere, which is continuously purified to keep levels of oxygen and water below 10 ppm. In this

installation, demonstration of the technical feasibility of electrorefining and reductive extraction concepts is being made. The stainless steel box has been equipped with a newly designed electrorefiner, fabricated and developed by CRIEPI as based on experience gained in a range of experiments. 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. At present, 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 is being processed. Experiments on irradiated metallic fuels and conversion of HLW into molten salt chlorides are also planned. For these purposes, the cell will be shielded with 150 mm of lead and installed in the hot cell facility of ITU. This joint research programme will also be reported on by CRIEPI. The experimental test plan for the joint study is shown in Figure 4.

**Figure 4. Experimental plan for the joint ITU/CRIEPI study**



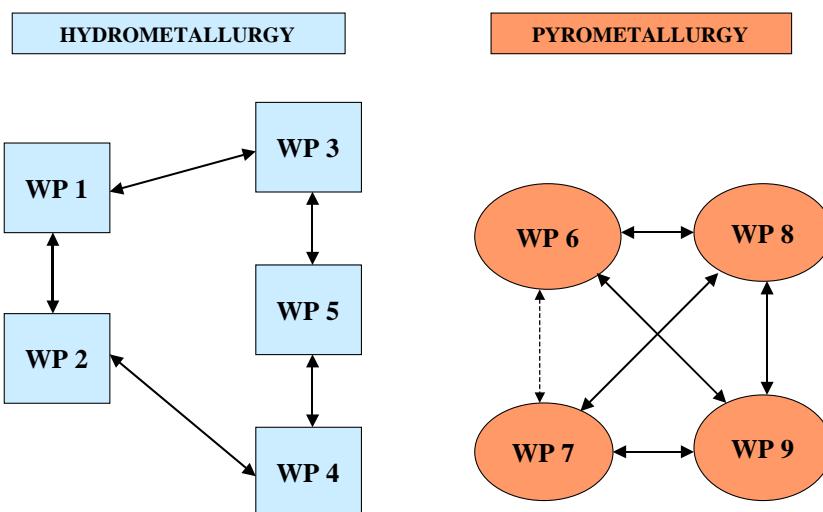
Use of the CRIEPI process to reprocess irradiated ThO<sub>2</sub> fuel is foreseen in a bilateral joint research project between ITU and ENEA (Italy). The study, which has not yet begun, will mainly deal with the electrochemical behaviour of protactinium. In the framework of the institutional (EU) research programme on pyrochemical separations, electrowinning of americium is studied. The overall purpose is to investigate the separation of MA from lanthanides by selective electro-deposition onto solid and liquid cathodes. For these experiments a double glove box has been constructed. The outer glove box is operated under nitrogen and the inner box under a purified argon atmosphere.

ITU-JRC and CRIEPI (Japan) also participated in a network of six European research organisations in an R&D project on pyrochemical reprocessing, called PYROREP, for the 5<sup>th</sup> Framework Programme for Technological Research and Development of the European Commission, and since 2004 in the EUROPART Project of the 6<sup>th</sup> Framework Programme. The partners are CEA (Marcoule, France), CIEMAT (Madrid, Spain) ENEA (Casaccia, Italy), NRI (Rez, Czech Republic) and BNFL (Sellafield, United Kingdom), together with AEA-T (Harwell, United Kingdom). The main objective of the

proposal, which includes both conceptual studies and experimental work, is to provide basic data, especially on the behaviour of minor actinides. The programme should yield sufficient basic data to assess and propose pyrochemical flow sheets for irradiated materials. It should also revive European research in the area of pyrochemical reprocessing and contribute to establishing long-term European expertise in this area.

The EUROPART programme is divided into nine work packages, five on hydrometallurgy and four on pyrometallurgy (Figure 5); ITU-CRIEPI is involved mainly in work package 7, which is devoted: (1) to determining basic properties of actinides (uranium to californium) and of some fission products in solution in molten halides; (2) to defining the different steps of pyrochemical processes, i.e. electrolysis, oxide precipitation, reductive metal extraction, for the co-separation of actinides (U-Cf) initially contained within advanced high burn-up spent fuels, such as those of the future ADS; (3) to defining the concepts of experimental devices (such as an electrorefiner) for process implementation. This information will be used during the second period of EUROPART to develop process flow sheet(s) which will be tested in hot cell laboratories.

**Figure 5. Work packages of the EUROPART programme**



## FRANCE

### Introduction

Separation studies for radionuclides found in irradiated nuclear fuel are, to a very large extent, based on hydrometallurgical processes. This is the reference path for the research effort on selective extractants for long-lived radionuclides instituted under the terms of the French law on long-lived high-level waste management passed on 30 December 1991. This choice is based on a number of considerations, which may be summarised as follows:

- A partitioning and transmutation strategy for the minor actinides or long-lived fission products (LLFP) can only be considered concurrently with or following a similar plutonium recycling strategy. As plutonium is presently separated by the PUREX process, it is not unreasonable to seek technological continuity for any subsequent downstream separation steps. Moreover, only processes similar to those already developed to industrial maturity appear to be suitable candidates in the possibility of a rapid industrial deployment after 2006.

- Operating experience acquired to date in the La Hague plants shows that these selective extraction technologies are capable of achieving remarkable separation performance (high recovery and purification percentages of the desired elements), while generating only small volumes of secondary waste. These are major advantages with regard to the objectives and criteria that must be taken into account in selecting a new separation process.

In spite of these considerations, assessing the potential of other technologies is not only an interesting prospect, but may be a necessary one in some respect. It is proposed to explore the possibilities offered by pyrochemical processes, as based on electrolytic or high-temperature extraction chemistry in molten-salt media.

The presumed inherent advantages of pyrochemical processes have often been described in prospective studies concerning future reprocessing techniques: compactness (a small number of basic operations performed on concentrated solutions) and more favourable criticality constraints (due to the absence of water). However, the absence of aqueous waste streams raises a number of major questions concerning the quantity and contamination level of the resulting technological waste.

The renewed impetus for further investigation of these processes is above all due to progress in the assessment of new concepts for transmutation and the corresponding fuel cycles. New matrices are being designed for the elements to be transmuted, including heterogeneous recycling targets, as well as dedicated fuel concepts for double-strata scenarios. Longer-term perspectives also include new fuels for homogeneous recycling processes. Some of the considered scenarios propose multiple recycling of targets or fuel to obtain a high effectiveness of transmutation (and thus a major reduction in radiotoxicity). The capability of pyrochemical processes to deal with highly irradiated materials could in such applications represent an advantageous alternative to hydrometallurgical processes, which could in some cases prove less compatible with the high burn-up and short cooling times proposed under some scenarios. The more distant future options, such as dedicated fuel cycles and transmutation in molten-salt reactors, provide further impetus for exploring pyrochemical processes. This is obvious in the case of molten-salt reactors, for which pyrochemical processes are the natural – and perhaps the only possible – approach.

Other concepts, however, which do not imply such a radical break with current technology, could also benefit from some features of pyrochemical cycles, e.g. reprocessing co-located with reactors, combined management of all the transuranic nuclides (plutonium and the minor actinides), and minimal inventory of radiotoxic materials confined in a dedicated cycle. As recommended by the French National Assessment Committee, and as already undertaken by research teams in Japan (OMEGA project), Russia (DOVITA) and in the United States (IFR concept), CEA proposes a research programme in these areas. In view of the wide range of transmutation options currently under consideration and the major conceptual evolution that can be expected in this area, it appears advisable to conduct a research programme addressing as broad an assessment as possible, with emphasis on acquiring fundamental knowledge that can be applied to the various scenarios under consideration. By the 2006 deadline imposed by the French law on long-lived high-level waste management, a selection of pyrochemical concepts should be proposed, and a thorough assessment of their potential advantages and drawbacks for the applications envisaged should be made, including more detailed data regarding scenarios of particular interest (e.g. multiple recycling of heterogeneous targets and the double-strata scenarios).

## R&D objectives

The proposed research programme basically consists in exploring and assessing an alternative to the reference path (i.e. hydrometallurgical processes) for the separation of long-lived radionuclides. The interest in this alternative will vary according to the scenarios considered; the most innovative

(and thus the most futuristic) are the most likely to benefit from the potential of pyrochemical processes, with perspectives for relatively long-term application. By 2006, it is important to provide a general overview of the potential of these processes with regard to the assessment criteria (expected performance, operating conditions, secondary waste production, etc.) covering the largest possible number of medium- or long-term applications. At this stage, an overall evaluation is of greater importance than a developmental approach that would favour target applications from the outset, at the risk of undertaking detailed development work for these anticipated objectives and defining basic options too early in the process to ensure that the initial choices were pertinent. It is therefore proposed to devote the period from 1999 to 2005 primarily to laboratory-scale research without seeking significant technological developments except those that might appear necessary to obtain a preliminary assessment of the operating conditions for the processes investigated. This approach addresses a broad spectrum of possible applications with the following objectives:

- to consolidate the knowledge of the concepts already described or tested elsewhere;
- to explore any promising options;
- to proceed with a preliminary selection of concepts for more thorough investigation of the aspects affecting their possible implementation;
- to perform one or more demonstrations on a few tens of grams of representative irradiated material as exhaustively as possible.

A related objective is to acquire a greater basic knowledge of the chemistry of the elements in the proposed media and of process engineering considerations in order to prepare for possible subsequent development of specific applications.

### **Proposed research programme: Scenario studies**

Two types of scenario studies will be conducted:

- simplified scenario studies, designed to obtain the radioactivity and mass properties of the fuel in the case of equilibrium recycling;
- detailed scenario studies to obtain the same characteristics together with the environmental and occupational impact in both transient and equilibrium recycling conditions.

Both types of studies will be used to characterise mass balances.

The scenarios proposed for assessment include for reprocessing purposes:

- *Homogeneous recycling*. The minor actinides are mixed with standard fuel in each type of reactor, producing irradiated fuel with limited activity for reprocessing.
- *Heterogeneous recycling*. The minor actinides or long-lived fission products are confined in targets and special core subassemblies, resulting in highly radioactive fuel for reprocessing.

Pyrochemical processes are of potential interest in the following scenarios:

- one hundred per cent (100%) fast reactor scenarios with homogeneous dilution of minor actinides in a metallic or nitride fuel;
- combined PWR and fast reactor scenarios in which the fast reactors burn metallic or nitride fuel while recycling the minor actinides in homogeneous mode (diluted with plutonium) or in heterogeneous mode with slightly modified devices;
- double-strata scenarios in which pyrochemical techniques are used to reprocess fuel with high actinide loading.

The expected results to be analysed are the mass inventories and flows, the impact on the major cycle parameters (residual power, gamma-ray emission, neutron emission, etc.) and the impact on criticality during reprocessing and fabrication operations for comparison with hydrometallurgical processes. The objective is to confirm the possibility of reprocessing either high-level targets or dedicated non-oxide fuel based on simplified scenario studies. These studies will iteratively characterise the preliminary mass flows and their activity and will assess the potential of pyrochemical methods for reprocessing the irradiated fuel within a limited time frame (residual power, activity, neutron emission, criticality, etc.).

Once these aspects have been confirmed, the detailed scenario studies will address the following issues:

- process input and output material flows;
- reprocessing losses;
- estimated occupational and environmental impact doses;
- reprocessing plant flow sheet;
- preliminary economic assessment.

The scenarios, applicable to molten-salt reactors, are the same as for solid fuel reactors, except that MSRs are capable of operating with a fraction of the fission products in the salt and thus simplify the salt reprocessing

## **Research domains**

### *Extraction flow sheets*

In the case of molten-salt reactors (MSR), the objective is to extract the fission products; the actinides remain in the salt, which is recycled in the reactor. Conversely, in the case of incineration targets or of any oxide mixture, the objective, after dissolution in a molten salt, is to extract the actinides while leaving the fission products in the salt. The chemistry required for these two flow sheets is obviously very different. At present, we have chosen to consider only the second option. The first option is considered only within the scope of a co-operation programme (ISTC#1606).

### ***Selection of a solvent medium***

It is not a simple matter to choose the salts or salt mixtures for these studies from among the wide range of possible candidates, including halides, hydroxides, oxidised salts (sulphates, nitrates, carbonates, etc.) and oxides. Numerous selection criteria are involved:

- *Melting temperature.* The higher the temperature, the more complex the technology.
- *Solubility of metallic species.* It must be relatively high.
- *Electro-activity range.* The wider the domain, the easier it is to control the oxidation and reduction reactions that are the basis of most separation processes.
- *Stability.* Although considered very stable, some salts may present difficulties (for example, nitrates involved in exchange reactions with  $O^{2-}$  generate  $NO^{2+}$ , which is unstable at the operating temperatures considered here).
- *Salt volatility.* It should be as low as possible.
- *Water affinity.* Most molten salts are very hydrophilic and the presence of water could inhibit many reactions by solvent hydrolysis.
- *Secondary waste management.*

The intention is not to perform a detailed analysis to define the “ideal salt”. On the basis of available data and past experience in France and abroad, it is initially proposed to consider only the halides (chlorides and fluorides) for process development purposes. However, other salts may be considered in the course of the studies for a better understanding of the phenomena involved.

### ***Separation techniques***

A wide range of techniques may be proposed to separate the actinides from the fission products dissolved in a molten-salt medium, including fractional distillation, liquid-liquid extraction, adsorption on a medium, fractional crystallisation, ultra-filtration on an inorganic membrane or electrolysis. In view of the foreseeable difficulties (high temperatures, corrosion, hydrodynamic properties), only electrolysis, extraction by a liquid metal or a combination of the two will be considered in this programme. Moreover, because of their inherent interest, two other subjects will be investigated within the scope of co-operative programmes:

- nitride processing, with JAERI (Japan);
- fractional crystallisation of actinides in a molten-salt medium, with RIAR (Russia).

### ***Exploratory studies***

It is planned to start “exploratory” radioactive testing shortly, in order to optimise this approach, as soon as possible, by identifying problem areas. There is no intention for these tests to affect the course of the basic research that will be necessary, or the choice of solvents or separation techniques that will be made at a later date. Their only role is to uncover the main stumbling blocks likely to be encountered.

Based on a few general questions (Which elementary operations should be tested? In what medium? On what material?), the following experimental issues have been identified:

- actinide separation in a molten fluoride bath by extraction in a liquid metal in the presence of a reducing agent;
- minor actinide separation by electrolysis in a molten chloride bath.

### **Related fundamental research**

The CEA and other laboratories (CNRS, universities and other institutes) will conduct fundamental research with the following objectives:

- understand the fundamental mechanisms involved (nature, structure of the chemical species, reactivity);
- provide data for selection of the previously mentioned options;
- compile a basic data bank for process studies;
- master the basic operations to be able to implement them when the final decisions are made.

The first point is of particular importance, not only to optimise the process implementation but also to anticipate any malfunction and thus to demonstrate the safety of the processes. The basic data must be determined with regard to the elementary operations proposed to constitute a complete process.

The following inventory may be completed as necessary as the work progresses. Some data will require only documentary research (e.g. melting temperatures), while others will require substantial experimental work. The task will therefore have to be ranked according to the primary programme objectives and the available resources.

### **Examination of process flow sheets**

Considering the general programme objectives (nature and quality of input and output products, recovery efficiency and degree of purification) and based on the findings of laboratory studies or published reports, the purposes of this task are to:

- establish a complete process flow sheet (the goal is to provide a general flow sheet for a specific type of fuel: dissolution, off-gas treatment, separation by salt/metal exchange and/or electrolysis or volatilisation, recovery of finished products and waste treatment);
- determine the data corresponding to the flow sheet (flow streams, concentrations, activities, etc.);
- provide a quantitative and qualitative assessment of the waste production.

The results will be used for an overall assessment of the process and thus for comparison of various flow sheets. The data may also be used for a technical and economic feasibility assessment.

Irrespective of the options that may be selected at a later date, a number of flow sheets can be proposed for this type of investigation:

- treatment of metal targets using the process developed by ANL for U-Pu-Zr fuel: electro-deposition of uranium and then of the other actinides in a molten chloride medium (actinide recycling in metallic form);
- treatment of an oxide target using the same process (with actinide recycling in oxide form);
- treatment of an oxide target in a molten fluoride medium: actinide separation by liquid-liquid extraction (actinide recycling in oxide form);
- treatment of molten-salt reactor fuel.

The molten-salt reactor in this case was designed by the CEA, EdF and Pechiney-Ugine-Kuhlman (PUK) between 1969 and 1982; a comprehensive design package (CEA-N-2341) was produced in 1977 before the project was terminated. This research task could also cover processing of fuel from the  $^{232}\text{Th}/^{233}\text{U}$  cycle to assess the potential of pyro-metallurgy in the thorium fuel cycle.

Other flow sheets developed abroad could also be analysed, such as:

- treatment of an oxide target by the RIAR process (Russia): electrolysis and crystallisation in a molten chloride medium (actinide recycling in oxide form);
- treatment of a nitride target by the JAERI process (Japan) including recycling of  $^{15}\text{N}$ .

The studies proposed above were carried out in part under a European research programme (PYROREP).

### **Chemical engineering studies**

Pyrochemical processes call on a wide range of techniques, based on the general classification of chemical engineering operations, including:

- *Fluid mechanics.* Solid-liquid separation (filtration, settling), liquid-liquid separation.
- *Material transfers.* Gas absorption, dissolution, liquid-liquid extraction, crystallisation and electro-deposition.
- *Chemical conversions.* Oxidation or reduction, chemical displacement.

It is essential to master some of these operations in order to meet the assigned programme objectives; yet, the subject is not widely covered in the literature. The initial effort will therefore address these points. Fundamental research topics include material and heat transfer near an electrode, material transfer between a molten salt and a liquid metal and liquid-liquid separation.

### **Corrosion, product recycling and secondary waste management**

For corrosion studies, the first task will be to identify one or more acceptable materials for the selected medium based on bibliographic research and prior experience, together with a few validation tests. The corrosion rates and mechanisms will then be characterised with greater precision.

The pyrochemical processes are intended to recycle actinides and long-lived fission products; the resulting products (metal, oxide or nitride) must therefore be compatible with the target fabrication processes. These studies will be undertaken in close collaboration with the teams working to define the fabrication process once the nature of the targets has been chosen.

In addition to classic technological waste, a pyrochemical process generates specific waste forms requiring suitable management routes. These include off-gas trapping solutions, un-trapped gases, contaminated salts and metals used for extraction. Although classic liquid waste treatment processes are available for the first category, the remaining waste forms will require substantial development work: first to estimate the waste quantities generated (based on the process flow sheet development work) and then to identify suitable treatment and stable conditioning processes. Decontamination processes may include electrostatic filtration (for gases), melting (for metals) or metal-salt exchange (for salts).

The first R&D task will be to acquire basic data under both inactive and radioactive conditions, including the effectiveness of electrostatic filtration, the distribution coefficients in salts and metals, the physicochemical properties of salts and metals, the activity coefficients of contaminants in salts and metals and the reaction kinetics involved. This information will then be used in the preliminary specification of the industrial reactor design.

The waste conditioning objectives include:

- defining a suitable containment material for the process by-products;
- defining the material fabrication requirements;
- characterising the material by determining its structural properties, thermal stability, physicochemical characteristics, etc.;
- investigating its long-term behaviour (leaching resistance, etc.) under various interim storage or disposal conditions.

### Selecting a reference flow sheet

The results of the exploratory experimentation, together with the findings of the scenario studies conducted in parallel with them, will provide the basis for determining the reference flow sheet on which much of the remaining effort will then be concentrated. The choice may not be definitive, particularly if the analysis identifies alternative flow sheets. The reference flow sheet will include specifications for the process feed material(s), the medium, the separation technique and the techniques used for ancillary operations.

### Demonstration experiment(s)

In order to ensure a feasibility assessment before 2005, the technological options selected for the process concepts described above must be validated experimentally. These tests will be conducted at limited scale under radioactive conditions with a representative material (the targets planned for irradiation in the PHENIX reactor). The experimentation will cover the key process steps – notably dissolution and separation – sequentially or separately and will demonstrate the scientific feasibility of the reference process.

## **Technical feasibility**

This step is intended to demonstrate that the selected process could be operated in an industrial environment. It cannot be defined at this stage of the project. Various facilities are required.

The following facilities operated by the Nuclear Energy Direction of CEA are currently available at Marcoule:

- *Test room in Building 208 and G1 facility.* Suitable for much of the non-radioactive test programme including chemical engineering and equipment tests.
- *ATALANTE laboratory L8.* Equipped with four dedicated pyrochemistry glove boxes and includes the necessary off-gas lines and a chloride treatment unit (the proposed experiments are also covered by its safety references).
- *Cell 10 in the ATALANTE facility.* A large cell suitable for experimentation on materials containing actinides and fission products.

Additional short-term availability of a shielded cell in one of the ATALANTE cell complexes is now being considered for exploratory testing. The “Process” hot cell complex in the ATALANTE DRA building has also been reserved in the future for installation of the equipment necessary to conduct an integral pyrochemistry experiment.

## **General research schedule**

The novelty of this research area makes it difficult at this stage to estimate the time necessary to accomplish the research activities described in this document. Nevertheless, it is advisable to take advantage of the future availability of targets irradiated in PHENIX (or in the HFR) to qualify some or all of the process options. Assuming that the demonstration experiments on actual targets are to be conducted in 2005, the research must be sufficiently advanced to allow a preliminary process selection before that date. In view of the scope of the tasks and the range of fields investigated, a major co-operative effort with CNRS laboratories and universities will be indispensable, notably for aspects concerning the fundamental research. Collaborative programmes with foreign institutes should also be developed, in particular for the application studies.

## **ITALY**

Since 1995, a growing interest in accelerator-driven system (ADS) concepts has taken place in Italy. This has given rise to several basic R&D activities as well as a technical programme involving ENEA (the Italian national research body for energy, environment and new technologies), INFN (the Italian national research institute for nuclear physics) and various industrial partners.

## **Technical programme**

The national R&D programme TRASCO (TRAsmutazione SCOrie – Italian acronym standing for waste transmutation) was funded and started in 1998 as a first step under the leadership of INFN for the accelerator and of ENEA for the sub-critical system. The TRASCO programme was intended to promote collaboration among groups of different competencies (accelerator, reactor physics, plant design), which will provide significant results in support of any related industrial programme.

Parallel to the basic activities of TRASCO, a technical programme was proposed in two main steps:

- Ongoing short-term activities in the Italian context to issue the preliminary design of the ADS experimental plant. A reference configuration has been proposed (known as Energy Amplifier Demonstration Facility, EADF) and submitted to the European partners as a contribution to the European Road Map for developing an ADS experimental plant. The preliminary design was completed in the first half of 2001, while the main supporting R&D needs were assessed. The experimental facility CIRCE for thermal-hydraulic testing using Pb-Bi of the main sub-systems of the experimental plant has been realised in the ENEA centre in Brasimone. Recently, the preliminary design has been proposed in the European project PDS-XADS as a reference for assessing the concept of a Pb-Bi ADS.
- Medium-term activities in a European and international context as described under international collaborations. The pyrochemical separations work is performed collaboratively with ITU, CRIEPI and organisations collaborating under the EU PYROREP programme.

## JAPAN

Development of pyrochemical technologies for irradiated fuel processing in Japan is being pursued by three separate entities: the Central Research Institute of Electric Power Industry (CRIEPI), the Japan Atomic Energy Research Institute (JAERI), and the Japan Nuclear Cycle Development Institute (JNC).

## CRIEPI

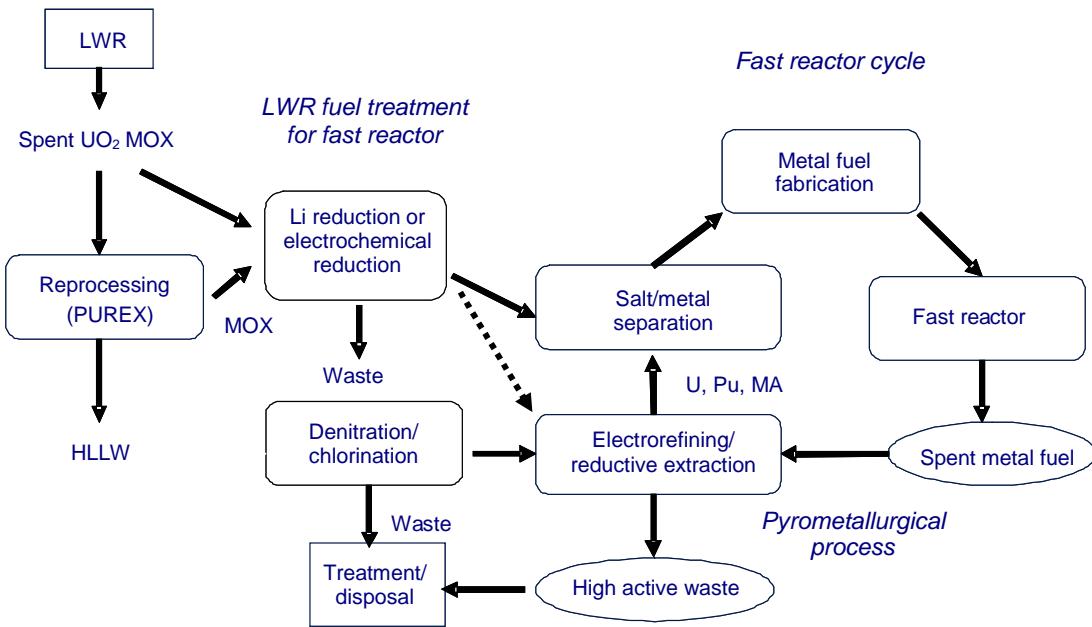
In Japan, CRIEPI is taking part in the feasibility study (FS) for the development of a fast reactor and fuel cycle system and in the OMEGA programme, which involves long-term research and development on partitioning and transmutation (P&T) technology. Under these programmes, CRIEPI's work is focused 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) originating 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 6. 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 pyrometallurgical application 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. Collaboration with JAERI, 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. A co-operative study with JNC on metal electrorefining has also started.

### Past and present studies in CRIEPI

#### *Thermodynamic properties*

The study of pyro-metallurgy 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,

**Figure 6. CRIEPI pyrochemical process for the recycle of actinides**



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. 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.

### **Separation of actinides from lanthanides**

Separate experimental devices for electrorefining and reductive extraction were examined for separation of actinides from lanthanides. 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 by 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 by electrorefining and reductive extraction.

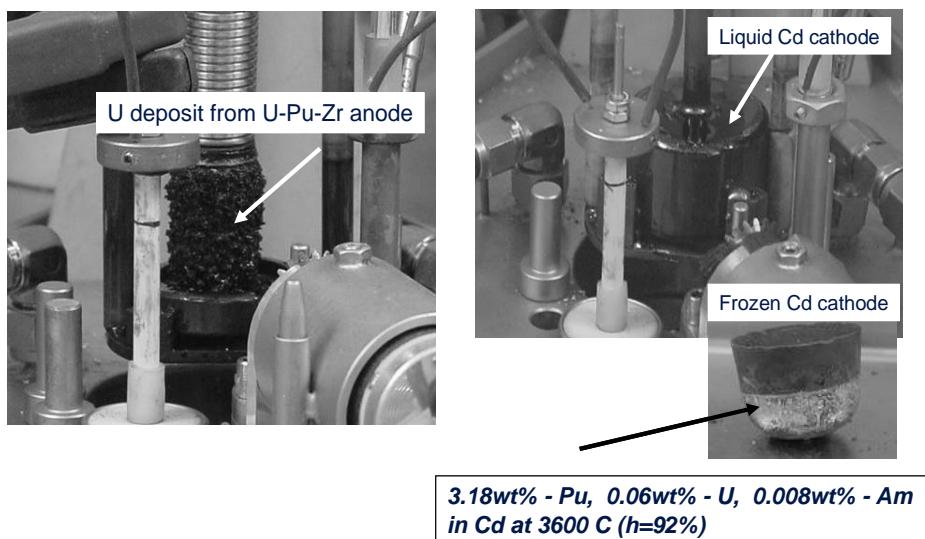
### **Process technology development**

#### ***U and Pu electrorefining process***

CRIEPI aims at optimising operating conditions for the use of electrorefining methods. Uranium tests at the 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. Due to the US policy of no utilisation of plutonium, engineering scale demonstration of transuranic recovery by pyroprocessing has not yet been realised by ANL. CRIEPI is proceeding to develop and demonstrate the electrorefining

of U, Pu and Np with solid and liquid cathodes in a joint study with JAERI. 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 7 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.

**Figure 7. Overview of uranium and plutonium collected on a solid cathode and in a cadmium cathode, respectively, by electrorefining**



### ***Reduction process for oxide fuel***

Experiments on the reduction of  $\text{UO}_2$ , carried out in co-operation with Kyoto University, have confirmed that more than 99% of the  $\text{UO}_2$  was converted into metallic form. Further experiments, using single elements of  $\text{PuO}_2$ ,  $\text{Am}_2\text{O}_3$  and  $\text{NpO}_2$ , as well as MOX pellets, showed the feasibility of conversion to metals. These studies were jointly conducted by CRIEPI and AEA Technology. 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.

### ***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  $500^\circ\text{C}$ , with some alkali nitrates remaining. The oxides formed are converted to chlorides by passing chlorine gas with carbon reductant through a  $\text{LiCl}-\text{KCl}$  bath at over  $700^\circ\text{C}$ . The demonstration using genuine HLLW is now in progress in a hot cell at ITU.

### ***Reductive extraction process for recovering transuranic elements***

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

## ***Waste treatment process development for pyroprocess wastes***

Two kinds of waste treatment process have been developed. Firstly, sodalite, in which waste chlorides are immobilised in a mineral matrix, is synthesised by heating NaAlO<sub>2</sub> and SiO<sub>2</sub> with waste salts at high temperature. The second process forms a borosilicate glass waste. Salt waste is converted to oxides through electro-reduction in liquid lead followed by vitrification with B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in an air atmosphere.

## **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 a feasibility study at JNC.

## **Future studies**

The future programme for the next five years is divided into the following three areas of activity:

1. The empirical demonstration of each process by using actual irradiated fuel and HLLW samples. This task includes the improvement of the technology and optimisation of the process flow sheet.
2. The development of devices suitable for commercial use. This study is carried out from the engineering point of view.
3. A design study of each engineering device and the overall facility is planned, based on experimental evidence, providing a basis for detailed cost estimates. To this end, equipment for electrorefining and reductive extraction, to separate actinides from actual fuel and wastes, have been installed in a hot cell facility at ITU. A glove box for chemical reduction and electrorefining is also being prepared for a process study using Pu. This study is performed in co-operation with JNC.

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## JAERI

In 1999, the Atomic Energy Commission (AEC) of Japan issued a progress report for the OMEGA programme in Japan; a long-term project for research and development on partitioning and transmutation (P&T) technology. The report proposed that:

- system design and implementation scenarios of P&T be studied;
- basic experiments be carried out to demonstrate the feasibility of the processes;
- engineering-scale experiments be conducted to obtain safety data for these systems.

JAERI 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 (MAs)(second stratum). For the transmutation of MAs, JAERI is considering a nitride-fuelled ADS (accelerator-driven system) as a reference, in which irradiated fuel is treated by pyrochemical processes. The schematic of the double-strata fuel cycle, as proposed by JAERI, is shown in Figure 8. Under the OMEGA programme in Japan, R&D activities have been stimulated by the collaborative efforts of JAERI, JNC and CRIEPI.

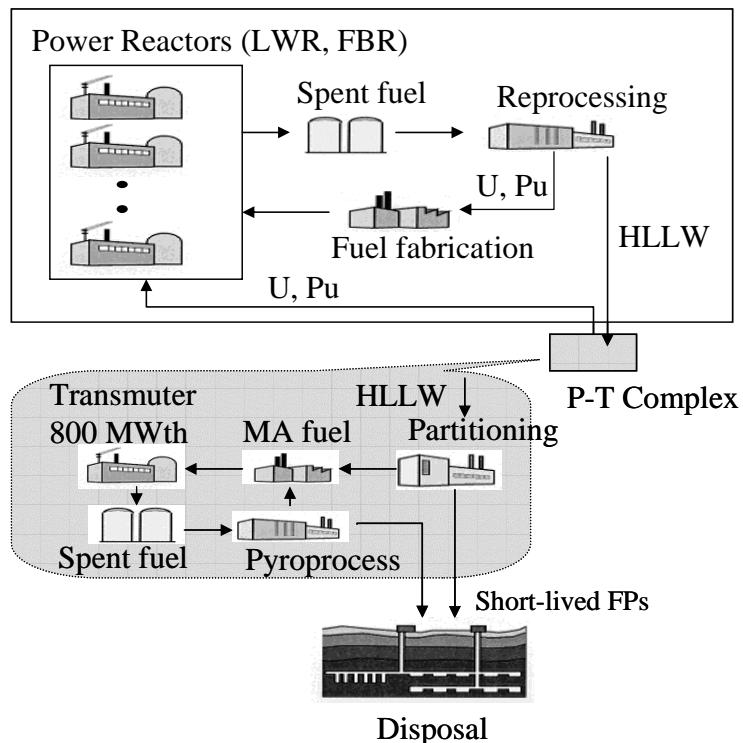
## Current activities

JAERI does not have a long history of pyrochemical study for P&T. Electrorefining of nitride fuel in LiCl-KCl molten salt was started in the mid-1990s in a co-operation with CRIEPI. 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:

- 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  $^{15}\text{N}$ ;
- 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  $\text{N}_2$  gas.

In parallel, some basic studies relating to pyrochemical separation are under way. They include preparation of a “pyrochemical database” under a joint research programme with JNC, investigation of the reaction  $\text{M}^{3+}/\text{M}^{2+}$ , thermodynamic properties of M-N-Cl and M-O-Cl systems (M: rare earth elements) by both electrochemistry and high-temperature spectrophotometry, structural study of the chloride molten salt by X-ray diffraction, and EXAFS and molecular dynamic calculations.

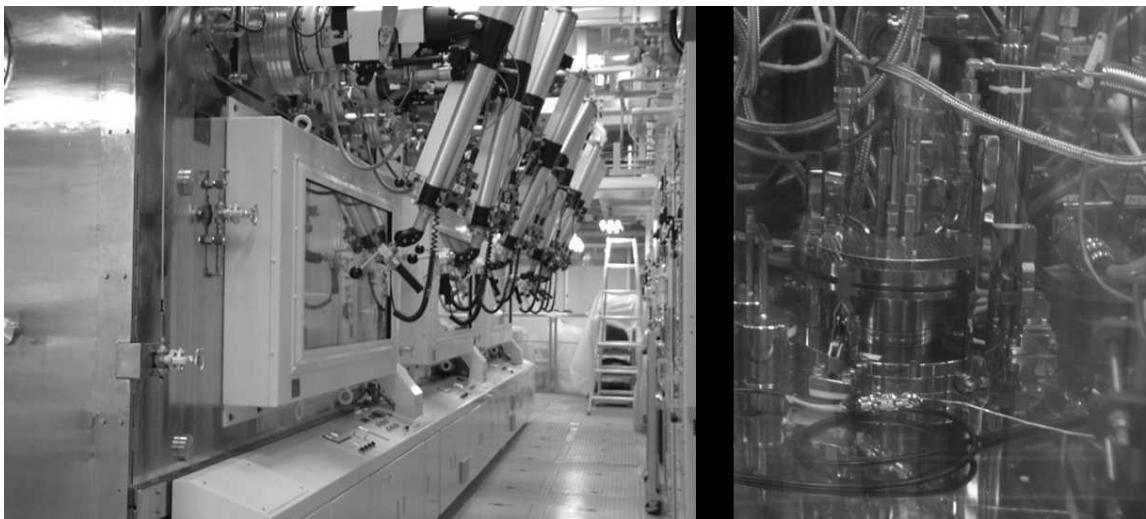
**Figure 8. Double-strata fuel cycle proposed by JAERI**



## Future studies

JAERI 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. JAERI thus 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. TRU-HITEC was completed in the NUCEF facility at JAERI-Tokai in 2003 (see Figure 9). Experiments at the ten-gram scale of Am and ten-milligram scale of Cm are planned, and research on Am, such as electrorefining of AmN, will start in 2004.

**Figure 9. Appearance of TRU-HITEC for pyrochemical study of MA**



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## **JNC**

### **Introduction**

The Japan Nuclear Cycle Development Institute (JNC) is leading a feasibility study (FS) in Japan concerning the development of a commercialised fast reactor and its associated fuel cycle system. Other partners in this feasibility study are the electric utilities, JAERI, CRIEPI, private industrial companies and universities.

The key targets are:

- safety of reactor and fuel cycle (safety-in-design);
- economic competitiveness, at least comparable to future LWRs;
- efficient utilisation of uranium resources;
- reduction of environmental burden;
- enhancement of nuclear non-proliferation.

In Phase I (JFY1999-2000), technical options were surveyed for a broad range of technologies and conceptual designs assessed against the above-mentioned targets. In Phase II (JFY2001-2005), intensive laboratory test work and engineering-scale trials of key technologies are being performed. JNC and partners are mainly considering four technologies for reprocessing FBR irradiated fuel: advanced PUREX, fluoride volatility, oxide electro-winning (modified RIAR process) and metal electrorefining (modified ANL process). The latter three are pyrochemical processes. The cost target is 0.27 million Yen per kg (initial heavy metal) corresponding to about \$2 100/kg (iHM).

### Past JNC pyrochemical studies

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<sub>2</sub>, Rh, Zr and CeO<sub>2</sub> in molten alkali salts, and electro-winning of noble metals and also UO<sub>2</sub> decontaminated from noble metals. Noble metal (Rh) separation was effective at small voltage corresponding to low current density (~0.02 A/cm<sup>2</sup>).

A design study concerning small-scale uranium and plutonium laboratory equipment for oxide fuel electro-winning tests has been undertaken. In addition, an assessment has been performed of oxide fuel electro-winning 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.

Installation work has been completed on an integrated process test for the metallic fuel cycle to be undertaken at the Chemical Process Facility (CPF) at the JNC Tokai Works. Licensing of equipment is complete for electrorefining of plutonium and uranium metals and oxides.

Laboratory explorations of lithium reduction of U<sub>3</sub>O<sub>8</sub>, distillation of metal chlorides and cadmium oxidation of uranium metal, and rare-earth element extraction between molten salt and liquid cadmium phases have been performed to further the understanding and the development of pyrochemical separation techniques.

### Current JNC pyrochemical studies

Preparation of an integrated process test in CPF for the metallic fuel cycle is being carried out. Construction of the equipment has been completed. For the oxide electro-winning process, test equipment is being commissioned for electro-dissolution and electro-deposition tests (~100 g simulant scale) using a molten salt/Cl<sub>2</sub> apparatus mounted in a vacuum glove box. Material studies, including corrosion rates of ~1 g samples in 50 g molten salt/Cl<sub>2</sub>, are also being performed. Molten salt handling, safety trials, and remote operation tests of a 20-litre graphite vessel suitable for oxide electro-winning, 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 a possible installation of the equipment in CPF. Conceptual studies for the scale-up of metal electrorefining and oxide electro-winning equipment and processes are being carried out. As described in the section dedicated to *International collaborations*, JNC also participates in significant co-operative studies with RIAR on the oxide electro-winning Dimitrovgrad Dry Process (DDP).

### Future JNC pyrochemical R&D

Besides completion of the present pyrochemical test work, one of the main future items is the process test using plutonium for the metallic fuel cycle, jointly undertaken at Tokai Works by JNC and CRIEPI. The objectives are to:

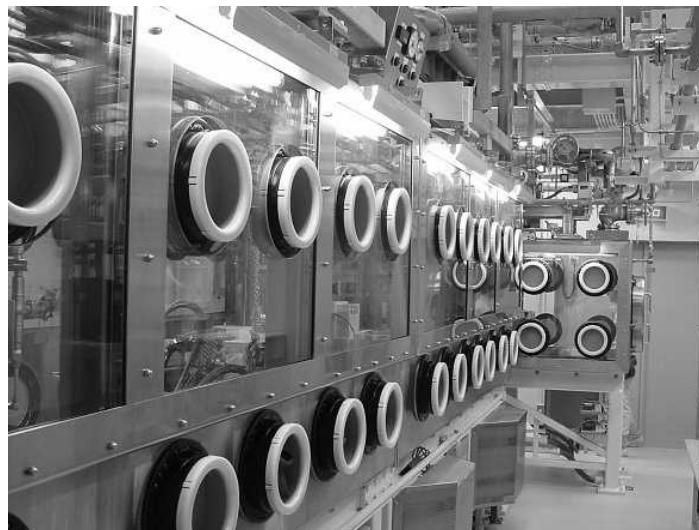
- accumulate a domestic database to evaluate feasibility of the metallic fuel cycle as adapted to oxide fuel;
- perform sequential process tests to simulate the actual fuel cycle operation and determine its realistic recovery efficiency;
- provide a domestic facility for process innovation and optimisation.

The schedule is as follows:

- completion of construction and installation in early 2002;
- commissioning and cold testing in mid-2002;
- U commissioning in early 2003;
- commencement of plutonium active work in late 2003.

Another important test and demonstration item currently in the planning and design stages is the process trial using plutonium for the RIAR-based oxide electro-winning fuel cycle. This will be performed by JNC within a glove box in CPF. Anodic dissolution of simulant-irradiated FR fuel, MOX electro-co-deposition and PuO<sub>2</sub> precipitation are amongst the stages likely to be investigated.

**Figure 10. Glove box facility at JNC for the demonstration of metal electrorefining of simulant oxide fuel**



#### **REPUBLIC OF KOREA**

#### **Introduction**

The nuclear power industry in Korea has grown dramatically since the first commercial nuclear power plant, Kori #1, started operation in 1978. Eighteen nuclear power plants (14 PWRs and four PHWRs) are currently in operation, supplying about 40% of the total electricity demand. As of December 2002, the accumulated irradiated fuel amounted to 5 982 t (heavy metal) which is stored at

four reactor sites. The cumulative amount is expected to reach 11 000 t (heavy metal) by 2010. However, the Korean government has not yet decided on any definite policy for the back-end fuel cycle, adhering to a “wait and see” strategy.

### Fundamental studies on partitioning and transmutation

In the field of R&D only, several options are being studied at the Korea Atomic Energy Research Institute (KAERI) in order to find an effective solution for the back-end of the fuel cycle. Options such as direct disposal, conditioned disposal (disposal of irradiated fuels after conversion of the oxide form into metallic form), direct use of PWR spent fuel in CANDU (DUPIC), and partitioning and transmutation are considered candidate methods for the long-term management of irradiated fuel.

As for partitioning and transmutation studies, KAERI is conducting a fundamental study according to the long-term plan for nuclear technology development set up by the Korean government. Partitioning studies are focused on the development of pyroprocessing because it is seen as a rather proliferation-resistant technology. The major experimental items for the pyroprocessing study include electrorefining, electro-winning, cadmium evaporation and molten salt waste treatment. Thus far, the thermodynamic properties of several molten salts of chlorides and fluorides, as well as the electrolytic behaviours of various metal halides in the molten salts, have been investigated in order to examine the applicability of electrolysis of molten salts for the separation of long-lived radionuclides. In addition, some basic experiments at the laboratory scale employing inactive materials for electrorefining, electro-winning and cadmium evaporation, were also carried out. The effect of the process conditions were analysed for each procedure. Based on this work, further studies for the development of key technologies for pyroprocessing will be continued in the coming years.

The molten salt waste is composed of mixtures of metal chlorides or metal fluorides, which have high solubility in water and also high volatility. Therefore, it will generate secondary waste during the solidification phase and the solidified substance will have a high leachability when disposed of underground. Its conversion into more stable chemical forms may thus be needed to overcome the above drawbacks. Gelation is at present being studied as a candidate method for conversion from chloride or fluoride into phosphate or oxide.

As for the transmutation concept, the Hybrid Power Extraction Reactor (HYPER) system, comprising a proton accelerator and a sub-critical reactor, is considered appropriate for the Korean situation, with priority given to the non-proliferation attributes of the treatment of nuclear fissile materials in the back-end of the fuel cycle. The sub-critical reactor features a fast flux of spallation neutrons that are created by an accelerated proton beam striking the spallation target. This system is expected to handle a certain level of impurities (fission products) left in the fuel at the time of transuranic recycling. It decreases the required effectiveness of partitioning of transuramics and also contributes to non-proliferation in the P&T cycle, since it is unnecessary to further purify the fuel material after partitioning. Long-lived fission products such as  $^{99}\text{Tc}$  and  $^{129}\text{I}$  can also be incorporated in the system as irradiation targets and then transmuted by neutron capture, which is made possible by local moderation of the fast neutron flux. In parallel with this, the partitioning study focuses on the development of pyroprocessing technology using the electrolysis of molten salts.

### Electrolytic reduction study

The development of electrolytic reduction technology aims to reduce the volume of irradiated fuels before final disposal. Volume reduction of irradiated fuels can be achieved by dismantling the irradiated fuel assemblies, removing the structural parts of the assemblies and then transforming the oxide fuel

materials into metallic form. An additional benefit of this technology lies in the possibility to remove heat-emitting radionuclides such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ . This engenders a favourable effect in that the thermal load is reduced, thus making it possible to diminish the distance between two neighbouring disposal pitches in a repository of irradiated fuels. Therefore, this technology can be applied as a promising pre-treatment method for the final disposal of irradiated fuels, reducing the demand for disposal space.

## ***RUSSIAN FEDERATION***

### **Introduction**

The Russian national strategy for the peaceful use of nuclear power in the 21<sup>st</sup> century is still based on the closed nuclear fuel cycle [1]. In September 2000, the President of the Russian Federation, Vladimir Putin, put forward the “Power, Sustainability, Safety, Ecology, Non-proliferation in the 21<sup>st</sup> Century: A Russian Federation Presidential Initiative” for the international development of a new nuclear reactor and fuel cycle concept. Solutions to problems related to the back-end of the fuel cycle require changes throughout the entire fuel cycle, up to and including reactors, fuel manufacturing, decommissioning and waste disposal. This could be realised on the basis of advanced aqueous technologies, as well as on the base of “dry” technologies – spent nuclear fuel (SNF) reprocessing in molten salts, fluoride volatility and other processes.

The flow sheets based on the use of the non-aqueous processes were proposed for both thermal reactors and fast reactors at the very outset of the nuclear era. The non-aqueous methods of fuel reprocessing exclude the use of both aqueous and organic media, and are based on the use of liquid metals, molten salts or halogens, usually at high temperatures [2]. The Russian nuclear effort in this area is divided into two main categories: pyro-electrochemical, which are the most compact, but provide only partial purification; and halogenide distillation, which can achieve the complete purification of uranium (mainly) and plutonium from fission products. Other applications of non-aqueous methods are currently under consideration, particularly flow sheets compatible with advanced fuel cycles, designed for more efficient use of resource materials and for minimisation of radiological impact of radioactive waste. In that context, points of interest are for fuels with high burn-up, short cooling times, multiple recycling and limited needs for partitioning for reactors.

The molten salt reactor concept process, based on a mixed fluoride salt fluid as a reactor fuel and coolant, is very important for consideration as an element for future nuclear energy systems. This integrated technology (reactor + processing unit) has the advantage of easy fuel preparation and recycling, because the fluid nature of the fuel provides extra flexibility and a simpler back-end fuel cycle. The molten salt reactor concept appears to have substantial promise not only as a transmuter of TRUs, but also as an advanced TRU-free system operating with the U-Th cycle [3].

### **Historical background of pyrochemical fuel processing**

In the former USSR attention was paid to the development of new methods of fuel reprocessing. As many metallurgical processes were already used in the technology of non-ferrous, rare metals, the usage of metallurgical principles seemed suitable for nuclear materials as well.

In the early 1950s, activities linked to the fluoride volatility process were started with regard to reprocessing of irradiated fuel. This work was initiated in Moscow at the RRC Kurchatov Institute and at the All-Russian Scientific Research Institute of Chemical Technology (VNIICHT). Both institutes possessed equipment for production of elemental fluorine and they developed processes for the production of  $\text{UF}_6$ , initially for the purposes of uranium isotopic enrichment [4,5].

In the late 1950s, the principles of molten salt application to reprocessing and refining of the nuclear fuel were formulated at the Ural Polytechnical Institute (UPI). Several research groups dealing with this scientific line were established, and, in parallel, they began to investigate the physical properties of the melts and the related electrochemical processes.

In the early 1960s, when the fundamental studies of the melts and engineering investigations on fluoride volatility method adaptation were under way, a radiochemical complex was put into operation at RIAR (Dimitrovgrad). The complex was designed for carrying out the investigation of the chemistry and technology of trans-plutonium elements. The experimental base made it possible to establish another two groups (laboratories) at RIAR, which developed engineering projects in the field of testing and implementation of non-aqueous methods:

- A fluoride volatility laboratory, which worked under supervision of RRC-Kurchatov Institute for a long period of time. Among the projects completed could be mentioned FREGAT and FREGAT-2 [6,7].
- An electrochemical laboratory, which began to investigate plutonium chemistry and the testing of various molten salt processes. This laboratory turned to another research line providing the ORYOL facility with fuel, and has now become one of the basic divisions at RIAR, where the methods involving molten salts are used and developed [8,9].

The work of these groups gained importance during construction and commissioning of the BOR-60 test fast reactor. It was decided to construct closed fuel cycle facilities near this reactor. Both of the above-mentioned technologies were considered candidates for implementing the procedure of irradiated fuel reprocessing prior to fuel pin fabrication [10].

Additionally, in the 1960s-1970s the practice of co-operation between institutes and universities (dealing with non-aqueous method studies) was widespread in the USSR. For instance, the following basic organisations were engaged in studying molten salt applications:

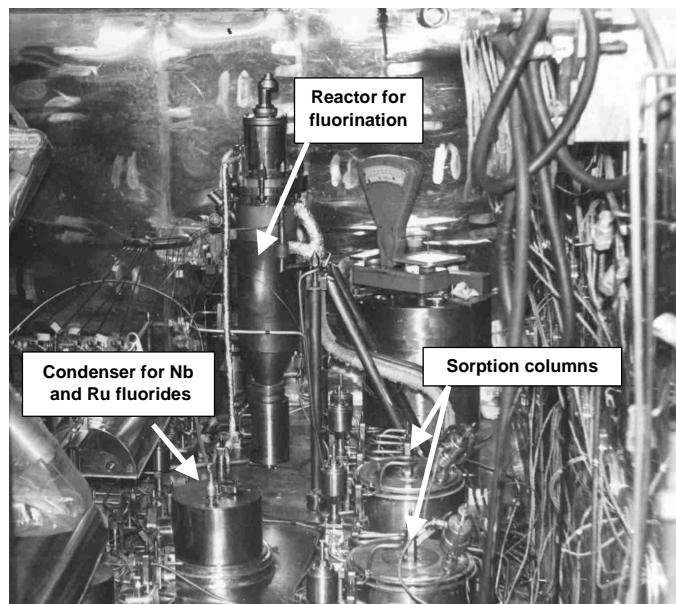
- *Research Institute of Atomic Reactors (RIAR, Dimitrovgrad)*. Study of the properties of uranium- and plutonium-containing molten salts, plutonium electrochemistry, detailed study of various technological and auxiliary operations, equipment design, technological and laboratory experiments with fuel simulators, demonstration experiments with real irradiated nuclear fuel, production of experimental fuel batches for irradiation, etc.
- *Institute of High-temperature Electrochemistry (Ekaterinburg)*. Fundamental studies of molten salt chemistry and electrochemistry, studies related to the theory of metal crystallisation during melt electrolysis, thorough investigation of uranium and thorium electrochemistry, study of electrode processes, data on the chemistry of fission products, engineering techniques of salts handling, etc.
- *Ural Polytechnical Institute (Ekaterinburg)*. Investigation of uranium- and thorium-containing melts, a series of investigations on fission product chemistry, systematic studies of alloys of low-melting metals and actinides, theory of liquid alloys, electrolysis, theory of non-stationary electrolysis in molten salts, metal refining.
- *SverdNIKhimmash (Ekaterinburg)*. Development of equipment for pyroprocesses.
- *Khlopin Institute (St. Petersburg)*. Fundamental spectral studies of actinide compounds in halogenide molten salts, study of various salts – nitrate, oxide and other salts.

- *VNIINM (Moscow)*. Study of specific methods for molten salt usage in various processes, investigations of oxide deposition in fluoride salts, study of molybdate melts.
- *Nizhny Novgorod State University*. Study of inorganic ceramic systems able to concentrate fission products and actinides in reprocessing of wastes resulting from pyro-processes; study of the behaviour of some fission products.
- *IPPE (Obninsk)*. Study and development of the processes for uranium spent nuclear fuel handling in molten salts.
- *Institute of Physical Chemistry (Moscow)*. Study of the systems for immobilisation of wastes arising from fluoride volatility and pyrochemical processes; some fundamental studies.

Other organisations from the USSR (Russia and Ukraine) also took part in this work, but the main development was performed by organisations from Ekaterinburg and RIAR. The main aim of this co-operative work (apart from the fundamental ones) was the closed fuel cycle for the fast breeder reactor, and by the middle of the 1970s, the main objective of reprocessing concerned oxide fuel of uranium, uranium and plutonium, uranium and thorium, as well as MSR fuel. However, studies of other systems were also pursued. In parallel, thorough studies of fuel preparation for reprocessing (de-cladding) using non-aqueous methods were carried out [11].

The FREGAT project demonstrated the possibility of uranium fuel recycling at the beginning of the 1970s [6,12] (Figure 11). In the second half of the 1970s, the ORYOL facility, a unique automated remote-controlled complex, was put into operation. This facility (jointly developed by the USSR and East Germany) was intended for the fabrication of BOR-60 fuel pins and assemblies in remote conditions using the vibropacking technique [9,13]. Since the production of granulated fuel through pellet crushing and the sol-gel method did not lead to successful results, it was decided to use the fuel produced by pyro-electrochemical and UF<sub>6</sub> pyro-hydrolysis methods. The extension of the ORYOL facility covered the application of both technologies [14].

**Figure 11. FREGAT facility**



After commissioning the ORYOL facility, the government of the USSR adopted a resolution in 1978 concerning the development of automated technology for deployment of “civil” plutonium in the fast reactor fuel cycle. It was a very strong spur for the development of both technologies. The objective was later narrowed, however, and was reduced to only MOX fuel production. The general concept of the closed fuel cycle of breeder reactors was at this stage considered as a development of principles using “civil” plutonium.

The second half of the 1970s was also very important for the development of MSR. Work on this project was based on the early-established co-operation between institutes in the field of development of fluoride volatility and pyrochemical processes. The initiator and leader of this programme was the Kurchatov Institute. In the late 1970s, in parallel with the ORYOL facility project, the project on feasibility studies of the plant for irradiated nuclear fuel reprocessing by fluoride volatility method was carried out in co-operation with the CEA (France).

The data obtained as a result of this project can be used for engineering analysis of the fluoride volatility method applicability. The conditions necessary for comparing pyro-electrochemical and fluoride volatility technologies were created at the RIAR site. The pyro-electrochemical technology enabled the production of MOX fuel in a shorter period of time and in amounts large enough for operation of the BOR-60 reactor using MOX fuel, in comparison with the fluoride volatility technology. However, the vibropacked fuel was subjected to improvements up until the second half of the 1980s, and a new type of vibropacked fuel, crystal MOX fuel, was developed with getter additive in the form of uranium metal [15,16].

In the mid-1980s, both the facilities for BN-600 fuel production by a pyro-electrochemical method and the FREGAT-2 facility were constructed at RIAR, based on the experience garnered from the ORYOL facility, which was then dismantled. The facility for BN-600 fuel production, fuel pins and assemblies, capable of a productivity of 1 500 kg of MOX fuel per annum, was constructed in its place over a two-year period [17]. The new facility was entirely developed in the USSR. The FREGAT-2 project was realised in co-operation with Czechoslovakia and it incorporated some new solutions, different from those determined at the FREGAT-1 facility. The designed productivity of the flame fluorination reactor was 3 kg per hour.

At RIAR, the complex of these facilities (ORYOL-2, pyro-electrochemical facility for MOX fuel production and FREGAT-2) was known as the Pilot Research Complex (OIK), though it is often referred to as the Semi-industrial Complex (Figures 12, 13). However, in the late 1980s and early 1990s almost all work at OIK, as well as that concerning many other research lines related to the fuel cycle, was stopped. Work on fluoride volatility technology was completely abandoned. Work on pyro-electrochemical technology was carried out very slowly, but co-operation with academic institutes and universities was preserved.

Furthermore, since 1990 many RIAR studies on pyro-electrochemical technology and the ORYOL facility have been declassified, contributing to the appearance of open contacts with the USA, Japan, and later with BNFL, CEA, KAERI and ITU. In the 1990s, co-operation with Japanese companies enabled further progress of the studies on the pyro-electrochemical process at RIAR. Co-operation with the CEA and the US DOE made it possible to analyse and test the application of pyro-electrochemical processes to weapons-plutonium disposition [18]. The DOVITA Programme formulated at RIAR in 1992 [19] was supported both by ISTC and through direct contracts.

During the 1990s, MinAtom was not able to take an active part in financing the work on new technologies because of the overall economic stagnation. Only a small “RECYCLE programme” was maintained, covering the investigation of pyrochemical process of americium recovery from wastes and fabrication of fuel with increased neptunium and americium content for transmutation in the fast reactor.

**Figure 12. Semi-industrial Complex of RIAR (Bld. 180)**



**Figure 13. Hot cell facility for pyrochemical production of MOX fuel in Semi-industrial Complex of RIAR**



The “renaissance” of non-aqueous reprocessing methods began over the period 1997-1999:

- A summing up of the experience gained in the field of non-aqueous methods was carried out by MinAtom, and it enabled consideration of possible application of non-aqueous methods on a new basis [20].
- Feasibility studies and experimental work on the development of the BREST reactor fuel cycle technology were started. This concept uses a closed fuel cycle based on non-aqueous fuel processing [21].

- Following an initiative of RIAR, Khlopin Institute and Krasnoyarsk-26, the work on the analysis of possible new concepts for the plant (RT-2 plant) for reprocessing of VVER reactor fuel was started. The first version of the combined scheme was subjected to economic analysis. At present this work is under way [20].
- A large-scale programme on weapons-grade plutonium disposition in power reactors with MOX fuel (including pyro-electrochemical method for fuel conversion) is underway [22].
- The RRC-Kurchatov Institute, VNIICHT, VNIINM and RIAR re-started experimental work on fluoride volatility technology and pyrochemical processing in molten salts.
- RIAR has started development work on non-aqueous methods applicable to:
  - closing of the BOR-60 fuel cycle;
  - reprocessing of the fuel arising from research reactors of different types;
  - conversion of HEU-containing materials into material which is less than 20% enriched in  $^{235}\text{U}$ ;
  - recycling of materials valuable for nuclear power engineering (enriched boron, zirconium).

Thus, Russia has accumulated broad scientific and practical experience that will serve as the basis for implementation of a new “Strategy for Nuclear Power Development in Russia for the First Half of the 21<sup>st</sup> Century” [1]. This document points directly to the use of pyrochemical reprocessing methods for realising the task of nuclear power engineering development.

### **Dry volatility irradiated fuel processing**

The fluoride volatility process' lack of sensitivity to radiation creates an opportunity to reprocess irradiated nuclear fuel with a short cooling period, which is especially important for the breeder reactors. The most notable feature of the process is the exceptional selectivity in the separation of uranium and plutonium from fission products. Uranium and plutonium hexafluorides separated from fission products can be easily transformed to either metal or dioxide. The radioactive waste, consisting of the fluorides of fission products, is produced directly in a very compact form.

Though the physical and chemical principles of the process are simple, there are technical problems connected with the properties of fluorine, such as its exceptional chemical reactivity and the high thermal output of the fluorination reactions. For commercialisation of the fluoride method to be feasible, the following key problems must be addressed:

- heat removal from irradiated fuel fluorination;
- purification of uranium hexafluoride from fission products;
- concentration of fission products;
- separation and purification of plutonium;
- development of remote-controlled equipment for high-temperature processes.

Although the industrial production of  $\text{UF}_6$  was mastered long ago, extensive R&D work was required to achieve efficient heat removal at sufficiently small (criticality safe) dimensions and to adequately filter the gaseous flow at the outlet of the apparatus, in order to optimise the process of irradiated fuel fluorination. Initially, the fluorination of  $\text{UO}_2$  pellets (or oxidised to  $\text{U}_3\text{O}_8$  before fluorination) within fluidised bed was used in experiments performed at the Kurchatov Institute [5]. An alternative method of fluorination of irradiated fuel, using a flame-type cold-wall apparatus, was also developed in the USSR.

The decisive advantage of the fluoride volatility process (the potential for producing non-volatile fission products in a compact form) has been experimentally demonstrated in the FREGAT facility. This special facility had permitted to carry out complex studies on the reprocessing of irradiated  $\text{UO}_2$  and MOX fuel from FBR [6,12].

The reprocessing flow sheet for irradiated uranium fuel of the BOR-60 reactor [6] includes the following stages:

- de-cladding (by voloxidation);
- fluorination in a fluidised bed reactor;
- some stages for  $\text{UF}_6$  purification from fission products by cooling, sorption on  $\text{NaF}$  and de-sorption;
- $\text{UF}_6$  condensation.

The fuel used in the tests had a burn-up of about 10% heavy atoms and a short cooling period (3-6 months). The  $\text{UF}_6$  product had a high decontamination factor from fission products ( $> 10^6$ ) after reprocessing. The total extraction of uranium from irradiated nuclear fuel was 99.4-99.6%, and the direct recovery rate into  $\text{UF}_6$  was 96.1-98.3%. The losses were 0.4-0.5%. Most of the fission products (~ 85%) were concentrated in residues of fluorination, and the radioactivity release into gas dumps was less than 10-5%. The main high-level wastes were:

- residues of fuel fluorination (fission products and impurity fluorides);
- sorbents ( $\text{NaF}$  with fission product fluorides and traces of  $\text{UF}_6$ );
- spent chemical sorbent ( $\text{Ca}(\text{OH})_2 + \text{CaF}_2$ );
- ceramics, coal heaters, traps and filters with sorbents, etc.; these high-level wastes were compacted by melting to cryolyte-type rocks [23].

The experiments on uranium fuel reprocessing stimulated the application of the method to MOX fuel. For  $\text{PuO}_2$  fluorination up to  $\text{PuF}_6$ , a higher temperature is necessary and the fluorination step was carried out in a special flame fluorinator [12]. The flame temperature where the fuel burns (in  $\text{Ar}/\text{F}_2$  mix) is about 1 300 K. The resulting gas mixture was filtered, fission product fluorides were condensed under 313-323 K, as were  $\text{UF}_6$  and  $\text{PuF}_6$  (under 213-233 K). The scheme of decontamination was similar to that described for uranium fuel.

Some types of fuel were reprocessed at RIAR [12]. The experiment with the BOR-60 fuel gave the following results:

- decontamination factors for  $\text{UF}_6$  was  $10^7$ , for  $\text{PuF}_6$   $10^3\text{-}10^4$ ;
- the recovery rate for U was >99%, for Pu 89-91%.

The low recovery rate of Pu is connected to the instability of  $\text{PuF}_6$ . It is probable that the  $\text{PuF}_6$  recovery rate can be increased. It was also proposed to carry out a low-temperature fluorination of fuel. This could improve the method, especially from the point of view of decreased release of fission products and TRU into the gas phase. A major advantage of the method is that  $\text{UF}_6$  can be used directly for re-enrichment. Also, hexafluorides can be transformed into dioxides just after reprocessing by pyro-hydrolysis in a gaseous mixture  $\text{H}_2\text{O} + \text{H}_2$ .

Such a process was developed at RIAR [24]. After irradiated fuel reprocessing,  $\text{UF}_6$  was converted to granulated  $\text{UO}_2$ , which was used for manufacturing vibropacked fuel pins, which were subsequently irradiated in the BOR-60 reactor up to 15.6% burn-up. Thus, the first four of the five key problems of the fluoride method were solved by the 1970s. Development of remote control (the fifth problem) techniques was held up because suitable equipment for observing the remote operations had not been developed. This became one of the main obstacles to developing the fluoride volatility process for large batches of irradiated fuel.

Costing studies carried out at the project and design institutions of MinAtom have shown the economical advantages of the fluoride volatility method of irradiated nuclear fuel reprocessing as compared to aqueous extraction technology, in particular for fuels with high plutonium content. The experimental programme came to a halt in the Soviet Union after the Chernobyl accident.

## Dimitrovgrad Dry Process (DDP)

### *Technological description*

Studies of irradiated oxide fuel reprocessing, obtaining U and Pu oxides and their mixture from molten alkali chlorides, were carried out in the former Hanford Engineering Development Laboratory (USA) [25]. In the USSR, work in this direction was begun in Sverdlovsk at the end of the 1950s, and has been taken up at RIAR, where the development has continued. In the RIAR work [2,17,26,27], the basic problems of the fast reactor fuel cycle, employing pyrochemical technology, were solved and the following basic principles of this fuel cycle were experimentally demonstrated:

- pyrochemical re-processing of irradiated nuclear fuel and waste treatment;
- production of reprocessed fuel in the form of dense granulated particles;
- manufacturing of fuel pins using the vibropacking method from granulated fuel;
- use of remote-controlled automated equipment for fuel reprocessing and fuel pin and assembly manufacturing.

In addition to scientific problems, the basic technical difficulties were also solved. Extensive reactor tests were carried out and all aspects of the safety of the cycle were investigated. Physical and chemical laws of the processes occurring in the molten alkali chlorides with U and Pu have now been studied in

more detail. Concerning oxide fuel reprocessing technology, the following properties of U and Pu are more important [28-32]:

- From the electrochemical point, U and Pu oxides behave like metals. During dissolution in the molten salt or anode oxidation they form the complex oxygen ions  $\text{MeO}_2^{n+}$ , which are reduced to oxides on the cathode.
- Under high temperatures ( $> 400^\circ\text{C}$ ),  $\text{UO}_2$  and  $\text{PuO}_2$  are electrically conductive. Thus, during electrolysis, the formation of crystals and an increase of the cathode deposit are possible. The lower electric conductivity of oxides, in comparison with the melt, provides a stable flat front of crystallisation and allows obtaining compact cathode deposits.
- In the molten alkali chlorides, uranium has the stable ions U(III), U(IV) and U(VI). At the same time, the highest states of Pu oxidation Pu(V) and Pu(VI) are stable only in a definite field of ratios for oxidation reduction potentials of the system. Therefore, during the joint electro-deposition of  $\text{UO}_2$  and  $\text{PuO}_2$ , it is necessary to treat the melt with a chlorine-oxygen gaseous mixture to create the required concentration of the ion  $\text{PuO}_2^{2+}$ .
- From any oxidation state, plutonium can be converted into oxide by changing the oxidation reduction potential of the system. This process is called “precipitative crystallisation”. Under oxidation conditions, uranium stays in the melt and, thus it is possible to fractionally separate plutonium from nuclear fuel.
- $\text{UO}_2$  and  $\text{PuO}_2$  are reduced in the electropositive area. The majority of fission products are reduced at more negative potentials, so during the electro-deposition process of  $\text{UO}_2$  and  $\text{PuO}_2$  the cleansing of impurities occurs.

The data on chemistry of U, Pu and fission products served as a basis for the development of technologies for the production of fuel compositions and reprocessing of irradiated nuclear fuel.

### ***Main technological processes (DDP)***

Technological processes for the production of oxide granulated fuel from the molten alkali chlorides are developed [26]. The initial products of the process are Pu and U oxides in the form of powder. However, the processes are considered for use with different types (on isotopic and chemical composition) of raw material.

- *Electro-deposition of uranium dioxide.* The process is carried out from molten  $\text{NaCl}-2\text{CsCl}$  (or  $\text{NaCl}-\text{KCl}$ )- $\text{UO}_2\text{Cl}_2$ , prepared by chlorination of uranium oxides. During electrolysis the formation of dense cathodic deposits of  $\text{UO}_2$  occurs. The special electrolysis modes allow obtaining a product with a recovery rate of 99.0-99.5% for the manufacture of vibropacked fuel pins with a high effective density (more than  $9.0 \text{ g/cm}^3$ ). The technology of crystal  $\text{UO}_2$  fuel production has passed the complete cycle of development from laboratory to the creation of a semi-industrial facility.

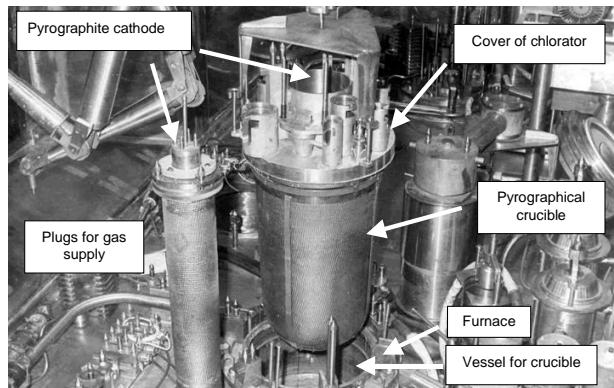
In the beginning of the 1970s experiments with irradiated  $\text{UO}_2$  of the BOR-60 reactor were carried out. The experiments show that the pyro-electrochemical method allows to reprocess irradiated nuclear fuel (burn-up – 7.7% heavy atoms, cooling period – six months) with a high recovery rate (99%) and satisfactory decontamination from fission products (DF = 500-1 000).

- *Precipitative crystallisation of plutonium dioxide.* The process is carried out with molten NaCl-KCl after chlorination-dissolution of PuO<sub>2</sub> or metal Pu. During treatment of melt with a gas mixture containing chlorine and oxygen, the formation of crystalline PuO<sub>2</sub> occurs. Three options present themselves for the production of granulated PuO<sub>2</sub>:
  - production of crystalline PuO<sub>2</sub> from reprocessed reactor-grade plutonium with purification from americium;
  - extraction of crystalline PuO<sub>2</sub> from irradiated MOX fuel, the process being tested on the irradiated MOX fuel of BN-350 and BOR-60 reactors;
  - conversion of military origin Pu alloy into dioxide.
- *Electro-co-deposition of uranium and plutonium oxides.* The process includes the operation of initial oxides chlorination in molten NaCl-2CsCl with formation of uranylchloride and plutonium chlorides and the operation of oxidation for transformation of Pu into plutonylchlorides. Electrolysis is carried out by treating the melt with a chlorine-oxygen gas mixture, resulting in a co-deposition of UO<sub>2</sub> and PuO<sub>2</sub>. The cathodic deposits which emerge are quasi-homogeneous crystals of (U,Pu)O<sub>2</sub>. After removal of captured salts and crushing, the product is used for vibropacked fuel pin manufacturing. The fuel recovery rate (with recycled products) is 98.5-99.5%. The technology was developed and applied on OIK for the production of MOX fuel. This facility has been operating since 1988. It manufactures fuel for the BOR-60 reactor and experimental fuel assemblies for the BN-600 reactor.

For all processes, the flow sheets are very similar. The products have a particle density close to the theoretical (10.7-10.9 g/cm<sup>3</sup>) that allows supplying high effective density of the fuel column during vibropacking. The necessary equipment was developed for realisation of technological processes in remote conditions. The head device (chlorinator-electrolyser) uses pyrolytic graphite as materials for bath-anode, cathode and gas tubes.

Different types of chlorinator-electrolysers are tested for fuel processing, differing only in volume. The present device has a working volume of 40 litres and is designed for loading 30 kg of initial material, corresponding to one fuel assembly in the BN-600 reactor (Figure 14). Apart from the chlorinator-electrolyser, other equipment is used for crushing cathodic deposits, for removal of captured salts from fuel, for drying and for classification.

**Figure 14. Chlorator-electrolyser in hot cell**



The processes described provided – and continue to do so – the fuel pins, manufactured with vibropacked oxide uranium and MOX fuel, for operation of the BOR-60 reactor and for tests in the BN-600 and BN-350 fast reactors (Table 1).

**Table 1. Pyrochemical production and reprocessing of oxide fuel in RIAR**

Facility	Fuel	Weight, kg	Period	Reactor
Facility in glove boxes for uranium fuel	UO <sub>2</sub>	900	1976-1983	BOR-60
	UO <sub>2</sub>	365	1983	BN-350
Test hot cell facility for MOX fuel production	PuO <sub>2</sub>	100	1980-1982	BOR-60
	(UPu)O <sub>2</sub>	550	1983-1987	BOR-60
	(UPu)O <sub>2</sub>	75	1984	BN-350
	(UPu)O <sub>2</sub>	70	1987	BN-600
Semi-industrial Complex (OIK)	UO <sub>2</sub>	120	1988	BN-600
	UO <sub>2</sub>	535	1988-1989	RBT-10
	UO <sub>2</sub>	1 300	1989-2002	BOR-60
	UO <sub>2</sub>	374	1993	BN-350
	(U,Pu)O <sub>2</sub>	325	1989-1998	BOR-60
	(U,Pu)O <sub>2</sub>	370	1989-2000	BFS
	(U,Pu)O <sub>2</sub>	300	1990	BN-600
OIK – military plutonium	(U,Pu)O <sub>2</sub>	111	1998-1999	BOR-60
		270	1999-2002	BN-600
Experimental fuels		30		BOR-60

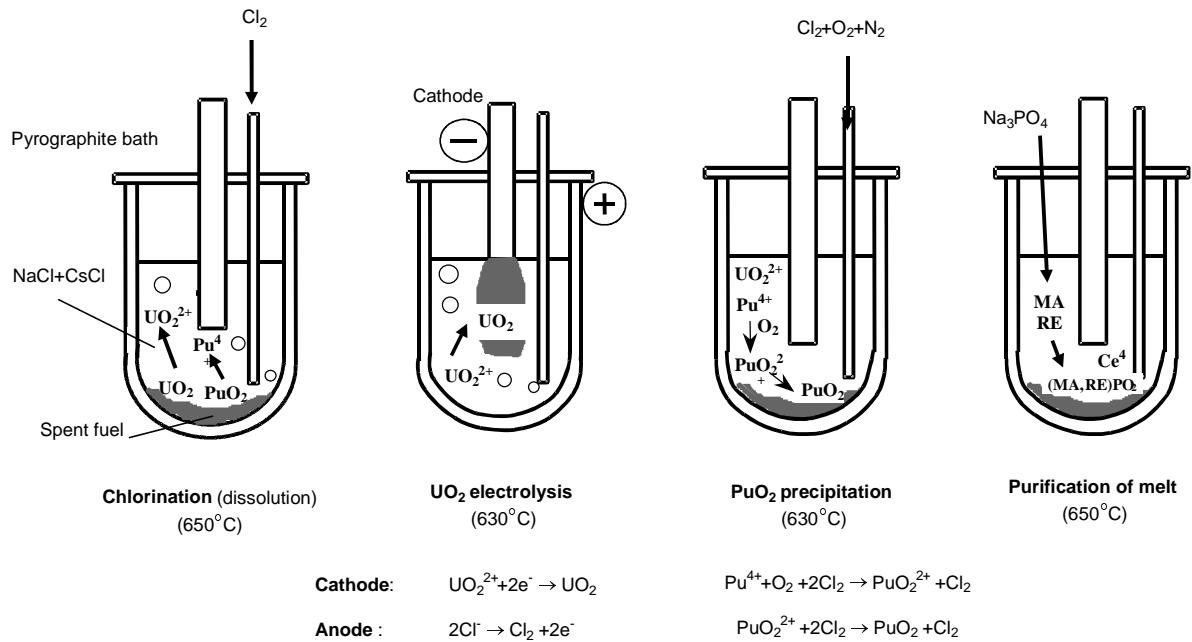
Irradiated fuel reprocessing				
Fuel	Burn-up	Weight, kg	Time for test	Reactor
UO <sub>2</sub>	1%	3.3	1968-1969	VK-50
UO <sub>2</sub>	7.7%	2.5	1972-1973	BOR-60
UPuO <sub>2</sub>	4.7%	4.1	1991	BN-350
UPuO <sub>2</sub>	21-24%	3.5	1995	BOR-60
UO <sub>2</sub>	10%	5	2000	BOR-60
UPuO <sub>2</sub>	10%	12	2000-2001	BOR-60

#### ***Reprocessing irradiated MOX fuel using the Dimitrovgrad Dry Process***

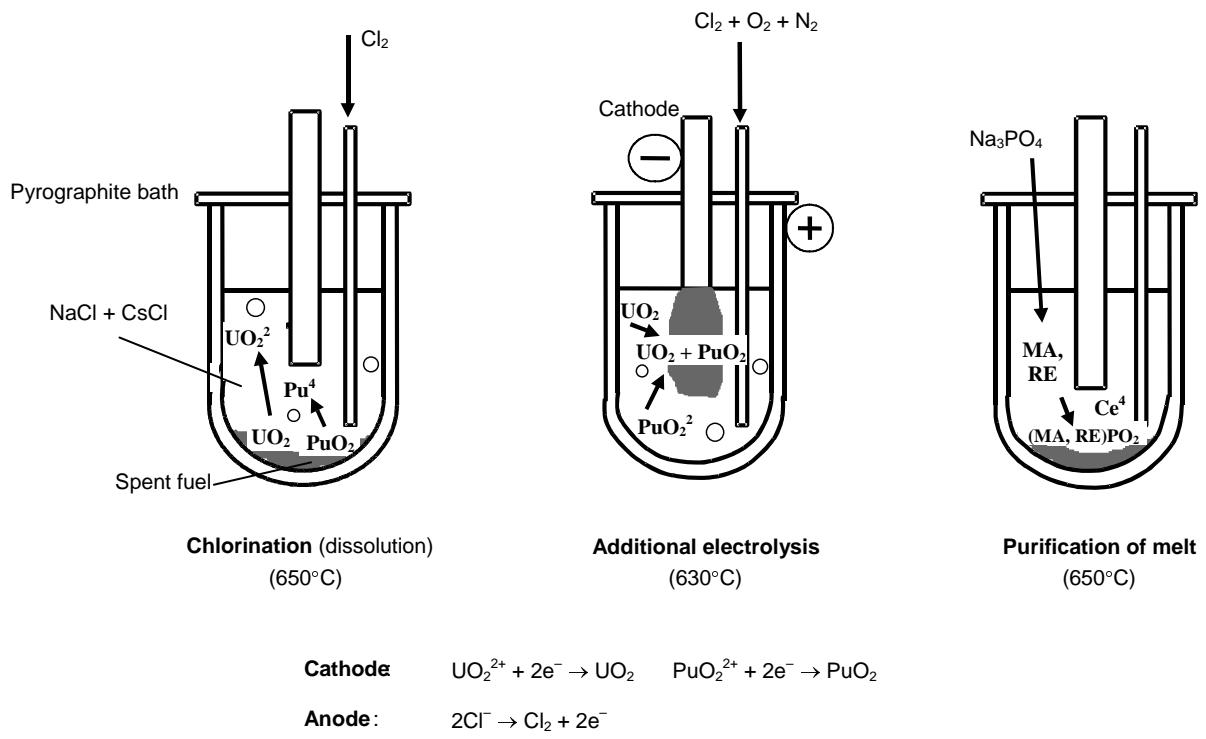
Three alternatives were considered and are now under development for reprocessing irradiated nuclear fuel in RIAR [33-36]:

- reprocessing uranium fuel with production of UO<sub>2</sub> for recycle;
- reprocessing MOX fuel for only plutonium recycle as the most valuable component (Figure 15);
- reprocessing MOX fuel with production of MOX fuel (Figure 16).

**Figure 15. Sequence of operation for pyroelectrochemical reprocessing of spent fuel in  $\text{UO}_2$  and  $\text{PuO}_2$**



**Figure 16. Sequence of operation for pyroelectrochemical reprocessing of spent fuel in MOX fuel**



The pyro-electrochemical process of PuO<sub>2</sub> extraction from core-irradiated nuclear fuel was developed to demonstrate a closed fuel cycle for the BOR-60 reactor. The thermal or mechanical de-cladding of fuel is considered a first stage of this technology. This sequence includes the following operations:

- Fuel chlorination in molten NaCl-KCl or LiCl-NaCl-KCl-CsCl. The complete dissolution of fuel components takes place.
- Electrolysis for removal of part of UO<sub>2</sub> free from Pu. There some fission products (Zr, Nb, Ru, Rh, Pd, Ag) are captured by cathodic deposit. The U/Pu separation factor at this stage is 120-140.
- Precipitative crystallisation of PuO<sub>2</sub> decontaminated from fission products that allows to obtain crystalline PuO<sub>2</sub> ready for vibropacking; 99.5-99.9% of Pu is collected in bottom PuO<sub>2</sub>.
- Additional electrolysis for removal of uranium. The main quantity of fission products is deposited simultaneously with UO<sub>2</sub> from melt.
- Molten salt purification from impurity. This operation is carried out by introducing sodium phosphate into the melt. As a result the formation and precipitation of impurity phosphates occur. These are insoluble both in molten chlorides and in water. Only Cs, Rb and, partially, Sr remain in the molten salt.

In 1991-92, the first test concerning reprocessing of irradiated MOX fuel was carried out. It took place at RIAR; the fuel was irradiated in the BN-350 fast reactor and subjected to thermal de-cladding. The reprocessing of fuel confirmed the comparability of laboratory and real tests. The experiment was carried out to verify predictions. Five hundred and twenty (520 g) grams of PuO<sub>2</sub> were obtained.

Decontamination factors are given in Table 2.

**Table 2. PuO<sub>2</sub>, UO<sub>2</sub> and MOX decontamination factors (DF) from main fission products**

Test/FP	Ru-Rh	Ce-Pr	Cs	Eu	Sb
DF for BN-350 test (PuO <sub>2</sub> , 1991)	50	220	> 3 000	40	200
DF for BOR-60 test (PuO <sub>2</sub> , 1995)	33	40 ÷ 50	4 000	40 ÷ 50	120
DF for BOR-60 test (UO <sub>2</sub> , 2000)	> 30	~	> 4 000	> 200	~
DF for BOR-60 test (MOX, 2001)	20 ÷ 30	25	~ 10 000	> 100	~

Two fuel assemblies of the BOR-60 reactor, having a burn-up of 21% and 24% heavy atoms, were chosen for the following experiment, for which the initial fuel was produced by pyrochemical methods before irradiation. The demonstration experiment was carried out in 1995 and studied:

- the material balance on U, Pu, minor actinides and some fission products;
- the influence of fuel reprocessing on radiation situation and environment;
- HLW composition and properties test of some for HLW treatment.

The most important result of the experiment was the high recovery rate of Pu – 95.6%. It is possible to reach higher recovery rates (over 99%) for cases of industrial organisation of MOX fuel reprocessing with extraction of PuO<sub>2</sub> when all recycled products will be returned to the “head-end” of the process. The decontamination of Pu is quite sufficient as concerns fuel nuclear physical properties (Table 2).

The study of the radiation conditions during the experiment showed that no appreciable “disturbance” in the normal work at RIAR had taken place. The PuO<sub>2</sub> produced (from both tests), as a mechanical mixture with pure UO<sub>2</sub>, was used to manufacture test fuel pins for irradiation in the BOR-60 reactor. The RIAR continues this line of research, one of the basic recent tests being the pyro-electrochemical reprocessing of irradiated UO<sub>2</sub> and MOX fuel of the BOR-60 reactors for production of UO<sub>2</sub> and MOX fuel for repeated irradiation (2000-2001). These tests included all technological aspects of fuel handling from storage to reprocessing in hot cells. In total, two UO<sub>2</sub> and four MOX irradiated fuel assemblies were removed from storage, unloaded from storage containers and de-clad by mechanical and voloxidation methods. The test resulted, for some batches of UO<sub>2</sub> and MOX fuel, in partial decontamination (Table 2), but their characteristics were close to fuel for vibropacking.

Recovered UO<sub>2</sub>, prepared by recycling, and one batch of MOX recovered fuel were used in the beginning of 2002 for production of a full-scale fuel assembly for the BOR-60 reactor. Data concerning this complex test will be published soon.

The wastes of all reprocessing tests were used to study both HLW solidification before disposal and HLW reprocessing (for extraction of Am and Cm) [37]. Two processes are currently being examined for phosphate and salt waste disposal and immobilisation:

- application of fluoride-phosphate glasses as joint matrixes for both salt and phosphate deposit;
- conversion of salts into NZP-type ceramics and pressing with phosphates.

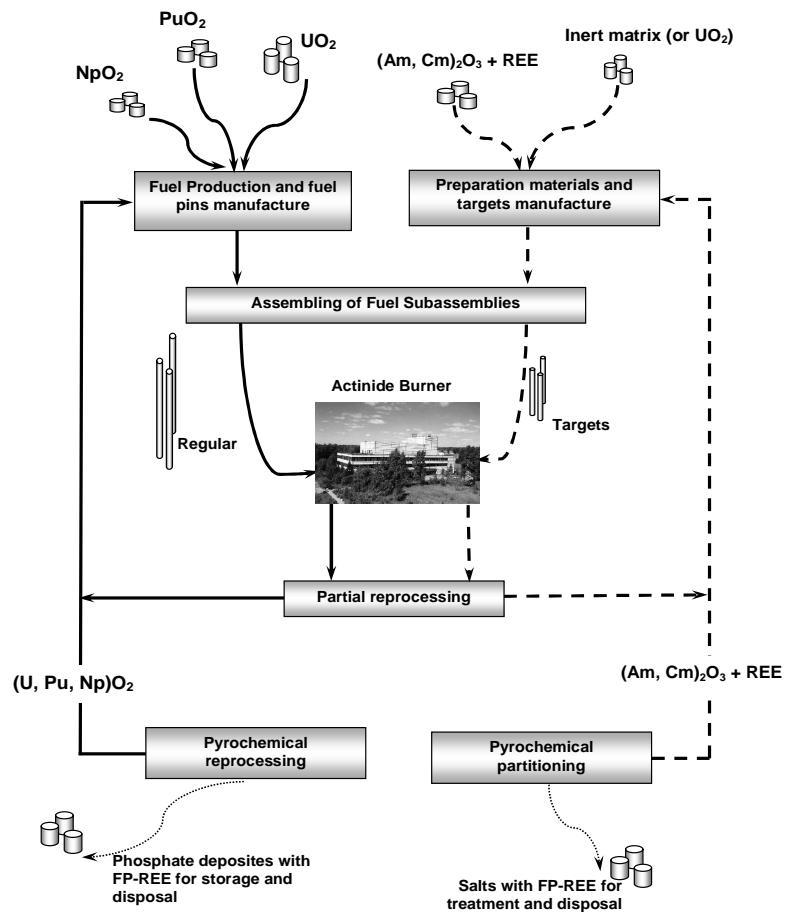
### ***The DOVITA programme***

Taking into account the advantages of pyrochemical technology and the vibropacking method, in 1992 RIAR began research under the DOVITA programme (Dry reprocessing, Oxide fuel, Vibropac, Integral, Transmutation of Actinides) [19,38,39] (Figure 17). It is a programme for the demonstration of minor-actinide burner reactors. The reprocessing of the irradiated fuel and targets is performed in two ways:

- pyro-electrochemical;
- non-complete vacuum thermal.

Vibropacking technology is applied to the manufacture of fuel pins. All products are reprocessed with the goal of having a complete recycle of Pu, Np, Am and Cm. A number of experiments on Np recycle were carried out. The study of electro-co-deposition of Np and Am with UO<sub>2</sub> from molten chlorides were fulfilled. Fuel with Np additives has already been irradiated in the BOR-60 reactor up to 20% heavy atom burn-up, and fuel with Am additives is prepared for irradiation. Studies in this domain are ongoing.

**Figure 17. DOVITA fuel cycle flow sheet**



### *Military plutonium disposition programme*

In accordance with the concept of Russian MinAtom on the utilisation of excess military plutonium, RIAR has begun to study the possibility of technological processing of metal military plutonium into MOX fuel. During 1998-2000, the first stage of this programme was fulfilled, and 50 kg of military-origin metallic plutonium was converted to MOX fuel for the BOR-60 and BN-600 reactors [22,40]. Plutonium conversion into MOX fuel is carried out with the technology described above. The flow sheet of pyrochemical conversion of metallic plutonium alloy into MOX fuel includes:

- dissolution of metal plutonium alloy and uranium oxide in molten salt  $\text{NaCl}-2\text{CsCl}$ ;
- electrolysis of molten salt with regulated co-deposition of  $\text{PuO}_2$  with  $\text{UO}_2$ ;
- treatment of cathodic deposit and reception of granulated fuel.

The MOX fuel produced is purified from alloy additives (Ga) and corresponds to the standard vibropacked fuel for fast reactors. A decrease of the gallium content in fuel up to 0.001% is attained. The manufacture of fuel pins for BOR-60 and BN-600 reactors are carried out using the standard procedure vibropacking method, which has been used at RIAR for over 20 years.

The resulting MOX fuel was used for the manufacture of 34 fuel assemblies for the BOR-60 reactor. These fuel assemblies have been successfully irradiated. The burn-up is 14.5% heavy atom (at the end of 2001). Three test fuel assemblies for the BN-600 reactor were manufactured using the MOX fuel, and the irradiation at the Beloyarsk NPP (BN-600) was finished in March 2002 with a burn-up of 11% heavy atom. Studies of military plutonium disposition include other work for which earlier-developed processes are applied. In the framework of Russian-French and Russian-American collaboration, the process of metal Pu conversion to  $\text{PuO}_2$  was also investigated.

### ***Feasibility studies for industrial application***

RIAR and design organisations in the USSR and Russia made some attempts to scale-up the Dimitrovgrad Dry Process (DDP) according to the following needs:

- In the 1980s, the evaluation for recycling plant serving two BN-800s showed a capital cost of 10% from two reactors.
- In the 1990s, more detailed evaluations were undertaken using drawings for a similar plant building and calculation of process cycles. This feasibility study showed a lower portion of the capital cost – about 7% from two BN-800s.
- In the 1990s, the feasibility comparison of various methods for military plutonium conversion to  $\text{PuO}_2$  was fulfilled. A pyrochemical method was found to be more economic and safe in comparison with aqueous methods (only one factor was negative: pyrochemical  $\text{PuO}_2$  powder was not adopted as standard technology for MOX fuel pellet production).
- All studies showed high economical and safety advantages for the pyro-electrochemical process.

Today the DDP is the only pyrochemical semi-industrial project in Russia. Fundamental and engineering studies actively continue.

### **High-temperature de-cladding**

Thermal de-cladding methods for the separation of fuel and clad materials have been the subject of investigation in the USSR. The best results were achieved employing the following methods:

- cladding material melting;
- gas-thermal embrittlement;
- cladding dissolution in molten metal or embrittlement in metal vapours.

A melting method was developed for the separation of steel cladding from FBR oxide fuel. This method was developed at VNIINM, KI, VNIIChT, etc. At RIAR, test experiments were carried out in one of the shielded cells of the FREGAT facility. The first type of apparatus was based on filtration principles. Good results were obtained from the hot tests [11,41].

During de-cladding of irradiated vibropacked oxide fuel pins ( $\text{UO}_2$  and MOX/ $\text{UO}_2$ -20%  $\text{PuO}_2$ ), the fuel recovery rate was  $99.8 \pm 0.2\%$  and  $99.7 + 0.2\%$ , respectively. The quantity of steel in  $\text{UO}_2$  after separation achieved 1.7%, and in MOX it was 3.2%. Total plutonium loss with the steel ingot amounted to 0.005%, and the loss with ceramic lining was 0.05%.

A less thermal de-cladding process was developed for oxide fuel pins. In the 1980s horizontal-type automatic apparatuses with end-tail heating of fuel assemblies were manufactured at SverdNIIKhimmash. The process was tested using full-scale BN-350 irradiated fuel assemblies. The mixture of fuel and steel droplets was subjected to voloxidation with further separation of  $U_3O_8$  by gas flow, and it resulted in a very high degree of component separation. In the experiments with MOX fuel, a satisfactory degree of separation was not achieved, as MOX fuel cannot be converted into the fine-crystal phase through oxidation. Improved models of the automated equipment were developed, but in the late 1980s this work was stopped.

When developing the concepts of the plant for BN-800 fuel reprocessing, RIAR considers this method as a basic one for preparation of the core fuel for reprocessing. For separation of zirconium claddings, gas-thermal de-cladding methods for LWR fuel were studied. The cladding hydrogenation method makes it possible to change zirconium properties, and then crush it, and to oxidise the fuel up to  $U_3O_8$ . The experiments demonstrated that the size of zirconium scraps was 2-30 mm, and  $U_3O_8$  particles were 1-10  $\mu\text{m}$  in size. Thus it is possible to separate zirconium and fuel (uranium content in the scraps is 0.02-0.05%).

The method of gas-thermal treatment of VVER fuel pin claddings using a  $N_2 + O_2$  mixture is very promising. The effect and possible flow sheet are very close to that of the cladding hydrogenation method. A method of high-temperature embrittlement of steel claddings in metal vapours (mostly in zinc) was studied with regard to its application to ceramic fuel. RIAR tested the equipment and method of stainless steel cladding removal from fuel pins irradiated in the BOR-60 reactor up to a burn-up of 11%. A method of complete dissolution of steel cladding in zinc was also subjected to laboratory testing. High-temperature de-cladding methods are regarded in Russia as a stage of fuel preparation for reprocessing by non-aqueous methods of any type.

### **Molten salt/liquid metal systems**

Molten salt/liquid metal systems are unique for the realisation of pyro-electrochemical processes. These methods were intensively developed in the USSR in the 1960s and 1970s although they were more suitable for metal fuel and therefore remained at the level of fundamental studies. Thorough investigations on electrochemistry and thermochemistry of alloys of low-melted non-ferrous metals, lanthanides and actinides were carried out. These theoretical studies were continued at UPI (Ekaterinburg) [42,43].

Parts of the experiments were performed by other organisations. In particular, the RRC Kurchatov Institute and the VNIINM experimentally studied reductive extraction of actinide and lanthanide fluorides in Li,Be/F and Li,Na,K/F systems [44]. The necessary database was established. From the methodological and hardware points of view this work could be elevated to the level of engineering experiments in a short time. It should be noted that fuel refining and reprocessing in systems using molten chlorides and fluorides, and liquid metals (Bi, Zn, Cd, Pb, Sn, etc.) is one of the most promising methods for the resolution of the problem of actinide and fission product partitioning. These approaches are considered as the basic ones for reprocessing of metal, nitride and molten salt fuels. A series of works related to the study of non-stationary processes at liquid electrodes during electrolysis could be distinguished from the developments that can make a significant contribution to a new stage of this fuel reprocessing methods development. The methods developed in UPI and IHTE make it possible to influence the surface layer of molten metal only by electrochemical methods produced at the non-stationary and even non-equipotential surface. Such approaches can exclude the mechanical effect on the liquid electrode, and this fact is of importance in designing the remote equipment.

## **Study of fluoride and oxide molten salts**

The method of fluorine-oxygen exchange in molten fluorides was studied at VNIINM [45,46]. This idea was initially discussed within the framework of a series of Soviet-French seminars in 1976-1981 as applied to fast reactor fuel processing development. The basic operation of the process is gas fluorination of the fuel, leading to volatilisation of uranium in the form of  $\text{UF}_6$ , followed by sorption purification of uranium hexafluoride. The solid residue of fluorination and the sorbent ( $\text{NaF}$ ), containing the main amount of actinides, are then processed by means of selective deposition of actinide oxides from a fluoride melt – the lithium and sodium fluorides eutectics. All experiments were performed at 800°C.

The solid residues of fluorination and spent sorbents have rather complex chemical composition. Besides actinides, they contain practically all of the fission products, forming non-volatile fluorides, such as alkaline, earth-alkaline, rare-earth elements, as well as fluorides of noble and semi-noble metals (from zirconium to platinum metals) and, eventually, the process equipment corrosion products (iron, nickel). The precipitation of the investigated metal oxides from the salt melts can be presented as the sequence: U, Zr, Th,  $\text{Pu}^{(+4)}$ , Be, Al, REE.

In this sequence, preceding elements are precipitated by oxides of succeeding ones, and this is the main factor of fractionating components of nuclear fuel, while its reprocessing in fluoride melts “semi-noble” metals (such as iron and nickel), as well as zirconium, co-precipitate in the form of oxides with actinide oxides. Evidently, they should be removed from salt melts prior to starting the process of fluorine-oxygen exchange. This could be done by means of element reduction and recovery in the form of metals, as implicated by the electromotive series in the molten fluorides solvent system.

The processes in molten fluorides were also studied at RIAR with regard to conversion of actinide oxide powders into metal form for metal fuel production. The study of sulphate application was carried out at IHTE [47]. Reprocessing in molten sulphates is carried out under working temperatures of 450-650°C. Dissolution occurs during fuel reprocessing in media of molten sulphates (for example,  $\text{Na}_2\text{SO}_4-\text{K}_2\text{SO}_4$ ) by gaseous sulphur oxides or vapour of sulphuric acid. Complex oxy-ions of uranium are formed. Electrolysis of such molten salt allows the extraction of uranium oxides  $\text{U}_4\text{O}_9$  ( $\text{U}_3\text{O}_8$ ). Plutonium oxide is removed from melt through temperature increase and decomposition of its sulphate. As a whole, the method does not have great advantages. Problems are related to high aggressive media and there are no obvious advantages in comparison with chloride salts. However, it has some prospect connected with reprocessing of fuel with a graphite matrix (for example, HTR), as molten sulphates are a very convenient media for burning carbon materials.

Studies of molten alkali nitrates for oxide irradiated nuclear fuel reprocessing were carried out at the Khlopin Institute. Oxidation-reduction reprocessing in molten alkali nitrates could be carried out at rather low temperatures (300-450°C) and is based on the fact that uranium oxides are dissolved.  $\text{PuO}_2$  does not dissolve in molten alkali nitrates, but rather is separated into components. Solid salt, containing uranates, could easily be dissolved in water for future reprocessing. Molten salt can be subjected to electrochemical decomposition to obtain  $\text{U}_3\text{O}_8$ . Interesting studies were carried out at the Bochvar Institute and IHTE related to the application of molybdate and tungstate salts for fuel reprocessing and production [48,49]. Reprocessing in molten molybdates is carried out at temperatures ranging from 800-1 200°C and is based on a “dissolution/precipitation” process with a change in the acidity of the melt. There the complex ions can form and actinide oxides can be removed through electrolysis.

Molten tungstates have lower working temperatures, 700-900°C. The following cycle is the most convenient:

- oxide U<sub>3</sub>O<sub>8</sub> dissolution into Na<sub>2</sub>[UO<sub>2</sub>(WO<sub>4</sub>)<sub>2</sub>] type compounds;
- electrolysis with production of UO<sub>2</sub>.

The method is interesting because it is carried out in a special atmosphere. Studies for production of crystalline PuO<sub>2</sub> through precipitation, electrochemical deposition of uranium and MOX fuel were carried out. This method is not currently targeted for future development, but has some advantages due to the low corrosion activity of salt.

Some other molten salt systems were under investigation for application to nuclear cycle problems, such as molten alkalis, mixed molten phosphates and chlorides, molten borates and phosphates.

### **Partial reprocessing and other applications**

Some other high-temperature methods can be applied for the treatment of fuel and HLW. They are illustrated by the following examples [39]:

- Partial reprocessing of irradiated oxide fuel for vibropac recycling. After de-cladding fuel is crushed, heated in a vacuum [for removal of volatile (Cs, Te, Sb) and gaseous fission products] and vibropacked into new clad with additions of fissile materials. This method was tested at RIAR. A similar approach could be applied for the recycling of targets for transmutation.
- Partial reprocessing of fuel, when it is transferred only in the intermediate form for storage. As an example, metallisation of LWR irradiated nuclear fuel, tested at RIAR in co-operation with KAERI.

Other relevant usage of pyrometallurgical methods is the application in recycling and refining of valuable materials of atomic engineering. The following three examples are worth mention [50]:

- In Russia and Ukraine research on zirconium recovery from scraps after VVER irradiated nuclear fuel reprocessing is under way with application of refining procedures in molten salts and sublimation of halogenides.
- Over an eight-year period, RIAR carried out the experimental reprocessing of enriched boron carbide from control rods of BOR-60 and BN-600 fast reactors. This is based on the volatility of boron chloride at chlorination of carbide and allows high purification from radioactive impurities. Re-fabricated control rods are already exploited in the BOR-60/BN-600 reactors.
- In the 1990s, RIAR developed the processes of <sup>99</sup>Mo isotope extraction from targets of molten salts for improved radiation safety. The Kurchatov Institute studies the capability of producing <sup>99</sup>Mo through irradiation of molten salt in a special loop.

### **Current programmes related to the pyrochemical process**

Non-aqueous methods are esteemed in different tasks at MinAtom (Russian Federation) and, as a rule, have a targeted nature. When programming a MinAtom conference on the fuel cycle, the following was stated [20]:

*Pyrochemical methods, as a rule, are convenient for the solution of concrete problems and could be hardly developed up to the universal application. Now it is necessary to consider four prospective directions of fuel reprocessing:*

- *combined pyrochemical and aqueous reprocessing method consisting of developed processes of dry reprocessing, aqueous method of uranyl-nitrate crystallisation and extraction recovery of plutonium;*
- *pyro-electrochemical reprocessing of MOX fuel tested at semi-industrial level on fresh fuel and checked on irradiated fuel;*
- *fluoride volatility reprocessing permitting to organise uranium recycling and its enrichment;*
- *pyro-electrochemical reprocessing of mixed nitride fuel of fast reactors in molten salts, both chlorides and fluorides (in frame of near-reactor reprocessing plant of the BREST reactor).*

*The main criterion for application of different techniques or their combinations should be their economic efficiency or benefit. Therefore, it is necessary to perform R&D work, including integrated testing of the technique and equipment at the pilot-industrial facilities, analysis of the real products, and compare the results obtained from the standpoint of their feasibility.*

Presently, the following programmes connected to non-aqueous processes are underway.

### ***RIAR programmes***

- *Military plutonium disposition by pyro-electrochemical technology.* SSC RIAR's plans for the most recent year of development of this method of military plutonium conversion into MOX fuel applying pyrochemical and vibropacking technologies is as follows:
  - production and irradiation of 21 MOX fuel assemblies for BN-600 reactor;
  - modernisation of facilities for production of granulated MOX fuel, fuel pins and fuel assemblies for the BN-600 reactor, planned annual capacity being 50 fuel assemblies (up to 1 500 kg of MOX fuel and conversion of 300 kg of military origin plutonium);
  - continuation of tests for production of powered PuO<sub>2</sub> for MOX pellet production;
  - study of methods for immobilisation of wastes after Pu conversion.

These activities continue with the strong support of JNC (Japan) and in the framework of the USA-Russia Agreement. One advantage of pyro-electrochemical conversion of military plutonium into MOX is avoiding the need for a special facility for conversion of Pu to PuO<sub>2</sub> before MOX fuel production. The developed technology can be applied for systematic utilisation of plutonium in the Russian fast reactors (BOR-60 and BN-600).

- *Development of pyroelectrochemical method.* The development of fuel reprocessing methods is carried out in the following areas:
  - improvements of processes duration;
  - optimisations of the equipment and processes, including process materials improvement;
  - stabilisation of recovered fuel quality;
  - demonstration tests on cycle as a whole.

Creation of a facility to recycle BOR-60 reactor fuel could become the best option for engineering-scale testing of the process. However, to date there are no confirmed funds for implementation of such a programme.

- *DOVITA programme.* Application of pyro-processes in fuel cycle with transmutation of minor actinides; the programme is continued with support of MinAtom (recycle programme) and foreign partners.
- *Reprocessing of irradiated fuel from research reactors.* This programme is directed towards the utilisation of enriched uranium from irradiated nuclear fuel from research reactors. As a rule, the fuel is considered as being not suitable for aqueous-extraction reprocessing in the RT-1 plant. These investigations are carried out with the purpose of returning the HEU into nuclear power engineering. In particular, the U-Mo fuel from pulse reactors is refined. The methods for processes of metal-ceramic fuel reprocessing are studied. This programme is partially connected with the programme of Material Consolidation and Conversion (MCC) supported by USDOE for HEU consolidation and conversion. RIAR uses dry methods to decrease uranium enrichment.
- *Closed fuel cycle for the new generation of fast reactors (BREST and BN).* The initial round of R&D to support the development of U-Pu-MA fuel reprocessing methods for the new generation of fast reactors, including transmutation of minor actinides, was carried out in 1999-2001 [21,51]. At the initial stage, the researchers explored the feasibility of meeting the above requirements using the following procedures:
  - upgraded PUREX process (VNIINM);
  - electrolysis of molten chlorides with reduction of actinides to metals or to nitrides – LINEX process (VNIINM, RIAR);
  - metallurgical process, with nitrides kept intact at all stages of reprocessing (VNIINM and collaborators);
  - pyrochemistry (ion exchange reactions) in molten fluorides and chlorides (Bochvar Institute, RRC-Kurchatov Institute, IHTE);
  - dry fluoride volatility process (VNIICHT, RRC-Kurchatov Institute);
  - re-crystallisation in molten molybdates and phosphates (VNIINM), etc.

Basic flow sheets have been prepared and equipment components have been identified. Laboratory experiments have been conducted to validate the key features of the process design. The capital and operational costs have been estimated and the feasibility of technological options has been assessed. The procedure examined has shown no fundamental difficulties for commercialisation with a production rate of 25-50 t of irradiated fuel per year; and the main requirements (see above) can be met under nominal conditions of the process. It is also possible to fulfil the radwaste partitioning requirements by combining various methods. According to economic estimations, the cost of a plant for fuel reprocessing and re-fabrication will be no more than 15% of the cost of the NPP with two BREST-1200 units ( $2 \times 1\ 200$  MWe) to be serviced by this reprocessing plant. Studies are in progress on non-aqueous methods, including ion-exchange reactions and electrolysis processes. Work on dry volatility process and advanced PUREX processes have been suspended due to its relatively easy transformation for plutonium extraction.

- *Feasibility study of dry methods application for the RT-2 reprocessing plant.* Engineering feasibility studies of different schemes of LWR fuel reprocessing are continued for a plant with a capacity of 1 500 tonnes (heavy metal) annually. The first phase of the feasibility study was completed. It was committed to compare a “classic” PUREX process with partitioning with a combined scheme including: fluoride volatility separation of uranium, aqueous partitioning of plutonium, and pyrochemical manufacturing of vibro-MOX-fuel. The first results have shown that the dry methods improve the economical performance indices of the plant. The studies are being continued. Five new schemes are taken into consideration, including: advanced aqueous method, combined methods and “dry” methods.

### Molten salt reactor concept

In Russia, the molten salt reactor (MSR) programme was started in the second half of the 1970s [3]. RRC-KI was the basic organisation under whose supervision a collaboration of specialised institutions was formed and functioned. In 1970s the objectives of the Russian MSR programme were as follows:

- identify potential advantages and intrinsic pitfalls of MSR concepts;
- search for a means of providing maximum advantages and minimum vulnerability;
- explore the feasibility of technical implementation of main MSR design features.

At that time, the main effort in the Russian programmes was focused on the development of the U/Th breeder and converter reactor concepts. As a result, the suggested key technical solutions had been optimised for application to this goal. Within the Russian programme, an MSR study was organised on the following issues:

- exploration of possible use and niches for MSR concepts;
- reactor physics;
- thermal-hydraulics and safety;
- containment materials for fuel and coolant salts;

- molten salt transport properties;
- fuel radiation stability;
- heat transfer and hydraulics of fuel and coolant;
- handling and circulation of fuel and coolant salts;
- process and radiochemical bench tests of model installations.

The first two issues constituted theoretical studies, and the rest were experimental ones. Several of the fluorides salts satisfy the characteristic properties of the thermal stability, radiation resistance, low vapour pressure and manageable melting point. To achieve lower melting temperatures, two or more salts are combined to produce still lower melting mixtures. Li,Be/F, Li,Na,K/F, Li,Na/F, Na,Be/F, NaF-NaBF<sub>4</sub>, Li,Be,U/F and Li,Be,Th,U/F fuel mixtures were used in these studies.

The design of the MSR core requires detailed information on heat and mass transport properties of the proposed fuel and coolant fluoride melts. The specific physical properties which were measured within the Russian MSR programme include phase diagrams behaviour, density, heat capacity, heat of fusion, viscosity, thermal conductivity and electrical conductivity. Particular emphasis has been placed on U/Th fuels. An important part of Russian MSR programme dealt with the investigation of the container materials. The development of domestic structural material for MSR was substantiated by available experience accumulated through the ORNL MSR programme on nickel-based alloys for UF<sub>4</sub>-containing salts. The results of the combined investigation of mechanical, corrosion and radiation properties of various Hastelloy N-type alloys permitted to suggest the Ti and Al-modified alloy named HN80MTY as an optimum container material for the MSR.

A number of pyrochemical processes (fluorination, reductive extraction and precipitation by oxidation) for removing the actinides and soluble fission products from the fluoride-based salt have been explored at RRC-Kurchatov Institute and VNIINM within the Russian MSR programme. Studies of the MSR fuel salt chemical processing system are not as far advanced, but small-scale experiments lead to a certain optimism that a practicable system can be developed.

Certainly, the R&D on materials for the fission product clean-up unit for MSR is at a very early stage. A layer of frozen salt will probably serve to protect surfaces that are worked under oxidising conditions, if the layer can be maintained in the complex equipment. Preliminary tests at molten salt loops showed that the thickness of the frozen film on the wall was predictable and adhered to the wall. The only materials that are truly resistant to bismuth and molten salts are refractory metals (W, Mo, Ta) and graphite (e.g. graphite with isotropic pyrolytic coating tested for both working fluids), neither of which is attractive for fabricating a large and complicated system. Development work to determine if iron-based alloys can be protected with refractory metal coatings should probably be considered with higher priority.

The above-mentioned activities decreased after 1986 due to the Chernobyl accident and the general stagnation of the nuclear power industry. Toward the end of 80s, however, there was an increase in conceptual studies as a result of the interest in inherently safe reactors of a new generation. An extensive review of MSR technology developments at RRC-KI through 1989 is given in a book [3]. Currently, interest in MSR technology is reviving, especially as applied to the back-end of the fuel cycle, including the management of plutonium, minor actinides and long-lived fission products.

A proposal from the RRC-Kurchatov Institute on the implementation of an innovative nuclear fuel cycle including the MSR, was considered and approved by MinAtom in 1998. The following tasks were outlined within the framework of the new programme:

- assessment of different versions of the MSR compatible to fuel cycle concept development, taking into account current state of technology and future requirements of the nuclear power;
- elaboration of an optimal scenario for the safe, sustainable, economic, low waste and proliferation-resistant development of nuclear power, including MSR;
- conceptual studies on prospective critical and sub-critical MSRs, fuelled by variable fuel compositions, including high contents of Pu and minor actinides for uranium-free matrix as well as U/Th fuel matrix.

At present work is being carried out aimed at the optimisation of the suggested process flow sheet within the framework of a collaboration between the RRC-Kurchatov Institute, VNIITF, IPPE, Hydropress, VNIINM, Radium Institute, RIAR, VNIPRIET and other institutions [52-54].

Current experimental work on molten salt technology development at the RRC-Kurchatov Institute under contract with MinAtom, particularly, includes the following areas:

- experimental studies on pyrochemical fuel treatment (electro-deposition and reductive extraction);
- AnF<sub>3</sub>-fuelled molten salt irradiation (“Ampula” test);

Finally, studies on integral evaluation of MSR technology potential as applied to commercial long-lived actinide transmutation are underway within ISTC #1606, entitled “Experimental study of molten salt technology for safe, low waste and proliferation-resistant treatment of plutonium and minor actinides in accelerator-driven and critical systems”. Project #1606 has a three-year duration, from February 2001 to February 2004. This project is carried out in close co-operation with the EC MOST project that is focused on analysing the potential of MSR technology to service future nuclear power development. The current stage of #1606 is devoted to the examination, mainly experimental, of the potential of the Molten Salt Advanced Reactor Transmuter (MOSART) for TRU in a Th-U free FLiBe based stream.

The major developments expected as result of Project #1606 are the following: reactor physics and fuel cycle considerations, experimental study of fuel salt key physical and chemical properties and corrosion studies in natural convection loop. The first experimental data have already been obtained for the selected Na,Li,Be/F salt system, including system phase behaviour, solubility of plutonium trifluorides/oxides, transport properties (density, thermal conductivity, viscosity and heat capacity). Experimental studies on An/Ln standard potentials measurements and RE recovery by electro-deposition, oxide precipitation and reductive extraction as applied to MOSART are currently under way.

The construction and study of a corrosion loop made from Ni-based alloy and Redox control in a Na,Li,Be/F system fuelled by PuF<sub>3</sub> is already finalised. Corrosion studies will involve three types of container material samples: RF HN80MTY, US Hastelloy NM and, as an additional effort, Czech MONICR. The last material sample was provided in the framework of the EC MOST and ISTC#1606 co-operation. The facility permits to perform tests on candidate structural materials for MOSART with a minimal temperature of circulated fuel salt up to 550-600°C, temperature salt heat up 80-100°C and a salt flow rate of up to 5 cm/s (Re > 3 000).

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## **SPAIN**

### **Introduction**

R&D activities in Spain on high-level waste (HLW) and irradiated nuclear fuel are defined by the 5<sup>th</sup> Research and Development Plan for Radioactive Waste Management (1999-2003) approved by the Spanish government in July 1999. Until 2010, R&D activities will be focused mainly on two areas: direct disposal of irradiated fuel and partitioning and transmutation (P&T) of long-lived radionuclides, in order to provide a sufficient database to support a decision in the future by government. Therefore, no definition of the selected option for the final HLW and irradiated nuclear fuel management will be taken before 2010.

Within the partitioning and transmutation activities, CIEMAT, the National Research Laboratory for Energy and Environment, is leading pyrochemical separation studies. Research is performed in collaboration with the University of Valladolid (UVA), which has a group specialised in molten salt technology. ENRESA, the National Waste Management Agency, is promoting and financing several lines of research on P&T, one of them being pyrochemical partitioning.

The strategy to be followed in all partitioning and transmutation activities has two main axes:

- to evaluate the viability of this technology in the framework of international collaboration by participating in studies promoted by international organisations (IAEA, OECD/NEA, EU, etc.);
- to create a Spanish infrastructure with groups of researchers and experts in various areas.

### **International collaboration**

Bilateral agreements have been established between CEA and CIEMAT and between ITU (JRC) and ENRESA/CIEMAT for international collaboration on pyrochemical partitioning. Furthermore, CIEMAT, together with UVA, participates in the 5<sup>th</sup> Framework Programme for the Technological Research and Development of the European Union, through the PYROREP project, in which five other European research organisations are partners.

### **Spanish infrastructure**

In this context, studies on the application of pyrochemical processes involving high-temperature separation of long-lived radionuclides in molten salt media began in 1998. For the near term (1998-2003), the research programme has settled on the investigation of chloride salt media. An *ad hoc* laboratory was constructed where alpha, beta and gamma emitters at trace levels are studied; operation began in 2003.

### **Programme**

The Spanish project involves the following stages:

- *1998-1999.* Several pyrochemical separation concepts developed and tested in other countries were reviewed to aid the definition of immediate future activities (media, technological requirements, etc.)
- *1999-2001.* CIEMAT facilities were adapted to molten salt technological requirements for performing laboratory-scale experiments with inactive and active materials (glove box with atmosphere control, electrochemical cells, etc.).

- 2001-2003. Basic data acquisition on the elementary chemical processes involved in several pyrochemical concepts (conversion to halide form, salt-metal extraction and electrochemical techniques for radionuclides separation, salt decontamination, etc.)
- 2003-2006. Definition of the selected concepts and proposal of applied research at laboratory scale with small quantities of radioactive materials (promising fuels compositions and expected waste generation will be taken into account). Waste stream treatment will be one of the main research items in this period; mainly, the studies will focus on an evaluation of the chemical treatment of chloride salt waste versus direct immobilisation.

## **Media and materials**

Many types of fuels and targets have been considered in recent years depending on the scenarios considered for the transmutation of long-lived radionuclides. Presently, materials being considered are simulated oxide-type fuels, uranium in oxide form, ThO<sub>2</sub> and an analogue of the calcinate of high-level liquid waste obtained from the PUREX process. Studies are focused on chloride media, i.e. LiCl-KCl and CaCl<sub>2</sub>-NaCl systems (working temperatures 450 and 550°C respectively), but without excluding studies of other salts.

## **Research activities (2000-2003)**

### ***Fuel conversion to halide form***

Dissolution of the elements of interest in the chloride salt medium is a necessary preliminary step for establishing various separation processes. Chlorinating agents such as HCl(g) and Cl<sub>2</sub>(g) are being investigated. The construction of generalised Pourbaix-type diagrams (E-pO<sup>2-</sup> diagrams) for chlorinating mixtures and comparison with E-pO<sup>2-</sup> diagrams of elements contained in the simulated fuel provide valuable parameters for the separation step. Specific tools, such as yttria-stabilised zirconia membrane electrodes (ysze), are used for the experimental determination of the stability of oxide and oxychloride species. Dissolution tests of oxides and oxychlorides show the effectiveness of the chlorinating agent considered.

### ***Electrochemical separation processes***

The objective of this activity is to provide separation factors of the elements of interest. Activities focus on the study of the electrochemical behaviour of uranium, lanthanides and other minor elements contained in simulated fuel. Solid and liquid metal cathodes are examined in the studies. Electrochemical techniques are used to determine thermodynamic and kinetic basic parameters including:

- standard potential;
- activity coefficient,  $\gamma(MCl_3)$ , of lanthanide chlorides;
- determination of the stable oxidation states of lanthanides;
- free energy, enthalpy and entropy of formation.

Electronic mechanisms are needed to provide metal electro-deposition conditions. Parameters such as diffusion coefficients and activation energies for diffusion are being studied.

### ***Separation by salt-metal extraction***

Actinide-lanthanide separation by extraction is based on the differences in the thermodynamic stability of their compounds or complexes and on changes in their oxidation states. It is studied by considering U, Ce and La as a first approach. The process is being studied in chloride media by reduction into a metallic cadmium phase (without excluding later examination of other metals or alloys). Studies will continue with simulated fuel to assess the feasibility of salt-metal extraction with inactive materials through measurement of the recovery yields.

### ***Salt de-contamination***

This stage is studied with the aim of recycling salt to reduce waste generation. The presence of various radionuclides in the molten salt after the separation step provides an undesirable radioactive content and volume increase, which may modify the physical and chemical properties and hinder salt recycling within the separation process. Chemical treatment of salt waste is considered in the Spanish research programme as a promising method to minimise fission product concentrations. The work plan includes electrochemical techniques based on thermodynamics.

### ***Materials selection***

Materials corrosion, even if so-called inert materials are considered, is expected to be a limiting factor as a result of combining halides and liquid metals, high temperatures and corrosive gases. Material characterisation after test termination will be performed in order to obtain a preliminary selection of resistant materials.

### **Future activities**

Pyrochemical reprocessing is an integral part of the strategic activities of CIEMAT and ENRESA on partitioning and transmutation, which began in 1998 and for which a minimum infrastructure has been put into place. Spain does not intend to be in the lead as may do other countries that have more substantial nuclear programmes. Nevertheless, this first step demonstrates the interest of the Spanish government in studying the back-end of the fuel cycle with new technologies. Spain intends to evaluate the influence of partitioning and transmutation in the definitive management of irradiated fuel and HLW and also to seek the best way to implement the preferred solutions. For these reasons, future research and development programmes on waste management must maintain, if not increase, research on this type of partitioning.

## **UNITED KINGDOM**

### **Introduction**

The UK pyrochemical programme is led by British Nuclear Fuels Ltd. (BNFL). The BNFL molten salt project operates within the company's commercial environment and is subject to its innovation management process. As such, the project is business-funded with assessment of potential value and risk at each stage of development. BNFL believes that the greatest challenge facing pyrochemical technology, along with the understanding of underpinning science, is the transformation into a commercially viable industrial-scale process against a given need. The BNFL programme [1] is geared towards understanding

process possibilities against commercial fuel management needs and examining the technical factors which impact on industrialisation and commercial viability. The project includes complete schemes of fuel treatment, from the head-end through a separation process to the immobilisation of salt wastes, and in depth from basic chemistry and materials science to engineering design studies.

### **The history of pyrochemical work in BNFL**

BNFL has a significant history of pyrochemical technology. A research programme was undertaken at the Springfields laboratory in the UK between 1963 and 1969 to investigate the production of uranium metal by electro-winning in high-temperature molten salt systems. The intention was to use the process for the production of Magnox fuel. At the close of the project, a 660 mm width cell had operated for several days with a mean output of 1 kg U/hour and current efficiencies of ~60%.

Pyrochemical technology is employed in the manufacture of Magnox (uranium metal) fuel on a scale of hundreds of tonnes per year at the Springfields plant. Uranium tetrafluoride is reduced with magnesium metal in a thermite-type reaction initiated at 650°C and reaching 1 500°C at its maximum. Uranium fuel rods are cast from liquid metal. In the 1990s, BNFL's advanced reprocessing programme examined a number of technologies for future fuel treatment and recycle applications. The molten salt project developed a capability within the company and established many links internationally as well. Small-scale experimental programmes were established with a number of assessments and pre-conceptual design studies. Molten salt technology was assessed initially as part of a fluoride volatility programme. Work, much of it now in the open literature, was performed on the dissolution of uranium dioxide in carbonate melts. Laboratory-scale studies of graphite corrosion by aggressive metal melts were also carried out. In 1997, it was decided that BNFL undertake work on the treatment and immobilisation of molten salt wastes. Practical laboratory work explored options for removing inactive fission product simulants from salt and their immobilisation in a durable waste form.

Again in 1997, Magnox Electric, which in 1998 was merged with BNFL, posted an assignee to the Argonne National Laboratory, USA. This assignment resulted in a study of the technology for application to BNFL's Magnox fuels. BNFL's Nuclear Sciences and Technology Services business unit has a team dedicated to the support of its existing vitrification facilities, and towards the development of future immobilised waste forms. Members of this team were involved in the molten salts development programme. BNFL has also developed powder-handling technologies including mills and classifiers for application in active glove-box environments. It is believed that this technology will be transferable to treatment steps within pyrochemical processes. In 1999, the molten salts project passed through BNFL's innovation process, and as a result has become structured on risk management and targeted towards the resolution of parameters key to the successful final application of the technology (potential showstoppers). The project has a broad remit, looking at all of the major aspects of the technology, engineering and industrialisation of the process, environmental and safety implications.

### **Current programme**

In October 2001, a new larger BNFL molten salts project was defined with a seven-year time frame. This has around twenty science and engineering staff in-house undertaking test and design studies. The alpha electrorefining experiments at AEA Technology (AEA-T) at Harwell, which involved participation in the European Commission 5<sup>th</sup> Framework (FP5) PYROREP programme, are now complete. Pyrochemical test work has commenced at bench-scale in the new BNFL Technology Centre (BTC) at Sellafield, which is progressively coming into operation (2002-2005). The facilities of BTC include radioactive laboratories, modular highly radioactive cells, alpha radioactive gloveboxes, U active

rig hall and non-radioactive large-scale plant. The BNFL pyrochemical programme is subject to review points at 2-3 year intervals. The first review was completed successfully in 2003 and the programme is continuing as described below. BNFL participates in the 6<sup>th</sup> Framework Programme (2002-2006), which is the EU's Framework Programme (FP6) for Research and Technological Development and a major tool to support the creation of the European Research Area (ERA). Pyrochemical separation studies are under way in various universities.

The aims of the current BNFL pyrochemical separation programme include:

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

The main technical parts of the BNFL Molten Salt Project are:

- laboratory-scale U and U-Pu-Am-Nd-Ce electrorefining (EU 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-salt dynamics rig;
- BTC alpha active laboratory-scale electrorefiner;
- other BTC rigs and laboratory tests – salt purification, direct electrochemical reduction of oxides, inactive electrorefiner visualisation, etc.;
- international collaborative studies;
- university studies.

### **The BNFL alpha active electrorefiner programme**

A major part of the BNFL molten salt programme in the period 2000-2003 has been the design, construction and testing of a 1 litre 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. A small part of the funding has been provided by a collaborative European P&T research proposal under the EU 5<sup>th</sup> Framework. Electrotransport to solid and liquid cathodes has been used together with selective reductive extraction, using Cd-Li, etc., and molten salts. Determinations of distribution coefficients between different salt and metal phases have been 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 concentration (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).

Test work used molten lithium-potassium eutectic chloride salt and liquid cadmium at 450-550°C under pure argon gas and performed within a dedicated alpha active glove box system in Harwell H220. The maximum inventory of Pu was 50 g. Modification of an existing alpha glove box to include two heated wells was implemented. Test equipment was designed and fabricated. The electrorefiner fits in one well and is a heated tank with ports that contain molten salt. It has means of inserting and withdrawing simulated fuel, U, etc., rotating electrodes, stirring salt, supplying low voltage at high current to electrodes, material addition, sampling and cover gas control. The second well is used for molten salt extraction experiments with reductive metal alloys as well as chemical preparation, analysis and other purposes. Equipment installation began in June 2000 [2]. Progress with the programme has been reported during the past several years [3].

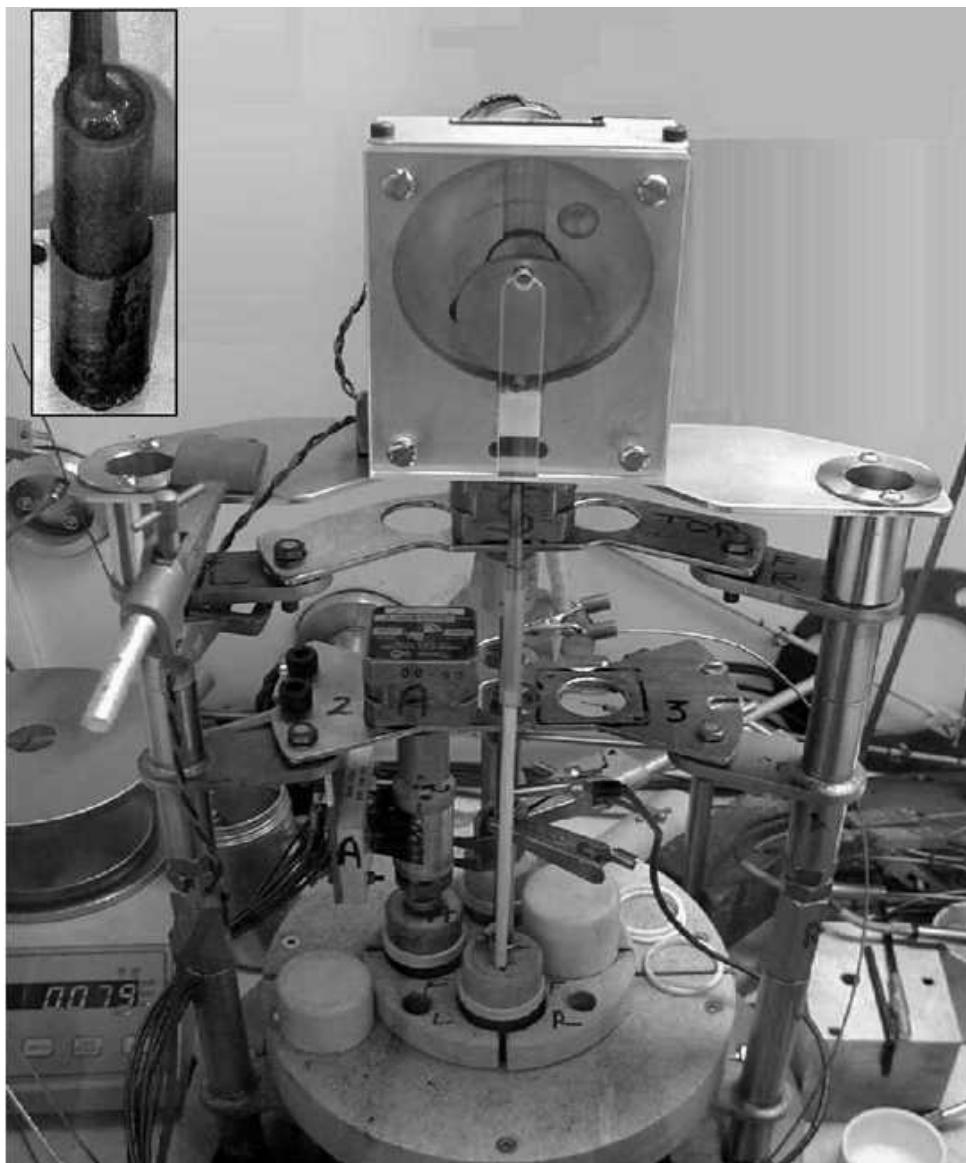
The following results have been obtained [4]:

- Good separation of uranium from other solutes by electrolytic deposition at a solid cathode (electrorefining) was achieved with typical “effective” separation factors of > 1 000 and > 500 for Pu and rare-earth elements, respectively.
- Electrorecovery of Pu-U-Am was achieved using liquid cadmium cathodes (LCC) operated with a low frequency plunger.
- 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
- The 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 affected but was not straightforward because of current limitations and chemical reaction between Li-Cd and U-TRU in the salt.
- Gamma spectroscopy was used for measurement of Pu, Am and Ce (tracer). Inductively coupled plasma – optical emission spectroscopy (ICP-OES) was used for Cd, U and other species.  $^{144}\text{Ce}$  was useful as a tracer for RE and  $^{137}\text{Cs}$  is recommended for future LiCl-KCl salt measurement.
- A simple numerical model was developed to simulate the salt/Cd interfacial concentrations in the LCC and accounts for declining separations at increasing current densities.

Although the pyrochemical separations data obtained are insufficient for flow-sheeting of the partitioning processes, it does generally confirm the feasibility of several key separation steps.

A picture of the BNFL electrorefiner is given in Figure 18. It shows the electrorefiner mounted within a hot well and inside an argon atmosphere glove box.

**Figure 18. BNFL Electrorefiner operating with liquid cadmium cathode and pounder (see inset) for Pu-U-Am electrorecovery**



### **Additional experimental studies**

The project has been divided into packages of work reflecting the process stages likely to be needed in an industrial process. If oxide fuels are to be treated by pyrochemical technology based upon electrorefining of metal feeds, as in the ANL process, they must first be converted to a metal form. Paper studies have identified the issues associated with the oxide-to-metal reduction, both from

a fundamental chemistry and an engineering perspective. BNFL has subsequently addressed the issues associated with this oxide reduction step by chemical and electrochemical means. Non-active electrochemical reduction experiments are under way.

Electrorefining is likely to be a key step in any pyrochemical process targeted at the separation and purification of irradiated fuels or streams derived from irradiated fuel treatment. As well as participation in the EC 5<sup>th</sup> Framework PYROREP programme, BNFL has undertaken additional studies in electrorefining. BNFL has collaborated with several international groups through assignment and contract research. Practical electrochemical measurements in nitride systems were undertaken by assignment to JAERI. A contract placed at a US university examined the pyrochemical separation of uranium from fuel cladding materials. This work concentrated on the decontamination factors of the uranium from the cladding material and vice versa, and how the electrochemical dissolution of the cladding material affects the behaviour of the melt system.

BNFL believes that the decontamination of the salt solvent from fission products, and the recycle of this salt, will be crucial to the economics of any process. Such recycle should minimise the volume of HA waste generated, which will require expensive storage and repository space, while optimising the necessary durability of the waste form. The alkali metal and chloride ions are particularly mobile, and can often be incorporated within wastes only at low percentages. A number of studies are ongoing to examine the separation of fission products from salt. Extensive studies have now been completed by BNFL on the treatment of various simulant salt wastes with phosphate precipitants. It is the intention to explore zeolite and other ion exchange materials in the future. BNFL's programme has examined the incorporation of inactive waste simulants, and has attempted to optimise the waste loading [5]. A number of waste forms including glasses, glass-ceramics and ceramics are considered. BNFL has a capability in thermodynamic modelling of molten salt systems. Understanding the thermodynamic properties of the systems will be important with regard to the successful application of this technology.

### **Engineering studies**

In 1998, BNFL commissioned a cost study in the US that examined the best publicly available information on electrometallurgical (EM) treatment technology for the management of gas-cooled metallic irradiated fuel. The study indicated the feasibility of EM treatment and developed cost and schedule information underpinned by a reference process and pre-conceptual designs for a facility. Information was developed using a bottom-up generic work breakdown system structured by the cost element. Pre-operational, operational and decommissioning costs were estimated to obtain an overall estimated life cycle cost. Statistical modelling of cost probability distributions was applied.

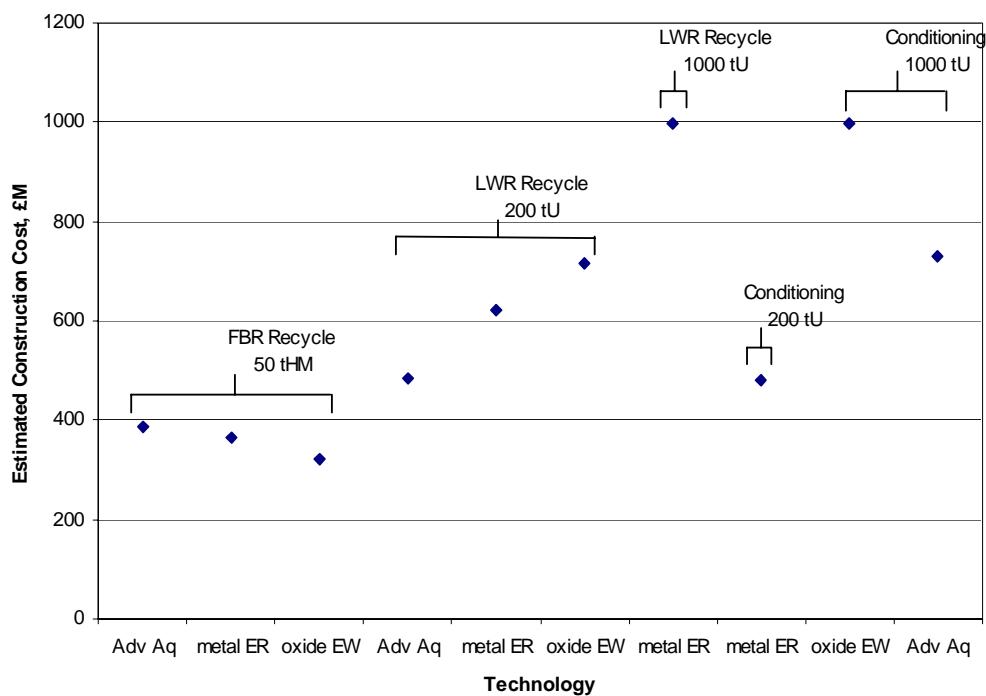
BNFL has examined various options for pyrochemical-based flow sheets to process spent nuclear fuel. Various engineering and modelling studies were performed (Table 3) to compare the suitability of these flow sheets against various treatment strategies [5]. Within the flow sheet, consideration of the detailed operating parameters, such as electrorefining efficiencies and decontamination factors, needs to be taken to allow engineers to size the equipment. However, equally important is the consideration of secondary processes and their effect on the overall size and economics of the facility. Potential was found for waste volumes to be reduced, to match those from advanced aqueous processes by effective use of salt recycle and selection of several clean-up processes using zeolites and phosphates.

The estimated construction costs of reprocessing facilities using a variety of technologies and for various throughputs are shown in Figure 19.

**Table 3. Summary of engineering studies by BNFL on pyrochemical processes**

Plant type	Throughput t/year	Operating mode	Novel stages	Parallel processing
MAGNOX conditioning: metal electrorefining	200	Mainly batch	Some	Little
LWR conditioning: metal electrorefining	1 000	Semi-continuous	Many	High
LWR conditioning: oxide electrowinning	1 000	Mainly batch	Some	Some
FR recycle: metal electrorefining	50	Semi-batch	Many	Some
FR recycle: oxide electrowinning	50	Mainly batch	Some	Little
FR recycle: advanced aqueous	50	Mainly continuous	Few	Negligible
LWR recycle: metal electrorefining	200	Semi-continuous	Many	High
LWR recycle: oxide electrowinning	200	Mainly batch	Some	Some
LWR recycle: advanced aqueous	200	Mainly continuous	Few	Little
LWR recycle: advanced aqueous	1 000	Mainly continuous	Few	Little

**Figure 19. Estimated construction costs for various spent fuel treatment facilities**



The following conclusions were drawn from the design and cost studies [5]:

- 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.

BNFL is also carrying out a pyrochemical process test case application, which helps focus the development programme. There is no commitment for construction but the test case is seen as a small, versatile plant [ $\sim 20$  t(HM)/a] capable of processing a variety of “legacy” fuels. Individually, these are relatively low tonnage irradiated fuels of several hundred tonnes total arisings from demonstration reactors or test fuel campaigns, which are not readily processed by the existing large-scale PUREX reprocessing plants operating commercially in the UK. TRU wastes or targets are other possibilities. The main outputs of the plant are foreseen to be LLW uranium oxide and immobilised HLW containing Pu and other transuranics.

Pyrochemical processing is seen to be at a pre-competitive stage and it is felt that pyroprocess plants are more likely to be installed in the longer term. A first radioactive demonstration is anticipated for the period 2015-2020. The UK programme is intended to enable commercial industrialisation with technology partners on an international basis. Present studies include: feed treatment, flow-sheeting, plant design, economics (including cost sensitivities), HAZOP, risk management, plant interfaces, environmental studies, location, shared infrastructure and waste management. These will enable BNFL to brief the planned UK Nuclear Decommissioning Authority on legacy fuel treatment in the future.

### ***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 Argonne National Laboratory (ANL) process as demonstrated recently by treatment at the  $\sim 1$  t(HM)/a scale at ANL-West. BNFL and JNC have a technical co-operation agreement in the fuel cycle area which includes 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 the commercial scale. Bench scale experiments, concept development and design work are underway leading to a pilot-scale, molten salt metal ER with features suited to an industrial-scale plant for processing irradiated nuclear fuel. 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 [6]. Design objectives have been based on the use of high-fissile-content fuel taking into account severe criticality safety constraints and with an initial facility throughput of 50 t(HM)/a and a possible later deployment at 200 t(HM)/a. A 1/5<sup>th</sup>-scale pilot plant, using depleted U and alkali chlorides, will be taken to the detailed design stage by 2005. Construction and testing is planned as a further phase. This study concentrates on the electrorefining of U and assumes that TRU electrorecovery may take place in a separate vessel through which molten salt is pumped. A previous study assessed the overall system design [7].

The three industrial ER candidates finally selected (in order of preference) were [6]:

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

The procedure used to select ER design concepts was described. Several novel electrode types, including “crusting” and “cast” cathodes, were identified and allied to design for continuous operation. To enable industrial use, radical design targets were adopted and a wide range of non-nuclear engineering practices, including aqueous electrolysis, metal winning and purification with molten salts, was used.

### ***Molten-salt dynamics rig***

A schematic of the BNFL molten salt dynamics rig is given in Figure 22. 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. RFDs are widely used in PUREX plant and in HLW storage tanks. They have no wetted moving parts, and utilise a jet pump pair that is alternately fed from a charge vessel and driven by gas pressure. Salt transport behaviour will be investigated during transfers and by flow between vessels. The salt inventory is around 60 litres. Commissioning started in late 2003.

## **The future programme**

### ***Planned experimental studies***

Further molten salt tests and equipment planned for construction and operation at BTC Sellafield in the period 2003-2005 include rigs for oxide reduction, U electrorefining, U and TRU electrorefining and partitioning, and waste processing. To support this programme, a general-purpose argon dry box ( $900 \times 1\,950 \times 1\,500$ ) with two hot wells, an alpha-active argon glove box (see Figure 20), and dedicated rigs with argon glove and port facilities for electrorefining and waste management are being constructed.

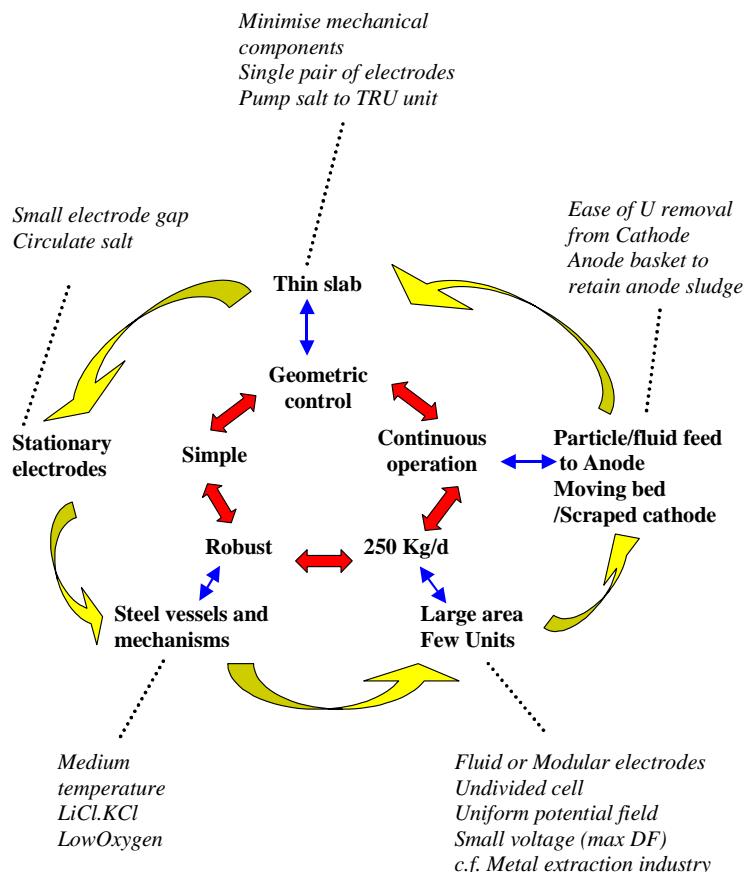
**Figure 20. BNFL BTC standard alpha box**



A laboratory-scale test rig for direct electrochemical reduction of refractory metal oxides in calcium chloride electrolyte is undergoing tests and significant conversions to metal form are established. Work is proceeding on electrolyte systems, electrodes, conversion and selectivity. A further rig for the direct electrochemical reduction of uranium and TRU oxides will be established using lithium chloride as electrolyte.

Some non-uranium active and some uranium active pilot facilities are in design as electrorefiner development modules (EDM) to model the key functional features of the selected industrial scale U electrorefiner concept. This is to support the detail design of the industrial electrorefiner that is planned for construction commencing in 2005 (Figure 21).

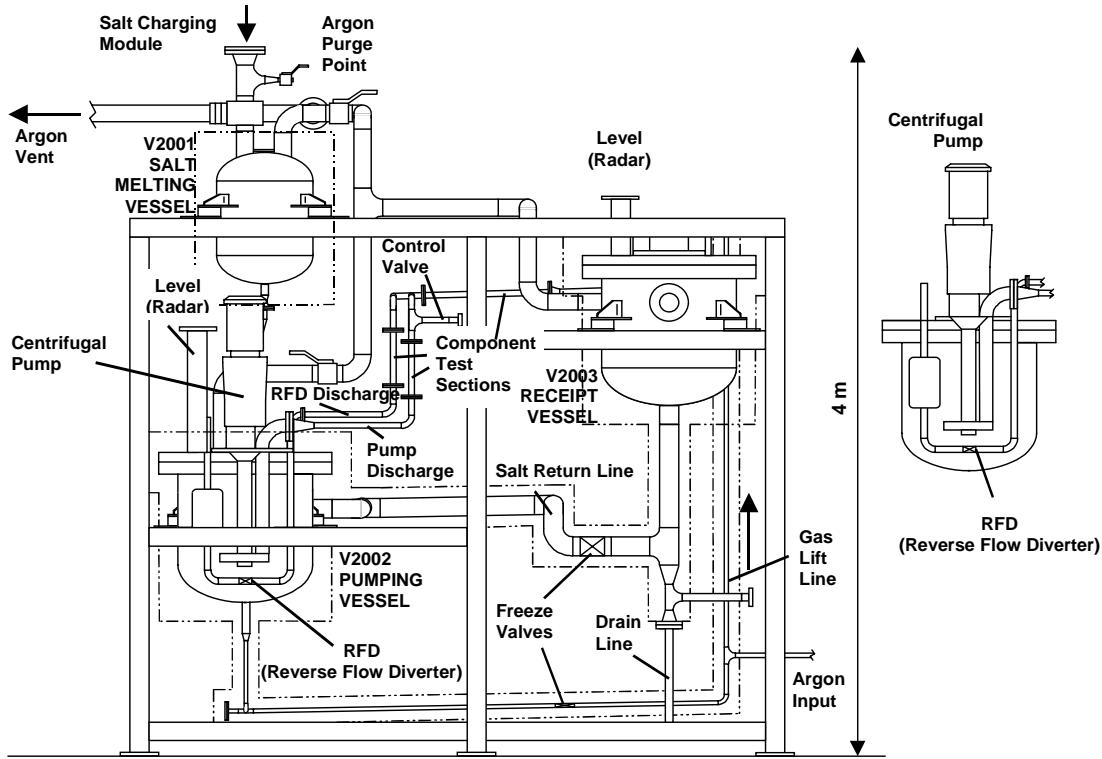
**Figure 21. Schematic summarising typical electrorefiner design requirements and potential options**



An alpha-active argon-filled glove box is being constructed for electrorefining and partitioning studies to follow up those initially conducted for BNFL at AEA-T, Harwell. Studies will be performed under well-defined scientific and/or engineering conditions such as rotating disc and rotating cylinder, and flow through parallel plates. The box incorporates four experiments, i.e. three furnaces and a waste bench. There is double-sided glove port access, 90 g Pu metal limit, shielding based on Magnox Pu (five-year cooled), and argon atmosphere control targets of 10 ppm oxygen and 3 ppm water vapour.

Programmes to be carried out in the general-purpose argon dry box include simulation of anode sludge, investigation of waste forms, salt clean-up using zeolites, phosphate and oxides, electrorefiner component investigation and the use of alternative electrolytes for direct electrochemical reduction. The molten salts dynamics rig (Figure 22) will be operated at Risley, Manchester. Successful overall development will require collaborative partnerships with international organisations involved in pyrochemical research and in the implementation of the technology.

**Figure 22. BNFL molten salts dynamics rig**



## Other UK programmes

### AEA Technology

Publications released in the 1960s show that UKAEA Harwell was involved in the early development of pyrochemical processes [8,9]. This included pilot plant studies for the electro-winning of crystalline uranium oxide from molten salts [10]. In more recent years, AEA-T, the privatised commercial division of UKAEA, has provided contract research services for a number of organisations including CRIEPI [11,12] and KAERI [13]. Work was performed for CRIEPI, examining the reduction of actinide oxides using lithium metal. Uranium, plutonium, americium and neptunium oxides and un-irradiated mixed oxide pellets were studied, and a number of publications made. KAERI and AEA-T have collaboratively performed electrorefining studies at Harwell on the electrolysis of actinide and lanthanide fluorides in LiF-NaF-KF melt. The Nuclear Sciences division of AEA-T, which operated the electrorefiner [3] as part of the participation of BNFL in the EU 5<sup>th</sup> Framework pyrochemical separation programme named PYROREP, has been a contractor to BNFL and more recently has become part of BNFL.

### UK universities

A number of universities have completed, are undertaking or are in discussions with BNFL to perform pyrochemical or supporting electrochemical studies. In the UK, these include Bath, Belfast (QUILL), Cambridge, Edinburgh, Leeds and Manchester. Collaboration with the Urals State Technical University (Ekaterinburg) is also proposed. Several of these institutes have subsequently published some of this research work in the open literature, for example [14-19]. This includes the University of

Leeds, where work concentrated on the dissolution of uranium oxides into molten carbonates. A small group of pyrochemists has been established at the Manchester Radiochemical Centre of Excellence, based in the Chemistry Department at Manchester University. The work emphasises chlorinative dissolution of uranium and fission product simulants in alkali chloride melts, including *in situ* spectroscopy studies. The Universities of Belfast, Cambridge and Edinburgh are undertaking electrochemical studies, the former on ionic liquids. The University of Bath is providing expertise in electrochemical engineering.

## Summary

The UK national programme is summarised as follows:

- BNFL, assisted by other UK participants, has considerable experience with pyrochemical separations, favours UK and international collaborations, encourages technical publication, and has an ongoing programme for technology industrialisation.
- Recent and future work comprises:
  - actinide electrorefining experiments performed using LiCl-KCl and providing 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 under way;
  - molten salt, LiCl-KCl, dynamics rig in commissioning;
  - selection of concept and detailed design of industrial U electrorefiner;
  - construction of new non-radioactive and alpha-active glove box facilities for a range of experiments at BTC Sellafield;
  - pyroprocess plant test case development (legacy fuels and waste);
  - pyroprocessing plant design and cost studies (LWR and FBR);
  - wide range of pyrochemical fuel processing and partitioning studies.

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## **UNITED STATES OF AMERICA**

### **Introduction**

The quest for pyrochemical alternatives to aqueous reprocessing has been under way in the United States since the late 1950s [1]. Approaches examined at various levels of development and for a variety of fuels include alloy melting, fission product volatilisation and adsorption, fluoride and chloride volatility methods, redox solvent extractions between liquid salt and metal phases, precipitation and fractional crystallisation, and electro-winning and electrorefining of actinide metals and oxides. The processes that won through to greatest acceptance internationally are considered to be metal electrorefining, oxide electro-winning and fluoride volatility. The first of these has been the most successful in the US.

### **Early US work**

The unusual behaviour of uranium, neptunium and plutonium in forming volatile hexafluorides has been the basis of many studies by the Brookhaven (BNL), Argonne (ANL) and Oak Ridge (ORNL) national laboratories for the chemical processing of irradiated fuels though the use of fluoride volatility (FV) [2]. Uranium metal dissolves in both halofluorides and hydrogen fluoride/nitrogen oxides and can be recovered as a hexafluoride which can be fed to a uranium diffusion plant. Excepting the noble gases, fission products are generally non-volatile and form few volatile fluorides. Tellurium is the main exception to the latter. The final decontamination of fission product fluorides can be performed by absorption or distillation. Oxide fuels are oxidised to U<sub>3</sub>O<sub>8</sub> and charged to a fluidised bed of alumina through which a fluorinating gas such as F<sub>2</sub>, ClF<sub>3</sub> or BrF<sub>5</sub> is passed. A flame fluorinator may also be used. ORNL has treated kg quantities of irradiated fuels including: Zr-HEU submarine type, HEU-Al research reactor type and salt from the ORNL molten salt reactor experiment (MSRE) [3]. The Morris, Illinois, fuel reprocessing plant also incorporated FV as a late uranium decontamination stage following PUREX stages, though this plant was never operated with hot fuels.

Development of FV processes decreased in the US following the cancellation of the MSRE project in 1973. Materials selection and conversion of Pu between volatile and non-volatile fluoride forms are potential drawbacks. It is convenient to consider FV to be a pyrochemical separation process though some variants, especially for metal fuels, do specify relatively low operating temperatures.

The phenomenon of electrolytic production of solid UO<sub>2</sub> from molten UO<sub>2</sub>Cl<sub>2</sub> was discovered at the end of the 19<sup>th</sup> century [4]. An oxide electro-winning process was developed at Hanford Laboratories as the Salt Cycle Process but terminated there in the mid-1960s after processing irradiated thermal oxide fuels at 0.1 m<sup>3</sup> salt batch pilot scale [5]. A 10 kg quantity of low plutonium mixed oxide was recycled for further thermal reactor irradiation. This system aimed for technical simplicity with low DFs while facilitating economical remote fabrication of “dirty” MOX fuel with vibratory compaction technology. The process depends on the chlorinative dissolution of fuel in salt, the stability of UO<sub>2</sub><sup>2+</sup>

in molten salts, the low reductive potentials of dissolved uranyl and plutonyl species to the solid oxides, the electrical conductivity of  $\text{UO}_2$  solid at higher temperatures, and the controlled oxidation reduction of  $\text{Pu}^{3+} - \text{PuO}_2^{2+}$  to enable MOX electro-co-deposition. Both precipitation of  $\text{PuO}_2$  solids and MOX electro-co-deposition were demonstrated but good process control was not achieved and the selection of materials suitable for electrolyser construction was very limited.

Oxidative-reductive extractions between molten metal and salt phases have been the basis of a number of fuel cycle processes for experimental reactor concepts with molten fuel types. Brookhaven National Laboratory studied the pyrochemical separation of uranium and fission products using redox extractions between chloride salts and molten bismuth for the liquid-metal fuel reactor (LMFR) with  $^{235}\text{U}$  dissolved in Bi as fuel [6]. Los Alamos National Laboratory (LANL) tested pyrochemical extraction methods to separate fission products from molten plutonium fuel in the LAMPRE system [7]. Oak Ridge National Laboratory investigated liquid bismuth with lithium reductant for separation of U and Pa from fission products and from salt in the MSRE [8].

In the early 1960s, LANL developed a molten salt process and constructed equipment to perform electrorefining runs to purify plutonium metal at the 3.5 kg batch scale as compatible with criticality safety. This equipment ran until 1977 at the original facility generating around 1.6 t of > 99.95% purity product from around 1.9 t of fabrication scrap, etc. of 99% purity [9]. Equimolar NaCl-KCl was used as electrolyte and a process temperature of 1 013 K maintained the Pu electrodes in the molten state while minimising container corrosion. Recycling of ~2 300 kg of short-cooled experimental breeder reactor II (EBR-II) fast reactor metallic fuel took place at ANL-West in the mid to late 1960s using a melt refining process based on volatilisation and selective reaction with the crucible material, Stevenson [10]. This was discontinued when EBR-II became a test bed for oxide fast fuels. Much of the ANL nuclear pyrochemical development work after 1960 was based on the salt-transport process using zinc and other low melting metals as solvents for extractions between metals and salts; this is reviewed by Steunenberg, *et al.* [11]. Materials of construction are limited with zinc and phase separations and solvent removal can be difficult. This work preceded electrorefining of irradiated nuclear fuels as identified by Burris, *et al.* [12,13], who presented the early proposals for the IFR fuel recycling system in the mid to late 1980s. Halide slagging and electrorefining were first proposed and then it was found that anodic dissolution obviated the need for slagging and/or chemical dissolution in liquid cadmium.

The definitive account of Integral Fast Reactor (IFR) irradiated fuel processing is probably that edited by Hannum [14]. For the IFR process, electrorefining of irradiated metallic fuel is performed in LiCl-KCl salt. Batches of fuel are anodically dissolved in salt. The uranium is electro-transported to a solid iron cathode where it deposits in purified form. Plutonium, minor actinides (MA) and reactive fission products convert to chlorides and accumulate in the salt. Fission products, that are un-reactive, generally accumulate as metallic solids in the anode baskets (anode sludge). When a number of fuel batches have been treated, the plutonium is recovered as a Pu-U-MA alloy in a liquid cadmium cathode that has a “pounder” (or other interfacial agitation device) to maximise TRU electro-deposition and prevent growth of pure uranium from the cathode-salt interface. When the salt from the electrorefiner is sufficiently loaded with fission products, it is treated by lithium reduction/molten metal extraction (titrated) using a “pyrocontactor”, to separate 95-99% of the actinides while nearly all of the rare earths are left in the salt. The partly reduced salt is then contacted with Cd-2 wt.% U reductive alloy to remove the remaining transuranic elements with a minority of rare earths which are returned to the electrorefiner. The residual fission products are then removed from molten salt by ion exchange using zeolite to enable immobilisation as high-level wastes. The IFR project was terminated in 1994 but the technology provided the basis for a fuel conditioning treatment to manage irradiated fuels at the ANL-West site and potentially others.

## Recent US pyrochemical separations work

Since the mid 1990s, an advanced pyrochemical process, called electrometallurgical treatment (EMT), has been developed by ANL for the conditioning of metallic fuels including EBR-II driver and blanket fuel assemblies for the disposal of fission product and transuranic elements. The EBR-II fuel inventory is largely U-5 wt.% fissium metallic fuel; later designs were U-10 wt.% Zr and an even smaller quantity of U-20Pu-10Zr, also metallic fuels. The total beginning-of-life enrichment of the EBR-II fuel was about 70%. Blanket elements were irradiated in EBR-II until they were replaced with stainless steel reflectors in the late 1960s; the blanket elements are depleted or natural uranium in metallic form. Both the core and blanket fuels included a metallic sodium thermal bonding agent internal to the fuel rods. Driver and blanket fuel elements are being processed by EMT, which involves the electrorefining of the uranium present in the fuel. Segments of chopped fuel, including the cladding and bond sodium, are placed in a mesh basket in an electrorefining cell containing LiCl-KCl electrolyte salt at the eutectic composition. The cell is operated at a temperature normally in the range 723-773 K. The basket containing the chopped fuel is made the anode and uranium is transported to a solid steel cathode. Provided that the U:TRU ratio in the electrolyte salt is kept sufficiently high, that is > 0.5 or so, high-purity uranium can be electrodeposited at the solid cathode. The bond sodium reacts with chloride ions to form NaCl, which tends to increase the melting temperature of the electrolyte and is a potential limiting factor in electrolyte lifetime (another possible limiting factor is the level of decay heat arising from the accumulation of fission products dissolved in salt which interferes with electrorefining cell temperature control).

Because EBR-II fuel conditioning is intended only as a waste management scheme, the uranium is consolidated and down-blended to LEU by melting for storage. The metallic uranium cathode deposit is freed of adhering electrolyte by vacuum melting and preferential vaporisation of salt. This consolidation is normally done at temperatures of around 1 700 K; at such temperatures the extremely reactive combination of uranium and salts leads to rapid attack of crucible materials. The transuramics and fission products present in the driver/blanket fuels collect in the electrolyte salt and are subsequently incorporated in a durable high-level glass-ceramic waste form. Cladding hulls and noble metal fission products, which collect in the anode basket, are melted to form the high-level metal waste form.

In 1996, Argonne National Laboratory (ANL) was authorised to begin a demonstration of the pyrochemical conditioning of EBR-II fuel and blankets, with a limit of 100 driver and 25 blanket fuel assemblies. The demonstration was successfully completed in 1999 and reviewed at US DOE request by the National Research Council of the National Academy of Sciences [15]. A further US government authorisation was provided to complete the processing of the full inventory of EBR-II driver and blanket fuel in storage, a total of approximately 30 t(HM). Most of this material is blanket fuel. Whereas the highly-enriched core driver fuel (about 57% enrichment at discharge) must be handled with concern for nuclear criticality and is thus limited to batches of 20 kg (HM) using rod cathodes, the depleted uranium blanket fuel material that amounts to over 90% of the fuel mass cannot be processed on a practicable schedule at the low rates [about 10 kg(U)/month] used for driver fuel. Therefore, ANL has developed a higher throughput anode-cathode module (ACM) that features cylindrical arrays of anode baskets rotating *in annuli* between concentric tubular cathodes. This design reduces the cell resistance and permits operation at the very high current levels necessitated by the fact that only 3 g of uranium can be electrodeposited for each ampere-hour of current passed between the anode and cathode. Four ACMs, each of 600 A rating, fit into a single Mark V electrorefiner vessel as now used at ANL-West, enabling overall processing rates in the range 150-450 kg(U)/month, while a newly designed electrorefiner that fits in the same hot cell floor space will have a capacity of 10-20 t(U)/a.

Processing of the EBR-II driver/blanket inventory is now in progress and is proceeding satisfactorily [16]. Uranium is being recovered and down-blended for storage, while the transuranic elements are left in the electrolyte salt and subsequently included in a ceramic waste form together with caesium, strontium, iodine and many of the rare-earth fission products. The transition metal fission products, including technetium, are placed in a metallic waste form for which the fuel cladding material (stainless steel) is the matrix. As of the end of 2002, nearly 3 tonnes of EBR-II driver fuel and blanket assemblies had been processed.

Besides treatment of DOE spent fuel wastes at Idaho, DOE is sponsoring some assessment work regarding application of pyrochemical separations to advanced fuel cycles. In 1999, DOE commenced work to identify, assess and develop a progressive, next generation of nuclear plant and new nuclear systems, called Generation IV. Because the system goals include sustainability, Generation IV concepts are complete energy systems including closed fuel cycles. A “Generation IV Nuclear Energy Systems Technology Roadmap” was recently published [17]. Six reactor systems have been selected for emphasis:

- 1) very-high-temperature reactor (VHTR);
- 2) supercritical light water reactor (SCWR);
- 3) gas-cooled fast reactor (GFR);
- 4) sodium-cooled fast reactor (sfr);
- 5) lead-cooled (or lead/bismuth-cooled) fast reactor (LFR);
- 6) molten salt reactor (MSR).

The project is divided into various groups including Working Group 3: Liquid Metal Reactors, for which many of the system proposals include pyrometallurgical processing for closure of the fuel cycle [18].

### **Pyrochemical partitioning of selected radionuclides for transmutation**

Further interest in pyrochemical processing of irradiated fuel arose with inception of the US programme for Accelerator Transmutation of Waste (ATW) [19]. The programme was motivated by the goals of:

- 1) reducing the toxicity of materials to be permanently emplaced in a geologic repository for high-level nuclear wastes;
- 2) eliminating a future “plutonium mine”;
- 3) increasing the efficiency of utilisation of energy resources by fission of the transuramics present in irradiated nuclear fuel.

It was originally envisioned that the system resulting from this development programme would deal with the very large quantities of commercial LWR irradiated fuel currently stored in the US (over 40 000 t(HM) now, and over 100 000 t(HM) by 2020). Pyrochemical separation processes that would find application in such a partitioning/transmutation system must meet demanding requirements on actinide recovery and, in some scenarios, on long-lived fission product recovery from irradiated fuel.

In the initial formulation of the US ATW programme, it was assumed that all transuranic elements contained in LWR irradiated fuel would be directed to an accelerator-driven sub-critical reactor for fission. The costs of operating this system would be offset in part by revenues derived from the generation and sale of electricity. An aqueous separation method was chosen for the initial partitioning of the LWR irradiated fuel, on the basis of a reasonable certainty that an aqueous system could economically deal with the very large quantities of irradiated fuel to be processed, without necessitating an extensive technology development programme. The aqueous method that was chosen incorporates a solvent extraction process for extraction of pure uranium and technetium, but leaves the transuranic elements and other fission products in the first cycle raffinate. That stream is calcined to produce TRU and fission product oxides, which are fed to a pyrochemical process (known as PYRO-A) for separation of the transuranic elements from fission products. The oxides are then electrochemically reduced to metallic form for TRU/fission product separation; several methods for oxide reduction were considered, including chemical reduction by lithium or calcium and direct electrochemical reduction. The electrochemical reduction process chosen is carried out in a LiCl carrier salt containing a small concentration of  $\text{Li}_2\text{O}$ , which then becomes the electrolyte for the next step, electrorefining, in which the fission products are separated from the transuranic elements.

A reductive extraction process might also serve to accomplish the separation of fission products from transuranic elements, and a process incorporating this method is under development; the oxide product is chlorinated in a LiCl-KCl carrier salt and the salt is then contacted with a molten dilute alloy of lithium in cadmium. The transuranics extract into the cadmium and the fission products remain in the salt. The transuranic elements are then recovered by distilling off the cadmium. The principal advantages of the PYRO-A process for transuranic element partitioning are:

- no separation of plutonium from the minor transuramics;
- efficient recovery of the transuramics present, of the order of 99% or greater;
- reasonable cost of processing.

Contamination of the transuranic product with a small amount (of the order of 5% or less) of lanthanides is considered acceptable, because the fuel is to be irradiated in a fast spectrum in which neutron absorption by the lanthanides is within acceptable limits.

The sub-critical reactor of the initial ATW scenario was assumed to operate to significant fuel burn-ups, of the order of 30 atom %, using a non-fertile fuel to preclude the generation of additional transuranic elements. After discharge, the fuel would be processed to recover unburned transuranic elements for recycle and to extract newly-generated long-lived fission products (i.e. Tc and I) for transmutation in thermalised regions of the reactor. Because it was economically desirable to process the irradiated transmuter fuel with short cooling times, and because the amount of fuel to be processed annually contains a comparatively small amount of heavy metal (relative to the annual throughput of heavy metal in LWR irradiated fuel), pyrochemical processing was chosen for the treatment of the transmuter fuel. Initially, a metal alloy fuel (TRU-Zr) was assumed as the transmuter fuel. The volume fraction of zirconium was assumed to be large, about 90%, and this large quantity of Zr coupled with high radiation and decay heat levels for the fuel drove the process selection toward pyrochemistry.

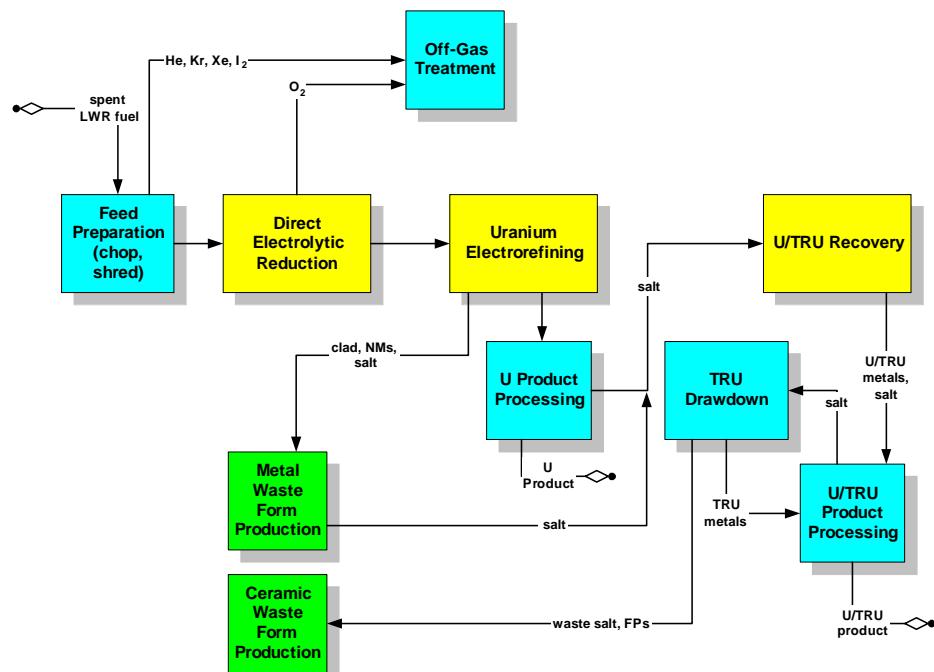
The process initially selected, known as PYRO-B, first involved the digestion of the zirconium matrix. This was done by chlorination of the fuel with  $\text{CdCl}_2$  in a KCl salt bath and then removal by volatilisation of the  $\text{ZrCl}_4$  formed. The extracted Zr could then be recovered for use in recycle fuel fabrication. The remaining salt, containing transuramics, fission products, and cadmium, was then treated by pouring off the cadmium bearing the noble metal fission products. Cadmium was separated by

distillation and recycled, and the noble metal fission products, including technetium, were processed to form a corrosion-resistant metal waste form. The residual salt was treated by electro-winning to recover the transuranics in metal form. In the process of electro-winning, fission product iodine was swept off with the liberated chlorine and recovered for transmutation or immobilisation, with the fission products remaining in the salt in a sodalite-based ceramic waste form. The entrainment of small amounts of cadmium in the recovered  $ZrCl_4$  led, however, to abandonment of the PYRO-B process in favour of a direct electrorefining process in which the transuranics are electrodeposited at a steel cathode and the zirconium is left behind with the noble metal fission products and incorporated as a matrix material in the metal waste form.

As the US programme has evolved over the years since the initial definition of the ATW programme in 1999, increasing attention has been paid to the scenario of a multi-tier system for transmutation. This concept is embodied in a new programme, the Advanced Fuel Cycle Initiative (AFCI) [20]. In the AFCI programme, the first tier is the existing commercial LWRs, and the second tier would be thermal spectrum reactors capable of burning fissile transuranics from the LWR irradiated fuel and transmuting long-lived fission products while generating electricity. The third tier would be fast spectrum reactors, either critical reactors or sub-critical accelerator-driven devices, intended for minor actinide burning that derives their feed from processing of irradiated fuel from LWRs and the second-tier thermal burners. Although the reactor types and fuel types have not yet been determined, this system presents a number of interesting separation challenges. While an aqueous solvent extraction process remains favoured for commercial LWR fuel processing, the quantity of LWR fuel that must be processed is so large (2 000 tonnes per year, not allowing for growth of nuclear generating capacity in the 21<sup>st</sup> century) that the potential for reduced costs presented by pyrochemical processing technologies cannot be ignored.

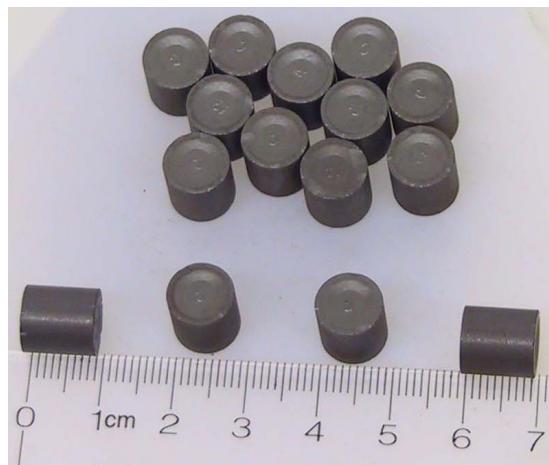
Accordingly, considerable effort is going into the development of a pyrochemical processing method for LWR irradiated fuel. The process, known as PYROX, is illustrated in Figure 23 and involves the direct electrochemical reduction of LWR oxide fuel to the metallic state using the same

**Figure 23. US PYROX process for the treatment of spent LWR oxide fuels**



technique as in the PYRO-A process. An electrolysis process is then used to produce a stream of separated pure uranium and a second stream of transuranics, largely free of fission products but with a small concentration of lanthanides. The transuranics can be sent directly to the fast reactor fuel fabrication step, using some of the recovered uranium as make-up feed. The balance of the recovered uranium can be used for blanket element fabrication if the fast spectrum reactor system is configured for breeding. Initial experiments with the PYROX process, using simulated irradiated oxide fuel, have shown excellent reduction efficiency for actinides and fission products (see Figure 24); anode material development has been the most challenging aspect of this process, as the anode is subject to extreme oxidising conditions at high temperatures ( $\sim 650^{\circ}\text{C}$ ). The PYROX process will be subject to small-scale testing with irradiated fuel materials in 2003, and an integrated engineering-scale (20-50 kg batch size) demonstration of the process will be carried out over the period 2005-2007. Planning for the AFCI programme calls for a decision in 2007 on the deployment of a large plant for the processing of irradiated LWR fuel, and a conceptual design of a processing plant incorporating PYROX technology will be available to support the deployment decision.

**Figure 24. High-fired uranium oxide pellets before (upper photo) and after (lower photo) electrochemical reduction in a lithium chloride bath at  $650^{\circ}\text{C}$**



Reactors being considered for the third-tier transmuter role will incorporate fuel systems that pose significant challenges to aqueous reprocessing methods (high discharge fissile content, short cooling time, inert matrices difficult to dissolve with nitric acid). Therefore, the treatment of discharged fuel from these reactors would almost certainly be by pyrochemical means. Electrorefining methods are suitable for metal alloy (TRU-Zr) and nitride (TRU N – ZrN) fuels, and experiments with such fuels have validated this process. Limited development work is now being done on alternative fuel types that might be utilised in other Generation IV reactor types, including dispersion fuels (cermet and cercer) based on both oxides and nitrides and on coated particle fuels for graphite reactors. Importantly, consideration is being given to the problems associated with industrial-scale deployment of pyrochemical processing systems, which is essential even at this early stage of system definition.

### Scale-up of pyrochemical processes for industrial application

Pyrochemical operations, at the present stage of technology development, are batch processes. The cost of such operations is approximately linearly dependent upon the number of batch operations to be run simultaneously. Some economies of scale can be expected from large-volume equipment fabrication, commonality of repair parts, and standardisation of procedures, but the effects are not at all comparable to the considerable economies of scale available with continuous aqueous processing. Furthermore, many pyrochemical processes require the recovery of materials from each batch operation and transport and loading of the materials to the next batch operation; this must generally be done by electromechanical means, as opposed to the simple liquid pumping operations in aqueous processing. All of these handling and transfer operations add complexity to the process, and duplication of complex equipment to provide for multi-batch operations means an increase in the probability for failure somewhere in the system. Intuitively, such considerations must impose a limit on the economic throughput capacity of a pyrochemical separations process. The limited industrial experience with such processes at present precludes a quantitative evaluation of the practical limits to throughput capacity. Nor is it yet possible to estimate with certainty the capital and operating costs of these processes. Therefore, the US programme is based on a series of successive scale-ups of the various separation processes, beginning with laboratory-scale process confirmation experiments with feeds of a few tens to hundreds of grams of heavy metal, initially with simulated irradiated fuel and proceeding to actual irradiated fuel as it becomes available. Demonstrations at near-industrial scale are planned to follow the completion of pilot-scale operations.

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## *Chapter 3*

### **COLLABORATIVE INTERNATIONAL DEVELOPMENT OF PYROCHEMICAL SEPARATIONS TECHNOLOGIES**

#### **Introduction**

In this chapter, the status of collaborative international activities involving the application and development of pyrochemical technology for nuclear separations is summarised. Goals and benefits of international collaboration are described. An attempt will be made to demonstrate the reasons for which international collaboration is now especially opportune.

The principal strategic applications of pyrochemical separations, as currently envisioned, lie in novel fuel cycles for future reactor systems, innovative waste management strategies and possible on-line processing of molten/liquid fuels from advanced reactor concepts including burner reactor types. These tend to be longer-term objectives that are well suited to pre-competitive research. The breadth of these issues and the complexity of the nuclear systems involved calls for wide international exploration, development and assessment. A successful global nuclear industry can greatly benefit from technological convergence, public acceptance of management approaches and a certain degree of standardisation of future processes and plants.

The costs of introduction of any new advanced reactor, e.g. the US Generation IV concepts, and the appropriate fuel cycles, are so high that any single institution or country may well be unable on its own to carry out the required technological development. Besides spreading costs, international collaboration helps ensure development for wide country and market conditions, and eventual international licensing and commercial deployment. Back-end issues as dealt with by pyrochemical separations are very significant to waste management and recycling issues as perceived by the public, electricity consumers and other stakeholders.

Some waste management concepts may be well suited to introduction in the very long term. International consensus on what is possible over the next few decades could help focus work in various countries and help guide the priorities of the national and international funding organisations. World-wide interest in partitioning and transmutation systems has grown recently because of the potential to reduce the engineering needs and chemical/physical performance of geologic disposal repositories. Transmutation brings more effective closure of the fuel cycle and also releases energy that may be used for electricity generation. However, avoidance of processes and plants with excessive complexity and cost and insufficient benefits will aid the international nuclear industry as a whole in reaching new generations of commercially successful reactor and fuel cycle plants.

Other potential applications of pyrochemical processing include fuel conditioning, conversion of weapons Pu to MOX fuel, Pu recovery and waste decontamination. These may be deployed on an early time scale. Some of these efforts are already internationally funded and others in the waste management and decontamination fields may be applied to specific national sites requiring clean-up. These particular applications still benefit from broad comparative assessments of cost and benefits for pyrochemical applications.

Research and development funding within the nuclear industry is now much more limited than in earlier decades, when major separations processes such as PUREX were developed and deployed. International collaboration is needed to ensure the best possible progress from the world-wide programmes that are underway. For maximum benefit, they should be mutually supportive and well co-ordinated. The existence of R&D programmes within a technology sector is often considered a prerequisite for long-term stability and growth in a world where resource supply, environmental discharges, regulatory requirements, intellectual property, human resource development and output efficiency are constantly becoming more demanding. Innovative reactor, fuel cycle and waste transmutation R&D areas are central to commercial advanced nuclear competence and the longevity of the world-wide nuclear fission industry where much of the work is strategic and nationally or supra-nationally funded.

International collaboration on pyrochemical separations is especially opportune due to renewed interest in nuclear electricity generation in the US as a result of the excellent safety, production and business performance of commercial nuclear power stations in recent years. This meshes well with projected increases in nuclear generating capacity and fuel cycle capabilities in Japan, the Russian Federation, China and the Republic of Korea. Growing world-wide attention is being paid to novel high burn-up reactor concepts with enhanced safety, non-proliferation and optimised fuel cycles, e.g. the US Department of Energy Generation IV and IAEA INPRO international projects. At the same time, there is an increasing world-wide awareness of the likely detrimental effects of greenhouse gas emissions on global climate change and a concern for limitation of such emissions. A recommendation in mid-2001 by the US National Energy Policy Development Group for re-examination of policies to allow for R&D of fuel conditioning methods (such as pyroprocessing) and consideration of technologies (in collaboration with international partners) to develop reprocessing and fuel treatment technologies provides strong political support for US laboratories to broaden their collaboration with international organisations possessing needed expertise and capabilities.

### **Current and past international collaborations in pyrochemical processing**

A substantial level of international co-operation in pyrochemical processing of nuclear materials has been carried out over the past several years, over and above the numerous international conferences that have covered the topic in various ways. A partial compilation of collaborative activities, on a country-by-country basis, appears in the following paragraphs.

#### **CZECH REPUBLIC**

The present research and development activities in the field of pyrochemical and pyrometallurgical separations of irradiated fuel derive from previous research and development activities in the former Czechoslovakia during its participation in the former Soviet Union Fast Breeder Reactor Programme.

In the 1970s and 1980s, the Nuclear Research Institute Rez plc (NRI Rez plc) took part in the bilateral Czechoslovak/Soviet Union co-operation concerning the development and verification of dry reprocessing technology for fast breeder reactor irradiated fuel. The development was motivated by the projected commercial utilisation of fast breeder reactors whose application in the power industry could be economically efficient only in the case of a closed fuel cycle. Therefore, countries that were planning the introduction of fast breeder reactors sought to develop suitable methods for reprocessing because the hydrometallurgical PUREX process was not well-matched to reprocessing short-cooled fuel.

One of the alternative methods, under development in the former Czechoslovakia in the 1970s and 1980s, was the Fluoride Volatility Process, involving the separation of uranium and plutonium (in the form of volatile hexafluorides) from fission products, the majority of which form non-volatile fluorides. The process was developed in the former Czechoslovakia in co-operation with the Soviet Union, under the agreement between the former Czechoslovak Atomic Energy Commission and the State Commission for Atomic Energy of the USSR. The Nuclear Research Institute Rez plc was the contractor for the Czechoslovak side and the Kurchatov Institute (Moscow) and the Research Institute of Atomic Reactors (Dimitrovgrad) were the contractors for the Soviet side. In the second half of the 1970s, work on development and realisation of the pilot-plant technological line, called FREGAT-2, was started. The line was intended to verify fluoride volatility technology by means of experimental reprocessing of irradiated fuel from the Russian research fast reactor BOR-60. Practically all of the equipment and apparatus of the FREGAT-2 line was designed and manufactured in the former Czechoslovakia, tested in the Nuclear Research Institute Rez plc, and then moved to the hot cell of the Research Institute of Atomic Reactors, Dimitrovgrad, for complex technological validation. Although the joint experimental programme on the FREGAT-2 line was stopped in 1988 (after the Chernobyl accident and re-evaluation of the fast breeder reactor programme in the former USSR), leaving the verification programme uncompleted, the functionality of the majority of apparatus, equipment and technological operations was confirmed.

At present, research and industrial organisations in the Czech Republic use the previous fluoride volatility process experience in the national programme of partitioning and transmutation technology development and in international co-operation in areas of partitioning and transmutation which are in good agreement with the Czech national programme concept. Pyrochemical and pyrometallurgical separation methods are part of the focus of interest.

The Czech national concept of partitioning and transmutation, as a basis for national R&D and international co-operation, was set up during the 1995-1998 period. The concept is founded on the belief in future use of transmutation reactors with fluoride-salt based liquid fuel (molten salt transmutation reactors). The fuel cycle is based on pyrochemical and/or pyrometallurgical fluoride partitioning of irradiated fuel. The Czech Republic, as a relatively small country, is conscious of the necessity of wide co-operation in international R&D as the only possibility of realising this concept.

Besides non-contractual co-operation with many foreign research institutions in the field of information exchange, there are two important collaborating partners at present: EC/EURATOM and RRC-Kurchatov Institute

### **Co-operation with the European Commission/EURATOM (multilateral international activity)**

In association with other European research institutions, the Nuclear Research Institute Rez plc is taking part in the pyrometallurgical processing research programme (PYROREP) project of the 5<sup>th</sup> Framework Programme of EC/EURATOM. The project started in 2000 and represents an R&D programme to provide sufficient basic data to establish and assess pyrometallurgical processing flow sheets as suited to advanced fuel cycles and designed to minimise the radiological impact of nuclear waste. NRI Rez plc is performing experiments mainly for the development of pyrochemical/pyrometallurgical separation methods using molten fluoride salt media.

The second relevant EC/EURATOM project, a review of molten salt reactor technology (MOST), involves twelve European research institutions and companies and will be completed in late 2003. The project includes pyrochemistry and pyrometallurgy. NRI Rez plc is performing a significant part

of the compilation of the review and analysis of fuel processing and waste form studies for the molten salt reactor. The study will include comparisons and designs of several suitable pyrochemical and pyrometallurgical technologies for fuel cycles of molten salt reactors.

### **Co-operation with Russia (bilateral international activity)**

The historical experience of Russian institutions in several areas of dry separation technologies, including fluoride volatility and molten salt chemistry, has been a good basis for the present co-operation between the Nuclear Research Institute Rez plc and the RRC Kurchatov Institute, Moscow, in the research field of neutron characteristics of actinides, transmutation reactions and chemical analysis following actinide transmutation. The objective of the joint “Ampula” experiment is the investigation of the behaviour of actinides in the fluoride melt medium during their transmutation in thermal and fast neutron spectra and the subsequent chemical analysis of the transmuted elements using pyrochemical or pyrometallurgical separation methods. The planned duration of the project, launched in early 2001, is three years. The first year was devoted to design and manufacture of the specialised and highly equipped probe (“Ampula”) and to carrying out preliminary irradiation experiments. The next two years were devoted to transmutation experiments, performing chemical analysis (after the necessary cooling period), and using these results for pyrochemical and pyrometallurgical separation studies.

### **Co-operation with OECD/NEA**

The Czech Republic, as a member country of the OECD/NEA, has a representative on the Nuclear Science Committee and is active in the working parties and working groups of this committee that have a focus on partitioning by means of pyrochemical separations.

## ***EUROPEAN COMMISSION***

Work sponsored by the European Commission has been performed at the Joint Research Centre-Institute for TransUranium elements (JRC-ITU), henceforth referred to as ITU, which is a part of the European Commission and located in Germany. At the present time, there are no other activities in this field in Germany. ITU's current activities in this field are a part of the overall research in the field of partitioning and transmutation and considered complementary to advanced aqueous separation methods of transuranics.

In the 1980s, ITU started collaboration with CRIEPI to develop a fuel cycle for a metal-fuelled fast breeder reactor. Minor actinide-containing fuels were developed and metal test fuels were fabricated to study fast breeder transmutation of transuranics. The latter are at present under irradiation in the PHENIX reactor in France. Scrap material from the fuel fabrication is being used for electrorefining tests following the pyrochemical process developed by ANL and CRIEPI. To accommodate these experiments a pilot electrorefiner, installed in a hot cell, has been put into place and the first active electrorefining separation tests have started.

### **Multilateral international collaborations: PYROREP**

Under a European Commission Shared Cost Action programme, pyrochemical separation of minor actinides from irradiated metal fuel, from targets or from reduced oxide fuels is being studied. The programme, known as the Pyrochemical Processing Research Programme (PYROREP), extended over three years and was finished at the end of 2003. Partners in the programme include research

organisations in France, Italy, Spain, UK, Czech Republic and the EU-CRIEPI collaboration. The major objective of the programme was to yield sufficient basic data to assess and propose pyrochemical flow sheets for irradiated materials. The programme was divided into three work packages, carried out by six major European laboratories and an associated Japanese laboratory:

- *CEA*, Commissariat à l'Energie Atomique in France;
- *CIEMAT*, Centro de Investigaciones Energéticas Medioambientales y Tecnologicas of Madrid in Spain;
- *ENEA*, Ente per le Nuove Tecnologie l'Energia e l'Ambiente in Italy;
- *BNFL*, British Nuclear Fuel Limited in Great Britain;
- *NRI*, Nuclear Research Institute Rez plc in the Czech Republic;
- *ITU*, Trans Uranium Institute (Joint Research Centre, Karlsruhe, Germany) and CRIEPI (Central Research Institute of Electric Power Industry of Japan) which is not funded by the European Union but is fully associated with the actions undertaken by ITU.

The total cost of the project was 3.6 M € for a three-year duration (September 2000-August 2003) co-funded by the European Community (50%) and by each laboratory (50%). The objective of this project was to determine the practicalities of separating uranium, plutonium and minor actinides from fission products from an irradiated fuel or target (metal or oxide fuel form), using pyrochemistry. This joint effort contributed to the consolidation and revival of European expertise in this field.

The PYROREP programme explored the most promising options: separation by salt/metal exchange and separation by electrolysis. The purpose of this contract was to build on the technologies based on chloride media, to assess the feasibility of using fluoride media, and to demonstrate process parameters for the separation of the minor actinides and plutonium from fission products. This integrated R&D programme yielded sufficient basic data to establish and assess pyrometallurgical processing flow sheets suitable for use with advanced fuel cycles designed to minimise the radiological impact of nuclear waste. It addressed, furthermore, the objectives of the work programme concerning the safety of the fuel cycle (partitioning and transmutation).

Within the scope of the PYROREP contract, substantial progress was made; e.g. many basic data values concerning the behaviour of fission products and actinides (U, Pu, and Am) in molten salts and metals were measured for the first time or confirmed in both fluoride and chloride media. The main R&D focus of the PYROREP contract was on the separation step, which represents the core of the future pyrochemical separation process(es). In fluoride media, the investigation of reductive salt/metal extraction yielded very promising results for both actinide recovery and fission product decontamination yields. For electrolytic processes in chloride media it has been shown that, from the strict standpoint of actinide/lanthanide separation, an aluminium cathode would provide better results than a cadmium cathode, although the latter could be used if it is not indispensable to recover and separate the actinides from the lanthanides with very high efficiency. Development work should be carried out on the use of an aluminium cathode to take advantage of these potentially interesting results.

The data acquired to date are sufficient to begin designing and quantifying preliminary schemes for reprocessing methods. From the standpoint of a fuel cycle policy based on partitioning and transmutation (P&T), effective implementation will require not only a very high actinide recovery factor (typically 99.9%), but also sufficient fission product decontamination to recycle less than 5% of the initial negative reactivity of the fission products with the actinides.

In the beginning of 2004, a new project called EUROPART was launched, wherein both aqueous and pyroprocessing methods will be investigated in parallel. The total duration of the project will be 36 months. The research on the pyrometallurgy part is organised in four work packages. The subjects of these work packages are the following: (1) two work packages concern the development of actinide partitioning methods, and one of these two work packages (i.e. WP7) also includes the study of the basic chemistry of trans-curium elements in molten salts; (2) one work package concerns the study of the conditioning of the wastes; and (3) the last work package is dedicated to systems studies. Moreover, a strong management team will be concerned not only with the technical and financial issues arising from EUROPART, but also with information and communication, science and society, gender issues and benefits for Europe. Training and education of young researchers will also constitute an important part of the project. Processes for possible industrialisation of partitioning strategies will be defined as part of the project.

### **Multilateral international collaborations: ISTC**

The European Commission, which is part of the International Science and Technology Centre (ISTC), is involved in examination of molten salt nuclear fuel as an actinide burner (transmuter) reactor concept.

### **Bilateral international activities**

The above-described collaboration with CRIEPI aims to demonstrate the feasibility of pyrometallurgical processes for separating actinide elements from actual irradiated fuel and HLW. This joint study is described in detail under the Japanese contribution. With ENEA (Italy), a study is foreseen to use the CRIEPI process for pyrochemical reprocessing of Th-based fuels.

## **FRANCE**

### **Principal areas of research**

The main broad areas within the French national programme are those of examining alternative methods of management of high-level wastes as put forward under the radioactive waste law of 1991 and providing R&D on fuel cycles to support nuclear energy for the future. One of the options for the former is pyrochemical separations for partitioning and transmutation, while for the latter recycle of thermal or fast high burn-up gas reactor fuels has been raised as a promising possibility. Several areas of research have been identified for collaborative efforts:

- assessment of separation performance (recovery yields, separation factors, etc.);
- fundamental or basic research, including both theoretical and experimental work;
- process engineering, for the development of new process flow sheets, for the purpose of comparative evaluation of test results obtained for the processes considered as “systems”, i.e. including assessment of secondary operations such as feed material preparation and secondary liquid and solid waste management;
- technical and technological research, notably (a) to select materials used to fabricate the process equipment and (b) to design and build equipment for laboratory- or pilot-scale testing.

Partners for these research topics are selected with a view to maximum efficiency by consulting the most competent organisations in the field. International collaboration within the scope of European research programmes appears necessary and is supplemented by individual agreements with various countries that have established expertise in this area: USA, Russia, Japan, Spain and ITU within the frame of the 5<sup>th</sup> Framework Programme funded by the European Union.

In France, collaboration is encouraged with laboratories operated by the CNRS, universities and engineering schools specialised in this area, notably within the GEDEON and PRACTIS research groups.

### ***The GEDEON research group***

The GEDEON research group, supported by CEA, CNRS, EDF and FRAMATOME-ANP was firstly oriented on the innovative systems for transmutation like minor actinides burners and long-lived fission product transmutation, including physics, design evaluation and optimisation of the core, spallation target, scenario analysis for plutonium management or thorium cycle, materials behaviour and corrosion resistance. The frame was open to the innovative systems, mainly Generation IV selected concepts such as gas-cooled reactors with thermal or fast neutron spectrum (HTR and GFR), molten salt reactors (MSRs) and also to hydrogen production. GEDEON organised workshops open to international scientists, and offered support by funding activities from laboratories for experiments or studies in the field of physics, scenarios, materials, corrosion resistance. The activities of the GEDEON research group are currently ongoing under the new label GEDEPEON.

### ***The PARIS research group***

The PARIS research group, previously named PRACTIS, backed by the CEA/DEN, CNRS/DSC, CNRS/IN2P3, EDF and ANDRA, has been active since 1995. Its mission was recently renewed for another four-year period (2003-2006) with the objective of co-ordinating various French research activities on the basic chemistry of the radionuclides found in spent nuclear fuel, undertaken in the context of the 1991 law. PARIS research topics include the following:

- physics and chemistry of radionuclides at the liquid-solid interface;
- modelling;
- physics and chemistry of radionuclides in solution and liquid-liquid transfer;
- molten salts and pyrochemistry;
- radiolysis;
- database.

Pyrochemistry research is related to all of the above topics.

It is considered important to establish a precise knowledge of solvated species, actinides and other radionuclides in various molten salts comprising molten oxides or halides and RTILs, so as to study phenomena related to liquid-liquid and liquid-solid transfer.

The following studies are carried out in this context:

- structure of solvated species;
- thermodynamic potential diagrams  $f(pX^{n-})$  for  $X = \text{oxygen or halide}$ ;
- temperature effects;
- deviations from ideality;
- ligand exchange and redox kinetics;
- molecular modelling of solvated entities and modelling of complex liquids by statistical physics methods;
- thermodynamics and kinetics of exchanges between the actinides and other radionuclides between molten salt and metal baths;
- phenomena occurring at the liquid-liquid interfaces;
- molecular modelling of entities at the interfaces and modelling of equilibria between phases;
- spent fuel or target dissolution mechanisms in molten salts;
- actinide electrodeposition mechanisms during electrolysis in molten salt media.

The French scientific community is increasingly co-ordinated in this area, as illustrated by the dedicated workshops which have been organised:

- joint workshop PRACTIS-GEDEON (16-18 September 98) in Pantin;
- workshop PRACTIS (31 May 99) in Villeneuve-lès-Avignon;
- workshop PRACTIS (22 May 01) in Orléans;
- joint workshop PRACTIS-GEDEON (19-20 June 02) in Cadarache.

## **Current international collaborations**

### ***Co-operation with the European Commission***

The CEA, in association with five other European research organisations under the 5<sup>th</sup> Framework Programme for Technological Research and Development (PCRD), is co-ordinating the PYROREP contract for R&D on pyrometallurgical reprocessing, including both conceptual studies and experimental work. This contract started in September 2000 (36 months long). Many aspects of the thermodynamics of actinides in metal and salt media are insufficiently documented and it is not possible at this time to compute operational process flow sheets suitable for new fuels. It is now necessary to undertake a major experimental programme to acquire the missing basic data. The programme therefore is broken

down into three closely related work packages (WP), each of which dedicated to homogeneous part of the research programme:

- WP1 assesses the possibility of separating the actinides and lanthanides by two methods, salt/metal extraction and electrorefining either on solid or liquid cathodes. CEA will perform investigations regarding molten fluorides.
- WP2 incorporates some of the steps necessary to implement separation processes such as salt decontamination. The goal of the CEA is to study the recovery of actinide traces contained in spent fluoride salts by reductive extraction.
- WP3 is dedicated to waste and system studies. CEA will perform leaching tests on sodalite prepared by ENEA. It also will participate in system studies in which the processes selected in the whole proposal will be compared and evaluated through the close collaboration of the participants with regard to segregation factors, decontamination factors, final product compositions and characteristics, recycling of reactants and waste amounts.

The experiments undertaken by the CEA are performed on radioactive materials at the ATALANTE facility (Marcoule site).

### ***Co-operation with Russia***

The Research Institute of Atomic Reactors (RIAR) in Dimitrovgrad, in association with the High-temperature Electrochemistry Institute of Ekaterinburg, long ago developed a novel oxide fuel cycle up to the prototype stage, based on fuel fabrication by vibrocompaction with pyrochemical reprocessing. Since the early 1990s, RIAR has been promoting this fuel cycle under the DOVITA programme (*Dry reprocessing of Oxide fuel with Vibropacking for Transmutation of Actinides*). As such investigations interest CEA, a general agreement on pyrochemistry has been signed with this Russian nuclear centre (May 2001). Topics of interest include fundamental studies in molten chlorides, enhancement of the performances of RIAR process with regard to new chemical and technological considerations, reprocessing of irradiated targets and exotic fuels, and waste treatment. As part of a study of americium recycling as targets in dedicated reactors, interest has grown in assessing the feasibility of a complete fuel cycle based on the fabrication of vibrocompacted targets (ViPac process) with pyrochemical reprocessing of the targets. The signature of a research contract between RIAR and CEA acting on behalf of ITU is underway. The initial phase of this programme covers the design, fabrication, irradiation and examination of the targets. The second phase will deal with processing of the targets. Reprocessing investigations will be focused on Am/rare-earth element (and matrix material) separation by selective precipitation in molten chlorides. In the 1990s, there was also a collaborative programme between CEA and RIAR concerning pyrochemical procedures for the conversion of military-origin metallic Pu into MOX. Finally, the Arzamas Centre and the Kurchatov Institute, under the auspices of the International Science and Technology Centre (ISTC project # 1606), proposed an evaluation of fundamental and applied research for molten salt reactors (with an epithermal or thermal neutron spectrum and a high TRU mass fraction) as a possible dedicated reactor for the second stratum. Expected results include:

- a database of the properties of fluorides with actinides (review of salt properties, phase diagram, Pu and minor actinide solubility, viscosity, conductivity, vapour pressure, redox potentials, etc.);
- preparation of molten salts, purification and means for determining impurities;

- behaviour of structural materials (graphite and Hastelloy-N) including experimental characterisation with salts;
- investigation of salt treatment, LLFP separation and secondary waste processing;
- preliminary characterisation of a concept with a process flow sheet;
- preliminary assessments of economic feasibility, proliferation and licensing.

A thermo-siphon loop will be built to test material specimens for up to 1 000 hours and measurements will be performed with plutonium and other TRUs. This unique three-year programme is backed by the European Commission, the CEA, EDF, KTH, FzK; it started in mid-2001.

### ***Co-operation with Japan***

Possibilities exist for co-operation on pyrochemistry under the bilateral programmes set up between the CEA and JAERI and between the CEA and JNC. JAERI has proposed and adopted the “double-strata” strategy based on transmutation in dedicated sub-critical (or possibly critical) reactors using nitride fuel and a pyrochemical process. Currently, scientific data of mutual interest are exchanged during annual CEA/JAERI meetings (alternately in France and Japan). JNC has adopted a transmutation strategy based on homogeneous recycle in fast neutron reactors burning oxide fuel. Fuel treatment processes now being investigated include the pyrochemical processes developed by RIAR and the CRIEPI version of the Argonne process (JNC is considering both processes). CEA has sought a close association with JNC for the analysis of both options, as the results are of obvious interest with regard to the CEA work.

### ***Co-operation with the USA***

An umbrella bilateral nuclear R&D agreement was signed between the CEA and the USDOE in Vienna in September 2000 and research grants were awarded to joint French-US teams in 2001. The Administrator General of CEA and Chairman of AREVA, M. Pascal Colombani, signed a bilateral agreement in July 2001 with the US Secretary of Energy, Mr. Spencer Abraham, concerning innovative reactors and fuel cycles. Research and development on accelerator-driven systems, pyroprocessing and partitioning are likely to be carried out under this agreement. Co-operative programmes with the United States could focus on the processes developed at the Argonne National Laboratory and on advanced fuel cycle chemistry within the scope of DOE-CEA bilateral co-operation in Advanced Nuclear Reactor Science and Technology (recently discussed in March 2001) with the Generation IV/I-NERI initiative. Joint topics deemed to be of the greatest priority are processability evaluation, electrorefining technology, instrumentation, fission product chemistry in molten salts, and TRISO fuel processing. Detailed programme co-operation is under discussion.

### ***Co-operation with Spain***

The objective of this bilateral agreement on pyrochemistry (five years in duration) is to get basic thermodynamic data on long-lived radionuclides and awkward fission products in molten chlorides. CEA will set up E-pO<sup>2-</sup> diagrams concerning actinides. Complementary studies on electrodeposition and salt decontamination will be focused on actinide behaviour.

## **ITALY**

Since 1995, there has been an increasing interest in Italy in accelerator-driven system (ADS) concepts. An industrial programme involving the ENEA (the Italian national research body for energy, environment and new technologies), INFN (the Italian national research institute for nuclear physics), and various industrial partners has been started together with several basic R&D activities that are being performed on an international collaborative basis. The national R&D programme TRASCO (Italian acronym standing for waste transmutation – TRAnsmutazione SCOrie) commenced in 1998 as a first step under the leadership of INFN for the accelerator and of the ENEA for the sub-critical system. Supporting R&D, including the fuel and fuel processing for waste transmutation in the experimental ADS and in the industrial transmuter is being performed under international collaborative arrangements.

### **Present international activities**

#### ***Collaboration with JRC-ITU***

In a bilateral joint research project between ITU and ENEA, a study is foreseen to use the CRIEPI process for pyrochemical separation in NaCl-KCl of the homogeneous oxide fuel for thorium high-temperature reactor (THTR) fuels as simulated by  $(\text{Th}, \text{U}, \text{Pa})\text{O}_2$ . The study will deal mainly with the electrochemical behaviour of protactinium. This study has not yet started.

#### ***Collaboration with CRIEPI***

Starting from 2002, CRIEPI and ENEA will co-operate on modelling studies on actinide and lanthanide elements in a pyrometallurgical process, using the TRAIL code developed by CRIEPI.

#### ***Collaboration within the EU***

ENEA and Politecnico di Milano participated in the PYROREP project of the 5<sup>th</sup> Framework Programme for the Technological Research and Development of the European Union.

### **System and performance assessment for pyrometallurgical processes (with CEA, NRI)**

This task is intended to assess the feasibility of one or more of the pyroreprocessing concepts (electrorefining or salt, liquid metal extraction). These processes would be suitable for oxides or metal fuels, targets with inert matrix and PUREX calcines. A system and performance assessment study will be performed for these processes; this task will estimate recycling of reactants, off-gas treatment, final products and the quantities and characteristics of the process wastes.

## **JAPAN**

Pyrochemical processes are included in many of the recently proposed novel nuclear fuel cycles and the international connections of the principal Japanese R&D institutes in this area are described below.

### **CRIEPI collaborative programmes**

CRIEPI is taking part in the Japanese feasibility study for the development of a safe and economic fast reactor and fuel cycle system for electrical and/or other energy generation including minimisation

of environmental impact through the recycle of long-lived radionuclides. CRIEPI also participates in the Japanese OMEGA programme, which is long-term research and development on partitioning and transmutation technology for minimisation of long-lived wastes from thermal reactors. Under these programmes, CRIEPI focuses on the research and development of pyrometallurgical process technology for the metal-fuelled FBR cycle and on the pyro-partitioning of transuranium elements from high-level liquid waste (HLLW) coming from PUREX-type reprocessing, which could contribute to a reduction of long-term radiotoxicity of transuranium elements. Collaborations with JAERI, Kyoto University and overseas institutes, Argonne National Laboratory, Missouri University, AEA Technology and the Institute for Transuranium Elements, help to provide experimental information concerning actinide behaviour. A co-operative study with JNC is also underway.

### ***Collaboration with the United States***

- DOE (1989-1995):
  - took part in the IFR project as devised and carried out by ANL;
  - obtained technical and engineering information on electrorefining, cathode processing, injection casting and other associated operations.
- Boeing (formerly Rockwell International)/Missouri University at Columbia (1988-1998):
  - measurement of thermodynamic data and distribution coefficients of U, TRU and lanthanides in LiCl-KCl/Cd and LiCl-KCl/Bi systems;
  - confirmation of TRU partitioning from high-level wastes simulated composition using transuranics at milligram scale.

### ***Collaboration with the United Kingdom***

- AEA Technology (1997-2000):
  - obtained the data of lithium reduction on actinide oxides and MOX.

### ***Collaboration with EU (ITU) (1998-present)***

Collaborative projects include:

- installation of a semi-hot experimental facility;
- confirmation of performance of devices for electrorefining, reductive extraction, distillation and chlorination by use of actual materials such as irradiated fuel and HLLW;
- validation of the predicted process flow sheets;
- measurement of characteristics of metal fuel with minor actinides and irradiation testing (1990-present, fuel irradiation began in the CEA PHENIX reactor in January 2004).

### ***Collaboration with ENEA (2001-present)***

- Co-operation on electrorefining, other devices and computer simulation.

### ***Collaboration with EU (2000-present)***

- Participation in the 5<sup>th</sup> and 6<sup>th</sup> Framework Programmes of EU, PYROREP (2000-2003), and EUROPART (2004-2007), together with ITU.

### **JAERI collaborative programmes**

JAERI has investigated minor actinide (MA) partitioning and transmutation (P&T) through the use of nitride-fuelled accelerator-driven systems (ADS) and pyrochemical processes. Although JAERI realises the importance of international collaboration in the field of pyrochemical separation, present activity is limited. In the area of pyrochemical separation, bilateral collaborations with CEA (France), NRG (The Netherlands) and BNFL (United Kingdom) have been carried out. However, the basic subject is addressed, not necessarily technological processes.

JAERI and CEA have a general co-operation agreement in the field of nuclear research and development. In the fuel cycle area, there is a co-operation agreement on radioactive waste and irradiated fuel management and one of the Specific Topics of Co-operation (STC) concerns the pyrochemical process. Areas of co-operation cover (1) exchange of information on pyrochemical process concepts for treating specific irradiated fuels and/or high-level wastes in the frame of long-lived radionuclide management; (2) exchange of information on basic studies supporting the process developments; (3) joint efforts to enlarge the molten salt database for nuclear applications, including laboratory-scale experiment; (4) exchange of staff. This collaboration has been in force since 1999. Annual meetings for information exchange in the field of pyrochemical separation have been held in Japan and France. Exchange of staff is being planned.

In 1999, JAERI and NRG signed a co-operative agreement regarding partitioning, transmutation and associated advanced technologies. Fundamental thermochemical data related to pyrochemical separation are included in this agreement. As items and activities, the joint experiments/assessments are made on thermochemical properties of selected compounds of interest in P&T; JAERI will supply either the actinide salt samples or the information on fabrication procedures of the samples, and NRG will perform the thermodynamic property measurements. In 2000, JAERI fabricated some chloride salt samples and shipped them to NRG, who measured their thermodynamic properties (enthalpy of solution, heat capacity and so on). Staff from JAERI also took part in the measurements at NRG and the results are presented under co-authorship.

Although there is no specific agreement between JAERI and BNFL in the area of pyrochemical separation, JAERI has been accepting BNFL staff since 1999 based on a visiting researcher programme. The BNFL staff member is involved in the JAERI P&T programme, nitride/pyroprocess. In 1999 and 2000, the BNFL scientist carried out experiments on the electrochemical behaviour of lanthanide nitride in chloride molten salt. The results are presented under co-authorship.

### **JNC collaborative programmes**

The Japan Nuclear Cycle Development Institute (JNC) is leading the feasibility study in Japan concerning development of a fast reactor (FR) and fuel cycle system. The study includes the support

of ten Japanese utilities, CRIEPI, JAERI, commercial industry and universities. Additional technical support is sought from overseas. The key targets for a commercialised system are: safety, economic competitiveness, efficient utilisation of uranium, reduced environmental impact and enhanced nuclear non-proliferation. During Phase I (JFY1999-2000), technologies were surveyed widely and conceptual designs were assessed against targets. Further design studies and engineering-scale tests of prime technologies will be performed in Phase II (JFY2001-2005). JNC is assessing four main technologies for reprocessing FR fuel: advanced PUREX, oxide-electro-winning, metal-electrorefining and fluoride volatility. These are integrated with candidate fuel fabrication technologies such as simplified pellet and spherepac/vibropack for MOX/metal nitride fuels and casting for metallic fuel. The cost target is ¥ 0.43 M/kg(HM) (~\$3 600/kg) including reprocessing, fuel fabrication and HLW immobilisation. The target for reprocessing only is ¥ 0.27 M/kg(HM) (~\$2 200/kg). Preliminary results of cost studies show that several plant types meet these targets at 200 tonnes (HM) per year capacity, while only one does so at 50 tonnes (HM) per year capacity.

JNC has implemented collaborations with France (CEA) for advanced processing technology; Russia (RIAR) for dry processing and safe disposition of plutonium as MOX fuel, with the UK for technical co-operation across the advanced fuel cycle field (BNFL) as well as for advanced technology (AEA Technology), and with the USA (DOE/JNC Agreement in the Field of Nuclear Technologies).

### **Japanese collaboration with RIAR**

Over the period 1990-2000, the Japanese utilities (ten electric power companies) have collaborated with the Research Institute of Atomic Reactors (RIAR) at Dimitrovgrad, Russian Federation. The work also included the Japanese companies Toshiba and Marubeni. These studies concerned the Dimitrovgrad Dry Process (DDP), which is an integrated process for the recycling of oxide fuel in particular, using oxide-electro-winning in molten salt within a pyrographite electrolyser. The recovered products ( $\text{UO}_2$ ,  $\text{PuO}_2$  and MOX), are fabricated remotely into fresh fuel using simplified techniques such as "vibropac". Studies in collaboration with RIAR also considered variations on existing flow sheets to suit Japanese objectives.

Japan has carried out design studies based on the above process, in collaboration with RIAR and in test work with simulants. Using  $\text{UO}_2$  and  $\text{CeO}_2$ , tests of simultaneous chlorinative dissolution and anodic dissolution with cathodic deposition of  $\text{UO}_2$  suggest the validity of this approach as concerns reduction of chlorine use and improving kinetics. The most recent Japanese design is based on MOX electro-co-deposition, which is considered more proliferation resistant. Other design aims have included increasing equipment scale, simplification of electrolyser operations, and shortening of cycle time. Additionally, Toshiba has carried out design studies for a fast reactor fuel reprocessing plant using "simultaneous" dissolution and  $\text{UO}_2$  electro-deposition operations coupled with MOX production by electro-co-deposition.

RIAR and JNC are collaborating on the design and installation of equipment at RIAR for the fabrication of Vipac fuel by the molten salt oxide electro-winning process using electro-co-deposition of MOX. This is done with the goal of converting the Russian BN-600 commercial fast reactor core to mixed oxide fuel for the safe disposition of surplus Russian weapons plutonium. This work is also in collaboration with the USDOE. Future collaboration studies with RIAR are likely to be carried out under the JNC-led Fast Reactor and Fuel Cycle Feasibility Study, which entered its second phase in early 2001. This study includes Japanese utilities, CRIEPI, JAERI, industrial companies and universities.

## **REPUBLIC OF KOREA**

Korea is operating a substantial nuclear power generation programme and has accumulated a significant amount of irradiated fuels. However, it has no recycle activities in the back-end of the fuel cycle; all irradiated fuel is currently stored in pools and silos at the four reactor sites. This is based on the background of a governmental policy of “wait & see” for irradiated fuel management. While no definitive back-end fuel cycle policy has been made, the near-term irradiated fuel management plan is that the irradiated fuel is to be transferred to a central interim storage facility, which is scheduled for construction by 2016. This plan stems from the limited irradiated fuel storage capacities of the existing power plants. Many people in Korea, particularly those belonging to environmental movement groups, are deeply concerned with the possible environmental impacts triggered by underground disposal of irradiated fuel in the future. They expect the development of a more reliable solution. Though not yet developed for commercial use, nuclear transmutation is seen as a proper option for future irradiated fuel management. It may be an efficient way to relieve the risks of radiological contamination of the environment caused by potential release of long-lived radionuclides from geological repositories. Because transmutation is an integral part of the partitioning and transmutation cycle where long-lived radionuclides must be recycled, partitioning is an essential procedure to complete transmutation.

Recently, pyrochemical separation, though it is still in the R&D stage, has been attracting great interest as a prospective method of partitioning long-lived radionuclides because of perceived advantages over wet processes, especially in terms of proliferation resistance and economy. KAERI's long-term R&D programme envisions the development of a partitioning and transmutation cycle based on a hybrid transmutation system and pyrochemical separation. As KAERI gives priority to proliferation-resistance, pyrochemistry seems to be a favoured technology, well suited for this purpose. However, having such limited activities in the area of the back-end of the fuel cycle, KAERI is eager to join international collaborative programmes in order to resolve irradiated fuel issues in common with other countries.

## **Collaborative study between KAERI and AEA Technology**

KAERI conducted a joint study with AEA Technology (AEAT) of the UK during the period August 2000-March 2001 in the area of molten salt electrolysis. This study was aimed at investigating the decomposition behaviour of metal salts in eutectic salt, FLINAK (LiF-NaF-KF) which has a eutectic point of 456°C at the composition of 46.5-11.5-42.0 mole-%, respectively. The voltammograms of representative transuranium (Np, Pu) and lanthanide (Nd, Gd) materials, and mixtures of these components, were obtained at 500°C. Since the decomposition potential of each metal fluoride during electrolysis is dependent on its Gibbs free energy of formation, the examination of decomposition behaviour of metal salts provides valuable information for the design of an electrolysis system. In addition, this information gives suitable conditions for selective deposition of such metals at the cathode. The experimental results have yet to be analysed. However, further studies seem to be required in order to determine an appropriate operational range to achieve a controlled deposition of relevant metals because the decomposition potential of each metal fluoride tends to vary with the composition of molten salt. In conjunction with this study, some specific works for further studies are described below. Though some of these topics may have already been touched upon in foreign laboratories, the results have not been reported sufficiently. Much fundamental work needs to be done before formulating an optimal pyrochemical separation process, including:

- examination of dual cathode behaviour in the molten salt electrolysis system;
- comparison of different molten salt media in the electrolysis system;
- comparison of different metal solvents as a cathode material;

- treatment of a liquid cathode in order to remove cathodically-deposited material;
- measurement of distribution coefficients of transuranium and lanthanide elements in different combinations of molten salts and metal solvents;
- development of an ideal electrolysis system.

### **Collaborative study between KAERI and RIAR Dimitrovgrad**

A co-operative programme is underway between KAERI and RIAR Dimitrovgrad, on the basis of the ISTC programme, in the area of uranium dioxide reduction using liquid lithium. A new concept for LWR irradiated uranium fuel storage has been developed at KAERI. This process consists of oxidation of irradiated PWR fuel by air during fuel de-cladding, the reduction of oxidised irradiated PWR fuel powder by molten lithium, lithium recovery from spent salts by electrolysis, casting of reduced irradiated fuel into metallic ingots, followed by the encapsulation and the dry storage of the rods. The SSC RIAR has been co-operating with KAERI since 1999. Under the joint ISTC Project (in co-operation with KAERI), construction of a non-radioactive facility has been under way since 2000 for process and equipment prototype studies using simulant materials. The mock-up facility was put into operation in the summer of 2001. The purpose of the work with un-irradiated fuel is in preparation for hot experiments on the lithium reduction of real irradiated fuel at the facility in the RIAR shielded cell K-16. The mock-up facility is a shielded stainless steel box equipped with standard manipulators, special ventilation and waste systems, that it makes possible to work with 5-10 kg of naturally occurring or depleted uranium. The box is placed in a full-size mock-up of the shielded cell K-16.

### **DUPIC programme**

*Direct Use of irradiated PWR fuel In CANDU reactors (DUPIC) technology is the fabrication of CANDU fuel from irradiated PWR fuel through a dry process, which deliberately avoids separation of fissile materials. At first, the irradiated PWR fuel is disassembled and then de-clad to retrieve the fuel material. The irradiated fuel material is treated by repeated cycles of oxidation and reduction, named the OREOX process, to make the irradiated fuel material finer and 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 assembling, except that all the steps must be remotely performed inside a hot cell. International collaborative research on dry recycling technology for irradiated nuclear fuel was first proposed by KAERI at the Joint Steering Committee on Nuclear Energy Co-operation between Korea and the USA in 1991. The dry recycling technology was termed “DUPIC” at the first joint meeting among KAERI, AECL of Canada and the Departments of State and Energy of the USA in 1991. The Phase I study on the feasibility of DUPIC fuel was performed over 1991-1993. Based on the results of the feasibility study, the OREOX (oxidation and reduction of oxide fuel) process was selected as a most promising fabrication method, and the safeguard ability of the DUPIC process was evaluated. The Phase II study on the experimental verification of DUPIC fuel performance continued from 1993-2002. In the Phase II study, several DUPIC pellets and elements were fabricated in the hot cells of KAERI and AECL. They are currently under irradiation test for the evaluation of performance at the Hanaro and NRU research reactors of KAERI and AECL, respectively. Furthermore, safeguards technology development and a compatibility study with the CANDU reactor system are being performed in a co-operation among KAERI, AECL and Los Alamos National Laboratory of the USA.*

The Phase III study on the demonstration of DUPIC fuel performance is planned to proceed from 2002-2007. More DUPIC pellets and elements will be fabricated using irradiated PWR fuel during Phase III, and various characteristics of the DUPIC fuel will be analysed. Also, further application of proliferation-resistant dry recycling technology, which is based on the DUPIC process, will be assessed.

## **RUSSIAN FEDERATION**

The future of nuclear power depends to a great extent on how efficiently its fuel cycle is organised with regard to both cost effectiveness and environmental safety. The back-end of the fuel cycle, including chemical processing of irradiated fuel, remains the most complex and least acceptable link due to the high radioactivity of the materials to be managed. In the commercial nuclear sector, light water reactors produce most of the electricity generated and their irradiated nuclear fuel is either stored or reprocessed using the PUREX process. However, alternative non-aqueous technologies do exist.

The September 2000 Initiative, launched by President Putin, concerns international development of a new nuclear reactor and fuel cycle concept. Also in the year 2000, IAEA established an international project on innovative reactors and fuel cycles, called INPRO. Russia is among the INPRO member countries. The main purpose is to enable nuclear energy to be an important contributor to the global energy supply in the 21<sup>st</sup> century by facilitating R&D on safe, economic, proliferation-resistant and low-waste reactor types and fuel cycles to be operational by 2050. During Phase I, INPRO will concentrate on scenarios of nuclear power development, requirements for innovative reactors and fuel cycles as well as the methodology of comparison of various options. The Phase IA report of INPRO is planned to be ready in 2003. MinAtom and RRC-Kurchatov Institute experts are contributing to all six INPRO subgroups from the start of project activity. Some scenarios based on multi-component structures of the future world nuclear power system, which would form as a result of a natural process of development, are now under consideration. Several alternative fuel cycles based on pyrochemical methods have been proposed which would enable much-improved use of raw material, minimal waste generation and enhanced proliferation resistance. Key issues include reducing the time elapse between fabrication, irradiation and processing, restricting the needs for partitioning by use of innovative reactors and reprocessing of highly-active irradiated fuel. In these scenarios, fast reactors can maintain the required neutron balance and basic electricity production. Thermal neutron reactors would make it possible to considerably extend the sphere of nuclear energy use. Fluid fuel reactors (possibly molten salt systems) would facilitate radioactive waste disposal. Obviously, the development of innovative reactors and fuel cycles must be mutually compatible.

## **Past international collaboration**

One of the biggest international projects related to pyrochemical technologies application was the ORYOL project. This project was realised jointly between the former USSR State Commission for Atomic Energy and the DDR government. The project included development, design, construction and commissioning of the automatic remote-controlled line in a hot cell environment for re-fabrication of fuel pins and assemblies for the BOR-60 fast reactors in Dimitrovgrad. DDR and USSR organisations collaborated and the results included an unique automatic line that operated from 1977 up to 1986. This line supplied the BOR-60 reactors with vibropacked fuel including MOX (from 1982). The fuel fabrication line included three complexes and the line demonstrated a high reliability (fuel pin production – reliability factor 0.93, fuel pin control – 0.85, fuel assembling – 0.98). Production of UO<sub>2</sub> fuel and MOX fuel for vibropacking were organised by two dry methods: pyroelectrochemical and pyrohydrolysis of UF<sub>6</sub>. Operational experience with the ORYOL facility made it possible to improve

both dry methods and to find the necessary conditions for production of good quality granulated fuel. The ORYOL facility was decommissioned in 1986 and a new automatic facility was commissioned in its place.

The USSR collaborated actively in the field of the fluoride volatility process with other countries. Cost-benefit studies of industrial fuel reprocessing for the Soviet BN-1600 and French Super Phenix-1 reactors, performed in the Soviet Union and France (CEA) respectively, confirmed the possibility of industrial realisation of the fluoride volatility process and its cost benefits compared to solvent extraction. Some problems with safety were unresolved, but now the project results can be used for other feasibility studies of fluoride volatility processes.

The FREGAT-2 project was carried out in the context of the collaboration between the USSR State Commission for Atomic Energy and the former Czechoslovak Atomic Energy Commission. The Kurchatov Institute and RIAR were collaborators from the USSR side. The work on development and realisation of this pilot-plant technological facility started in the late 1970s. The FREGAT-2 facility was a continuation of the FREGAT facility. It was intended to verify fluoride volatility technology by experimental reprocessing of irradiated fuel from the BOR-60 test fast reactor. Some key unique technological units were delivered from Czechoslovakia and mounted in the hot cell of RIAR (Bldg. 180). Unfortunately this facility was not put into operation, but functional tests were completed. The programme was interrupted due to political and financial reasons.

In the beginning of the 1990s and after the disclosure of pyrochemical development work in Russia, an initial contact was made between RIAR and ANL staff. Over the following decade, RIAR was the main participant in international collaboration on pyrochemical reprocessing. Only in the last few years have other Russian institutes begun to participate in that collaboration.

In 1991, RIAR started contract work with TEPCO (through Marubeni) in 1991. Up to 1995 this collaboration mainly involved the preparation of descriptive reports for TEPCO and PNC (now JNC) on the RIAR pyrochemical process and vibropacking experience.

In the middle of the 1990s, in the framework of the AIDA-MOX programme, a CEA-RIAR collaboration was started on molten salt treatment for military plutonium conversion. Joint tests in Dimitrovgrad and Marcoule (ATALANTE) were carried out with Pu-Ga alloy. Research was stopped because this process was not chosen for future application for VVER MOX pellet fuel production.

In 1994, BNFL and RIAR signed the Framework Agreement for Technical Co-operation. Some information exchanges were fulfilled, but this collaboration has not been active for the past few years. In 1996, RIAR proposed that KAERI consider the vibropacking options for realisation of the DUPIC concept. A feasibility study report was issued, but RIAR proposals were not adopted.

The RIAR transmutation programme, DOVITA, evoked interest from international organisations and, as a result; two ISTC Projects were authorised. The EU and Japan (PNC) supported these projects. ISTC Project #272 was dedicated to the feasibility study and development of particular flow sheets for closed fuel cycles of fast burner reactors. Preliminary economic evaluations were made. ISTC Project #279 was dedicated to the removal of fission products from irradiated fuel of a fast burner reactor. Tests with irradiated fuel with partial reprocessing and tests with MOX fuel were carried out. It was shown that both processes could be used for fuel recycling. A project supported by PNC/JNC then followed that was dedicated to reactor irradiation and post-irradiation examination of fuel containing neptunium as well as other vibropacked fuels (ISTC #1357).

## **Current international collaboration**

### ***RIAR multi-lateral co-operation on military Pu disposition***

A large international programme directed to disposition of military plutonium is now under way in Russia. Bilateral and multilateral agreements (USA-Russia, France-Germany-Russia) started this activity. The Japanese government supports some of these actions. From the Russian side many institutes and enterprises participate: the Kurchatov Institute and IPPE are involved in development of scenarios for Pu disposition, while VNIINM, VNIPRIET and RIAR are responsible in technological matters. The Kurchatov Institute, OKBM, Hydropress, AEP and others are responsible in the reactor area. Mayak and Krasnoyarsk-26 are considered to be the main sites for future location of industrial facilities. An advanced method for Pu disposition is the option developed by RIAR (with the participation of IPPE, OKBM and Beloyarsk NPP). This option includes pyroelectrochemical conversion of military Pu to MOX fuel fabrication by vibropacking and application of these technologies for Pu disposition in fast reactors (BN-600 and BOR-60). The main RIAR activities in this field are listed below:

- Production of converted MOX fuel for the BN-600 (supported by JNC). Three lead test assemblies were irradiated in BN-600. A new agreement for production and continuation of irradiation is in preparation.
- Modernisation of the MOX fuel production facility is being carried out under the JNC-RIAR agreement. The facility will produce 1 500 kg of MOX per annum by pyroelectrochemical method for loading the BN-600 hybrid core. Design institutes are also taking part in this work (VNIPRIET and SverdNIIChimmash).
- Feasibility studies have been undertaken for the evaluation of a large-scale plant for pyrochemical production of MOX fuel for BN reactors.
- Development of a method for conversion of metallic Pu to PuO<sub>2</sub> was supported by CEA and Los Alamos National Laboratory through the Bochvar Institute. RIAR is now awaiting the decision by USDOE, but some activity continues, with application of low-melting salts and testing whether the resulting PuO<sub>2</sub> is suitable for pellet production.
- A feasibility study of the immobilisation and treatment of wastes produced by a MOX fuel pyrochemical facility is being supported by Lawrence Livermore National Laboratory. This key political task could have the additional benefit of demonstrating the advantages of new pyrochemical fuel production technologies.

### ***RIAR bilateral international collaboration***

RIAR has active collaborations with Japanese organisations in the field of the closed fuel cycle of the fast reactor, based on the electro-winning process for oxide fuel. The main contractor from the Japanese side is Marubeni, which services electric power companies (TEPCO and others), JAPC, JNC and other participants (Toshiba, Hitachi, *et al.*). The first stage of collaboration included only collection and compilation of existing information. In 1995, RIAR started experimental and feasibility studies in the framework of contracts for the Japanese electric companies. The data obtained were discussed and analysed by specialists from Toshiba and TEPCO. Beginning in 1999, JNC also took part in this collaboration. The collaboration includes many studies related to pyroelectrochemical processes and validation of the process for vibropacking of fuel, such as:

- experimental facility and equipment improvement and renovation;
- demonstration reprocessing tests on BOR-60 irradiated fuel in the K-16 hot cell large-scale laboratory facility, including studies on actinide and fission product behaviour, materials balances, fuel quality vs. conditions, safety aspects, etc.;
- analysis of data on pyroprocess mass balance, rare-earth element behaviour, laboratory tests, etc.;
- testing new processes: anodic dissolution of MOX fuel, new modes of chlorination and electrolysis, etc.;
- study of the influence of impurities on electrolysis and other operations;
- corrosion tests of new materials;
- experimental recycling of reprocessed fuel, in-pile tests and PIE of vibropacked fuel;
- studies on vitrification of pyroprocess wastes (including salt);
- chlorine recycle studies.

Initial data for the Japanese feasibility study were prepared as reports. Additionally RIAR has non-financial scientific contacts with CRIEPI and Japanese universities. Renewed activity is being undertaken on the fluoride volatility process. The Kurchatov Institute, together with RIAR, VNIIkHT, and the Khlopin Institute, are involved in collaboration with JNC and Hitachi. Demonstration tests are now under way at the Kurchatov Institute. Also, a desire to collaborate in the field of fluoride salt and volatility process studies has been expressed by NRI of the Czech Republic, RIAR and the Kurchatov Institute.

RIAR collaboration with France (CEA) is now related mainly to transmutation and partitioning activity. A general agreement on pyrochemistry was signed by CEA and RIAR in 2001. The subjects are as follows: fundamental studies in molten chlorides, enhancement of the performance of pyroprocesses in new technological applications, reprocessing of irradiated targets and non-standard fuels and waste treatment. A study of americium recycling as targets is now under contract, directed to the feasibility of the complete cycle and covering fabrication of vibropac targets and their pyrochemical reprocessing. ITU also takes part in this work. The design, fabrication, irradiation and examination of the americium targets are under way. Initial steps for processing the targets also have started, including consideration of americium and rare-earth element separation by selective precipitation in molten chlorides. Another Academician Institute (IITE, Ekaterinburg) also collaborates with CEA in the field of molten salt fundamental studies.

Collaboration of KAERI and RIAR is under way under the aegis of ISTC Project #1705p. This work is directed toward the development of a new technology for storage of irradiated LWR fuel. RIAR is carrying out cold and hot tests for uranium oxide reduction using liquid lithium in molten salt media, with subsequent examination of the reaction products. Under the ISTC project, construction of a non-radioactive facility has been carried out for prototype equipment studies. Cold tests (5 kg of uranium oxides) were completed successfully. Hot tests with real VVER irradiated fuel will start in 2002 in hot cell K-16. This conception is under discussion in Russia for RBMK irradiated fuel storage consideration.

Collaboration of RIAR and other Russian institutes with American organisations in the field of pyrochemical processes is not presently very active. RIAR currently has a grant project from the US Civilian Research and Development Foundation on “Utilisation of Room Temperature Ionic Liquids and Low-temperature Molten Salts to Elucidate Gallium”. The Institute for High-temperature Electrochemistry also participates in these studies.

In 2002, RIAR and BNFL (UK) had no new joint activity; both sides, however, expect the continuation of joint projects in the future. Some discussions concerning collaboration in the field of fluoride salt and volatility process studies have been held between NRI (Czech Republic) and RIAR, but work is not yet in an active phase. In 1997-1998 RIAR had limited contacts with India (Indira Gandhi Centre for Atomic Research, Kalpakkam) where pyrochemical processes are under study. This contact came to an end, however, for reasons related to export control. In 2000, a preliminary agreement was reached with Ukrainian organisations for the development of pyrochemical processes for Zr recovery from wastes and checking of new materials for application of pyroelectrochemical process. Discussions are continuing.

### **Prospective areas for future collaboration**

Russian specialists and organisations welcome active participation in international programmes on development and industrial introduction of pyrochemical technologies. The following features should be recognised:

- availability of a wide network of organisations and institutes in the Russian Federation, which can achieve integrated solutions in the nuclear fuel cycle;
- availability of specialised laboratories and organisations, which possess experience in this area – IHTE, RIAR, SverdNIIChimmash, groups in the Kurchatov Institute, Bochvar Institute, VNIICHT and universities;
- availability of specialised experimental base, for example in RIAR;
- experience accumulated over a 40-year period.

The most advantageous perspectives may be:

- creation of harmonious technologies for the reprocessing of irradiated fuel, especially for fast reactors;
- creation of simple technologies for plutonium utilisation;
- development of new principles for LWR fuel reprocessing as complete and partial processes;
- minimisation of radioactive waste volume and extraction of actinides and some fission products;
- development of advanced technologies for the production and reprocessing of new fuels with short cooling times;
- recycling of valuable radionuclides for nuclear power engineering.

## **The molten salt reactor concept**

### ***Technical and strategic background***

The use of molten salts as fuel material has been proposed for many different reactor types and applications. In the United States, Russia, France and Japan, molten salt reactor (MSR) concepts have been studied for fast breeders and thermal cores/blankets, operating in critical and sub-critical modes. The present general approach employs a single salt stream which can contain not only fissile materials (transmuting), but also fertile materials for generating  $^{233}\text{U}$ . Note, however, that in this case  $^{233}\text{U}$  can be removed in a relatively short time without  $^{232}\text{U}$  and  $^{234}\text{U}$  contamination. Though the molten salt nuclear fuel concept has been demonstrated by successful operation of the MSRE experimental reactor at ORNL, this approach has not yet been implemented industrially. The fuel chosen for operation of MSRE and for subsequent reactor designs of this type was a mixture of  $^7\text{Li}$ , Be, Zr, U/F and  $^7\text{Li}$ , Be, Th, U/F.

In recent years, important R&D efforts have been implemented world-wide to find ways to reduce the long-term radionuclide inventory resulting from nuclear power generation. This approach calls for the introduction of innovative solutions in future nuclear power system concepts. It is natural to expect that in the future MSR technology could find a role in symbiosis with standard reactors as concerns the management of transuranic elements and long-lived fission products, as well as in thorium utilisation. The interest in this technology stems mainly from an increased neutron flux density and burn-up time in the system, reduced actinide mass flow rate and relatively small quantities of wastes generated from purifying and reconstituting the fuel. The advantages of the MSR system include the effective combination with pyrochemical techniques of fuel processing, which have prospects of low cost and small waste volume, and the capability to use fuel of different heavy nuclide composition in continuous operation with no special modification of the core. Furthermore, the MSRs can tolerate denaturing and dilution of the fuel, as well as contamination by lanthanides. A useful attribute of the molten salt breeder reactor is the capacity to contain long-lived fission products like zirconium, caesium and iodine in the form of fluorides.

### ***Previous international collaborations***

The MSR programme was started in the former Soviet Union in the second half of the 1970s. The RRC-Kurchatov Institute was the basic organisation under whose supervision a collaboration of specialised institutions was formed and functioned. The main part of Russian MSR developments was substantiated by available experience accumulated by the ORNL MSR programme for Th/U-containing salts. Also, some information exchange was performed in the 1970s-1980s between molten salt groups in the RRC-Kurchatov Institute and various Japanese universities, including Furukawa. A reduction of activity transpired after 1986 due to the Chernobyl accident and the general stagnation of nuclear power and the nuclear industry. Interest in MSR technology is currently reviving in Russia, especially as applied to the back-end of the fuel cycle for management of plutonium, minor actinides and long-lived fission products. The RRC-Kurchatov Institute performs a significant part of these studies under international co-operative arrangements.

### ***Current collaborative international activities***

#### ***ISTC***

A feasibility study concerning molten salt fuel as applied to Pu burning and long-lived radwaste transmutation in accelerator-driven system (ADS) was supported in Russia from 1994-1996 by the International Science and Technology Centre (ISTC) within Task #17 (funding source: US and EU).

Within this framework the RRC-Kurchatov Institute, VNIITF (Institute of Technical Physics), IVTEX (Institute of High-temperature Electrochemistry) and VNIIKHT (Institute of Chemical Technology) focused their attention on sub-critical molten salt blanket conceptual development, technology for the preparation of fuel salt components and preliminary capsule corrosion studies with a Li,Be,Zr,Pu/F mixture.

Currently, studies on integral evaluation of MSR technology potential as applied to commercial long-lived actinide transmutation are underway within ISTC Task #1606, entitled "Experimental Study of Molten Salt Technology for Safe, Low-waste and Proliferation-resistant Treatment of Plutonium and Minor Actinides in Accelerator-driven and Critical Systems". Participating Russian institutions are: RRC-Kurchatov Institute, VNIITF, IVTEX and VNIIkHT. The project duration is three years; it started in February 2001. Foreign collaborators are: CEA, Cogema, BNFL, KTH, FZR and FZK. This study is being carried out in close co-operation with the EU MOST (review of MSR technology) project. Major developments are expected from the following Task #1606 work packages:

- WP1 – reactor physics & fuel cycle considerations;
- WP2 – experimental study of fuel salt key properties;
- WP3 – corrosion studies in natural convection loop for fuel salt selected.

The last two objectives are considered crucial to further development of the molten salt transuranic burner concept. The experimental data would be fed into the conceptual design efforts. The objectives of the conceptual design and development programme are first to identify candidate flow sheets (reactor fuel correction unit) for the MSR concept that will be technologically feasible.

Within WP1, two types of general partitioning and transmutation scenarios with innovative MSR concepts are now under consideration:

- a scenario based on a standard LWR (PWR or BWR) employing enriched uranium fuel and special-purpose MSR burners, which consume plutonium and higher actinides (produced by other reactors) in a fuel without uranium or thorium support;
- a scenario based on MSR allowing homogeneous recycling of (thorium- or uranium-based) fuel, while minimising the generation of radioactive wastes.

FLIBE-based (F-Li-Be salt) solvent systems selected for MSR configurations appear, on the basis of present knowledge, to resolve all technological problems and in addition, to offer operational advantages regarding increased trifluoride solubility, not yet proven, compared to compositions used in prior MSR designs. The freezing point and radiation stability criteria clearly favour all compositions proposed. The differences in levels of corrosivity of the melts towards Ni-based alloys, as yet unproven for transuranic-fuelled systems at increased fuel outlet temperatures (up to 750°C), are not expected to be great. Maintaining the desired redox potential in the fuel salt is clearly possible for U-based fuels, but is not yet proven for U-free systems. Obviously, rare-earth fission product removal procedures must be more complicated for Th-based fuels.

A direct comparison within WP1 between the attractive solvents for molten salt breeder reactor (MSBR) concepts can not now be made at full scale, because of a lack of knowledge on some key physical and chemical properties as well as various aspects of fuel and materials behaviour (operational constraints). This is particularly true in the case of the ternary sodium-lithium-beryllium fluoride melt, which is not as well characterised as the binary Li,Be/F, ternary Li,Be,Zr/F or Li,Be,Th/F compositions. Additional experimental work is necessary to permit the needed evaluation and comparison.

After discussions with EU collaborators it was decided to place the main experimental emphasis within WP2 and WP3 on salts without uranium and thorium content, particularly on the Na,Li,Be/F salt composition with:

- minimisation of LiF content for tritium and economical concern;
- identification of a salt able to provide a solubility of PuF<sub>3</sub> up to 2 mole-% or possibly more, by minimisation of the beryllium content;
- ability to sustain a minimum fuel salt temperature up to 600/650°C and maximum temperature up to 750-800°C.

The goal for WP2 is experimental measurement of some key characteristics for the solvent salt composition selected:

- determination of phase relationships and solubilities of actinide/lanthanide trifluorides and oxides;
- salt transport properties;
- standard potentials for the rare earths and Pu trifluorides;
- pyrochemistry processes for rare-earth fission product recovery from the chosen solvent;
- redox potential measurements.

Within WP3, three main types of candidate structural materials for the MSR primary circuit will be tested. The first is the Ni-based alloy Hastelloy-NM of ORNL, the second is the alloy HN80MTY of the RRC-Kurchatov Institute and the last is the MONICR alloy of Skoda-Plzn, Czech Republic. On the basis of these studies, a conclusion about the candidate structural materials' compatibility with the selected salt will be possible.

Another ISTC task, #1486, titled “Experimental and Theoretical Justification of the Cascade Scheme of the Sub-critical Molten Salt Reactor for Transmutation of Long-lived RW of the Nuclear Fuel Cycle” is currently under way. Russian participating institutions are: RRC-Kurchatov Institute, MUCATEX, VNIIEF and RIAR. The project duration is two years; it started in March 2001 (funding parties: US and Japan). The following scientific and technical problems will be studied in the frame of this project:

- comparative analysis of the schemes of closed nuclear fuel cycles based on the sub-critical MSR (SCMSR);
- development of the comprehensive mathematical model of the SCMSR;
- nuclear calculations of the SCMSR core with various compositions, configurations and external neutron sources and calculation of the equilibrium states of SCMSRs at different core salt compositions;
- studies of the SCMSR core composition behaviour under high neutron flux conditions of the high flux research reactor;

- formulation of the requirements regarding nuclear-physical, chemical, physical-chemical, thermal-physical properties of the materials and compositions of the core, the structural materials and the main equipment of the reactor;
- choice of the prospective cores with respect to neutron balance and efficiency of the long-term radioactive waste incineration (initially for Np, Am and Cm);
- estimations of the core component burn-up rate, determination of the conditions for the optimum nuclide balance, the range of rates of the fuel supply and fission products extraction. Analysis of two options: thorium and uranium fuel cycles;
- estimation of the needed nuclear, chemical and thermal-physical properties of the core elements and composites;
- development of the database cataloguing the properties and behaviour of materials of the nuclear-chemical system based on SCMSR;
- analysis of nuclear and radiation safety of the SCMSR and of its influence on the environment.

## Bilateral co-operation

The historical experience of Russian institutions in several areas of dry separation technologies, including fluoride volatility and molten salt chemistry, is a good basis for further co-operation of the RRC-Kurchatov Institute with CEA (France) as well as Czech institutions (NRI, Rez/Skoda, Pilsen/Brno University). Currently, CEA collaborates with the RRC-Kurchatov Institute within the framework of the Agreement on Innovative Reactor Concepts and Advanced Closed Fuel Cycle and Minimisation of Radwastes, which includes a work package on non-aqueous reprocessing methods.

In bilateral co-operation with Czech institutions the top research priorities include MSR fuel cycle aspects, molten salt irradiation chemistry, container materials (mainly MONICR alloy) and clean-up of fuels with emphasis on experiments. The objective of the joint “Ampula” in-reactor experiment is the irradiation studies of the transuranic-containing fluoride-based salts. The planned duration of the project for Phase I, launched in early 2001, is three years. The first two years were devoted to design and manufacture of the test section (“Ampula”) and preparation of salt components. The programme includes irradiation experiments and post-irradiation analyses.

BNFL (UK) and ORNL (US) have also had some linkage with the RRC-Kurchatov Institute concerning the MSR programme, and it is believed that there will be opportunities for future collaborative programmes.

## SPAIN

The Spanish R&D plan for radioactive waste management (1999-2003) defines direct disposal of irradiated fuel and partitioning and transmutation of long-lived radionuclides as the research items in this field until 2010. CIEMAT, as the Spanish national research laboratory for energy and environment, is leading the long-lived radionuclide separation studies that are performed in collaboration with several Spanish universities (UVA, UAM, etc.) and in the framework of international collaborations.

Research on pyrochemical processes is carried out in collaboration with UVA. The aim of the studies is to establish a fundamental database on the several separation steps, mainly by considering oxide-type fuels and chloride salt media.

### Past international activities

CIEMAT (formerly JEN) was created in 1951 as the national research centre for developments in the nuclear field, with two main areas of activities: staff formation and the development of technologies concerning the several steps of the fuel cycle. Collaboration with other countries was promoted and considered as the only way to achieve a consistent and competitive technology. In August 1955, a collaboration agreement was signed between the USA and Spain for the peaceful use of nuclear energy. In the frame of this collaboration from the end of the 1950s to the end of the 1960s, several Spanish scientists from JEN were involved in research centres in the United States (Argonne and Oak Ridge National Laboratories) working on hydro-reprocessing, waste treatment and molten-salt reactor reprocessing. In parallel, an agreement was established with CEA (France) wherein JEN scientist were involved with Pu studies (chemistry and analyses), mainly at the Fontenay-aux-Roses site.

From 1963 to 1970, a reprocessing pilot plant (M-1) was constructed and operated at the JEN site in Madrid. In 1966, the US Atomic Energy Commission provided permission to reprocess irradiated fuel from the JEN-1 experimental reactor. From 1967 to 1970, irradiated fuel plates (U-Al type fuel) and irradiated fuel from the experimental SAPHIR reactor (Switzerland) were processed. At this time, as the result of Spanish participation in EUROCHEMIC, several researchers from JEN worked on reprocessing at Mol (Belgium). This collaboration was also focused on personnel development. Between 1964 and 1967, design and construction of the experimental fast reactor (CORAL) was carried out at JEN. It operated from 1968 to the beginning of the 1980s. In 1970 a liquid sodium loop belonging to the fast reactor programme was constructed at JEN. In the 1970s, Pu studies were also carried out in agreement with KfK (Germany) within the frame of a wider bilateral agreement.

JEN scientists have been involved in international working groups, some of them promoted by international agencies such as IAEA and OECD/NEA. For example, at the end of 1977, a US proposal promoted the International Nuclear Fuel Cycle Evaluation (INFCE) formed by eight working groups; a JEN scientist led Working Group 6 (irradiated fuel management).

### Present international activities

#### *Collaboration with EU*

CIEMAT, in collaboration with UVA, participates in the PYROREP project of the 5<sup>th</sup> Framework Programme for Technological Research and Development of the European Union. Spanish studies within the collaborative project involve chlorinative dissolution of a simulated UO<sub>2</sub>-type fuel and fundamental electrochemical separation studies of uranium and rare-earth elements in chloride salt media (LiCl-KCl). The objective of the task on conversion to the chloride form is to determine the stability of the compounds and the reaction rates when direct chlorination from the oxide form (i.e. SIMFUEL) is performed. Dissolution studies of rare-earth oxides and oxohalides are being carried out. Separation activities are focused on the application of electrochemical techniques for separation of the elements contained in a spent fuel analogue (SIMFUEL). The studies involve fundamental experiments to determine the electrochemical behaviour of a selection of elements of interest, definition of possible separation paths and separation of minor elements of SIMFUEL. Examination and construction of thermodynamic diagrams are performed for several chlorinating mixtures and

elements under study, showing stable phases as a function of potential and oxygen concentration. Kinetic and thermodynamic data are being determined for electrochemical separations processes involving both solid and liquid cathodes.

Thermodynamic and kinetic studies will continue in the frame of the 6<sup>th</sup> Framework Programme of the European Union through participation in the EUROPRT project. Activities will mainly be focused on continuation of the basic data acquisition performed in the PYROREP project; actinides will be studied at the laboratory scale and the work will include the study of the chemical treatment of the waste stream chloride salt, with the twin objectives of fission product reduction and chloride recycling.

### ***Collaboration with France***

This collaboration is carried out in the framework of a CEA-CIEMAT bilateral agreement having a five-year duration. Activities on pyrochemical studies are focused on fundamental data acquisition. CIEMAT is concentrating on E-pO<sup>2-</sup> diagram construction concerning lanthanides and on separation by salt-metal extraction in chloride media. Various chloride systems are under consideration.

### ***UNITED KINGDOM***

In the present era, development of any major new nuclear process is probably beyond the means of any single organisation. The costs of development of a new process, both in financial terms and in the training, development and maintenance of the required skills base, will be prohibitive to any one organisation, and indeed perhaps to any one nation. If pyrochemical technology is to be successfully deployed on a commercial basis in the future, there will be an ongoing need for collaborative projects at all stages of the development process. This will have to be the case over a broad spectrum: from creating a better understanding of the fundamentals of the chemistry, such as the establishment of comprehensive thermodynamics databases, through to the very specific design of individual pieces of full-scale process equipment.

BNFL's core fuel management process for the separation of uranium and plutonium from irradiated fuel is based on solvent extraction technology, specifically PUREX. The company operates two reprocessing plants, with a combined annual capacity greater than 2 000 tonnes per year, using this technology. Currently, BNFL is considering whether molten salt technology can offer any benefits over improved PUREX technology for fuel treatment within *future* fuel cycles or for fuel services which current plants may not offer. The programme includes international collaboration and is focused towards objective assessment of the potential for industrial technology application. BNFL's operation of industrial-scale processes on a commercial basis places it in a strong position to assess the viability of any new technology and, if justified, to recommend the correct development methodologies to adopt. BNFL's competencies include process development, engineering and industrialisation of nuclear technology to deliver safe, efficient plants. Thus, the company's involvement in the development of the technology may be a significant factor in successful industrial deployment.

BNFL considers that pyrochemical research should be broadly based, but further considers that issues of industrialisation are key to the justification of work and successful development. Although pyrochemical processes are becoming increasingly well developed, especially the US process developed at Argonne National Laboratory and the Russian process developed at the Research Institute of Atomic Reactors (Dimitrovgrad), there are significant technical and engineering hurdles to overcome before large-scale deployment. An added complication is that each nation, and indeed organisation, at the moment has a different development goal. If successful deployment is to be achieved, then effective collaborative partnerships will be required. If collaboration is to be successful, good understanding and

trust between the partners is needed. To this end, and given the relative immaturity of the technology, the intellectual property aspects can be properly managed to mutual benefit. Development should be targeted towards overcoming all hurdles to towards successful industrialisation of the technology, and the particular needs of any one organisation should be not be dominant. That said, there should be a rational assessment of the real commercial viability and other key objectives, so that it may be determined whether indeed it is worth continuing with development.

BNFL wishes to enhance its technological capability in the pyrochemical area so that it can offer commercial process services, act as an informed buyer or user, and be able to adapt to international technical and commercial developments. It has constructed a large and diverse set of nuclear process plants at Sellafield and other sites and possesses extensive engineering, project management and operational skills in the industrialisation of radioactive process facilities; it is prepared to partner on a case-by-case basis with organisations with complementary skills such as technology developers and researchers.

A collaborative partnership with AEA Technology has been developed over the last few years and this will be discussed further in the text below.

## Past and present international activities

### *Japan*

International collaborative pyrochemical activities have taken place between Japan and the UK in recent years, and it is expected that these will increase in the future. JNC is studying development of a fast reactor and fuel cycle system. In April 2001, BNFL and JNC signed a technical co-operation agreement that includes advanced fuel cycle activities. Collaboration activities are under way in reprocessing, fuel fabrication and waste management areas that include pyrochemical studies. A BNFL engineer was seconded for two years (2000-2002) to participate as a JNC International Fellow at the JNC Tokai Works. The fellowship involved the investigation of pyrochemical processes applied to fast reactor fuel reprocessing. Work addressed the scale-up of pyrochemical equipment.

A BNFL research scientist was seconded to JAERI during the period April 1999 to April 2001, the time divided between the Tokai and Oarai sites. The work concentrated on the measurement of fundamental thermodynamic properties and electrochemical studies. JAERI has proposed the development of a “double strata” strategy based on transmutation in reactors using nitride fuel. As part of the secondment, the chemistry of dysprosium and its nitrides in molten salts were studied. In this particular case, dysprosium was used as an inactive simulant for americium.

BNFL has performed a number of pyrochemical plant design and feasibility studies under contract with other Japanese organisations. CRIEPI and BNFL are involved with the PYROREP European Commission 5<sup>th</sup> Framework Project.

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, and a number of publications released.

The collaborations have allowed the UK to increase its skill base in molten salt technology. In return, it is hoped that the Japanese organisations have gained from BNFL an improved perspective of the requirements for future development of nuclear technologies, and some of the issues which are required to be overcome to enable industrialisation of pyrochemistry.

### ***United States of America***

Links between BNFL and the US have been active in the past. A BNFL (Magnox Electric) attaché worked for two years at Argonne National Laboratory, learning about the technology and exploring the possible application of an electrometallurgical process to the fuel conditioning of UK metallic irradiated fuel. Subsequent to this in 1998, BNFL commissioned a cost study in the US with Babcock and Wilcox and Burns and Roe Enterprises (again with BNFL attaché participation) that examined the best publicly available information on electrometallurgical (EM) treatment technology for the management of gas-cooled metallic irradiated fuel. The study indicated the feasibility of EM treatment and developed cost and schedule information underpinned by reference process and facility pre-conceptual designs. Information was developed using a bottom-up generic work breakdown system structured by cost element. Pre-operational, operational and decommissioning costs were estimated to obtain an overall estimated life cycle cost. Statistical modelling of cost probability distributions was applied. General and specific design requirements were developed. The design assessment included safety, operability and HAZOP studies. Process option studies were performed and the logic/justification to select the reference EM treatment process design was formalised. An industrial engineering study was conducted to confirm that the specified throughput and required maintainability could be achieved using process cells and other areas as described. In addition, BNFL have established links with other US national laboratories and universities. This has included research contracts with the Colorado School of Mines (CSM). CSM completed a research programme investigating electrometallurgical separation of magnesium from uranium.

### ***Russian Federation***

BNFL considers that the SSC RIAR Dimitrovgrad is a cornerstone in the development of molten salts technology. (This sentiment is shared by a number of other countries.) BNFL has also had a number of visits, collaborative projects and work packages with RIAR Dimitrovgrad, whereby BNFL have sought information about the electro-winning process, to determine its possible success and applicability to BNFL's possible future requirements. The company has also had some linkage under ISTC with the RRC-Kurchatov Institute at Moscow concerning their molten salt reactor programme, and believes that there will be opportunity for future collaborative programmes.

### ***Europe***

BNFL is party to the European Commission 5<sup>th</sup> Framework Partitioning and Transmutation programme (PYROREP), with the collaborative participation of CEA Marcoule (France), CIEMAT Madrid (Spain), NRI Rez (Czech Republic), ENEA Casaccia (Italy), ITU Karlsruhe (Germany) and CRIEPI (Japan). BNFL is subcontracting a portion of its work to AEA Technology Harwell, who has extensive links with BNFL's research programmes and a proven history of working together with BNFL. The PYROREP programme is targeted at achieving a greater understanding of the application of pyrochemical technology to partitioning, in particular the separation of minor actinides. The R&D programme should yield sufficient basic data to assess pyrometallurgical processing flow sheets for use with irradiated fuel and targets. The experiments carried out will provide an opportunity to develop specific methods and apparatus and identify materials compatible with pyrometallurgical processes. Each elementary chemical process will be investigated, i.e. oxide fuel conversion to halide form, radionuclide separation by electrolysis or metal/salt exchange, recycling of process reactants, liquid and solid process waste treatment. The performance of each step (yields, decontamination factors, etc.) will be assessed. It is also hoped that the research collaboration will increase the European resource base trained in pyrochemistry.

BNFL uses fundamental thermodynamic information obtained through links and contracts with the UK National Physical Laboratory. There is a hope to extend collaborations with both French and Japanese researchers within this subject.

## Future international activities

BNFL continually reviews its development programmes and the prioritisation/scope of the work justified. So that a greater understanding of the issues involved in the industrialisation of pyrochemical processes can be obtained, current work includes a variety of experimental projects, including:

- a rig where the handling and pumping of salts will be tested;
- alpha-active glove boxes for testing electrorefining equipment and the electrochemistry of the actinides;
- an inactive glove box for salt treatment and the measurement of fundamental electrochemistry of metals;
- a large-scale uranium-active electrorefiner, where a BNFL-designed electrorefiner will be built and tested to operate on tens of kilogram quantities of metal;
- a rig for the testing and handling of a salt clean-up process which will operate on inactive simulant materials.

In consideration of future collaborative opportunities, it is believed that successful development of industrial-scale pyrochemical processing will be a collaborative endeavour. Given the justification to proceed, BNFL is likely to pursue a number of areas of development as collaborative programmes of work with others who can contribute skills or resources to mutual benefit.

## UNITED STATES OF AMERICA

The United States has been in an awkward position regarding international collaboration on the development of pyrochemical processing technology almost since the inception of the work on metallic fuel reprocessing in the mid-1980s. The technology was considered by the US government to be a sensitive nuclear technology, with very explicit export control restrictions spelled out under US law (Title 10, Code of Federal Regulations, Chapter 810). This law expressly forbids the transfer of sensitive nuclear technologies (including reprocessing technologies) in the form of process or plant design information to other countries without specific authorisation by the US government. Furthermore, the pyroprocessing technology for application to metallic fast reactor fuel was developed in support of the Integral Fast Reactor concept, a technology that was considered in the 10-year period from 1985 to 1994 to be a commercially sensitive technology. Therefore, all research results developed under this programme fell under the dual restrictions of (1) sensitive nuclear technology and (2) commercially sensitive technology, and open publications of research results were restricted.

In 1990, it became clear that at least one industrially-connected organisation in Japan (the Central Research Institute of Electric Power Industry, CRIEPI) was seriously considering the introduction of a metal-fuelled inherently-safe reactor like the US Integral Fast Reactor (IFR), with an integrated closed fuel cycle. As a consequence, the US Department of Energy negotiated a contract between CRIEPI and Argonne National Laboratory wherein CRIEPI would in essence buy in to the development of the IFR and support continuing research and development at Argonne in exchange for access to the results of

the development programme, including the assignment of a specified number of CRIEPI staff members at Argonne National Laboratory for a period of 18 months per assignee, subject to extension by mutual consent. This contract extended until 1994, when the US Department of Energy determined that the contract amounted to an unauthorised transfer of sensitive nuclear technology and caused the contract to be terminated. Coincidentally, the IFR programme was cancelled at the same time and Argonne shifted the emphasis of pyroprocessing development to the treatment of irradiated nuclear fuel that existed in the Department of Energy inventory. This ended all international collaboration connected with the development of pyrochemical processes for the treatment of irradiated metallic alloy fuels for fast reactors. The pyroprocessing programme of Argonne then became focused on the conditioning of EBR-II reactor-irradiated driver fuel and blanket assemblies, which was favoured because these fuel and blanket designs involved thermal bonding of the fuel or blanket material to the cladding with elemental sodium, which is precluded from direct disposal in a US geologic repository for high-level nuclear waste.

In 1999, the US Congress directed the preparation of a technology road map for the accelerator transmutation of wastes coming from commercial light water reactors. This led to the implementation, in 2000, of the Accelerator Transmutation of Waste (ATW) programme, which was directed toward the partitioning and transmutation of transuranic elements and long-lived fission products present in commercial LWR irradiated fuel. Because this programme was not considered commercially sensitive, nor a nuclear proliferation issue, the development of ATW technology became eligible for international collaboration. The US participated actively in international forums, including strong involvement in OECD/NEA expert groups such as those involved in fast reactor/accelerator-driven systems comparisons and in evaluation of pyrochemical applications. In 2001, the US Department of Energy and the CEA (France) initiated discussions on possible collaborative efforts that have since developed into a detailed programme of joint activities extending well into the middle of this decade. The collaboration concerning chemical processing includes specific activities in pyrochemical processing technology development.

The US programme has now transitioned into the Advanced Fuel Cycle Initiative, which has the multiple roles of (1) facilitating the disposal of high-level nuclear wastes coming from commercial LWR irradiated fuel; (2) eliminating the highly-radiotoxic minor actinide elements; and (3) closing the fuel cycle of the next generation of nuclear power plants. With large-scale deployment of these technologies extending well into the middle of the century, and with formidable cost projections, it has become clear that achieving the goals of this programme will be possible only through highly-focused collaboration with international partners having the needed expertise in pyrochemical separations technologies. Accordingly, the managers of this programme are considering collaborative efforts with a number of other nations, hoping to establish mutually beneficial co-operative research initiatives in the very near future. A collaborative agreement with CEA (France) was implemented in 2000, and similar agreements are being negotiated with the European Commission, Republic of Korea, Canada and Japan.

### **Connections with additional countries, organisations and initiatives**

Pyrochemical separation and relevant molten salt technology studies are known to be underway or have taken place in various additional countries including Belgium, e.g. University of Liège; China, CIAE India, e.g. Indira Gandhi Centre, Kalpakkam; and the Netherlands (e.g. the NRG).

### **OECD/NEA**

Collaborations have been enhanced by the series of International Information Exchange Meetings on Actinide and Fission Product Partitioning and Transmutation, which have been held biennially by

the OECD/NEA since the first in Mito City, Ibaraki, Japan in 1990. The last meeting was held in Madrid, Spain in 2000 [7]. The OECD/NEA 7<sup>th</sup> International Information Exchange Meeting on P&T will be held at Jeju in the Republic of Korea on 14-16 October 2002. The last OECD/NEA status report in this area was published in 1999 [8].

The OECD/NEA/NSC has recently established a Working Party on Scientific Issues in Partitioning and Transmutation (WPPT). The working party will deal with the status and trends of scientific issues in partitioning and transmutation (P&T) and comprise four sub-groups for accelerators, chemical partitioning, fuels and materials, physics and safety of transmutation systems. The first meetings were held in Madrid on 10 December 2000 and on 8 June 2001 at OECD/NEA HQ Paris. The chairman of the Pyrochemical Separations Working Group also chairs the WPPT Chemical Partitioning Sub-group. The WPPT covers the recycling or destruction of Pu, MA and some FP, and mainly aqueous partitioning processes will be considered. The work of these two groups will be maintained separate though some experts will be present in both.

As mentioned, development of pyrochemical separations partly proceeds in relation to advanced reactors, accelerators and fuels. A joint study has been performed by OECD/NEA, OECD International Energy Agency (IEA) and IAEA on “Innovative Nuclear Reactor Developments – Opportunities for International Co-operation”. The report of the study is due for publication in late 2001/early 2002.

Another connection through the OECD/NEA is the OECD/NEA Working Party on the Physics of Plutonium Fuels and Innovative Fuel Cycles [9]. The Workshop on Advanced Reactors with Innovative Fuels (ARWIF 2001) was hosted by British Nuclear Fuels Limited under the auspices of the OECD/NEA Nuclear Science Committee and held 22-24 October 2001 at Chester, UK. The home page is: <http://www.nea.fr/html/science/meetings/arwif2001/>.

## IAEA

The International Atomic Energy Agency started an effort to integrate data on minor actinides which is available in the world. The first step was to seek recommendations and guidance of experts on MA data such as thermodynamic, electrochemical, phase-diagram and physical properties of MAs. Accordingly, a consultancy meeting, with experts from France, Germany, Japan, Russia and USA, was held on 4-6 November 2002 at IAEA headquarters in Vienna.

The status of the existing databases on minor actinides was discussed. Recommendations were issued on the development of the database on minor actinides used for advanced nuclear fuel cycles. They include the important MA-based materials and associated properties and also the working method for collection, assessment and evaluation of the data.

It was recommended that the IAEA foster a collaboration with ongoing activities in this field within other organisations and that duplication of efforts be avoided.

Although it is believed that the IAEA does not presently maintain a technical group dealing specifically with pyrochemical separations, nonetheless it does hold “Advisory Group Meetings on Spent Fuel Treatment”. These are held periodically; a recent meeting was held on 29-31 October 2001. The objective is to review the status and trends of irradiated fuel treatment and to define the emerging issues in this field. It is known that the group is examining pyrochemical separations within this context. The IAEA has commissioned the writing of an IAEA technical document (“Tech Doc”) on “Spent Fuel Management for the Sustainability of Nuclear Energy”. It is to be completed in 2002. The co-ordinator for the editing of this document is Mr. J.S. Lee of KAERI.

The IAEA conducts a programme covering P&T activities from non-OECD/NEA countries and focuses on safety, environmental and non-proliferation aspects. The IAEA has launched an internet site, <http://www.iaea.org/inis/aws/fnss/> for researchers working on ADS and also provides links to ADS-related sites. The most recent IAEA status reports in this area were issued in 1997 [10,11].

The IAEA has set up an international project on innovative reactors and fuel cycles, called INPRO, which first met on 27-28 November 2000 to define the terms of reference and start the project. INPRO member countries include Argentina, Canada, China, France, Germany, India, Netherlands, Russian Federation, Spain and Turkey. The main purpose is to help enable nuclear energy to be an important contributor to global energy supply in the 21<sup>st</sup> century by facilitating R&D on reactor types to be operational by 2050. In the early stage, INPRO will concentrate on user requirements for innovative reactors and fuel cycles in addition to economic, environmental, safety and non-proliferation criteria.



## *Chapter 4*

### **FUTURE APPLICATIONS OF PYROCHEMICAL TECHNOLOGY**

#### **Introduction**

International development within the field of pyrochemical technology is directed towards a wide variety of potential future applications. Five main applications of pyroprocesses in the nuclear industry have been described in the literature:

- the processing of existing stockpiles of metallic fuel from early reactors;
- the processing of present and future irradiated fuel from fast reactors;
- a candidate for processing of LWR oxide fuel if an alternative to the PUREX process is needed;
- the partitioning step in a partitioning and transmutation (P&T) strategy of transmutation of long-lived radioactive waste before disposal;
- the irradiated fuel treatment module of a future integrated reactor/recycle system.

These applications would have to meet very different demands:

- different drivers for development, ranging from clean-up concerns, recycling of nuclear materials, and non-proliferation, to cost-competitiveness and safe waste management;
- very different time frames of deployment, linked with the deployment of the reactor technology and/or the requirements and the enforcement of the policies of radioactive waste disposal;
- very different scales of implementation depending on the quantity of material available for treatment.

For future application there should be a good understanding of the advantages and disadvantages of deployment of the technology. The claimed advantages and drawbacks of irradiated nuclear fuel pyrochemical processing can be summarised as follows:

- Main advantages:
  - compact, with a limited number of operational steps; small devices with small hold-up of nuclear material;
  - molten salts are inorganic, non-aqueous media, less sensitive to radiolysis hazards than aqueous processes and believed to be less subject to criticality limitations;

- material with limited solubility in nitric acid can be more easily dissolved in molten salts, especially by electrochemical means;
- expected to be able to process high burn-up, short-cooled fuels with no significant penalty.
- Main drawbacks:
  - high temperature and strongly corrosive reagents, especially in fluoride systems, will create difficult challenges in highly active industrial cells;
  - current pyroprocesses have limited separation efficiency and are presently limited to a batch mode, which restricts the scale of industrial operation;
  - the management of volatile species at large scale will be challenging;
  - generation of process wastes outside the bounds of current standards;
  - production of some awkward technological wastes.

## Possible applications of pyrochemical technology

### *Fuel conditioning*

Fuel conditioning can involve the treatment of irradiated fuel using pyrochemical technology without the separation of fissile material in the process. The process will produce a number of products of different classification, which may include a uranium waste form, a ceramic/glass high-level waste and a metallic high-level waste form. The purpose of the process is to produce waste forms of greater stability for repository disposal than untreated irradiated fuel. Ideally, there would be a reduction in the volume of high-level waste. A representative example is the ANL pyroprocess, as applied to EBR-II fuel and blanket elements.

### *Fuel recycle*

The treatment of irradiated fuel with a separation of fissile material during the process can provide valuable recycle materials. The process will produce a uranium-based product, with the aim of returning this material to reactor. The process will also create a plutonium/minor actinide product, also eventually intended for return to reactor. The fission products will form a ceramic/glass waste form for disposal. A cogent example is the RIAR-Dimitrovgrad process applied to vibropac oxide fuel recycle, where the fissile material is returned to a fast reactor.

### *Partitioning and transmutation*

There are several methods of applying pyrochemical technology in partitioning and transmutation applications.

It might be applied to the treatment of the highly-active (HA) waste stream which has been derived from a PUREX plant. The process would first convert the HA raffinate to a suitable form for dissolution in a molten salt. The process would bring about the separation of the minor actinides from

the rare-earth elements. The actinides would be then processed for subsequent transmutation, and the rare-earth elements processed into a suitable waste form. Other selected elements may also be removed from the stream for transmutation or immobilisation.

In application of the technology to bring about the partitioning directly from irradiated fuel, products would include a purified uranium-based material and a waste form that includes elements such as the rare-earth elements. Plutonium and elements suitable for transmutation such as the minor actinides would be partitioned from the fuel. Once again, transmutation might be via fast reactor or accelerator systems.

In a molten-salt reactor application, as applied to molten salt-based reactor fuels, the fuel would be passed through an on-line separation process, in which fission products would be removed from the salt. In addition, the fissile content of the fuel would be corrected prior to return of the salt to the reactor. An example of such an application is the Molten Salt Reactor Experiment of Oak Ridge National Laboratory in the US in the 1960s.

There are some waste management applications of molten salts where they can be used to treat waste streams to produce waste forms of greater durability and reduced volume. An example is the Lawrence Livermore Molten Salt Oxidation process. In this process, a range of wastes, which may be inorganic residues or organic wastes such as contaminated miscellaneous waste (gloves, tissues, etc.), are added to a molten salt in a stream of oxygen or air. The organic material is catalytically oxidised within the salt, predominantly to CO<sub>2</sub>. Inorganic residues such as radioactive metals remain in the salt, where they become increasingly concentrated. These materials can eventually be recovered and converted to a suitable waste form.

## **Future application of pyrochemical technology – national intentions**

### **CZECH REPUBLIC**

Czech research institutions, industrial companies and governmental authorities are parties to a decision to engage in the development of advanced partitioning and transmutation technologies, in connection with the development of a new reactor concept that may help to support the sustainable development of nuclear power in this century. The main criterion was to select a reactor technology that will serve to transmute accumulated transuranium elements from PWR irradiated fuel, while minimising the production of radioactive waste (in effect, a self-transmuter). The molten salt reactor (MSR, utilising the Th-U fuel cycle) was chosen as one of the prospective reactor systems.

Pyrochemical processing methods were judged to be the only technologies suitable for the fuel cycle of MSRs with integrated reprocessing technologies. Because the liquid fuel for MSR is a mixture of molten fluorides, the fuel processing and reprocessing technologies planned are pyrochemical or pyrometallurgical technologies, based on separations in molten fluoride salts.

The systems scenario based on the future use of the molten salt transmutation reactor is grounded in two pyrochemical/pyrometallurgical separations technologies – the fluoride volatility method and electrochemical separations processes in a molten fluoride salt mixture. The simplified scheme of the MSR fuel cycle was shown previously (see Figure 1).

Pyrochemical/pyrometallurgical technologies have practically no alternatives in case of the MSRs with integrated fuel processing and reprocessing, as in the case of the Pu and MA burner (molten salt transmuter) as well as for the MSR utilising the Th-U fuel cycle as a “self-transmuter”.

According to the Czech Atomic Act, the state guarantees the safe disposal of all radioactive wastes, including irradiated fuel. The construction and operation of an underground repository is planned, possibly accepting the first irradiated fuel and/or high-level waste after 2065. Financing of the back-end of the nuclear fuel cycle is realised through the so-called “Nuclear Account” administered by the Radioactive Waste Repository Authority. The main revenues of the Nuclear Account come from fees paid by radioactive waste and irradiated fuel producers (mainly the Czech power company CEZ, which operates Czech nuclear power plants). The period of time up to 2065 is envisioned to provide the opportunity for development and deployment of partitioning and transmutation technologies as the practical alternative to the direct underground disposal of irradiated nuclear fuel.

In 1996, the consortium of research institutions and industrial companies called “Transmutation” was established. The task of the consortium is to take part in the development of selected partitioning and transmutation technologies (including the fluoride pyrochemical partitioning for molten salt transmutation reactors). The Nuclear Research Institute Rez plc, which also plays the role of the R&D base of the Czech power company CEZ is the co-ordinating centre of partitioning and transmutation research and development in the Czech Republic. Research and development on pyrochemical technologies is financially supported by the Ministry of Industry and Trade and by the Radioactive Waste Repository Authority. The basic research and development period is projected to be finished in approximately 10 years. At that point, the evaluation of results and assessment of new intentions and objectives will be achieved. As the Czech Republic is a relatively small country, a substantial emphasis is devoted to broad international collaboration. It is assumed that the molten salt transmutation reactors with an integrated fuel cycle based on pyrochemical processing/reprocessing technologies could be deployed in the second quarter of this century.

## **THE EUROPEAN UNION**

In the EU there are only two states concerned with industrial reprocessing: the United Kingdom and France. However, the European Atomic Energy Community (EURATOM) has recently joined the Generation IV International Forum (GIF) with the goal to foster research and development activities related to next-generation reactor systems with closed fuel cycles within its territory and among member states. To achieve this objective, the European Commission relies on the multi-annual EURATOM Framework Programme and on two modalities for funding research and training activities in the field of nuclear fission and radiation protection: Direct Actions and Indirect Actions. For the Direct Actions, the European Commission directly finances its own R&D establishment, the Joint Research Centre (JRC), which contributes directly in GIF projects. For Indirect Actions, the European Commission partly or totally funds R&D and training activities carried out by consortia of member states’ research bodies (research organisations including the JRC, industry and universities). One of these projects is the EUROPART project dealing with both aqueous and pyrochemical separation techniques. The objectives of the research related to pyrochemistry are the following:

- determining basic properties of actinides (including the transcurium elements) in molten halides (chlorides and fluorides), the media to be selected for the development of pyrometallurgical partitioning processes;
- defining partitioning process of actinides from high-level wastes issued from the reprocessing of UOX and/or MOX spent fuels by the PUREX process;
- defining processes for advanced dedicated fuel cycles (such as those of accelerator-driven systems, ADS);

- defining conditioning methods for the wastes generated by partitioning processes;
- defining the overall organisation of the methods to be implemented within pyrometallurgical partitioning processes.

In addition, member states which wish to contribute directly in GIF projects may channel their contribution via EURATOM participation in the GIF and thus ensure an optimised consistency at the community level.

Fuel fabrication applications include several pyrochemical processes; e.g. pyrolysis of solutions in plasma to produce oxides, pyrolytic covering of kernels (for high-temperature reactors) with graphite and SiC layers, oxidative and reductive sintering of pellets, cermets and pyrometallurgical fuel fabrication (casting, powder metallurgy). Waste solidification processes include vitrification, ceramics, cermets, etc., with the corresponding processes. As to fuel reprocessing, apart from electrorefining, one should consider voloxidation for fast reactor fuels (as already used for PWR in the DUPIC concept) alone or as one step in a refining process for example. The burning of the graphite coatings of TRISO gas reactor fuel is another example. The salt cycle/transport processes with dissolution of oxides by halogenisation in salts for electrorefining is a potential future process. Counter-current extraction from molten salts by metal alloys (e.g. a CRIEPI proposal based on ANL work) is also a possibility. Fractionated precipitation (see the Dimitrovgrad Dry Process) is another possible process. Volatilisation, also in combination with aqueous processes or to reduce excessive uranium when switching from LWR to fast reactors, has promise. Last but not least, the various molten salt (breeder) reactor concepts must be considered.

## **FRANCE**

The Commissariat à l'Énergie Atomique (CEA) foresees two areas of possible applications for pyrochemical technology. First, within the framework of the December 1991 Legislative Act on the management of nuclear waste, CEA is studying long-lived radionuclide partitioning and transmutation scenarios and technologies. Several cases are under consideration, especially for the transmutation of minor actinides. Opposed to once-through transmutation, there is the recycling of targets or dedicated fuels. In that case, processing the irradiated material to recover the actinides is necessary and for such processing hydrometallurgy may not be adequate because of the high activity and specific nature of the material. Pyrochemistry, on the other hand, is probably a good candidate. Second, for mid- and long-term strategies, there is a renewed interest in gas-cooled reactor technology. For this future nuclear system, innovative fuels and the associated recycling technology will have to meet ambitious requirements compared to current processes:

- All the actinides will have to be recycled together.
- Very high burn-up is targeted and with the shortest cooling time attainable to minimise the out-of-reactor inventory of actinides.
- In order to gain in overall energy yield, there may be no secondary cooling loop for the reactor. Thus, the fuel will have to exhibit a very high level of radionuclide confinement and highly refractory ceramics are proposed to ensure that this is the case.

- To minimise transportation of nuclear materials, it is proposed that future recycle units integrate both processing of irradiated fuel and re-fabrication of fresh fuel. For the same reason, on-site processing is preferable, meaning that the closure of the fuel cycle can be accomplished in a small, compact unit.
- Releases (either gaseous or liquid) must be minimised.

It should be mentioned that CEA is considering both hydrometallurgy and pyrometallurgy for these two fields of application. France has a strong background in aqueous processes and has already demonstrated the ability of such processes to cope with most of the important issues. Nevertheless, pyrochemical processes have known (or presumed) advantages that may make them suitable for applications such as:

- ability to treat refractory materials (e.g. TRISO particulate fuels);
- no sensitivity to radiolytic degradation;
- large fissile material loading (criticality constraints are less restrictive than with aqueous processes);
- compactness of equipment (integrated concept).

However, a number of drawbacks and uncertainties will have to be overcome before one can enter an industrial expansion. The major ones are the following:

- *Separations performance.* CEA has conducted a detailed bibliographical survey of many pyroprocesses studied in the past or at present in several countries. It was found that no demonstration has been made of the ability to quantitatively recover all of the actinides, even at a level of 99%. This is a strong requirement for multiple recycling scenarios and a serious issue for future investigation.
- *High-level waste management.* Vitrification is presently recognised as a standard technology for the confinement of fission products. In the case of pyroprocessing with fluoride salts it is possible to vitrify the stream of fission product fluorides; with a chloride salt-based process, vitrification of the waste stream becomes virtually impossible and other means for waste form preparation must be used.
- *Corrosion.* This matter is of primary importance for industrial applications and has not been resolved, in particular as concerns fluoride salts. The solution could come from emerging technologies (like ceramic coatings).
- *Sophisticated technology* (high temperature, controlled atmosphere).

Considering all of these difficulties, pyrochemistry has a long way to go before it becomes a practical industrial technology. Thus, the French research strategy concentrates on the issue of primary importance (i.e. separations performance). The basic chemistry of actinide separation in molten salt is being studied in order to answer this simple question: Is it possible to find the right combination – media and technique – that allows a quantitative recovery of all the actinides? Due to the genuine complexity of the subject, an answer is not expected for several years (perhaps by 2005-2006). If the answer is positive, this will lead to the initiation of a more comprehensive development programme.

***Future applications to the fast breeder reactor fuel cycle***

JNC is leading a phased feasibility study in Japan concerning the development of a fast reactor and fuel cycle system. The feasibility study involves a collaborative effort by JNC, electric utilities, nuclear research organisations including JAERI and CRIEPI, design and construction companies, and universities. Emphasis is being placed on international collaboration to optimise the quality and minimise the cost of the project. The key targets for a commercialised system are:

- safety of reactor and fuel cycle (safety in design);
- economic competitiveness – at least comparable to future LWRs;
- efficient utilisation of uranium resources;
- reduction of the environmental burden imposed by fuel cycle activities;
- enhancement of nuclear non-proliferation characteristics of the nuclear fuel cycle.

In the first phase (JFY1999-2000), options were surveyed from a broad range of technologies and conceptual designs were assessed against targets. In the second phase (JFY2001-2005), further conceptual design studies and engineering-scale tests of key technologies are underway.

JNC is presently considering three main technologies for reprocessing FBR irradiated fuel: advanced PUREX, oxide electro-winning and metal electrorefining. The latter two are molten salt pyrochemical processes. The cost target is ¥0.27 M/kg(HM) [about \$2 500/kg(HM)].

The Japanese feasibility study for the fast reactor and its associated fuel cycle emphasises safety and economics. Newly proposed processes – both wet and dry – represent simplifications of past reprocessing and fuel fabrication practices. Lower decontamination factors and simplified fabrication routes as suited to remote fabrication are favoured.

The expected high burn-up of fast reactor fuels reduces the scale of the recycle plant compared to thermal oxide systems and tends to help the current dry processes. This is also true for decentralised recycling systems attached to nuclear-generating sites that decrease the need for irradiated fuel transport.

The feasibility study has a primary purpose in creating a future electrical-power-generating system, but the reduction of the environmental impact of the fuel cycle may be enhanced by recycle of higher actinides. Two dry processes are being studied with this aspect in mind.

Pyrochemical processes are viewed as potentially simpler, more compact and probably lower cost. They may accommodate TRU partitioning and recycle more easily than PUREX processes. In addition, they are suited to high burn-ups and high dissolved TRU concentrations.

Pyrochemical technologies are considered to have higher technical risk and require more development. The current small scale of batch equipment for pyrochemical processes leads to less than optimal plant designs. The oxide electro-winning process is compatible with both thermal and fast oxide fuels and could ease the expected future transition between these reactor types. It also deals with thermal MOX fuels for recycle to fast reactors.

Advanced PUREX, oxide electro-winning and metal electrorefining are the competing technologies and these must be integrated with simplified fabrication methods. JNC has not made a definitive choice between these technologies. At some point in the future, the choice may be narrowed to one wet and one dry technology.

The projected plant scale to be deployed may be between 50 t(iHM) and 200 t(iHM) per year. Accordingly, design and cost studies are being performed against both of these scales. JNC is studying small, medium and large FBR types of various fuel and coolant materials. In the past, JNC has proposed construction of a 10 kg(iHM) per hour fuel reprocessing line in the Recycle Equipment Test Facility (RETF). This line would process fully active fast reactor fuel assemblies from the JOYO and MONJU reactors. As a test facility, the annual throughput would be low compared to the hourly rate.

Further scientific data is required for all candidate FR fuel recycle technologies, especially the dry process ones. The current Japanese “simultaneous” oxide electro-winning process, as developed for the feasibility study (principally by Toshiba and TEPCO, in collaboration with RIAR), is a relatively new approach and requires various data, and possibly some further modification of process steps. It is at moderate scale and may require further scale-up.

Issues for resolution in oxide electro-winning include the short vessel lifetime and the need to develop alternative structural materials. The partitioning of electro-deposited uranium oxide and noble metals is an important unresolved issue. A quantitative understanding of MOX electro-co-deposition is needed for design and control purposes. The influence of fission product species on MOX electro-co-deposition is significant and may require more frequent salt purification than would otherwise be necessary.

Through an initial collaborative agreement with Argonne National Laboratory in the US, and in subsequent internal investigations, CRIEPI has acquired considerable scientific data concerning the metal electrorefining process, but once again scale-up may be needed. (The principle is based on the process developed by ANL, but some process modifications are being investigated by several Japanese laboratories.)

JNC and CRIEPI, jointly, have designed and constructed plutonium active (100 g scale) metal electrorefining test equipment in the Chemical Process Facility (CPF) at Tokai Works, and JNC will also install oxide electro-winning test equipment in the CPF. These complement collaborative radioactive trials by CRIEPI at ITU, Germany, and at JAERI, Oarai Centre.

Reactor design and assessment work is underway, principally at the JNC Oarai site. JNC is seeking the restart of the MONJU FBR after some modifications. JNC also operates the JOYO fast breeder test reactor that is now being up-rated to 130 MW(t). These reactor and recycle activities will bring the capability to design a commercial FBR cycle system in the second or third decade of the 21<sup>st</sup> century.

JNC is responsible for leading the phased feasibility study in Japan concerning the development of a fast reactor and fuel cycle system. JNC is funded by and reports to the Japanese government as represented by the Japan Atomic Energy Commission and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the Ministry of Economy, Trade and Industry (METI).

#### ***Future applications to accelerator-driven system (ADS) fuel cycle***

A double-strata fuel cycle has been proposed by JAERI. It comprises an electricity production cycle (first stratum) coupled with a minor actinide (MA) and long-lived fission product (LLFP) transmutation cycle (second stratum). JAERI is applying pyrochemical technology to separation of the

irradiated fuel of the second stratum. The proposed transmutation plant is a nitride-fuelled ADS. In this concept, each stratum may be independently optimised. The first stratum focuses on economy, effective utilisation of plutonium, and so on without being affected by the existence of MA and LLFP. Although the second stratum deals with hazardous MA and LLFP in high concentrations, the amount of materials handled is quite small compared with the first stratum (~1/50). Pyrochemical separation of the irradiated fuel is one of the key technologies in the second stratum. The object of transmutation of MA and LLFP is, of course, to lighten the burden of geological disposal of high-level wastes.

In the JAERI programme, pyrochemical technology is being applied to separation of the irradiated fuel of the ADS because of:

- reduced plant size and cost;
- increased proliferation resistance;
- reduced criticality constraints;
- no solvent degradation through radiation damage.

In addition, the JAERI ADS concept uses nitride fuel with  $^{15}\text{N}$  enrichment in order to limit the formation of  $^{14}\text{C}$ . In this case, recovery and recycling of expensive  $^{15}\text{N}$  is essential for economic reasons. Pyrochemical processes are advantageous as concerns recovery and recycling of  $^{15}\text{N}$  (as  $^{15}\text{N}_2$  gas) in comparison to wet processes that normally use nitric acid, which tends to result in isotopic dilution of the nitrogen.

In the JAERI deployment planning, one commercial ADS plant would transmute about 250 kg of minor actinides to stable or short-lived nuclides per year. This corresponds to the amount of minor actinides produced by approximately 10 LWRs each generating 1 GW(e) per year. The second stratum receives about 250 kg of minor actinides from a partitioning plant per year. Assuming a minor actinide fuel burn-up of about 20% over 600 days of irradiation, with a cooling time after discharge of about two years, a pyrochemical separation plant deals with ~1 000 kg of minor actinides per year. The scale (batch size) of a molten salt electrorefining system to support this operation would thus be similar to that of an FBR reprocessing plant, which is considered technically feasible.

Increasing electrorefiner efficiencies, development of material accountability (Pu, Np, Am, Cm), reduction of the wastes (reduction of volume and radiotoxicity, lengthening the life span of salt and crucible), and so on are necessary for future application of pyrochemical technologies for commercial use. In addition, in the case of nitride fuel, the fabrication characteristics of nitride fuel (pellet-type or vibropacked fuel pin) originating from the electrodeposits at a cathode should be investigated. Furthermore, in case of an inert-matrix fuel (with a diluent such as ZrN), an important consideration is how to effectively recycle or dispose of the diluent material.

JAERI plans to demonstrate the feasibility of partitioning and transmutation of minor actinides and long-lived fission products in an ADS system by about 2030. JAERI is planning construction of a small-scale ADS and associated pilot plants for partitioning, fuel fabrication and pyrochemical separation (~1/10 of commercial plant scale) by about 2025, in which feasibility of the complete system is to be demonstrated. Efforts for the ensuing 10 years will focus on R&D of basic technology, R&D for designing and licensing the plants, and scale-up (quantity and quality) tests, all as related to pyrochemical separation.

JAERI is the Japanese research institution responsible for developing ADS. Some domestic and international collaborations are in place. As JAERI is a national institute, MEXT is responsible for funding and setting the technical direction. Every five years, JAERI's partitioning and transmutation programme, including pyrochemical technology, is subject to a "Check and Review" process by the government, in which the results of R&D are analysed and determination is made as to how to proceed in the future.

## **REPUBLIC OF KOREA**

It is well known in the global nuclear community that matured nuclear power technology stemming from LWR development would not guarantee the ultimate resolutions for vital issues of nuclear safety, non-proliferation and high-level waste management. Due to these concerns, countries technically advanced but poorly endowed with resources persevere in their research and development efforts, to seek nuclear options other than the LWRs for long-term energy security. Because long-lived radionuclides are not all transmuted in one life cycle of loading in a transmutation system, partitioning is an essential step in the partitioning and transmutation cycle. There are basically two methods of partitioning: wet and dry. The latter is being developed in several countries with a focus on the enhancement of its economic features as well as its proliferation resistance, which are the disadvantages associated with the former. Pyrochemical processing, which is a sort of dry process, is being considered in Korea as a suitable partitioning method applicable to the recycling of long-lived radionuclides in the future transmutation systems.

### ***Advanced irradiated fuel conditioning***

Electrolytic reduction technology can be applied for the conditioning of irradiated fuels for disposal. It is a kind of pre-disposal treatment of irradiated fuels, involving chemical reduction of oxide fuel materials into metallic forms by electrolytic reduction in a system of Li<sub>2</sub>O-LiCl molten salt. It will lead to the reduction of disposal volume as well as to the reduction in size of the repository area. The former advantage can be achieved by decreasing the volume of fuel material due to the change in its chemical form and also by removing the structural parts of fuel assemblies, while the latter can be achieved by removing the heat-emitting radionuclides such as <sup>137</sup>Cs and <sup>90</sup>Sr in the process.

### ***Partitioning and transmutation***

Pyrochemical technology would be a promising method to recover transuranic (TRU) elements for use as fuel materials and as transmutation targets in the transmutation systems. The TRUs will be manufactured as transuranic fuels and then loaded into transmutation systems such as the Hybrid Power Extraction Reactor (HYPER), the Advanced Molten-salt Break-even Inherently-safe Dual-mission Experimental and Test Reactor (AMBIDEXTER) and the Proliferation-resistant Environmental-friendly Accident-tolerant Continual Economic Reactor (PEACER). Conceptual studies on these transmutation systems are being or have been carried out in KAERI, Seoul University and Ajoo University.

The conceptual design for HYPER, which is an accelerator-driven transmutation system, is scheduled to be completed by the year 2006 at KAERI. The HYPER core will be designed to have a fast neutron system for effective burning of TRU. About 258 kg of TRU is expected to be transmuted while generating 1 000 MWth per year. Two kinds of metallic fuels, alloy type (TRU-Zr) and dispersion type [(90TRU-10Zr)-Zr] are presently under consideration. Both types of fuel forms will be designed to have a discharge burn-up of at least 30 atom%.

AMBIDEXTER is a sort of molten salt reactor. It consists of two independent circuits of molten salt fuel treatment and a generation system placed at the same site as an integrated system. It will therefore be capable of treating the used molten salt fuel continuously, confining the inventory of the molten salt in the system. In addition, the in-reactor inventory of fission products, such as sources of decay heat and radioactivity, can be kept as low as possible. The standard design of the AMBIDEXTER adopts the Th/<sup>233</sup>U fuel cycle instead of the <sup>235</sup>U/Pu cycle, eliminating the possible accumulation of TRU.

The concept of PEACER was established so as to overcome the drawbacks of conventional sodium-cooled fast reactors. Lead-bismuth alloy is being considered as a candidate coolant in the PEACER because of its higher chemical stability compared with that of sodium. The actinides un-burned or newly generated during the operation will be recycled through pyroprocessing.

## **RUSSIAN FEDERATION**

The State Scientific Centre-Kurchatov Institute foresees several areas of possible applications of pyrochemical technology. Currently, two reactor types dominate global nuclear power generation (PWRs and BWRs). For long-term sustainable nuclear power development, uranium resource limitations demand the consideration of innovative technologies which provide more efficient use of nuclear fuel, including breeder reactors and the closing of the nuclear fuel cycle for uranium and plutonium. Without a closed fuel cycle, it will be impossible to create the fuel materials necessary to ensure the system's sustainability – through production of a virtually renewable fuel resource – using as a basis the large reserves of <sup>238</sup>U and thorium. It is expected that over the next 50 years the PUREX aqueous fuel reprocessing technology, presently widely used by the industry, would remain the basic means for fuel cycle closure. The main deficiency of the PUREX process in the past has been connected with the generation of inadmissibly large amounts of water and organic wastes, which could result in considerable expenses for waste processing and disposal. After decades of commercial application, the possibilities for further improvement of this technology are somewhat limited. In recent years, many results of fundamental and applied research have made possible a considerable improvement in the irradiated nuclear fuel reprocessing technologies presently used and have led to the identification of the potential for use of alternative technologies. This could be realised in the form of aqueous technological processes (with the use of new, more radiation-resistant agents, etc.), as well as in "dry" technologies, i.e. irradiated nuclear fuel reprocessing in molten salts, halide volatility and other technologies. Obviously, the future of nuclear energy depends on a solution to the problems of long-lived radioactive waste management. A few chemical elements (including Pu, Am, Cm and I, Tc) contained in irradiated fuel are responsible for its long-term radiotoxicity. In some nuclear power development scenarios, partitioning and transmutation is considered a tool for radioactive waste management as regards eliminating transuranic elements and long-lived fission products. The development of a system with incineration efficiency for these elements will require high fuel burn-up and multiple fuel recycling with short cooling times. The solution to the problems related to closure of the nuclear fuel cycle for all actinides may require the consideration of a three-component nuclear power structure, which would include, in parallel with solid-fuel thermal and fast reactors, molten salt reactors intended for burning the minor actinides and, possibly, for transmutation of some long-lived fission products; in other words, the incorporation of transmutation reactors into the structure of nuclear power systems.

A radical means of simplifying the back-end of the nuclear fuel cycle, making realisation possible on the basis of only one fuel carrier into the integrated nuclear system (reactor + reprocessing system), is usually connected to the development of molten salt reactors with pyrochemical fuel clean-up. This permits the elimination of the stages of nuclear fuel fabrication and re-fabrication in case of multiple recycling. Transition to the closed fuel cycle should be based on an evaluation of the viewpoints of the most appropriate technology, the industrial readiness to accept this technology, the environmental

situation and the economic efficiency of the process. Also, the possibilities of new fuel cycles for production of radionuclides which could find application in other fields, such as in medical applications, should also be noted.

## **UNITED KINGDOM**

In the UK there is presently around 10 GW(e) capacity of oxide-fuelled commercial nuclear power generation which is mainly of the advanced gas reactor type but includes a single recently-operational large PWR, Sizewell B. The BNFL thermal oxide reprocessing plant (THORP), with nominal throughput of 1 000 tonnes (HM) per year is of the modern PUREX type. It entered service in the mid-1990s and has more than enough capacity to process these irradiated fuel arisings, if required. The THORP plant also reprocesses significant quantities of fuel from overseas. Additionally, there is around a 2 GW(e) capacity of older, metal-fuelled gas-cooled (MAGNOX) commercial reactors in the UK for which the BNFL B205 PUREX plant, due to close around 2012, presently provides fuel processing.

Two prototype fast reactors (the Dounreay Fast Reactor, DFR, and the Prototype Fast Reactor, PFR) were designed and constructed in the UK; dedicated aqueous reprocessing lines were developed to support these reactors. The larger of these, PFR, had a capacity of 250 MW(e) and used oxide fuel; both are presently being decommissioned. Design studies were made for a PUREX-type reprocessing plant to be capable of supporting several full-scale [1 GW(e)] fast breeder reactors. This plant received construction approval at a public inquiry but ultimately was not built. The UK has operated material test reactors including use of HEU, low-power experimental reactors, and prototype power reactors of various sizes. Besides these irradiated fuel arisings, there are fuel residues in various chemical states from fuel fabrication, handling and processing.

The UK currently has no plans for construction of future fast reactors and is not planning the use of facilities for partitioning and transmutation of long-lived radioactive wastes. However, work (led by BNFL) is being carried out in both these areas in order to maintain an informed position, co-operate in international studies and monitor technical developments. BNFL participates in the Generation IV international forum (GIF) which seeks innovative reactor and supporting fuel cycle solutions for installation by around 2030. Pyrochemical technology is envisaged for some of the sustainable reactor system concepts within this study. Regarding nearer-term reactor options, BNFL participates in the consortium developing the pebble-bed modular reactor (PBMR) and offers the AP-600 and AP-1000 advanced water reactors through ownership of Westinghouse. With these reactor options, BNFL presently has no intentions for closing the nuclear fuel cycle.

As an international commercial company with strong expertise in the nuclear fuel cycle, BNFL currently uses high-temperature pyrochemical processes in fuel production and carries out R&D work on pyrochemical fuel processing. BNFL recognises the increasing worldwide interest in pyrochemical separations for new and diverse applications and notes the complementary capabilities of pyrochemical and PUREX separations. The company has no plans for early deployment of a pyrochemical separations plant but is developing experimental and technology skills in the area, has undertaken test case design work, and has performed a range of cost studies for various small and larger plants. The latter are ongoing. BNFL takes a wide interpretation of pyrochemical processes that includes electrorefining, electro-winning, reductive extraction between molten salt and metal phases, halogenation, precipitation, evaporation and volatilisation using halides. There is an open view on the merits of various pyrochemical separations steps, because diversity is valuable for application to a wide range of fuels and it is considered too early to narrow down to any single process.

BNFL considers that pyrochemical separation technology is generally at a pre-competitive stage and, given the success of the present generation of large-scale PUREX plants, envisages that pyrochemical plants may be installed in the longer term. Such plants may initially be constructed at small industrial scale for processing existing niche fuels and wastes or for demonstration of fuels or targets for advanced fuel cycles. In future years, BNFL is likely to act as site manager and operating and maintenance contractor for the proposed Nuclear Decommissioning Authority (NDA) which, when formed, will act on behalf of Her Majesty's Government in Britain.

### ***Potential future applications in the UK***

The main possible applications for pyrochemical separation technology in the UK are considered to be:

- conditioning of fuel and fuel residues for disposal;
- fuel processing for recycle;
- advanced waste processing, which could potentially include waste management options such as separation of heat-generating or long-lived wastes.

In this context, conditioning of irradiated fuel for disposal entails the removal of chemical reactivity, separation of uranium and immobilisation of fission products and transuranics. There are no products apart from uranium, which may or may not be considered a waste stream. Conditioning is seen as particularly relevant to "legacy" fuels and fuel residues of limited quantity and little fissile value that are chemically reactive.

Processing for recycle is considered appropriate for fuels of high chemical reactivity, notably where components can cost-effectively reduce demand for fresh resources. It is particularly applicable to high burn-up and highly-rated fuels such as in the liquid- or gas-cooled fast spectrum reactors. These have lower quantities of irradiated fuel arisings and are less suited to transport at short cooling times, which may favour small, co-located fuel cycle facilities. They may also include separation requirements suited to effective recycle of minor actinides, etc. as a step toward reduction of toxicity and lifetime of wastes for disposal. The lower decontamination factors (DF) of pyrochemical processes as compared to products from classic PUREX plants have increased the emphasis on product quality for recycle and the use of simplified fuel fabrication processes such as vibropac and spherepac. Both the ANL electrorefining and RIAR electro-winning processes are seen as well suited to fast reactor metallic and oxide fuels, respectively. The future application of pyrochemical technology to large quantities of irradiated commercial LWR fuel is not excluded, although considered unlikely at this stage, as the challenges are amplified by the scale of production required. Also, development is needed for process concepts and plant designs suited to continuous processing that is likely to be required for the treatment of large quantities of uranium oxide thermal reactor fuels. Application to smaller quantities of multi-recycle thermal MOX irradiated fuel for product feed to fast spectrum reactors may be favoured in the near term until continuous processes are developed.

The technologies, needs and benefits of partitioning and transmutation as an advanced waste management option are being examined world-wide and include the publication of technology road maps [1,2] by some of the major economic blocs. The potential needs for partitioning will derive from these transmuter/target designs. The processing of fuels dissolved in molten salt coolants as used for molten salt reactors (MSR) is an option being examined by several countries world-wide; BNFL has no

plans for use of the MSR, but participates in funding several ISTC projects in this area being performed by various institutions within the Russian Federation. This includes study of pyrochemical processing of fluoride salts for reactivity, waste management and chemical coolant control.

The potential advantages of pyrochemical separations plants as perceived in the UK are as follows:

- compact plant with few stages and vessels;
- low neutron multiplication factor for fissile materials dissolved in molten salts;
- economic for construction at low industrial throughput;
- suited to various advanced reactor and fuel cycle types, including transmuter targets;
- few additional steps for minor actinide recycle to homogeneous fuels;
- potential simplification of head-end steps;
- un-reactive cover gas that may simplify recovery and immobilisation of volatile radioactive wastes;
- likely reduction in waste discharges;

Potential disadvantages include:

- not yet well established as plant concepts for high fuel throughputs of the order of  $10^3$  tonnes (HM) per year;
- present configurations have poor economics due to substantial process equipment replication;
- potential actinide oxide precipitation in salt with air or water ingress;
- high-level waste forms that differ from the present UK vitrified high-level waste.

### ***Pyrochemical separations development for future applications***

As described above, the UK pyrochemical separations programme is currently directed toward enabling commercial industrialisation of the technology in partnership, in the long term, rather than comprising a specific planned deployment. The present programme is phased over seven years and R&D funds are released at approximately two-year intervals within BNFL, using a formal management assessment technique known as the "BNFL Innovation Process". To this end, various activities are under way in the period 2001-2005 including:

- uranium electrorefining and plutonium electro-recovery in the presence of americium, neptunium and several rare-earth elements in molten salt using a laboratory scale electrorefiner (this is part financed under the EC 5<sup>th</sup> Framework as a collaborative European pyrochemical programme);
- demonstration of salt handling and hydraulic behaviour at large scale (50-100 kg);
- cost studies for ANL and RIAR type fuel processing plants;

- studies of industrialisation of major process components;
- review of technical risks for deployment of pyrochemical plant within BNFL including risk assessment, flow sheet, components, sensitivities on cost and throughput, and interfaces with existing site services;
- experimental and systems studies are under way in the EC 6<sup>th</sup> Framework programme.

BNFL has performed cost studies for LWR and FBR pyrochemical recycle plants using both metal electrorefining and oxide electro-winning processes [3]. Cost studies have also been performed for pyrochemical conditioning of LWR oxide and gas reactor metallic fuels at various throughputs. These showed that pyrochemical separation plants potentially have the clearest economic advantage at low design throughputs and that despite the central importance of electrorefiner availability and throughput, waste management and waste quantities are also important to the economic case. There is a need to simplify the existing head-end processes, for example bulk shear or dismantling and shearing, to match the simplicity of the electrorefining stage and contain overall costs.

### ***Pyrochemical processing plant test case for UK***

Processing of a variety of British “legacy” fuels and fuel residues is presently perceived as the first possible commercial application in the UK. This could be for recovery of high fissile inventories, conditioning of fuels with low recycle value, or possibly both, in a single flexible plant. There is no commitment to build such a plant, but for this test case a date for first operation is considered for the period 2015-2020. The feeds considered include fast reactor metallic and oxide driver fuel, MAGNOX residuals and reactor physics metal fuels, and prototype reactor oxide fuels. A pre-treatment step to convert oxide fuels to metallic form may be required depending on the feeds selected. The design incorporates head-end, reduction, electrorefining, uranium separation from salt, waste recovery from salt and immobilisation. The plant case is based on a 20-30 year lifetime with a total fuel feed of 400-500 tonnes (HM) which equates to a capacity of 75 kg (HM) per day assuming 200 days operation per year. The engineering study performed will provide the basis for risk assessments and cost studies with a view to defining further needs for R&D and programme definition. Any such plant will need significant development to satisfy stakeholders on such issues as safety, environmental performance, product recycle, economics, waste properties and disposal routes. The level of development must be high to compete with processes that are already deployed. Keen regulatory interest is expected in the nuclear and conventional safety areas from the Nuclear Installations Inspectorate, which is part of the Health and Safety Executive in the UK.

### **UNITED STATES OF AMERICA**

A considerable amount of experience relevant to future applications of pyrochemical processing has been gained in the course of treatment of irradiated driver fuel and blanket elements discharged from the EBR-II reactor. This treatment is actually an irradiated fuel conditioning process, because only uranium is recovered while the transuranic elements are directed to high-level waste streams along with fission products. Nevertheless, many of the essential unit operations required for the processing of a broad variety of irradiated fuels have been incorporated in the treatment of the EBR-II materials. High-throughput electrorefining equipment concepts have been developed that will support operations at the rate of one tonne of metallic or nitride fuel or feed material per day. Waste form production operations that can be universally applied to any molten chloride electrorefining process have been perfected and waste qualification for geologic repository acceptance is nearly complete.

Emphasis in the US programme is now being placed on optimisation of pyrochemical methods for the treatment of fuels discharged from advanced (Generation IV) reactors. Processes for the treatment of metal and nitride fuels have been shown to be technically feasible, and the treatment concept for oxide fuels that is most advanced at present (aside from the RIAR process) involves the electrochemical reduction of the oxide in a LiCl-Li<sub>2</sub>O electrolyte, followed by electrorefining to separate the bulk of the uranium content and then by an electrolysis step to recover the transuramics and the balance of the uranium. An alternative process concept is the direct chlorination of the irradiated fuel in a LiCl-KCl salt bath, followed by the usual electrorefining and electrolysis steps. A hybrid process is also under study in which the LWR fuel is dissolved in nitric acid as in a conventional PUREX process, followed by removal of the bulk of the uranium by crystallisation at reduced temperature. The remaining acid solution can be de-nitrated by calcination, with the oxide product (consisting of TRU and fission-product oxides plus a small amount of residual uranium oxide) sent to a chlorination step and subsequent electrolysis to separate the actinides from the fission products.

It is presently expected that advanced reactor systems in the US likely to emerge from the Generation IV development programme will be based upon closed fuel cycles that largely involve pyrochemical separations. The technical feasibility of pyrochemical processing of metal or nitride fuels discharged from fast spectrum reactors designed either for power production or transmutation purposes has been demonstrated, at least at laboratory scale. Once a decision has been made as to the potential deployment of such reactors, an intensified effort of process demonstration and validation will be carried out. For gas reactors utilising coated-particle fuels, a limited concept evaluation process has been completed, and it appears that pyrochemical processes involving direct electrorefining or halide volatility methods can be successfully applied to the treatment of such irradiated fuels. But, since deployment of these Generation IV reactors is not expected for at least two decades, the overriding emphasis in the US programme continues to be on the treatment of LWR irradiated fuel, for purposes of extending the capacity of the proposed Yucca Mountain geologic repository for high-level wastes and significantly delaying the decision point for construction of a second repository.

The development of treatment processes for advanced fuel cycles will be carried out at the R&D level, but without a substantial commitment of resources until the need is more urgent. In the meantime, advanced pyrochemical processing methods are being investigated for potential near-term and long-term applications. The use of organic salts that are liquid at room temperature, the so-called "room temperature ionic liquids", is being explored in a series of laboratory-scale experiments. It may prove possible to utilise these electrolyte salts in specialised applications, such as in the removal of uranium from irradiated fuel or in the separation of specific actinides. Halide volatility methods for treatment of certain fuels, such as a dispersion of fuel material in an inert matrix (e.g. yttria-stabilised ZrO<sub>2</sub>) are also being examined, as are concepts involving zone melting of irradiated fuel rods.

A simplified characterisation of the US programme would be something like the following: pyrochemical processing methods for irradiated nuclear fuel have great promise, but the processes have not been demonstrated at large scale with the specific fuels of interest. Pyrochemical processing of commercial LWR irradiated oxide fuel may be technically feasible, but its application on an industrial scale has not been proven and its ability to yield products with sufficient decontamination of unwanted radionuclides has not been verified. There are variants on the currently studied pyroprocess for LWR irradiated fuel that may make pyrochemical processing more practical, such as head-end chlorination processes. Pyroprocessing seems eminently suited to the treatment of specialised fuels discharged from fast-spectrum reactors, but those reactors are presently such a long time from extensive deployment that the development of specific processing methods is premature at this time. The incorporation of pyrochemical processes in hybrid schemes for the treatment of commercial LWR irradiated fuel may be the most effective near-term application of this very important technology.

## **References**

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## *Chapter 5*

### **RESEARCH NEEDS**

#### **Introduction**

It is only in the last decade of the 20<sup>th</sup> century that the concept of actinide and fission product partitioning to reduce the long-term radiotoxicity of nuclear wastes gained support. Pyrochemical separation and conditioning techniques are not fully developed for nuclear materials and their applicability remains to be proved in many cases. However, within the first decade of the 21<sup>st</sup> century it will be necessary to choose the most promising processes to treat nuclear wastes and start experiments at pilot-plant-scale for the processes, experiments that never reached this scale in the past. Today the evaluation of pyrochemical treatment capability demands more experimental demonstration than has been achieved to date. It is not an easy task, as the material to be treated is not completely defined and because many options for reducing the hazardous radionuclide inventory are still under examination.

Many features are common to the treatment of all types of nuclear waste; the existence of these common features enhances interest in an international exchange of knowledge and technology even though national policies are not, or will not be, identical. In this section, the evolution of irradiated fuel processing from the separation of pure uranium and plutonium products from residual radioactive waste toward more complex partitioning schemes is described. The latter includes co-recovery of actinides, separation of long-lived radionuclides for transmutation and immobilisation of shorter-lived highly active waste for geological disposal. The example provided by the pyrochemical separations development programme of the Russian Federation is given. Quantitative criteria for separation efficiencies and material recoveries have been proposed by the United States. Plant sizes for industrial- and demonstration-scale processing of fuels and targets arising for various reactor and transmuter types are identified. A wide range of research areas are recognised, for example by France, especially for support of pyrochemical separations for partitioning and transmutation targets, and the United Kingdom, particularly in support of industrialisation of pyrochemical separations. Finally, besides fundamental research, this chapter draws attention to three main areas of research and development: that is to say, exploratory studies, demonstration experiments and process development. Listings of significant research areas are made, and conclusions are drawn concerning the deployment of research and development work in the identified areas.

#### **Research situation**

##### ***The past in pyrochemical treatment of nuclear materials***

In the past, from the 1950s to the 1970s, studies of pyrochemical processes were largely devoted to separation of the main fuel constituents, U and Pu, from the minor actinides and fission products. The research almost completely stopped when the PUREX process and light water reactors were adopted world-wide. It is only recently, with the appearance of the concept of partitioning and transmutation, that this kind of research has been revived.

As many data are available on the processes that were examined decades ago, it is natural to try to adapt the oldest techniques to present-day targets. Indeed, some of these techniques have been demonstrated with radioactive species, which is always very expensive to achieve. Some were also developed or used at a significant scale with real nuclear materials (even though these materials sometimes were of military use). These “known” pyrochemical processes are not always, however, efficient in separating the minor actinides, even if they were proven so in the extraction of U and Pu. This is the reason why, today, alternate routes are also envisaged to solve the pressing present problem of long-lived nuclear wastes.

The nuclear material to be treated can be in the form of metal (such as U-Pu-Zr fuel or irradiation targets), of oxides (such as the present-day PWR fuel), or fluoride (such as a possible fuel for molten salt reactors). Today the nuclear material can be a fuel, or a residue from the fuel treatment by another technique (PUREX), or even wastes accumulated during experiments. When the fuels were the main targets, trials were made to keep the nature or the treated fuel identical to that of the recycle fuel, because it is more economical and creates less waste than a transformation of the fuel type. For this purpose, electrorefining was studied for metallic fuels (US, ANL), dissolution and precipitation of oxides in a chloride bath (Russia, RIAR Dimitrovgrad Dry Process) was applied to PWR fuel, reversible fluoride bath/liquid metal exchange was envisaged as a mean of treatment of molten salt reactor fuel (US, ORNL).

Now, the nature of the fuel can be changed to take advantage of some process specificity. This is the case for the fluorination process, in which U is volatilised by formation of gaseous  $\text{UF}_6$  from uranium oxide or uranium tetrafluoride. For minor-actinide partitioning, there are no economical reasons to prevent this change of fuel type if it is for the sake of efficiency. This is why minor-actinide separation may now be considered independently of the nature of the fuel where they have been produced.

### ***The common principles of chemical separation***

In this document the similarity between all of the national research situations will be used to present the research needs as much independent of the research objectives as possible in order to facilitate international collaborations. The separation processes that are presently studied involve:

- fluoride volatility (extraction of U and Np);
- oxide or nitride precipitation in a chloride bath (Th, rare earth, minor actinides);
- electro-winning on a solid or liquid cathode (actinides including U and Th);
- reduction by a metal in a liquid metallic bath (for halides or oxides);
- electrorefining in molten salts (for metallic actinides).

These processes apply to different fuel types or irradiation targets (oxides, salts, metals) or to different types of waste. They raise the same common questions about the effectiveness of the elementary processes, the consistency of the elementary processes involved for a specific treatment, and the experimental verification with active material that is so essential for an informed decision on process selection.

## ***Consistency of research needs with past options and present evolutions***

An illustration of the relationships between past experience and choices and the present evolution in nuclear waste treatment is given in Table 3, a summary of development work on pyrochemical processing at the State Scientific Centre of the Russian Federation, Research Institute of Atomic Reactors (RIAR), representing the status of research and development as of 2002.

## **Specifications**

In order to provide a good basis for future technology decisions, one must bear in mind the specifications for a pyrochemical treatment of nuclear materials and the industrial constraints that could impact on its efficiency. The specifications of a treatment process and of the various research steps before its implementation at pilot-plant scale come from considerations of different nature: the amount of material to be treated, the quality requirements for the input and output, the needs for a progressive acquisition of scientific and technical knowledge, and the specific considerations for an economical management of the treatment facilities. These constitutive elements of the specifications for the development of a pyrochemical process are examined in the following sections.

### ***Quantitative requirements***

For a few decades to come, LWRs based on uranium oxide fuel will constitute the major source of nuclear wastes. However, other reactor types are available or may be developed in the near future, such as fast reactors (FRs). It is also envisaged that the transmutation of minor actinides or transuranic elements will take place in dedicated reactors which are not yet clearly defined. Similarly, the future development of thorium-based reactors must be considered.

For a nominal 1 GW(e) PWR with heavy-metal inventory of about 100 t(HM), the approximate annual fuel charge is 30 t heavy metal. The mass flows<sup>1</sup> in the corresponding discharged irradiated fuel are as follows:

Uranium	28 600 kg
Plutonium	300 kg
Minor actinides	15 kg (Np+Am+Cm)
Fission products	1 000 kg

This material flow may be considered as corresponding to the minimum annual capacity of a treatment unit associated with a single reactor of about 1 GW(e). A dedicated industrial plant could process a few hundred times more material. Therefore the capacity of a processing unit is generally considered to be sized at between 10 and 3 000 t of HM/year. If pyroprocessing is restricted to the TRUs and long-lived fission products (LLFP), this annual capacity drops down to 0.5 to 50 t/year. In the case of dedicated treatment of minor actinides coming from 1 000 t of irradiated fuel a year, the capacity should be less than 1 t/year. These figures may change depending on the reactor type (LWR, fast reactor and molten salt reactor) and the local strategy for waste treatment and nuclear material transportation. However, the orders of magnitude will remain the same, especially for heavy metals

<sup>1</sup> Based on ORIGEN2 calculation for 4.1%  $^{235}\text{U}$  enrichment fuel with burn-up ~34 000 MWd/t(U), using the cross-section library based on JENDL-3.2 for a PWR 17 × 17 fuel assembly.

**Table 3. Main lines of pyrochemical fuel cycle development at the RIAR**

Fuel	Object	Type	Purpose	Production		Collaboration	Reprocessing		Research needs
				Type of process	Status of investigation		Type of process	Status of investigation	
Oxide	UOX	Vibropack	FBR	Pyroelectro-chemical, chloride salt	Semi-industrial level, updating equipment	MINATOM	Pyroelectro-chemical, chloride salt	Large scale experiments with actual irradiated fuel in K-16 hot cell	MINATOM, JNC
	LWR			Pyroelectro-chemical, chloride salt	Feasibility phase	None	OR	Feasibility phase of hot cell facility refurbishment (FREGAT-3)	Optimisation/development of process/equipment
				Pyrohydrolysis of UF <sub>6</sub> in fluidised bed apparatus	Refurbishment of lab-scale facility KS-2	None			
Pellets	FBR			–	–	–	Fluoride volatility process	Large lab-scale test in mock-up facility with non-irrad. fuel	Hot test with actual irradiated LWR fuel in K-16 hot cell
	LWR			–	–	–	Metallisation by Li in molten chloride salt for advanced storage		
MOX	Vibropack	LWR	Pyroelectro-chemical, chloride salt	Initial lab-scale experiments	–	–	–	–	Feasibility phase of process
	FBR		Pyroelectro-chemical, chloride salt	Semi-industrial level, updating equipment	MINATOM, MAYAK, Siberian Chemical Combine	Pyroelectro-chemical, chloride salt	Large-scale experiment with actual irradiated fuel from BOR-60 in K-16 hot cell	MINATOM, TEPCO, Toshiba, JNC	Optimisation/development of process/equipment
Pellets	LWR		Production of PuO <sub>2</sub> powder using the precipitation crystallisation process	Lab-scale experiments	MINATOM, Bochvar Inst.	–	–	Optimisation/development of process	

**Table 3. Main lines of pyrochemical fuel cycle development at the RIAR (*cont.*)**

Fuel	Object	Type	Purpose	Production			Reprocessing		Research needs
				Type of process	Status of investigation	Collaboration	Type of process	Status of investigation	
Oxide	MA oxide	Vibropack	FBR fuel pins with Np based on $\text{UO}_2$	Pyroelectro-chemical, chloride salt	Irradiation of two $(\text{U}, \text{Np})\text{O}_2$ fuel pins in BOR-60 done; now under PIE	MINATOM, CEA	—	—	Optimisation/development of process
			FBR Am oxide fuel pins	Pyroelectro-chemical, chloride salt	Lab-scale experiments	MINATOM, CEA	Pyroelectro-chemical, chloride salt	Feasibility phase of experiments	Optimisation/development of process
			FBR targets with Am, inert matrix	Pyroelectro-chemical, chloride salt	Lab-scale experiments	MINATOM, CEA	Pyroelectro-chemical, chloride salt	Feasibility phase of experiments	Optimisation/development of process
Nitride	U-Pu mixed mononitride	Pellets	BREST reactor fuel	—	—	LINEX process (ANL flow sheet uses liquid Cd cathode)	Lab-scale experiments	MINATOM, ENTEK, Bochvar Inst.	MA recovery, comparative feasibility phase of experiments
	MA containing fuel based on inert matrix	Pellets	Conventional ABR	Unselected	Preliminary feasibility phase	IPPE CEA, planning ISTC project	—	—	Preliminary feasibility study
Metallic	U-containing fuel	U-Al alloys	Research reactors	—	—	—	Pyroelectro-chemical, chloride salt	PRESTO, Energoatom, IHE, Ekaterinburg	Lab-scale experiments with non-irrad. fuel
		U-Cu alloys	Research reactors	—	—	—	Pyroelectro-chemical, fluoride salt	Lab-scale experiments with Pu and MA	Pu and MA fluorides solubility; study of different flow sheets
Molten salt	MSR fuel	Fluoride salt	Molten salt reactor	—	—	—	Pyroelectro-chemical, fluoride salt	KI, Bochvar Inst., ISTC Project #1486	

**Table 3. Main lines of pyrochemical fuel cycle development at the RIAR (*cont.*)**

Object	Type	Purpose	Production			Type of process	Status of investigation	Collaboration	Type of process	Status of investigation	Collaboration	Research needs
			Type of process	Status of investigation	Collaboration							
<i>Non-fuel materials</i>												
High-level waste	Salt	Chloride salts	–	–	–	–	–	–	Vitrification (aluminum fluoride glass)	Sampling scale experiment with actual irradiated fuel	MINATOM, TEPCO, Toshiba, JNC	Optimisation/development of process
Fission product concentrate	Phosphate precipitate	–	–	–	–	–	–	–	Ceramisation (NZP – ceramic)	Lab-scale experiment with simulated irradiated fuel	MINATOM, Nizhny-Novgorod University, TEPCO, Toshiba	
Pu-containing wastes	–	–	–	–	–	–	–	–	Immobilisation into ceramic (NZP-ceramic)	Lab-scale experiments with $^{238}\text{Pu}$	LANL	Optimisation/development of process
B <sub>4</sub> C	Enriched boron carbide	–	–	–	–	–	–	–	High-temperature chlorination	Lab-scale processing of actual spent B <sub>4</sub> C	MINATOM	Optimisation/development of process
<sup>99</sup> Mo	U-Zn alloy target	–	–	–	–	–	–	–	Pyrochemical reprocessing	Large lab-scale experiments with irradiated targets	MINATOM	Optimisation/development of process/equipment
<sup>99</sup> Tc	Metallic Tc target	Transmutation and production of marketable Ru	–	–	–	–	–	Unselected	Feasibility phase of experiments	Institute of Physical Chemistry of RAS, MAYAK, planning ISTC project	Institute of Physical Chemistry of RAS, MAYAK, planning ISTC project	Feasibility study and process optimisation

and fission products, because 1 tonne of fissile material will always roughly be needed to produce 1 GW(e)year. For Pu and minor actinides this could be different in the future, depending on the options taken: higher Pu flow for MOX fuels or FR fuels, lower TRU flow for the Th-based cycle.

The industrial scale may be defined at 10 to 100 t/year capacity for the fertile elements, and at 1 t/year capacity for fissile elements. For a pilot-scale unit, one may consider that a demonstration should reach a treatment rate of about 0.1 t/year with TRUs and 1-10 t/year for fertile elements (scale 1/10). For a laboratory-scale experiment, performing batch treatment on nuclear material, the typical required capacity would be of the order of about 1 kg/day of fertile elements and 0.1 kg/day of TRU (scale 1/100).

The capacities of a laboratory-scale unit are easily accessible for fertile elements (natural isotopic composition) but the radiotoxicity of TRU results in the need for use of a shielded glove box or for remote handling of the material in hot cells. Specific care must be devoted to the effluents and the wastes generated during the tests. This is why an international collaboration would be very valuable for experiments on TRU elements.

### *Chemical specifications*

As soon as a nuclear irradiated fuel is treated, either for recycling U (or U and Pu), or for reducing the radiotoxicity of long-lived radionuclides in the stored nuclear wastes, partitioning of each radionuclide is required, to an extent that is yet to be specified. The more demanding scheme is the partitioning and transmutation (P&T) option that is of current world-wide interest. This scheme is valid for present-day nuclear fuels, but it should also be applicable to future nuclear reactor fuels with the main objective of increasing long-term public safety. Three types of radionuclides are considered here: the fertile-fissile couple (U-U, U-Pu or Th-U), the minor actinides (MA: Np, Am, Cm) or the transuranics (Pu and MA) and the long-lived fission products (LLFP:  $^{99}\text{Tc}$  and  $^{129}\text{I}$ ).

A fourth group is the lanthanide group, a set of neutron poisons, the concentration of which should be limited in fuels or in transmutation targets. The concentration limits for each group can depend on:

- efficiency of radiotoxicity reduction by transmutation;
- nuclear physics of each reactor;
- heat produced during the decay period for each fuel or target.

As it is difficult to cover the entire range of possible fuels and reactors, only typical examples will be given here.

Purity requirements for the fertile-fissile couple depend on the type of reactor used for recycling and on the national policy. For instance, the US presently proposes to incorporate Pu and Np in the recycle LWR nuclear fuel, whereas other nations have chosen to recycle only Pu or U and Pu. In the US case, neptunium is kept with plutonium for non-proliferation purposes (denaturing with  $^{238}\text{Pu}$  from neutron absorption by  $^{237}\text{Np}$ ). The main requirement for this separation is that the amount of Pu and Np lost to the waste stream should be less than 0.5% of the amount originally present in the irradiated LWR fuel.

In the US scheme, reprocessed uranium (in fuel burned to greater than 50 MWd/kg) is of little value in view of the vast amounts of un-reprocessed depleted uranium remaining from enrichment operations. The concentration limit for lanthanides in recycle fuel is fixed by reactor physics considerations and depends on the reactor type (thermal or fast neutrons, solid fuel or molten salt) and on the chosen operating conditions (breeding factor, burn-up).

For the U-Pu mixture, the radiotoxicity is due to Pu, and only reactor physics considerations apply in the establishment of limitations on minor-actinide concentrations. The same holds true with minor-actinide transmutation targets. However, another limit appears due to the heat produced during the decay of the fuel materials. This decay heat comes primarily from  $^{241}\text{Am}$ , with lesser contributions from  $^{238}\text{Pu}$  and  $^{244}\text{Cm}$ ;  $^{238}\text{Pu}$  can derive from neutron absorption in  $^{237}\text{Np}$  or by alpha decay of  $^{242}\text{Cm}$ . The heat limit arises from the creation of problems in product handling (once it has been converted to solid form) and in recycle fuel fabrication steps. Different limits will apply in different handling and fabrication scenarios.

In the US, at the onset of the ATW programme, it was determined that an attempt will be made to dispose of the separated uranium as a Class C low-level waste as defined by the US Nuclear Regulatory Commission. Those limits are as shown in Table 4.

The US programme has also established tentative specifications for losses of actinides (Table 5) and on the decontamination requirements for transuranic materials that are to be sent to recycle fuel or transmutation target fabrication (Table 6).

The US programme is also currently operating with an assumed requirement of a 95% recovery efficiency for long-lived fission products, projected to be the principal contributors to the off-site dose rate for people living in the vicinity of the Yucca Mountain geologic repository in the first 10 000 years

**Table 4. Limits on the contamination of separated uranium, as fixed in the case of the US programme for partitioning and transmutation**

Radionuclide	Maximum content/ tonne separated U
TRU	6.8 mg
$^{99}\text{Tc}$	9.3 g
$^{129}\text{I}$	24.2 g
$^{137}\text{Cs}$	2.8 g
$^{90}\text{Sr}$	2.7 g

**Table 5. Tentative limits on recovery efficiency established in the US programme for irradiated fuel treatment**

Element	Criterion	Recovery efficiency
U lost in TRU stream	Residual U should not produce more than 1% of the TRU fissioned during transmutation	99% U
Pu lost in HLW	Residual Pu radiotoxicity should contribute less than 0.01% of the radiotoxicity of the irradiated fuel	99.5% Pu
MA lost in HLW	Same as for Pu	

**Table 6. Tentative decontamination specifications for recovered transuramics***Controlling factors are indicated parenthetically*

Fuel \ Reactor	Thermal spectrum		Fast spectrum	
	MOX	TRUOX	TRU	MA
Pu limit	(up to enrichment limit)	(up to enrichment limit)	<1% $^{238}\text{Pu}$ (decay heat)	(up to enrichment limit)
Np limit	<5% (neutron capture)	<10% (neutron capture)	(core physics limit)	(core physics limit)
Am limit	<0.33% (decay heat)	Yet to be determined	<2.32% (decay heat)	Yet to be determined
Cm limit	<0.02% (decay heat)	Yet to be determined	<0.12% (decay heat)	Yet to be determined
Ln limit	<0.3% (neutron capture)	Yet to be determined	<5% (fuel-cladding interaction)	Yet to be determined

after emplacement of high-level wastes in the repository. Validation of the criteria shown in Tables 4-6 is a clear research need, because the criteria have a significant impact on the scope (and costs) of separations processes that must be carried out in a partitioning and transmutation system.

Other countries are considering required recovery efficiencies and necessary waste or product purities. There is difficulty in establishing unequivocal targets for differing technologies. One issue is the selection of targets based on radiotoxicity, a measure of potential maximum harm, versus that of predicted repository release, an estimate of expected harm. Another is the differing national categorisation and regulatory limits for management of radioactive wastes. Also transmuter, fuels and partitioning processes are not well established such that conversions and number of recycles are not well known. Although some of the targets may be considered somewhat arbitrary, they are likely to form the best current basis for the comparative assessment of candidate processes. The OECD/NEA Working Party on Scientific Issues in Partitioning and Transmutation has instituted a fifth sub-group to address the above issues.

### Research needs for pyrochemical separations

Presently, the main thrust of research on pyrochemical treatment concepts is to determine their theoretical efficiency and to predict their technological feasibility. In most cases, the work to be carried out is at an early stage of development. For this reason, the most pressing research needs are considered to be of a more fundamental nature.

Four stages of development will be considered here. The first one is the search for principles which could be applied to the separation of actinides from the other constituents of a given fuel or waste. It is called here "Exploratory studies", because it is open to any idea irrespective of technical consideration or economics. The idea at this stage is to check what principles may serve to provide a first screening among a wide variety of elementary operations concerning the most important question for any nuclear material treatment process: actinide separation. The second one is designated the "Demonstration experiment" stage. The purpose of this stage is to demonstrate that the principles selected in the previous stage are actually applicable to nuclear materials. This requires operations

with synthetic or real nuclear materials, under the usual operating constraints of a nuclear environment. The demonstration can, however, usually be reduced to a single elementary step and not necessarily made for the entire chain of treatment, from the initial material to the treatment of the secondary wastes generated during the treatment itself. The third step is the “Process development” stage, which includes technological considerations such as the compatibility of the succession of elementary operations and the front- and back-end operations. The scale of this third stage is not necessarily the full production scale of the process, but it should be at a sufficiently large scale to be representative of possible problems and solutions for full-scale operations.

The reasons for this classification, representing stages far from industrialisation, are first, that up to now, no pyroprocess has reached the industrial scale consistent with commercial nuclear fuel processing (the most advanced of these processes, the Argonne National Laboratory electrorefining method for metallic fuel and the RIAR-Dimitrovgrad dry oxide fuel treatment process, have operated only at the rate of kilograms per year for fuels with high fissile content) and second that the matter of industrialisation belongs to the competitive commercial field and thus is less suitable for international open collaboration. The field of international collaboration is better suited to the pre-competitive level and, particularly, to the exploration of as many routes as possible to document the best possibilities of pyrochemical processing for each kind of nuclear material that will require treatment.

This section also addresses the “fundamental” knowledge that could be useful in the development of specific nuclear fuel treatment processes. Indeed, the basic data and chemical engineering innovations needed for nuclear fuel and target treatment are common to other, non-nuclear, applications. Knowledge coming from non-nuclear studies can be helpful in understanding general process behaviour or in providing a simulation of what could be done with nuclear materials. An obvious common interest is in process or property modelling and also in property measurement techniques. The discussions to follow will examine what is needed to adapt existing methods to the treatment of nuclear materials.

The research that has been identified below does not exactly reflect the national research programmes presently under way (and presented in this document), partly because some questions are expected to be clarified during these programmes and also because, after these programmes, other problems will arise to be addressed, but with a priority that is still to be determined. The selected topics are also suited for effective international collaboration because they are sufficiently independent from a given fuel material or reactor system option.

The OECD-NE Pyrochemistry Working Group concludes that research should be conducted with the following objectives:

- *Fundamental research.* To understand the fundamental mechanisms involved (nature, structure of the chemical species, reactivity) in pyrochemical processes and provide data for the selection of process options.
- *Exploratory studies.* To master the basic operations, to be able to implement them if a technological expansion is decided upon and to identify the technical feasibility of certain processes.
- *Demonstration experiments.* To confirm the industrial feasibility of selected process options and to identify needed areas for process improvements.
- *Process development.* To develop the engineering technologies (process equipment design, process control instrumentation) necessary for the industrial-scale implementation of pyrochemical processes.

The first point is of particular importance, not only to optimise the process implementation but also to anticipate any malfunction and thus to demonstrate the safety of the processes. Basic data must be determined with regard to the elementary operations proposed to constitute a complete process. Specific research needs identified by the working group follow.

### ***Fundamental research***

Some physical and chemical properties are not known for substances or materials that could be involved in pyrochemical processes of interest for nuclear applications. In the more common case, these properties are known for systems that are much simpler than the multi-component ones composing the reactive medium of pyrochemical processes. In any event, measurements are required in order to be able to proceed further with confidence in a sound database. From an engineering point of view it is often valuable to model the physics and chemical behaviour of the substances that will be used to better simulate the processes, including under conditions that are far from the best operating ones. All this relies on data acquisition on non-radioactive systems and such acquisition may thus be carried out in general-purpose research facilities by researchers having experience in the field and in possession of specialised equipment.

Elements such as natural thorium and uranium can be handled in the same facilities as non-nuclear materials. For fissile isotopes or minor actinides this is not the case, and the measurement equipment must be transferred or rebuilt in nuclear facilities, which can be a long and very expensive process. For property modelling there is not such a constraint and very often the model validation may be carried out on surrogate materials before application to fissile ones.

To the extent that this “fundamental data needs” section is related to non-nuclear materials, there is no very specific demand from the nuclear community. However, such kinds of research may provide a transfer from the non-nuclear field that is beneficial to the nuclear community. It is thus worth being attentive to any opportunity of attracting experts who could adapt their methods (equipment or software) to nuclear pyrochemistry needs. As this kind of exchange already exists, it may be valuable to promote it further in meetings (on nuclear pyrochemistry or general pyrochemistry) or by starting new, specific collaborations on an international basis.

### ***Thermodynamic properties***

Different categories of thermodynamic properties are required at different stages of process development. Some are very basic, such as the free energy of formation of compounds and their vapour pressures. This is mainly true for the actinide compounds but also for some fission products. Other categories involve more sophisticated data such as the phase diagrams of complex mixtures. In general, thermodynamic properties of actinides and other fission products are needed for oxides, fluorides, chlorides and iodides because they are either unknown or not accurate for all oxidation states. This includes free energy of formation and vapour pressure. For instance, the vapour pressure of actinides and fission products in chloride salts (especially for elements with high potential volatility such as Cd, Am, I) are needed. This is because all the ionic phases involved in fuel processing or waste treatment belong to these systems. The same is true for metals and inter-metallic compounds because many processes involve a metallic phase that allows an easy physical separation from an ionic phase. Such metallic phases can be a solid metal or an inter-metallic compound for electro-deposition, or a liquid alloy for electro-deposition or reduction by a metal (Al, Ca, Li). But they can also be metallic phases appearing in molten salt reactors or metallic fuels due to the presence of fission

products. In some applications where the extraction of certain long-lived fission products is a system requirement, the vapour pressure of metallic fission products such as technetium is an important data requirement.

Phase diagrams for liquid ionic or metallic phases are also needed, either for the behaviour of minor actinides or for very complex mixtures containing the numerous actinides and fission products. This is true for the evaluation of the solubility of actinide ionic compounds (oxides, chlorides and fluorides) in molten salts (for molten salt reactors or separation of elements in nuclear wastes) and for identification of the liquidus temperature of complex alloys and complex salts. For complex ionic or metallic liquids another kind of thermodynamic property is sought after: the free energy of mixing of some elements or compounds. For instance, the free energy of mixing of actinides and/or lanthanides in alloys would be useful information in choosing the best metallic solvent for separation purposes using liquid alloys (electrochemical or metallothermic reduction). Evaluation of the activity coefficients of transuranic elements in molten chloride salts with a high concentration of transuranic elements is also needed, because data have only been obtained with very low concentration, thus too far from the operating conditions.

Modelling thermodynamic properties for evaluation purposes or for extrapolation of measured properties is also of great general interest. Two types of thermodynamic modelling may be considered: the Calphad type of extrapolation-interpolation models or *ab initio* evaluations. The first consists of a polynomial representation of the free energy of mixing of each phase that can appear in a given mixture. This representation allows the calculation of phase equilibrium in all the composition ranges and at every temperature. To achieve this, two things are required: experimental information (phase equilibrium, free energy of mixing, compound stability) and a representation that is consistent with all of the data in the corresponding database. The second corresponds to models that do not use thermodynamic mixing data as parameters but are based on the first principle of physics. They are not as accurate as the previous ones, but they do not require as much physical data. They are more predictive models than representation models. Their interest is that they can be validated on a few members of the actinides or lanthanides series and then they can be used to predict the behaviour of the other elements of these series. This is also true for each column of the periodic table and can be applied to various fission products. *Ab initio* models have been developed for liquid metals and salts.

Modelling of the thermodynamics of mixing of molten salts or alloys would allow a calculation of the phase diagrams and the distribution coefficient of the elements between the various phases under a wide span of conditions, even larger than the range of experimental application. This assumes, first, that reliable measurements are available (phase diagrams, component activity measurements, enthalpies of mixing or formation) and that databases for assessed thermodynamic mixing properties already exist for the main constituents. Then a choice of software associated with the existing database is to be made and new specific data added after assessing their consistency with respect to the existing base. This is a long-term effort covering a large variety of needs and thus conducive to a collaborative effort.

### **Mass transfer kinetics**

Mass transfer kinetics are usually specific to a process type and a scale of equipment. However, chemical engineers have developed models to adapt data to each reactor type and size. In order to use them properly the first thing is to identify the nature of the limiting step of mass transfer, which is not always what would be expected by analogy with the known pyrochemical processes of the non-nuclear industry. The identified information needs are:

- the nature of the limiting step of mass transfer in molten salt/liquid metal reactions or in the vicinity of an electrode;
- the corrosion mode of container materials by molten salts or liquid metals;
- the nature of high temperature gaseous species for modelling deposition or volatilisation kinetics (sorption and de-sorption);
- the heterogeneous non-catalysed reaction kinetics in the fluoride volatility method for treatment of the fluorides coming from molten salt reactors (transmutation of MA or Th-U cycle);
- conversion of oxides to fluorides in the front-end of the MSR fuel cycle (for transmutation of Pu and minor actinides).

### ***Electrochemical behaviour***

The general use of molten salts as a medium to handle nuclear materials or as a source of nuclear material (e.g. the molten salt reactor) leads to the consideration of electrochemistry as an obvious means of treatment or characterisation and an obvious source of corrosion. Therefore, all the specific techniques of molten salt electrochemistry are of great interest:

- cyclic voltammetry (various shapes of potential versus time);
- chronopotentiometry;
- integration techniques.

This is also true for the modelling of transport properties (diffusion, electro-migration) that could result from the understanding of the electrochemical mechanisms. As organo-metallic salts could provide a low-temperature medium for electrochemical treatments, it would be helpful to determine the electrochemical properties of organo-metallic halide salts and their stability to radiation.

### ***Physical properties of liquid metals and molten salts***

These data are particularly important for chemical engineering studies, for equipment specification and for implementation of the processes. The following data must be determined for any given compound: density, heat capacity, molar volume, melting temperature, melting heat and entropy, viscosity, thermal conductivity and saturation vapour pressure, as well as the possible effects of temperature on these parameters. Data on the physical properties of ionic or metallic liquids are needed for hydrodynamic calculations and analysis of heat and mass transfer conditions; the needed data include density, viscosity and heat capacity of molten salts and alloys. A specific mention is to be made of density and thermal expansion of molten salts for molten salt reactors because of critical safety concerns. Data on the speciation of actinides and fission products in salts for on-line analytical purposes (optical properties) or for modelling thermodynamic or electrochemical properties (stability or transport properties) are also needed.

### ***Chemical properties of liquid metals and molten salt***

Major chemical properties to be investigated for salts include salt stability, phase diagrams (notably the existence of eutectic or peritectic mixtures and specially-defined compounds), element solubility and electro-inactivity domain (decomposition voltages). For the metals, phase diagrams of complex alloys and activity coefficients of diluted actinides and lanthanides are required.

### ***Speciation and redox properties in salts***

This aspect is both the most important and the most challenging. Regardless of the separation technique that is ultimately selected, it will be based on the possibility of modifying the oxidation state of an element (by electrolysis or by adding a chemical agent) to separate it from another. In a molten salt medium, this process is complicated by complexation phenomena and by the very significant influence of temperature. The first task is to identify the species liable to exist in the reaction medium (speciation). This is a difficult step, requiring the use of sophisticated equipment including a variety of spectrophotometers (UV-visible, Raman, NMR, XAS, etc.) but it is indispensable. Determining the redox properties involves measuring the normal apparent potentials as a function of the temperature but also as a function of variables such as pX (where X stands for  $\text{Cl}^-$ ,  $\text{F}^-$  or  $\text{O}^{2-}$  depending on the chemical system considered). The thermodynamic possibilities of separating the desired metallic species could then be predicted.

### ***Reaction processes in complex media***

The mechanisms and reaction equilibrium must be assessed in situations that may be far from ideal thermodynamic conditions. This phenomenon is particularly significant in the case of extraction by a liquid metal.

### ***Kinetics***

Although generally considered rapid, pyrochemical reactions may be slow under some conditions when several phases are involved:

- gas-liquid-solid for dissolution;
- liquid-liquid for extraction by a metal;
- liquid-solid for electrolytic deposits.

It is thus of critical importance to determine the parameters controlling mixing, diffusion and transfer phenomena. Specific studies, generally with non-radioactive media, must be carried out in close collaboration with chemical engineering studies.

### ***Exploratory studies***

Exploratory studies are defined here as consisting of speculative research involving any elementary operation that could take place in the processing of nuclear fuel materials in one of the many scenarios that have been proposed. The very first stage in the development of a new concept is to ascertain whether the physics and the chemistry that are involved work as expected. These studies may only

be undertaken for elucidation of the principal elementary operations of the concept to be evaluated. Simulant materials and simplified technologies may be used to shorten the evaluation period. The aim is to obtain some kind of order-of-magnitude estimate of the potential efficiency and to reveal the main drawbacks or technical difficulties for each of the elementary processes involved. Diluted uranium and/or thorium are generally the only actinides to be used in such exploratory studies, to avoid the use of the specialised equipment that transuranic elements would require. Experiments with Pu and other minor actinides are described in the “Demonstration experiments” section below. For non-radioactive elements, the complexity of the chemical systems under examination would be greatly simplified at this base level.

The study of some details of already-known processes, including duplication of earlier work at other institutions, is useful in that it helps to improve the general state of knowledge and to generate reliable data on the main characteristics of these processes. But refining the state of knowledge has another objective: the establishment of a network of researchers and the dissemination of understanding of the basic technologies that follows. Indeed, this stage of development is cheap and suited to knowledge acquisition. Training on simple handling and measurement techniques saves time, money and material when switching to experiments in a nuclear environment. Because the research is simplified, it also allows trials on many variations of operational parameters.

### ***Electrorefining of metallic fuel***

The treatment of irradiated metallic fuel containing U-Pu-MA (minor actinides)-RE (rare earth)-Zr consists of an anodic dissolution of the fuel into a molten LiCl-KCl salt eutectic mixture, followed by electro-deposition on a solid or a liquid cathode. Uranium is largely recovered on a solid cathode, whereas the remaining actinides (U, Pu and MA) are recovered by a subsequent electrolysis step or in a liquid Cd cathode, together with a small amount of uranium and lanthanide fission products. This process has already reached the scale of hundreds of kilograms per year at Argonne National Laboratory in the processing of depleted U blanket elements. It is also presently investigated by Japan (CRIEPI), Korea (KAERI), the European Commission (JRC-ITU) and countries of the European Union, at the tens-of-grams level with active materials. Important aspects of the electrorefining process that should be investigated are:

- the effect of impurities, such as fission products, in the salt or in the atmosphere ( $O_2$  or  $H_2O$ );
- the lifetime of presently-used vessel materials (AlN,  $ZrO_2$ ,  $Al_2O_3$ , BeO) and the search for a new long-lasting material compatible with the salt and the active metals.

### ***Electrorefining of oxide fuel***

This is a new process that has been suggested to treat oxide fuels or targets. It consists of electro-deposition of actinide oxides in a chloride melt of insoluble actinide oxides. The influence of salt composition, temperature and potential must be investigated with uranium oxide before going to irradiated oxide fuel; such work is in progress at SSC-RIAR, Dimitrovgrad. The design of the electrochemical cell must be improved to optimise the process yield.

### ***Chlorination of high-level wastes (HLW)***

The CRIEPI concept for HLW treatment foresees the conversion of the high-level waste obtained from the PUREX process into chloride form for subsequent pyrochemical separation of minor actinides

from lanthanide fission products. This is accomplished by a chain of processes such as de-nitration, calcination and salt-bath chlorination. It is important to know the behaviour of each fission product and transuranic element during the chlorination process, including:

- the conversion ratios of each element for several temperatures and operating time;
- the type and stability of the chemical species formed in the salt;
- the volatility of some elements (such as Ru and Mo).

### ***Preparation of salts***

Reduction or electro-transport experiments may have to deal with reduced species in the salt [U(III) for instance] or at least with a controlled potential [ratio U(III) to U(IV)] to simulate real situations (molten salt reactor) or reduction conditions. One will have to find practical ways to prepare a molten salt (chloride or fluoride) in a given state of oxidation, or a given potential, prior to the experiments. Similarly, the oxygen (or moisture) content of a salt in small-scale experiments is awkward to reduce to the level (~1 000 ppm) where it could be maintained in large-scale operations. It would be useful to find simple ways to fix the oxygen content at a low level (100 ppm for instance) in already-prepared chloride or fluoride salts.

### ***Process for separation of metallic actinides and fission products from salts***

In several processes (electrochemical deposition or chemical reduction), actinide particles (such as uranium) are present in the salt. In other cases, metallic fission product (Mo, Ru) may also be present. Thus, there is an interest in finding efficient processes to extract these metallic particles from the molten salt.

### ***Separation of actinides from lanthanides by salt/metal reductive extraction***

There are several situations in which the fission products are dissolved in a molten salt, either after reprocessing of irradiated metallic fuel or by chlorination or fluorination of high-level wastes. Minor actinides (and U or Pu residue) are then the main radioactive elements to be extracted from the molten salt. In this extraction, actinides should be separated from the lanthanides (RE) in view of their incineration or simply to minimise the amount of matter classified as high-level waste (HLW). A possible solution is a selective reduction into a liquid metal such as Bi. The reductive salt/metal extraction process needs to be better characterised to:

- find the solubility limit of actinides (U, Th) and lanthanides in the metallic solvent and the composition of inter-metallic compounds that could precipitate;
- investigate the extraction kinetics to find the most efficient kind of reactor;
- investigate the influence of impurities, especially oxygen or water, on the kinetics.

### ***Reduction of oxide fuels***

The reduction of  $\text{UO}_2$  by metallic lithium in a liquid lithium chloride bath or through direct electrochemical reduction in a suitable electrolyte such as  $\text{CaCl}_2$ ,  $\text{LiCl-KCl}$  eutectic, etc., in view of

storing high-density bulk metallic uranium instead of oxide powder, could be a way of reducing the space needed for storage or final disposal of irradiated fuel. The oxidised Li can be recovered by electrochemical reduction in the salt. Irradiated oxide fuels can also be treated by the electrochemical reduction method, followed by electrorefining to separate actinides from fission products, as a means for recovering valuable actinides for recycle in a nuclear system.

#### ***Adsorption of Cs and Sr by zeolites in molten salts***

Caesium and strontium chloride tend to remain in the electrolyte salts after treatment of nuclear materials. In order to avoid wasting these salts or in order to decrease their residual radioactivity for final storage, it is important to find a way of extracting these fission products. Their removal by adsorption on zeolite could be a possibility that should be tested. Electrochemical methods should also be evaluated.

#### ***Cleaning and recycling salts and alloys***

The solvents for the actinides and fission product, molten salts and liquid metals as well, typically represent a mass of material in excess of the nuclear material to be treated (10 to 100 times more). This added material should not become an extra nuclear waste. Most of the dissolved (or trapped) nuclear material has to be removed from these solvents after use. If this is possible, recycling or permanent storage are possible. There are a number of methods already available, but new techniques are still needed to address this key issue.

#### ***Immobilisation of chloride waste***

Chloride salts are the most frequently studied molten salts for waste treatment, but their insertion in glass is limited and a way of increasing the amount of chloride salt immobilised in a glass or in an alternate waste form must be explored.

#### ***Development of process flow sheets***

Considering a particular application of a given process (nature and quality of input and output products, recovery efficiency and degree of purification) and based on the findings of laboratory studies or published reports, the purpose of this task is:

- to establish a complete process flow sheet (the goal is to provide a general flow sheet for a specific type of fuel: dissolution, off-gas treatment, separation by salt/metal exchange and/or electrolysis or volatilisation, recovery of finished products and waste treatment);
- to determine the data corresponding to the flow sheet (flow streams, concentrations, activities, etc.);
- to provide a quantitative and qualitative assessment of the waste production.

The results can then be used for an overall assessment of the process and thus for comparison of various flow sheets. The data may also be used for a technical and economic feasibility assessment.

## ***Chemical engineering studies***

Pyrochemical processes call on a wide range of techniques, based on the general classification of chemical engineering operations, including:

- fluid mechanics, i.e. solid-liquid separation (filtration, settling), liquid-liquid separation;
- material transfers, i.e. gas absorption, dissolution, liquid-liquid extraction, crystallisation, electro-deposition;
- chemical conversions, i.e. oxidation or reduction, chemical displacement.

It is essential to master some of these operations and yet the subject is not widely covered in the literature. Research topics include the following.

### ***Material and heat transfer near an electrode***

In view of the rheological properties of molten salts and considering that electro-deposition combines material transfers and heat transfers, it must be determined whether the Chilton-Colburn analogy is applicable; if so, the general transfer modelling methods based on the Nusselt and Sherwood criteria will also be applicable. This analysis will require measuring the coefficients of diffusion (e.g. by electrochemical means with a few representative species) and thermal diffusivity, as well as determining the viscosity and heat capacity of the molten salts.

### ***Material transfer between a molten salt and a liquid metal***

This is an unusual liquid-liquid transfer and a fundamental approach is necessary to describe and model these systems and to design efficient contactors. Material transfer phenomena must be analysed to predict the limiting steps, notably in the case of exchanges involving several species (reductive extraction), to determine whether classic chemical engineering models (e.g. the double boundary layer model) are applicable.

### ***Liquid-liquid separation***

Despite the different densities, it may be difficult to obtain complete separation between a molten salt and a liquid metal. This problem has often been attributed to capillarity phenomena and is particularly troublesome when the metal phase is produced by reduction in a homogeneous salt phase. It may considerably limit the recovery yield even with a favourable system chemistry. For the relevant salts and metals, this task will consist in estimating the possibilities for separation by settling alone, by more sophisticated means (e.g. centrifugation) or by adding compounds to enhance coalescence. Surface tension measurements may also be necessary. Chemical engineering studies will then attempt to define the design principles of pyrochemical reactors compatible with the process flow sheets developed previously.

### ***Materials studies***

Corrosion is expected to be a limiting factor in the development of processes combining high temperatures, corrosive gases, halides and liquid metals. The first task should be to identify one or more

acceptable materials for the selected medium based on bibliographic research and prior experience, together with a few validation tests. The corrosion rates and mechanisms will then be characterised with greater precision.

### ***Product recycling studies***

Pyrochemical processes are intended to recycle actinides and long-lived fission products; the resulting products (metal, oxide, carbide or nitride) must therefore be compatible with the target fabrication processes. These studies must be undertaken in close collaboration with teams working in charge of defining the fabrication process.

### ***Secondary waste management studies***

In addition to classic technological wastes (e.g. failed equipment, cleaning wastes, etc.), a pyrochemical process generates specific waste-forms requiring suitable management routes. These include off-gas trapping solutions, un-trapped gases, contaminated salts and metals used for extraction. Although classic liquid-waste-treatment processes are available for the first category, the remaining waste forms will require substantial development work: first, to estimate the waste quantities generated (based on the process flow sheet development work) and second, to identify suitable treatment and stable conditioning processes. Decontamination processes may include electrostatic filtration (for gases), melting (for metals) or metal-salt exchange (for salts). The first R&D task could be to acquire basic data under both inactive and radioactive conditions, including the effectiveness of electrostatic filtration, the distribution coefficients in salts and metals, the activity coefficients of contaminants in salts and metals and the reaction kinetics involved. This information can then be used in the preliminary specification of the industrial reactor design. The waste conditioning objectives include:

- defining a suitable containment material for the process by-products;
- characterising the material by determining its structural properties, thermal stability and physicochemical characteristics;
- investigating its long-term behaviour (leaching resistance, etc.) under various interim storage or disposal conditions.

### **Demonstration experiments**

Demonstration experiments represent the stage following the exploratory experiments, where an elementary process or a succession of elementary processes is tested in nuclear facilities. The aim of these demonstration experiments is to confirm that the efficiency found with simulant material is valid with all the actinides, the elements that are the usual target of the concept. More reliable data than those obtained in the exploratory studies are determined in these demonstrations, to establish the technological feasibility of a particular process. These experiments could deal with a single elementary process or with a chain of elementary processes, to check their compatibility. They would not necessarily be at full scale or carried out with a proven technology. They could be operated with synthetic nuclear material. The use of glove boxes for alpha-active material dramatically increases the cost of the research, hot cells even more so. Some confidence in the success of the experiment or the process is required before such work is undertaken. This confidence is based on the results of the “Exploratory studies” and on the experience of the research team in carrying out pyrochemical tests under radioactive conditions.

### ***Electrorefining of metallic fuel***

The electrorefining process for metallic fuel should be demonstrated first with non-irradiated alloys (U, Pu, minor actinides, rare earths and Zr) in glove box equipment. Special emphasis should be placed on the behaviour of Zr. Secondly, the process should be applied to fuel irradiated in a fast reactor, in a radiation-shielded installation. The details to be investigated are the different electrorefining steps:

- anodic dissolution behaviour of metals and metallic fuel;
- deposition behaviour of the different elements onto a solid cathode;
- deposition behaviour of the different elements into a liquid Cd cathode.

### ***Cadmium distillation***

A cadmium distillation process must be demonstrated with transuranic elements. The behaviour of these elements should be investigated with respect to particle formation, size distribution and Am volatilisation.

### ***Separation of actinides from lanthanides by salt/metal reductive extraction***

The salt/metal reductive separation of actinides from lanthanides should first be performed with synthetic material containing minor actinides and later with genuine radioactive wastes under concentrations expected to be reached in a real process. This is valid for chloride and fluoride salts and for several liquid metals that were not already investigated using real nuclear materials.

### ***Chlorination of high-level oxide wastes***

In the case of the potential application of pyrochemical processing to the extraction of actinides from aqueous processing wastes (e.g. the PUREX process raffinate), experiments on the chlorination of genuine high level oxide wastes from the PUREX process should be carried out. Off-gas treatment and chlorine gas recycling must be demonstrated in nuclear facilities.

### ***Inactive and fully active experiments with uranium and plutonium***

As a general point of note, for any new concept under development, there are a series of steps which should be followed. Initial demonstration experiments would normally start with inactive simulant materials. These would test a process or a piece of equipment with no radioactive materials present. This simplifies modification of the process or the equipment. A uranium active stage follows. This checks that the process or equipment still operate successfully for uranium. The next stage of the process involves the actinide elements. Alpha active studies have to be conducted in a rigorously controlled environment in high-integrity glove boxes, and the nature of the work dramatically increases the cost of the research. There should be confidence in the success of the equipment or the process before work of this nature is undertaken. The final set of demonstration experiments would involve use of small quantities of the actual fuel (or an active simulant) to be processed. This checks that the process is suitable applied to the material it is required to treat. For such work hot cells are required, and once again the cost of tests significantly increases.

### ***Comparison of process alternatives***

During the demonstration stage, a number of possible process options should be tested, and the most suitable option taken forward for process development.

### ***Understanding of electrorefining***

For a given process requirement or fuel type, it must be demonstrated that the process does fundamentally work. Does it achieve the separations and decontamination factors that are needed? What are the process limitations? How can products best be recovered? How can solutes within the salt be recovered? How can the salt most efficiently be recycled in the process?

### ***Understanding of electro-winning***

How is the fuel best chemically dissolved in the salt system? What are the implications of using particularly aggressive oxidising agents? What are the materials issues? What control can be exerted on the chemistry of using different oxidising agents and process conditions? What materials are electro-won to the cathode? What are the decontamination factors that are achievable, and are these within the intended range of process requirements? How can the product be cleaned of entrained salt? What particle size range is achieved, and what is needed?

### ***Understanding of salt/metal extraction***

What processes are available for performing salt/liquid metal extractions? What are the distribution coefficients for the species of interest? Can the process be used to bring about the separation factors and purification, which is required? What are the process limitations?

### ***Optimisation of waste forms***

Performed at a very basic level, what are the waste forms which could be used to immobilise the salt waste and fission products? Testing of many different possible forms and determination of the fundamental principles which control achievable waste form loading are necessary. Can those non-radioactive species which create problems within the waste form and therefore limit fission product loading be removed from the stream? For instance, there is a limitation to the amount of chloride ion which can be incorporated within a waste. This then limits the fission product ion concentration which can be incorporated. If the chloride ions can be released from the system and replaced by another anion, such as oxide, then the final fission product loading of the waste can be increased. Investigations are required into all the available methods of performing this.

## **Process development**

The process development stage is the means whereby a new technology is tested under realistic operating conditions in order to provide a basis for economic evaluation of the process. Certain aspects of different processes may have common technological issues, such as corrosion resistance or mechanical operations, for instance, that are specific to high-temperature processes. It is only at this stage that the industrialisation needs can be evaluated on a sound basis. The experimental set-up that is

defined must aim at providing viable technical solutions, and its operation should give data directly relevant to the main criteria that have been defined as critical for industrialisation of the process. From this point of view, the process development stage is in essence the stage of building a “pilot process”; this is followed by the industrialisation stage. Process development should include pilot-scale testing of all the processes comprising a particular pyrochemical technology. For this reason, the process development stage is not complete unless there is appropriate attention to the back-end of the process.

Engineering questions are of utmost importance, but in most cases they cannot be addressed before a process choice has been made. However some techniques will be used in the future, to an extent that is not known, for example fluorination for  $\text{UF}_6$ , distillation (salts or metals), electro-deposition (liquid or solid cathode), reduction by a metallic element and chemical precipitation (oxides, nitrides). They present common needs such as vessel corrosion, monitoring techniques and process modelling. Research on these issues may fruitfully be shared.

### ***Vessels for high-temperature processing***

High-temperature processing involving the simultaneous presence of various phases raises the problem of finding vessel and internal structure materials that are resistant to multiple-phase corrosion. Physical or chemical corrosion creates contaminated wastes when the equipment must be replaced and results in contamination of the products of the process. This is a major concern with pyrochemical processes. For example, durable structural materials are needed:

- for processes involving a combination of molten salts (chlorides or fluorides) and uranium;
- for extended exposure to molten salts, such as an electrorefiner;
- that are more robust than graphite (crucibles, electrodes) or quartz (tubings), to withstand high-temperature corrosion by chlorine gas during the chlorination process of oxide wastes or by oxygen gas during electrochemical reduction of oxides.

With liquid salts or metals, an alternative is to freeze the liquid on a cooled container wall. Then the requested mechanical property and tightness is provided by a material that is not submitted to high-temperature corrosion by the hot fluids. The container material is in contact with a solid metal or salt only at a rather low temperature with respect to the treatment temperature. The presence of a frozen protective layer is also a solution for the use of highly corrosive high-temperature gases (fluorination of liquid salts to extract  $\text{UF}_6$ , for instance). The heat extracted by maintaining the wall at a low temperature has to be compensated for by heating the fluids inside the reactor. Induction heating is a solution to heat up the ionic or metallic phases through the cold wall. Induction stirring or circulation can be applied to these fluids for engineering purposes, without mechanical contact. The advantages of “cold wall induction-heated crucible” processing with molten salts and highly reactive materials make it imperative to evaluate such methods in the future.

### ***Process equipment engineering***

The design of process equipment for the treatment of nuclear materials imposes specific requirements that have not been encountered in non-nuclear chemical engineering applications. Even if the adaptation of standard process equipment can be accomplished without modifications for handling radionuclides, special attention is still required for specific nuclear material needs. Examples are:

- efficient distillation devices that minimise entrainment and provide high output for salts (chlorides) or metals (Cd);
- large-scale electrorefiners capable of actinide recovery at realistic material throughput rates;
- electrochemical process to recover actinide oxides from irradiated fuel with high efficiency.

### ***Instrumentation***

Instrumentation is required to operate, without maintenance but with high reliability, under conditions combining high temperature, high radiation, electric field and a highly corrosive environment, for periods far more demanding than those prevailing in current nuclear facilities. New monitoring techniques must be conceived and tested for normal operation and for material accountancy and safeguards. An on-line measuring technique of transuranic element concentrations in the molten salts (chloride and fluoride) must be developed and validated for continuous monitoring of the chemical state of the salts during operation and for rapid detection of anomalous behaviour.

### ***Process control***

Transient regimes during operation of pyrochemical processes must be thoroughly investigated, including: process start-up, shut down, incident recovery, and adaptation to the variability of feed materials. This is necessary to allow safe transient management. This will have to be carried out after the selection and sufficient development of a given process with a defined technology.

### ***Process simulation***

The development of computer codes for simulating different experimental set-ups and to help in scaling-up is a general need. The existing commercial codes must be checked for the specific applications related to nuclear materials, taking into account the observed behaviour of these processes and the constraints due to the needs for radiation protection. Once developed, such computer codes can have important applications in process control.

### ***System ageing***

Understanding the ageing factors of the system is important for its viability. This includes its resistance to thermal cycling and corrosion, erosion and debris accumulation. In some cases experience has been accumulated in the non-nuclear industry. However, many techniques proposed today have not been extensively used in the industry in the last several decades such that the experience, if any, has been, or is nearly, lost.

### ***Assessment of waste generation***

Waste generation is also an issue to be documented. It includes technical waste production, release of effluents (mainly gases) and the normal secondary waste material expected after processing. Targets to be met by these wastes and the waste management regime must be established and compared with process practicability.

### ***Formulation of flow sheets for each of the process steps***

At an early stage of flow-sheet development it is necessary to record all of the possible process steps. As development work proceeds, many of the options that were initially forthcoming will become redundant and a final flow sheet will become apparent. This flow sheet will form the basis for a record of mass balance data and a full understanding of what goes where within the process.

### ***An understanding of head-end and pre-treatment requirements***

For any application of pyrochemical technology, the “molten salt” step will impose certain requirements on its feed material, necessary for maintaining chemical and process stability. An example is to remove certain cladding materials and all residual moisture. Research needs must be targeted at establishing what levels of contamination of certain materials are allowable in the salt before any process starts to deviate from the process boundaries

### ***Development of head-end techniques***

Head-end techniques must be investigated to ensure that the fuel feed or fuel-derived feed are in a suitable form for addition to the “pyrochemical” stage of the process. This might be a bulk shearing of irradiated fuel, or may be a process such as AIROX, which forms the fuel into a finely divided oxide powder.

### ***A detailed understanding of control of separation factors***

What are the achievable separation factors within variation of process parameters, to allow safe transients of the operation within a manageable operating envelope? Experimental characterisation will be required in this area. This must include process start-up, shut down, and incident recovery and variability of material between batches. Separation factors must be good enough to avoid multi-step processes and to meet the product purity required. The simplicity of elementary pyrochemistry cannot be compromised by complex secondary process flow sheets. Research is required to understand separation factors and their control.

### ***Sensitivity of electrorefiner components such as electrodes to thermal cycling and corrosion***

Appropriate design and construction must maximise reliability and operational life and reduce maintenance needs. Inactive piloting and trials must demonstrate high availability, minimum technological waste and low cost. This must be supplemented by active trials with key species present.

### ***Understanding of system ageing***

Systems which work well in a new electrorefiner or highly-maintained rig can deteriorate with time due to corrosion, erosion, accumulations of debris or excessive wear in a highly-utilised, low-maintenance application. Studies based on the experience accumulated in the non-nuclear industry are probably advisable to avoid significant remedial work after limited operation. Research must be performed to start to address these issues during the industrialisation stage of development.

### ***Development of new monitoring and maintenance techniques***

New monitoring techniques will have to be conceived and tested. Remote maintenance, while undesirable, will probably be needed in many areas, especially in areas of contact with the molten salt. Instrumentation (perhaps on-line) must be developed to satisfy process requirements.

### ***Development of instrumentation for measurement and control to industrial standards***

Instrumentation will have to operate, without maintenance but with high reliability, in conditions combining high temperature, high radiation, electric fields and strong corrosion, for periods far more demanding than those prevailing in current nuclear facilities. It will be necessary to understand the process control envelope, the consequences of an incident, and to demonstrate the capability for timely detection (and recovery).

### ***An understanding of “hold-ups” in the process***

The batch mode generally induces active material hold-ups and “heels” which are in some cases difficult to track or even to localise. This will create difficulty in criticality control and nuclear materials accountancy in a larger-scale plant. This item could be addressed by trials and modelling.

### ***Establishment of a safeguards regime***

Process phases may be less homogeneous than in aqueous processes and some radioactive species are likely to accumulate or deposit locally in the plant. Substantial amounts of fissile material could be lost in the waste streams generated by cells with limited separation factors. This complicates plant scale-up and raises challenges in establishing an industrially viable safeguards system.

### ***An assessment of the waste generation, including release of effluents, production of process and technological waste***

Like any other nuclear facility, those using a pyroprocess will have to minimise the generation of gaseous, liquid and solid wastes. The assessment must consider both the radioactive and chemical impact of the expected wastes. This will have to be done for each proposed flow sheet. Targets to be met for effluent and waste management must be established and compared with process practicability.

### ***Advanced development of suitable waste forms***

Any new kind of waste form will be compared with existing forms. The latter will set the standards in term of characterisation, transport, storage and disposal conditions. A pyroprocess-based facility will be expected to generate waste forms consistent with existing standards and practices. Processes avoiding “first of a kind” waste forms or showing a large margin of progress in waste characteristics will be favoured.

### ***Behaviour of dross, sludge and their control***

Any pyrochemical process is likely to have residues which are not soluble within the molten salt under process conditions. For any given process, a full understanding of the content, form, morphology

and behaviour of this dross and “sludge” must be fully understood, particularly if the content is fissile. Treatment and disposal routes must also be researched.

#### ***Study of volatile emissions from all stages of the process and their control and abatement***

By their high-temperature nature, pyrochemical processes are likely to produce volatile species. There may be methods of controlling the bath chemistry to minimise the volatility, but the extent of volatility of key species such as ruthenium, caesium and iodine must be well understood. There are some species, such as the noble gases, which will readily volatilise during processing, probably during head-end processing. Suitable abatement systems will have to be developed to ensure that the species removed from aerial effluent streams do not reach the environment.

#### ***Clear definition of the process envelope***

Most industrial processes only work efficiently and effectively if they are operated within a carefully defined and refined process envelope. Deviation from this process envelope can at best cause the process to operate inefficiently, and at worst result in a failure within the system. For any new process based on pyrochemistry, there will be a need for very careful definition of the process envelope and the capacity to recover from credible excursions.

#### ***Product processing***

There are development issues with processing the product material which is created in the main process. Any products created that are required to be returned to the reactor will require processing, and determination of the most suitable method to achieve this requires research.

#### ***Alloy treatment***

A means for separation of the metal products from process materials such as cadmium must be developed.

#### ***Waste form process development***

In addition to the development of suitable waste forms, significant research is needed into process development for making the chosen waste form in the most efficient and economic manner, while fulfilling all quality requirements. This will require a broad range of approaches and disciplines. What will the waste form be, glass, glass-ceramic or ceramic? Will the process rely on in-can calcination or a melt-and-pour process? If in-can processing is required in combination with high-pressure systems, what are the requirements and the limitations of these pressure systems? What is the easiest processing method to adopt which provides the required product?

#### ***Waste form licensing***

Any new waste form developed will require extensive testing of its long-term performance and reliability. This will go on to the licensing and acceptance of the waste form. The process of licensing is stringent and long. There will be a large research requirement during this licensing phase.

### ***Off-gas waste stream treatment***

If methods are developed to capture volatile species from any process, then there will be waste streams associated with these process steps. Again, it will be necessary to develop processes to ensure that these wastes are encapsulated within suitable waste-form materials, preferably with minimum development of new waste types.

### ***Pumping, handling and moving salts***

Any process developed to use molten salts will require a means of handling and transporting the salt around the process. Even in the simplest batch process, there will still be a requirement to be able to transport salt, either to empty the vessel or in a fault condition. Any development of a continuous process will have a requirement for salt pumping. Reliable and efficient pumping of salt will require extensive research into pump technology. There will be a need for materials studies across a broad range of demands. Studies will have to examine the effect of both corrosion and erosion.

### ***Criticality studies***

One of the main safety issues with any process which involves the handling of irradiated nuclear fuel is the content of fissile material within the system and the possibility of a criticality accident. Extensive studies will be required of any process designed, and in particular process vessels, for their criticality safety. Particular attention must be applied to precluding the chance of criticality during fault scenarios. For instance, in an electrorefining process, if there is ingress of oxygen and moisture into the equipment, could one obtain information on the formation of plutonium dioxide? Would this plutonium dioxide precipitate in the vessel, and how would one know this was happening? Would it be possible under this fault scenario to precipitate a critical mass of material? Can process control equipment be incorporated to prevent this fault condition? Can process equipment be designed to mitigate against the chance of criticality? Would the regulating authorities grant a license for the process?

### ***Safety studies***

Research will be required into the main industrial safety issues of operation of any potential plant, and how hazards can be made safe.

### ***Decontamination, maintainability and decommissioning***

In the design of plants or processes, consideration must be given to the eventual closure of the plant and the clean-up and decommissioning operations. In certain cases, closure and decommissioning operations may require the introduction of ancillary processes and plants. These issues must be considered at an early stage so that the total cost of a plant (construction, operation and decommissioning) is known. Research work is required during the various stages of the programme, to ascertain what the decontamination and decommissioning issues are likely to be. By way of example: If processes are based on volatile species such as cadmium or zinc, where within the process equipment will the cadmium or zinc be contained? On what surfaces will the vapour condense? How can these surfaces be decontaminated? The volatile species waste stream may also contain some fission product elements, so what is the likely classification of this waste? Development work will be required to identify the most suitable forms for these wastes.

### ***Environmental impact assessments***

Supporting the whole development programme, there will be a need for full environmental impact assessment of the technology to be used, and the final plant to be operated. There can be a great deal of research needed to determine some of these issues, such as:

- What are the inputs to the process?
- What is the environmental burden the reagents impose?
- What are the waste streams, and their long-term environmental impact?
- What are the aerial and liquid discharges, and are these likely to fall within the authorised discharge limits?
- What are the energy requirements of the process, and how can these be minimised?

### ***Engineering studies***

There will be a need for engineering studies to support and help focus the development programme. There are many stages of engineering development and expertise. The first stage will involve feasibility studies, looking at the process flow diagram. Issues to be addressed are numerous, such as: What are the stages of the process? How do all the stages link together? What are likely to be the overall feasibility and cost of the process? These engineering feasibility studies will set the structure of the development programme. More detailed engineering will be performed on each of the pieces of process equipment. This will go through different stages, from laboratory equipment through to pilot-scale equipment and in the later stages, design and engineering of the plant equipment, including scale-up, materials, fabrication and failure/reliability assessment. Detailed equipment design will have to be concomitant with the entire process design and engineering.

### ***Materials issues***

Throughout the development programme there is a need to perform material studies. The best materials of construction for each of the components must be identified. The rates of corrosion under different conditions must be determined. And the effects of material constraints on plant maintenance requirements must be evaluated in detail.

### ***Process modelling***

High-temperature process modelling has been developed for most large industrial pyrochemical processes. The techniques involved in nuclear material processing are often different than those in use in the heavy industry, not only for a question of size but also because the basic reactions are not the same. Indeed, there are many foreseen processes with halides or metals that correspond to a pyrochemistry of highly reactive elements with a relatively low melting point. Such properties do not correspond exactly to known large industrial process applications. Thus there is an interest in developing new software or in adapting existing ones that would be more suited to nuclear pyrochemical processing. This includes coupled transfers: momentum, heat and mass. An example is the heat transfer and combustion for the fluorination of salts.

### ***Continuous processing***

Although almost all industrial pyrochemical processes are batch processes, there is always a potential for the development of more efficient continuous processes. This is not necessarily true from an economical point of view, as handling and storing liquid or gases at high temperature is awkward. But in the case of a high level of radiation, batch operations are difficult and time-consuming even for solid materials. It is thus worthwhile to keep a permanent watch for the possibility of introduction of continuous processes or partly continuous processes, when this improves the process efficiency.

### **Process development and industrialisation – conclusions**

If pyrochemical processing is to progress beyond an interesting area of investigation with limited application, a clear objective of industrialisation and commercial application must be pursued at some point. The resultant research and development programme will be large and complex and, because of its scale, will probably require international collaborative projects.

Technical viability and operability are the fundamental criteria to meet to decide whether or not pyrochemistry is ever adopted as a standard industrial production process in any part of the nuclear cycle. This should be borne in mind throughout all stages of research and development, and used to maintain focus to programmes, and to “cull” process ideas where feasibility appears unlikely.

There is a requirement for an intimate link between all stages of process development. Typically it is considered that good ideas from elementary studies lead to further development in demonstration experiments, and that these may go on to process development and implementation. However, such routes of research are often wasteful in terms of ideas, resource and finance. So as to maintain focused and well-managed programmes, research at all stages should be driven by the process requirements, i.e. what does the process need to achieve, and what are the bounding conditions in which the process needs to operate? Immediately upon the conception of a process idea, consideration of the feasibility of industrialisation should be addressed. What does the plant look like? What are the inputs to the process, and what are all the likely waste streams? What are the types and design of the equipment that are required? Engineering feasibility studies can be applied to gain this information, and the results of these studies should then be applied to drive the research programme towards the process which appears the most technically and economically feasible at the industrial scale.

In addition to the above list of development requirements, the demands of society and regulatory licensing will dictate much broader requirements of the whole industrial process than just primary process viability. These broader key factors, which determine whether a process can be successfully industrialised, must be recognised and assessed from the earliest stages of development. If prudent investment is to be made in a successful “winning” industrial technology such topics as, for example, economics, process safety, environmental impact, plant engineering, and social acceptability or “licensability” must be considered relatively early in an industrial concept development. Many of these issues are interlinked and dependent on fundamental technical factors. Early recognition of this linkage and dependency will assist in ensuring that the key obstacles, and hence primary development objectives, are defined and prioritised, and also ensure that impractical concepts can be eliminated early.



## *Chapter 6*

### **RECOMMENDATIONS**

As OECD/NEA member countries are presently involved mainly in monolithic programmes for the development of pyrochemical technologies, even though some of this work is duplicative of prior work in other countries, it is probably premature to recommend a programme of intensive multilateral collaboration. It is important at this time that each country, to the extent possible, establish its own elementary understanding of the scientific principles underlying pyrochemical technologies, preparatory to the development of the engineering skills necessary for the practical deployment of such technologies.

Due to the disparity in degrees of development, it seems appropriate at this time to propose a general information exchange, rather than a comprehensive programme of shared development, in which individual parties would take responsibility for a particular aspect of the technology. This is probably true even though there is considerable laboratory capability available for joint programmes. Some countries may wish to accelerate their own technology development programmes by purchasing access to other more developed programmes, while others may be content to observe the progress of development, while contributing to the overall knowledge base in highly specific specialities.

In any case, it is important that the avenues of communication remain open and unrestricted. The commercial value of these technologies is not likely to be realised for several decades, and open discourse at this time can only serve to increase the future value of pyrochemical technologies. As the course of technology development proceeds, it may be possible to identify fruitful areas of international collaboration. It is necessary to maintain channels of communication among the various countries involved in the development of pyrochemical technologies in order to exploit these opportunities.

It is recommended that this be accomplished through regular multilateral and international information exchanges, perhaps best accomplished as part of the continuing series of the biannual OECD/NEA Information Exchange Meetings on Partitioning and Transmutation. Should circumstances warrant, it could be possible to augment these meetings with specialists meetings on pyrochemistry applications held in alternating years with the OECD/NEA Information Exchange Meetings. These specialists meetings could also be conducted under the auspices of the OECD/NEA.



## Appendix

### **List of Working Group Meetings**

	<i>Date</i>	<i>Place</i>
First meeting	30-31 October 2000	NEA Headquarters, France
Second meeting	16-17 May 2001	Issy-les-Moulineaux, France
Third meeting	14-15 September 2001	NEA Headquarters, France
Fourth meeting	25-26 April 2002	NEA Headquarters, France
Fifth meeting	24-25 February 2003	OECD Headquarters, France

### **Members of Pyrochemistry Working Group**

<i>Name</i>	<i>Country</i>	<i>Institute</i>
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UHLIR, Jan	Czech Republic	NRI
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BROSSARD, Phillippe	France	CEA
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GAUNE-ESCARD, Marcelle	France	IUSTI Marseille
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