ACTINIDE AND FISSION PRODUCT
PARTITIONING AND TRANSMUTATION
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Good morning Ladies and Gentlemen,

It is a great pleasure for me to welcome you and deliver the opening address on the occasion of the 4th OECD/NEA International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation.

Nowadays, nuclear power has become a very important energy source and accounts for about 17% of gross electric power in the world. From the viewpoint of stable energy supply in the future, it is strongly expected that nuclear energy could play a more important role as a reliable energy source on a large scale, once we overcome the basic problems, such as technical and economical difficulties.

Because of plentiful oil production and of low oil prices thereof, people have tended to use oil as if it is an inexhaustible resource. But oil and other fossil fuels are not only for energy but are also as raw materials for various essential products of daily uses. Increase in consumption of fossil fuels is believed to cause global warming, which is one of those global environmental problems to be resolved urgently. Nuclear energy is able to cope with these global problems. The success of nuclear energy use will greatly influence global society in the 21st Century.

For these reasons, Japan intends to guarantee its energy security by carrying forward research and development efforts for commercial implementation of nuclear fuel cycle which includes secure supply of uranium resources, Pu utilization and radioactive waste disposal. For the matured nuclear fuel cycle, the establishment of ways of appropriate management and disposal of radioactive waste, especially high-level radioactive waste, is one of the most important tasks.

Therefore, Japan is implementing significant research and development efforts for realization of consistent high-level radioactive waste disposal measures. In 1995, in order to proceed systematically with high-level radioactive waste management and to promote understanding on the part of Japanese Public for implementing the high-level radioactive waste disposal, the Atomic Energy Commission set up a round table conference for
discussing social and economic aspects of disposal. In the same year, the Advisory Committee on fuel cycle backed management was also set up for reviewing and deliberating on planning and technical issues of research and development of high-level radioactive waste disposal.

At the same time, Partitioning and Transmutation is deemed in Japan to be quite an interesting subject from the perspectives of potential utilization of resources and possible alleviation of environmental burden caused by long-lived radioactive waste. The R&D program is jointly carried out by the collaborative efforts of relevant organizations.

Partitioning and Transmutation is one of the options for processing high-level radioactive waste before final disposal. Significant efforts are needed to implement this concept. I believe this information exchange meeting is very useful for international collaboration in pursuing efficient R&D.

I am also a strong supporter of basic research. This type of work must continue at all times because policy changes can occur in the future and basic research has a long lead time. It is not inconceivable that our study of, for instance, star formation and nucleosynthesis can give us insight into better and novel methods of transmutation which can, in turn, help solve the problems of high-level radioactive wastes.

Therefore, it is a great pleasure and pride for us to host the 4-th OECD/NEA Information Exchange Meeting in Japan.

I would like to conclude the opening address hoping fruitful discussions and also for the promotion of nuclear energy developments in each country of the participants.
Ladies and Gentlemen,

It is a great privilege and pleasure to welcome you on behalf of the NEA to the 4th International Information Exchange Meeting on Actinide and Fission Product Separation and Transmutation. It is a particular pleasure for me as it was here that the first of these meetings was held in 1990, and I treasure my memories of that occasion.

At a number of recent meetings related to nuclear energy but not specifically to nuclear science or to waste management, I have noticed a tendency to believe that there does exist some magic spell that will somehow relieve us of the difficulties of managing highly radioactive wastes. I, too, wish that there could be such a "spell" but I do not believe in alchemy. I do believe that patient research and ingenuity in development will improve our capabilities to meet the challenges of long-term waste management within a cost-competitive fuel cycle. I see no reason to modify the position that has been taken since the outset of this Programme, that successful application of Partitioning and Transmutation would not replace the need for geological disposal for high-level waste.

Since the NEA was invited to take up this topic in 1988, the interest in it has grown in several of our Member countries. The task is one of long-term scientific research, but it is recognised that certain short- or medium-term benefits could also be derived. There is quite a rich network of bilateral agreements on P&T between OECD countries. However, judging from the number of participants who have come a long way to this meeting there is a clear view that substantial benefits can be achieved from wider international activities and co-operation. I am very glad to see so many friends and colleagues from around the globe.

There are also some newcomers to this forum and I am glad about that too. Mainly for their benefit let me describe briefly the NEA’s role and responsibilities in the field we are here to discuss. When the NEA agreed to work on the Japanese proposal for an international activity, it was entrusted to the Nuclear Development Committee. They agreed that it would be sensible to sponsor an information exchange. This led to the first Mito City meeting in 1990. That generated the idea of holding specialist meetings on particular scientific aspects. Subsequently the establishment of the NEA’s Nuclear Science Committee made it more practical to hold such meetings under that committee. The Secretariat ensures close cooperation between these committees. The topic is one of great interest to the waste managers and this is recognized in the reporting of the activities we make to the Radioactive Waste Management Committee and in the nomination by it of one of its members, M. Lefèvre, as their special liaison person.

In November 1992, the Argonne National Laboratory hosted the second NEA International Information Exchange meeting. The papers presented indicated that one common thread was the need for some means of taking an integrated view of the expected benefits and possible disadvantages of including P&T in the
nuclear fuel cycle. Among other results of such an approach would be guidance on research needs. A number of emerging important issues were identified during the meeting, including the legal background, the incentives and the implications for the whole fuel cycle in different countries.

These views were carried forward at the third NEA Information Exchange meeting, hosted by the CEA at its Cadarache site in December 1994. Several participants from 11 countries, together with Russia, the IAEA and the European Commission attended the meeting which primarily focused on P&T strategic systems studies. The meeting provided a solid base for approaching a more co-ordinated NEA project, which has started in early 1996, on the benefits and penalties of adding P&T to the nuclear fuel cycle.

At that meeting, interesting papers were also presented on national policy orientations and on scientific and related data aspects. There was a wealth of wide ranging ideas and suggestions for future activities. It was noted that real progress since the Argonne meeting had been achieved in three fields:

- chemistry of separation;
- experimental irradiation of actinide-based fuels and targets had been launched in the frame of national or international programmes;
- preliminary cost estimates were presented for a P&T scenario in the frame of the EU strategic systems study.

There is a clear need for objectives against to which to measure potential benefits of P&T. Discussion at the Cadarache meeting indicated that a final set could not yet be established. Therefore, working hypotheses should be adopted for goals which can be adjusted as knowledge improves. This remains our approach.

In addition, the NEA Nuclear Science Committee (NSC) and the NEA Data Bank are co-ordinating a number of technical activities in the field of P&T. The NSC task force on different transmutation concepts has issued specifications for a calculation benchmark comparing activities from various fuel cycles after passage through different reactor and accelerator concepts. The NSC is also preparing a state-of-the-art report on the separation chemistry of actinides. An important part of the technical activities is related to nuclear data questions for transmutation applications. The data activities cover both conventional reactor and intermediate energy applications, and include the compilation of a high priority request list for nuclear data, as well as the compilation of basic experimental data themselves. The Data Bank is also setting up a collection of evaluated intermediate energy nuclear data libraries and is conducting nuclear model code comparison to validate the computational methods used.

I am looking forward to hearing in this meeting of progress in ways of evaluating a number of different P&T systems and their integration into the nuclear fuel cycle. I have no doubt that we shall also have lively discussion on the scientific ideas and results that have been coming out in the last two years. Please forgive me if I have a biassed view on these matters, but I firmly believe that exchanges of information and opinion in this sort of meeting is one of the most effective ways to carry forward R&D in this complex and, in some ways, politically sensitive area. I am grateful for the support that the Japanese Government has given the NEA in order that we can continue to be sufficiently active in this field.

I know that organising a meeting like this is hard work, so I particularly wish to thank our Liaison officer Dr. Mukaiyama and his colleagues in the STA, JAERI, PNC and CRIEPI, who have, I am sure, laid the basis for a very successful and stimulating meeting. Thank you all for being here. I wish you all an interesting, instructive and profitable three days.
1. Introduction
Thank you Mr. Chairman for your kind introduction. Distinguished guests, and Ladies and Gentleman, I'm very honored and glad to have this opportunity to make a speech here today.

On behalf of the Science and Technology Agency, I'd like to present here, recent topics in the field of radioactive waste management.

2. Policy Development for the Geological Disposal of High Level Radioactive Waste
The Atomic Energy Commission of Japan put forward a road map for the geological disposal of the high-level radioactive waste in its “Long-Term Program for Research, Development and Utilization of Nuclear Energy” issued in June 1994. The Program attached particular importance to the program of the management of radioactive waste, especially to ensure the smooth implementation of disposal of high-level radioactive waste. The Program stipulates that the high-level radioactive waste generated through the reprocessing of spent fuels be disposed of in geological formation after vitrification and temporary storage for cooling (for about 30-50 years). The role and responsibility of the related organizations concerned with the geological disposal have been confirmed and the schedule and procedures are shown for the implementation of the disposal.

Along with the basic philosophy and milestones set at the Long-Term Program said above, the Atomic Energy Commission set course to promote the discussion and preparation of high-level radioactive waste disposal in September 1995. The Atomic Energy Commission set up “Special Committee on the Disposal of High-Level Radioactive Waste”. The Special Committee will make a wide range of study including social and economic aspects in order to pave the way for public understanding and approval of specific measures for actual implementation of the disposal of high-level radioactive waste. “Advisory Committee on Nuclear Fuel Cycle Backend Policy”, which was set up by the Atomic Energy Commission last year, is intensively studying and deliberating technological items concerning disposal such as formulation of a research and development plan on geological disposal of high-level radioactive waste.

The special Committee has produced general consensus to promote implementation and research and development for disposal of high-level radioactive waste positively by our own responsibility. On the other hand, the Advisory Committee has started its discussion to produce a research program concerning the high-level radioactive waste disposal forwarding year 2000, when Power Reactor and Nuclear Fuel Development Corporation will publish a report on the results of research and development as said above. The Advisory Committee is now discussing how to evaluate the report. The Advisory Committee is also considering the implementation system as well as research and development for the other radioactive wastes and the decommissioning of nuclear facilities etc. in the future.

Steering Committee on High-Level Radioactive Waste Project (SHP) was established in May 1993. SHP is responsible to prepare measures to encourage the establishment of organization to execute the disposal of the high-level radioactive waste under the public understanding and cooperation. The recent activities of SHP are as follows:

- considering what kind of organization is the most appropriate to conduct the disposal project
- developing mid- to long-term, public relation strategy
- investigating a policy to collect the fund for the disposal project
- investigating the plan for regional developments for site incentive

SHP published the first interim report in May 1996, which includes coexistence with the host communities, define the nature of and funding for the implementing entity including its legal and regulatory aspects, and public information programs and activities for promoting public understanding and acceptance.
4. Underground Research Laboratory

On 28 December 1995, the Power Reactor and Nuclear Fuel Development Corporation (PNC) signed an agreement with the prefectural and local governments concerned with the construction of an underground research laboratory at Mizunami city in Gifu prefecture, central Japan. It is the first underground laboratory to be able to provide undisturbed conditions of deep underground in Japan, which is of great advantage compared with in-situ test facility using mining galleries. It is expected to conduct a comprehensive geoscientific research, and provide fundamental knowledge of groundwater and rock mass in deep underground to the research and development for geological disposal.

The research projects in the deep underground research laboratory, which will last 20 years, are expected to executed with the participation of researchers from not only other research organization concerned in Japan but also ones abroad.

5. Partitioning and Transmutation Technology

The Partitioning and Transmutation technology, which would reduce the environmental impact of the disposal by utilizing useful nuclides in the high-level radioactive waste, is considered to be future technology in the Long-Term Program. The Japan Atomic Energy Research Institute (JAERI), the Power Reactor and Nuclear Fuel Development Corporation (PNC) and other organization such as the Central Research Institute of Electric Power Industry (CRIEPI) are carrying out the basic research and development of these technologies. Research and Development activities of this technology are being continued according to the Long-Term Program for Partitioning and Transmutation, which was published by the Atomic Energy Commission in 1988. The activity which follows this program is called OMEGA project (Options for Making Extra Gains of Actinides and Fission Products generated in Nuclear Fuel Cycle). The check and review based on the progress of these activities will be carried out in the second half of this decade and consideration will be given to how to further proceed with development of this technology.

Now, it's time to close my presentation. Thank you very much for your attention.
RESEARCH ACTIVITIES OF THE EUROPEAN COMMISSION ON NEW FUEL CYCLE CONCEPTS

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ABSTRACT

This paper presents the objective and the research work of the eight projects partly funded by the European Commission in the field of new fuel cycle concepts, which includes three areas of work: (i) strategy studies, (ii) partitioning techniques, (iii) transmutation techniques. This field is part of the specific programme on Nuclear Fission Safety of the Framework Programme for the European Atomic Energy Community (1994-1998).
INTRODUCTION

In its fourth five-year shared-cost research and development programme on "Management and Storage of Radioactive Waste 1990-1994", the European Commission (EC) included the study of the potentialities of partitioning and transmutation (P&T) of long-lived radionuclides. The activities partly supported by the EC were dealing with experimental work on partitioning of long-lived radionuclides from high level waste (HLW) and an overall strategy study on the potentialities of P&T for nuclear waste management. Besides, research work on P&T, mainly on partitioning experiments and fuel and target development, was carried out at the Joint Research Centre of the European Commission in Karlsruhe, the Institute for Transuranium Elements (ITU).

The main results and conclusions of the strategy study have been presented elsewhere [1]. This study has led to an order of priorities for the radionuclides to be recycled. Plutonium should have the first priority because of its very large radiotoxicity and of proliferation risks. At present, the main issue is to improve the burning rate of plutonium in reactors to decrease its stock. Americium is the most radiotoxic actinide after plutonium up to 50,000 years and also contributes to the potential radiotoxicity of HLW through neptunium formation beyond 50,000 years. The problem to be solved is to find a selective partitioning process for americium only from the liquid HLW coming from PUREX reprocessing, which does not generate unacceptable amounts of secondary waste. When removing all plutonium and americium from HLW, the resulting waste will become less radiotoxic than uranium ore after 1000 years. Fast reactors appear at present to offer the best prospects for plutonium and americium incineration, when compared to light and heavy water reactors and high temperature reactors.

Nuclear Fission Safety is one of the specific programmes of the Framework Programme for the European Atomic Energy Community (1994-1998). It has been launched by the European Union on 15 December 1994. Exploring new fuel cycle concepts is part of this programme with three research tasks: (i) strategy studies, (ii) partitioning techniques, (iii) transmutation techniques. Eight research proposals to be partly funded by the EC have been selected in 1995 by the Commission on the basis of an evaluation made by independent experts. The objective and the research work of these projects are briefly described in this paper.

STRATEGY STUDIES

Four projects cover the strategy studies.

Evaluation of Possible P&T Strategies

The first project is a global assessment of different possible P&T scenarios and of the technical feasibility of P&T techniques and of advanced fuel and target fabrication. Eleven European laboratories are participating to this study, which is coordinated by CEA Cadarache (F). Five scenarios have been defined. The first one is the reference scenario with one-through cycle for pressurised water reactors (PWRs) with uranium oxide (UO$_2$) fuel. The four other scenarios have the same common basis from 2000 to 2040: the reactor park consists of PWRs with UO$_2$ fuel and PWRs with a mixture of 70% of UO$_2$ fuel and 30% of mixed oxide (MOX) fuel; plutonium (Pu) is recycled once, i.e. spent UO$_2$ fuel is reprocessed to recover Pu for MOX fuel fabrication and spent MOX fuel is placed in interim storage. From 2040, spent MOX fuel is also reprocessed following the requirements in Pu, minor actinides are partitioned and recycled in homogeneous mode for neptunium (Np) and heterogeneous mode for americium (Am) and curium (Cm). A PWR loaded with 30% MOX fuel is replaced every year by an over-moderated PWR with 100% MOX fuel in the second scenario and by a CAPRA type fast reactor (FR) incinerating Pu in the third scenario. The fourth scenario starts like the third one until a shutdown of nuclear energy is decided: special actinide burners are then built. The beginning of the fifth scenario is similar to the third one; at a certain time, fast breeder reactors are coupled to the network with the objective of having only FRs as burners and breeders in the reactor park.

The consequences of the use of fuels with high Pu content in PWRs and FRs on partitioning will be assessed: the dissolution of spent MOX fuel in nitric acid becomes more difficult, as the content in PuO$_2$ increases. Reprocessing of MOX with 45% PuO$_2$ and uranium free fuel and the effect of inert matrices will be studied. Both enhanced "PUREX based" and/or pyrometallurgical processes will be investigated.
Transmutation in PWRs and FRs will be assessed by computing actinide consumption and core safety parameters for advanced MOX fuels (highly enriched in Pu and/or containing Np) and/or specific targets containing americium and/or curium. Pu consumption will be optimised, while keeping the core safety parameters at a reasonable level. The moderator-to-fuel ratio of full MOX fuel cores in PWRs will be increased to maximise the Pu consumption. "U-free" PWRs and FRs will be studied.

The fabrication processes of the advanced fuel and target will be investigated: sol-gel fabrication and MOX fuels adapted to enhanced moderation and full core loading. The consequences of the presence of more radioactive nuclides in the fuel on the dose rates received by the workers during the different steps of fuel fabrication and handling will be evaluated.

Finally, the long term risk and residual dose to man from different waste to be disposed of in an underground repository will be compared: spent PWR UO₂ fuel at high burn-up, spent PWR MOX fuel, vitrified HLW, actinide depleted vitrified HLW, separated actinides conditioned in advanced matrices, spent FR MOX fuel after multiple recycling. The retardation efficiency of three geological barriers (clay, hard rock, salt) will be investigated.

Supporting Nuclear Data for Advanced MOX Fuels

Belgonucléaire (B) coordinates this project, which involves six European research institutions altogether. The objective of this project is to provide the strategy study above with more accurate nuclear data for the scenarios aiming at reducing the waste toxicity in MOX recycling schemes either in PWRs or FRs.

The accuracy of strategy studies involving the use of PWRs with enhanced moderation and full MOX loading will be assessed. The experimental basis is provided by the analysis of the composition of MOX fuel after irradiation at very high burn-up (80 GWd/t) in the overmoderated BR3 reactor. Experimental data are also available for MOX fuel irradiated in the Saint Laurent B1 PWR. These data will be compared with the results of calculations using the European JEF 2.2 library. Sensitivity and uncertainty analyses will be performed on the basis of the JEF 2.2 library and the EAF transmutation and uncertainty file.

A similar exercise will be performed for FRs. The experimental data are provided by the measurements of the isotopic composition of samples irradiated in Phenix and KNK-II in Karlsruhe. These data will be interpreted with the European JEF 2.2 library.

A critical analysis and intercomparison of the nuclear data files for the isotopes ²⁴⁰Pu, ²⁴²Pu and ²⁴¹Am will be performed especially in the range of resonances.

The corrected nuclear data will be introduced into working libraries for transport and radionuclide inventory computations. The computational techniques of the different partners will be compared to integrate all results in a common data base. Finally, the uncertainty margins of the isotopic compositions will be estimated for the P&T strategy studies.

Thorium Cycles as Nuclear Waste Management Option

The third project is coordinated by ECN Petten (NL) and involves six other European laboratories. The objective is an assessment of the thorium (Th) fuel cycle to limit nuclear waste production and to burn waste. This study will cover the major aspects of the thorium fuel cycle, i.e. mining, fuel fabrication, reactor operation, reprocessing, waste disposal and non proliferation.

The work on mining consists of a study of the quantities of tailings for available thorium minerals, the extraction performances and the composition of radionuclides in the extraction waste. The health impact on workers, the potential radiotoxicity of the generated waste and possibly the residual short and long term risks to the public will be also calculated.

The different types of thorium oxide fuels will be reviewed with special emphasis on the radioactivity of fresh and recycled fuels. Mixed oxide fuels will be considered with uranium, protactinium (Pa) and plutonium.
Three types of thorium fuelled reactors will be assessed: a PWR core with minimum actinide waste production; a PWR to bum as much as possible plutonium and minor actinides (MA) (Np, Am, Cm); a FR as an energy generating system with low actinide production or with high capability to bum Pu and MA. Limits imposed by reactor safety parameters, neutron economy and maximum achievable burn-up will be taken into account.

Concerning reprocessing, the THOREX process will be reviewed on the basis of previous experience with special attention to partitioning of Th, U, Pu and Pa.

The long term residual risk of geological disposal of the different HLW generated by the three types of reactors considered above will be computed. The basic migration parameters of Pa and Th will be measured in order to assess their behaviour in two generic geological environments (clay and granite).

The technical proliferation characteristics of Th and U based fuel cycles will be compared. The basic problems (neutron emission and heating rates) associated with the fissile $^{233}$U and $^{239}$Pu isotopes will be addressed.

**Impact of the Accelerator-based Technologies on Nuclear Fission Safety (IABAT)**

Kungliga Tekniska Högskolan (S) is coordinating this research contract, which involves a total of eleven European research institutions. The possibilities of Accelerator Driven Systems (ADS) for safe energy production, minimum waste production and nuclear waste transmutation will be assessed in this project. The objectives of the IABAT project are to perform system studies on accelerator driven hybrid systems, to assess accelerator technology, to obtain basic data on nuclear reaction cross-sections and on radiation damages at the spallation target walls and to study the radiotoxicity of the ADS fuel cycles.

The system studies on ADS will address several items: a safety and economical assessment; the physics of molten salt systems with fast and thermal neutron spectrum; the stability, time response and dependence of dynamics on subcriticality; a 2D/3D neutron kinetics study; an actinide incineration system with liquid lead as an actinide carrier; spallation target optimisation with respect to transmutation efficiency; estimation of the spallation product yields and of the radiotoxicity of the spallation target.

The technological aspects of accelerator technology related to construction, proton current and energy levels will be assessed. A cost analysis will be performed for linear and circular accelerators with an energy of e.g. 1GeV and a current of 10 mA.

As the high energy transport codes are not very reliable in the 100 MeV energy region, basic nuclear data are necessary. Evaluated nuclear data files will be assembled for protons on lead and isotopes for energies up to 200 MeV. Some cross sections above 20 MeV will be measured and validated for neutron and proton induced reactions (e.g. fission of Pb, Bi and $^{238}$U and transmutation of some nuclides). The measurement of yields for $^{233}$U thermal fission and $^{232}$Th fast fission will be performed. The radiation damages at the lead spallation target enclosure walls will be estimated.

Different aspects of possible fuel cycles for ADS will be addressed. The radiotoxicity of the residual waste and the non-proliferation resistance of the reprocessing technology will be investigated for a LWR waste transmutation system based on molten salt fuel and thermal neutron spectrum. Different thorium fuel options will be considered for an ADS with liquid lead coolant/carrier. The radiotoxicity of the thorium based ADS fuel cycle will be evaluated for thermal, epithermal and fast systems.
PARTITIONING TECHNIQUES

Experimental work on partitioning is carried out in two projects.

New Partitioning Techniques (NEWPART)

Seven European laboratories are participating to this project, which is coordinated by CEA Marcoule (F). The objective of this project is to develop processes for the separation of minor actinides from very acidic aqueous solutions containing HLW without generating secondary solid waste, while avoiding the problems encountered previously (e.g. radionuclide precipitation and difficulties in the back-extraction of actinides from the solvent).

To meet this objective, two principles have to be applied: (i) the molecules (extractants, diluents, aqueous soluble reagents) used in the processes must be totally incinerable, once they have been spent; in other words, they are converted into gases, which can be released into the atmosphere; (ii) the very acidic liquid HLW to be processed must not be neutralised.

There are two possible routes for the separation strategy:

- route N° 1 has two extraction cycles, the first one to co-extract the actinides and the lanthanides from the very acidic liquid HLW, and the second one to separate the actinides from the lanthanides in aqueous acid solutions, 0.05 to 0.5 mole/L. Some work will be done on the Am/Cm separation.

- route N° 2 has a single cycle, which extracts selectively the actinides, leaving the fission products and lanthanides in the very acidic aqueous solution (> 2 mole/L). This route corresponds to the second step of route N° 1, except that the separation is done at a higher acidity, which makes it much more difficult from an experimental point of view. Its basic criteria must be carefully established using molecular design, synthesis and testing of new extractants.

It is proposed to use weak bases such as diamide reagents for the first cycle of route N° 1 and to develop the DIAMEX process further. For the second cycle of route N° 1 and for route N° 2, tripyridyltriazine (TPTZ) derivatives and new heterocyclic N donor atom extractants will be investigated.

Extraction and Selective Separation of Long Lived Nuclides by Functionalized Macrocycles

This research project involves CEA Cadarache (F) as coordinator and eight European universities. Its objectives are to synthesise and test new macrocycles for the selective extraction of strontium and actinides from MLW (after a sufficient decontamination, the resulting waste could be disposed of in surface repositories) and for the partitioning of trivalent actinides (Am, Cm) from trivalent lanthanides in HLW.

The work programme of this project has three different items: (i) synthesis of macrocycles; (ii) measurement of the extracting properties of the macrocycles; (iii) molecular modelling and X-ray and NMR structures of the complexes formed by the extractant and the radionuclide.

The synthesis of various extractants such as bis-crown ether and calixarene derivatives will be investigated for the removal of strontium. Calixarenes bearing phosphine oxide and diamide groups will be synthesised for the extraction of actinides. Macrocycles (calixarenes, resorcarenes, and others) with soft and hard donor groups will be studied for the actinide/lanthanide separation.

The extracting properties of these compounds will be thoroughly investigated by determining the complexation constants, measuring the distribution coefficients of the nuclides of interest and carrying out transport experiments through supported liquid membranes.

These experimental results will be compared with molecular mechanics and molecular dynamics simulations to understand the selective complexation of cations and to provide guidance for the synthesis of macrocycles. The measurement of NMR and X-ray structures of the complexes between the macrocyclic extractant and the cation, both as crystal and in solution, will provide additional data for modelling.
TRANSMUTATION TECHNIQUES

Two projects are dealing with transmutation techniques. The neutrons are produced in a nuclear reactor in the first project and by spallation using an accelerator in the second one.

Joint EFTTRA Experiment on Am Transmutation

This project aims at demonstrating the feasibility of $^{241}\text{Am}$ transmutation in a high thermal flux reactor. For this purpose, an irradiation experiment of a target containing $^{241}\text{Am}$ embedded in an inert matrix (e.g. cerium oxide or spinel) will be performed in the High Flux Reactor (HFR) at Petten.

The project includes different steps: fabrication of the target (stainless steel cladding encapsulating pellets made of a mixture of americium oxide and inert matrix); preparation of the irradiation facility; irradiation of the target during one-and-half year; non-destructive analyses (i.e. visual inspection, $\gamma$-ray spectrometry and tomography, neutron radiography); destructive post-irradiation examination (after de-cladding, the sample will be prepared for microscopic examination and a part of it sent to chemical analysis to determine its isotopic composition and hence the transmutation rate); interpretation of the results.

The work will be carried out by the EFTTRA (Experimental Feasibility of Targets for TRAnsmutation) group, which consists of six European laboratories and institutes. The coordinator is ECN Petten (NL).

Neutron Driven Transmutation by Adiabatic Resonance Crossing (TARC)

This project is coordinated by CERN and involves five other European research institutions. Its main objective is to develop both theoretically and experimentally a new method, the adiabatic resonance crossing (ARC), which enables to enhance strongly the capture rate of neutrons by the radionuclides to be incinerated. An experimental test will be carried out with a neutron spallation source driven by the CERN proton synchrotron. The transmutation of the radionuclides exposed to the neutron flux will be detected by the de-excitation $\gamma$-rays and the decay of the daughter nuclei with electronic methods. A first test will be made with $^{99}\text{Tc}$, for which the predicted cross sections are sufficiently accurate.

The peak cross sections for neutron energies corresponding to the resonance region are much larger than for the other neutron energies. For instance, the cross section of $^{99}\text{Tc}$ is 4000 barn at the peak of a resonance at 5eV, but it is only 20 barn at thermal energy. Access to the resonance region can be achieved by using a transparent medium where the neutrons lose their energy in very small decrements following successive nuclear encounters (i.e. the lethargy is minimal) and their absorption is very small. In such a medium, the neutron flux per unit energy is correspondingly larger and the neutron energy decreases slowly through the resonances, leading to a very large probability of capture during crossing. Lead appears to be one of the best elements which satisfy these criteria.

All the measurements will be performed in a large lead volume with a spallation target (initially the lead itself) and several types of detectors. The radionuclides to be transmuted will be introduced in the lead assembly through thin channels. A narrow hole brings the proton beam from the CERN proton synchrotron deep inside the structure. Protons create neutrons after interaction with the lead.

The first task is to construct the lead assembly and to equip the proton beam line with instruments. Then, different types of experiments on ARC will be carried out. The transport properties of lead for neutrons at different energies will be studied. An appropriate formalism and new time-efficient Monte Carlo simulation methods for parallel computers will be developed for ARC. Finally, a conceptual design of an incinerating device based on ARC will be made.
CONCLUSION

The three areas of the research activities on new fuel cycle concepts are covered with more emphasis on strategy studies and balance between the two experimental areas. These research activities gather different scientific fields from basic chemistry (partitioning) to nuclear physics and accelerator technology. About forty different European research institutions are participating to the projects, which have started in 1996. It is expected that, at the end of the specific programme on Nuclear Fission Safety in three years from now, the scientific community will have a clearer picture on the possibilities offered by the different options investigated to reduce efficiently the radiotoxicity of nuclear waste.

ACKNOWLEDGEMENT

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REFERENCE

Abstract

In 1990, the IAEA received a request from Member States to review the status of research and development on partitioning and transmutation of actinides and fission products. In response to this request the Advisory Group Meeting (AG) was held in the fall of 1991. AG advised the Agency to play an active role in coordinating international activities in this area. A series of meetings that followed identified considerable interest among many Member States and international organizations in the P&T options as a potential complement to the reference concepts of the back-end of nuclear fuel cycle. Inherent difficulties for the Agency to actively explore this programme were identified including non-proliferation concerns from some Member States about partitioning technology and possible duplication of effort in other international organizations, especially OECD/NEA. But, there remain fundamental questions to be addressed on the objectives of and motivations for P&T and it is clear that some common international understanding would be necessary. In order to contribute to the solution of this problem, and considering the existence of programmes being implemented by OECD/NEA, the Agency has initiated a CRP entitled "Safety, environmental and non-proliferation aspects of partitioning and transmutation of actinides and fission products" (1995-1998). The documents on accelerator-driven systems and on the status of transmutation studies in non-OECD countries are being prepared.
1. Introduction

There is considerable interest among many Member States in the Partitioning and Transmutation (P&T) of long-lived radionuclides as a potential complement to the reference concept of the closed nuclear fuel cycle comprising: fuel fabrication, energy generation, intermediate storage of spent fuel, reprocessing, plutonium use in fuel and disposal of solidified high-level waste (HLW) in a deep geologic repository.

P&T is a complex issue involving safety, technological, economic and public acceptance aspects. Until now, there is no clear indication that P&T of actinides and long-lived fission products offers a more safe and effective waste management option. Current national (China, France, Japan, Russia) and international (OECD/NEA and CEU) programmes on P&T tend to be more concerned with the development of techniques for the separation of actinides, preparation of fuel and targets and for transmutation of actinides and long-lived fission products rather than with the studies of safety implications of P&T.

The IAEA's involvement with the problem of partitioning and transmutation of actinides and fission products goes back to 1976 when the Agency carried out a Co-ordinated Research Programme (CRP). The results of the CRP were published in a Technical Report Series No. 214 in 1982. The conclusion of this report on P&T was rather negative. In 1990, the Agency received a request from some Member States to re-activate the programme. The Advisory Group Meeting (AGM) held in the autumn of 1991 advised the Agency to play an active role in coordinating international activities in this area. A series of meetings (two Consultant Meetings (CS) and one Technical Committee Meeting (TCM)) that followed identified considerable interest among many Member States and international organizations in the P&T options as a potential complement to the reference concepts of the back-end of nuclear fuel cycle.

The meetings also gave the opportunity to review the current status and progress of national and international programmes on P&T, to identify the most important directions of national and international cooperation. The meetings provided advice regarding the IAEA programme on P&T.

2. Main results of IAEA meetings on P&T

There is a scientific consensus that the current waste management concept provides an adequate protection to the population and the environment by sufficient confinement of radionuclides. According to the experts' opinion, the purpose of P&T is to reduce the long-term effects of radioactivity of actinides and long-lived fission products but cannot eliminate the need for a geologic repository. In some countries (France, Japan, Russia) it has already received political or institutional backing as a complementary future strategy to the current fuel cycle. The specific role of P&T in the nuclear fuel cycle needs to be defined further within the general trend to minimize waste and the growing concern about a maximum degree of safety in the very long term.

A general guidance with respect to hazard reduction by P&T cannot be given since the local geological, hydrogeological and confinement conditions of proposed repositories vary from country to country. However, qualitative indications will be very useful to establish an order of priority in the radionuclides to be studied regarding the hazard reduction involved.

It was emphasized that from the point of view of potential hazards (potential hazard involves the source term without taking into account the geological barriers), the actinides are the most important nuclides to be investigated in a P&T concept, however, some long-lived mobile fission products constitute the main residual hazard (residual hazard means the radionuclides released to the biosphere) over a long term period of time.

The following are main conclusions of meetings concerning the progress being made in the fields of partitioning, of fuel and target developments and of transmutation.
Partitioning

Two main fields of work are involved in the partitioning of plutonium, minor actinides and long lived radionuclides: wet separation methods that are implemented in association with the PUREX process; pyrometallurgical processes, which may follow the PUREX process or completely replace it.

Significant progress has been achieved in reducing the losses of plutonium from the PUREX process and in the improvement of neptunium and technetium separation through flow sheet alterations. Progress has also been made with the partitioning of other elements.

Fuel and Target Development for Transmutation

The technical feasibility of the use of U-Pu and U oxide fuels for the recycling of minor actinides in a fast reactor has been proven to some extent. Oxide, metal alloy and inert matrix fuels and targets containing MA and Tc-99 are fabricated, at a laboratory scale, and scheduled for irradiation. Concepts of nitride and molten salt fuels have been proposed for the advanced transmutation systems, e.g. actinide burners and accelerator driven systems.

Transmutation

An overall reduction of the radiological hazards requires the development of new technologies, e.g. with an accelerator driven transmutation system. Only with a major break-through in technology are we likely to reach the expected goal.

3. Role and involvement of IAEA

The participants of IAEA meetings stressed that OECD/NEA and CEU have managed international P&T programmes. However, a number of countries are not yet covered by these international bodies, therefore the IAEA might play a significant role by coordinating the efforts of these countries with OECD/NEA and CEU countries.

Based on the recommendation of experts from Member States and considering the existence of technologically oriented programmes being implemented by OECD/NEA and CEU, the IAEA established a complementary programme on the safety, environmental and non-proliferation aspects of P&T that could be beneficial in assisting Member States.

A series of topics are to be addressed as:

1. the definition of hazard criteria;
2. the evaluation of hazard reduction;
3. the definition of a priority list of nuclides to be considered.

Since each of the three above-mentioned topics are strongly dependent on the geological nature of the repositories and on their technological implementation it is deemed necessary to widen the scope of the P&T discussion to the general waste management issue involved with such an option. It is, therefore, suggested to associate plutonium and waste management experts in the P&T discussions.

In the mainstream of this programme, IAEA with the P&T, Pu, and Waste Management expert groups will be able to make a comprehensive evaluation of the following tasks:

4. establish a worldwide inventory of the radionuclide source term;
5. identify the possible fundamental safety benefits of a series of P&T options and scenarios;
6. evaluate the waste conditioning processes in the perspective of a future transmutation option;
7. identify the influence of secondary waste arisings on the net safety benefit of the overall P&T processes;
8. examine the non-proliferation implications of an extended fuel cycle activity over a long period of time.

This recommendation became a basis of a CRP on P&T initiated by the IAEA in 1994.


Scientific scope and programme goals

The CRP will promote the exchange of information on the results gained by different countries in order to clarify the objectives and motivation of P&T and to obtain a common international understanding from the standpoint of safety and non-proliferation. The results of this programme will also give the opportunity to Member States to define the scope of further research and development-work required in this field. The intended beneficiaries of the proposed programme are both the policy makers and the research programme managers in the fuel cycle field.

In the framework of the CRP the radionuclides hazard is to be studied in order to identify the critical nuclides to be considered in a P&T strategy and to quantify their radiological importance in a global nuclear fuel cycle analysis. A priority list of radionuclides for P&T is to be established according to the hazard definition.

The necessary extent of P&T for achieving the radiological hazard reduction should be clearly defined. It may turn out that not all long-lived radionuclides will have to be partitioned to the same degree and hence their contribution to the disposed waste will have a different effect on the overall hazard reduction. The achievable goals in hazard reduction by different P&T systems will be examined.

The construction and operation of various nuclear facilities needed for P&T may involve increasing risk for the personnel and additional detriment to the environment. The safety aspects of the modified fuel cycle are to be realistically assessed.

Non-proliferation implications of different P&T systems will be assessed in order to define the most promising and effective schemes in this regard.

Programme Subjects

A list of proposed subjects is given below:

a) Critical Radionuclides for P&T
   These studies will define the hazard criteria and consider the hazards of different radionuclides in HLW. As a result of the studies a priority list of critical radionuclides will be established for partitioning and transmutation.

b) Radiological Hazard Reduction by P&T
   The aims of the radiological hazard reduction will be defined and the necessary extent of P&T
for achieving the hazard reduction will be studied. Attainable hazard reduction by different P&T systems will be assessed. For different partitioning processes under development, the influence of secondary waste arisings and the quantification of unseparated radionuclides which must be sent to a repository will be evaluated.

c) Safety assessments of different P&T processes
These studies will include investigations of the operational safety aspects of different P&T systems including the management of the secondary waste in order to assess the safety of the modified fuel cycle.

d) Non-proliferation aspects of P&T processes
These studies will be aimed at the potential of P&T for the technical contribution to the non-proliferation regime.


The preparation of a Status Report on Actinide Transmutation in Advanced Nuclear Reactors in non-OECD countries was initiated in 1994. Its objective is to review the status of research activities in non-OECD countries and to discuss relevant programmes on transmutation development in these countries.

Participating Countries: Belgium, China, Czech Republic, France, India, Japan, Republic of Korea, Russian Federation.


The IAEA has also started to prepare a status report on Accelerator Driven Systems (ADS), as recommended by participants of a Special Scientific Programme on "Use of High Energy Accelerators for Transmutation of Actinides and Power Production" held at the Austria Center in Vienna, on 21 September 1994 in conjunction with the 38th IAEA General Conference. The general purpose of the Status Report is to provide, in particular for planners, decision makers, and other parties that are not directly involved in the development of ADS, an overview of on-going development activities, different concepts being developed and their project status, as well as typical development trends.

Participating Countries and Organizations: France, Japan, Russian Federation, Sweden, USA, EC-JRC (Ispra Site), CERN.


This CRP was established in 1995. It will examine the different fuel cycle options in which Pu can be recycled with Th to eliminate of Pu, or replace Pu with materials that are more acceptable to the public. Potential of Th-matrix will be examined through computer calculations. Each participant can choose his own cycle, and the different cycles can be compared through certain predefined parameters (e.g., annual reduction in Pu inventory). The toxicity accumulation and a transmutation potential of Th-based cycles for current, advanced and innovative nuclear power reactors, including hybrid systems, will be investigated.

The CRP consists of two parts (Benchmarks):
Part 1: Calculation of the isotopic composition, cross-sections and fluxes for a typical PWR-cell loaded with (Pu-Th)\textsubscript{2}O\textsubscript{2} fuel, as a function of the fuel burnup.

8 countries are participating in the Benchmark. Data set was distributed by IAEA in 1995 and all participants have already sent us the results of calculations. As all results of calculations are available, RCM is planned to be held in October 1996 in Vienna to discuss the results of calculations and to approve the next stage of the programme.

Part 2: Accelerator Driven Systems (ADS) - Neutronic Calculations

Goal of Stage 1 of this Benchmark was defined as a verification of reactivity swing during burnup, as well as some important reactivity effects for a fast spectrum ADS (\textsuperscript{235}U - \textsuperscript{232}Th fuel) with an external (spallation type) neutron source at different subcriticality levels. 9 countries and 1 International Organization (CERN) are participating in this Benchmark. The final data specification was distributed in July 1996 and RCM is planned for February-March 1997.
EFTTRA IRRADIATION EXPERIMENTS FOR THE DEVELOPMENT
OF FUELS AND TARGETS FOR TRANSMUTATION

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ABSTRACT

The EFTTRA collaboration (Experimental Feasibility of Targets for Transmutation) between CEA (France), ECN (The Netherlands), EDF (France), FZK (Germany), LAM and ITU (European Commission) was launched in 1992, with the aim of performing joint experiments for the study of materials for the transmutation. Irradiations have started in parallel in the Phénix fast reactor in France, and in the high flux thermal reactor HFR in the Netherlands. One of these experiments, concerning technetium and iodine, has been completed; post-irradiation examinations of the Tc metallic samples are performed by ECN, CEA and ITU, and a summary of the last results is presented. The other ongoing EFTTRA experiments are described, with a report on the application of fabrication methods for matrices with up to 10% americium content. Finally, some considerations on the strategies for americium are given.
INTRODUCTION

In the field of the research on nuclear wastes management, the problem of the long-lived radioactive nuclides requires careful consideration. The possibility of separating and transmuting these long-lived radioactive nuclides, with the aim of reducing the radiotoxicity of the final waste, has to be investigated. To carry out such experimental or theoretical investigations in the frame of an international collaboration presents many advantages, one of them being to split the costs of the studies. Therefore, the decision to form the EFTTRA (Experimental Feasibility of Targets for Transmutation) group, devoted to technical problems, together with European partners, was taken [1].

EFTTRA PROGRAMME AND RESULTS

The EFTTRA programme presently consists of the study of the transmutation of Tc-99 (metal), and of the development of materials (inert matrices) for the transmutation of americium. One experiment on Tc (EFTTRA-T1) concerned also iodine.

Technetium

Metallic Tc rods have been produced and welded in 6 cylindrical target capsules (3 for HFR and 3 for Phénix), at ITU, for irradiation in HFR and in Phénix. The irradiation of 3 target capsules in HFR, an experiment called EFTTRA-T1, was completed in 1994, and "the first results of the post-irradiation examination at ECN, which have been presented earlier [2-4], show that the burn-up is about 6.4 % and that no swelling of the rods has occurred. Part of these irradiated samples have been sent to ITU and CEA for comparative examination ; the results from the three laboratories will be discussed and interpreted in common, and a detailed report will be published. The observations at ITU and CEA confirm the results obtained earlier at ECN that the irradiation had no significant effect on the structure of the material, and no swelling was detected. It will be checked if this good behaviour of technetium metal remains for higher burnup (see below, EFTTRA-T2). The distribution of the Ru concentration along the radius of the sample, determined at ITU by EMPA (Electron MicroProbe Analysis), showed the same sharp decrease as for the ECN sample, from ~ 13 % at the surface, down to 8 % at 0.1 mm depth and 6 % at 1mm depth (diameter of the samples : 4,8 mm). The value obtained at the surface of the sample is slightly below the ECN value : this can be due to the very steep slope of the concentration curve near the surface, or to the orientation of the sample. No significant variation of the Ru concentration was found along the axis of the samples. The PIE observations are in excellent agreement with the results of detailed KENO Monte-Carlo calculations, as performed at ECN [5].

Two technetium rods have been re-packed at ECN for a re-irradiation in the HFR. This irradiation (EFTTRA-T2) was started in February 1996 and will last for about 500 full power days during which a burn-up of more than 20% will be achieved.

The irradiation of the 3 other Tc target capsules is planned in the fast reactor Phénix (EFTTRA-F2) ; depending on the schedule of the Phénix reactor, the irradiation should start in 1997. The samples will be placed in the radial blanket of the reactor, in a thermalized neutron flux ; the moderator is CaH₂. The experiment aims at a transmutation of 15%.

Iodine

The iodine capsules (containing natural I-127) of the EFTTRA-T1 irradiation were examined at ECN [4,6]. The capsules containing Cet₃ and Nal did not show any degradation and the burn-up was 5-6 %, the capsules containing PbI₂ were heavily corroded and leakage had occurred. Taking also into account the information from the fabrication of the targets, Nal seems to be the best of the three candidate materials. However, because the necessity of iodine transmutation is still under discussion and the implementation of the transmutation of iodine in the fuel cycle is very complicated (large inventories, long transmutation half lives, vented pins concepts to release Xe pressure), the EFTTRA cooperation will stop its efforts on this element.

Inert matrices

The heterogeneous recycling of Am supposes that targets for the transmutation, with a high percentage of americium (10 to 40%), are produced, irradiated, and reprocessed. The choice of a suited inert matrix depends on its thermodynamic, physico-chemical, and mechanical properties, and on its behaviour under irradiation or during cooling.

The preliminary studies are done in the laboratory, for a first selection of matrices [7,8]. Techniques have to be developed for the fabrication of the materials ; if reprocessing by the Purex process is envisaged, the solubility of the matrix in nitric acid, possibly after crushing of the material, is an important factor : MgO was found to be the most easily soluble. Once the matrix has been fabricated, a range of parameters has to be
measured: the ideal matrix material should have high thermal conductivity and melting point temperature, low creep and swelling properties, low activation coefficient, low neutron absorption, and should not react with the cladding or the coolant. Radiation damage can also be studied out-of-pile, by ion implantation. Table 1 shows the main criteria and the present situation on the evaluation of candidate (oxide) matrices. A similar study is now underway for nitride matrices.

For the study of the behaviour under irradiation of the candidate matrices, several experiments are planned. UO₂ may be added to the samples, to simulate the presence of americium oxide. The EFTTRA-T2 experiment, already mentioned in the above section on Tc, also includes the irradiation in HFR of samples of Al₂O₃, YAG (Y₃Al₅O₁₂) and spinel (MgAl₂O₄). A shorter, parallel irradiation, with also a sample of CeO₂, started at the same time in HFR (EFTTRA-T2bis), and should give a quicker indication of the behaviour of the matrices in a high thermal neutron flux environment.

The start of the EFTTRA-T3 experiment, in which a selection of inert matrices is mixed with UO₂, 20% enriched in U-235, is planned for the end of November 1996. Table 2 gives a list of the samples which have been selected for this irradiation.

Details on the EFTTRA-F1 and EFTTRA-F1bis experiments, also called Matina 1 and Matina 1bis, in the Phénix fast reactor have been given earlier [8-10]; changes in the programme may occur, depending on the operation planning of the Phénix reactor, and of possible new orientations in the strategy.

**Amerium targets**

The same preliminary studies on fabrication, properties, and reprocessing, have to be done with the matrix material containing americium. This was started with the AmO-MgO system [11].

The irradiation in HFR of a sample of americium oxide embedded in a spinel matrix, the EFTTRA-T4 experiment, is now under preparation. This experiment is partly financed by the European Commission, through the shared cost actions of the Framework Programme 1994-1998 on Nuclear Fission Safety. The samples have been produced by ITU, using an impregnation method developed in the frame of a research programme of the Institute on innovative fabrication techniques for the fuels of tomorrow; a publication is under preparation, which will give detailed information on the technique. Dose measurements have been performed on the samples, giving indications on the protective measures to be considered for the future developments of the technique; it can already be stated that the impregnation technique elaborated at ITU presents two main advantages in this respect, compared to the classical powder mixing method: the low amount of wastes produced, and the possibility to remotely control the process, i.e. to produce the samples with a good radiological protection of the operator.

The samples, containing 10 wt% of Am-241, will be encapsulated in a stainless steel cladding. The irradiation is planned to start in September 1996; the duration will be about 400 full power days, with a fluence of the order of 4x10²⁰ m⁻². According to the calculations [12,13], the actinide density in the sample could be reduced by 35%.

**UNDERLYING STRATEGIES**

The efforts of the EFTTRA group are concentrated on the technological aspects of the transmutation, namely the development of targets for the transmutation of technetium and americium. However, the connection of our programme with the studies on strategies cannot be denied: it has to be consistent with the possible options for the future, and the final choices will be made taking also into account our results on the technical practicability of the proposed solutions. As such, EFTTRA is participating in the shared cost action of the European Commission on the Possible P&T Strategies, where it will contribute to the work package on the assessment of the feasibility of advanced fuel or target fabrication.

In most of the countries using nuclear energy, no strategy has been chosen yet for the long term, concerning the back-end of the fuel cycle, i.e. the fate of the plutonium and of the minor actinides. Different scenarios have been defined, which could be classified according to the recycling scheme, considering the available reactor park: the CEA studied 4 scenarios, PWRs only (recycling of Pu and minor actinides in MOX fuel), PWRs and recycling in fast reactors, PWRs with Pu monorecycling and subsequent recycling in fast reactors, or fast reactors only. Sometimes, separate dedicated devices for the transmutation are proposed, like for the Japanese "double-strata" system [14], based on fast reactors or hybrid (accelerator) systems. The scenarios include also the possible evolution of the nuclear energy in the coming years: decrease, stability, or increase (possibly with the development of new reactor technology). The final aim of the study of the various scenarios is an appreciation of their impact on the reduction of the radiotoxicity of the end waste disposal. For each scenario, many elements have to be investigated, like the consequences on core operation, safety, on cycle operation; the reactor parameters have to be optimised, and the materials tested. There are also other items entering in the appreciation of the value of a scenario:

- should it be a strategy for today, with the present technology, or a solution for the future?
- weight of the economic factor
- capacity of reducing the losses from reprocessing
- is there a request for reprocessing, or is once-through permitted?
- technological possibility to go to high burn-up
- can the reprocessing technique be different from PUREX?

Concerning the field of interest of the EFTTRA group, i.e. the transmutation of americium, Table 3 shows the spectrum of envisaged possibilities. The advantage of an inert matrix is the reduction of the production of plutonium isotopes; but a UO$_2$ matrix is easier to reprocess, has the best behaviour under irradiation, and it has been shown that the extra radiotoxicity produced is negligible. If the once-through solution is adopted, there will be no reprocessing, but very long irradiation times will be necessary, with the problem of finding suitable materials.

**CONCLUSION**

Before a definitive choice of the right strategy for the future can be made, the study of the different scenarios must be pursued, in order to have enough elements of decision available. EFTTRA is participating in this effort, with a range of complementary irradiation experiments, both in a thermal and in a fast neutron spectrum, including the fabrication tests, the determination of the properties of the candidate materials, and the post-irradiation examination programme.

**REFERENCES**


Table 1: Evaluation of candidate inert matrices for the transmutation of minor actinides

Candidate oxide matrices for M.A. transmutation in a PWR

<table>
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<tr>
<th>Technical steps</th>
<th>MgO</th>
<th>MgAl₂O₄</th>
<th>Al₂O₃</th>
<th>CeO₂</th>
<th>Y₂O₃</th>
<th>Y₃Al₅O₁₂</th>
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Candidate oxide matrices for M.A. transmutation in a Fast Reactor

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<th>MgO</th>
<th>MgAl₂O₄</th>
<th>Al₂O₃</th>
<th>CeO₂</th>
<th>Y₂O₃</th>
<th>Y₃Al₅O₁₂</th>
<th>CePO₄</th>
<th>ZrSiO₄</th>
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<td>Yes</td>
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Table 2: EFTTRA-T3, irradiation of candidate inert matrices in HFR Petten

<table>
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<tr>
<th>level 1</th>
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<th>Y₂O₃ + UO₂</th>
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<td>YN</td>
<td>ZrN †/UN</td>
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Also for CAPRA-programme

Table 3: Possible strategies for the transmutation of americium

<table>
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<th>inert / heterogeneous</th>
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<th>fast spectrum</th>
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<td>once-through</td>
<td>reprocessing</td>
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<td>few % Am</td>
<td>&gt; 20% Am</td>
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<tr>
<td>UO₂ / heterogeneous</td>
<td>X</td>
<td>&gt; 20% Am</td>
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<td>MOX / homogeneous</td>
<td>X</td>
<td>few % Am</td>
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A COMPARATIVE SYSTEMS-ANALYSIS APPROACH
ON FUEL CYCLES WITH PARTITIONING AND TRANSMUTATION

by L.H. Baetslé

Abstract

A system's analysis approach aims at the definition of the optimum strategy in future P&T research and development activities. Since all nuclear electricity production leads to the production of waste, a general discussion must lead to an agreement on the risk analysis assessment. Two concepts are in opposition: the intrinsic radiotoxicity versus the site specific risk analysis.

The objectives of the P&T systems analysis are:
- provide a synthetic and comparative overview of current projects
- investigate the feasibility of the proposed approaches
- bridge the gap between waste management issues and P&T options
- select promising developments for further international cooperation.

The fuel cycle with P&T should be compared with the currently practised fuel cycles: the once-through fuel cycle with direct disposal and the conventional fuel cycle with U+Pu recovery and MOX use in LWRs and disposal of vitrified waste.

In the once-through cycle the criticality issue and the long term stability of spent fuel are the most important radiological safety aspects to be assessed.

The conventional fuel cycle reduces Uranium mining needs and the resulting radiologic impact of the mill tailings. The short term increase of dose to man in LWR-MOX fabrication and the longterm impact of depleted and reprocessed uranium should also be discussed.

The separation and recycling of Minor Actinides from HLLW will reduce the intrinsic residual radiotoxicity of vitrified waste, but may not influence the risk analysis.

Separation of actinides and a recycling strategy to stabilize the total actinide inventory is probably the most ambitious goal of P&T in the present circumstances.

The longlived fission products can only partially be eliminated either by dilution e.g. .1129, or by transmutation (Tc99), in dedicated very specialised facilities and at very high cost.

The advanced fuel cycle with a complete set of waste recycling steps should be analysed from comparative cost benefit point of view. Fully new technologies e.g. actinide burner reactors and accelerator-driven-transmutation facilities can only be assessed in a generic way since their development is still in their infancy. A very extensive set of parameters might influence the outcome and the credibility of the comparative analysis.
Adaptation of existing technologies will be more easily approached: a.o. reprocessing of high burnup fuel from LWR-MOX and FR-MOX, fabrication of concentrated actinide targets and fuels especially those containing Pu238, Am241, Cm244., processing losses etc but are fundamental issues in the judgment on P&T.

The realization of a comprehensive systems analysis study will require contribution from all involved countries and require the participation of a multidisciplinary task force.

1. DEFINITION OF PARTITIONING AND TRANSMUTATION

Partitioning is a complex series of Chemical and/or Metallurgical operations, intended to separate selected radiotoxic nuclides or groups of nuclides from the bulk of radionuclides occluded in the spent fuel elements which are periodically discharged from a nuclear reactor. The separated nuclides or group of nuclides can be stored as such or transformed into new fuel elements or irradiation targets.

Transmutation is the general term covering as well elementary nuclear transmutation as a result of single neutron capture or more complex phenomena as fission of heavy nuclei, spallation and other nuclear reactions involving neutrons produced in nuclear reactor cores or in subcritical nuclear facilities connected to high energy proton accelerators.

The ultimate aim of the transmutation is to reduce the radiotoxicity by transforming the initial nuclide either into short lived radionuclides or into stable isotopes.

2. ROLE OF P&T IN THE FUEL CYCLE SCENARIOS.

2.1 The Once Through Cycle (OTC)

The OTC is the scenario by which all spent fuel discharged from a nuclear reactor is stored in engineered facilities till sufficiently cooled to be transferred to a permanent disposal site in deep geological formations.

The OTC scenario implies that with continuing nuclear power throughout the world the quantity of Uranium mining remains at present day levels, and that the residual fissile material content of the spent fuel (1% Pu 0.8% U235) is lost for ever.

The main longterm potential radiotoxicity is associated with the actinide elements particularly the TRU nuclides (Pu,Np,Am,Cm...) which constitute over periods of hundred thousands of years the radiological source term within the geosphere. However the intrinsic insolubility of actinides in deep geological formations reduces the effective contribution of the TRUs to the longterm dose to man.

The fission products (FP) are in the short term the most limiting factor in designing the repository facilities due to the decay heat emission which increases proportionally with the burnup. After some 300 to 500 years the major part of the FP have decayed except for some longlived nuclides (Cs135,Tc99,I129,Zr93...) with half lives of hundred thousands to million years. Some of them are relatively mobile in the geosphere and contribute to the dose to man in the vicinity of repository structures or may even enter a worldwide circulation.

The radiologic impact of the OTC can only be controled by man made barriers which are as longlived as the radiological source term they confine. The very long time periods involved require a full public acceptance of such scenario which goes far beyond the reference lifetime of a geologic repository i.e. 10,000 years.
At the present time there is no worldwide agreement on the time intervals for confinement of high level radioactive wastes in a geologic repository. Periods of 100000 years and longer have in the past been considered as a necessary or a wishful target but no internationally accepted confinement periods have been established.

The working group might investigate the consequences of the duration of the confinement period in a geologic repository on the requirements for a P&T approach.

A number of specific regulatory and safety aspects are associated with the OTC scenario:
- the maximum inventory of spent fuel is (in the US) limited to 70000 THM per repository.
- there is an inherent criticality potential associated with the quantity of fissile material in the repository
- the longterm heat emission on the surrounding geosphere due to the TRUs.

Indirectly the OTC scenario implies the continuous production of mill tailings which accumulate at the mining sites.

By not recycling fissile or fertile materials the energetic significance of the nuclear energy in the global world energy economy is rather limited. P&T is incompatible with OTC.

2.2 Conventional Fuel Cycle with Reprocessing and U-Pu recycling. (CFC)

Since natural Uranium contains only 0.72% of fissile U235 isotope, the recycling of U-Pu from spent fuel through the CFC has been from the beginning of the nuclear era the standard scenario of nuclear energy production. Since 1972 this policy has been rejected by the US administration for economic and non-proliferation reasons.

The CFC scenario incorporates the "reprocessing" step which aims at the recovery of U and Pu from dissolved fuel elements and the transfer of FP and Minor Actinides (M.A.=Np,Am,Cm) to the High Level Liquid Waste (HLLW) which is stored for a number of years till vitrification of this highly active solution. The glass-blocks are stored in engineered facilities till their transfer as HLW to a geological repository.

By proceeding according to this CFC scenario the major fraction (99.7%) of the U and Pu streams are extracted and only a very minor fraction of the so called "major actinides" are transferred to the HLLW (and consequently to the HLW) and eventually to the geologic repository.

Partitioning of Minor Actinides (M.A.) from HLLW in order to further reduce the radiological potential of HLW has been studied since the 1970ies. Initially the R&D activities were focussed on the quantitative removal of MA in order to eliminate the need for any longterm storage or final disposal in geologic formations. This option was abandoned, because unrealizable.

However, if the public and/or political acceptance of very long term disposal of HLW could not be obtained, the removal of MA from HLLW is a technical solution which might reduce the residual radiotoxicity of the HLW. With increasing burnup the generation of MA becomes more and more important.

The addition of a MA Partitioning module to the standard reprocessing plant would in such a case be the most obvious step to be added to the current CFC.

Countries with a reprocessing infrastructure (France, UK, Japan, Russia, China) and their associated partners could in a medium term realize a partial partitioning scenario by which the actually produced HLW would be practically free from longlived TRUs.

However the question arises what to do with the recovered U, Pu, and TRU fractions?

The countries which chose to reprocess their spent fuel did this with the main purpose to recover the major actinides (U and Pu), to save on fresh uranium purchase (20%) and to use
the residual fissile components of the spent fuel (1% U235, 1% Pu) corresponding to about 25% of the regular SWU expenses in the uranium enrichment step.

For a number of decades the Pu recycling was envisaged in a Fast Reactor (FR) option but for technical, economic and political reasons this longterm option of nuclear energy production has been slowed down and sometimes even put to an end.

The stock of Pu already accumulated at the reprocessing plants and which was intended to be used in LMFBRs became redundant in a cheap uranium market economy.

Some years ago the recycling in LWRs of Pu recovered in the reprocessing operations became an industrial practice. The use of LWR-MOX in a CFC option got industrial significance in Western Europe where increasing quantities of PuO2 were transformed into LWR-MOX fuel and irradiated in specially licensed reactors in France, Germany, Switzerland and Belgium.

**The reuse of Pu is to a certain extent a first step in a global P&T scenario which has to be brought into broader perspective of reuse of resources and reduction of the radiotoxic legacy from the nuclear age.** The recycling of Pu as LWR-MOX is a posteriori a step to recover the expenses spent during the conventional reprocessing step by producing a fraction of the electricity in a subsequent reactor core. But from radiotoxic point of view the overall gain is rather limited since only ~ 25% of the recycled Pu is fissioned and about 10% is transformed into a longterm radiotoxic MA source term.

Spent LWR-MOX is for the time being the most important radiotoxic source term which has been reduced in overall mass (a factor of about 5) but not significantly in total radiotoxicity. Multiple recycling of LWR-MOX is theoretically possible in LWRs but the resulting radiotoxicity increases throughout the subsequent recycling campaigns.

In order to reduce the global radiotoxicity it is necessary to transfer the TRU content of spent LWR-MOX fuel into a FR-MOX fuel cycle scenario which becomes a part of the next-generation scenario: the AFC.

In the meantime retrievable storage of spent LWR-MOX fuel is the most appropriate fuel cycle option till a fast Burner reactor technology will become industrially available.

Reprocessing of spent LWR-MOX fuel in view of recycling the TRUs in a FR energy scenario is conceptually possible in present reprocessing plants but these are equipped with extraction facilities for U+Pu recovery and transfer the MA fraction to the HLLW. Since the MA generation in spent LWR-MOX fuel is much higher than that in LWR-UO2 fuel the radiotoxicity of HLLW resulting from LWR-MOX reprocessing is much more important.

**The potential radiotoxicity of HLLW produced during reprocessing of LWR-MOX fuel would require an additional TRU separation module to significantly reduce the residual radiotoxicity of HLW in comparison with spent LWR-MOX fuel.** The same technology as that proposed for HLLW from LWR-UO2 would be adequate.

The recovery of U from spent fuel was from the beginning of the nuclear era an obvious option which was followed because the extraction in the PUREX process was carried out with TBP. For many decades U has been recovered during reprocessing but very little of this stockpile has been reused in subsequent reactor loadings.

Reprocessed U contains some disturbing radioisotopes (U234 and U236) which are the mother isotopes of natural decay chains with radiotoxic decay nuclides. Any delay in recycling reprocessed U leads to the buildup of the (4n+2) Radium chain from U234 with outspoken residual radiotoxicity due to Ra226. The buildup of U236 in reprocessed U, has economic consequences, since it is a neutron poison which decreases the reactivity of reprocessed U versus natural U. For all these reasons and particularly because fresh mined U became so cheap, reprocessed U has not been recycled on an industrial scale and might become a medium level waste type which cannot be disposed of in surface repositories.
If there is no medium term solution to this potential U waste stream, the residual radiotoxicity of reprocessed U will surpass that of Np237, one of the MA. Recovery of Np237 from the U- Pu product stream which is technically possible in the PUREX process, might this way become unnecessary from radiotoxic point of view. This problem ought to be investigated from many viewpoints to end up in a recommendation for the elaboration of the AFC scenario. Indeed one of the TRU nuclides with the longest half life (2,140,000 years) is Np and very few natural barriers are capable to confine this radiotoxic element over such an extended time period.

The quantitative removal of Am241,243 from HLLW resulting from the reprocessing of LWR-MOX is without any doubt the most important task to be investigated, since these nuclides determine to a major extent the potential radiotoxicity of this type of HLW within the time interval of 500 to 4000 years. Part of the Np 237 problem is solved when Am241, its mother isotope, has been quantitatively separated from HLLW before vitrification.

As a conclusion we might say that the recovery of TRUs from spent LWR-MOX fuel would be a first significant step in implementing the P&T option for LWR fuel. The costs incurred in this option might become prohibitive unless the dose-benefit/cost-increment ratio remains acceptable in comparison with the Pu extraction and recycling.

2.3. Advanced Fuel Cycle with TRU recycling. (AFC)

P&T has to play an essential role in the future AFC which is intended to reduce as much as possible the residual radiotoxicity of the Waste streams. The ideal AFC scenario with P&T will be treated in this note as a long term objective to be reached, knowing that economic constraints will damp the enthusiasm for this futuristic option.

Any AFC scenario must rely on the use of reprocessing of spent fuel as an indispensable first step.

A comprehensive AFC scenario with Partitioning and Transmutation comprises the following steps:
- Conventional reprocessing of LWR-UO2 fuel.
- Separation of MA from HLLW resulting from LWR-UO2 reprocessing.
- Fabrication of MA targets for heterogeneous irradiation in LWRs.
- Separation of certain fission products with long half lives if required for the disposal step.
- Quantitative recycling of U and Pu into LWR-MOX fuel.(single or multiple recycling)
- Reprocessing of spent LWR-MOX fuel in adequate facilities (higher Pu inventory).
- Separation of MA from HLLW and conditioning of individual elements (Np, Am, Cm)
- Fabrication of FR-MOX fuel with limited MA content.
- Irradiation of FR-MOX fuel in Fast Burner Reactors. (very high burnup)
- Reprocessing of spent FR-MOX fuel in specially designed and licensed facilities.
- Quantitative separation of all TRUs from the spent FR fuel solution.
- Revision of the fission product management: Tc99 separation (head end, HLLW)
- Investigation of the radiological impact of the minor long-lived Fission Products.
- Impact of Platinum metals separation on the overall economics of Partitioning.
- Multiple recycling of FR-MOX fuel with major TRU content until significant depletion.

The most important of these steps will be briefly commented:
2.3.1 Conventional reprocessing of LWR-UO2 fuel.

The current separation factors obtained for major Actinides (99.7%) are in a first approach sufficient to reduce their content in HLLW. The only improvement which might have a significant influence on the longterm toxicity and waste management is the reduction of Medium Level Waste (MLW) which is not vitrified before disposal and occupies a rather large volume compared to HLW.

2.3.2 Separation of MA from HLLW.

The current reprocessing technology does not separate quantitatively all the MA. Am and Cm (+ shorter lived TRUs, Bk, Cf...) are quantitatively (>99.5%) transferred to HLLW but Np is partly transferred to the High Active Feed (HAF) solution and partly directed towards the HLLW.

The partitioning of Np needs further chemical extraction steps to insure a quantitative transfer to one single waste or product stream, from which further separations could be performed. Partitioning of all MA from HLLW is presently under investigation in many laboratories throughout the world. (Japan, France, China and some minor nuclear countries) and was studied formerly in the US national laboratories (ANL, ORNL, Hanford...).

Several processes have been studied at the conceptual level and tested in hot facilities among the most important are: the TRUEX, DIDPA, TRPO and DIAMEX processes. The systems analysis should emphasize the merits and drawbacks of each of these approaches in existing reprocessing facilities or the adaptations to be made to the current flowsheets and their translation into technological modifications to be implemented in present facilities or to be designed in future reprocessing plants with incorporated Partitioning steps.

Separation of Am(+Cm) is from radiotoxic point of view the first priority, but the Am(Cm) fraction contains all the Rare Earth (RE) elements which are in terms of quantity, 10 times more important than actinides. (12.4 Kg RE compared to 1.27 Kg MA). In order to obtain a TRU fraction with 90% purity a separation factor of 100 is required for the RE fraction. A 99% purity involves a separation factor of 1000, which is a technical limit for elements such as the Lanthanides and the Actinides, with very similar chemical properties.

2.3.3. Fabrication of MA targets for heterogeneous irradiation in LWRs.

In the medium term only thermal reactors and particularly LWRs are available for irradiation of MA targets. Fabrication of irradiation targets with industrially representative quantities of MA are difficult to prepare even in pilot-scale hot-cell facilities. Experience has been gained in the production of isotopic heat sources, but the radiologic context and the ALARA limitations to be expected from regulatory bodies on industrial activities are probably very different from what has been done for military- and space applications.

The presence of large quantities of Am241 accompanied by 1 to 10% RE will require fully gamma shielded and remote operated fabrication facilities. The presence of 5% Cm244 in an Am241-243 target will multiply the degree of technical complexity due to the additional neutron shielding resulting from the spontaneous fission rate and from the alpha-n reaction in oxide-type isotopic targets.
The report should emphasize the order of magnitude of advanced fuel fabrication capacity required to cope with the potential output from an industrial advanced reprocessing plant, equipped with an Am(Cm) separation module. Recycling of such targets to achieve a significant TRU depletion in the target could be discussed in connection with the issue of multiple recycling of fuels and targets (see section 2.3.9) in fast reactors.

2.3.4. Separation of long-lived fission products.

A number of radiologically important fission/activation products play a potentially important role in the assessment of a geologic repository. In order of importance the following nuclides have to be assessed: the fission products Tc99, I129, Cs135, Se79, Zr93, and the activation product C14.

Tc99 is a fission product with a half-life of 210,000 years which occurs as Tc (TcO2) metal in the insoluble residues and as Technetate ion in the HLLW solution. In order to effectively address the longterm radiotoxicity problem both fractions ought to be combined before any nuclear action is taken towards depletion by transmutation. The similarity between Tc and the Platinum metals and the nature of the separation methods (pyrometallurgical techniques) makes this partitioning operation very difficult. Tc displays only a radiotoxicological hazard when submitted to oxidative underground conditions (Tuff, Yucca Mountains). In reducing deep underground aquifers the migration of Tc99 is negligible.

I129 is separated from the HLLW during the conventional reprocessing operations. The separated fraction can either be stored on a specific adsorbent or discharged into the ocean. Since I129 has a half-life of 16 million years it will in any scenario enter into a worldwide dispersion in the geo- or biosphere. I129 is one of the critical nuclides when considering landbased repositories of spent fuel. In a worldwide dispersion scenario its radiotoxic importance is rather limited.

Zr93 and Cs135 are two longlived (1.5 resp. 2 million years half-life) nuclides occurring in spent fuel. Separation of these radionuclides from the other fission products for eventual transmutation is almost excluded since they are accompanied by other radioisotopes which are very radioactive (Cs137) or are present in much larger quantities (736 g Zr93 with 3327 g Zr per THM). In order to effectively reduce the radiotoxic potential by neutron irradiation a series of isotopic separation processes ought to precede any target fabrication and this route is presently considered as an almost impossible endeavour from economic point of view.

C14, with a half-life of 5730 years, is a difficult case because it can potentially enter into the biosphere through its solubility in groundwater and play an important radiotoxicological role because of its incorporation into the biochemical life cycle. Its role in the longterm radiotoxicity is dependent on the physico-chemical conditions occurring in deep underground aquifers or in water unsaturated geospheres.

Some radionuclides discussed in this section ought to be examined in depth by the working group in order to establish their risk and potential radiotoxic role in comparison with the TRUs. Their radiotoxicity is between 1000 and 100,000 times less important than TRUs but their contribution to the long term risk is predominant because migration to the biosphere may be much more rapid and generate in the very long term a certain radiation dose to man.
2.3.5 Quantitative recycling of U and Pu into LWR-MOX fuel.

Up to now it has been assumed that in the CFC scenario all major actinides (U+Pu) were recycled and used in a next fuel loading scheme: LWR-MOX or FR-MOX. For reasons explained above this has not yet been realized and large quantities of reprocessed U and recovered Pu are still in the engineered storage facilities. The management of Pu has recently been examined by a OECD-NEA working group and the conclusions should be used to establish the most probable scenario for the recovery and future use of this very controversial spent fuel constituent.

Three alternatives are open:
- CFC with partial use of U+Pu as LWR-MOX
- CFC with use of U+Pu as feedstock for FR-MOX
- AFC with quantitative recovery of U and Pu for LWR-MOX followed by its transfer to FR-MOX at a later stage.

The working group should assess whether the AFC scenario should preferably be situated as a follow up of the LWR-UO2 reprocessing step or whether it is indicated to transfer all the Pu first to the LWR-MOX step before starting a FR-MOX recycle. If quantitative recovery of all major actinides is not a viable route, it will have a direct impact on the overall separation factor to be achieved for TRUs in general and MAs in particular.

Recycling, or not, of U has a direct influence on the significance of separating Np from spent fuel solutions. The degree of Pu recycling will directly affect the radiotoxic significance of TRU partitioning.

2.3.6 Reprocessing of LWR-MOX

Up to now the reprocessing of LWR-MOX has been done by diluting the LWR-MOX fuel with LWR-UO2 fuel according to the ratio it occurs in the reactor-core. (UO2/MOX=2). Reprocessing of spent LWR-MOX can be performed industrially if the reprocessing plant has been licensed for the treatment of increased Pu concentrations and a much higher total Pu inventory.

The radiotoxicity of spent LWR-MOX is ~ 8 times higher than that of LWR-UO2. Conventional reprocessing will remove U+Pu which accounts for about 30% of the total alpha activity the residual 70% enters into the HLLW stream and is composed of Cm244 and Am241+243. In a perspective of P&T it would be indispensable to remove the TRUs from the HLLW before vitrification. The techniques to be used are in principle the same as for the LWR-UO2 fuel (see 2.3.2), but the higher alpha activity level will interfere with the extraction because of increased radiation damage.

Another option is to store the spent LWR-MOX fuel for example during 50 or more years and to let Cm244 decay (18 years half life) to Pu240 before carrying out the reprocessing. The chemical extraction processes are after the "cooling" period much easier as the alpha decay heat is reduced by a factor of 7 or more.

2.3.7 FR-MOX Fuel fabrication with limited TRU content.

The largest industrial experience has been gained in the FR-MOX fuel fabrication since for several decades FR programmes were undertaken in many nuclear countries. The fabrication of
FR-MOX fuel with 15 to 25% Pu has been realized routinely. But the Pu quality used for these purposes was derived from low burnup UO2 fuel with low Pu238 and 241 contents.

In a perspective of the use of advanced FRs (CAPRA) still higher Pu concentrations are envisaged. (up to 45%) 

In the mean time the burnup of spent LWR-UO2 fuel has increased to 45 MWd/THM and that of LWR-MOX may reach 50 MWd/THM. The isotopic composition of Pu resulting from the reprocessing of such fuels is seriously degraded. High Pu238 and Pu242, low Pu239 and Pu241.

A thorough study of the issues involved was published in 1989 by OECD-NEA and is still valid as source book for the working group on P&T. (PLUTONIUM FUEL An Assessment)

The recycling of FR-MOX containing high Pu238 levels and limited amounts of MA is still more difficult and requires the design and construction of remotely operated fuel fabrication plants.

For homogeneous recycling of MA in FR-MOX, admixtures of 2.5% Np237 and/or Am241 are currently studied. Since Np237 is a pure alpha emitter there is no handling problem involved; but the admixture of Am241 at the 2.5% level will induce a gamma field around the glove boxes or hot cells. However the major interfering nuclide is Pu238 at the 3% level which is a heat and neutron source (5KWth/THM; 5.10 E8 neutrons/s per THM.)

The FR-MOX fuel fabrication with limited TRU admixture will also be influenced by the degree of separation of the Rare Earths (strong gamma emitters) and last but not least by Cm244 which will accompany Am241 and 243 when separated from HLLW. The presence of even small Cm244 impurity levels will boost the neutron emission of the resulting fresh FR-MOX fuel.

The working group should establish which separation coefficients ought to be obtained from Rare Earths and from Cm244 to allow for industrial fuel fabrication operations. Heterogeneous recycling of MA is means to avoid the dilution of troublesome nuclides, e.g. Cm244, throughout the fuel fabrication step and carry this operation in small but dedicated facilities.

2.3.8 Metal Fuel fabrication for ALMRs and advanced fuels for Burner reactors

In the frame work of the Integral Fast Reactor project a specific fuel fabrication technology has been developed and tested on cold (and hot) pilot scale. At the FFTF facility metal fuel has been recycled by casting a UPu-Zr alloy on laboratory- and hot pilot scale.

It is obvious that these processes are still in the exploratory stage and cannot be considered as proven technology but their potential should be investigated since metal fuel permits to reach very high burnups and has good neutronic characteristics for transmutation of TRUs.

The working group could summarize the results obtained and draft a series of recommendations for further work in the countries (Japan, and possibly the US) involved in this type of pyrometallurgical development.

Very recently the attention was drawn on the potential of Nitride and Carbide fuels for Fast Burner Reactors (FBuR)

Nitride TRU fuel containing macroscopic quantities of MA can be produced by a combination of an internal gelation method and a carbothermic synthesis. These nitride fuels can be reprocessed by electrorefining methods similar to the technology developed for metal fuel.

A short analysis of the potential and limitations of this type of new fuel cycle should be included.
2.3.9. Fast Burner Reactors (FBuR)

In the framework of P&T the Fast Breeder Reactor (LMFBR) is not a goal in itself because it produces more TRUs than initially present in the reactor. But very much technological experience has been accumulated since thirty years of R&D&D all over the world which can be transferred to FBuR technology. The decision of the French government to modify the objective of the Super-Phenix (SPX) reactor will have far-reaching consequences on the future FR programme. Gradually the large SPX prototype reactor working with FR-MOX fuel, will be used as a semi-industrial tool to investigate the feasibility of accelerated TRU burning. Therefore it is necessary to modify the reactor configuration (removal of blankets) and even to fundamentally change the fuel and core design. The recently launched CAPRA project will primarily investigate accelerated Pu burning technologies (very high Pu concentrations in the fuel), but MA incineration is also considered. In order to reduce as much as possible the TRU formation, U free TRU fuel with inert matrices are receiving increasing attention.

Several years ago from 1988 on, the Japanese government launched new transmutation projects in the framework of the OMEGA project. The Minor Actinide Burner reactor (MABR), the Particulate Bed Burner Reactor (P-ABR). These projects are being further developed but apart from FR-MOX fuel other types e.g. Nitrides and Carbo-nitrides are investigated as possible alternatives. The IFR project of ANL evolved into an industrial sodium cooled FR prototype design called the PRISM reactor which is supposed to use metallic fuel (UPuZr) with adjacent pyrometallurgical reprocessing facilities to recycle TRU fuel and discard the fission products. Core design studies and core performance analysis are underway to increase the TRU incineration.

The working panel should comparatively investigate:
- the transmutation capacity of TRUs as a function of neutron fluence and spectrum
- the influence of burnup on the fuel behaviour and the cycle time
- the overall mass balance of TRU input and output inventories
- the evolution of the residual radiotoxicity
- the fuel recycle aspects, total cycle inventory, TRU depletion, residual core content.

This analysis would lead to a better understanding of the relative merits and drawbacks of each conceptual design and help the international nuclear community to better grasp the significance and purpose of the many new reactor concepts which were launched in the frame of P&T.

2.3.10 FR-spent fuel reprocessing

The reduction of the radiotoxic inventory resulting from multiple recycling of spent FR-MOX or FR-Metal fuel is only possible if repeated reprocessing of FR-spent fuel is part of the AFC scenario. Irradiation of FR-MOX or FR-Metal fuel is carried out till very high burnup levels. Compared to LWR-MOX fuel the target burnups of FR-fuel are 2 to 3 times higher, i.e. burnups ranging from 120 to 180 MWd/THM are currently to be envisaged, and even higher burnup
levels should be attained in a more distant future. But even these very high burnup levels still correspond to a rather small transmutation or incineration %.

After a prolonged irradiation campaign of e.g. 5 years and a burnup of 150 GWd/THM the degree of depletion is only about 15 to 20 % of the initial TRU inventory. In order to reach an overall TRU depletion yield of 90% it is necessary to recycle the FR-spent fuel between 15 to 17 times according to the expected percentage of losses during each of the chemical extraction operations.

Any reprocessing campaign of spent FR-fuel based on the use of the PUREX process or on an equivalent aqueous extraction process cannot be carried out within a short time interval after the discharge from the fast reactor because the decay heat is much too high. Cooling times between discharge and reprocessing are, as a result, increased from 7 to 10 or 12 years. The duration of the total AFC cycle becomes 15 to 17 years per cycle. The time interval to reach a global depletion of 90% is consequently of the order of 250 years.

Pyrochemical reprocessing of spent FR-fuel was developed in the frame of the IFR project. In this case FR-Metal fuel irradiated at very high burnup is transferred to a "on-site" pyrometallurgical hot-cell for reprocessing. The molten salt bath (CdCl₂,LiCl,KCl..) is not subject to alpha radiation damage and much shorter cooling times can be envisaged. However this type of reprocessing technology is still in its infancy and will require extensive R&D before reaching industrial maturity in the civil nuclear sector.

The process involves electrefining of spent metal fuel with a Cadmium anode, solid and liquid cathodes, and a molten salt electrolyte (LiCl+KCl) at 500°C. The heart of the process is a pyrochemical dissolution process of mechanically declad spent fuel. Pure U (free of Pu) is electro-transported to the solid Cd cathode. The mixture of Pu+MA with some U is electro-transported to a second but liquid Cd cathode and separated from the bulk of fission products. The Pu+MA fraction is recycled as metal and casted into the new fuel pins.

Similar pyrometallurgical processes are being developed in Japan by the CRIEPI institute and may in a distant future become an alternative to aqueous reprocessing with the PUREX process for highly irradiated FR-Metal/Nitride spent fuel.

The fundamental advantage of the pyrometallurgical reprocessing processes is their insensitivity to burnup of the spent fuel and the possibility to reduce the overall AFC fuel cycle to 6 or 7 years. By doing so, a given depletion yield could be reached in half the time period scheduled for an AFC with aqueous reprocessing. The material problems due to corrosion, the degree of separation of the TRUs and the waste handling are the most important issues which await fully convincing answers before this type of pyrometallurgical process will become a serious contender for the reprocessing of FR-Metal fuel.

The P&T working group should assess the merits and drawbacks of each of the approaches taking into account that improvements are possible in the PUREX process and that the pyrometallurgical processes are still in their laboratory phase.

2.3.11 Transmutation issues of longlived fission products

Transmutation of longlived FP is a very difficult task, because the capture cross sections to transmute the radioactive nuclide into a short lived or stable isotopes requires dedicated and large reactor capacities. Thermal reactors and dedicated Accelerator driven Transmutation (ADT) facilities are the only possible choices for carrying out this very expensive endeavour.
From reactor- technological point of view the transmutation of Tc99 is the easiest approach since the metallic Tc target is transmuted into metallic Ru100, a stable isotope. However the thermal n-gamma cross section for thermal neutrons is only 20 barns (b) which is extremely low for practical transmutation purposes. The transmutation "half life", i.e. the time necessary to deplete the target with 50 percent varies from one thermal reactor to another but amounts to about 30 years in the best conditions. The reactor must be overenriched to compensate the reactivity loss due to the antireactivity of the Tc targets in the fuel assemblies.

The simultaneous production of Tc99 by fission in the LWR-UO2 driver fuel decreases the net transmutation rate and necessitates large Tc loadings. The reactor ought to be dedicated for that purpose.

Transmutation of I129 is from pure neutronic point of view very similar to that of Tc99, but is from chemical-metallurgical standpoint a much more difficult process since the target product is chemically unstable and the neutron capture reaction product is a noble gas: Xe 130 which has to be vented from the irradiation capsule during its stay in the reactor. Any temperature excursion would result in a release of I129 into the reactor off gases.

ADT technologies with extreme high thermal neutron fluxes (10E16 n/cm2/s) should be capable of reducing the transmutation half life. This technology is presently in the conceptual phase. However any type of thermal neutron transmutation will be energetically very expensive.

The radionuclides Zr93 and Cs135 cannot be considered for reactor transmutation since they have to be isotopically separated from the other Zr and Cs isotopes before being submitted to irradiation.

The transmutation of C14 has up to now not yet been considered in the P&T context. Theoretically the C14 released from the spent fuel could be removed from the reprocessing off-gases and transformed into a solid target e.g. BaCO3, but the cross section of C14 for thermal neutrons is nearly zero.

Transmutation by charged particles in high energy accelerators is a theoretical alternative in some cases, but the practical feasibility and the economy of such approaches is very questionable.

The working group should evaluate whether the transmutation of long-lived fission products is a realistic way to pursue and assess the dose benefit/ cost increment ratio for a significant (e.g. 90%), source term reduction of Tc99 and I129. Since these radionuclides have very long half lives, the effect on the dose to man is stretched over geologic periods and surpasses by far the reference lifetime of a repository and even the confinement times of natural barriers.

2.3.11 Conclusions on the role of P&T in the AFC option.

The P&T option within the AFC scenario, as described above, is the most comprehensive approach which can be reasonably proposed and constitutes a very important extension of the fuel cycle activities in comparison with the CFC and a priori with OTC scenario.

The Working Group on P&T should identify the most attractive of the subscenarios to be pursued in the future within a comprehensive and often wishful type of AFC scenario.
Transmutation : Physics and Strategies

M. Salvatores, A. Zaetta
Nuclear Reactor Directorate, CEA-Cadarache
- Much can be said (and has been said) about "criteria".

- However, the simple parameter represented by the activity of the materials stored in a repository (or the "source of potential radiotoxicity") is still widely used. Much debate, not many new suggestions.

- Long-lived fission products: since 1990 (1st OECD Exchange Meeting here in MITO) no much progress towards a clear assessment of the relevance of their associated toxicity.
Transmutation (with neutrons):

- everything has already been said!

few clear guidelines:

- fission should be privileged and neutron economy is essential,

- the evaluation of the consequences on the physics parameters of the fuel cycle is crucial. Again, it is better to "transmute" by fission than by capture,

- Np is not a priority : Americium is!

- Cm : no unique strategy is easily available,

- when evaluating benefits/drawbacks of transmutation, the role of the strategy chosen for Pu management is dominant.
The Physics of Transmutation

- At equilibrium:

\[ \frac{dN_J}{dt} = AN_J + S_J = 0 \quad \text{ (} S_J \text{: continuous feed of isotope J to the system)} \]

\( \Rightarrow \) equilibrium is readily achieved!

- At each isotope J, one can associate a "neutron consumption/fission"

\[ D_J \quad \text{(} D_J < 0 \text{ means "production")}. \]

One can define a \( D_{\text{comb}} \) for a fuel, which is a mixture of isotopes J with fractions \( \varepsilon_J \):

\[ D_{\text{comb}} = \sum_J \varepsilon_J D_J \]
# DJ values

<table>
<thead>
<tr>
<th>ISOTOPE (or fuel type)</th>
<th>Neutron Spectrum and flux level (n/cm².s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fast spectrum</td>
</tr>
<tr>
<td>Th (with extraction of Pa-233)</td>
<td>-0.39</td>
</tr>
<tr>
<td>Th (without extraction of Pa-233)</td>
<td>-0.38</td>
</tr>
<tr>
<td>U-238</td>
<td>-0.62</td>
</tr>
<tr>
<td>Pu</td>
<td>-1.36</td>
</tr>
<tr>
<td></td>
<td>-1.46</td>
</tr>
<tr>
<td></td>
<td>-0.96</td>
</tr>
<tr>
<td></td>
<td>-1.24</td>
</tr>
<tr>
<td></td>
<td>-0.44</td>
</tr>
<tr>
<td>Np</td>
<td>-0.59</td>
</tr>
<tr>
<td>Am</td>
<td>-0.62</td>
</tr>
<tr>
<td></td>
<td>-0.60</td>
</tr>
<tr>
<td>Cm</td>
<td>-1.39</td>
</tr>
<tr>
<td></td>
<td>-2.51</td>
</tr>
<tr>
<td>DTRU (fuel unloaded from a PWR)</td>
<td>-1.17</td>
</tr>
<tr>
<td>DTRPu + Np (fuel unloaded from a PWR)</td>
<td>-0.70</td>
</tr>
<tr>
<td>DPu (fuel unloaded from a PWR)</td>
<td>-1.1</td>
</tr>
</tbody>
</table>
The system neutron balance can be expressed in terms of a (positive or negative) neutron "surplus" $G$:

$$G = - D_{\text{comb}} - (CM + L)$$

($CM$ and $L$ are the neutrons/fission lost in parasitic captures or by leakage).

Since $CM + L$ is generally equal to $\approx 0.3 \text{ n/fission}$ (for most systems) one can assess what system can allow "transmutation" (fast reactors or thermal reactors with increased fuel enrichment).

For a source-driven subcritical system:

$$G = S_{\text{ext}} - D_{\text{comb}} - (CM + L)$$
In a subcritical system driven by an accelerator which supplies protons of \( \sim 1.5 \text{ GeV} \) to a target producing \( \sim 40 \) neutrons/proton (i.e. \( \text{Max } S_{\text{ext}} \sim 1 \div 1.5 \text{ n/fission} \)),

\[
\Rightarrow \text{The relations among the subcritical } K_{\text{eff}}, \text{ the fraction } f \text{ of the fission energy used to feed the accelerator, the proton current } i \text{ and the power } P \text{ of the subcritical core give for example:}
\]

\[
\begin{align*}
K_{\text{eff}} & \sim 0.95 & f & \sim 10 \% & P & \sim 300 \text{ MWth} & i & \sim 5 \text{ mA} \\
K_{\text{eff}} & \sim 0.9 & f & \sim 20 \% & P & \sim 1000 \text{ MWth} & i & \sim 30 \text{ mA}
\end{align*}
\]

\[
\Rightarrow \text{The surplus of neutrons has a price } (f). \text{ However, can help to provide an alternative option to critical fission reactors for transmutation if:}
\]

- fuels very exotic (better \( K_{\text{eff}} \ll 1 \))
- possible to concentrate all minor actinides in a limited number of dedicated machines (\( \sim 2 \div 5 \% \) of a total power reactor park).
Transmutation in critical reactors (Homogeneous recycling):

- Both LWRs and FRs:
  - Reactivity loss over the cycle: reduced
  - Temperature coefficients (and boron effectiveness): worse
  - Coolant void reactivity effect: less negative (or more positive).

- For LWRs: need of over-enrichment (neutron economy).
  However: Higher moderator-to-fuel ratio is beneficial.

- Maximum allowable MA: 5% of total HI for FRs - 1 ÷ 2% for LWRs.

Heterogeneous recycling:

- Targets at the periphery of the core for minimum perturbation to power distributions.

⇒
  - Performances (mass inventory)
  - Consequences on the physics characteristics of the fuel cycle
## Mass inventories after 1 recycle

<table>
<thead>
<tr>
<th></th>
<th>FR of EFR type (1500 MWe)</th>
<th>FR of EFR type Heterogeneous recycling in radial blankets (content : 40 %)</th>
<th>PWR-MOX with $V_m/V_F = 3$ (content : 1 %)</th>
<th>PWR-UOX Heterogeneous recycling in the core BU = 42 GWd/t</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Np</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumption (Kg/TWhe)</td>
<td>10</td>
<td>13</td>
<td>11</td>
<td>15</td>
</tr>
<tr>
<td>Consumption rate (%)</td>
<td>60</td>
<td>60</td>
<td>45</td>
<td>38</td>
</tr>
<tr>
<td>Fission rate (%)</td>
<td>27</td>
<td>24</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td><strong>Am</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumption (Kg/TWhe)</td>
<td>9</td>
<td>14</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Consumption rate (%)</td>
<td>45</td>
<td>60</td>
<td>42</td>
<td>70</td>
</tr>
<tr>
<td>Fission rate (%)</td>
<td>18</td>
<td>22</td>
<td>6</td>
<td>13</td>
</tr>
</tbody>
</table>
## Consequences on physics parameters of fuel cycle

<table>
<thead>
<tr>
<th>Type of recycling</th>
<th>HOMOGENEOUS</th>
<th>HETEROGENEOUS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5 % Np</td>
<td>2.5 % Am</td>
</tr>
<tr>
<td>Actinide content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>× 1</td>
<td>+ 71 %</td>
</tr>
<tr>
<td>Activity</td>
<td>× 1</td>
<td>+ 3 %</td>
</tr>
<tr>
<td>Gamma source</td>
<td>× 1</td>
<td>× 4</td>
</tr>
<tr>
<td>γ-dose at 1 m</td>
<td>× 4</td>
<td>× 76</td>
</tr>
<tr>
<td>Neutron source</td>
<td>× 1</td>
<td>+ 40 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>FABRICATION</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decay heat</td>
<td>+ 2 %</td>
<td>+ 1 %</td>
</tr>
<tr>
<td>Activity</td>
<td>+ 0.3 %</td>
<td>+ 1 %</td>
</tr>
<tr>
<td>Gamma source</td>
<td>- 0.7 %</td>
<td>- 1 %</td>
</tr>
<tr>
<td>γ-dose at 1 m</td>
<td>+ 6 %</td>
<td>+ 2 %</td>
</tr>
<tr>
<td>Neutron source</td>
<td>- 5 %</td>
<td>× 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>End of irradiation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decay heat</td>
<td>+ 80 %</td>
<td>× 3</td>
</tr>
<tr>
<td>Activity</td>
<td>+ 5 %</td>
<td>+ 13 %</td>
</tr>
<tr>
<td>Gamma source</td>
<td>+ 1 %</td>
<td>+ 5 %</td>
</tr>
<tr>
<td>γ-dose at 1 m</td>
<td>- 1 %</td>
<td>- 2 %</td>
</tr>
<tr>
<td>Neutron source</td>
<td>- 6 %</td>
<td>× 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>End of irradiation + 5 years</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decay heat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gamma source</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-dose at 1 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron source</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Am transmutation in a FR

- Heterogeneous mode

- Multirecycling? Large amounts of Cm are produced

- Cm: what strategy?

- Temporary storage $\rightarrow$ decay to Pu (60 ÷ 100 y !)
- Recycle as for Am - Higher mass MA production
- Reduce its production:

  $\rightarrow$ fission Am to 90 ÷ 95 %
  long irradiation in a high flux (thermalised) at the periphery of a FR.
  However, high DPA (> 200 DPA NRT ?)
  Also: optimisation to avoid too small initial Am loadings
Application to a reactor park

- Whatever the strategy, Pu recycling reduces potential radiotoxicity by factor $\sim 2 + 3$ (in particular if FRs are used): this is a first step in the right direction!

- If Am is recycled, in an equilibrium park:

<table>
<thead>
<tr>
<th></th>
<th>PWR-UOX</th>
<th>PWR-MOX</th>
<th>FR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70 %</td>
<td>10 %</td>
<td>20 %</td>
</tr>
</tbody>
</table>

the potential source of radiotoxicity is reduced by factors $f$:

<table>
<thead>
<tr>
<th>At t (years)</th>
<th>$\Rightarrow$</th>
<th>$10^2$</th>
<th>$10^3$</th>
<th>$10^4$</th>
<th>$10^5$</th>
<th>$10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>$\Rightarrow$</td>
<td>71</td>
<td>75</td>
<td>84</td>
<td>140</td>
<td>80</td>
</tr>
<tr>
<td>(theoretical $f$)</td>
<td>$\Rightarrow$</td>
<td>510</td>
<td>480</td>
<td>630</td>
<td>700</td>
<td>570</td>
</tr>
</tbody>
</table>

If Cm is not put to wastes - Losses: Pu 0.1 % Am, Cm, Np 1 %

If Cm is put to wastes, $f$ are reduced:

| $f$ | $\Rightarrow$ | 10 | 11 | 7 | 94 | 32 |
Conclusions

- Data and methods for transmutation:
  ⇒ Need of improvements (reduction of uncertainties).
  However, present uncertainties allow reasonable evaluations.

- Physics analysis (at equilibrium) allows to point out major features and to intercompare different systems/strategies.

- Accelerator-driven systems: a few extra neutrons available, but at a cost. Can help if dedicated (i.e. MA-fuelled) reactors are envisaged in a "double-strata" type of approach.

- Fast reactors can do most of the job. Limited consequences on the fuel cycle. Transmutation in PWRs: less "attractive".

- Major issue: target development for (once-through) Am irradiation.
  ⇒ Role of SUPERPHENIX: irradiations foreseen.
THE FRENCH PARTITIONING-TRANSMUTATION PROGRAMME,
ASSETS AND PROSPECTS

Michèle VIALA, Commissariat à l'Energie Atomique, Fuel Cycle Division
Massimo SALVATORES, Commissariat à l'Energie Atomique, Nuclear Reactor Division
Henri MOUNEY, Electricité de France, Equipment Division

ABSTRACT

Partitioning-transmutation studies are covered by the 1991 French law concerning radioactive waste management.

The programme is progressing with a dual approach:

- What can be done in partitioning-transmutation? At what cost? In what timescale?
- How can long-term gains and short-term disadvantages be qualified and quantified?

The first approach concerns technical know-how. The studies based on today's technologies are continuing (reactors, fuels and targets, separation of radionuclides by solvents).

The second approach involves an assessment activity, based firstly on studies of scenarios. Pertinent assessment criteria must be brought out.
INTRODUCTION

The French law of December 1991 on radioactive waste management requires this management to comply with the protection of nature, environment and health, taking the rights of future generations into consideration. It explicitly indicates that solutions must be found to enable the partitioning and transmutation of the long-lived radionuclides present in these wastes.

In 2006, the French Parliament will have to come to a decision as to the construction of an underground disposal and the continuation of other research paths.

The French Assessment Commission consisting of twelve members (1), set up in 1994, is in charge of assessing the studies. It published two progress reports in June 1995 and June 1996.

Its principal recommendation, to set up the scientific and technical coordination and a research plan, was followed by a letter from the Ministry (December 27, 1995) organising the management of the R&D and by the publication of a research programme.

Among these technical recommendations, the Commission requested that thought concerning the order of precedence to be assigned to the long-lived radionuclides to be separated and transmuted be continued and that quantified goals be defined. It also requested that the studies and research be organised so as to distinguish between the short and medium-term options concerning already industrial systems, or those undergoing industrialisation, and the longer-term options which are based on the overall foreseeable innovative systems. Lastly, it considered scenario studies and their contribution in the acquisition of highly diversified data bearing on radionuclide inventories, flows of material, economics, safety, etc. These studies are necessary to assess the partitioning-transmutation systems that result in particularly complex schemes.

Deputy Christian Bataille (Member of Parliament) published a report on the "evolution of research on the management of high level nuclear waste", on behalf of the French Office of Scientific and Technological Choices. He recalled the genesis and the content of the 1991 law, underlining its beneficial effect in calming down the discussion, indicated that the research on the transmutation of radionuclides, the underground disposal of waste and the long-duration interim storage of wastes, is progressing most satisfactorily. In conclusion, he noted that no domain, even technical in appearance, is outside the realm of democracy and that today, the law-maker's will is done. However, the change in the European economic context has modified the picture and he recommends适应对 the postponed reprocessing strategy by promoting new research on the possibilities of long-term surface interim storage as well as on the possibilities of direct disposal of non-reprocessed assemblies.

The expose below gives the state-of-the-art on the research programme concerning partitioning-transmutation carried out by CEA in collaboration with those "directly concerned by the law" (EDF, COGEMA, CNRS, ANDRA, ...), and replies to two questions:

- What can be done in partitioning-transmutation? At what cost? With what timescale?
- How can long-term gains be qualified and quantified? Are there short-term disadvantages?

(1) The Commission consists of six people (including at least two international experts) appointed by the French National Assembly and by the Senate, and proposed by the French Office for Parliamentary Scientific and Technological Choices, two people appointed by the Government and proposed by the Conseil Supérieur de la Sûreté et de l'Information Nucléaire (Higher Council for Nuclear Safety and Information), four scientific experts appointed by the Government and proposed by the French Academy of Sciences.
THE ASSETS AND LIMITATIONS OF PARTITIONING-TRANSMUTATION

Partitioning-transmutation fulfills the desire to transform long-lived radioisotopes (>31 years) into short-lived radioisotopes or stable isotopes which could then be managed by confinement and natural decay over periods of some hundreds of years.

It is not planned for short-lived radionuclides (< 31 years) for which confinement pending decay is clearly preferable and already implemented, for instance, in the Aube Storage Centre (CSA).

Both operations, partitioning and transmutation, call upon different types of techniques the limitations of which should be clearly understood.

1. Assets and Limits of partitioning-transmutation

1.1. Partitioning: Assets and Limits

Radionuclides are found in non-reprocessed spent fuels, in type B wastes and in glass (table 1, diagram 1).

To achieve transmutations or fissions, the radionuclides must be submitted to a sustained neutronic flux. These conditions lead to the use of ceramic-type materials able to withstand high temperatures, thermal flux and mechanical constraints. It is therefore necessary to have concentrated and purified radionuclides. (The ideal would be an isotopic purity). With the removal of the long-lived radionuclides from the wastes as a goal, the partitioning must be performed with the highest possible efficiency before proceeding to the purification, concentration and production of the ceramics.

The type B wastes represent large volumes in which the radionuclides are diluted. They must be decontaminated to a point where they can be stored on the surface. The feasibility of such operations depends on the type of waste (concrete, metals, etc.) and on the nature of the contamination (labile, fixed etc.). The performance required is beyond our present know-how. On the other hand, the quantities of radionuclides recovered would be small and easy to manage with those from the bulk of the spent fuel.

The spent fuel, when reprocessed, is quasi-totally dissolved. The valuable materials, U and Pu, are separated and purified (with a recovery yield of 99.9%). Iodine and other fission gases (krypton, ...) are discharged. The fission products and minor actinides (Np, Am and Cm) are contained in a so-called "high level effluent" (which contains 98% of the $^{137}$_{S} activity and the $\alpha$ activity exclusive of plutonium). The glass is made from the high level effluent. (Figure 1).

The high level effluent containing most of the radioactivity is the subject of long-lived radionuclide separation studies.

In a first stage, the partitioning-transmutation applies to spent fuels only. It does not apply to type B wastes.

Extraction by solvent techniques are extremely efficient (they are the ones that enable the industrial recovery of uranium and plutonium), on condition that a good solvent is used. The latter must extract the desired element with very high affinity (recovery yield) and good selectivity (without extraction of unwanted species), allow the subsequent recovery of the element (back extraction) and enable the implementation of operations under industrial conditions without generating new waste.

Partitioning is first of all a question of molecular chemistry (discover the functionalities of the molecules of the solvent and tailor the molecule to the extraction conditions), then of chemistry and of chemical engineering (operating conditions).

For neptunium, zirconium and technetium, the research pertains to implementation, as the solvent is well-known (TBP).
For caesium, the calixarenes functionalised by etheroxide chains have been discovered. The development of a molecule for the solvent and process implementation remain to be achieved.

For the co-extraction of actinides and lanthanides, a molecule has just been developed (DMDBTDMA) and the Diamex process is to be defined (chemistry and implementation).

For americium and curium, unsatisfactory solutions exist (very tricky implementation and large secondary wastes) and interesting functionalities are under study (TPTZ and picolinamides). It is hoped that they will be suitable and, if so, the molecules will have to be tailored to the extraction conditions and the implementation made.

Table 2 gives the research status for the partitioning of actinides and fission products.

Concerning partitioning, once the feasibilities have been acquired, performances will be excellent and a preliminary calculation may be made by assuming losses of long-lived radionuclides from 0.1% to 1% in the high level effluent sent to vitrification.

1.2. Assets and limits of transmutation for actinides

Incineration-transmutation (1) is seen by an overlapping of phenomena with the disappearance and the creation of nuclei: the limits of the process therefore have to be clearly defined.

Chemical separation leads to radioisotope mixes. Each one interacts with neutrons in a specific way, which is the only interaction possible today to transmute on a large industrial scale.

Actinides may undergo fissions generating radioactive fission products as well as neutronic captures which produce other actinides. The radioactive decay of actinides spans a very long time and belongs to one of four main families of decay which end with stable isotopes of lead or bismuth.

a) Physical feasibility

Studies to date have shown that it would be possible theoretically, and exclusive of any industrial and economic feasibility studies, to very appreciably reduce the final production of radiotoxic heavy nuclei (plutonium and minor actinides) resulting from the supply of electricity, using fission reactors in a park of reactors that produce and consume these heavy nuclei. Such a park is said to be balanced (in mass and isotopic composition) when it reaches a steady state in which all the radiotoxic heavy nuclei it produced are fissioned.

Various scenarios of multiple recyclings of plutonium alone or with minor actinides in parks consisting of PWRs, RMAs (AMRs?) or FBRs have been studied to strike a balance between production and consumption of actinides, hence a final zero production within the park. (Diagram 2).

These studies tend to show that there are neither outstanding nor even significantly different scenarios for the recycling of plutonium alone (Table 3). They all result in balanced Pu inventories in the cycle, of the same order of magnitude (a few hundred tons). They also show that the in-cycle plutonium inventory is higher for these scenarios than for a PWR open cycle that produces the same amount of energy but discards the plutonium for waste. On the other hand, the amount of plutonium sent to waste in these scenarios depends only on the separative performances of the cycle knowing, moreover, that the production of minor actinides is considerably increased.

(1) The term transmutation is used when the atomic nucleus captures a neutron, and incineration when it fissions.
These studies also indicate that the dynamics of the systems is very slow (about 100 years to reach equilibrium) and that a controlled phasing out of nuclear power must also be provided for to progressively eliminate the plutonium inventory in the cycle. (1% may be reached in more than 100 years).

The same theoretical studies began with the recycling, besides plutonium, of the minor actinides. They started with the study of the reactivity of various reactor cores and the verification of the main safety parameters. Thus the acceptable limit in minor actinides was set at 5% in FBRs and 1 to 2% in PWRs when the minor actinide is homogeneously distributed within the UO2-PUO2 mixture in the ceramic fuel. These cores result in actinide incineration performances of 18 to 27% in FBRs and from 6 to 9% in PWRs at standard burn-ups and allow a positive balance in the consumption versus the production of minor actinides (Table 4). Multiple recycling scenarios are under study. It seems that the same type of results would be obtained as with the recycling of Pu alone, slightly more contrasted depending on the reactors. The study with CAPRA reactors is partly completed (Table 5).

The management of curium is difficult owing to its strong neutron and gamma emission. Interim storage may be envisaged (100 years) and then transmute the plutonium from decay or accept to send it to waste pending very strongly reduced production. This could be obtained by separating the americium and by its single-recycling once only in targets. (Then an americium destruction rate by fission higher than 90% is required).

The manufacture of plutonium fuels has already reached the industrial level, and their in-reactor performances mastered. The fuels also containing neptunium raise little problem (an experimental assembly was produced for SPX). On the other hand, the americium targets require further fundamental research on the chemical nature of the americium combination (AmO₂, AmO₂₋ₓ, AmₓO₂₋ₓ), and of the inert matrix able to behave properly under irradiation (choice of the material, Al₂O₃? MgO?...). It is also necessary to improve the behaviour of the cladding under long irradiation and very great deformation of the ceramics. Table 6 recapitulates the status of the research in progress.

Furthermore, innovative options for transmutation such as hybrid systems based on accelerators are being considered. Their potentialities remain to be analysed.

b) Technical and technological feasibility

Several scenarios should be selected, chosen for their technical and industrial credibility and the broad range of choices offered to decision-makers, and technical work should be performed on the feasibility of reactors, the feasibility of the cycle, the dynamics of the systems, the inventories per cycle and the wastes, and the consequences on the risks and costs. Unsteady state periods will deserve special attention.

1.3. Assets and limitations of transmutation for fission products

Long-lived fission products can be transmuted by neutron capture only. Therefore, a system must be used that produces a large available excess of neutrons. This is why fission reactors (in the theoretical parks mentioned above) are not very efficient for transmuting long-lived fission products.

Each fission product must be studied individually to assess the technical feasibility of its transmutation in reactors or in innovative dedicated systems. Sensitive points appear: the making of thermally stable iodine targets able to withstand the irradiation, the isotopic separation of caesium (without this separation, caesium 133 and 134 generate more caesium 135 than is transmuted, without mentioning the occurrence of the highly radioactive caesium 137), the recovery of carbon 14 which is an activation product of nitrogen 15 and oxygen 17 (can it be separated?)... One case is favourable: that of technetium 99. The others have not yet been studied.

2. Conclusion and prospects

Partitioning-transmutation can be considered from the technical point of view, in a dual approach at the medium and long-term.
At medium term, it is theoretically possible to design nuclear reactor parks that fission all the transuranic heavy nuclei they produce.

The main sensitive points identified today are actinide-lanthanide separation, making americium targets and managing curium.

Major technical changes are necessary, in reactors, reprocessing and fuel fabrication.

These points make up the essential part of the technical research programme.

This management of materials should be performed on a large scale and on an extended timescale. It will not eliminate the "high level and long-lived" wastes as the long-lived fission products and the actinide losses from the cycle (~ 0.1%) will remain in the glass. Type B wastes could be increased in proportion to the flows processed. Furthermore, the controlled phasing out of nuclear must be taken into account.

Several studies of complete scenarios over time, inventory of material, wastes, risks and costs according to the service rendered will be useful to the 2006 decisions and are included in the research programme.

For the long-term, innovative techniques may be required. They could include new hybrid reactor systems allowing to incinerate the capturing only isotopes as well. Their potentiality and the whole of the associated cycle remain to be studied.

A rather fundamental assessment-oriented research programme has been launched.

In any case, type B wastes will remain. Endeavours to rationalise and reduce the volumes are being made in the framework of current reprocessing (Pu partitioning).

The Puretex research programme deals with this subject.

HOW CAN THE ADVANTAGES AND DISADVANTAGES OF PARTITIONING-TRANSMUTATION BE QUALIFIED AND QUANTIFIED?

Transmutation is a complex operation, easier to contemplate today for plutonium than for minor actinides or fission products. It meets the desire to get rid of wastes by destroying them, but it does have limitations. Since it concerns only separated radionuclides and refined products, it cannot not deal with type B wastes.

It does, however, enable the composition of future "high level and long-lived" wastes to be changed by modifying the inventory of the long-lived radionuclides they contain. So it is a technical step in the management of wastes, upstream from their production, and which cannot be assessed independently.

1. Can partitioning-transmutation complement geological disposal?

Projects for disposing of radioactive wastes in geological formations aim at isolating the radionuclides from man and the environment for a long enough time for their impact to have decreased below the regulatory limit of 0.25 mSv/year. The performance of the multibarrier confinement system (package, engineered barrier and geological formation) is assessed by means of safety models taking into account:

- the behaviour of the waste packages,
- the transfer rate of the various radionuclides through the engineered barrier,
- the transfer rate of the various radionuclides in the geosphere,
- the transfer paths and times of the various radionuclides within the biosphere,
- the effects of the various radionuclides on man.
The different confinement barriers allow to limit the flux of radionuclides at the outlet and hence their impact on man. The safety assessment allows this impact to be assessed for each radionuclide versus time, and hence to identify and classify the radionuclides that are important for safety. In particular, it allows to identify those that would be at the origin of a relatively greater impact, linked either to their properties, or to the uncertainty concerning their behaviour. These calculations are performed right from the design phase, taking the conditions offered by the site into account.

In the event the impact of some radionuclides from storage in a given site were too great in view of regulatory requirements, means must be found to reduce it. If their management involved technical conditions that are difficult to achieve, other processes must be considered. Several paths may then be envisaged, including:

- a reduction at the source of the wastes disposed of, corresponding to a reduction in the radionuclide inventory. This is the partitioning followed by transmutation system,

- partitioning for special conditioning,

- adapting the performance of the engineered barrier to meet the safety requirement,

- adding an extra barrier, of the over-packing type or similar.

Each of these systems must be examined and assessed with respect to the safety objectives and the technical means to reach them.

Some orientations may already be provided based on generic type exercises, including the international exercises. They indicate that, in a normal evolution scenario:

- the actinides are well contained by the multibarrier system. Owing to their very low solubility in a reducing medium, they are immobilised by precipitation either in the barriers or within the natural system,

- the only significantly predominant impact could be due to mobile fission products. Iodine is often mentioned, and to a lesser extent caesium. Elements for which the data on behaviour in a natural medium are still uncertain are also mentioned: technetium, palladium, niobium and selenium.

A specific request concerning partitioning and transmutation originating from disposal studies can therefore not be considered before the end of 1997, namely in the framework of the first choice of concept, once the inventory per radionuclide has been specified, the long-term behaviour of the packages described and the specifications laid down.

2. What does partitioning-transmutation contribute as a way to reduce the inventory of long-lived radionuclides in waste?

It may first be considered that P&T fits into a simple rationale to reduce the inventory of long-lived radionuclides sent to waste to potentially reduce the dangers that future generations may be subjected to. In that case, it results only from a subjective need to reduce "potential" dangers independently of any waste management scenario.

The analysis of the concentration of radioisotopes in a spent fuel, of their specific radioactivity and of their dose factor when ingested or inhaled has shown that the "radiotoxic inventory" after 1000 years was linked only to the actinides a thousandfold to ten thousandfold more than to the long-lived fission products. Plutonium represents 90% of the inventory, minor actinides 10%. Plutonium and minor actinides are therefore the priority challenge (Figure 2).

Let us recall that the "radiotoxic inventory" is only a global indicator. It is obtained by weighing each element in the inventory (its concentration) by a coefficient which is strictly valid only in the event of inhalation or ingestion in small doses.

Reducing the inventory of plutonium and minor actinides in wastes obliges global scenarios to be taken into account when they are recycled in a reactor park.
These theoretical scenarios compared with the once-through scenario where the spent fuel is considered a waste, brings out the following conclusions:

In the case of multirecycling plutonium alone, the radiotoxic inventory of the wastes is only reduced by a factor less than 10 (from 2 to 5 depending on the reactor type), since 10% of the plutonium is transmuted into americium and curium (Figure 3 and 4 give an example for Pu recycling in PWRs).

In the case of multirecycling of plutonium and minor actinides, the inventory gain in wastes will then practically depend only on the partitioning performances.

A P&T strategy in a reactor park really makes sense only if it is mastered from beginning to end: reaching a steady state in the park, operating this balanced park over the desired period of time, programmed phasing out necessary to eliminate the inventory in the cycle and putting an end to the nuclear programme. Any brusk interruption in the sequencing of these phases would heavily penalise, or even annihilate the expected gains in the tonnage to be disposed of.

The establishment, operating and programmed phase-out times for nuclear in a P&T strategy is counted in centuries. The problem of the availability of the foreseeable uranium resource in a PWR park will then be acutely felt for carrying out such a strategy. In this regard, the position of FBRs is much more favourable in all respects: sufficient uranium resources, proven physical feasibility of multirecycling, lower production of minor actinides, etc.

The inventory of fission products in wastes can hardly be reduced using fission reactors and dedicated, potentially more efficient, innovative systems must be considered. However their feasibility remains to be proven.

CONCLUSION

Partitioning-transmutation applied to the management of materials is an operation that could modify the composition of the wastes and act on the long-lived radionuclide inventory (especially actinides). We do not know today how to assess the gain of such operations, or the disadvantages resulting from a service rendered, namely the TWhe of electricity produced.

This step will have to be included in nuclear power evolution and waste management scenarios to bring out more significant parameters of the pros and cons, for example the short-term radiologic impact on the workers, the impact that could be produced in the future by geological disposal, the costs, the consumption of raw material resources, etc.

Typical scenarios could perhaps suffice to bring out easier to use assessment critera by showing "classes" of radionuclides (fissile materials, γ n emitters, mobile elements, very low radioactive β emitters, etc.).

However, the difficulty in short-term and long-term risk intercomparisons will remain.

Acknowledgments:

The results quoted were obtained at CEA and through a very large number of research partners. In France: EDF, COGEMA, CNRS. In Europe: the European Communities, TUI, PSI (Switzerland), ECN (Holland), FZK (Germany). In Japan: PNC, JAERI. In Russia: Minatom, IPPE, IPC.

May they all be thanked.
TABLE 1

LONG LIVED NUCLIDE INVENTORY IN 2010, ACCORDING TO EDF’S PLAN (GLOBAL 1995)

FUELS:

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Quantity (mtHM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWR operation buffer (UOX)</td>
<td>8 500</td>
</tr>
<tr>
<td>PWR in storage (UOX)</td>
<td>3 440</td>
</tr>
<tr>
<td>PWR in storage (MOX)</td>
<td>1 900</td>
</tr>
</tbody>
</table>

WASTES:

<table>
<thead>
<tr>
<th>Waste Type</th>
<th>Quantity (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLASSES</td>
<td>2 800</td>
</tr>
<tr>
<td>Type B</td>
<td>70 000</td>
</tr>
</tbody>
</table>

ACTINIDES (metric tons)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Pu</th>
<th>Np</th>
<th>Am</th>
<th>Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>in glass and type B waste</td>
<td>0.15</td>
<td>7.6</td>
<td>7.1</td>
<td>0.9</td>
</tr>
<tr>
<td>in stored fuels and operation buffer</td>
<td>223 (1)</td>
<td>6.9</td>
<td>17</td>
<td>2.3</td>
</tr>
</tbody>
</table>

LONG LIVED FISSION PRODUCTS (metric tons)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>75Se</th>
<th>93Zr</th>
<th>99Tc</th>
<th>107Pd</th>
<th>126Sn</th>
<th>129I</th>
<th>135Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>in glass and type B waste</td>
<td>0.01</td>
<td>9.7</td>
<td>13.7</td>
<td>3.7</td>
<td>0.4</td>
<td>---</td>
<td>6.3(2)</td>
</tr>
<tr>
<td>in stored fuels and operation buffer</td>
<td>0.01</td>
<td>11</td>
<td>13.8</td>
<td>4.4</td>
<td>0.4</td>
<td>3</td>
<td>7.2</td>
</tr>
</tbody>
</table>

(1) Including 100 tons of Pu in MOX fuel assemblies

(2) 135Cs = 6.3 tons for Cs total = 44 tons
LES FLUX DANS LE CYCLE
DU COMBUSTIBLE NUCLEAIRE

Unat naturel (Unat) 8200 t 4 ans

Enrichissement (U.T.S.) 4700000 U.T.S. 2 ans

Unat appauvri pour le Mox 125 t

Fabrication 955 t 1 an

Transport vers La Hague 850 t 2 ans

Retraitement UP2 / 800 850 t

Transport entreposage C.I. 350 t

Entreposage N.I.E. 1200 m³ NON IMMEDIATEMENT EVACUABLE

Pu 8,5 t

Conversion URT 820 t

MOX Melox 135 t 9,5 ans

UTS - URT 530 000 U.T.S. 8,5 ans

URT appauvri 710 t

Fabrication URT 110 t 9,5 ans

Schéma 4
PROCESSING THE GASES

DISSOLUTION

FIGURE 1: BEHAVIOUR OF LONG-LIVED ELEMENTS IN THE PUREX PROCESS

Am, Cm
Np (<30%)
Cs, Zr (100%)

Tc (80 to 90%)
Np (>70%)

Glass
βγ 98 %
α 45 %
M.A. 100 %
Tc, Zr: 100 %

99.9 % U
99.9 % Pu

acqueous phase  solids
solvent  gas
### TABLE 2

**RESEARCH STATUS ON ACTINIDE AND F.P. PARTITIONING**

<table>
<thead>
<tr>
<th></th>
<th>Basic R &amp; D</th>
<th>Process Development</th>
<th>Process Industrialisation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>U/Pu partitioning</strong></td>
<td></td>
<td>X &gt; 99 %</td>
<td>X 95 %</td>
</tr>
<tr>
<td><strong>Np partitioning</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Am/Cm partitioning</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamex</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ac/Ln</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oxidised Am partitioning</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc partitioning</td>
<td>X insoluble fraction</td>
<td>X soluble fraction</td>
<td></td>
</tr>
<tr>
<td>I partitioning</td>
<td>X</td>
<td></td>
<td>X 95 %</td>
</tr>
<tr>
<td>Zr partitioning</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs partitioning</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd, Se, Sn partitioning</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*X*: Present status of research

Once the feasibility is demonstrated, performances will be excellent and 99 to 99.9% of the radionuclides should be separated.
SCENARIOS OF MULTIRECYCLING OF PLUTONIUM ALONE OR WITH MINOR ACTINIDES

PWR OPEN CYCLE

Pu REP/RMA RECYCLING

Pu FBR RECYCLING

Pu and FBR M.A. RECYCLING

DIAGRAM 2
### TABLE 3

**MULTIRECYCLING OF PLUTONIUM ONLY**  
**STEADY STATE CONDITIONS**  
60 GWe - 400 TWh

<table>
<thead>
<tr>
<th>Reactor</th>
<th>N4 MOX heterogeneous</th>
<th>N4 MOX homogeneous</th>
<th>RMA heterogeneous</th>
<th>RMA homogeneous</th>
<th>CAPRA</th>
<th>N4 UOX</th>
</tr>
</thead>
<tbody>
<tr>
<td>U, associated to Pu (%235U)</td>
<td>2.8%</td>
<td>3.8%</td>
<td>0.25%</td>
<td>3.8%</td>
<td>0.19%</td>
<td>2</td>
</tr>
<tr>
<td>Pu concentration (%)</td>
<td>9.6%</td>
<td>2%</td>
<td>18%</td>
<td>1.2%</td>
<td>54%</td>
<td>0</td>
</tr>
<tr>
<td>Cycle inventory in tons of Pu</td>
<td>400</td>
<td>200</td>
<td>390</td>
<td>112</td>
<td>310</td>
<td>35</td>
</tr>
<tr>
<td>Pu in wastes (kg/year)</td>
<td>28</td>
<td>16</td>
<td>31</td>
<td>10</td>
<td>37</td>
<td>11600</td>
</tr>
<tr>
<td>MA in wastes (kg/year)</td>
<td>3600</td>
<td>3250</td>
<td>3450</td>
<td>2500</td>
<td>2800</td>
<td>1520</td>
</tr>
</tbody>
</table>
TABLE 4

PHYSICAL FEASIBILITY OF RECYCLING MINOR ACTINIDES IN REACTOR

<table>
<thead>
<tr>
<th></th>
<th>Maximum concentration in M.A.</th>
<th>Transmutation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWR N₄ or RMA (47 GWJr⁻¹)</td>
<td>1 to 2 %</td>
<td>6 to 9 %</td>
</tr>
<tr>
<td>FBR (EFR type) (120 GWJr⁻¹)</td>
<td>5 %</td>
<td>18 to 27 %</td>
</tr>
</tbody>
</table>

Homogeneous recycling (minor actinide dispersed in a standard fuel).

Results: 3 to 15 kg/TWhe transformed depending upon reactor type and recycling conditions against 3 kg/TWhe produced in a PWR (UOX) at 33,000 MWdr⁻¹
TABLE 5

EXEMPLARY OF INVENTORY REDUCTION (Pu and M.A.)
IN WASTES (Pu and M.A. RECYCLING)

400 TWh/year

<table>
<thead>
<tr>
<th>PWR open cycle (UOX)</th>
<th>Steady state park with FBRs (CAPRA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Yearly uprisings:</td>
<td>• Yearly uprisings:</td>
</tr>
<tr>
<td>Pu 12 mt/year</td>
<td>Pu ~ 0</td>
</tr>
<tr>
<td>M.A. 1.3 mt/year</td>
<td>M.A. ~ 0</td>
</tr>
<tr>
<td>• Yearly amounts to waste:</td>
<td>• Yearly amounts to wastes:</td>
</tr>
<tr>
<td>Pu 12 mt/year</td>
<td>Pu ~ 0.1 mt/year</td>
</tr>
<tr>
<td>M.A. 1.3 mt/year</td>
<td>M.A. ~ 0.1 mt/year</td>
</tr>
<tr>
<td>• In-cycle inventory~In-reactor inventory</td>
<td>• In-cycle inventory ~ In-reactor and in-plant inventory</td>
</tr>
<tr>
<td>Pu 34.8 mt</td>
<td>Pu ~ 460 mt (170 tons in reactors)</td>
</tr>
<tr>
<td>M.A. 3.9 mt</td>
<td>M.A. ~ 120 mt (50 tons in reactors)</td>
</tr>
</tbody>
</table>

A STEADY STATE FBR PARK VERSUS A PWR OPEN CYCLE

<table>
<thead>
<tr>
<th>Inventory in wastes</th>
<th>Over 10 years</th>
<th>Over 100 years</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Total inventory (cycle and wastes)</td>
<td>X 3.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

75
<table>
<thead>
<tr>
<th></th>
<th>Basic R&amp;D</th>
<th>Process development</th>
<th>Process industrialisation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FUELS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂ or PuO₂ + Np + Am + Cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TARGETS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Am targets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cm targets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc targets</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X: Present status of research
FIGURE 2: Radiotoxic inventory of one ton of UOX1 fuel

The graph shows the radionuclide inventory over time, with the y-axis representing radiotoxic inventory in Sv (Sievert) and the x-axis representing time in years. The lines represent:

- Plutonium
- Minor actinides
- Fission products
FIGURE 3: Contribution of the various initial actinides to the radiotoxic inventory of wastes (UOX1 fuel case)
FIGURE 4: Contribution of the various initial actinides to the radiotoxic inventory of wastes
(MOX fuel case)
PARTITIONING AND TRANSMUTATION PROGRAM
"OMEGA" AT JAERI

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ABSTRACT

During the last two decades, JAERI has been carrying out the partitioning and transmutation program in the following areas: (a) development of the four-group partitioning process, (b) design study of the transmutation systems, one with actinide burner reactor, the other with an accelerator-driven subcritical reactor, (c) development of an intense proton accelerator, (d) development of nitride fuel manufacturing and pyrochemical reprocessing, and (e) basic research for supporting the development of transmutation systems. Activities and recent achievements are overviewed.

JAERI is about to launch the Neutron Science Project which aims at bringing scientific and technological innovation for the 21st century in the fields of basic science and nuclear technology using neutrons. The accelerator-driven transmutation system study and the development of an intense proton accelerator are also under way as important parts of this project.
I. INTRODUCTION

Since the mid 1970s, JAERI has been developing a partitioning process of high-level waste (HLW) and a concept of a dedicated transmutation system of minor actinides (MAs) as an effective and efficient measure to alleviate the long-term burden of nuclear energy which may arise from the management of HLW. During these studies, the double strata fuel-cycle concept was developed. JAERI's activities cover the following areas of the partitioning and transmutation: (a) development of the four-group partitioning process, (b) design study of the actinide burner reactor and the accelerator-driven hybrid system, (c) development of an intense proton accelerator, (d) development of nitride fuel cycle technologies, and (e) basic research for supporting the development of transmutation systems.\(^{(1)}\)

In the course of planning of an intense proton accelerator for transmutation, we recognized that neutron scattering researchers need intense neutron beams for basic science. JAERI is planning to launch the Neutron Science Project which aims at accomplishing the scientific and technological innovation using neutrons for the 21st century. An intense proton accelerator will be constructed for dual duty as a neutron producer for transmutation and for basic science including neutron scattering.

II. DOUBLE STRATA FUEL CYCLE

JAERI has been proposing the concept of the double strata fuel cycle consisting of the power reactor fuel cycle and the Partitioning-Transmutation (P-T) cycle.\(^{(2)}\) In this scenario, a reprocessing plant, a partitioning plant and a transmutation plant will be co-located in one site. This configuration of plants composes a high level radioactive waste (HLW) management park.

The concept of the double strata fuel cycle is illustrated in Fig. 1. The final HLW from this fuel cycle contains only short-lived fission products. The separate treatment or the isolation of MAs from the commercial cycle is preferable from two reasons: (a) complete recovering and transmutation of MAs and long-lived fission products are possible, and (b) MAs are strong neutron emitters, and, thus, MA recycling through the conventional fuel cycle may cause problems in the radiation shielding of the fuel cycle facilities. This may cause the cost of electricity generation to increase.\(^{(3)}\)

III. DEVELOPMENT OF FOUR-GROUP PARTITIONING PROCESS\(^{(4,5)}\)

Firstly, a partitioning process was developed for separating elements in HLW into three groups, namely, transuranium elements (TRU), Sr-Cs, and others. The process consists of three steps: (a) the solvent extraction of U and Pu with tributylphosphate (TBP), (b) the solvent extraction of Am and Cm with diisodecylphosphoric acid (DIDPA), and (c) the adsorption of Sr and Cs with inorganic ion exchangers. The process was demonstrated with actual HLW and more than 99.99% of the Am and Cm were extracted with DIDPA.

Later, a four-group partitioning process has been developed in which one step for separating the Tc-PGM group was developed in addition to the three-group separation. Effective methods for separating TRU (especially Np) and Tc have been developed.

(a) Np Separation

Neptunium, which is dominant in HLW, is the most difficult actinide element to be extracted with general organic solvents. A new process was developed in which more than 99.97% of penta-valent Np was extracted when hydrogen peroxide was fed to a level to compensate for its decomposition in the DIDPA extraction process.

(b) Am and Cm Separation from rare earths

Selective stripping of Am and Cm from DIDPA with the complex agent DTPA is being studied for their separation from rare earths (RE). Batch experiments showed that the separation factor between Am and RE (ratio of distribution ratios) is larger than 10. Experiments are now in progress to find the optimum process conditions.
Tc Separation

Two methods have been developed to separate Tc, precipitation by denitrating HLW and adsorption with active carbon. More than 95% of Tc in a simulated HLW was recovered as precipitate by denitration of HLW. An active carbon column was used for the quantitative adsorption of Tc from a 0.5 M nitric acid solution. Desorption of Tc from the column was achieved quantitatively by the use of an alkaline thiocyanate solution as eluant.

The four-group partitioning process was developed as shown in Fig. 2. This process is to be tested with actual HLW at NUCEF (Nuclear Fuel Cycle Safety Engineering Facility). Hot operation with actual HLW is scheduled in 1998.

IV. DESIGN STUDY OF THE TRANSMUTATION SYSTEMS

A transmutation system with a very hard neutron energy spectrum and high neutron flux would be very efficient and effective for MA transmutation. The concepts of MA burner reactors (ABR: Actinide Burner Reactor) and a proton accelerator-driven MA transmutation system have been developed at JAERI. When a dedicated transmutation system becomes available, the scheme of an entire fuel cycle will be a strata structure fuel cycle.

IV.1. MA BURNER REACTORS (ABR: ACTINIDE BURNER REACTOR)

Two types of ABRs are designed at JAERI. Fuel material of these ABRs is MA-U nitride mixture. One type is a lead-cooled pin fuel ABR (L-ABR) and the other is a He-cooled particle fuel ABR (P-ABR). Nitride was selected as the fuel material of these ABRs because of its good thermal property. The other advantage of nitride fuel is that it can be processed with the pyrochemical reprocessing, and, hence, the fuel cycle facilities can be very compact and cost effective. The fuel concept of P-ABR is shown in Fig. 3. The reactor core design parameters of these ABRs are given in Table 1. In these ABRs, neutron energy spectrum is very hard and the core-averaged neutron energy is around 720 keV. These hard neutron spectra are very effective for direct fission of MAs which has fission threshold above 600 keV. The MA burnup in the ABRs of 1 GW thermal output is 190 to 200 kg per year.

IV.2. ACCELERATOR-DRIVEN TRANSMUTATION SYSTEM

Two types of accelerator-driven system concepts are being studied; namely, a solid system a molten-salt system. Either system utilizes the hard neutron spectrum of spallation neutrons to transmute MAs efficiently by fission.

(a) Concept of solid target/core system

An accelerator injects proton beam through a beam window into the solid tungsten target located at the center of the target/blanket. Surrounding the target is the subcritical blanket loaded with actinide alloy fuel. Spallation neutrons emitted from the target induce fission in the actinide blanket region. The schematic diagram of the proposed transmutation system concept is shown in Fig. 4. With a 1.5 GeV, 39 mA proton beam, a sodium-cooled solid target/core having $k_{eff}$ of 0.89 produces 820 MW of thermal power. Assuming a load factor of 80%, MA burnup is approximately 250 kg/y, or 8% of inventory per year.

(b) Concept of molten-salt target/core system

The molten salt acts both as fuel and as target material, and also serves as coolant. Its main advantage is the capability of continuous on-line processing of MAs and reaction products. Chloride salt is chosen based on the consideration about actinide solubility and nuclear characteristics. The molten-salt target/core with $k_{eff}$ of 0.92 produces 800 MW thermal power with a 1.5 GeV, 25 mA proton beam. Assuming a load factor of 80%, the MA burnup is approximately 250 kg/y, or 4.6% of inventory per year.
The support factor, which is defined as the number of power reactor units whose MAs are transmuted by one unit of a transmutation system, is about 10 to 15 for dedicated transmutation systems, while the support factor of FBR proposed so far is between 4 to 6.

V. TRU NITRIDE FUEL AND FUEL CYCLE \(^{(10,11)}\)

In a double-strata concept, MAs from the commercial fuel cycle flow into the second-stratum of transmutation ("dedicated actinide-burner") cycle. MAs are concentrated and confined in the second stratum, exiting only after being converted to fission products. Considering the inherent difficulty in handling MAs, an innovative approach is required in designing a fuel cycle system for the actinide burning.

Concepts of dense fuel cycles for the second stratum (Fig. 5) have been proposed, where high atom densities of the actinides are maintained throughout the whole cycle, and the system volume and envelope are minimized. JAERI is studying the feasibility of employing the nitride fuel and pyrochemical reprocessing. The favorable thermal properties of the nitride fuels that make full utilization of a cold-fuel concept possible are: (a) lower fuel temperatures and hence lower fission gas release, (b) a thinner cladding to achieve a harder neutron spectrum, and (c) a relatively large Doppler effect in the over-power events.

Efforts are directed to technical developments and fundamental property studies of (a) the sol-gel process to obtain nitride microspheres from the actinide nitrate solution, and (b) the electrorefining process of the nitride fuel with a LiCl-KCl-AnCl\(_3\) (An: actinides) melt.

(a) Nitride fabrication from actinide salts

Actinide nitrate solution from the partitioning of HLW can be solidified to a ceramic form by an internal gelation method. A droplet of the actinide nitrate solution with a carbon suspension turns into a solid mixture of oxide (hydroxide) and carbon in a form of microspheres. A microwave gelation apparatus has been developed and tested at JAERI. The (oxide+carbon) microspheres thus obtained are converted to the nitride by a carbothermic synthesis.

The nitride fuels can be used in the form of either pellets or TiN-coated particles. In the particle-fuel concept, the TiN coating consists of both high-density and low-density layers.

(b) Electrorefining of nitrides

In the proposed pyrochemical process, the irradiated nitride fuels are electrorefined in a LiCl-KCl eutectic melt. Like metal fuels, the actinide nitrides would be anodically dissolved. The design of the electrorefiner may be very similar to that for the metal fuels. The recovered metals then have to be converted to nitrides.

Laboratory runs of the fused salt electrolysis of UN have been made. The recovery of uranium metal has been demonstrated. During the electrolysis, the system was purged with purified helium. Conversion of the metal to the nitride has been readily made in liquid Cd with nitrogen cover gas. The reaction products were \(\text{U}_2\text{N}_3\) and \((\text{U}, \text{Gd})\text{N}\).

VI. DEVELOPMENT OF A HIGH-INTENSITY PROTON ACCELERATOR \(^{(12)}\)

A high-intensity proton linear accelerator with a beam power up to about 10 MW has been proposed for basic science and various engineering tests of the transmutation system.

The R&D work has been carried out for the components of the front-end part of the proton accelerator: ion source, radio-frequency quadrupole (RFQ), drift tube linac (DTL), and RF source. In the beam test, a current of 70 mA with a duty factor of 10% has been accelerated from the RFQ at an energy of 2 MeV. A hot test model of the DTL for high-power and high-duty operation has been fabricated and tested.

For the high-energy portion above 100 MeV, superconducting accelerating cavity is studied as a main option. The superconducting linac is expected to have several favorable characteristics for high-intensity accelerator such as shorter length acceleration, large bore radius resulting in low beam losses, and cost effectiveness for construction and operation. The design work for superconducting cavities is in progress in collaboration with the KEK (National Laboratory for High Energy Physics). A test stand with the equipment of cryogenics system, vacuum system, RF system, and cavity processing and cleaning has been prepared to test the physics issues and
fabrication process.

The main accelerator components such as high-current hydrogen-ion source, RFQ, DTL, and RF power source have been constructed and tested. A high brightness (140 mA) hydrogen ion beam has been extracted.

The first 2 MeV beam test with the ion source and RFQ in combination of a single unit of high power RF source was successfully carried out with the peak acceleration current of 70 mA (a duty factor of 10%). (13)

VII. BASIC RESEARCH SUPPORTING THE DEVELOPMENT OF TRANSMUTATION SYSTEMS

To support the above-mentioned activities on transmutation system development, several basic research activities are in progress.

VII.1. NUCLEAR DATA FILE FOR TRANSMUTATION SYSTEM DESIGN STUDY (14)

Two types of nuclear data files are being compiled. The JENDL Actinide File is compiled for use in the ABR design study. It contains neutron-induced reaction data for about 90 nuclides from $^{231}$U to $^{252}$Fm. This compilation will be completed by 1997. The JENDL High-Energy File contains the data for protons and neutrons up to a few GeV which are used for the design of the accelerator and for studying an accelerator-driven transmutation system.

VII.2. MEASUREMENT AND EVALUATION OF ACTINIIDE NUCLEAR DATA

Actinide nuclear data are measured for fission-neutron yields, delayed-neutron yields, and fission yields in collaboration with the Oak Ridge National Laboratory (ORNL) and Texas A&M University. Actinide nuclear data in the JENDL File are evaluated using the integral experiments at the fast critical facility FCA. (13)

Spallation integral experiments have been carried out to obtain data on nuclide production, to estimate the yields of neutrons and spallation products, and to evaluate the validity of the simulation code system. The 500 MeV booster proton synchrotron facility at the National Laboratory for High Energy Physics (KEK) is used for the activation experiments. In general, the calculation with the codes agree fairly well with the experimental results. There are however some discrepancies in both the nuclide production cross section and the neutron energy spectrum. (9, 16)

VII.3. FUEL MATERIAL THERMODYNAMIC DATABASE (9, 11)

In view of the feasibility study of the above dense fuel cycles, thermodynamic data base needs to be expanded in three major areas: actinide alloys and intermetallics, nitrides, and actinide-containing molten salts. In JAERI, a pure substance and solution data base, related to the actinide burning, is being formed as a minor supplement to the existing thermodynamic data base.

VIII. NEUTRON SCIENCE PROJECT OF JAERI

Neutron scattering has achieved some notable successes in recent years, such as unraveling the crystal structures of high-temperature superconductors, and is now exciting a lot of interest among biologists for probing large organic molecules. A limiting factor for neutron scattering is the intensity of the neutron beams. High intensities of neutron beams allow researchers to carry out experiments that would otherwise be impossible. In Europe, the European Spallation Source ESS is under design, and in the USA, the National Spallation Neutron Source (NSNS) will be constructed at ORNL, both with 5 MW proton beam power.

JAERI is preparing to launch the neutron science project next year. The objective of the project is to construct an intense proton accelerator with proton energy of 1.5 GeV, proton beam power of 6 to 8 MW, and research facilities to be dedicated for the neutron science research center of JAERI Tokai. The spallation neutron source has double duty as a neutron source for basic science and as a neutron source for nuclear-energy-related research such as an accelerator-driven transmutation study.
Basic science in this center covers the fields of structural biology for investigating the structure and function of biological molecules such as DNA, advanced material science (e.g., under extreme conditions), high-energy neutron science (e.g., spallation phenomena), nuclear cross-section measurements for transmutation study, heavy-ion science for creating unstable heavy nuclei through spallation, and decay property measurements of extremely-neutron-rich nuclei.

The layout of the proposed facilities and the proposed schedule for construction of facilities are shown in Figs. 6 and 7.

Transmutation study at this facility will cover the two steps of accelerator-driven transmutation system development. The first step will be the feasibility study of the hybrid system concept at low power level of uranium subcritical system. These experiments will check the stable operation of a hybrid system and MA burnup with use of MA foils or pellets for activation measurements or destructive analysis. The data base for designing a spallation target for high-power experiments will be obtained at the second step. In the first step, most of the transmutation experiments will be performed with pulse-mode operation so that proton beams from the accelerator can be shared in time among the other experiments.

Once the feasibility of the hybrid system concept for the MA transmutation is proven, a test reactor facility with 10-30 MW thermal power will be proposed for the second phase of development. Operation of the hybrid system with uranium subcritical system will be tested at this high power level and transmutation capability will be tested using MA target pins. Technical feasibility of spallation target and beam window will be also tested in the second-step experiments.

REFERENCES

(12) M. Mizumoto et al.: "Development of a High Intensity Proton Accelerator", Proc. 2nd


Fig. 1 JAERI's Concept of Double Strata Fuel Cycle for Complete HLW Management
Fig. 2 Flow Sheet of Four Group Partitioning Process

Fig. 3 Fuel element and coated fuel particle for He gas cooled reactor
Fig. 4  Conceptual Layout of Intense Proton Accelerator with Superconductive Cavity
Fig. 5  Double Strata Fuel Cycle with Nitride/Pyrochemical Process
Fig. 6 Layout of proposed Facilities for Neutron Science
Fig. 7 Proposed Schedule for Construction of Neutron Science Research Facilities

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September 11, 1996
PARTITIONING AND TRANSMUTATION OF NUCLEAR WASTE: THE DUTCH RAS PROGRAMME AND ITS RELATION TO INTERNATIONAL STUDIES

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ABSTRACT

In the present paper a review of the Dutch RAS programme is presented. The objectives and achievements of the programme are described. Special attention is given to a recent assessment of the international status of P&T that has been made for the Dutch authorities. The major conclusion of this assessment is that P&T is an important instrument in the management of nuclear waste to achieve the technical limits (ALARA) with respect to radiotoxicity of the waste inventory as well as radiological effects of the disposal. The technology for P&T is, however, only partially available at present and recommendations for the directions of the RAS programme are given.

1. INTRODUCTION

Spent fuel elements from nuclear power plants contain many radioactive elements (actinides, fission products) which are a possible thread to mankind if released to the biosphere. Disposal in geological repositories is considered to be the final destination of spent fuel or the waste produced by reprocessing of the fuel elements, but is, however, not considered safe by a significant fraction of the population in many countries. This could be overcome if the actinides can be removed efficiently from the spent fuel and the radiotoxicity of the waste can be reduced to that of the uranium ore it was produced from, in a reasonable period of time (e.g. 250 years). Reprocessing, partitioning, recycling and transmutation are techniques to achieve this goal.

In 1991 the Netherlands Energy Research Foundation ECN started a research programme on recycling and transmutation of long-lived nuclides that are present in the spent fuel from nuclear power generation. This programme, which is known under the Dutch acronym RAS, is concentrated on the following five topics:

1. reactor physics and scenario studies,
2. chemical and material studies of fuels and targets,
3. irradiations in the High Flux Reactor at Petten,
4. radiological effects and risks,
5. non-proliferation.

In the present paper a short description of the objectives and achievements of the RAS programme is given, followed by the present views on the state-of-the-art of partitioning and transmutation of actinides and fission products. Strategies and (innovative) fuel cycle technology required for the recycling of plutonium, minor actinides and fission products are discussed and their possibilities and limits are identified. Also the potential of future options with low actinide production (thorium cycle, accelerators) is considered. An extended report on this work is given in Ref. [1].

2. OBJECTIVES AND ACHIEVEMENTS OF THE RAS PROJECT

In the Dutch RAS programme the ALARA principle is applied to the radiotoxicity of the waste as well as to the risk of disposal to the benefit of future generations. As a consequence, the investigations in the field of P&T are focused on:

1. the actinides, in particular Pu and Am, which dominate the medium- and long-term radiotoxicity of HLW,
2. long-lived mobile components (in particular Np, Tc, I, Cs), which dominate the long-term radiological effects of disposal.
However, the justification of the work is not based on scientific arguments since the risks of geologically stored waste to future generations are estimated to be very low. The RAS programme should rather demonstrate the maximum possible measures that are necessary to relieve public concern.

In the first phase of the RAS programme considerable attention was given to the transmutation of the fission products technetium and iodine. In the frame of the EFTTRA cooperation [2], an irradiation experiment (EFTTRA-T1) was performed in the HFR to study the behaviour of several target materials [3-5]. In parallel, scenario studies for the transmutation of these fission products in various reactor types have been made [6,7]. The overall conclusion of the work is that transmutation of technetium is technically possible although the irradiation times in most reactor types are (very) long and the technetium inventories are high. The transmutation of iodine in existing fission reactors does not look feasible (see below).

Currently, the RAS programme is focused on the transmutation of actinides. Different recycling modes for plutonium and americium are being studied by calculational methods and experiments, including MOX fuel in current LWRs and TRU fuels in future reactors. Again, the efforts within the EFTTRA programme are an essential part of this work: three irradiation experiments are planned in the HFR (Table 1) to study the irradiation behaviour of various ceramic materials that can be used as inert matrix in non-fertile fuels or targets [8]. In addition, laboratory experiments are performed to characterize a number of inert-matrix materials and to determine their physico-chemical properties. Various scenarios for the transmutation of plutonium and americium have been analysed [9-11]. An overall conclusion is not yet available but the preliminary results show that recycling of Pu is possible, whereas recycling of Am is only feasible if the technological problems with respect to reprocessing and fuel fabrication can be solved, as will be discussed below.

The use of the thorium cycle in fission reactors as a means to minimize the production of actinides has also been investigated. The state-of-the-art of the technology of thorium-based fuel has been reviewed [12] with respect to reactor physics, chemical and material aspects and actinide waste. In this study it was concluded that a substantial reduction of actinide radiotoxicity can be achieved by using thorium-based fuels if efficient partitioning and multiple recycling of uranium and thorium can be realized. Finally, a limited effort is devoted to the study of accelerator-based transmutation, including contributions to nuclear data for these systems [13].

In 1996, an assessment of the international status of P&T has been made for the Dutch authorities in order to define the next phase of the RAS programme [1]. The report has been reviewed by a national committee of experts from government, science and industry. In the following three sections, the views expressed in this report are summarized.

Table 1. Irradiation programme in the HFR at Petten.

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<td>transmutation of the fission products technetium (~6% burn-up) and iodine</td>
<td>1994</td>
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<td>EFTTRA-T2</td>
<td>• re-irradiation of technetium (&gt; 20% burn-up)</td>
<td>1996-1998</td>
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<td>• irradiation of ceramic materials for the development of fuels for actinide burning (inert matrices)</td>
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3. STATUS OF PARTITIONING AND TRANSMUTATION

3.1 Plutonium and Uranium

Separation of plutonium (Pu) and uranium (U) from spent fuel will lead to a decrease of the radiotoxicity of the remaining waste by a factor 10. Using current PUREX technology, Pu and U can be separated from spent fuel with high efficiency (99.5-99.88%). From the point of view of P&T, further improvement of the separation efficiency is only useful if also the minor actinides, in particular americium, are removed from the high level waste.

Pu and U can be recycled in thermal reactors in the form of mixed oxide (MOX) fuel. In case of 30% MOX loading, as is current practice, Pu recycling in LWRs will slow down the growth of plutonium stocks. Higher MOX loadings (up to 100%) will lead to net Pu consumption in future reactor designs. The effect of Pu recycling in LWRs on the radiotoxicity is, however, limited due to build-up of non-fissile Pu isotopes. Ultimately, the use of reactors/devices with fast neutron spectra is inevitable to reach substantial reduction of the plutonium radiotoxicity. The technology for the design of devices and fuels with maximum incineration rates needs to be developed.

3.2 Minor Actinides

Partitioning and transmutation of minor actinides, and especially americium, is necessary because a reduction of the radiotoxicity greater than 10 is wanted. If separation is realised with a 99-99.9% efficiency, a reduction of the radiotoxicity by a factor greater than 100 is within reach, provided that recycling is performed efficient as well. However, at present partitioning of the minor actinides americium and curium from PUREX waste solutions is not yet possible at an industrial scale. In several countries liquid-liquid extraction processes have been developed (Table 2) but in all cases the lanthanides, an important group of fission products, are co-extracted as a result of their chemical similarity to the trivalent actinides. New techniques to separate the trivalent actinides and lanthanides as well as the actinides mutually are required. The use of macrocyclic extraction molecules in Supported Liquid Membranes (SLM) is a promising development in this field and is studied in several European laboratories, among which ECN.

Transmutation of the minor actinides can be done efficiently in a fast-neutron flux but also the benefits of a "once-through" incineration in a thermal flux have to be evaluated. Neptunium can be recycled in MINOX fuels, americium in special targets containing an inert matrix. In practice, recycling of curium does not seem feasible at the moment because of the α-, γ- and neutron doses due to decay and spontaneous fission which extremely complicate the fabrication curium fuels and targets.

When transmutation of the minor actinides is introduced in the fuel cycle, existing non-proliferation measures have to be extended to cover P&T. Most of the problems to the minor actinides are similar to those of reprocessing and MOX fabrication plants which have been proven to be adequately safeguardable. However,

<table>
<thead>
<tr>
<th>process name</th>
<th>country</th>
<th>extraction molecule</th>
<th>HNO₃ concentration</th>
<th>typical results</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIAMEX</td>
<td>France</td>
<td>diamides</td>
<td>0.5 - 5 M</td>
<td>Am+Cm &gt; 95%</td>
</tr>
<tr>
<td>DIDPA</td>
<td>Japan</td>
<td>DIDPA/TBP</td>
<td>0.5 M</td>
<td>Am+Cm &gt; 99.9%</td>
</tr>
<tr>
<td>TRPO</td>
<td>China</td>
<td>TRPO</td>
<td>0.1 - 1 M</td>
<td>Am+Cm &gt; 95%</td>
</tr>
<tr>
<td>TRUEX</td>
<td>USA</td>
<td>CMPO/TBP</td>
<td>0.1 - 3 M</td>
<td>Am+Cm &gt; 99.9%</td>
</tr>
</tbody>
</table>
specific P&T issues need to be addressed, such as the potential of misuse of minor actinides and the new facilities. Until today the civil fuel cycle has shown to be a rather difficult route for proliferation and it is of utmost importance to maintain this characteristic also for new installations and fuel cycles.

3.3 Fission Products

Partitioning and transmutation of long-lived fission products is only relevant from the point of view of reduction of radiological effects. In this respect, the following three fission products need to be considered: cesium (\(^{133}\text{Cs}\)), iodine (\(^{131}\text{I}\)) and technetium (\(^{99}\text{Tc}\)). The technology to separate these elements from HLLW is available on a laboratory scale, but has not been implemented in the PUREX process. Technetium and iodine can be transmuted by single neutron capture, but the transmutation half-lives and inventories in most reactor types are high. In addition, transmutation of these fission products requires additional enrichment. Transmutation of cesium is not feasible because of the low neutron absorption cross section of \(^{135}\text{Cs}\) and parasitic absorptions in \(^{137}\text{Cs}\) and \(^{133}\text{Cs}\) which are present in the fuel in about equal quantities as \(^{133}\text{Cs}\).

3.4 Survey of transmutation devices

Recycling of plutonium is possible in existing LWRs with respect to reduction of masses. However, as multiple recycling of Pu in LWRs is limited and transmutation of minor actinides in existing thermal reactors is not effective, a significant radiotoxicity reduction is only obtained in follow-up transmutation in dedicated burners. These burners should have low Pu production, a high specific power and for minor actinide incineration, a fast neutron spectrum. Nearby technology indicates CANDU and CAPRA burner types as interesting candidates; future developments hint in the direction of accelerator-based systems. Also fission-product transmutation can best be achieved in dedicated thermal burners or in moderated subassemblies of fast reactors since transmutation half-lives and inventories in LWRs are very high. The potential of existing, near-by and future reactor technology is summarized in Table 3.

Table 3. Review of the recycling capabilities of various transmutation devices; MA denotes minor actinides, FP fission products.

<table>
<thead>
<tr>
<th>device</th>
<th>Pu</th>
<th>MA</th>
<th>FP</th>
</tr>
</thead>
<tbody>
<tr>
<td>LWR</td>
<td>limited(^a)</td>
<td>poor</td>
<td>no</td>
</tr>
<tr>
<td>HWR</td>
<td>moderate(^ab)</td>
<td>poor</td>
<td>moderate</td>
</tr>
<tr>
<td>HTR</td>
<td>limited(^c)</td>
<td>poor</td>
<td>no</td>
</tr>
<tr>
<td>ALMR</td>
<td>good</td>
<td>good</td>
<td>no</td>
</tr>
<tr>
<td>CAPRA</td>
<td>excellent</td>
<td>good</td>
<td>reasonable(^d)</td>
</tr>
<tr>
<td>Pb-cooled burner</td>
<td>excellent</td>
<td>good</td>
<td>reasonable(^d)</td>
</tr>
<tr>
<td>molten salt reactor</td>
<td>good?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>accelerator-driven thermal burner</td>
<td>good?</td>
<td>?</td>
<td>good</td>
</tr>
<tr>
<td>accelerator-driven fast burner</td>
<td>excellent</td>
<td>good</td>
<td>?</td>
</tr>
</tbody>
</table>

\(^a\) Multirecycling of MOX is limited due to production of even-mass Pu and other actinides.
\(^b\) 100% Pu in an inert matrix.
\(^c\) Reprocessing is difficult.
\(^d\) In a moderated subassembly.
4. OPTIONS WITH LOW ACTINIDE PRODUCTION

4.1 Radiological clean energy production?

The use of pure fissile material, in particular fissile U isotopes, gives lowest long-lived radiotoxic actinide production. This requires fissile material from either (high) enrichment or breeding. Use of uranium, highly enriched in $^{235}\text{U}$ (HEU), is not recommended from the point of view of non-proliferation. The alternative is the use of $^{232}\text{U}$ produced in the thorium cycle, which is more proliferation resistant, due to hard $\gamma$-rays from co-generated $^{232}\text{U}$. At present, extension of burnup of LWR fuel is a good measure to limit the actinide production per unit of generated electricity in the current open U/Pu cycle.

4.2 Thorium cycle in reactors

The effective use of thorium in an open cycle requires fissile topping material and a high burnup. The radiotoxicity of waste is lowest if $^{233}\text{U}$ or $^{235}\text{U}$ (HEU) is used as topping material. Further reduction of the radiotoxicity is obtained in a closed cycle using thermal reactors and $^{233}\text{U}$ or $^{235}\text{U}$ (HEU) as topping material and recycling of uranium. The best result should be obtained in a fast reactor with recycling of all actinides and without topping material. The main obstacle for introduction of the closed cycle is that reprocessing and fuel fabrication have to be introduced on an industrial scale, including adequate safeguards. A good introduction to the thorium cycle could be to burn Pu in a thorium oxide fuel matrix.

4.3 Accelerator-based energy production

Accelerator-based systems have probably some safety advantages and produce excess neutrons. These two aspects give flexibility to design future systems for safe, clean and acceptable nuclear energy production and/or waste transmutation. The accelerator offers the possibility for applying a closed thorium cycle, due to excess neutrons (when coupled to thermal reactors) or additional safety (when coupled to fast reactors). The Fast Energy Amplifier is one of the examples with high potential. Other advanced features are related to waste transmutation of difficult long-lived components, like minor actinides and long-lived fission products and the possibility of incinerating the radioactive inventory at the end of a nuclear era.

5. CONSEQUENCES FOR DISPOSAL

The radiological effects of disposal of waste in a (geological) repository are not only determined by the radiotoxicity but also by the performance of the natural and engineered barriers of the disposal concept. The safety-relevant radionuclides that are identified 'normal evolution' release scenarios used in performance assessments, are the fission products $^{133}\text{Cs}$, $^{129}\text{I}$, $^{79}\text{Se}$, $^{99}\text{Tc}$ and the actinide $^{237}\text{Np}$ and its decay products. However, the calculated maximum exposures in 'altered evolution' scenarios are far below the natural background. For human intrusion scenarios the maximum exposure is more significant and in these scenarios the actinides $^{241}\text{Am}$, $^{243}\text{Am}$ and $^{240}\text{Pu}$ predominate the radiological effects.

Table 4. Some results of performance assessments for disposal of vitrified HLW in a salt formation in the Netherlands.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Maximum exposure</th>
<th>Dominant radionuclides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>magnitude (Sv/y)</td>
<td>time (y)</td>
</tr>
<tr>
<td>Normal evolution</td>
<td>$10^{-7}$</td>
<td>$10^{6}$</td>
</tr>
<tr>
<td>Ground water intrusion</td>
<td>$10^{-4}$</td>
<td>$10^{6}$</td>
</tr>
<tr>
<td>Human intrusion</td>
<td>$10^{-4}$</td>
<td>500</td>
</tr>
</tbody>
</table>

$^{237}\text{Np}$, $^{233}\text{U}$, $^{133}\text{Cs}$
$^{133}\text{Cs}$, $^{79}\text{Se}$, $^{226}\text{Ra}$
$^{241}\text{Am}$, $^{243}\text{Am}$, $^{240}\text{Pu}$
It should be realised that the separation of the actinides alone, as a result of which the radiotoxicity of the waste is reduced below the level of natural uranium ore after 250 years, does not imply that disposal in a (geological) repository is no longer needed. But if such waste is disposed in a carefully selected geological formation, the risk can be as low as that of natural uranium ore in its geological situation.

6 CONCLUSIONS

Partitioning and transmutation of actinides are important elements in the management of the waste from nuclear power generation. They are means to achieve the limits (ALARA) with respect the radiotoxicity of the inventory of disposal sites as well as the radiological effects of human intrusions of disposal sites in the future. The technology required for the implementation of P&T of actinides in the fuel cycle is only partially available at present and much research is still needed. In the coming years the efforts of the RAS programma should be concentrated on:

- Improved partitioning methods for trivalent actinides.
- Transmutation of actinides using non-fertile fuels.
- Scenario studies using 100 % MOX, HWRs and fast burners.
- Innovative systems for future "clean" energy production and transmutation using the thorium cycle and/or accelerators.

To reduce the (small) effects of exposure of radionuclides due to normal evolution, transmutation of long-lived fission products should also be realised. However, on the basis of the present technology this does not seem feasible and partitioning and immobilisation might be a more realistic way of achieving this. Study of this topic is recommended.

ACKNOWLEDGEMENT

Dr. J.L. Kloosterman is acknowledged for his critical comments and his willingness to present this paper at the meeting.

REFERENCES

This meeting.


TRANSMUTATION OF TRANSURANICS: NEUTRONICS, ACTINIDES BALANCE,
SAFETY AND FUEL PROVISION ASPECTS

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Abstract

A review is given of the selected works on the subject in Russia with the emphasis on the latest results published or presented after GLOBAL95 Conference. The main attention is concentrated on following problems: evolution of the actinides isotopic mixtures during multiple recycling in thermal and fast neutron systems operating separately or in combinations; compatibility of the transmutation with the breeding of secondary fuel; influence of plutonium composition, including weapon-grade, on the recycling process; nuclear safety related problems of actinides recycling; nuclear data for transmutation; criteria of assessment of radiological and environmental consequences of actinides transmutation; excess neutrons available for transmutation in accelerator-driven facilities; activation of neutron producing accelerator targets.
Introduction

During last three years some new attitudes toward nuclear fuel cycle were developing fast as the new series of GLOBAL-93 and GLOBAL-95 [1,2] conferences clearly demonstrated. These new trends included: increased attention to transmutation of minor actinides and possibly of some fission products; fast disposition of the excess separated plutonium, especially weapon grade; extensive analyses of the transmutation and plutonium utilization potential of accelerator-driven facilities. These problems are closely interconnected and in Russia the interest in P&T research is mainly stimulated by the importance of plutonium problem.

In 1995 the IAEA has undertaken efforts to produce Status Report on Transmutation in Non-OECD Countries as an IAEA Technical Document. The text was compiled, corrected and approved last September and now is about to be published. It contains rather comprehensive general review of the progress in P&T covering the activity of about dozen largest Russian institutions during last few years. So present paper is focused on the results obtained quite recently and best known to the author which means mainly A.I.Leipunskiy IPPE publications. At first short general review is given and then a few points are outlined in more details.

The strategy of P&T research in Russia is determined by following considerations. Due to obvious slowing down of the development of nuclear power industry the balance of research efforts between evolutionary and innovative approaches shifted to the latter. In the domain of basically evolutionary designs, which means critical fission reactors with solid fuel and liquid coolant, an ideal facility included in closed fuel cycle with multiple recycling, aimed at as complete utilization of natural resources as possible, should have:

- all principal reactivity coefficients of proper signs and values;
- fuel burn-up not less than 100 GW days/thm;
- breeding ratio not less than 1.3;
- ability to burn, in equilibrium regime, all Np and Am of its own and, if needed, some quantity of MA from outside;
- proliferation resistant fuel cycle;
- transparent ability to withstand design basis accidents without catastrophic consequences;
- good economy.

If these requirements are conflicting or some of them just may not be realized then we should look into a broader domain of designs.

1. General review

Transmutation related research at IPPE connected with the topic of present paper consists of following interacting sectors:

- analysis of the status and prospects of closed fuel cycles technologies aimed at transmutation of minor actinides and probably selected fission products;
- extensive calculations of the properties and parameters of the plutonium fueled fast reactor cores used as actinide burners;
- experiments on critical facilities, imitating the cores of large fast reactors, coordinated with the calculations and analysis programs and used to verify both input data and calculation methods.
- measurements and evaluation of basic microscopic nuclear data;
- designing, related experiments and calculations on the neutron producing accelerator targets of accelerator-driven transmutation facilities.

Present paper deals mainly with the reactor side of the transmutation problem because in ADTT research in Russia the Institute of Theoretical and Experimental Physics (Moscow) is main driving and coordinating force as demonstrated by the latest ADTT Conference in Kalmar [3]. But some important work is done in IPPE also and those results are discussed briefly.

1.1 Closed nuclear fuel cycle as the way of developing long term sustainable nuclear power industry.

Mining of uranium does not satisfy present demand and situation will get worse in coming 15 years with fuel fabrication relying significantly on the stored uranium reserves. Spent fuel reprocessing rate is only a fraction of the discharge rate and does not prevent piling up of large masses of SNF consisting of almost untouched natural uranium with uncertain future. So a time will come, most probably in the second half of the next century, when nuclear power industry will face following situation in raw materials: millions of tons of depleted uranium and a limited quantity of assorted plutonium and minor actinides, mostly in the spent fuel
form. Let's call the time "Day X". Sustainable level of nuclear power after the Day X, P(t>X), depends on the quantity Mpu(X) and quality of plutonium available determined by the global scenario of plutonium utilization which is combination of national scenarios, formed today and varying drastically. Mpu(X)=0 means P(t>X)=0 i.e. the end of the nuclear power industry based on critical fission reactors because no system critical on depleted uranium only is possible. We made an attempt to estimate X and P(X) for Russian national nuclear power industry and to investigate the sensitivity of these values to some features and parameters of the selected scheme of the nuclear fuel cycle within different concrete scenarios [4]. Basic assumptions are:

- thermal and fast reactors are used in varying proportion;
- regenerated uranium is recycled both in thermal and fast reactors;
- plutonium is recycled in MOX fuel of fast reactors;
- the possibility of utilization of excess weapon-grade plutonium is considered.

The results indicate that:
- in the model adopted X is close to 2080;
- P(X) is considerably lower than the maximum value of mainly uranium nuclear power capacity reached earlier;
- weapon-grade plutonium is essential; if added to reactor-grade plutonium as 20 per cent admixture and used in fast reactors with breeding ratio 1.3 it may add up to 30 per cent to P(X);
- BR=1.3 increases P(X) by some 70 per cent as compared to the case with BR=1.0.

Delay of the introduction of fast breeders into national nuclear power industry obviously decreases P(X) considerably. From the point of view of nuclear power industry development in the next century there is no plutonium surplus in Russia. The same well may be true in global scale if present trend to develop primarily net plutonium burners prevails (warnings of this kind may be found elsewhere, see, for example, [5]). The best way to deal with weapon-grade plutonium is to convert it to "spent fuel standard" in fast breeders with as good breeding ratio as possible and keep the spent nuclear fuel for later recycling, thus solving non-proliferation problem and using plutonium's energy producing potential.

Pu recycling and breeding may be combined with MA burning neutronically but safety should be studied further; already nearest generation of new reactors with life-time expectancy of at least 50 years should be designed flexible to meet the requirements of steadily growing plutonium breeding when necessary. Recycling of U in thermal reactors increases total electricity production during the considered period by 14 per cent, recycling of Pu in thermal reactors - by further 4 per cent only. Introduction of fast reactors with BR=1.0 brings 21 per cent increase which rises to 43 per cent at BR=1.3.

1.2 Recycling of plutonium and minor actinides: nuclear safety related consequences.

Plutonium and minor actinides may be recycled in both thermal and fast reactors. The efficiencies of these two options depend not only on the physics and technology of corresponding systems but on many varying and not always predictable external conditions like availability of competing energy sources, natural uranium prices, public acceptance, general national energy policies etc. But there is a set of much more definite safety related problems which should be considered first:

Core neutronics: worsening of Doppler and void reactivity effects, control rod worth, delayed neutrons parameters.

Power density distribution: sharper non-uniformities starting at the pellet level; strong and non-monotonous time-dependence, possible complications of loading and reloading schemes.

Accidents development: higher recriticality dangers in a case of melt down with high Pu content; worse kinetic parameters with resulting increase of the energy release during an excursion.

Proliferation issues: separated plutonium of practically any composition is most proliferation sensitive substance unlike plutonium in spent fuel.

All these aspects are closely investigated and some of the latest results are to be presented in a few papers at PHYSOR-96 Conference, September 16-20, 1996, Mito, Japan, [6-8].

Experience with liquid metal coolants in IPPE is not restricted by sodium cooled fast reactors but includes the reactors cooled by liquid heavy metal, lead-bismuth eutectics first of all. This concept is revisited nowadays in connection with the possibility to use fast reactors cooled by heavy metals for Pu utilization and MA transmutation (see, for example [9-10]).
1.3. Experiments on BFS facilities.

Actinide integral measurements were carried out on BFS similar to those on a set of FCA-9 assemblies to test the fission and capture cross sections of minor actinides (MA) described in [11]. The integral data measured are:
- the central fission rate ratio (FRR);
- the central sample worthies (CSR).

The core of BFS-67 assembly was composed with 96% enriched metal plutonium, depleted uranium dioxide, sodium and stainless steel. This composition was similar to the SUPERPHENIX core. About half of uranium dioxide in this composition was replaced with sodium for constructing of BFS-69 assembly core.

For both BFS assemblies the spectra were similar to the spectrum averaged over FCA assemblies. The integral data measured are:
- FRR of Np-237 and Pu-239 relative to fission in U-235;
- CSW of Np-237, Pu-239 and U-235.

All samples sizes were less than in FCA experiments. The Np and Pu samples were of three different size. The exact description of the assemblies, experimental devices and obtained results of measurements were given in [12]. Some of the results provided by the authors are given in Tables 1-4.

The starting point of neutron data testing is homogeneous calculation of FRR and first order perturbation theory using ABBN approach [13]. Evaluation of experiments means taking into account the heterogeneous structure of core cells, finite sizes of samples and group constant correction at calculation of CSW.

Heterogeneous structure of critical assembly's cell is taken into account by using the integral-transport approximation. Undisturbed group fluxes and adjoint fluxes are obtained from solutions of corresponding integral-transport equations in the cell approximation. Criticality is attained by modification of a neutron leakage. Perturbation of collision probabilities are taking into account too by calculation results using perturbation theory (first type of correction). Consideration of a detailed energy structure of adjoint solution gives the additional contribution into the reactivity worth ratio (second type of correction). Taking into account the finite size of samples have consisted the third type of correction.

The results of measurements and evaluation are presented in Tables 1 and 3 for CSW ratios of Pu-239/U-235, in Table 2 for CSW ratios of Np-237/Pu-239 and in Table 4 for CSW ratios of Np-237/U-235.

**Table 1. CSW ratio U-235 / Pu - 239**

<table>
<thead>
<tr>
<th>Assemb. FCA</th>
<th>EXP. Correction of 1 and 2 types</th>
<th>Correction of 3 type for Pu</th>
<th>3 Correction of 3 type for U</th>
<th>EXP. evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-1</td>
<td>1.476</td>
<td>-0.023</td>
<td>-0.146</td>
<td>+1.109</td>
</tr>
<tr>
<td>9-2</td>
<td>1.617</td>
<td>-0.100</td>
<td>-0.127</td>
<td>+1.124</td>
</tr>
<tr>
<td>9-3</td>
<td>1.713</td>
<td>-0.009</td>
<td>-0.008</td>
<td>+0.016</td>
</tr>
<tr>
<td>9-4</td>
<td>1.708</td>
<td>-0.006</td>
<td>-0.079</td>
<td>+0.089</td>
</tr>
<tr>
<td>9-5</td>
<td>1.750</td>
<td>0</td>
<td>-0.075</td>
<td>+0.081</td>
</tr>
<tr>
<td>9-7</td>
<td>1.745</td>
<td>-0.002</td>
<td>-0.065</td>
<td>+0.060</td>
</tr>
</tbody>
</table>

**Table 2. CSW ratio Np-237 / Pu - 239**

<table>
<thead>
<tr>
<th>Assemb. FCA</th>
<th>EXP. Correction of 1 and 2 types</th>
<th>Correction of 3 type for Pu</th>
<th>3 Correction of 3 type for U</th>
<th>EXP. evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-1</td>
<td>-0.865</td>
<td>+0.179</td>
<td>-0.220</td>
<td>-0.073</td>
</tr>
<tr>
<td>9-2</td>
<td>-2.42</td>
<td>+0.072</td>
<td>-0.042</td>
<td>-0.013</td>
</tr>
<tr>
<td>9-3</td>
<td>-0.014</td>
<td>+0.021</td>
<td>-0.014</td>
<td>+0.005</td>
</tr>
<tr>
<td>9-4</td>
<td>+0.054</td>
<td>+0.006</td>
<td>-0.005</td>
<td>+0.006</td>
</tr>
<tr>
<td>9-5</td>
<td>+1.58</td>
<td>+0.002</td>
<td>-0.004</td>
<td>+0.010</td>
</tr>
<tr>
<td>9-7</td>
<td>+1.17</td>
<td>+0.001</td>
<td>-0.003</td>
<td>+0.007</td>
</tr>
</tbody>
</table>
Table 3. CSW ratio Pu - 239/U - 235

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Type of sample</th>
<th>EXP VIRGIN</th>
<th>ZERO SIZE of samples</th>
<th>correction of 1 and 2 types</th>
<th>EXP evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS 67</td>
<td>Pu - A</td>
<td>1.350 ± .020</td>
<td>1.327 ± .021</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pu - B</td>
<td>1.406 ± .008</td>
<td>1.365 ± .009</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pu - C</td>
<td>1.404 ± .005</td>
<td>1.352 ± .007</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>averaged value</td>
<td></td>
<td>1.353 ± .019</td>
<td>+.011</td>
<td>1.364 ± .019</td>
</tr>
<tr>
<td>BFS 69</td>
<td>Pu - A</td>
<td>1.591 ± .018</td>
<td>1.560 ± .020</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pu - B</td>
<td>1.607 ± .007</td>
<td>1.552 ± .008</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pu - C</td>
<td>1.592 ± .004</td>
<td>1.528 ± .006</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>averaged value</td>
<td></td>
<td>1.541 ± .019</td>
<td>-.002</td>
<td>1.539 ± .019</td>
</tr>
</tbody>
</table>

Table 4. CSW ratio Np-237 / U-235

<table>
<thead>
<tr>
<th>Assembly</th>
<th>VIRGIN EXP</th>
<th>ZERO SIZE of samples</th>
<th>correction of 1 and 2 types</th>
<th>evaluated experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>67-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np - A</td>
<td>-.240 ± .011</td>
<td>-.250 ± .011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np - B</td>
<td>-.228 ± .006</td>
<td>-.240 ± .008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np - C</td>
<td>-.228 ± .005</td>
<td>-.245 ± .007</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>averaged value</td>
<td>-.245 ± .010</td>
<td>+.023</td>
<td>-.222 ± .011</td>
</tr>
<tr>
<td>69-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np - A</td>
<td>-.120 ± .010</td>
<td>-.128 ± .010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np - B</td>
<td>-.119 ± .006</td>
<td>-.130 ± .007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np - C</td>
<td>-.114 ± .003</td>
<td>-.131 ± .004</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>averaged value</td>
<td>-.130 ± .005</td>
<td>+.021</td>
<td>-.109 ± .006</td>
</tr>
</tbody>
</table>

1.4. Nuclear data measurements and evaluations.

Improvement of nuclear data for minor actinides is important for transmutation projects using actinide burner reactors and needed for the nuclides $^{237,238}\text{Np}$, $^{238,242}\text{Pu}$, $^{241,242,243}\text{Am}$ and $^{242,245,244,245,246}\text{Cm}$. Some of the most important cases are now investigated in the framework of ISTC Project-304 "Measurement and Analysis of Basic Nuclear Data for Minor Actinides". The latest works include:

- preliminary results of precise measurements of the fission cross sections of $^{241,245,246,247}\text{Cm}$ and $^{242}\text{Am}$ by 0.15-7.0 energy neutrons;
- first runs of measurements of secondary neutron spectra, fission product yields, delayed neutron yields and inelastic scattering cross section for Np-237;
- improved evaluations of the most important cross sections for Np-237.

Extensive calculations and evaluations of the nuclear data are now done for higher energy range to satisfy the needs of ADT research and development. The latest results:

- special library is developed (MENDL-2, Medium Energy Nuclear Data Library) for the investigations of the activation and transmutation of the materials irradiated by the nucleons of intermediate energies (neutrons up to 100 MeV, protons up to 200 MeV, more than 100 000 reactions). First, neutron, part is described in [14], proton part is to be converted to an agreed format and then released;
- systematics were developed of the cross sections of the threshold reactions on 14 MeV neutrons based on a new approach taking into account both equilibrium and non-equilibrium mechanisms of nuclear reactions [15-16].
1.5. Research on the accelerator targets for ADTT.

Efforts are undertaken in collaboration with Design Bureau “Gidropress” on the development of neutron producing liquid heavy metal targets irradiated by very powerful proton beams in GeV energy range. Both beam-window and windowless targets are investigated. This research includes:
- calculations of thermophysical and hydrodynamic properties of the targets and optimization of the designs;
- material studies;
- calculations of the diaphragm behavior, energy release, activation, including the accumulation of long-lived radionuclides, and gas production in liquid Pb-Bi and Pb targets;
- release of radionuclides from liquid and solid targets.
A few papers on these subjects were presented at Kalmar Conference [17-21].

2. Selected results on the actinides balance in various scenarios of Pu and MA recycling

2.1. Comparison of thermal and fast reactors in actinides recycling.

Transmutation of MA is closely linked with Pu utilization and would influence the actinide balance. The problem is whether MA burning is compatible with Pu breeding needed to support stable to say nothing of developing nuclear power industry. Another problem is whether nuclear safety requirements to Pu and MA containing cores may be met in fuel cycles involving Pu breeding. It’s very wide domain so here we consider only some most prominent differences between thermal and fast reactors used for multiple long-term recycling of transuranics. A simple calculational model based on KARE code [22] was chosen to make the comparison (the results were presented in [4]). Basic features of the model are:
- the fuel of the first cycle is MOX-fuel, mixture of depleted uranium with reactor plutonium (isotopic composition of the latter is given in Table 5); enrichment by plutonium is sufficient to support chain reaction for planned campaign period and to reach planned burnup (parameters of the first cycle are given in Table 6);
- neutron spectra, fluxes and one-group constants coincide with those of BN-800 for fast reactor and with the parameters of Pu fueled VVER-1000 for thermal reactor;
- after each cycle the spent fuel is cooled for three years, fission products are eliminated completely, plutonium of initial composition and depleted uranium are added in the quantities necessary to complete the next cycle;
- all the actinides are left in refabricated fuel.

Table 5. Isotopic composition of fresh plutonium used in calculational model.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Concentration, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu-238</td>
<td>0.5</td>
</tr>
<tr>
<td>Pu-239</td>
<td>60.0</td>
</tr>
<tr>
<td>Pu-240</td>
<td>24.5</td>
</tr>
<tr>
<td>Pu-241</td>
<td>10.9</td>
</tr>
<tr>
<td>Pu-242</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 6. Parameters of the first cycle.

<table>
<thead>
<tr>
<th>Parameter of the cycle</th>
<th>Reactor type</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fast</td>
<td>Thermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time of irradiation, days</td>
<td>420</td>
<td>920</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pu enrichment, per cent</td>
<td>18.9</td>
<td>5.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron flux, cm$^{-2}$ c$^{-1}$</td>
<td>$6.0 \times 10^{15}$</td>
<td>$4.0 \times 10^{14}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burn up, per cent of heavy atoms</td>
<td>6.6</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of fissions/number of captures</td>
<td>0.98</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Final actinide composition was calculated for every cycle and then the quantities of plutonium and depleted uranium to be added to the fuel were determined. The behavior of fast and thermal reactors was compared by following parameters: plutonium enrichment of the fuel; average value of neutron flux; share of the fissioning isotopes in plutonium; concentration of minor actinides. The results are presented in Figs. 1-6 as a function of total burnup for all cycles (which may be more than 100 per cent if the number of cycles is large enough - more than 15 for fast reactors and more than 25 for thermal reactors which refers to rather long periods of time).
These results demonstrate that:

- enrichment grows slower in fast reactor, almost stabilizing asymptotically; it's important because enrichment in thermal reactors is restricted by safety requirements at about 10 per cent;
- average flux is practically stable in fast reactor but it's almost halved in thermal reactors and this decrease is to be compensated by enrichment;
- degradation of Pu isotope composition is much faster in thermal reactors;
- accumulation of neptunium is almost identical in both reactors up to 50 per cent burn up and then americium decay will increase it in TR (burn up is four times faster in fast reactors);
- accumulation of americium and especially of curium is more intense in TR.

These calculations were done for FR without breeding blankets.

2.2. The effects of plutonium composition and breeding ratio value on recycling of the actinides in fast sodium cooled reactors of BN type.

Multiple recycling of plutonium and MA in sodium cooled fast reactors BN-800 with highly Pu-enriched MOX-fuel was considered for the cases of civil Pu (BR=1.0 and 1.3) and weapon-grade Pu (BR=1.0) with irradiation cycle of 420 days. Following values were calculated:

- initial enrichment and final burn up in all three sub-cores for every cycle;
- plutonium isotopic composition at the beginning of every cycle;
- actinides concentrations at the end of every cycle.

Some of the results are illustrated by Figs.7-12. Following conclusions may be made:

1. There is prominent difference in the evolution of Pu isotopic composition during the recycling in converter and breeder modes: plutonium quality (the concentration of fissionable isotopes Pu-239 and Pu-241) is degrading significantly in converter mode while it is even improving slightly in the breeder mode, first of all due to accumulation of Pu-239 (see Fig.7) because very high grade plutonium is produced in the radial blanket (more than 96 per cent of Pu-239).

2. Minor actinides pile up slower in the breeder mode as may be seen in Figs.9-10 for the case of the most important nuclides Am-241 and Cm-244.

3. Switching to weapon-grade plutonium reduces accumulation of MA in converter mode drastically (see also Figs.9-10).

4. Tendencies mentioned in the points 2-3 are consequences of the reduced concentration of the key nuclide Pu-241 in the fuel (see Fig.8).

5. Practically all accumulation of Am-241 in plutonium fuel is due to the decay of Pu-241 in the load which may be seen in Fig.11 where the mass of Am-241 Vs Pu-241 mass in the load is shown. These masses are practically directly proportional both in for civil and weapon-grade plutonium.

6. Strong correlation exists also between the accumulated mass of most important curium isotope Cm-244 and Pu-242 concentration in the fuel load (Fig.12).

2.3. On combining thermal and fast reactors in Pu utilization and MA transmutation.

Various possibilities to create a combined system of fast and thermal reactors capable of recycling all the plutonium and MA are analytically explored now. Some of the latest results [23] are outlined below. The system considered includes two types of reactors: VVER-1000 with either uranium or 30 per cent MOX fuel and BN-800 with various cores. Basic parameters of the systems and some results of the calculations are given in Tables 7-9.

Table 7. Parameters of BN-800 cores.

<table>
<thead>
<tr>
<th>Model number</th>
<th>Parameters of the model</th>
<th>Volume share of the fuel</th>
<th>Average Pu enrichment, per cent</th>
<th>Actinides burn up, kg/GWe/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Uranium fuel with high Pu enrichment</td>
<td>0.29</td>
<td>37.0</td>
<td>57</td>
</tr>
<tr>
<td>2.</td>
<td>Inert matrix fuel without U-238</td>
<td>0.10</td>
<td>100</td>
<td>110</td>
</tr>
</tbody>
</table>
Table 8. Equilibrium fuel composition in VVER-BN system (kg/t).

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Model 1</th>
<th>Model 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Burnup 10%</td>
<td>Burnup 20%</td>
</tr>
<tr>
<td></td>
<td>Tc=1 year</td>
<td>Tc=3 years</td>
</tr>
<tr>
<td>U-235</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>U-238</td>
<td>564.1</td>
<td>521.4</td>
</tr>
<tr>
<td>Pu-238</td>
<td>12.3</td>
<td>13.5</td>
</tr>
<tr>
<td>Pu-239</td>
<td>151.4</td>
<td>170.1</td>
</tr>
<tr>
<td>Pu-240</td>
<td>137.6</td>
<td>153.6</td>
</tr>
<tr>
<td>Pu-241</td>
<td>30.0</td>
<td>38.1</td>
</tr>
<tr>
<td>Pu-242</td>
<td>38.6</td>
<td>47.3</td>
</tr>
<tr>
<td>Np-237</td>
<td>6.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Am-241</td>
<td>12.4</td>
<td>13.8</td>
</tr>
<tr>
<td>Am-242</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Am-243</td>
<td>14.3</td>
<td>18.0</td>
</tr>
<tr>
<td>Cm-242</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Cm-244</td>
<td>7.8</td>
<td>10.4</td>
</tr>
<tr>
<td>Cm-245</td>
<td>2.1</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 9. The number of VVER-1000 reactors with the actinide output utilized by one BN-800.

<table>
<thead>
<tr>
<th>BN model</th>
<th>BN burnup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10%</td>
</tr>
<tr>
<td>Model 1</td>
<td>1.5 (1.0)*</td>
</tr>
<tr>
<td>Model 2</td>
<td></td>
</tr>
</tbody>
</table>

* Figures in brackets refer to 30 per cent MOX fueled VVER-1000.

3. The neutrons available for transmutation of fission products.

The price and value of the neutrons used for transmutation may be estimated by considering the income provided by nuclear electricity production. The approach [24] based on such considerations is used below in a simplified form. These results were presented in [25].

Modifications in energy producing system decreasing sales of electricity is the price of achieving environmental goals. To get one neutron as a result of interaction of high energy proton with specially designed target one needs not less than 20 MeV of beam energy. Taking thermal efficiency of electricity production equal to 30 per cent and accelerator beam efficiency 40 per cent we conclude that production of one "external" neutron takes the energy almost equal to that released in an act of fission. Thus the production of 4.2 kg of neutrons in the proton target means the loss of income equivalent to selling electricity generated by 1 t of fissioned heavy metal, i.e. approximately 1 GWt(e) year. If every neutron transmutes 1 nucleus of Tc-99 then that's the price of transmuting 420 kg of Tc-99.

Not only "external" neutrons may be used for transmutation but also reactor excess neutrons not used for energy production. Their alternative use may be breeding of Pu, so their price is not less than the value of lost Pu.

In the case of actinides transmutation in equilibrium mode when every nucleus of fresh fuel is sooner or later fissioned after a chain of nuclear transformations consuming neutrons the price of the neutrons is not easy to determine.

Hybrid transmutation concept when accelerator-driven blanket both produces energy and multiplicates neutrons is most popular now. In this case both "external" and "multiplied" neutrons are used to transmute FP. But it does not a priori mean that one "external" neutron provides transmutation of more than one fission fragment.
Let’s consider the neutronics of FP transmutation in accelerator-driven blanket. Notations used: \( V \) - the number of fission neutrons, \( \Sigma_f \) - macroscopic fission cross section of the fuel; \( \Sigma_T \) - macroscopic total absorption cross section; \( \Sigma_U \) - macroscopic cross section of FP placed in the blanket to be transmuted; \( k = V \Sigma_U / (\Sigma_T + \Sigma_U) \) - blanket multiplication; \( k_0 = V \Sigma_f / \Sigma_T \) - initial multiplication of the blanket free from FP. The maximum number of fissions initiated by one external neutron in the blanket is \( \varphi = k V / (1 - k) \). The share of neutrons absorbed by FP being transmuted is

\[
\eta = \frac{\Sigma_U}{\Sigma_T + \Sigma_U} = 1 - k/k_0 \quad (1)
\]

This definition differs from that of Takahashi [26] by a factor \((1 - k/V)\) because in [26] the share of absorptions used is \( \eta_{FP} = \Sigma_U / (\Sigma_T - \Sigma_f + \Sigma_U) \) which does not provide direct information on the share of neutrons used for transmutation.

The number of FP transmuted per one “external” neutron (the transmutation “value” of external neutron) is the product of \( \eta \) and the number of multiplied neutrons:

\[
\tau = \eta (1 + \varphi V) = (1 - k/k_0)(1 - k) = 1 - \rho \varphi \rho \quad (2)
\]

where \( \rho = (k - 1/k) \) is blanket reactivity. Let’s now consider different reactivities of initial blanket (without FP added). If it were critical, \( k_c = 1, \rho_c = 0 \), we get \( \tau = 1 \), i.e. each “external” neutron provides transmutation of one FP just compensating added absorption. If initial blanket is subcritical (\( k_0 < 1 \)) then \( \tau < 1 \), i.e. “external” neutron transmutes less than one fragment in spite the multiplication in the blanket. And, finally, \( k_0 > 1 \) results in \( \tau > 1 \).

If some quantity of FP is placed in initially supercritical blanket, making it precisely critical, the blanket will operate in reactor mode transmuting \( 1 - 1/k_0 \) of fragments per every “internal” neutron, \( \varphi = k V / (1 - k) \) fissions will transmute \( \tau^* = k(k_0 - 1)/k_0(1 - k) \) fragments.

If the power of such a blanket, i.e. the rate of fissions, is equal to the power of subcritical accelerator-driven blanket, “combined” transmutation of FP in such a critical blanket plus direct transmutation by “external” neutrons will bring the same results as hybrid transmutation in subcritical accelerator-driven blanket with the same number of external neutrons: \( \tau = \tau^* + 1 \).

4. Criterion of radiation equivalence in environmental assessment of nuclear fuel cycles

Accumulation of highly radiotoxic nuclear wastes created a problem unique in the history of science - it’s necessary to choose the direction of the development of nuclear technologies optimized both to ensure safety of our descendants in dozens and hundreds of thousands of years and to minimize radiological risks and economic losses for the present and nearest generations of nuclear electricity consumers who are not only to pay for those long-term safety measures but to learn how to handle and actually handle large volumes of radioactive materials taking risks and damages.

Now hazards of the nuclear power radwaste are estimated by comparison of its radiotoxicity with that of the excavated uranium ore (see, for example, [27,28]). This approach is typical for the use of traditional mineral resources - their volume reflects directly both their value and its environmental price. Nuclear power falls out of this picture in both aspects. Useful effect, i.e. the quantity of electricity produced, may be increased by almost two orders if we switch from today’s open nuclear fuel cycle (ONFC) to closed one (CNFC).

We propose a modification of the assessment which is outlined below (see also [24]). In the estimates we shall assume the fission energy release equal to 200 MeV per act for all the actinides, differences in individual fission products (FP) yields for various actinides will be also neglected. In this approximation accumulation of 1 t of fission products corresponds to a little more than 1 GWt(e) year for standard thermal reactors. Consumption of uranium components and pile-up of the actinides are close for all major types of thermal reactors. Normalization of waste to 1 t of FP allows to compare hazards of various nuclear installations and cycles.

We shall use following mass notations: \( M_{ore,i} \) - ore components, \( M_S \) - all spent fuel, \( M_{BP,i} \) - components of the fuel load, \( M_{SS,i} \) - components of the discharged spent fuel, \( M_{FP} \) - fission products, \( \Delta_i = m_{SS,i} - m_{BP,i} \) where \( m_i \) are normalized to 1 t of FP. If specific “danger” of \( i \)-th nuclide is \( d_i \) then total danger of nuclides mixture is

\[
D = \sum_i M_i d_i \quad (3)
\]
What follows is true no matter what concept of “danger” is used, it may be mass, volume, activity, radiotoxicity, masses of diluting substances etc. Criterion of radiation equivalence of the spent fuel and excavated uranium usually used is the ratio of their dangers:

\[ K_{\text{eq}} = \frac{\sum M_{i} d_{i}}{\sum M_{\text{exc}} d_{i}} \]  

(4)

Only about 0.7 per cent of natural uranium nuclei react in ONFC. More than 99 per cent of them were dislocated but their radiotoxicity was unchanged. Whether such “displaced” nuclei are taken into account or not almost does not influence the numerator value in Eq(4) but is very essential for the denominator - the mass of uranium excavated is by two orders larger than the mass of uranium transmuted, the ratio of their activities being about 40. If one applies the criterion (4) to ideal CNFC where all the uranium excavated is turned into FPs with some 200 times more electricity produced we get a paradox - most efficient use of natural uranium formally results in increased environmental danger because the accumulation of FPs per ton of natural U increases correspondingly. In practice lower specific consumption of natural uranium in CNFC is not taken into account in comparisons of the waste radiotoxicities of various NFCs. Such a “default” refusal to use the criterion (4) needs justification.

Let’s now formulate a criterion of radiation equivalence which takes the specific ways of using raw materials in nuclear power into account. The idea is to compare the accumulated danger with the danger of transmuted (not only fissioned) uranium excluding “displaced” nuclides. The ratio of the dangers summed up over all the power and transmutation plants (index k) is

\[ K_{\text{WU}} = \frac{\sum_{k} M^{k}_{\text{FP}} \sum_{i} \Delta_{i}^{k} d_{i}}{\sum_{k} M^{k}_{\text{FP}} \sum_{i} \Delta_{\text{exc}}^{k} d_{i}} \]  

(5)

\( \Delta_{\text{exc}}^{k} \) includes not only U isotopes but co-extracted products of their decay chains. Total energy produced is proportional to \( \sum_{k} M^{k}_{\text{FP}} \sum_{i} \Delta_{i}^{k} \). The numerator includes total accumulation of FPs and accumulation or burning of actinides, the denominator - total quantity of the transmuted uranium. In CNFC without FP transmutation only FP and irretrievable losses of actinides in reprocessing enter the numerator, and denominator includes 1 ton of U per every ton in the numerator. This criterion makes obvious the advantages of CNFC compared to ONFC in a very long run (thousands of years) when the main contribution to radiotoxicity is made by actinides, burnt in CNFC and accumulated in ONFC. This criterion is valid for the case of FP transmutation as well but it is not without deficiencies also - according to it burning of less active \(^{238}\text{U}\) is 6 times more dangerous (due to small destroyed radioactivity) then burning of U-235.

The use of Eq (5) (accumulated danger/annihilated danger) instead of (4) (danger of spent fuel/danger of excavated uranium) increases the relative danger of ONFC correcting the traditional approach. It should be stressed that absolute indices of waste dangers do not depend on the choice of any of the two criteria.

Conclusions

Research and development efforts on transmutation should be aimed at the methods of closing nuclear fuel cycle efficient in a few senses:
- saving natural uranium by breeding secondary fuel;
- producing and directing to the radwaste less long-lived alpha-emitters;
- ensuring nuclear and radiological safety of all power producing plants and reprocessing installations;
- reducing proliferation dangers by keeping most of plutonium in spent fuel and strictly regulating quantity of separated plutonium.
- prompt introduction of fast reactors using Pu is vital for solving these problems;
- already nearest generation of new reactors with life-time expectancy of at least 50 years should be designed flexible to meet the requirements of steadily growing plutonium breeding when necessary;
- using of high-grade Pu in CNFC reduces the accumulation of minor actinides;
- useful energy produced should enter the denominator in any numerical criteria describing radiological hazards of NFC.
REFERENCES


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Fig. 1. Increasing of enrichment in multiple recycling of actinides.

Fig. 2. Flux degradation in multiple recycling of actinides.

Fig. 3. Degradation of Pu isotopic composition in multiple recycling.
Fig. 4. Accumulation of neptunium in actinides recycling.

Fig. 5. Accumulation of americium in actinides recycling.

Fig. 6. Accumulation of curium in actinides recycling.
Fig. 7. Evolution of Pu isotopic components in multiple recycling in BN-800 fast reactor at different values of breeding ratio.

Fig. 8. Total accumulation of Pu-241 in the core of BN-800 operating in various recycling modes.

Fig. 9. Total accumulation of Am-241 in the core of BN-800 operating in various recycling modes.
Fig. 10. Total accumulation of Cm-244 in the core of BN-800 operating in various recycling modes.

Fig. 11. Accumulation of Am-241 as a function of Pu-241 concentration in the fuel load of BN-800 during recycling of civil and weapon-grade plutonium in the converter mode (BR=1) and of civil Pu in breeder mode (BR=1.3).

Fig. 12. Accumulation of Cm-244 as a function of Pu-242 concentration in the fuel load of BN-800 during recycling of civil and weapon-grade plutonium in the converter mode (BR=1) and of civil Pu in breeder mode (BR=1.3).
ADVANCED FUEL RECYCLE SYSTEM CONCEPT
TO REALIZE MINOR ACTINIDES RECYCLE

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and T.Kawata
Power Reactor and Nuclear Fuel Development Corporation (PNC)

ABSTRACT

MA recycle has several benefits such as ease of waste problems and enhancement of proliferation resistance,
but MAs by means of aqueous process apparently needs more equipment, which requires more capital cost. For the PNC R&D activities, process optimization and simplification and integration of reprocessing and fabrication, which is one candidate goal of the Advanced Fuel Recycle System, is necessary to realize MA recycle.

In the present paper, PNC proposes an drastically improved recycle concept which is integrated system of reprocessing and fabrication. This concept mainly consists of a simplified PUREX process with single cycle extraction process flowsheet which gives rather low decontamination factors around $10^3$ and simplified fabrication process such as vibro-packing. Such simplified extraction process can radically reduce number and volume of contactors, vessels, waste treatment components, and all auxiliary equipment which can brings forth the economical innovation.

The concept shows enough economical performance for application of MA recovery process.
1. INTRODUCTION

In compliance with the "Long-Term Program for Research, Development and Utilization of Nuclear Energy" issued in 1994 by the Atomic Energy Commission of Japan, PNC is expanding its development program for Advanced Fuel Recycle System as a new concept of fast breeder reactor (FBR) fuel cycle.

The primary objective of this program is to strengthen the performance of fuel cycle at various criteria. In the currently developed mixed oxide (MOX) of uranium (U) and plutonium (Pu) -fueled cycle, PNC recognizes that there are still issues to be substantially improved, particularly with respect to economics, generation of radioactive wastes both in terms of volume and quality, and international concerns about proliferation of nuclear material.

Recognizing the above-mentioned necessity of improvement, PNC believes that the following basic steps must be taken.

(1) Improve the system's economics as a total fuel cycle system (system simplification)
(2) Achieve Pu recovery without perfect purification
(3) Make the most of the features of the fast neutron system. In addition to the breeding, pursue other function as MA (Minor Actinide such as Np, Am, and Cm) burning.

By following the above steps, the effective utilization of all actinides can be achieved, resulting in a reduction of the cumulative production of MAs, reduction of long-lasting toxicity in the high level liquid waste (HLW), and so on. This is the way to realize MA recycle.

Among several candidate system for Advanced Fuel Recycle System, PNC's main concern has been focused on the improvement of the system composed of the PUREX process and MOX fuel fabrication which have been well experienced by PNC through the past three decades.

2. FEATURE OF THE IMPROVEMENT

In the current commercial light water reactor (LWR) reprocessing, decontamination factor (DF) for fission products (FPs) in the order of $10^7$ to $10^8$ is required because of easy handling of the product U and Pu in the grove box for fuel fabrication.

On the other hand, we have to consider the trend of burn-up extension in the LWR system. The recovered Pu even with such high DF will have higher activity of gamma and neutron emission. This fact shows that the system of remote fuel fabrication should be essential in future.

If we allow the remote fabrication, the DF around $10^3$ or even smaller are acceptable in the product materials for recycling it to the FBR, because FBR has the low neutronic sensitivity to its fuel material impurities. The FBR system doe not require the fuel materials to be so pure like as the product from conventional reprocessing and such low DF can be attained easily by improved PUREX process with only one (single) cycle extraction.

In the conventional LWR reprocessing plant based on the PUREX technology using tri-butyl phosphate (TBP) as an extractant, the chemical separation process is composed of several extraction cycles in order to achieve high purity in both U and Pu products. Such multiple extraction cycles, usually consists of co-decontamination, partition of U and Pu and purification steps, become the multiple sources of aqueous and organic waste generation and then require quite a large capacity for the component to treat these waste. Figure 1 shows the ratio of liquid volume to be treated in each process of conventional reprocessing plant. It is apparent that around 70% or more are coming from partitioning of U and Pu and purification process.

Considering the single extraction process, we can eliminate all of partition and purification steps, which will result in the drastic reduction of total volume, i.e. 70% or more, and number of process component. Such reduction will lead to the proportional reduction in the required capacity of the waste processing and the reduction of waste itself. Thus the overall process is down sized and a significant reduction will be achieved on both plant capital and operating cost.
At present, the MOX fuel is usually fabricated in the form of sintered pellet at the facilities in the PNC Tokai Works as well as European countries. This fabrication method is featured with the powder preparation and pressing, sintering in furnace, chemical and physical inspections arraying pellets in a stack and inserting them into a cladding tube. Since most of these processes depend on very precise mechanical handlings with complicated devices, they are not well fitted to the remote operation and alternative methods are to be explored. Considering these facts, the gelation and vibro-packing method has been proposed as one of the methods suitable for remote fuel fabrication in the Advanced Fuel Recycle System.

3. DETAIL OF SINGLE CYCLE EXTRACTION PROCESS

One of the extremely simplified reprocessing flowsheet proposed as a part of Advanced Fuel Recycle System is shown in Figure 2, which is the improved PUREX process with single cycle extraction process as mentioned before.

In this case, both core and blanket fuel dissolved in nitric acid solution are treated by the process which consists of an extraction bank, a Pu and U co-stripping bank and a strip bank for residual U. The Pu and U co-stripping bank is made so that the Pu content is slightly higher than that required for core fuel fabrication. The process is also distinguished to extremely reduce amount of liquid waste by means of

(1) eliminate scrubbing process, and
(2) control process condition such as temperature, flow rate and so on in order to enable co-extraction of U and Pu without any reductant.

As for MA's behavior in this process, Np will be able to be recovered together with U and Pu if its valence in solution is adjusted in extractable form, but both Am and Cm will go to the raffinate from the extraction bank.

Further simplification will be made possibly by incorporating the supplemental technique to reduce heavy metal quantity to be fed to the extraction process in order to reduce aqueous and organic waste. One of the methods under study is crystallization technique which is to collect, prior to solvent extraction, a large portion of uranium from the feed solution by crystallizing it as uranyl nitrate hexahydrate (UNH) at lower temperature. As the solubility of Pu is less than U and total amount of MAs and FPs are far below than the amount of U, only U cristallizes from the dissolved solution. After the crystallization, the residual solution with Pu/U ratio enriched to nearly 30% will be fed to the solvent extraction system which

![Fig. 2 Single-Cycle Extraction Flowsheet](image-url)
consists of just an extraction and a stripping banks.

In either case, a major adjustment of Pu content in the product solution is to be made by the addition of recovered U before it is recycled for fuel fabrication.

It should be noted that the proposed process will completely eliminate the necessity for separation and handling pure Pu.

4. DETAIL OF REMOTE FUEL FABRICATION

Despite the automation of the process and inspection lines, radiation exposures to the workers tend to increase owing to occasional access for maintenance activities. In their aspect, a remote fuel fabrication process with an appropriate shielding is desirable or even necessary for the next generation MOX plants. And if we adopt the remote fabrication method for FBR fuel, we can drastically simplify the reprocessing process as discussed earlier.

Mixed solution of U and Pu with suitable concentration for MOX fabrication is fed to the gelation process to get particles with adequate diameter. Then particles are calcined and sintered to form granules. Finally granules are directly poured into cladding tube by applying vibration for dense filling.

In this case, most of the processes are fluidized, and therefore they are more suitable for remotization and easy to integrate into the reprocessing plant as its end process.

As shown in Figure 3, the system composed by gelation and vibro-packing can significantly shorten the fabrication process compared with the conventional process such as pelletization method. The inspection procedures will also be less complicated for the gelation process than in the pellet process.

5. EVALUATION ON ECONOMICSS

Since the major portion of electricity generation cost depends on the capital cost of the power reactor plant, significant effort is required for FBR plant to reduce its construction cost to become economically competitive. Also much effort to reduce the cost is needed for fuel cycle area which contributes about 20 to 30% of total electricity generation cost. About the fuel cycle cost comparison of LWR and FBR cycle, Figure 4 shows the relative effect of each constituents. As FBR fuel reprocessing has both functions of U purchase and conversion/enrichment in LWR cycle because of Pu recovery from spent fuel, it occupies larger portion in the fuel cycle cost than LWR fuel reprocessing. Innovation of reprocessing may brings forth larger cost effect. We believe the single cycle extraction process is one of the most effective method for this purpose.

In addition to the simplification and improvement of the process, the integration of reprocessing and fabrication processes into one fuel cycle plant will contribute to further reduction of the fuel cycle cost. It is often conceived that the remote handling might be more costly
than the automated directly handling. However, the remote fuel fabrication based on gelation and vibro-packing has a very good chance to achieve far better economy than the conventional pelleting process, because the number of process steps in gelation is much smaller than in the pellet process preceded by the conversion process.

In Figure 5, a block flow diagram of an integrated fuel cycle plant based on Advance Fuel Recycle System is compared with that of conventionally separate reprocessing and fabrication plants. Based on a conceptual image of the Advanced Fuel Recycle Plant (AFRP), a preliminary cost evaluation has been carried out and compared with conventional reprocessing and fabrication plants with same throughput in Figure 6. As indicated in the Figure, the concept of AFRP will bring forth nearly 60% reduction in the plant capital cost for fuel recycling.

6. CURRENT STATUS TOWARD MA RECYCLE

As the drastically improved recycle system signifies good performance on the economics, the addition of MA recovery system by means of aqueous process, that is TRUEX process in which CMPO is used as an extractant for MAs, may be acceptable, taking into account of merits of MA recycle such as easing the waste problem and strengthening the proliferation resistivity.

The cost gain due to addition of MA recycle function to the AFRP is estimated around only a few percent up. Of course, the MA recovery process such as TRUEX process should be reasonably improved.

It has been examined by TRUEX process that MA nuclides can be recovered almost 100% from the PUREX process raffinate generated from FBR spent fuel reprocessing test in the Chemical Processing Facility (CPF) in Tokai Works, PNC. Besides this, process condition to co-extract Np with Pu in PUREX process has been confirmed. Now, CPF is under modification to carry out more effectively the examination of the proposed single
cycle extraction process together with the basic study on the crystallization method focusing on the Pu solubility and the TRUEX process modification.

The possible recovered amount of MA from CPF is far below for conducting systematic irradiation test of MOX fuel containing MA nuclides, so that equipment to recover Am, which accumulates in the plutonium as a product from conventional LWR reprocessing plant, is going to be operation in near future at the Plutonium Fuel Development Facility (PFDF) in Tokai Works.

Enough amount of Am for irradiation test will be prepared into several pins at the cell of Alpha Gamma Facility (AGF), in Oarai Engineering Center, PNC, by remote technique to ensure workers exposure at low level. Irradiation test on MA contained fuel will be conducted at the Fast Experimental Reactor "Joyo" after getting the commission. It is expected that the test will be initiated around 2001.
ABSTRACT

Any strategy related to radioactive waste management has to provide first a consistent answer on the Plutonium management. In fact, Plutonium build-up with standard PWRs should be accounted for and, if reprocessing is adopted, long-term solutions have to be found to use Plutonium in an effective way, and to minimise the associated minor actinide build-up.

The present paper gives the results obtained for different scenarios related to a nuclear power park of 60 GWe.

These results are given to show main trends and features, but do not account for detailed, economic and technological feasibility aspects, that will be the aim of future work.
1. INTRODUCTION

Any strategy related to radioactive waste management has to provide first a consistent answer on the Plutonium management. In fact, Plutonium build-up with standard PWRs should be accounted for and, if reprocessing is adopted, long-term solutions have to be found to use Plutonium in an effective way, and to minimise the associated minor actinide build-up.

In the frame of the studies required by the French Parliament law of 1991 on Waste Management, and according to the requirements of the National Commission (CNE) in charge of Evaluating these studies, the CEA Nuclear Reactor Directorate has launched a wide range of assessments on different scenarios of Pu utilisation in different reactor types (PWRs, FRs) and on the consequent approaches to the residual minor actinide management, and in particular to specific options to transmute them. The goal is to help feasibility assessments, to quantify fuel cycle characteristics and eventual benefits for deep storage.

This type of far-reaching studies is the closest to what can be considered a full system study, related to Plutonium management and partitioning/transmutation, and are an essential part of the SPIN program.

The present paper will give results and present trends.

2. THE SCENARIOS CONSIDERED IN THIS STUDY

The following scenarios have been characterised:

- Open cycle scenario.
- Pu recycling in light water reactors. Two major options for PWRs are considered: a) 100 % MOX-PWRs with a high moderator-to-fuel ratio, RMA, b) PWRs with MOX fuel on a $^{235}U$ enriched support, with standard moderator-to-fuel ratio.
- Pu recycling in PWRs (RMAs) followed by FR (CAPRA-type) utilisation for Pu multirecycling. Two hypothesis are considered: a) Only one recycle of Plutonium in PWRs, b) Two recycles of Pu in PWRs. Both cases attempt to consider delays in the introduction of FRs in a nuclear power park.
- In two cases: a) Full Pu recycling in PWRs, b) One recycle of Pu in a standard PWR followed by multirecycling in FR ; the explicit management of separated Np, Am, and Cm is considered.

All PWRs have a burn-up of 55 GWd/t, with fuel reloading frequency equal to six. Fast Reactors are of the CAPRA type (140 GWd/t burn-up, frequency 3).

For each of these seven scenarios, mass flow (Pu, minor actinides) throughout reactors and in the fuel cycle installations (reprocessing, fabrication) has been obtained.

All scenarios are relative to the same installed power (60 GWe, producing 400 TWh/yr).

Moreover, the detail of the reactor core characteristics is also given (enrichments at equilibrium, Pu vectors, detailed minor actinide inventories).

Finally the full Plutonium inventory at equilibrium is explicitly given. In terms of benefits for waste management in the storage, potential radiotoxicity and its evolution in time is presented for the scenarios where minor actinide transmutation is studied.

3. RESULTS OF THE SCENARIOS STUDIES

The results for the seven scenarios indicated above, are summarized in figures 1-7. Some comments on each scenario is given below.
3.1 Open cycle (figure 1)

This is the standard reference scenario. To be noted the high burn-up which has been chosen (and which is applied to all PWRs, whatever the fuel loading, in all subsequent scenarios).

The figure shows both the Uranium resources needed (in terms of annual mass flow) and both the resulting depleted Uranium (U-235 enrichment: 0.25 %) and the "wastes", which, in that case, include Plutonium.

3.2 Pu recycling in high moderation PWRs (R_{mod} = 4) (Figure 2)

In this scenario, all Plutonium is multirecycled in PWRs with a high moderator-to-fuel ratio, HMR, (R_{mod} = 4), which previous studies [1] have indicated as a particularly interesting option. Since the multirecycling is shown at equilibrium, one has an unlikely high Pu content in the fuel (~ 18 %). This scenario implies a 190 t MOX fabrication capability (to be compared to the present MELOX plant potential).

The HMRs represent ~ 20 % of the reactor park.

As far as resources, this scenario allows a ~ 20 % reduction of natural Uranium requirements.

As far as wastes, the Am and Cm production goes up of a factor of 4, with respect to the open cycle scenario.

3.3 Pu recycling in standard MOX PWRs with enriched Uranium support (figure 3)

In order to avoid potential problems related to the increase of Pu content in MOX PWRs (and the consequent potential problems related to reactivity coefficients), one can envisage a mixed enriched U-235-MOX fuel.

An equilibrium park is obtained with only one type of PWR. The fuel Pu content is ~ 2 %, and the U-235 enrichment is 3.8 % (to be compared to the standard 4.5 % value, see figure 1).

Multirecycling seems then feasible from a physics point of view. However two main drawbacks should be noted: a) Fuel fabrication costs will probably grow significantly, and MOX fuel fabrication plants should account for the annual need of 880 tons (~ 7 MELOX plants); b) The Cm produced in this scenario goes up about a factor of 2.

In fact, the U-235 dominated core spectrum with a high thermalisation, favours the Cm production (the reduced Am production is an extra source of Cm build-up).

3.4 Scenarios with fast reactors for Pu recycling (figures 4 and 5)

Both scenarios of figures 4 and 5 account for the use of CAPRA-type fast reactors [2]. This seems to be still the most promising option, in view of the difficulties encountered in both the full-PWRs scenarios described above. For both scenarios, it has been considered realistic to envisage one or two recyclings of Plutonium in standard MOX-PWRs. The difference between the two scenarios is then represented by the delay in introducing fast reactors into the reactor park and the relative proportion of reactor types in the park (the fast reactor share is never higher than ~ 18 %). In fact, two recyclings of Pu in PWRs is envisaged in the scenario of fig. 5.

As far as resources, both scenarios allow a 30 % decrease of the natural Uranium supply requirement. In terms of MOX fabrication for both PWRs and FRs, one MELOX-type should be enough for the scenario of fig. 4. More fabrication capability is obviously required, if two recycling have to be foreseen in MOX-PWRs (fig. 5).

The waste production in these types of reactor parks, is close to that of the reactor park with HMRs (see figure 2). In fact, the potential benefits of using fast reactors, are reduced by the limited amount of these
reactors in the park and by the fact that the Pu recycled in fast reactor has already been degraded by one (or two) recycling(s) in PWRs.

Finally, it should be noted that the Pu content at equilibrium in the CAPRA-type reactors is close to 50 %, which is slightly higher of what is suggested in the CAPRA feasibility studies, but which can be easily adjusted to the required value (~ 45 %).

3.5 Scenarios with Minor Actinide (MA) recycling (figs. 6 and 7)

Minor actinides are recycled according to two scenarios which have been presented previously, namely a full PWRs scenario, with only one type of fuel loading (mixed enriched-U-235 and MOX fuel, shown in figure 3) and a MOX-PWR (one recycling) plus CAPRA-type reactors (shown in figure 4).

The mixed enriched-U/MOX PWRs have been chosen, since the MA recycling in PWRs generally worsens the core parameters [3], and, if an homogeneous MA recycling is chosen, one has to take that general trend into account. However, even in that case, the equilibrium composition (shown in fig. 6 : 4.1 % U-235, 2.6 % Plutonium, 1 % MA) can give rise to feasibility problems. As expected, the Cm production (see fig. 6) is very relevant with negative consequences on the physics parameters of the fuel cycle. Once more, it seems that the only reasonable way out to envisage a MA recycling in PWRs is the heterogeneous mode, and a specific scenario has to be envisaged, possibly with a temporary, long-term out-of-pile storage of Cm, or with a very long irradiation of MA targets, in order to fission them at a very high degree.

The scenario of figure 7 implies the use of FRs of the CAPRA-type. The relative fractions of the different reactor types are very close to those of fig. 4 (i.e. no MA recycling). The minor actinide recycling is of the homogeneous type for Np-237, and of the heterogeneous type for Am. Cm is separated and left to decay out-of-pile into Pu, and successively recycled [4].

This scenario does not present feasibility problems from the physics point of view. It has to be noticed that all the features of the specific, MA-burner CAPRA cores, are presently being experimentally studied in SUPERPHENIX [5] (high-Pu content fuel S/A in the CAPRA 1 and 2 irradiations, Np-bearing fuel in the homogeneous mode in the NACRE experiment. Am targets are foreseen to be introduced in SUPERPHENIX early 1998 : ECRIN experiment).

To optimise this scenario, the option of a once-through irradiation of Am targets is also being studied.

Finally, it is of interest to notice the overall amount of Am targets to be fabricated annually (~ 5 tons).

4. THE POTENTIAL RADIOACTIVITY SOURCE IN THE STORAGE

It is easy, starting from the mass balances obtained in the studies described above, to evaluate the potential radiotoxicity source in a deep geological storage.

This parameter (when normalized to the energy which is produced), even if not to be taken as an absolute reference, is a simple way to characterize the activity inventory in a storage and its evolution with time. The Scenarios described in figs. 6 and 7 show a potential reduction of the radiotoxicity source term with respect to the open cycle scenario, of a factor which varies between 50 and 100, according to the time scale, when a decontamination factor of 0.1 % is applied to the Plutonium reprocessing and of 1 % to the MA partitioning (see fig. 8).

This factor is reduced to approximately 3 for all the scenarios, where only Pu is recycled, and MA are sent directly to the wastes (see fig. 8).
5. MASSES INVENTORY

All the previous discussion has been based on annual mass flows. However, an interesting point is to consider the total isotope masses which are present in the fuel cycle. These quantities will help to understand the implications of the equilibrium scenarios, in the case, for example, of the need to reduce drastically a nuclear power park.

Fuel cycle inventory is defined as the total isotope masses present in Reactors and in the different fuel cycle plants (reprocessing, storage, fabrication). We consider five years for cooling time before reprocessing and two years for fabrication operations.

For the different scenarios, masses inventories are given in the following table:

<table>
<thead>
<tr>
<th>Pu recycling in HMR (fig. 2)</th>
<th>Pu Inventory (tons)</th>
<th>Minor Actinides Inventory (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu recycling in PWR with U235 support (fig. 3)</td>
<td>430</td>
<td>/</td>
</tr>
<tr>
<td>Pu recycling in CAPRA (once in PWR (fig. 4))</td>
<td>230</td>
<td>/</td>
</tr>
<tr>
<td>Pu recycling in CAPRA (twice in PWR (fig. 5))</td>
<td>370</td>
<td>/</td>
</tr>
<tr>
<td>Pu + M.A recycling in PWR with U235 support (fig. 6)</td>
<td>300</td>
<td>95</td>
</tr>
<tr>
<td>Pu + M.A recycling in CAPRA Pu once in PWR (fig. 7)</td>
<td>440</td>
<td>90</td>
</tr>
</tbody>
</table>

Scenarios with Pu recycling in dedicated Reactors (PWR or FR) show a quite similar amount of Pu inventory (around 400 tons).

For the scenario with Pu recycling in standard PWR with U235 support, Pu inventory is rather smaller about 200 tons. This is mainly due to the fact that in these case, the fissile isotope inventory necessary to reach Reactor's criticality is partially provided by the U235 support.

When Minor Actinides are recycled, the Pu inventory is increased by about 20 % to 30 % and Minor actinides inventory is slightly smaller than 100 tons for both scenarios.

REFERENCES


FIGURE 1
PARK OF PWRs (60 GWe) - 400 TWhe/year
Burn-up = 55 GWD/t    Frequency = 6

1. OPEN CYCLE

7930 t Unat

ENRICHMENT
4.6 MUTS

U5: 0.25%

Depleted
Uranium
7050 t

U5: 4.5%

FABRICATION
880 t

PWR (UOX)
60 GWe

ANNUAL MASS FLOW

WASTES
IRRADIATED FUELS
860 t

Pu: 11.6 t
U: 812 t
Act. M.: 1.4 t

Np 0.8 t
Am 0.6 t
Cm 0.1 t
FIGURE 2
PARK OF PWRs (60 GWe - 400 TWhe/year)
EQUILIBRIUM STATE
BURN-UP : 55 GWD/t  Frequency = 6

2. RECYCLE OF PU IN HIGH MODERATED REACTOR (Rmod = 4)

ENRICHMENT 3.7 MUTS

6220 t Unat

U5 : 0.25 %  U5 : 4.5 %

Depleted Uranium 5530 t

FABRICATION (UOX) 690 t

FABRICATION (MOX) 190 t

PWR (UOX) 47 GWe (78 %)

HMR (MOX) 13 GWe (22 %)

REPROCESSING UOX : 690 t

REPROCESSING MOX : 190 t

ANNUAL MASS FLOW

U  637 t
Pu  9.1 t
Np  0.7 t
Am  0.4 t
Cm  0.09 t

WASTES
U  0.8 t
Pu  0.03 t
Np  0.7 t
Am  2.4 t
Cm  0.5 t

Pu : 25 t
3. RECYCLE OF Pu IN STANDARD MOX WITH ENRICHED URANIUM SUPPORT

FIGURE 3
PARK OF PWRs (60 GWe - 400 TWh/year)
EQUILIBRIUM STATE
BURN-UP : 55 GWD/t  Frequency = 6

ANNUAL MASS FLOW

WASTES

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.8 t</td>
<td></td>
</tr>
<tr>
<td>Pu</td>
<td>0.02 t</td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>0.6 t</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>1.8 t</td>
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</tr>
<tr>
<td>Cm</td>
<td>0.9 t</td>
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</tr>
</tbody>
</table>

Pu : 17.6 t
FIGURE 4
PARK PWR + CAPRA (60 GWe - 400 TWhe/year)
EQUILIBRIUM STATE

BURN-UP PWR = 55 GWD/t
BURN-UP CAPRA = 140 GWD/t

Frequency 6
Frequency 3

4. RECYCLE OF Pu : once in PWR and after in CAPRA

ANNUAL MASS FLOW

WASTES

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Pu</th>
<th>Np</th>
<th>Am</th>
<th>Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.7 t</td>
<td>0.03 t</td>
<td>0.6 t</td>
<td>2.0 t</td>
<td>0.35 t</td>
</tr>
<tr>
<td>Pu</td>
<td>8.4 t</td>
<td>5.8 t</td>
<td>0.01 t</td>
<td>0.5 t</td>
<td>0.12 t</td>
</tr>
<tr>
<td>Np</td>
<td>0.6 t</td>
<td>0.01 t</td>
<td>0.5 t</td>
<td>0.12 t</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>2.0 t</td>
<td>0.5 t</td>
<td>0.12 t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cm</td>
<td>0.35 t</td>
<td>0.12 t</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uranium

5760 t Unat

ENRICHMENT
3.4 MUTS

FABRICATION (UOX)
640 t

PWR (UOX)
43.6 GWe (72.6 %)

Pu : 8.4 t

REPROCESSING
UOX : 640 t

FABRICATION (MOX)
83 t

PWR (MOX)
5.8 GWe (9.6 %)

Pu : 5.8 t

REPROCESSING
MOX : 83 t

FABRICATION (MOX-CAPRA)
49 t

CAPRA
10.6 GWe (17.7 %)

Pu : 20.5 t

REPROCESSING
CAPRA : 49 t

Depleted
Uranium
5120 t

74.7 t

83 t

49 t

22.7 t

640 t

640 t

83 t

49 t
Figure 5

Park PWR + CAPRA (60 GWe - 400 TWh/year)

Equilibrium State

Burn-up PWR = 55 GWD/t
Burn-up CAPRA = 140 GWD/t

5. Recycle of Pu: twice in PWR and after in CAPRA

Annual Mass Flow

Wastes

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.7 t</td>
</tr>
<tr>
<td>Pu</td>
<td>8.1 t</td>
</tr>
<tr>
<td>Np</td>
<td>0.6 t</td>
</tr>
<tr>
<td>Am</td>
<td>0.4 t</td>
</tr>
<tr>
<td>Cm</td>
<td>0.08 t</td>
</tr>
</tbody>
</table>

Depleted Uranium 4930 t

Enrichment 3.2 Muts

U5: 4.5%

Fabrication (UOX) 616 t

Pu: 8.1 t

PWR (UOX) 42 GWe (70%)

Fabrication (MOX) 136 t

Pu: 4.7 t

PWR (MOX) 9.5 GWe (16%)

Reprocessing UOX: 616 t

Pu: 5.6 t

Reprocessing MOX: 136 t

Pu: 16.5 t

Fabrication (MOX-CAPRA) 39 t

CAPRA 8.5 GWe (14%)

Reprocessing CAPRA: 39 t
FIGURE 6
PARK OF PWRs (60 GWe - 400 TWh/year)
(55 GWD/t, Frequency = 6)
EQUILIBRIUM STATE

6. RECYCLE OF Pu + Np + Am + Cm in MOX PWR with enriched uranium support:

7060 t Unat

ENRICHMENT 4.1 MMTS

U5: 0.25 %

U5: 4.1 %

FABRICATION (MOX) 880 t

880 t

PWR (MOX) 60 GWe

880 t

REPROCESSING UOX: 880 t

Np 0.9 t
Am 2.6 t
Am 3.7 t
Pu 23 t
7. RECYCLE OF: once in Pu in PWR and after in CAPRA, Np + Am + Cm

in CAPRA:

5680 t Unat

ENRICHMENT
3.3 MUTS

U5 : 4.5 %

FABRICATION (UOX)
630 t

PWR (UOX)
630 t

630 t

REPROCESSING
UOX: 630 t

Pu : 8.4 t

FABRICATION (MOX)
85 t

PWR (MOX)
85 t

85 t

REPROCESSING
MOX: 85 t

Pu : 5.6 t + Np = 0.6 t

Depleted Uranium
5050 t

76.9 t

FABRICATION (MOX-CAPRA)
56 t

56 t

CAPRA
56 t

11.6 GWe
(19 %)

REPROCESSING
CAPRA: 61 t

Pu : 28 t + Np = 0.8 t

21 t

Targets
4.7 t

ANNUAL MASS FLOW

Np 0.6 t
Am 0.4 t
Cm 0.08 t

Np 0.01 t
Am 0.5 t
Cm 0.12 t

Np 0.8 t
Am 3.7 t
Cm 0.7 t
FEASIBILITY STUDIES ON MA AND FP TRANSMUTATION IN FAST REACTORS

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Abstract

Feasibility studies have been performed to develop an optimized fast reactor core for reducing long-term radiotoxicity of nuclear waste by minor actinide (MA) and long-lived fission product (FP) transmutation, taking into consideration fuel cycle technology. Systematic parameter survey calculations were implemented to investigate the basic characteristics of MA and FP transmutation in a fast reactor core. The hybrid MA-loading method, where Np nuclide is dispersed uniformly in the core and target subassemblies containing Am, Cm and rare earth nuclides are loaded into the blanket region, has the potential to achieve the maximum transmutation of MA with no special fuel design considerations. The introduction of target subassemblies using duplex pellets - a moderator annulus surrounding a $^{99}$Tc core - has a great potential to transmute long-lived fission products in the radial blanket region of the fast reactor core.
1. INTRODUCTION

One of the distinctive features of a fast reactor is its good neutron economy. Utilizing the excess of neutrons enables us to construct flexible cores such that they breed or burn plutonium in consideration of plutonium stockpile balance, and also incinerate minor actinides (MA) and long-lived fission products to reduce radiotoxicity.

Some of the MA nuclides (Np, Am, Cm) and fission products (99Tc, 129I, etc.) contained in residual waste from reprocessing have extremely long-term radiotoxicity. Partitioning and transmutation of the MA and fission products are attracting considerable attention at present as an option to reduce the long-term radiological hazard of the high-level nuclear waste. There is general agreement that the implementation of partitioning and transmutation in waste management is technically feasible.

Means of reducing the radiotoxicity of the MA nuclides are presently under investigation. The MA nuclides could produce useful energy if converted into short-lived fission products by neutron bombardment. From this standpoint, a nuclear reactor provides the obvious means for transmutation of MA nuclides. Among the various nuclear reactors, a fast reactor is considered to have the greatest potential to transmute MA effectively, because of its hard neutron spectrum (1)-(5).

The beta-emitting fission products technetium (99Tc, half-life 2.13x10^5 year) and iodine (129I, half-life 1.57x10^7 year) are among the important long-lived nuclides in high-level waste, they dominate the beta radiotoxicity for more than a million years. Transmutation of 99Tc and 129I by neutron capture as a result of irradiation in nuclear reactors will yield the stable isotopes 100Ru and 130Xe, respectively. However, due to the small neutron cross sections, the transmutation efficiency in LWRs is low. Moderated subassemblies in fast reactors are more appropriate devices for the transmutation of the fission products.

Feasibility studies have been performed to investigate the basic transmutation characteristics of MA and long-lived fission products in the fast reactor (6,7).

2. MA Transmutation

Systematic parameter survey calculations were implemented to investigate the basic characteristics (transmutation rate, burnup reactivity, Doppler coefficient, sodium void reactivity, maximum linear heat rate, etc.) of a fast reactor core with MA transmutation, the following items were considered:

(1) Study on loading method of MA in the core (homogeneous, heterogeneous, hybrid, blanket, etc.)

(2) Selection of fuel material for MA transmutation (oxide, inert matrices such as Al2O3, CeO2, etc.),

(3) Study on the maximum tolerable amount of rare earth (RE) nuclides,

(4) Effect of MA recycling on core characteristics and fuel cycle system.

(1) Study on MA Loading method

Since MA loading considerably affects not only core characteristics but also fuel material properties, it is necessary to investigate MA loading methods taking into account this influence upon
core characteristics and fuel material properties. Possible MA loading methods (homogeneous, heterogeneous, hybrid, blanket, etc.) were investigated for fast reactor cores with no special design adaptation for MA loading. The MA is dispersed uniformly throughout all the fuel in the core in the homogeneous method. In the heterogeneous method, a small number of fuel subassemblies with concentrated MA (target S/As) are loaded into the core. The hybrid MA loading method is a combination of the homogeneous and heterogeneous methods: the Np nuclide is loaded in the core region uniformly and a small number of subassemblies containing Am, Cm and RE nuclides are loaded into the blanket region.

The comparison of core performance for various MA loading methods is shown in Table 1. The MA transmutation in a fast reactor core has no serious drawbacks in terms of core performance, provided that the homogeneous loading method can be employed with a small ratio of MA to fuel (~5wt%). Since a 1000MWe-class LWR produces about 26 kg of MA per year, a fast reactor with 5%wt MA loading can transmute the MA mass from six LWRs.

The heterogeneous MA loading method can be made feasible by optimizing the fuel design, loading pattern and the coolant flow of the MA-loaded fuel subassemblies. The reduction of the fuel pin diameter and the Pu enrichment is essential to reduce the power of MA-loaded fuel in the heterogeneous MA loading method.

The hybrid MA loading method can transmute a large amount of MA without serious drawbacks in terms of core performance. The transmuted mass of MA is about 530kg/cycle, which is almost 16 times the mass produced by an LWR of the same power output.

The MA loading in the blanket region causes no problems from the viewpoint of core performance. Minor actinides are transmuted at a rate of 6% per cycle in the axial and radial blanket regions.

It was found that the hybrid MA loading method, where the Np nuclide is dispersed uniformly in the core and target subassemblies containing Am, Cm and rare earth nuclides are loaded into the blanket region, has the potential to achieve the maximum transmutation of MA with no special design considerations.

(2) Selection of fuel material for MA transmutation

Different types of inert matrices, instead of UO2, for the heterogeneous MA-loading method have been investigated, they avoid the buildup of higher actinides via 238\text{U} and achieve a high MA transmutation rate. Inert matrices of Al2O3 and CeO2 were examined in this study. The MA transmutation rate of the target subassembly using inert matrices is larger than that of the target subassembly using UO2. The use of inert matrices in the target subassembly effectively increases the MA transmutation rate.

(3) Study on the permissible RE level in homogeneously loaded MA

Systematic parameter survey calculations were performed to investigate the basic characteristics of a fast reactor core loaded homogeneously with MA which contains RE, and also to establish a MA and RE loading method which has no serious influence on the core design. The homogeneous loading of MA and RE has no serious effects on the reactor core performance, provided that the amounts of MA and RE in the fuel are less than 5 and 10wt% respectively. In the case of adding Am, Cm and RE in the radial blanket region, it is possible,
from the viewpoint of core performance, to insert ~50wt% of Am and Cm, and ~50wt% of RE in the target assemblies, as is shown in Table 1.

(4) Effect of MA recycling on core characteristics and fuel cycle system.

The effects of MA recycling on the core characteristics and the fuel cycle system in the homogeneous loading method were evaluated. The absolute value of the Doppler coefficient is increased by MA recycling, the value at the 8th recycle is ~14% larger in comparison with that in the initial core, as is shown in Table 2. This is caused by the reduction in Pu enrichment with MA recycling, this increases the resonance absorption of $^{238}$U. Sodium void reactivity decreases with MA recycling, and the value at the 8th recycle is ~7% smaller than that in the initial core. The recycling of MA in a fast reactor is feasible from neutronic and thermal-hydraulic points of view. However, during multi-recycling the Np fraction is significantly reduced compared to the unirradiated feed, and the fraction of Cm is greatly increased because of neutron capture in Am. The accumulation of Cm as a result of the MA recycling will bring about some problems concerning fuel handling and reprocessing, because of an increase in both the decay heat and the neutron emission rate from $^{244}$Cm.

3. FP Transmutation

To calculate the transmutation rate of $^{99}$Tc in a neutron flux spectrum it is insufficient to account for the thermal neutron capture only; the epithermal part of the neutron spectrum also has a contribution. There is a large resonance peak at 5.6eV and a series of minor resonances between 10 and 100eV. This suggests that a neutron spectrum where there is more absorption in the resonance region than in the thermal region is advantageous in order to increase the absorption rate of $^{99}$Tc. This is because such a spectrum helps to suppress absorption by structural materials. Therefore, the appropriate loading mass of moderator depends upon its moderating power.

Systematic parameter survey calculations were performed to investigate the basic characteristics of FP($^{99}$Tc) transmutation in the blanket region of a fast reactor. A moderated target subassembly was used for $^{99}$Tc transmutation. The subassembly consists of moderator pins containing ZrH1.7 and $^{99}$Tc target pins distributed between the moderator pins. The moderated target subassemblies were loaded in the radial blanket region of the fast reactor core. The arrangement of the moderator and the target pins in the subassembly, the volume ratio of target to moderator and the moderator materials were selected as parameters in the present study. A new concept of duplex pellet - a moderator annulus surrounding a $^{99}$Tc core - for $^{99}$Tc transmutation was also adopted in the present study to get a better transmutation performance.

The core configuration and main parameters of the 600MWe-class fast reactor core used in the study are shown in Fig. 1. The arrangements of the moderator pins and the FP pins in the subassembly are shown in Fig. 2. The Monte Carlo computer code for neutron photon transport (MVP) was adopted for FP transmutation calculations in the moderated target subassembly because of its versatility and comprehensive geometry features.

The dependence of $^{99}$Tc transmutation performance on the number of FP pins in the 127-pin target assembly is shown in Table 3. The transmutation rate of $^{99}$Tc increases as the
number of FP pins in the target subassembly decreases, because the moderating power increases.

The sensitivity of the $^{99}$Tc transmutation performance to the neutron spectrum in the target subassemblies was calculated by changing the moderator materials (ZrH$_{1.7}$, BeO, Al$_2$O$_3$, SiC). Table 4 shows the results of $^{99}$Tc transmutation performance for various moderator materials. Neutron spectra and capture reaction rate distributions of $^{99}$Tc in the FP pin region for various moderator materials are shown in Fig. 3 and 4, respectively. It was found that the moderating power of ZrH$_{1.7}$ and of BeO is better than that of Al$_2$O$_3$ or SiC for $^{99}$Tc transmutation.

The FP transmutation performance of a new target subassembly concept using duplex pellets consisted of $^{99}$Tc and ZrH$_{1.7}$ was investigated. Configurations of moderated target subassemblies using duplex pellets are shown in Fig. 5. The results of the calculations are shown in Table 5. The transmutation rate of $^{99}$Tc in the new target subassembly is larger than that in the subassembly consisting of separate ZrH$_{1.7}$ moderator pins and $^{99}$Tc target pins as shown in Fig. 2. As a result of the present study, a maximum $^{99}$Tc transmutation rate of about 10%/year was obtained by using the new target subassembly loaded in the blanket region of the fast reactor. The new target subassembly can achieve the optimum transmutation performance by adjusting the volume ratio of ZrH$_{1.7}$ and $^{99}$Tc in the duplex pellet.

The effects of loading target subassemblies on main core characteristics were also analyzed. It was found that the power density of the core fuel adjacent to the target is rather high and is about the same as the maximum in the core. However, the power spike is much mitigated compared to the case of loading target subassemblies in the core region.

4. CONCLUSION

Feasibility studies have been performed to investigate the basic characteristics of MA and FP transmutation in fast reactors, and also to clarify the feasibility of MA and FP transmutation.

MA transmutation in a fast reactor core has no serious drawbacks in terms of core performance, provided that the homogeneous loading method can be employed with a small fraction of MA in the fuel (~5wt%). The hybrid MA-loading method, where Np nuclide is dispersed uniformly in the core and target subassemblies containing Am, Cm and rare earth nuclides are loaded into the blanket region, has the potential to achieve the maximum transmutation of MA with no special fuel design considerations.

The introduction of target subassemblies using duplex pellets - a moderator annulus surrounding a $^{99}$Tc core - gives the maximum transmutation rate of Tc-99 in the radial blanket region of the fast reactor core.

It was found that the fast reactors have an excellent potential for transmutating MA and FP effectively. However, much research needs still to be done to improve the partitioning of the radionuclides as well as to resolve the technological problems of the transmutation, to make the process industrially attractive.

REFERENCES

(1) M. YAMAOKA, M. ISHIKAWA and T. WAKABAYASHI, "Feasibility Study of TRU Transmutation


Table 1 Comparison of Core Performance for Various Ma Loading Methods

<table>
<thead>
<tr>
<th>Item</th>
<th>Reference (No MA)</th>
<th>Homo. Loading</th>
<th>Hetero. Loading</th>
<th>Homo. Loading</th>
<th>Hybrid Loading</th>
<th>Hybrid Loading</th>
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<tbody>
<tr>
<td>MA and RE Loaded in the Core Region</td>
<td>-</td>
<td>Np,Am,Cm</td>
<td>Np,Am,Cm</td>
<td>Np,Am,Cm</td>
<td>Np : 9.8%</td>
<td>Np : 9.8%</td>
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<tr>
<td></td>
<td></td>
<td>:5% RE :0%</td>
<td>:4% RE :0%</td>
<td>:5% RE :10%</td>
<td>RE :0%</td>
<td>RE :0%</td>
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<tr>
<td></td>
<td></td>
<td>(Number of target S/A:39)</td>
<td>(Number of target S/A:39)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MA and RE Loaded in the Blanket Region (Target)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Am,Cm: 46%</td>
<td>Am,Cm: 46%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>RE :46%</td>
<td>RE :46%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Number of target S/A:72)</td>
<td>(Number of target S/A:72)</td>
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<tr>
<td>Matrix of Target</td>
<td></td>
<td>UO₂</td>
<td>UO₂</td>
<td>Al₂O₃</td>
<td></td>
<td></td>
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<tr>
<td>Pu Enrichment (wt%)/(IC/OC)</td>
<td>15.4</td>
<td>16.6</td>
<td>15.4</td>
<td>20.0</td>
<td>19.0</td>
<td>19.0</td>
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<td>/18.6</td>
<td>24.2</td>
<td>23.4</td>
<td>23.4</td>
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<td>Burnup Reactivity (%Δk/kk')</td>
<td>3.31</td>
<td>2.12</td>
<td>1.83</td>
<td>3.71</td>
<td>0.87</td>
<td>0.90</td>
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<td>Max. Linear Heat Rate (w/cm) (Driver/Target)</td>
<td>420</td>
<td>407</td>
<td>439/309</td>
<td>413</td>
<td>405/217</td>
<td>406/174</td>
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<tr>
<td>Na Void Reactivity</td>
<td>1.0</td>
<td>1.3*</td>
<td>1.3*</td>
<td>1.4*</td>
<td>1.5*</td>
<td>1.5*</td>
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<tr>
<td>Doppler Coefficient</td>
<td>0.6*</td>
<td>0.7*</td>
<td>0.5*</td>
<td>0.45*</td>
<td>0.45*</td>
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<td>MA Trar Amount (µg/cycle)</td>
<td>-</td>
<td>172</td>
<td>186</td>
<td>164</td>
<td>514</td>
<td>529</td>
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<tr>
<td>Rate (Core) (%/cycle)</td>
<td>-</td>
<td>10.9</td>
<td>11.3</td>
<td>10.3</td>
<td>13.9</td>
<td>14.0</td>
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<tr>
<td>Rate (Blanket) (%/cycle)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
<td>3.3</td>
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* Relative Value
Table 2  Effect of MA Recycling on Core Performance (Homogeneous Loading Method)

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<tr>
<th>Item</th>
<th>Reference (Initial Core)</th>
<th>4th Recycle</th>
<th>8th Recycle</th>
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<tr>
<td>MA (wt%)</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<tr>
<td>Pu Enrichment (wt%)</td>
<td>17.8 (Inner)</td>
<td>17.6 (Inner)</td>
<td>16.9 (Inner)</td>
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<tr>
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<td>21.6 (Outer)</td>
<td>21.3 (Outer)</td>
<td>20.4 (Outer)</td>
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<tr>
<td>Burnup Reactivity (%Δk/Δk')</td>
<td>1.6</td>
<td>0.4</td>
<td>0.5</td>
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<tr>
<td>Na Void Reactivity (Ref.)</td>
<td>1.0</td>
<td>0.96</td>
<td>0.93</td>
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<tr>
<td></td>
<td>(Relative Value)</td>
<td>(Relative Value)</td>
<td>(Relative Value)</td>
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<tr>
<td>Doppler Coefficient (Ref.)</td>
<td>1.0</td>
<td>1.08</td>
<td>1.14</td>
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<tr>
<td></td>
<td>(Relative Value)</td>
<td>(Relative Value)</td>
<td>(Relative Value)</td>
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<tr>
<td>MA Transmutation Rate (%)</td>
<td>10.3</td>
<td>10.5</td>
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</table>

Table 3  Dependence of ⁹⁹Tc transmutation performance on the number of FP pins in the 127-pin target assembly.

<table>
<thead>
<tr>
<th>No. of FP pins</th>
<th>Radius of FP pins (cm)</th>
<th>( V_{fp}/V_{mod} )</th>
<th>Transmutation Rate (%/y)</th>
<th>Transmuted ⁹⁹Tc amounts (kg/y)</th>
<th>Loaded ⁹⁹Tc amounts (kg)</th>
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<tbody>
<tr>
<td>52</td>
<td>0.5</td>
<td>0.69</td>
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<td>27</td>
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<td>22</td>
<td>0.5</td>
<td>0.17</td>
<td>2.5</td>
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</table>
Table 4  Difference of $^{99}$Tc transmutation performance on moderator material

<table>
<thead>
<tr>
<th>Moderator</th>
<th>Transmutation Rate(%/y)</th>
<th>Transmuted FP amounts(kg/y)</th>
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</thead>
<tbody>
<tr>
<td>ZrH$_{1.7}$</td>
<td>2.1</td>
<td>34.4</td>
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<tr>
<td>BeO</td>
<td>2.2</td>
<td>36.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.7</td>
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<tr>
<td>SiC</td>
<td>1.6</td>
<td>27.0</td>
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Table 5  Results of parameter survey calculations on $^{99}$Tc transmutation performance using duplex moderator pins.

<table>
<thead>
<tr>
<th>No.of duplex pins</th>
<th>FP pin Radius (mm)</th>
<th>Transmutation Rate(%/y)</th>
<th>Transmuted amounts(kg/y)</th>
<th>Loaded amounts(kg)</th>
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<tr>
<td>127</td>
<td>2.00</td>
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<tr>
<td>127</td>
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<td>217</td>
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<td>0.63</td>
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Fig. 1  Core layout and main parameters

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<tr>
<td>Shielding</td>
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</tbody>
</table>

**Volume Fraction**

**Reactor Power**: 1600MWth

**Core Height**: 100cm

**Axial bracket**: 35cm

**Core Diameter**: 275m

**Fuel Type**: MOX

**Pu Enrichment**: 15.30/18.90

**Pu composition**: 8/9/0/1/2

**Core Pitch**: 160.7mm
Fig. 2  
$^{99}$Tc pin arrangements in Target Assembly (based on 127-pin assembly)
Fig. 3 Neutron spectra in $^{99}\text{Tc}$ region for various moderator materials (27 FP pins in 127 pins model)
Fig. 4 Capture Rates in $^{99}$Tc region for various moderator materials
(27 FP pins in 127 pins model)
Fig. 5  Duplex pin arrangements in Target assembly  

(Radius of FP($^{99}$Tc) = 0.6mm or 2.0mm)
TRANSMUTATION OF TECHNETIUM IN THE PETTEN HFR:  
A COMPARISON OF MEASUREMENTS AND CALCULATIONS

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Abstract
Within the framework of the EFTTRA cooperation between CEA, ECN, EDF, FZK, IAM and ITU, six metallic \(^{99}\)Tc rods have been irradiated in the Petten HFR for 193 effective full power days. During this irradiation, more than 6\% of the \(^{99}\)Tc has been transmuted to the stable \(^{100}\)Ru. At ECN, one of the six rods has been examined in the hot cell laboratory. The ruthenium concentration in the rod measured by Isotope Dilution Mass Spectrometry reaches 6.4\% at 5 mm from the bottom of the rod and 6.0\% at 5 mm from the top. Also the axial and radial distributions of the ruthenium have been measured by Electron Probe Micro Analysis. The ruthenium concentrations calculated by the three-dimensional Monte Carlo code KENO reach 6.1\% at 5 mm from the bottom of the rod and 5.7\% at 5 mm from the top. These values are in reasonable agreement with the measured ones. However, the calculated radial distribution of the ruthenium concentration is not in agreement with the measurements. The radial profile calculated by the Monte Carlo code MCNP, which uses a point-wise cross-section library, agrees much better with the measurements. To solve the remaining small differences between the measured and calculated ruthenium concentrations in the rod, the thermal absorption cross section of \(^{99}\)Tc will be measured in the Petten HFR in the course of this year.
1 Introduction

The long-lived fission products $^{99}\text{Tc}$ and $^{129}\text{I}$ are among the most important nuclides that dominate the beta activity of spent fuel after a hundred thousands of years. Because of their high solubility in (ground)water, technetium and iodine are easily transported to the biosphere once they are released from the deep-geological waste repository. To reduce the dose risks to future generations, technetium and iodine should be partitioned from the spent fuel and treated separately, e.g. transmuted in nuclear reactors or conditioned by chemical immobilization.

In 1992, the EFTTRA collaboration (Experimental Feasibility of Targets for TRAnsmutation) was founded between CEA, ECN, EDF, FZK, IAM and ITU, with the aim to investigate experimentally the behaviour of targets during irradiation in fast and thermal nuclear reactors and to demonstrate the applicability of scenarios for the transmutation of long-lived fission products and minor actinides [1].

This paper describes the irradiation and the results of the Post Irradiation Examinations (PIE) of one $^{99}\text{Tc}$ rod irradiated in the Petten thermal High Flux Reactor (HFR) within the framework of the EFTTRA cooperation. During the irradiation, the long-lived $^{99}\text{Tc}$ is transmuted to the stable $^{100}\text{Ru}$. The measured ruthenium concentration and profiles are compared with results of three-dimensional Monte-Carlo calculations.

2 Target fabrication and Irradiation

Six metallic technetium rods of 4.8 mm diameter and 25 mm length were fabricated by ITU in Karlsruhe. Details of the fabrication method are described in reference [2]. The specific density was higher than 99.9% of the theoretical density. Analysis by glow-discharge mass spectrometry showed that the ruthenium concentration in the metal was less than 1 ppm. The rods were enclosed in stainless steel capsules (Phenix cladding material), provided by CEA. Each capsule contained two rods on top of each other.

The targets were positioned in peripheral holes of an aluminium sample holder. Three holes were occupied by the six $^{99}\text{Tc}$ rods (two rods on top of each other) and the other six holes were filled by iodine targets. The sample holder was placed in an aluminium filler element and loaded in the core position C5 of the Petten HFR. At this position, the total neutron flux in the targets exceeds $10^{15}$ cm$^{-2}$s$^{-1}$ with a thermal component higher than $2 \times 10^{14}$ cm$^{-2}$s$^{-1}$. Close to the technetium and iodine targets, fluence detectors ($^{59}\text{Co}$ and $^{56}\text{Fe}$) and gamma scan wires were located to monitor the thermal and fast neutron fluences. Also nine thermocouples were installed to measure the temperature of the facility. The geometry of the irradiation facility is shown in figure 1.

Fig. 1: Horizontal cross section of the irradiation facility surrounded by HFR fuel assemblies.
The irradiation lasted for eight cycles (192.95 effective full power days in total) and ended at the beginning of 1995. Due to gamma heating, the temperature of the rods exceeded 900 K. At the end of the irradiation, the thermal neutron fluence (E<0.7 eV) averaged over the technetium rods has reached a value of $3 \times 10^{21}$ cm$^{-2}$ and the total neutron fluence a value of $2 \times 10^{22}$ cm$^{-2}$.

3 Post Irradiation Examinations

A joint PIE programme has been defined by CEA, ITU and ECN for four rods, whereas the other two rods are being re-irradiated again in the Petten HFR to reach a transmutation level of 20%.

Visual inspection after the irradiation showed that almost no irradiation damage and no swelling has occurred. Measurements by means of a micrometer and micrographic examinations confirmed these conclusions. Results of these measurements are given in Table 1.

Table 1: Dimensions of some technetium rods before and after the irradiation in the Petten HFR [2].

<table>
<thead>
<tr>
<th>99Tc sample</th>
<th>Diameter (mm)</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-irr</td>
<td>post-irr</td>
</tr>
<tr>
<td>A</td>
<td>4.80±0.01</td>
<td>4.83±0.01</td>
</tr>
<tr>
<td>B</td>
<td>4.81±0.02</td>
<td>4.84±0.01</td>
</tr>
<tr>
<td>D</td>
<td>4.81±0.02</td>
<td>4.83±0.03</td>
</tr>
</tbody>
</table>

Electron Probe Micro Analysis (EPMA) has been used to measure the radial profiles of the ruthenium concentration at two intersections of rod D: one located at 5 mm from the bottom (section D1) and one at 5 mm from the top (section D2). These intersections are shown in figure 2. The EPMA method has also been used to measure the axial profile along the rod axis at intersection D3 (see figure 2). The absolute values of the ruthenium concentration at D1 and D2 have been measured by Isotope Dilution Mass Spectrometry (IDMS), which is expected to be more accurate for absolute measurements.

Table 1: Dimensions of some technetium rods before and after the irradiation in the Petten HFR [2].

The ruthenium concentration as a function of the cross-sectional area of the rod at intersection D1 is shown in figure 3. The two curves are the results of two measurements at different azimuthal angles perpendicular to each other. The vertical line at an area of 18.1 mm$^2$ denotes the outer edge of the rod with a diameter of 4.8 mm. The results at intersection D2 are very similar to the ones in figure 3 and shown in figure 4. In both figures, the so-called Rim effect caused by the resonance shielding of the neutrons is clearly visible. The difference between the profiles at the outer edge of the rod (area 18.1 mm$^2$) is most probably due to the position of the sample and the roughness of the surface of the rod.
The cross-sectional averaged ruthenium concentration measured by EPMA equals 7.2% at D1 and 6.8% at D2. However, as mentioned before, the EPMA method is not very accurate for absolute measurements. Therefore, two slices at each intersection D1 and D2 of the rod were dissolved in HNO3 and the ruthenium concentration in each slice was measured several times by IDMS. The results are given in table 2.

Table 2: Ruthenium concentrations at intersections D1 and D2 measured by Isotope Dilution Mass Spectrometry (IDMS).

<table>
<thead>
<tr>
<th>Slice</th>
<th>Ruthenium concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D1</td>
</tr>
<tr>
<td>1</td>
<td>6.39±0.15</td>
</tr>
<tr>
<td>2</td>
<td>6.39±0.24</td>
</tr>
<tr>
<td>Average</td>
<td>6.39±0.23</td>
</tr>
</tbody>
</table>

Fig. 3: The profile of ruthenium concentration at D1 as a function of the cross-sectional area of the rod. Vertical line denotes the outer edge of the rod.
The ruthenium concentration at D3 as a function of the axial distance in the rod is shown in figure 5. The average ruthenium concentration is about 5.4%. Although there is a large spread in the results, the slope of the linear least squares fit indicates a small gradient of the ruthenium concentration as a function of the axial distance. According to this fit, the difference between the ruthenium concentrations at the intersections D1 and D2 along the rod axis would be $5.54 - 5.30 = 0.24\%$. 
4 KENO Monte Carlo Calculations

To assess the accuracy of the calculational methods and of the nuclear data files used in technetium transmutation studies, calculations have been performed by the Monte Carlo code KENO-Va [3] and associated nuclear data libraries based on the JEF2.2 evaluated file [4].

The standard three-dimensional core model of the Petten HFR has been used, which implies that the control members are at a fixed representative position and that a single type experimental facility was used to fill the experimental positions in the HFR model. This is done because it is too cumbersome to change the core model from one cycle to the other. The influence of these assumptions on the results is probably very small, because the experiment itself, which was loaded at position C5, has been modelled accurately, including the details on the fluence detectors (foils) and the gamma scan wires. Also the three-dimensional fuel distribution has been correctly represented. Figure 6 shows a horizontal cross section of the HFR core model with the experiment loaded at position C5, and figure 1 shows the irradiation facility in more detail.

In the calculations, the resonance shielding for all nuclides have been performed by the NITAWL-II code [5] (Nordheim method) in the resolved energy region and by the BONAMI-S code [6] (Bondarenko method) in the unresolved energy region, except for $^{99}$Tc for which no resonance shielding in the unresolved region has been performed. This is due to the large background cross sections of $^{99}$Tc in the unresolved region which may lead to negative cross sections when the resonance shielding is too large. Because the total contribution of the unresolved region to the capture rate is only 6.5%, this has no large effect on the results.
Fig. 6: Horizontal cross section view of the HFR core model used in the calculations. The experimental facility is loaded at position C5 with (x,y) coordinates (55,73).

The calculations yield the integrated number of $^{54}\text{Fe}(n,p)$ and $^{59}\text{Co}(n,\gamma)$ reactions in the detector foils, the ruthenium concentration averaged over each of the two rods, the axially averaged radial distribution and the radially averaged axial distribution in the two rods.

The integrated number of $^{54}\text{Fe}(n,p)$ and $^{59}\text{Co}(n,\gamma)$ reactions in the detector foils are given in table 3. It is seen that the calculated neutron spectra at the detector positions are quite accurate. The two foils closest to the investigated technetium rod (numbers 6 and 7) give results within 7% for the fast $^{54}\text{Fe}(n,p)$ reaction and within 1% for the thermal $^{59}\text{Co}(n,\gamma)$ reaction.
Table 3: Calculated reactions in the $^{54}\text{Fe}$ and $^{59}\text{Co}$ detector foils and the associated C/E ratios.

<table>
<thead>
<tr>
<th>Detector foil</th>
<th>$^{54}\text{Fe}(n,p)$ C/E ratio</th>
<th>$^{59}\text{Co}(n,\gamma)$ C/E ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.84±0.10 1.02±0.02</td>
<td>3.67±0.05 1.03±0.02</td>
</tr>
<tr>
<td>2</td>
<td>4.80±0.10 1.01±0.02</td>
<td>3.66±0.05 1.02±0.01</td>
</tr>
<tr>
<td>3</td>
<td>4.89±0.10 1.03±0.02</td>
<td>3.63±0.06 0.97±0.02</td>
</tr>
<tr>
<td>4</td>
<td>4.94±0.10 1.05±0.02</td>
<td>3.67±0.05 1.01±0.01</td>
</tr>
<tr>
<td>5</td>
<td>5.10±0.10 1.08±0.02</td>
<td>3.69±0.06 1.01±0.01</td>
</tr>
<tr>
<td>6</td>
<td>5.05±0.10 1.07±0.02</td>
<td>3.57±0.05 1.00±0.01</td>
</tr>
<tr>
<td>7</td>
<td>4.86±0.10 1.03±0.02</td>
<td>3.58±0.05 1.01±0.01</td>
</tr>
<tr>
<td>8</td>
<td>5.02±0.10 1.05±0.02</td>
<td>3.63±0.05 1.01±0.01</td>
</tr>
<tr>
<td>9</td>
<td>5.06±0.10 1.07±0.02</td>
<td>3.57±0.05 0.99±0.01</td>
</tr>
<tr>
<td>Average</td>
<td>1.05±0.02</td>
<td>1.01±0.02</td>
</tr>
</tbody>
</table>

Fig. 7: The calculated ruthenium concentration as a function of the axial position in the rods. The dots indicate the measurement values at D1 and D2.
The axial distribution of the ruthenium concentration in the two rods calculated by the Monte Carlo code KENO is shown in figure 7 as a function of the axial position in the rods. Also the two measurement values at D1 and D2 are shown. The lower rod (0<z<25 mm) has been examined by ECN. The vertical bars at each interval denote one standard deviation due to the Monte Carlo process. Clearly the ruthenium concentration shows an axial gradient, but the volume averaged ruthenium concentration of the lower rod (5.92±0.05%) does not differ significantly from that of the upper rod (5.87±0.05%). These calculations support the measured axial gradient as shown in figure 5. The calculated ruthenium concentrations at intersections D1 and D2 have values of 6.10±0.11% and 5.72±0.10%, respectively, which are in reasonable agreement with the measured values given in table 2 (6.39±0.23% at D1 and 5.98% at D2).

The radial distribution of the ruthenium concentration averaged over the two rods in axial direction is shown in figure 8. Clearly, the calculated distribution is not in agreement with the EPMA measurements. Most probably, this is due to the resonance shielding method used in the resolved energy range. By use of the Nordheim method, pin-averaged group cross sections are calculated which conserve the total neutron absorption. However, due to resonance absorption, the group cross sections change as a function of the distance to the moderator-rod interface.

Fig. 8: Comparison of the measured and calculated profile in the rod. The measured curve is the average of the four curves shown in figures 3 and 4.
To demonstrate the inadequacy of the Nordheim resonance shielding method for these purposes, a simple one-dimensional model of the experiment has been defined and the radial distribution of the ruthenium concentration has been calculated by both the KENO and the MCNP-4A [7] Monte Carlo codes. The latter code uses a point-wise cross-section library also based on the JEF2.2 nuclear data file. The results are shown in figure 9, where the radial distribution of the ruthenium concentrations normalized to the same value are shown together with the results of the EPMA measurements. Clearly, the MCNP results are in much better agreement with the measurements than the KENO results, due to the point-wise sampling of the cross sections. It is emphasized, however, that the model used in this benchmark is only a simple one-dimensional mockup of the actual experiment. Therefore, the differences between the KENO and MCNP results are meaningful, while the (small) differences between the calculations and the EPMA measurements may be due to the simplified geometry.

Fig. 9: The radial profile of the ruthenium concentration calculated by KENO, MCNP and measured by EPMA.
Conclusions

Six metallic $^{99}\text{Tc}$ rods have been irradiated in the Petten thermal High Flux Reactor with a total neutron fluence of $2 \times 10^{22} \text{cm}^{-2}$. About 6% of the $^{99}\text{Tc}$ has been transmuted to the stable $^{100}\text{Ru}$.

The absolute ruthenium concentrations in the rod have been measured by Isotope Dilution Mass Spectrometry, and the radial and axial profiles of the ruthenium concentration have been measured by Electron Probe Micro Analysis (EPMA). The measured ruthenium concentration in the rod ranges from 6.4% at 5 mm from the bottom of the rod (intersection D1) to 6.0% at 5 mm from the top (intersection D2).

Calculations have been performed by the group-wise Monte Carlo code KENO in a detailed three-dimensional model of the HFR core. The calculated ruthenium concentrations of 6.1% at intersection D1 and 5.7% at D2 are in reasonable agreement with the measurements. This shows the validity of the HFR core model and of the cross sections used.

The group-wise Monte Carlo code KENO in combination with the cross-section generation code NITAWL-II (Nordheim resonance shielding method) cannot be used to calculate accurately the radial distribution of the ruthenium concentration in the rods. A Monte Carlo code using point-wise cross sections like MCNP appears to give much better results.

Further work on the transmutation of $^{99}\text{Tc}$ consists of the re-irradiation of two $^{99}\text{Tc}$ rods in the Petten HFR up to a transmutation level of 20%, and the measurement of the thermal absorption cross section. According to reference 8, the thermal capture cross section of $^{99}\text{Tc}$ is 10 to 15% higher than the value in the JEF2.2 evaluated nuclear data file (about 19 barn).

References

STUDIES ON ACCELERATOR-DRIVEN TRANSMUTATION AT JAERI

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Abstract

Research and development on intense proton accelerator-driven transmutation of long-lived radioactive nuclides are being carried out at the Japan Atomic Energy Research Institute (JAERI) under the Japanese long-term program for research and development on nuclide partitioning and transmutation technology, called the OMEGA Program. In the conceptual design study of transmutation system, two options of solid system and molten-salt system have been pursued as dedicated transmutation systems with hard neutron spectrum and high neutron flux. Spallation integral experiments are being made on a lead assembly with 500 MeV proton beam to validate and improve the cascade code NMTC/JAERI. Front-end components for the prototype intense proton accelerator such as ion source, RFO, DTL, and RF source were developed and tested successfully. JAERI is proposing the development of an intense proton linear accelerator of 1.5 GeV class with a maximum beam power of around 10 MW for tests in accelerator-driven transmutation technology and various experiments in basic sciences. The project of the accelerator-based research complex is expected to be launched in 1997 with conceptual designs of the accelerator and research facilities.
1. Introduction

Under the framework of the Japanese long-term research and development program on nuclide partitioning and transmutation (P-T) technology, called the OMEGA Program, the Japan Atomic Energy Research Institute (JAERI) is carrying out R&Ds on P-T [1,2]. The OMEGA Program is aiming at establishing P-T technologies to provide an attractive option for high-level waste (HLW) management in the future. The technologies under study include an advanced partitioning to separate HLW into four element groups [3], transmutation with actinide burner reactor [4], and transmutation with accelerator-driven system. The proposed transmuters are dedicated systems specifically designed for nuclear waste transmutation purpose. With dedicated transmuters, the fuel cycle for P-T can be separated completely from the conventional commercial fuel cycle for power reactors, forming a double strata structure of nuclear fuel cycle [5].

The project on accelerator-driven transmutation technology at JAERI includes the conceptual design study of transmutation plants, the development of spallation simulation code system [6], the spallation integral experiment [7], and the development of a high-intensity proton linear accelerator [8].

In the conceptual design study of accelerator-based transmutation plant, two types of dedicated system concepts are being investigated; solid system and molten-salt system. The design of the solid system is based on the current technology and design practice for sodium-cooled fast breeder reactors. Another option is the molten-salt system with flowing actinide chloride that plays three principal roles of as fuel, target material, and coolant. Its main advantage is the capability of continuous on-line processing of actinides and reaction products.

JAERI is proposing the development of an intense proton linear accelerator for tests in accelerator-driven transmutation technology together with various experiments in basic sciences. The project is called the Neutron Science Project. The proposed accelerator will be of 1.5 GeV class with a final beam power of around 10 MW. It will share the beam among research facilities, which altogether form an accelerator-based research complex.

This paper describes the conceptual designs of accelerator-driven solid system and molten-salt system for nuclear waste transmutation. Outline of the program plan of tests in accelerator-driven transmutation is presented.

2. Accelerator-Driven Transmutation System

JAERI is aiming to develop technologies of an advanced partitioning process of transuranic elements (TRUs) and long-lived fission products from HLW and dedicated systems for their subsequent transmutation. The dedicated transmutation system is specially designed to burn minor actinides (MAs) efficiently in a very hard neutron energy spectrum and high neutron flux.

In this context, JAERI has been pursuing feasible concepts of accelerator-driven system as dedicated transmuters to be introduced in the second stratum (P-T fuel cycle) of the double strata fuel cycle. The concept of the double strata fuel cycle is schematically depicted in Fig. 1.

In the conceptual design study of accelerator-driven transmutation plant, two types of system concepts are being investigated. One is the solid target/core system consisting of tungsten target and solid fuel core cooled by liquid sodium. Mononitride fuel is selected mainly on the basis of its good thermal performance and adaptability of dry reprocessing. The design of the solid system is based on the current technology and design practice for sodium-cooled fast breeder reactors.

Another advanced option is the molten-salt system with flowing chloride fuel. The molten-salt fuel also serves as target material and as coolant. One of the main advantages of fluid fuel is the capability of continuous on-line processing of actinides and reaction products. Chloride salt is selected mainly on the basis of actinide solubility.

2.1 Solid System

The design of the solid target/core system is based on the state of the art of technology for a sodium-cooled fast breeder reactor. An accelerator injects proton beam through a beam window into the solid tungsten target located at the center of the target/core. Surrounding the target is the subcritical core loaded with actinide nitride fuel. Spallation neutrons emitted from the target induce further fission in the actinide core region.

The target consists of multiple layers of tungsten disk with through holes for coolant passage. The target is designed to maximize the number of emitted neutrons and to flatten the shape of axial distribution of
neutron flux. The coolant holes are arranged to stagger from layer to layer to avoid the possibility of direct penetration of high energy particles through the target.

The target/core is surrounded by reflectors made of stainless steel. The target and fuel subassemblies are cooled by forced upward flow of primary sodium. The whole target/core including reflectors is contained within a target/core vessel made of steel as shown in Fig. 2. The target/core is of loop type configuration, having two sodium primary loops. A vertical duct for beam path is inserted into the target/core vessel down to just above the target region. The bottom end of the duct is the hemispherical beam window made of oxide dispersion strengthened (ODS) steel. The beam window is cooled by impinging coolant flow from the target exit.

Mononitride of minor actinides is used as fuel in the design of the solid system. Nitride fuel has advantages of a high thermal conductivity around 15 W/m/K and a high melting point around 3100 K. This excellent thermal performance permits a high linear rating and high power density, leading to a high transmutation rate. It also results in a low fission gas release.

High atom density of actinides is beneficial to achieve a hard neutron energy spectrum. This is also preferable to realize a dense fuel cycle for the second fuel cycle stratum, where actinides are maintained in a high concentration throughout the whole cycle [9]. The mutual miscibility of actinide mononitrides also leads to the fuel design of high concentration of actinide elements and simplifies the process of fuel fabrication. For reprocessing, an innovative fuel cycle combined with molten-salt electrorefining will be available in the case of nitride as well as metallic fuel.

With a 1.0 GeV-22 mA incident proton beam, the target/core having an effective neutron multiplication factor of 0.927 produces 360-MW thermal power. The net MA transmutation rate is approximately 110 kg per year, or 9.7%/y, at a load factor of 80%.

Heat transport and power conversion systems in the plant design are similar to those for a sodium-cooled fast breeder reactor plant. The heat generated in the target/core is transported through the primary and the secondary sodium loops to the power conversion system. In the energy conversion system, thermal energy is converted into electricity through conventional steam turbine. A part of electric power is supplied to its own accelerator.

Major parameters of the nitride fuel solid system are summarized in Table 1. Further study is needed to detail and optimize the system design, taking full advantage of the excellent thermal performance of nitride fuel.

2.2 Molten-Salt System

A conceptual design study is being performed on a molten-salt target/core system as an advanced option for an accelerator-based transmutation system. Figure 3 schematically shows the proposed molten-salt system concept. Chloride salt with a composition of 64NaCl-5PuCl3-31MACl3 is chosen as the fuel for its sufficiently high actinide solubility. The molten-salt fuel serves also as target material and as coolant. This eliminates the physical and functional separation of target and core, and thus significantly simplifies the target/core configuration.

One of the attractive features of the molten-salt fuel is the possibility of continuous fuel feed and on-line processing of reaction product removal.

The target/core is designed for 800-MW thermal power. Proton beam at 1.5 GeV is injected vertically into the central target/core region through the beam window. The target/core region is surrounded by an internal reflector. Intermediate heat exchangers and salt pumps are installed in the annular region around the internal reflector to reduce radiation damages. The intermediate heat exchangers are of compact type with plate-and-fin configuration, where heat in the primary sodium loops is transferred to the secondary fluid of molten fluoride salt.

In the fluid fuel system, the heat removal problem usually appears in the intermediate heat exchangers than in the core itself. External shell-and-tube type heat exchangers of conventional design would require a large volume, leading to an unacceptably high actinide inventory and low transmutation rate for a dedicated transmutation system. In the present design, highly efficient compact type heat exchangers are incorporated within a reactor vessel. This in-vessel heat exchanger arrangement minimizes the total volume of the primary system and thus the total actinide inventory.

Another leading candidate fuel for a fast spectrum molten-salt system is PbCl2-3AnCl3 (An: actinide). A preliminary nuclear calculation was made for the lead-based molten-salt system with the same geometry and dimensions as the sodium-based molten-salt system. The energy of incident proton is 1.5 GeV. Table 2 lists the calculated results in comparison with the sodium-based salt system.

A comparison is also made for two candidate molten salts from the point of thermal-hydraulics design view.
Primary flow cross section area $S$ in a heat exchanger can be estimated from the Blasius equation $f = 0.3164 \ Re^{-0.25}$ for friction and the Dittus-Boelter equation $Nu = 0.023 \ Re^{0.8} \ Pr^{0.4}$ for heat transfer, where $f$ = friction factor, $Nu$ = Nusselt number, $Re$ = Reynolds number, $Pr$ = Prandtl number. In case when the maximum fluid velocity is a limiting factor in the design, $S$ is expressed as

$$S = c \left( \frac{d Q \lambda}{\Delta \theta A} \right) Re^{-3} Pr^{-4},$$

where $d$ = hydraulic diameter of the flow channel, $Q$ = thermal power exchanged, $\lambda$ = thermal conductivity, $\Delta \theta$ = temperature drop through heat exchanger. It is noted that $S$ is independent on the temperature difference between primary and secondary coolants. Assumptions were made that the maximum fluid velocity is limited by the pressure drop and the dynamic pressure in the primary system and the viscosity, thermal conductivity, and thermal capacity of the fluid are constant. Under these assumptions, $S$ becomes proportional to the square root of the fluid density $\rho$. For other primary flow cross sections, the same relation holds if the pressure drop and dynamic pressure are to be unchanged. This results in the relation that the total volume of the primary system varies as $\rho^{1/2}$.

Table 3 compares system parameters of the sodium-based molten-salt system and those of the corresponding lead-based molten-salt system. The total inventory of the lead-based salt in the system is about 65% larger due to its higher fluid density than that of sodium-based salt, but the actinide inventory is about 25% smaller. The comparison is preliminary since reliable data of thermodynamic and transport properties are lacking for lead-based salt.

3. Spallation Integral Experiment

In the design study of accelerator-based transmutation system, a nucleon meson transport code, NMTC/KAERI is used to simulate nuclear reactions and the particle transport in the energy range above 15 MeV. To estimate and validate the accuracy of the code system, a spallation integral experiment using a large scale lead assembly is in progress. The lead assembly is bombarded with 500 MeV protons at the booster synchrotron facility of the National Laboratory for High Energy Physics (KEK).

The lead assembly was 60 cm in diameter and 100 cm in length. The protons were injected through the beam entrance hole into the target of 16 cm in diameter and 30 cm in length installed in the assembly. The target is made of lead or tungsten alloy. High purity metal activation samples of Al, Fe, Ni, Cu and Au were inserted into irradiation holes drilled parallel to the beam axis in the assembly at various radial distances. The gamma-ray spectrometry was used to obtain yields of the nuclides produced in the samples.

Neutron energy spectrum from thick lead target and nuclide yield distributions of various threshold reactions in a lead assembly were measured in the experiment. In general, the calculation with the codes NMTC/KAERI and MCNP4.2 was agreed fairly well with the experimental results.

There are however some discrepancies in both the nuclide production cross section and the neutron energy spectrum, requiring further improvements in the calculation model. Comparison of the yield of proton induced spallation products is planned in the next step in the integral spallation experiment to validate the accuracy of the NMTC/KAERI prediction.

4. Intense Proton Accelerator and Transmutation Test Facility

JAERI is proposing the development of an intense proton accelerator for tests in accelerator-driven transmutation technology together with various experiments in basic sciences. The plan called the Neutron Science Project is aiming at the scientific and technological innovation for the 21st century using neutrons. The study on accelerator-driven transmutation and the development of an intense proton accelerator are under way as the important part of the Project. The proposed accelerator will be of 1.5 GeV class with a beam power around 10 MW and employ superconducting linac in the high-energy portion. It will share the beam among research facilities, comprising an accelerator-based multi-purpose research complex.

To develop intense accelerator technology, R&D work has been carried out for the accelerator components for the front-end part: ion source, radiofrequency quadrupole (RFQ), a drift tube linac (DTL), and RF source. Prototype components of the ion source, RFQ, and RF source have been developed and tested successfully. The design study for an intense proton accelerator is also underway and efforts are focused on a superconducting
accelerating cavity as a main option for the high-energy portion above 100 MeV. The superconducting linac has attractive features for a high-intensity accelerator such as shorter length acceleration, large bore radius resulting in low beam losses and possible cost reduction in the construction and operation. A test stand equipped with cryogenics system, vacuum system, RF system and cavity processing and cleaning is being prepared to test the physics issues and fabrication process.

The preconceptual study for the transmutation experimental facility started in the late 1995. The experimental program is to be proceeded in two steps. The first step will be the feasibility study of the hybrid system concept with a spallation target and a uranium subcritical system at a low power level with a pulsed beam. The experiments will demonstrate the stable operation of a hybrid system and MA burnup with use of MA foils or pellets. It will provide and verify the database for the development and design of a test reactor facility in the second step.

In the second phase, a test reactor facility will be constructed to perform tests of integrated target/core system at a moderate thermal power level of 10-30MW with a CW beam. Transmutation capability of the hybrid system will be tested using MA target pins. These system level tests will demonstrate the technical viability of the accelerator-based transmutation system. Technical feasibility of spallation target and beam window will be also tested at a high beam power in the second step experiments. These experiments are expected to open up possibility for the development of a future nuclear option of accelerator-driven system for not only waste transmutation but also energy production and fuel breeding.

The JAERI Neutron Science Project of the accelerator-based research complex is planned to start in 1997 with conceptual design of the intense proton accelerator, transmutation test facility, and other research facilities. Construction will be started around 1999. Operation with 1.5-MW beam power is expected to begin as early as 2003, and upgrading up to the full beam power around 10 MW will be completed in 2006.

5. Summary

The conceptual designs of accelerator-driven solid system and molten-salt system for nuclear waste transmutation were presented in this paper together with brief outline of the program plan of tests in accelerator-driven transmutation technology.

JAERI accelerator-driven transmutation project is being proceeded under the Japanese long-term R&D program on P-T technology, called OMEGA. In the conceptual design study, both solid system and molten-salt system are being pursued as dedicated transmuters to be introduced in the second stratum of the proposed double stratum fuel cycle system.

In either system, an MA-loaded subcritical core is driven by a high-intensity proton accelerator and makes use of hard neutron energy spectrum to transmute MAs efficiently by fission. The design of the solid system is based on the status of liquid-metal fast reactor technology, whereas the design of the molten-salt system relies on the next generation technology.

The solid system employs actinide mononitride fuel that has several favorable features as fuel for dedicated transmutation systems in the intense proton stratum fuel cycle. Its main advantages are excellent thermal performance and high atom density of actinides. It is expected that further improvement in the transmutation performance can be achieved by taking full advantage of the excellent thermal performance of nitride fuel.

The molten-salt system employs flowing chloride salt fuel which also acts at the same time both as target material and as coolant. The fuel salt selected for the reference design is NaCl-AnCl$_3$. Another leading candidate salt is PbCl$_2$-AnCl$_3$. A preliminary comparative nuclear and thermal-hydraulics design study was made for these two compositions of fuel salts. Results obtained seems to be not conclusive mainly due to the lack of reliable property data for PbCl$_2$-AnCl$_3$.

JAERI is proposing the development of an intense proton linear accelerator with a beam power of around 10 MW for tests in accelerator-driven transmutation technology together with various experiments in basic sciences. The preconceptual study for the transmutation test facility was initiated recently. The project is planned to start in 1997 with conceptual design of the accelerator and research facilities. Operation with 1.5-MW beam power is expected to begin as early as 2003, followed by gradual upgrading to the full beam power around 10 MW.
References

### Table 1 Major Parameters of Nitride Fuel Solid System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>Mononitride (90MA-10Pu)N</td>
</tr>
<tr>
<td></td>
<td>MA: Np, Am, Cm</td>
</tr>
<tr>
<td>Target</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Actinide Core Height</td>
<td>800 mm</td>
</tr>
<tr>
<td>Target/Core Volume</td>
<td>0.06/0.35 m³</td>
</tr>
<tr>
<td>Actinide Inventory</td>
<td>1150 kg</td>
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<tr>
<td>Neutron Multiplication Factor</td>
<td>0.927</td>
</tr>
<tr>
<td>Proton Beam, Energy - Current</td>
<td>1.0 GeV - 22 mA</td>
</tr>
<tr>
<td>Average Neutron Flux</td>
<td>$5.2 \times 10^{13}$ n/cm²/s</td>
</tr>
<tr>
<td>Power Density Average/Maximum</td>
<td>1020/1600 MW/m³</td>
</tr>
<tr>
<td>Thermal Power</td>
<td>360 MW</td>
</tr>
<tr>
<td>Burnup</td>
<td>110 kg/y (9.7 %/y)</td>
</tr>
<tr>
<td>Coolant Temperature Inlet/Outlet</td>
<td>663/793K</td>
</tr>
<tr>
<td>Clad Temperature, Maximum</td>
<td>988 K</td>
</tr>
<tr>
<td>Fuel Temperature, Peak</td>
<td>1440 K</td>
</tr>
</tbody>
</table>

### Table 2 Neutronics of Na-based Salt and Pb-based Salt Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Neutron Multiplication Factor</th>
<th>Spallation Neutron Yield (n/p)</th>
<th>Average Neutron Energy * (keV)</th>
<th>Power Density (keV/cm²/p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64NaCl-36AnCl₃</td>
<td>0.93</td>
<td>37</td>
<td>800</td>
<td>27</td>
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<tr>
<td>70PbCl₂-30AnCl₄</td>
<td>0.88</td>
<td>40</td>
<td>768</td>
<td>16</td>
</tr>
</tbody>
</table>

* averaged over target/core region, excluding IHX region.

### Table 3 Property and System Parameters for Na-based Salt and Pb-based Salt

<table>
<thead>
<tr>
<th>System</th>
<th>Fluid Density (kg/m³ at 923K)</th>
<th>Melting Point (K)</th>
<th>Primary System Volume (m³)</th>
<th>Molten-Salt Inventory (kg)</th>
<th>Actinide Inventory (kg)</th>
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</thead>
<tbody>
<tr>
<td>64NaCl-36AnCl₃</td>
<td>3800</td>
<td>~726</td>
<td>2.7</td>
<td>10,000</td>
<td>5,400</td>
</tr>
<tr>
<td>70PbCl₂-30AnCl₄</td>
<td>5300</td>
<td>~783</td>
<td>3.2</td>
<td>17,000</td>
<td>4,100</td>
</tr>
</tbody>
</table>
First Stratum of Fuel Cycle
(Commercial Power Reactor Fuel Cycle)

Second Stratum of Fuel Cycle
(P-T Cycle)

Fig. 1 Double-stratum fuel cycle
Fig. 2 Accelerator-driven nitride fuel solid target/core system

Fig. 3 Conceptual drawing of molten-salt target/core system
A Study on the Transmutation Capability of Accelerator Driven System

Won Seok Park, Hee Sung Shin, Tae Yong Song
Korea Atomic Energy Research Institute

A preliminary investigation was performed to evaluate the capability of accelerator driven thermal neutron system for the transmutation of minor actinides and fission products. Although the accelerator driven thermal neutron system was introduced long before by LANL, there has not been that much of research on minor actinide and fission product burning. LANL has focused its research mainly on the plutonium destruction.

For the analysis, 1GeV, 20mA proton linac was employed and the LAHET code developed by LANL was adopted for the simulation. The systems are molten salt fluoride with graphite moderator and in order to keep the system subcriticality 0.95, the ratio of plutonium to MA was adjusted. For the depletion calculation, ORIGEN2 code was used and systemwise one group cross section was generated by HMCNP.

The system was believed to have the neutronic characteristics something between LWR and FBR. The system was found to have about 14 %/yr transmutation rate for MA with a capacity factor 0.8. However it showed negligible capability for FP.
I. Introduction

Korea Atomic Energy Research Institute (KAERI) has performed a transmutation research since the middle of 1992. It had finished its first stage research in July of 1996 and obtained the tentative conclusion on its future transmutation research direction.

KAERI tried to estimate which option would be the optimal transmutation technology among LWR, FBR, accelerator-driven subcritical reactor concepts. The estimation works were done by evaluating the transmutation capability, the technical feasibility, the resistance to NPT (the possibility of commercialization), the safety, the economical advantages of each concept. A spent fuel problem is not the problem of one or two countries any more. It is the problem of world because nuclear power has been a worldwide energy source. In order to solve that worldwide problem, the technology to be developed should have something that any country can access and employ. From those points of view, weightings were assigned to the NPT resistance, transmutation capability, safety, technical feasibility, economical benefits in descending order. As results, the optimal concept was determined to be an accelerator driven subcritical reactor.

The detail neutronic analysis for an accelerator driven system will be done throughout the second stage research period from 1996 to 1999. No specific design parameters were determined yet. As a starting point, the thermal neutron system with molten salt fuel was selected. In this paper, some basic results obtained from the preliminary studies on the selected system was presented.

II. System Model Description

A program called KOMAC(KOrea Multipurpose linear ACcelerator) is under planning to build 1.0 GeV, 20mA linear proton accelerator in KAERI. KOMAC will be developed in a way to be applicable to transmutation. The proton beam of 1GeV, 20 mA was assumed for the spallation calculation. Basic concepts for the thermal system were derived from the ATW designed by LANL. Fig. 1 shows the schematic layout of the subcritical blanket and Table 1 represents the material specifications of the system. Lead target with the diameter 75cm and the height 100 cm was employed to get the neutrons induced by spallation reaction and graphite was adopted for neutron moderation. Because of very low solubility of TRU in molten fluoride, 1.0 mol% of TRU was assumed and the chemical form of fuel was 66LiF-33BeF$_2$-1(TRU)F$_4$. The reason using fluoride instead of chloride is to enhance the neutron moderation. The operating temperature was assumed to be 650°C and the physical density of molten salt was at the operating temperature. Because a thermal neutron is the most effective tool for fission product burning, a couple of sites were assigned for fission product incineration in the graphite region.

III. Calculational Methodology

LCS(LAHET code system) developed by LANL was employed to perform the neutronic analysis in the sample model. LAHET and HMCNP are the main codes in LCS.[1] Fig. 2 shows the input-output flow between codes. By adjusting the amount of Pu in total TRU, the subcriticality was kept to be 0.95. LAHET code analyzes the spallation reactions and deals with high energy neutrons(>20MeV).[2] LAHET provides HMCNP with a sort of fixed external neutron sources(energy and location). HMCNP performs the calculation of neutron flux and thermal power in the blanket.[3] HMCNP generated one group, corewise cross sections to be used for the calculation of transmutation capability using ORIGEN2.[5]

IV. Results

By using the kcode function in MCNP code, the nuclide composition of TRU to keep the system subcriticality 0.95 was searched. In that condition, the nuclide composition of Pu and MA was found to be 72:28 and the loading amount of MA was 775 kg.

The isotope composition of lead target was that of natural lead(Pb-204:Pb-206:Pb-207:Pb-208=2:24:22:52). The neutron production rate depends on the isotope composition and the size of the target. The more stable the nuclide is, the less the neutron production rate is. The neutron production rate was 34n/p in the proposed system and Fig. 3 shows the number of neutrons produced by the spallation reaction versus its energy. The figure shows that the most of spallation neutrons have the energy ranging from 2MeV to 10 MeV which is much higher than the fission neutron energy. A considerable amount of heat is generated by spallation reaction. In the proposed model, 1.3MW was deposited in the target.
As it is expected, maximum flux occurs at the target region. The average neutron flux in the target is about 80 ~ 90 times higher than that of blanket while the neutron flux of the reflector is 10 times less than that of blanket. Table 2 gives the neutronic parameters generated. For a given condition, the system produced the thermal power of 967 MW. Fig.4, 5 show the neutron energy spectrum in the blanket, and graphite region, respectively. In order to evaluate the transmutation capability, one group cross sections for 21 actinides and 17 fission product nuclides were produced using the average neutron energy spectrum in the blanket and reflector region, respectively. Table 3, 4 represent the transmutation capability of the system for actinides and fission products, respectively. The proposed system is supposed to transmute MA with the rate of 14%/yr when a capacity factor is assumed to be 0.8. On the other hand, it has negligible capability for fission product burning.

V. Discussion and Conclusion

A preliminary calculation was done to evaluate the neutronic performance of the accelerator driven thermal neutron system. Because the criticality of the system was 0.95, about 5% of neutrons were come from the spallation reaction. Therefore the average source neutron energy is supposed to be somewhat higher than the fission neutron energy. In addition, the moderator was positioned in a way to surround the blanket like a reflector. Such an array can not moderator the high energy neutron efficiently. As results, the neutron energy spectrum of the system was found to be something between LWR and FBR. Epithermal neutron can be suggested to be more effective for the transmutation. It might be true for some nuclides but not for some others. Table 5 shows one group absorption cross sections of some important long lived fission products. This table tells that the proposed system is more efficient for burning I-129 while LWR is for Te-99. The system was believed to have a considerable capability for MA transmutation. On the other hand, it had negligible for fission products. The main reason for that was due to the difference in the neutron flux. Therefore FP burning sites should be moved to somewhere a high neutron flux can be obtained. As it is known, a thermal neutron has an advantage of higher MA transmutation capability and a disadvantages of producing lots of higher actinides while a fast neutron has a reverse characteristics. Further detail studies should be done to decide which neutron is more efficient for the transmutation. Also some attention has to be paid on the definition of the transmutation when only MA is considered to be transmuted. In other words, it has to be answered whether it is transmutation or not when Np-237 is transformed to Pu by the successive absorption.

References

### Table 1 Material Specifications for the proposed system

<table>
<thead>
<tr>
<th>Component</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>• Material: Lead</td>
</tr>
<tr>
<td></td>
<td>• Density: 11.34 g/cm(^3)</td>
</tr>
<tr>
<td>Fuel</td>
<td>• Chemical Form: Molten Salt (66LiF-33BeF(_2)-(TRU)F(_4))</td>
</tr>
<tr>
<td></td>
<td>• Density: 2.06 g/cm(^3)</td>
</tr>
<tr>
<td></td>
<td>• TRU Composition: Pu/MA = 72/28</td>
</tr>
<tr>
<td>Moderator</td>
<td>• Material: Natural Graphite</td>
</tr>
<tr>
<td>Target and Blanket Container</td>
<td>• Material: HT-9</td>
</tr>
<tr>
<td></td>
<td>• Density: 7.75 g/cm(^3)</td>
</tr>
<tr>
<td></td>
<td>• Composition: Fe: Ni: Cr: Mo: Mn = 67.50:11.25:17.0:2.25:2.0 (at./wt.%)</td>
</tr>
</tbody>
</table>

### Table 2 Some Neutronic Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Target Region</th>
<th>Blanket Region</th>
<th>Graphite Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spallation Neutron</td>
<td>34 n/p</td>
<td>negligible</td>
<td>negligible</td>
</tr>
<tr>
<td>Avg. Flux (10(^{15})n/cm(^2)·sec)</td>
<td>656.0</td>
<td>8.2</td>
<td>0.88</td>
</tr>
<tr>
<td>Thermal Power</td>
<td>4.8</td>
<td>966.6</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### Table 3 Transmutation Rate for MA

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Loading Amount</th>
<th>After-30-days</th>
<th>Amount(^{a}) (kg/yr)</th>
<th>Rate(^{b}) (%/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{239})Np</td>
<td>3.419E+02</td>
<td>3.296E+02</td>
<td>-1.476E+02</td>
<td>-43</td>
</tr>
<tr>
<td>(^{238})Np</td>
<td>0.000E+00</td>
<td>1.231E+00</td>
<td>1.477E+01</td>
<td>-</td>
</tr>
<tr>
<td>(^{237})Pu</td>
<td>3.062E+01</td>
<td>4.13E+01</td>
<td>1.321E+02</td>
<td>431</td>
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<tr>
<td>(^{236})Pu</td>
<td>1.155E+03</td>
<td>1.113E+03</td>
<td>-5.04E+02</td>
<td>-44</td>
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<tr>
<td>(^{240})Pu</td>
<td>5.269E+02</td>
<td>5.335E+02</td>
<td>7.92E+01</td>
<td>15</td>
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<tr>
<td>(^{241})Pu</td>
<td>1.701E+02</td>
<td>1.715E+02</td>
<td>1.680E+01</td>
<td>10</td>
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<tr>
<td>(^{243})Pu</td>
<td>9.945E+01</td>
<td>1.016E+02</td>
<td>2.580E+01</td>
<td>26</td>
</tr>
<tr>
<td>(^{241})Am</td>
<td>3.710E+02</td>
<td>3.473E+02</td>
<td>-2.844E+02</td>
<td>-77</td>
</tr>
<tr>
<td>(^{242})Am</td>
<td>0.000E+00</td>
<td>9.869E+00</td>
<td>1.184E+02</td>
<td>-</td>
</tr>
<tr>
<td>(^{243})Am</td>
<td>0.000E+00</td>
<td>4.311E+01</td>
<td>5.173E+00</td>
<td>-</td>
</tr>
<tr>
<td>(^{243})Am</td>
<td>6.119E+01</td>
<td>5.492E+01</td>
<td>-7.52E+01</td>
<td>-123</td>
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<tr>
<td>(^{242})Cm</td>
<td>0.000E+00</td>
<td>1.038E+01</td>
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<tr>
<td>(^{243})Cm</td>
<td>1.950E-01</td>
<td>2.144E-01</td>
<td>2.328E-01</td>
<td>119</td>
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<tr>
<td>(^{244})Cm</td>
<td>1.147E+01</td>
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<td>9.744E+01</td>
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<td>(^{245})Cm</td>
<td>6.290E-01</td>
<td>1.062E+00</td>
<td>5.196E+00</td>
<td>826</td>
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<tr>
<td>U</td>
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<td>3.04E-02</td>
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<td>Np</td>
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<td>Pu</td>
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<td>Am</td>
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<td>Cm</td>
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<tr>
<td>MA*</td>
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<tr>
<td>TRU**</td>
<td>2.768E+03</td>
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<tr>
<td>ACT***</td>
<td>2.768E+03</td>
<td>2.736E+03</td>
<td>-3.914E+02</td>
<td>-14</td>
</tr>
</tbody>
</table>

* Total minor actinide nuclides, ** Total transuranium nuclides, *** Total actinide nuclides.  
\(^{a}\) (loading amount - after-30day amount) \* 365/30.  
\(^{b}\) (transmutation amount/loading amount) \* 100.
### Table 4 Transmutation Rate of Fission Products

(单位：kg, kg/yr)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Loading Amount</th>
<th>After-1-year Amount</th>
<th>Amount(^a) (kg/year)</th>
<th>Rate(^b) (%/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{99})Tc</td>
<td>2.60E+02</td>
<td>2.59E+02</td>
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<tr>
<td>(^{100})Ru</td>
<td>0.00E+00</td>
<td>5.64E-01</td>
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<tr>
<td>(^{127})I</td>
<td>1.51E+01</td>
<td>1.51E+01</td>
<td>-2.00E-02</td>
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</tr>
<tr>
<td>(^{138})Xe</td>
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<td>1.63E-02</td>
<td>1.63E-02</td>
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<tr>
<td>(^{129})I</td>
<td>4.87E+01</td>
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<tr>
<td>(^{138})Xe</td>
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<tr>
<td>(^{133})Cs</td>
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<td>7.43E-02</td>
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</tr>
<tr>
<td>(^{134})Ba</td>
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<td>1.32E-02</td>
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<tr>
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<td>-4.00E-03</td>
<td>-0.05</td>
</tr>
<tr>
<td>(^{134})Ba</td>
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<td>4.49E-03</td>
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<tr>
<td>(^{137})Cs</td>
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<td>Ru</td>
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<td>6.56E+01</td>
<td>-6.20E-01</td>
<td>-0.94</td>
</tr>
<tr>
<td>Ba</td>
<td>0.00E+00</td>
<td>6.22E-01</td>
<td>6.22E-01</td>
<td>-</td>
</tr>
<tr>
<td>Total LLFP*</td>
<td>3.90E+02</td>
<td>3.90E+02</td>
<td>-3.62E-02</td>
<td>-0.01</td>
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<tr>
<td>Total FP*</td>
<td>3.90E+02</td>
<td>3.90E+02</td>
<td>-3.62E-02</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

* Total amount of long-lived fission products.
** Total amount of fission products.
a) (loading amount - after-30day amount)\(\times\)365/30.
b) (transmutation amount/loading amount) \(\times\)100.

### Table 5 Absorption Cross Section Comparison for Major FPs

(单位：barn)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Proposed System</th>
<th>Absorption Cross Section</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>PWR</td>
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<tr>
<td>(^{99})Tc</td>
<td>6.910E+00</td>
<td>9.136E+00</td>
</tr>
<tr>
<td>(^{127})I</td>
<td>5.984E+00</td>
<td>4.846E+00</td>
</tr>
<tr>
<td>(^{128})Xe</td>
<td>2.547E+00</td>
<td>6.541E-01</td>
</tr>
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<td>7.140E+00</td>
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<td>(^{131})Xe</td>
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<td>(^{133})Cs</td>
<td>1.296E+01</td>
<td>1.072E+01</td>
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<td>(^{134})Cs</td>
<td>3.330E+01</td>
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<td>(^{135})Cs</td>
<td>4.085E+00</td>
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<tr>
<td>(^{137})Cs</td>
<td>3.843E-02</td>
<td>2.559E-02</td>
</tr>
</tbody>
</table>
Fig. 1 Schematic Layout of the System.
Fig. 2 Data Flow between Codes

Fig. 3 Spallation Neutron Energy Spectrum
Fig. 4 Neutron Energy Spectrum in Blanket

Fig. 5 Neutron Energy Spectrum in FP Burning Region
The present status of the research and development of nitride fuel cycle for burning transuranium elements in actinide burner reactors and fast reactors at JAERI is described, especially focusing on the progress in the recent two years. The research and development cover fuel fabrication technology, property measurements such as thermal conductivity, basic irradiation tests at Japan Materials Testing Reactors (JMTR), electrorefining of actinide nitrides in fused salts, and the evaluation of mass balance in the reprocessing process of nitride fuel.
1. Introduction

Actinide nitrides provide advantageous thermal properties such as high thermal conductivity and high melting temperature. By applying the cold fuel concept to fuel design for the transmutation of minor actinides (Np, Am and Cm), it would become possible to realize lower fuel temperature and hence lower fission gas release. Therefore, thinner cladding material might be acceptable and neutron spectrum could be harder. Furthermore, the mutual miscibility of actinide mononitrides might also lead to the fuel design with high concentrations of transuranium elements (TRUs). Considering the characteristics of nitride fuel, the actinide burner reactor (ABR) concept with a nitride fuel cycle has been proposed from Japan Atomic Energy Research Institute (JAERI) [2]. The research and development on nitride fuel cycle carried out at JAERI include fabrication technologies, property measurements, irradiation tests, and electrorefining of TRU-bearing nitride fuel. In addition to the above experimental studies, the mass balance in the pyroprocess has been evaluated. In the present report the progress of the studies on the nitride fuel cycle after the previous meeting [3] is mainly described.

2. Fuel Fabrication

2.1 Fabrication of nitride fuel particles by sol-gel method

The fabrication technology of nitride particle fuel by a sol-gel method has been investigated [3]. Minor actinides separated from the high-level waste (HLW) as nitrates will be converted to the solid particles by a sol-gel technique with a high yield. The gel particle is formed as a mixture of the actinide oxides and carbon, which is converted to mononitride by carbothermic reduction in a nitrogen atmosphere. The particles of uranium mononitride, UN, have been fabricated in order to study the fabrication process.

The feed solution with a C/U ratio of 2.75 was prepared by mixing uranium nitrate solution, carbon powder, hexamethylenetetramine (HMTA) and urea. The HMTA decomposes to form ammonia on heating to about 360K. The liquid droplets then turns into gel particles. The gel particles were washed, dried and calcined at 753K. The oxide with carbon was converted to nitride by first heating to 1.773K in N2. Further heating at 1.673K in N2-8%H2 promoted the reaction of UO2 with carbon through HCN and the removal of the residual carbon. Photo. 1 shows the UN particles thus produced. High purity UN particles with 660 ppm oxygen and 30 ppm carbon have been fabricated. Further efforts are being made:

1) Controlling the particle density.
2) Fabricating the mixed nitride of uranium and rare earth elements. The latters are substitutes for minor actinide.

2.2 Fabrication of nitride fuel pellets

Pellets-type uranium-plutonium mixed nitride, (U,Pu)N, has been fabricated by a conventional route with carbothermic reduction of the dioxides with graphite, followed by ball-milling, compacting and sintering [4,5]. The carbothermic reduction is carried out at about 1,920K in H2-8%N2 mixed gas flowing for about 36 ks.

For irradiation tests, the thermally stable pellets were fabricated by introducing relatively large pores in dense fuel matrix by use of pore former [5] so that pellet density could be kept about 85%TD. Fine nitride powder was used to obtain dense matrix because of its poor sintering characteristics. Sintering was performed at about 2,000K for 18 ks in an Ar-8%H2 atmosphere followed by the heat treatment at 1,730K in N2-8%H2 mixed gas stream. The microstructure of the pellet is shown in Photo. 2, where black circles were pores introduced by pore former.
3. Fuel Property Measurements

The lattice parameters of the quasi-binary systems of plutonium mononitride, PuN, with UN and neptunium mononitride, NpN, were determined by X-ray diffraction analysis of the solid solutions. It is found that the NpN-PuN system shows completely mutual solubility over the whole range of compositions, similarly to the UN-PuN systems[6]. It is also indicated that its lattice parameter deviates positively from the Vegard’s law, especially in the PuN-rich compositions as well as that of the system of UN-PuN. The deviation from the Vegard’s law could be explained by the behavior of 5f electron.

Knudsen-effusion mass-spectrometric experiments of NpN and the solid solutions of NpN and PuN were carried out. It was reported from the preliminary experiments of NpN that NpN showed the congruent evaporation[3], but further studies have led to the conclusion that the NpN might be considered to decompose into liquid neptunium and nitrogen gas as follows;

\[ \text{NpN(s)} = \text{Np(l)} + \frac{1}{2} \text{N}_2(g) \]
\[ \text{Np(l)} = \text{Np(g)} \]

The standard free energy of formation of NpN estimated from the data can be represented by the following equation[7];

\[ \Delta G_f = -295,870 + 91T \text{(J/mol)} \]

With regard to the vaporization behavior of the solid solutions of NpN and PuN, Np(g) and Pu(g) were detected as predominant gas species. The temperature dependence of the partial pressures of Np(g) suggested the precipitation of liquid neptunium. On the other hand, the temperature dependence of the pressures of Pu(g) was rather complicated; at higher temperatures, it showed a similar behavior with PuN, but, at lower temperatures, the precipitation of liquid plutonium might be suggested.

The thermal diffusivities of actinide nitrides have been measured by use of a laser-flash method for estimating the thermal conductivities. The results on the thermal conductivities of UN, PuN, NpN and the solid solutions of UN-PuN were reported in earlier papers[8,9]. It is confirmed from the estimated values that the thermal conductivity of actinide mononitrides decreases with the atomic number of heavy metals as shown in Fig. 1. The thermal conductivities of the solid solutions of NpN and PuN were also determined. The solid solutions have a similar temperature dependence with NpN and PuN and show intermediate values between those of NpN and PuN.

The details of the properties of the solid solutions of NpN and PuN will be presented at this meeting[10].

4. Irradiation Behavior

Four encapsulated fuel pins of uranium-plutonium mixed nitride, (U0.8Pu0.2)N, were irradiated at JMTR up to the maximum burn-up of 5.5%FIMA at maximum heating rates of 650 - 730 W/cm as shown in Fig. 2. Thermal stable nitride pellets were fabricated for the tests as described above. The typical characteristics of fuel pins are shown in Table 1. No pin failure was observed in all the cases. The preliminary results of FP gas release from the nitride fuel are plotted in Fig. 3 as a function of burn-up, together with those of mixed carbide fuel irradiated in JMTR and Japan Research Reactor-2 (JRR-2). It is obvious that nitride fuel shows very low fission gas release; 2-3 % at the burn-ups of 4-5%FIMA because of its advantageous thermal characteristics and also the stabilization of fuel matrix by introducing the thermal stable pellets. Furthermore, it is confirmed that the maximum diameter increase rate of the fuel pins was about 1 %/FIMA or less and the fission gas retained in fuel matrix does not significantly accelerate gas swelling of nitride fuel, at least up to the burn-up of 5.5%FIMA.
At present, two pins of mixed nitride fuel are under irradiation in the experimental fast reactor JOYO for a target burn-up of 4.5%FIMA as a joint research with JAERI and Power Reactor and Nuclear Fuel Development Cooperation (PNC).

5. Reprocessing Technology

5.1 Estimation of process and mass balance evaluation

The process of the molten-salt electrorefining of nitride fuel is similar to that of metal fuel: nitride fuel is anodically dissolved and the actinide metals are deposited on the dual cathodes, which consists of a solid cathode for the recovery of U and a liquid-Cd cathode for that of TRUs. Simulation calculations for nitride FBR fuel were made with use of the PALEO code to determine the amounts of actinides recovered in the electrorefiner and to estimate decontamination factors of fission products. The PALEO code, which is similar to the TRAIL code, calculates electrochemical behavior for Pu or U using diffusion layer model. In this calculation, the basic data such as standard potentials of actinides and lanthanides were taken from Ref. 13, and rare earth elements were represented by Ce which is one of the most difficult elements to be separated from actinides. It was found from preliminary calculation that the Ce concentration in the salt should be lower than 4.0wt% to keep the decontamination factor of about 5.

Equilibrium concentrations of main elements in LiCl-KCl eutectic melt were set to be 7.0wt% for Pu, 4.0wt% for U, 0.19wt% for minor actinides (Am) and 4.0wt% for rare earth (Ce) so that the Pu concentration in the output actinides from the electrorefining process might be almost same as that in the input actinides. The anode and cathode potentials were controlled to be -0.50V and -1.4V versus Ag/0.1wt%AgCl during electrorefining. As a result of the simulation calculations, the time dependent concentration of each element in the salt is shown in Fig. 4. At the first stage, Pu, Ce, Am and then U are well resolved, and U is deposited on the solid cathode. After exchanging the cathodes, Pu, U, Ce and Am are deposited on the liquid Cd cathode. The process time is about 7 hours for the first stage, and about 2.5 hours for the second stage.

In order to keep the rare earth concentration in salt around 4.0wt%, some amount of the salt (6.7% of the salt) have to be removed at each batch from the electrorefining vessel. The removed salt first goes through a stripping step with Cd-Li, and then an extraction step with Cd-U. The process calculation was made using the distribution coefficients (wt% in salt/wt% in Cd) [14]: 1 for U, 2 for Pu, 4 for minor actinides, 40 for rare earths, and 1,000 for alkali and halogen. Considering the Pu recovery rate and the rare earth concentration in Pu, the values of 1 for U distribution coefficient in the stripping process and 3 for Cd/salt ratio in extraction process were selected. The stripping and extraction steps remove almost all the actinide from the salt to Cd and leave about 72% of the rare earth in the spent salt. Actinides recovered in the Cd solution are returned to the electrorefiner.

Table 2 summarizes the mass flow in the electrorefining and salt treatment processes. The annual processing capacity is set to be 44 ton-HMeq (heavy metal equivalent) which corresponds to the amount of spent fuels from 4GWe nitride FBR. Average burnup of the discharged fuels is 100GWD/ton for core fuels and 12 GWD/ton for blanket fuels. About 220kg-HMeq per day are processed when the annual working day is assumed to be 200 days. Without considering the process loss, 99.45% of U and 99.95% of Pu can be recovered after adding those from the salt process.

5.2 Electrolysis of actinide nitrides

Anodic dissolution of UN in the eutectic melts of LiCl and KCl has been studied to provide a basis for the feasibility study of the electrorefining of irradiated nitride fuels [13]. The threshold potential of the anodic dissolution of UN was observed as shown in Fig. 5, where the working electrode was first cathodically polarized to -2.40 V and then potential was raised from the rest potential, about -1.6 V, to -0.2 V. It was consistently explained with the thermochemical
database of pure substances. The anodic dissolution of UN as U\(^{3+}\) into LiCl-KCl begins at the standard electrode potential of \(E = -0.82\) V referring to the equilibrium Ag/Ag\(^+\). It is considered that the threshold potential is determined by the formation of solid UC\(_3\) on UN. At present the possibility of direct nitriding of actinides in molten Cd-alloys is investigated.

Laboratory-scale electrorefiners for handling NpN and PuN have been installed in gloveboxes of 5 m\(^3\) in which purified argon gas is circulated at a rate of about 50m\(^3\)/hr and the concentrations of oxygen and water impurities are kept less than 1 ppm. The photograph of the argon gas atmosphere gloveboxes is shown in Photo. 3. The experiments are planned to start in 1996.

6. Summary

The present status of the research and development of nitride fuel cycle for TRU burning at JAERI is described. The fabrication technology of nitride fuel particles by a sol-gel method has been investigated and UN particles with high purity have been successfully fabricated, beside that pellet-type mixed nitride fuel by an conventional route. The properties of NpN-PuN solid solutions such as lattice parameter, thermal conductivity and evaporation behavior were determined. From the irradiation tests of mixed nitride fuel pins at JMTR, it is confirmed that nitride pellets shows very low FP gas release as expected. The pyroprocess for nitride fuel was estimated and the mass balance in the process was described.

References

List of table, figure and photograph

Table 1  Typical characteristics of nitride fuel pins irradiated at JMTR.
Table 2  Mass flow in the electrorefining and salt treatment process (1GWe × 4FBRs equivalent)

Fig. 1  Thermal conductivity of actinide mononitrides
Fig. 2  Irradiation program of nitride fuel
Fig. 3  FP gas release from carbide and nitride fuels irradiated in JRR-2 and JMTR
Fig. 4  Element concentration in salt at electrorefining of nitride fuel  
          (U/Pu/Am/Ce=4.0/7.0/0.19/4.0),
Fig. 5  Results of potentiodynamic measurements of UN

Photo. 1  UN particles fabricated by sol-gel process followed by carbothermic synthesis.
Photo. 2  Microstructure of thermal stable nitride pellet
Photo. 3  Appearance of gloveboxes in which electrorefiners for PuN and NpN are installed
<table>
<thead>
<tr>
<th>Characteristic</th>
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<td>Smear density</td>
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**Fuel pellet**

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<td>Pellet/cladding diameter gap</td>
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**Bonding material**

He
Table 2 Mass flow in the electrorefining and salt treatment process

(1GW·e x 4 FBRs equivalent) (kg/day)

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<th>Element</th>
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<th>(c)</th>
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<td>0.58</td>
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<td>0.14</td>
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</table>

MA : Minor Actinide  
RE : Rare Earth  
NM : Noble Metal  
HL : Halogen  
ALM : Alkali  
VFP : Vaporous FP  
SM : Structural Material

(a) - (j) : See below
Fig. 1 Thermal conductivity of actinide mononitrides

![Thermal conductivity graph](image)

Fig. 2 Irradiation program of nitride fuel

![Irradiation program graph](image)

* Under collaboration research program with PNC

Fig. 3 FP gas release from carbide and nitride fuels irradiated in JRR-2 and JMTR

![FP gas release graph](image)
Fig. 4 Element concentration in salt at electorefining of nitride fuel (U/Pu/Am/Ce=4.0/7.0/0.19/4.0),

Fig. 5 Results of potentiodynamic measurements of UN
Photo 1. UN particles fabricated by sol-gel process followed by carbothermic synthesis.

Photo 2. Microstructure of thermal stable nitride pellet.

Photo 3. Appearance of gloveboxes in which electrorefiners for PuN and NpN are installed.
CONSTRAINTS OF THE FABRICATION OF AMERICIUM OXIDE TARGETS

A. Renard, A. La Fuente, S. Pilate (BELGONUCLEAIRE, Brussels)
A. Harislur, M. Mouney, M. Rome (ELECTRICITE DE FRANCE, Paris & Lyon)

Abstract

If a special fabrication chain is devoted to prepare AmO₂ target pins in a MOX fuel fabrication plant, the dose rates will be considerably increased with respect to the present MOX (UO₂, PuO₂) fuel pin fabrication practice.

This memo shows results of orientation calculations, as recently performed at BN, with the close follow-up by EDF.

The accent is stressed on the validation of the calculational route via the evaluation of measurements available.
1. INTRODUCTION

After plutonium, americium is the second most important transuranium radio-isotope for what concerns the long-term waste radiotoxicity. With its half-life of 433 years, americium 241 contributes to a large part of the activity and toxicity of waste after 1000 years, while its decay raises the content in Np237. Americium 243 is less important as its half-life is 7380 years.

Ways to reduce the amount of americium by transmutation via reactor irradiation, either in pressurised water reactors (PWR) or in fast reactors, are thus under investigation.

At BELGONUCLEAIRE, the merits of homogeneously spreading americium oxide, supposed recovered at reprocessing, into the mixed oxide (MOX) fuel, have first been identified. Core physics calculations were first run to define the range of Am mixing fractions and Pu enrichments which would be required for such fuels in PWRs. Then, the radioprotection implications of manufacturing these special fuels have been determined from an extrapolation of the fuel fabrication conditions in present MOX fuel plants like that of BELGONUCLEAIRE at Dessel (1).

The results of these investigations were published at the preceding OECD meeting in Cadarache (2) and later on in open conference (3).

The heterogeneous irradiation of Am in PWR is being considered in turn. Target fuel pins would contain AmO\(_2\) with an inert material, like (Al\(_2\)MgO\(_4\)), transparent to neutrons. These pins could be inserted either in the bundle of MOX fuel assemblies, or in dedicated assemblies containing only target pins. A paper has presented solutions which seem acceptable from the point of view of reactor designers and operators (4) : they would allow to reduce the americium content by irradiation in a way which does not deteriorate reactor performances and safety.

What would be the burden of heterogeneous Am recycling on the MOX fuel fabrication plants ? This is the subject of current studies ; first results are presented in this paper. The accent is stressed on the validation of the results obtained.

ASSUMPTIONS ON OXIDE POWDERS AND TARGET PINS

The first assumption is that the MOX fuel fabrication plant would have a chain dedicated to AmO\(_2\) fuel, in parallel to the usual PuO\(_2\)-UO\(_2\) chain.

The front-end and back-end could stay in common, i.e.:

- it is imagined to receive AmO\(_2\) powders from the reprocessors in the same packing and in similar storage vaults than for PuO\(_2\)-UO\(_2\) at present,

- bundles of target fuel pins could be directed to assembly mounting halls, shipped in containers suited to on-site transportation.

In practice, for the sake of comparative calculations, the storage vault currently used has been supposed to contain pure AmO\(_2\) powder instead of pure PuO\(_2\) powder.

The incoming Am contains the following isotopic fractions : Am 241/242/243 = 62.4 % / 0.3 % / 37.3 %.

They are typical of americium fully recovered (with a 99 % yield) from the PWR fuel discharged after a burnup of 44 Gwd/t, 5 years after discharge. The isotopic Pu composition retained for comparison is :

Pu 238 / 239 / 240 / 241/242/ Am 241 = 2.4 / 53.4 / 23.6 / 12.3 / 7.1 / 1.2 %
The target pin is supposed to contain 20% AmO$_2$ diluted with Al$_2$O$_3$. This relatively low AmO$_2$ content has been found optimal in view of a large reduction factor by irradiation, of 90% for Am241 and 50% for Am242 (4). The MOX pin retained as a reference for comparison contains 7.8% Pu, i.e. an enrichment equivalent to 3.7% U235 in PWRs, which becomes typical of MOX fuel nowadays.

The AmO$_2$ dedicated assembly to be constituted would consist, as the standard 900-MWe PWR assembly, of 264 active pins and 25 guide-tubes, arranged according to a 17 x 17 square lattice; the active height is 3.66 m.

**COMPUTER CODES USED**

Three-dimensional dose-rate calculations have been performed using the codes QAD-CGGP (6) for gamma-rays and MCNP-4A (7) for neutrons. The radioactive sources have been established using ORIGEN-2 (8), taking into account irradiation history and the hypotheses given above.

**PRELIMINARY COMPARATIVE RESULTS**

- **Storage of powders**

  Figure 1 shows a sketch of the storage vaults; each vault can comprise a maximum of 5 cans containing each 3 kg oxide powders. The dose rates are calculated at 30 cm distance from the shielded doors.

  Table I gives dose rates calculated for the presence of PuO$_2$ or AmO$_2$ powders, respectively, and their ratios.

  For gamma-rays, the rise from PuO$_2$ to AmO$_2$ is by a factor 185; for neutrons this is by a factor 3.

  To reduce the dose rates to the same levels needs the addition of 7 cm lead thickness to the shielded door.

  **TABLE I**
  
  Powder Storage Vaults
  Dose rates at 30 cm distance from the door (mSv/h)

<table>
<thead>
<tr>
<th>Powder</th>
<th>Gamma dose</th>
<th>Neutron dose</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td>PuO$_2$</td>
<td>0.015</td>
<td>0.019</td>
<td>0.034</td>
</tr>
<tr>
<td>AmO$_2$</td>
<td>2.77</td>
<td>0.060</td>
<td>2.83</td>
</tr>
<tr>
<td>Ratio</td>
<td>185</td>
<td>3</td>
<td>82</td>
</tr>
</tbody>
</table>

- **Handling and transportation of pins**

  A transfer of 200 pins is considered towards the assembly mounting hall, inside of a steel canister of a square section by 21 x 21 cm and a 5 mm thickness.

  The IAEA rules for transportation of radioactive materials limit the dose rates to 2 mSv/h on surface and 0.1 mSv/h at 2 m distance. These limits have only an indicative value, as the considered transfer remains inside of the site, and is not a public road transportation.

  Table II gives dose rates calculated at 1 m distance, for 200 pins either corresponding to the reference MOX conditions, or to AmO$_2$ target pins.

  For gamma-rays, the rise from MOX to AmO$_2$ is by a factor 2780; for neutrons it is about 7. To reduce the dose rates to the same levels needs typically the addition of about 4 cm lead and 4 cm resin to the shielding, and to transport only half of the pins, i.e. 100, at the same time.
VALIDATION OF THE COMPARISONS

Much work has been focused on the validation of the results, especially because the extrapolation to be done from the present MOX fuel fabrication experience is huge.

Some aspects of this validation are detailed hereafter.

1. Dose from storage of MOX fuel

The dose rate has been measured at BELGONUCLEAIRE Dessel in front of the door of a storage vault containing 5 PuO$_2$ powder cans (double boxes), and compared to calculations.

The measurement was made at 63 mm distance from the external face of the door, which is made of sandwich layers of stainless steel, lead, boron containing glass, polythene and cadmium, see Figure 1.

Each of the 5 cans contained about 3 kg of PuO$_2$, with the following isotope composition:

Pu$_{238}$ / 239 / 240 / 241 / 242 / Am$_{241}$ = 1.32 / 57.38 / 24.15 / 6.11 / 5.11 / 5.93 %.

This measurement was selected for calibration of the methods, as it refers to an aged plutonium with as much as nearly 6 % Am$_{241}$ / Pu.

The comparison between calculation and measurement is given in Table III below.

<table>
<thead>
<tr>
<th>Dose Rates (μSv/h)</th>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>from gamma-rays</td>
<td>22.5</td>
<td>23*</td>
</tr>
<tr>
<td>from neutrons</td>
<td>33</td>
<td>29</td>
</tr>
</tbody>
</table>

* 23 : is the average of 5 measurements ; the extreme values were 23 ± 7 ; background was discounted.

The differences between calculation and measurement are quite acceptable.
Similar measurements were also made with the door open; the differences (C-E)/E were about 20% for gamma-rays, what is also acceptable. For neutrons, the calculations overestimate the dose as above.

Note that with this type of Pu, Am241 contributed to about 50% of the gamma dose.

2. Dose from a transport container

The case of the transport of 2 fresh MOX assemblies into a specific container with 2 positions has been considered. Results of measurements are available for 3 m-long MOX assemblies of 14 x 14 pins, with an average Pu enrichment of 5.3%.

A double steel wall, 4 cm-thick in total, comprises a 4-cm thick resin layer.

Table IV gives the comparison of calculated and measured dose rates on the surface of the container.

<table>
<thead>
<tr>
<th>Dose Rates (μSv/h)</th>
<th>Calculated</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>from gamma-rays</td>
<td>28.8</td>
<td>32</td>
</tr>
<tr>
<td>from neutrons</td>
<td>241</td>
<td>208</td>
</tr>
</tbody>
</table>

The comparison is satisfactory. The neutron calculation, by Monte-Carlo method with a statistical uncertainty of 3%, overestimates the measurement by 15%; fluctuations of the resin composition could explain this deviation.

3. Dose from a SUPERFACT pin

The irradiation experiment SUPERFACT has been conducted in the fast reactor PHENIX, up to a burnup of 5%. The capsule contained in particular special pins loaded with americium, which had been fabricated at TU Karlsruhe, see (5).

Pin SF No.14 contained mixed oxide, the metal being 20% Am241, 20% Np237 and 60% depleted uranium. The radial pin dimensions were typical of PHENIX: 5.42 mm pellet o.d., 6.55 mm cladding o.d.

For this fresh pin, dose rates have been measured at TUI. The measurement retained for this calibration is at a distance of 1 m from the pin, without any additional shielding. According to TUI (5), their calculation reproduces well the measurement.

Table V below compares two sets of calculation results, the one from TUI (5), and the other one with the BELGONUCLEAIRE methods, described above.

Both calculated routes have been applied in parallel to a standard PHENIX pin, of same radial geometry, containing mixed oxide UO₂-PuO₂ with a Pu enrichment of 25% and a Pu isotopic composition of:

Pu238 / 239 / 240 / 241 / 242 / Am241 : 1.3 / 60.4 / 23.4 / 9.9 / 4.5 / 0.5 %
TABLE V
Calibration of Methods

### 3. SUPERFACT pin with Am

<table>
<thead>
<tr>
<th>Dose Rates (mSv/h)</th>
<th>Calculated at TUI</th>
<th>Recalculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUPERFACT pin 14 :</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- from gamma-rays :</td>
<td>0.25 (^1)</td>
<td>0.33</td>
</tr>
<tr>
<td>- from neutrons :</td>
<td>(0.0065)</td>
<td>(0.00057)</td>
</tr>
<tr>
<td>Standard PHENIX pin :</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- from gamma-rays :</td>
<td>(0.0065)</td>
<td>(0.0068)</td>
</tr>
<tr>
<td>- from neutrons :</td>
<td>(0.00018)</td>
<td>(0.00028)</td>
</tr>
</tbody>
</table>

\(^1\) measured: 0.26
\(^2\) no measurement quoted

For the SF14 pin, Table V shows an overestimate of about 30% for the gamma-ray dose. While our calculations are showed to be conservative, the difference could be associated with the gamma source spectrum found with ORIGEN2 (TUI used a source from the KFK improved version KORIGEN).

For neutrons, the values for the PHENIX pin shows a difference by about +50%; the dose due to neutrons is anyhow much smaller than the gamma dose.

From the PHENIX pin to the SF14 pin, the gamma dose increases by a factor 40 to 50, and the neutron dose by a factor 2.

These cross-checks may be considered satisfactory for the sake of orientation calculations.

PROVISIONAL CONCLUSIONS

The fabrication of AmO\(_2\) target pins in a MOX fabrication plant indicate that, with respect to the dose rates experienced in present MOX (UO\(_2\), PuO\(_2\)) fuel fabrication, the dose rates emanating from AmO\(_2\) powders, from target AmC\(_2\) pins and from bundles of such pins, would be significantly higher if no reinforced shielding was applied. The raise of the dose rates would reach factors like:

- 80 in front of the shielded doors of the oxide powder storage vaults
- 50 from a single Am target pin compared to a standard fast reactor pin geometry,
- 2800 from a canister transferring 200 pins to the mounting hall.

The increase in shielding thickness necessary to lower dose rates to the levels currently observed in MOX fabrication, has been determined by calculation.

It appears that the fabrication of AmO\(_2\) target pins should preferably be done in shielded hot cells.
As the americium mass recoverable from PWR irradiated fuel (after 5 years) is about 6 % of the plutonium mass, and considering the assumption made here (MOX pins with 7.8 % Pu, target pins with 20 % AmO₂), the production of Am target pins would amount to about 1/50 of the MOX pins.

The transportation of dedicated AmO₂ assemblies obviously needs a re-inforced shielding on the containers. The practicability of such transportation is being studied in further details.

A large effort has been spent to check the validity of the calculations. To that aim, 3 important steps of the fabrication chain have been covered by experimental validation:

- the storage of incoming powders for which measurements are obtained from BN/Dessel for relatively aged PuO₂ batches,
- the transport container, for which measurements are obtained for current MOX assemblies,
- and the constitution of single pins containing 20 % AmO₂, for which TUI Karlsruhe had measured and calculated dose rates.

The comparisons made bring confidence in the validity of the predictions.
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OECD/NEA

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Experimental Nuclear Data in Relation to Irradiation Experiments of Minor Actinide Targets in Fast
Reactors
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for Neutron and Gamma-Ray Shielding Calculations using the GP Buildup Factor
Contributed by JAERI and ORNL - CCC-493 (1987)

[7] J. BRIESMEISTER (Editor)
MCNP, a General Monte Carlo Code for Neutron and Photon Transport
LA-7396-M (September 1986, revised April 1991)

[8] A.G. CROFF
ORNL/TM 7175 (July 1980)
19 mm borated glass

3 mm lead

0.5 mm cadmium

110 mm polythen

3 mm lead

1.5 mm stainless steel

Outside

Inside

Door of storage cavity

Air exhaust

Position of the 5 Powder Cans in the Storage Cavity

Storage cavity

Borated concrete

Air inlet

Door

Fig. 1. Plutonium Storage Rack
MOLTEN SALT ELECTROREFINING TO SEPARATE TRANSURANIUM ELEMENTS FROM RARE EARTH ELEMENTS

Takatoshi HIJIKATA, Yoshiharu SAKAMURA, Tadashi INOUE, Turk STORVICK and Richard GAY

1) Central Research Institute of Electric Power Industry (CRIEPI)
2) University of Missouri-Research Reactor
3) Rockwell International Corporation

ABSTRACT

CRIEPI has proposed a pyrometallurgical process to separate actinides from high level radioactive waste (HLW) and solvent scrubbing waste. In the concept, HLW is converted to chlorides, and the molten chlorides are reduced into liquid cadmium and/or bismuth by the addition of lithium metal as reductant. Then, the actinides are purified by electrorefining. Since rare earth elements (RE), which are chemically similar to actinides, are existing an order of magnitude more than actinides in the HLW, a key issue in the pyrometallurgical process is the efficient separation of the actinides from RE.

This study shows the separation between actinides and RE by the electrorefining with two stages. The first stage was carried out to transport actinides to the molten salt electrolyte and the Ta cathode from Cd anode. After removing the actinides was removed from Cd, the anode was changed to Li₂Sb for the following electrorefining, in which actinides were reduced on the Ta cathode from molten salt. The chemical composition in the system was adjusted according to the ratio of actinides to RE (Y, La, Ce, Nd and Gd) with HLW, except U and Pr. In the result, U and Np were easy to separate from RE, and Pu and Am showed small separation factor from RE, because the concentration of Pu in molten salt and Cd is quite low ( log Xₚ₄ < -4 ) and the redox potential was similar to RE. The current efficiency in this experiment was less than 30 %, since the deposition of actinides, especially U, dropped from the cathode. In the second stage, as the concentration of actinides in the salt, the separation of actinides from RE became more difficult. The final ratio of actinides to RE on the cathode was more than unity through this experiment.

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INTRODUCTION

Central Research Institute of Electric Power Industry (CRIEPI) in Japan has proposed a concept to separate actinides from HLW by a pyrometallurgical process and then to transmute them to short-lived nuclides in a metallic fuel FBR [1]. The pyrometallurgical process has been predicted to reduce the total amount of radioactive waste and has been suggested to favor compact facilities as compared with the aqueous processes such as solvent extraction, ion exchange etc., in spite of a relatively low purity of actinides elements in a final product. The pyrometallurgical partitioning process of HLW from PUREX process is shown in Fig. 1. The pyrometallurgical process consists of (1) denitration to form oxides, (2) chlorination of oxides to form chlorides, (3) reductive extraction of actinides from molten chlorides into liquid cadmium (Cd) or bismuth [2-6] and (4) electrorefining of actinides from fission product [7,8].

Since the amount of rare earth elements (RE) are in order of magnitude more than that of actinides in HLW, a key issue in the pyrometallurgical process is the efficient separation of actinides (U, Np, Pu, Am and Cm) from RE. In this study, separation of actinides from RE was carried out by the electrorefining in following two stages. In the first stage was transported actinides from Cd anode to the Ta cathode through the molten salt electrolyte. In the second stage, the anode was replaced by Li$_2$Sb, and actinides in the molten salt were reduced on the Ta cathode.

EXPERIMENT

The electrorefining apparatus was equipped in the furnace well of glove box where circulating argon gas was purified by DRYTRAIN and NITRAIN. During the experiments, oxygen and water content were both maintained at < 1ppm and nitrogen content was at < 500ppm. The electrorefining cell is shown in Fig. 2. The cell which contained molten salt and liquid Cd was made of Ta tube with a half inch size in an outside diameter. A Ta wire of 1 mm diameter was used as a cathode in the cell. As shown in Fig. 2 (A) and (B), actinides-Cd alloy was used as an anode for the electrorefining of first stage and the anode was replaced by Li$_2$Sb for the second stage. All experiment was controlled by galvanometry in the range of 2 mA to 5 mA in the first stage and 2 mA to 3 mA in the second stage.

The initial amount of the elements in liquid Cd and molten salt were determined as Table 1. According to the ratio of actinides (U, Np, Pu and Am) to RE (Y, La, Ce, Nd and Gd) in HLW, excepting U, Cd alloy was prepared by mixing Cd with U-Cd, Np-Cd, Pu-Cd and Am-Cd alloy at about 773 K. The resulting concentration of each element in the alloy was determined by Inductively Coupled Plasma atomic emission spectrometry (ICP). The salt was prepared by mixing the weighted amount of LiCl-KCl eutectic salt with YCl$_3$, LaCl$_3$, CeCl$_3$, NdCl$_3$ and GdCl$_3$ according Table 1. The alloy and the salt were put into Ta tube and then, heated to 723 K.

Ta wire with 1 mm $\phi$ was immersed in the molten salt and was connected to the cathode. A liquid Cd alloy was then connected to the anode through Ta tube. The cathode of the first stage was covered on the alumina tube of a quarter inch in an outside diameter with a small window and a small amount of Cd was placed in the tube, in order to catch the dropped deposits. The molten salt and liquid Cd were stirred by Ta stirrer. After passing about 10 to 20 coulomb, the cathode deposit and /or a trace amount of Cd alloy and salt were taken
out for the analysis by ICP, and then the new cathode was inserted. The amount of metal deposit were derived by subtracting the amount of salt entrained in the deposit. The amount of entrained salt was estimated from the concentration of potassium in the deposits.

After removing actinides from Cd alloy, Cd was taken out from the cell and then, the anode was changed to Li$_2$Sb in order to remove actinides from the salt, as shown in Fig. 2 (B). After passing about 20 to 50 coulomb, the cathode deposit and the salt were analyzed.

RESULTS AND DISCUSSION

Figure 3 shows the concentration change in the salt with the total charge passed. It was observed that the U concentration decreased faster than Np with passing charge. While, the final deposit was consisted of ca.42% - U, ca. 42% - Np, 0.7% - Pu, 1% - Am and 15% - RE. The total charge needed for removal of all actinides from Cd alloy three times as much as the calculated value of 77 coulomb. This was due to the drop of actinides deposited from Ta, because the content of U and Np in a catch Cd and a catch tube were higher concentrated than the other part. These results suggest that some portion of U deposits dropped into the salt. On the other hand, the concentration of Am in the salt was increased with increasing charge passed, and suggesting that Am was hard to deposit on the cathode. The content of RE in the salt didn't change with passing charge, which means to no deposition on the cathode at this electrolysis condition.

Figure 4 shows that the relationship between the current efficiencies and the total passed charge. The current efficiencies of cathode and anode were defined as the equations of (1) and (2), respectively.

\[
\text{The cathode current efficiency} = \frac{\sum \text{amount of deposit observed}}{\sum \text{amount of deposit calculated from the coulomb passed}} \quad (1)
\]

\[
\text{The anode current efficiency} = \frac{\sum \text{amount of elements removed from Cd phase}}{\sum \text{amount of removed elements calculated from the coulomb passed}} \quad (2)
\]

This figure indicates that the current efficiencies of the cathode and anode were ca. 20% and ca. 30%, respectively. If the dropped deposits were recovered by a catch tube, the anode current efficiency was still far less than 100%. Hence, most of the dropped deposit was returned to Cd anode through a window in a catch tube as a form metal fog [9]. The existence of the floating particles like metal fog was supported by salt entrained in the cathode deposit showed gray color with small black particles.

Figure 5 shows that the relationship between the separation ratio of actinides from RE at an use of Cd anode and total charge. This separation ratio was defined as the equation of (3).

\[
\text{Separation ratio} = \frac{\sum \text{amount of M deposit}}{\sum \text{amount of RE deposit}} \quad \frac{\text{amount of M before the electrolysis}}{\text{amount of RE before the electrolysis}} \quad (3)
\]

\[(M: \text{U, Np, Pu or Am})\]
The amount of M and RE were shown in Table 1. Figure 5 shows the separation ratios as ca. 20 for U, ca. 40 for Np, ca. 8 for Pu, ca. 1 for Am. Assuming that thermodynamic equilibrium are established, the separation ratio of actinides from RE can be derived from the standard redox potential in molten salt [7]. The derived values of separation ratio of U was larger than that of Np, although the measured value of U was smaller than that of Np. This difference could be attributed to drop of U from the deposit as mentioned above. Figure 5 shows that the tendency of separation ratio among actinides was in order of Np > U > Pu > Am, which agreed with the prediction from the standard redox potential [7], except U. In this stage, only small amount of Pu and Am were deposited on the cathode, resulting in the small separation ratio of Pu and Am. It means that Am were still remained in the salt after most of actinides were removed from Cd anode in this stage. The averaged separation ratio of actinides kept ca. 20 during the electrolysis using Cd anode. This value was dominantly affected by U and Np, because the deposits consisted mainly of U and Np in the first stage.

Figure 6 shows the concentration of each element in the salt with passing charge at the use of Li$_2$Sb anode. It was seen in this figure that the concentration of all elements decreased with charge. In contrast at the case of Fig.3 with use of Cd anode, we observed the decrease of Am content, which indicated the deposition of Am on the cathode. Hence, the important factor in order to deposit Am could be that the concentration of Am in the salt increased an order of magnitude over the concentration of U and Np in this electrolysis. On the other hand, it was seen in Fig.6 that the concentration of RE was also decreasing with passing charge. Ce and Nd showed remarkable decrease among RE, especially, because the standard redox potential of Ce and Nd was close to Am [7], and then Ce and Nd were higher content in the salt than another RE as shown in Table 1. Consequently, the electrolysis accelerated to deposit RE in particular Ce and Nd as well as Am on the cathode. It might be predicted that much amount of RE was accompanied on the cathode when Am was further removed (> 99%) from the salt. As shown in Fig.6, the concentration of Ce and Nd in the salt decreased remarkably after 220 coulomb passed. In this last deposit, the content of Ce and Nd became higher than all actinides. It should be ascribed the extremely low concentration of Am in the salt after 220 coulomb passed.

The cathode current efficiency in the second stage was lower than that of first stage. This may be come from the minimized current for getting better separation and from increase of the drop of the deposit with decreasing the concentration of actinides in the salt.

Figure 7 shows the relationship between the separation ratio and the total charge passed at an use of Li$_2$Sb anode. This separation ratio was replaced the denominator in the equation of (3) with the amount of actinides and RE before using of Li$_2$Sb anode. It was seen in Fig. 7 that the separation ratio became ca. 8 for U, ca. 60 for Np, ca. 20 for Pu and ca. 2 for Am, except the last deposition. As compared with Fig.5, the separation ratio of Np, Pu and Am from RE increased. It was due to low the concentration of U in the salt and high the content of Np, Pu and Am in the deposit. The order of the separation ratio was Np > Pu > U > Am. This behavior of U does not agree with the prediction from the standard redox potential[7]. It may be due to the low concentration of U in the salt and the fall of U deposit. The separation ratio of all actinides from RE became 10 in the second stage and was a half value of the case using Cd anode. This is because the main deposit of actinides was changed from U and Np to Am. It means that U and Np were easy to be separated from RE, but Am was difficult.
The recovered ratio of TRU (Np, Pu and Am) to RE was defined as the total amount of deposited TRU in divided by that of RE, and was derived to be 1.2 for this experiment. Since the ratio of TRU to RE before the electrolysis was 0.14, the molten salt electrorefining can be multiply the TRU ratio to RE about 8.6 times in this experiment.

CONCLUSION
1. The separation ratio of actinides to RE became 22 by using Cd anode.
2. The separation ratio became 10 by using Li₂Sb anode and was a low compared with the case of Cd anode. It was due to the change of the main deposit of actinides from U and Np to Am.
3. The molten salt electrorefining could be separated 8.6 times TRU from RE in this experiment.

ACKNOWLEDGMENTS
The author also would like to express his appreciation to Dr. Koyama in CRIEPI and also wish to thank TRUMP-S members in University of Missouri and Rockwell International Corporation for this work.

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<table>
<thead>
<tr>
<th>LiCl-KCl</th>
<th>Total (mg)</th>
<th>Cd Phase (mg)</th>
<th>Salt Phase (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>4.4962 (g)</td>
<td>7.4214 (g)</td>
<td></td>
</tr>
<tr>
<td>U**</td>
<td>37.0</td>
<td>30.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Np</td>
<td>15.0</td>
<td>9.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Pu</td>
<td>1.6</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Am</td>
<td>16.9</td>
<td>9.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Y</td>
<td>11.7</td>
<td>D.L.</td>
<td>11.7</td>
</tr>
<tr>
<td>La</td>
<td>36.4</td>
<td>0.5</td>
<td>35.9</td>
</tr>
<tr>
<td>Ce</td>
<td>69.0</td>
<td>2.9</td>
<td>66.1</td>
</tr>
<tr>
<td>Nd</td>
<td>110.0</td>
<td>5.2</td>
<td>104.8</td>
</tr>
<tr>
<td>Gd</td>
<td>7.3</td>
<td>0.3</td>
<td>7.0</td>
</tr>
</tbody>
</table>

*: The chemical composition in the system was adjusted to the ratio of actinides to RE (Y, La, Ce, Nd and Gd) with HLW.

**: Uranium was one fourth of the simulated composition, and praseodymium was none in the composition.
Fig. 1 Schematic flow diagram for TRU pyrometallurgical partitioning from high level wastes.
Fig. 2 Schematic diagram of the experimental cell. (A) Cd anode (B) Li$_2$Sb anode

Fig. 3 The concentration change in the salt with the charge passed at an use of Cd anode.
Fig. 4 The relationship between the current efficiencies and the charge passed at an use of Cd anode.

Fig. 5 The relationship between the separation ratio at an use of Cd anode and the total charge.
Fig. 6 The concentration change in the salt with the charge passed at an use of Li₂Sb anode.

Fig. 7 The relationship between the separation ratio at an use of Li₂Sb anode and the total charge.
In the Japan Atomic Energy Research Institute (JAERI), a partitioning process has been developed to separate elements in a high-level liquid waste (HLLW) into four groups: transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others.

The present paper deals with the partitioning process flow sheet, behaviors of objective elements and other constituents in the process, recoveries of objective elements, chemical purities of the products, the sorts and constituents of the secondary wastes, and the volume of solid materials generated from HLLW after the partitioning process.

The complete separation of TRU elements, including pentavalent Np, might be accomplished by using the partitioning process. However, further improvement will be required in the separation of Am and Cm from rare earths, back-extraction of U and Y from the DIDPA solvent, etc. to reduce the secondary waste generation and the handling liquid volume.
1. Introduction

Nuclear energy is the most promising option for the future generation when considering the global environmental protection. The management of high-level radioactive waste containing long-lived nuclides is one of the most important problems to be solved before the future deployment of nuclear energy in the global scale.

In 1988, Japan's Atomic Energy Commission published the report entitled "Long Term Program for Research and Development on Nuclide Partitioning and Transmutation Technology". In this program, a partitioning technology should be developed for separating elements in high-level liquid waste (HLLW) into four groups; transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others. Among them, long-lived nuclides such as TRU nuclides should be transmuted by using an actinide burner reactor, FBR, etc.

2. Development of partitioning process

At JAERI, development of a partitioning method started about 23 years ago. From 1973 to 1984, a partitioning process was developed for separating elements in HLLW into 3 groups; TRU, Sr-Cs and others. The partitioning process consists of three steps; solvent extraction of U and Pu with tributylphosphate (TBP), solvent extraction of Am and Cm with diisodecylphosphoric acid (DIDPA), and adsorption of Sr and Cs with inorganic ion exchangers. The process was demonstrated by using an actual HLLW.

Since 1985, a four group partitioning process has been developed, in which a step for separating the Tc-PGM group was developed in addition to the three group separation. Effective methods for separating TRU, especially Np, and Tc have been developed.

3. Four group partitioning process

Through the fundamental study, the four group partitioning process has been constructed as shown in Fig. 1. Main characteristics of this flow sheet are as follows: (1) All TRU elements including pentavalent Np are extracted with DIDPA after the denitration of HLLW, reducing the nitric acid concentration from 2 M to 0.5 M. (2) Tc and PGM are separated by precipitation through denitration or by adsorption with an active carbon. (3) Sr and Cs are separated by adsorption with inorganic ion exchangers, titanic acid and zeolite, respectively.

3.1 TRU separation

The TRU elements in the DIDPA solvent are sequentially back-extracted with 4 M nitric acid for Am, Cm and rare earths, 0.8 M oxalic acid solution for Np and Pu, and 1.5 M sodium carbonate solution for U. A chemical flow sheet is shown in Fig. 2. Back-extracted Am, Cm and rare earths are extracted again with DIDPA, and then Am and Cm are preferentially back-extracted with 0.05 M dietylenetriaminepentaacetic acid (DTPA) solution, leaving rare earths in the DIDPA solvent.

Recoveries of TRU elements and chemical behaviors of fission products and corrosion products in each chemical step can be estimated with data so far obtained through experiments with actual or simulated HLLW. Following results might be expected under optimized process conditions.

Recoveries of Am, Cm, Pu and U are more than 99.99% and Np more than 99.95% in the DIDPA extraction step. More than 99.99% of Am, Cm and rare earths are back-extracted with 4 M nitric acid, more than 99.9% of Np and Pu with the 0.8 M oxalic acid solution, more than 99.9% of U with the sodiumcarbonate solution and more than 99.99% of Am and Cm with the DTPA solution.
As to the chemical behaviors of fission and corrosion products, rare earths and Fe are quantitatively extracted with the DIDPA solvent. Rare earths behave like Am and Cm, but finally are separated from them in the DTPA back-extraction step. The rare earth content in the Am and Cm fraction might be reduced to lower than 25% under the operating condition of 99.99% recoveries of Am and Cm. Among rare earths, the chemical behavior of Y fairly differs from those of other rare earths. Most Y is back-extracted along with U in the sodium carbonate back-extraction step. The Fe is back-extracted along with Np and Pu with the 0.8 M oxalic acid solution.

3.2 Tc and PGM separation

Two chemical methods have been developed for the Tc and PGM separation from the DIDPA raffinate; the precipitation method by a denitration with formic acid and the adsorption method with active carbon column. The former method might be more effective in practical use because of no generation of secondary wastes even though the recovery of Tc is estimated to be about 95% as compared with more than 99.9% in the latter method and the former method is not applicable to the solution in which concentration of Rh and Pd is lower than 0.005 M. More than 90% of Tc might be preferentially leached out, leaving PGM in the precipitate, with a hydrogen peroxide solution.

3.3 Sr and Cs separation

The adsorption method with inorganic ion exchangers, titanate acid and zeolite, has been developed for the Sr and Cs separation. More than 99.9% of Sr and Cs might be separated from the filtrate by this adsorption method after the Tc and PGM separation.

4. Products from four group partitioning process

4.1 TRU products

4.1.1 Am and Cm

The recovery which is the ratio of the amount in the product to the initial amount in HLLW might be more than 99.97% for Am and Cm under the estimation that less than 0.03% of them are lost in the chemical steps; DIDPA extraction, 4 M nitric acid back-extraction, DIDPA re-extraction and DTPA back-extraction. About 1% of rare earths might be contained in the Am and Cm product and the chemical purity of the product might become about 75%.

In the chemical flow sheet as shown in Fig. 2, the Am and Cm product is obtained as the DTPA solution. Finally, a conversion method to oxide or nitride to be subjected to the nuclide transmutation should be developed.

4.1.2 Np and Pu

The recovery of Np might be more than 99.85% under the estimation that less than 0.05% is lost in the DIDPA extraction step and less than 0.1% in the 0.8 M oxalic acid back-extraction step. Almost all Fe and slight amounts of Rh, Ru, Zr and Mo might be contained in the Np and Pu product. The purification of the product from Fe and other impurities should be considered in the conversion step from the oxalic acid solution to oxide or nitride to be subjected to the nuclide transmutation.

Estimation of the Pu recovery is very difficult because more than 70% of Pu might be precipitated during the preparation step of HLLW from the TBP raffinate generated in the Purex.
process, long-term storage of HLLW and the denitration step of HLLW prior to the DIDPA extraction even though the recovery of Pu from the filtrate after the denitration of HLLW is more than 99.9%. In order to accomplish the complete recovery of Pu, the dissolution of the precipitate and the separation of Pu from the resulting solution should be developed.

4.1.3 U

The recovery of U might be more than 99.9% under the estimation that less than 0.01% is lost in the DIDPA extraction step and less than 0.1% in the sodium carbonate back-extraction step. Almost all Y, slight amount of Fe, less than 0.1% of Np and less than 0.01% of Am and Cm might be contained in the U product which is obtained as the sodium carbonate solution. This product should be recycled to a fuel reprocessing plant.

4.2 Tc and PGM products

Estimation of the recoveries of Tc and PGM is difficult as the same as in the case of Pu because about 10% of Tc and about 20% of Ru and Rh might be precipitated during long term storage of HLLW and the denitration step of HLLW prior to the DIDPA extraction. In order to increase the recoveries of Tc and PGM up to more than 90%, a treatment method for the precipitate should be developed. However, higher recovery more than 90% for Tc will not be needed from the standpoint of reducing the potential hazard index of a vitrified HLLW.

The recoveries from the filtrate after the denitration of HLLW are estimated to be about 95% of Tc, 92% of Ru, 87% of Rh and 99% of Pd when the precipitation method is applied to the DIDPA raffinate. The Tc product obtained by the leaching of the precipitate with hydrogen peroxide might contain trace amount of PGM. Conversion of the Tc chemical form present in pertechnetate ion should be studied for the nuclide transmutation or a beneficial use. The PGM obtained as the precipitate might be present as a mixture of metal and oxide. Mutual separation of Ru, Rh and Pd should be studied for their beneficial uses. However, the necessity of this study might not be so urgent since the PGM contains long lived nuclides of which half-lives are longer than one year and a very long-term cooling will be needed before practical use.

4.3 Sr and Cs product

The recoveries of Sr and Cs might be more than 99.9%. Most Ba and Ni might be also adsorped on the inorganic ion exchangers. The U and TRU contents compared to their initial amounts in HLLW might be less than 0.01% and less than 0.0001%, respectively.

The exchangers loaded with Sr and Cs can be solidified into a very stable form by direct calcination. This greatly contributes to the reduction of waste volume because the material used for the adsorption can be used as the mother material for the Sr and Cs solidification and the thermal stability of the product is very high compared with that of vitrified material. Therefore, large amount of heat generating nuclides can be included in the small volume of the solid material. Leachabilities of Sr and Cs are extremely low by a factor of four order of magnitude as compared with that for vitrified material.

The Sr and Cs product might be used as a heat source and a radiation source during the period of storage prior to a deep underground disposal.

5. Wastes from four group partitioning process
5.1 Others group

The others group in the four group partitioning process is waste in a direct sense. This group contains elements collected from 4 kinds of fractions; the precipitate after the denitration of HLLW, the rare earths fraction separated from Am and Cm, the effluent from the Sr and Cs adsorption column, the Fe and Y fractions separated from the Np and Pu fraction and the U fraction, respectively.

From the precipitate fraction, most Zr, Mo and Te are estimated to be recovered and transferred to the others group. The Pu quantity transferred to the others group is estimated to be less than 0.01%. The rare earth fraction is estimated to contain most rare earths and less than 0.01% of Am and Cm, the effluent fraction to contain Na which is released by an ion exchange reaction with Cs, and the Fe and Y fraction to contain most of them.

Total amount of elements to be contained in the others group is estimated to be 26 kg in their oxides for one ton of the spent fuel burned up to 33 GWd/t.

5.2 Solvent waste

The DIDPA solvent is estimated to contain less than 0.1% of U, less than 0.001% of TRU and trace amounts of Ru, Fe and Zr after treatment with the sodium carbonate solution. Total amount of the DIDPA solvent waste generated for one ton of the spent fuel is estimated to be 10 L, corresponding to 8.2 kg of CaHPO$_4$ under the conditions that 3000 L and 4000 L of the DIDPA solvent are used respectively for the TRU extraction step from HLLW and the separation step of Am and Cm from rare earths and the number of its recycle use in each step is estimated to be 50 and 100 times, respectively.

5.3 Washing solution

The DIDPA solvent after the treatment with the sodium carbonate solution should be washed with nitric acid to convert the Na form to H form for its recycle use. Therefore, the waste of the washing solution contains sodium ion of which amount is estimated to be 128 kg in NaNO$_3$ for one ton of the spent fuel. Amounts of U and Pu-TRU are estimated to be less than 0.0001% and less than 0.00001%, respectively.

5.4 Sodium carbonate solution and other wastes

In the U back-extraction step with sodium carbonate solution, about half of Na remains in the carbonate solution. Therefore, the amount of Na in the carbonate solution after the U back-extraction is estimated to be 128 kg in NaNO$_3$ for one ton of the spent fuel.

The liquid wastes generated after treatment of the Am and Cm fraction and the Np and Pu fraction are the DTPA solution and the oxalic acid solution, respectively. For these liquid wastes it might be possible to decompose to water and carbon dioxide which enable no generation of solid wastes.

6. Volume of the solid materials

Table 1 shows the volume of the solid materials generated in the four group partitioning process.

The volume of the Sr-Cs group was estimated for the solid material generated by the direct calcination of the inorganic ion exchangers loaded with most Sr, Cs, Rb, Ba and Ni, and the volume of the others group was estimated for the vitrified material containing 30 wt% of oxides of fission and corrosion products. This content might be not so high for the vitrification because the others group
contains less heat generators such as Sr-90 and Cs-137. Cementation was considered for the secondary wastes such as CaHPO₄ and NaNO₂.

Total volume of the four groups generated from the partitioning process was estimated to be 45 L which is smaller by a factor of 3.3 compared with that in the vitrification of HLLW without partitioning.

For the others group it might be possible to dispose directly into a deep underground without any long term cooling. For the cemented waste, a shallow land disposal might be suitable because alpha activities concentration is estimated to be negligible.

7. Conclusion

The four group partitioning contributes to the reduction of the high-level waste volume and the enhancement of the utilization of valuable elements or nuclides in HLLW as well as the promotion of the transmutation of long-lived nuclides which contributes to the reduction of long-term burden into natural environment.

Complete separation of TRU elements, including pentavalent Np, can be accomplished by using the DIDPA solvent. However, a chemical method using a salt-free reagent should be further developed for the back-extraction of U and Y from the DIDPA solvent to reduce the secondary waste generation and an advanced chemical method should be considered for the separation of Am and Cm from rare earths to reduce the handling liquid volume. The recovery of TRU elements, especially Pu, should be studied for the precipitate formed during the preparation step to HLLW from the TBP raffinate generated in the Purex process, long term storage of HLLW and the denitration step of HLLW.
Table 1 Volume of solid materials after partitioning for one ton of the spent fuel burned up to 33 GWd/t

<table>
<thead>
<tr>
<th>Group</th>
<th>Main nuclides or elements</th>
<th>Solid form</th>
<th>Volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRU</td>
<td>Np-237, Am-241</td>
<td>oxide</td>
<td>0.09</td>
</tr>
<tr>
<td>Tc-PGM</td>
<td>Tc-99, Ru, Rh, Pd</td>
<td>metal</td>
<td>0.39</td>
</tr>
<tr>
<td>Sr-Cs</td>
<td>Sr-90, Cs-137</td>
<td>calcined product</td>
<td>14</td>
</tr>
<tr>
<td>Others</td>
<td>Zr, Mo, Fe, rare earths</td>
<td>vitrified material</td>
<td>31</td>
</tr>
<tr>
<td>Secondary wastes</td>
<td>NaNO₃, CaHPO₄</td>
<td>cemented material</td>
<td>330</td>
</tr>
</tbody>
</table>
Fig. 1 The four group partitioning process
Fig. 2 The DIDPA extraction process including the separation of Am and Cm from rare earths.
Cesium possesses two long lived isotopes $^{135}$Cs and $^{137}$Cs, the first one of which the half live is very long must be selectively separated either for transmutation, either for encapsulation in a very specific matrix. As for $^{137}$Cs, it is interesting to remove it with strontium and actinides in order to decategorize immediate level radioactive wast. Cesium must be removed with a very high selectively in the first case from very acidic medium (HNO$_3$ 3-4 M) in the second one from acidic high sodium nitrate concentration liquid waste. Calix[4]arenes crown or bis crown in the 1,3 alternate conformation exhibit a tremendous efficiency and selectivity for cesium. These exceptional performances, much higher than those obtained with the best crown ethers, were obtained on simulated wastes and confirmed in two hot tests by liquid-liquid extraction and by implementing supported liquid membranes.
1 - INTRODUCTION

Nuclear Fuel reprocessing operations produce both high and medium level activity liquid wastes. Studies are launched, in the framework of SPIN programm to selectively remove actinides or long lived fission products like $^{137}$Cs in order to destroy them by transmutation or to dispose of them in very stable matrices. On the other hand medium level activity wastes are treated by evaporation this treatment leads to large volume of concentrates composed mainly of inactive salts. It is desirable to remove the long-lived radionuclides (actinides, $^{90}$Sr and $^{137}$Cs) from the concentrates, this allows these decontaminated wastes to be directed to surface repositories, only a small volume containing these radionuclides being disposed of in geological formation. We have to point out that in both cases, high or medium activity liquid wastes, it is interesting to selectively and efficiently remove cesium isotopes.

2 - EXTRACTION OF CESIUM BY ION EXCHANGERS OR EXTRACTANTS

For several decades, inorganic ion exchangers or absorbers were used to remove cesium, recent reviews concluded, from the study of these compounds that Cristalline Silico Titanates (CSTs) were the most promising (if reuse of material was not required) followed by ammonium molybdo phosphate, ferrocyanides and other phosphates [1][2]. However the authors concluded that elution, if possible, had to be studied in order to minimize the volume of waste produced.

Two classes of extractants were particularly studied for the extraction of cesium: Dicarbollides and crown ethers. Czechs carried out extensive studies for the synthesis and extraction properties of dicarbollides [3]. These lipophilic anions withstood protonation in very acidic medium and removed cesium effectively in nitric solution up to 3 M, the stripping occuring at higher acidity (5 M), but the extraction abilities sharply decreased in presence of sodium nitrate. Crown ethers, were also proposed for the extraction of cesium, bis (tert butyl benzo) 21 crown 7 or bis (hydroxyheptyl) 18 C 6 synergized by organic soluble anions like dinonyl (or didodecyl) naphtalene sulphonic acid were able to remove cesium from very acidic solutions but not in presence of high sodium concentration due to the high coextraction of sodium [4] [5]. Blasius showed that, among the classical crown ethers, DB 21 crown 7 was the only crown ether providing the required selectivity towards sodium, however to accomplish an extraction from sodium nitrate medium, the crown ether had to be combined with heteropolyacids or hexachloroantimony acid [6]. Lipophilic tert butyl (or decyl) benzo 21 crown 7 failed to quantitatively remove cesium from simulated acidic high sodium concentrates, we directed our efforts towards a new promising class of macrocycles functionalized calixarenes [7].

3 - CALIXARENES

Calix[4]arenes are macrocycles made up of phenolic units (generally n = 4 to 8) linked by methylene bridges. Butyl[4]calixarene, the cyclic tetramer, is an important building block because it can be synthesized in large amounts from inexpensive starting materials, it can be functionalized either using the phenolic oxygens, either by it’s para position. Moreover calix[4]arene is conformationally mobile and can assume four conformations: cone, partial cone, 1-2 alternate, 1-3 alternate (Fig. 1). The analogy of calix[4]arene in cone conformation with a beaker (calix in greek) led D. Gutsche to call them calixarenes. The functionalization associated with the conformational properties led to a large variety of « tailored » macrocycles.

![Figure 1]

calix[4]arene conformations
In search for better extractants than crown ethers, efforts were devoted to crown ethers built on calixarene molecular platform. Since the synthesis of a crown compound with two opposite phenolic groups linked by a penta ethylene glycol chain many calix[4]arenes with crown ether moieties were produced and proved to be efficient for the complexation of alkali and alkaline earth cations due to the presence of the crown ether link [8]. The selectivities of the complexation were strongly dependent on the conformation of the calixarenes. R. Ungaro and J. Vicens, blocked the calixarene crown into a 1,3 alternated conformation by adding respectively, either two alkyl chains either a second polyethylene glycol on the two remaining phenolic units.

Thirteen calix crowns have been studied, the extraction results are given in Table 1, the main conclusions are:

For alkxyo crown 6 and bis crown 6, the extraction is mainly dependent on conformation, the compounds in the 1,3 conformation displays the highest cesium distribution coefficients and very low sodium distribution coefficients hence the highest Cs/Na selectivity [10].

The extraction is at a lesser extent linked to the crown's size, the highest results are obtained for two classes of calixarenes with polyethylene glycol bridges containing six oxygens.

The exceptional selectivity of these two classes of calixarenes for cesium, much higher than those of the most efficient crown ethers, can be explained by the stabilization of the complexes calixarene-cesium by the bonding interactions with the four phenyl units of the calix[4]arene [11].

Table 1

<table>
<thead>
<tr>
<th>Extraction of cesium and sodium - Selectivity Cs/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous feed solution, $5.0 \times 10^{-4} \text{ M } M^+(\text{NO}_3^-)$ in 1 M HNO$_3$;</td>
</tr>
<tr>
<td>Organic solution, $10^{-2}$ M extracting agent in 1,2-nitrophenyl hexyl ether</td>
</tr>
<tr>
<td>$D_{Na}$</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>1,3-calix[4] dimethoxy crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] hydroxy ethoxy crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] dipropoxy crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] di isopropoxy crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] di n oxtyloxy crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] di methoxy crown 7</td>
</tr>
<tr>
<td>1,3-calix[4] biscrown 5</td>
</tr>
<tr>
<td>1,3-calix[4] biscrown 6</td>
</tr>
<tr>
<td>1,3-calix[4] biscrown 7</td>
</tr>
<tr>
<td>1,3-calix[4] bis-p-benzo-crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] bis-o-benzo-crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] bisnaphthyl-crown 6</td>
</tr>
<tr>
<td>1,3-calix[4] bisdiphenyl-crown 6</td>
</tr>
<tr>
<td>n-decylbenzo-21-crown 7</td>
</tr>
<tr>
<td>tert-butylbenzo-21 crown 7</td>
</tr>
</tbody>
</table>
4 - TRANSPORT OF CATIONS THROUGH SUPPORTED LIQUID MEMBRANES

4.1. Supported Liquid Membranes

The selective extractants used for extraction are often very expensive and thus limit the use of the techniques mentioned previously; work was therefore carried out in this study on the use of selective extractants with liquid membranes technology.

Supported liquid membranes (SLM) are made up of two-aqueous phases separated by an organic phase. The aqueous phase, called the feed phase, contains the radioelements to be extracted by means of the organic phase. They are then carried to the other aqueous phase, called the stripping phase. The organic phase, constituted by an extractant dissolved in a diluent, impregnates a microporous support placed between both aqueous phases. The driving force of the process is attributable to the difference of the nitrate concentrations in the feed phase [NaNO₃ (4 M), HNO₃ (1 M)] and in the stripping phase (no nitrate). The transport mechanism that takes place is called co-transport, as the cation and the extractant transit through the membrane in the same direction.

The use of neutral carriers, such as a calix[4]arene crowns, leads to a coupled co-transport of cations and nitrate anions through the SLM [12]. When concentrates or acidic solutions are used as feed solution, and demineralized water as stripping solution, the concentration gradient of the nitrate anions will force the transport of cesium against its own concentration gradient thus leading to their concentration in the stripping solution.

4.2. Permeability Determination

The transport of ¹³⁷Cs from synthetic aqueous solutions of NaNO₃ (4 M) and HNO₃ (1 M), was followed by regular measurement of the decrease of radioactivity in the feed solution by γ spectrometry analysis. This allowed graphical determination of the constant permeabilities $P$ (cm.h⁻¹) of cesium permeation through the SLM by plotting the logarithm of the ratio $C/C^o$ vs.time, as described in the model of mass transfer proposed by Danesi [13]

$$\ln \frac{C}{C^o} = -\frac{\varepsilon \cdot S}{V} \cdot P \cdot t$$

where

- $C$ is concentration of the cation in the feed solution at time $t$ (mol.l⁻¹);
- $C^o$ is initial concentration of the cation in the feed solution (mol.l⁻¹);
- $\varepsilon$ is volumic porosity of the SLM (%);
- $S$ is membrane surface area (cm²);
- $V$ is volume of feed and stripping solutions (cm³);
- $t$ is time (h).

Transport experiments were carried out with the most promising compounds; their permeability are given in the Table 2.
Table 2

\[ ^{137}\text{Cs Transport Experiments through Flat Sheet-Supported Liquid Membranes: Permeability Determination after 6 h of Permeation} \]

Aqueous feed solution, \( \text{NaNO}_3 \) (4 M) and \( \text{HNO}_3 \) (1 M); aqueous strip solution, deionized water; organic solution, \( 10^{-5} \text{M} \) carrier in 1,2-nitrophenyl octyl ether.

\[
P_{\text{Cs}} \ (\text{cm.h}^{-1})
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( P_{\text{Cs}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-calix[4] hydroxy ethoxy crown 6</td>
<td>0.4</td>
</tr>
<tr>
<td>1,3-calix[4] dipropoxy crown 6</td>
<td>1.6</td>
</tr>
<tr>
<td>1,3-calix[4] di iso propoxy crown 6</td>
<td>1.3</td>
</tr>
<tr>
<td>1,3-calix[4] di n octyloxy crown 6</td>
<td>1.9</td>
</tr>
<tr>
<td>1,3-calix[4] bis crown 5</td>
<td>( 9 \times 10^{-2} )</td>
</tr>
<tr>
<td>1,3-calix[4] bis crown 6</td>
<td>1.3</td>
</tr>
<tr>
<td>1,3-calix[4] bis crown 7</td>
<td>( 4 \times 10^{-2} )</td>
</tr>
<tr>
<td>1,3-calix[4] bis p benzo crown 6</td>
<td>( 3 \times 10^{-3} )</td>
</tr>
<tr>
<td>1,3-calix[4] bis o benzo crown 6</td>
<td>2.8</td>
</tr>
<tr>
<td>1,3-calix[4] bis naphtaphyl crown 6</td>
<td>2.7</td>
</tr>
<tr>
<td>1,3-calix[4] bis diphenyl crown 6</td>
<td>0.1</td>
</tr>
<tr>
<td>n-decylbenzo-21-crown 7</td>
<td>( 9 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

5 - TESTS ON REAL LIQUID WASTES

Two types of measurements (distribution coefficients, transport through SLMs) were carried out on two real wastes. The experiments were performed respectively in the CARMEN hot cell of CEA/DCC/DRDD on an acidic HA liquid waste provided by this Department and in the facilities of COGEMA Marcoule /Service on a M.A. concentrate provided by COGEMA Marcoule.

Several calixarenes were tested in the experiment carried out in CARMEN cell (bis crown-6-calix[4]arene, 1,3 diisopropy-2-4-crown-6 calix[4]arene and 1,3-di(2 nitrophenoxy octyloxy)-2,4- crown-6-calix[4]arene this calixarene has been conjointly synthesized by the Universities of Parma (Pr UNGARO) and Twente (Pr REINHOUDT), the latter was a very interesting compound due to its very high lipophilicity and to its great solubility in NPHE or NPOE but available in low amount. 1,3 di octyloxy-2-4-crown-6 calix[4]arene was used for decontaminating the concentrates.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{compound.png}
\caption{Structure of crown 6 calix[4]arenes}
\end{figure}

\begin{itemize}
\item Compound 1: bis crown-6-calix[4]arene
\item Compound 2: 1,3-diisopropoxy-2,4-crown-6-calix[4]arene
\item Compound 3: 1,3-di(2-nitrophenoxy octyloxy)-2,4-crown-6-calix[4]arene
\item Compound 4: 1,3-diocetyl oxy-2,4-crown-6-calix[4]arene
\end{itemize}
5.1- Test on HA liquid waste

The H.A. liquid waste is a dissolution of a MOX Fuel (Burn up 34 650 MWJ/NU) where Uranium and Plutonium have been previously extracted by TBP (classical PUREX process). Composition of the waste is summarized in Table 3.

### Table 3

**Chemical and radiochemical composition of the real raffinate to reprocess**

<table>
<thead>
<tr>
<th>Acidity</th>
<th>Concentration (mol/l)</th>
<th>Activity (Ci/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>$4.5 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>$5.1 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>$4.9 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>$4.9 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>$3 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Pu</td>
<td>$&lt;2 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>$&lt;4.2 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>$&lt;5 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>$&lt;2.1 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>$4.15 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$^{106}$Ru</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>$^{132}$Sb</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>$^{144}$Ce</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>$^{223}$Am</td>
<td>1.22 (17.8 %)</td>
<td></td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>5.57 (81.3 %)</td>
<td></td>
</tr>
<tr>
<td>$^{242}$Cm</td>
<td>0.024</td>
<td></td>
</tr>
</tbody>
</table>

Distribution coefficient measurements were carried out by putting into contact a calixarene crown 6, 0.1 M, diluted in NPHE, with the real waste, cesium distribution coefficients higher than 60 were obtained, then this cation was easily stripped in demineralized water (Table 4). Moreover the high selectivity of this class of calixarene, observed with synthetic waste was confirmed by this test: for all radionuclides (actinides or fission products: $^{106}$Ru, $^{134}$Eu, $^{132}$Sb, $^{144}$Ce) the decontamination factors (Ratio of initial activity of the elements in waste to activity of these elements in organic phase) were higher than 100 and ranging from 12 to 60 for Fe, Mo, Zr, Ce, Nd. (Table 5).

### Table 4

**Calixarènes**

<table>
<thead>
<tr>
<th>Calixarènes</th>
<th>Cesium distribution coefficients ($D_{Cs}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Extraction</td>
</tr>
<tr>
<td></td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>Back-extraction</td>
</tr>
<tr>
<td></td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>**</td>
</tr>
<tr>
<td>Compound 1</td>
<td>55±5</td>
</tr>
<tr>
<td></td>
<td>50±5</td>
</tr>
<tr>
<td></td>
<td>10±1</td>
</tr>
<tr>
<td>Compound 2</td>
<td>61±6</td>
</tr>
<tr>
<td></td>
<td>55±5</td>
</tr>
<tr>
<td></td>
<td>10±1</td>
</tr>
</tbody>
</table>

* aqueous phases mass-balance

** measurements of organic and aqueous phases
of liquid-liquid extraction of a real raffinate (Table 1) by crown calixarenes.

Cesium distribution coefficients and cesium decontamination factors towards other elements

<table>
<thead>
<tr>
<th>Calixarenes</th>
<th>Decontamination factors of cesium towards M, DF(Cs/M) :</th>
<th>Chemical elements</th>
<th>Actinides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{106}$Ru</td>
<td>$^{122}$Sb</td>
<td>$^{154}$Ce</td>
</tr>
<tr>
<td>Compound 1</td>
<td>9</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Compound 2</td>
<td>7</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Compound 3</td>
<td>73</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

Calixarene 0.1 M in 1,2-NPHE, $t = 30^\circ$C, stirring speed 1000 rpm, back-extraction : demineralized water. note : two Dcs measurements were performed. $D_{Cs} = \frac{[DCs]_{org}}{[Cs]}$. DF(Cs/M) = $D_{Cs}/D_M$.

A small percentage of nitric acid was coextracted (5 to 7 %) which is an interesting factor knowing that we observed a competitive extraction of nitric acid and cesium cation.

Calix[4]arene bis crown, diisopropoxy calix[4]arene crown 6 and di NPOE calix[4]arene (not available in sufficient amount to perform distribution coefficient measurements) were used as carriers in supported liquid membranes (0.1 M NPHE). Respectively 58.3 %, 77.5 % and 86.3 % of cesium was transported from liquid waste to the demineralized water, higher cesium activities could have been transported by increasing the duration of an experiment (Table 6). Only cesium was significantly transported during these tests, Molybdenum and Zirconium were detected in stripping phase at very low level when diisopropoxy calix[4]arene crown 6 was used, with di NPOE calix[4]arene crown 6 Molybdenum, Zirconium, Iron, Neodymium, Cerium were detected at a very low level. The decontamination (concentration of element in feed solution/concentration of elements in stripping solution) factors obtained were higher than 100 for all elements or radionuclides (Table 7).

### Table 6

Extracted cesium percentage during transport experiments

<table>
<thead>
<tr>
<th>Compound</th>
<th>Extracted cesium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>after 4 h</td>
</tr>
<tr>
<td>Compound 1</td>
<td>30.4</td>
</tr>
<tr>
<td>Compound 2</td>
<td>55.7</td>
</tr>
<tr>
<td>Compound 3</td>
<td>63.1</td>
</tr>
</tbody>
</table>

* the transport test lasted (xh)

It is obvious that bis-crown-6-calix[4]arene was the less efficient molecule. This molecule is the less lipophilic one. Because of the high ratio (aqueous phases/organic phase) used in SLM experiments (~3000-4000), the loss of extractant molecule in the aqueous media is far from negligible. Further transport kinetics of bis-crown-6-calix[4]arene were slower.

Cesium decontamination factors were highly satisfactory (Table 7). No other element (except Rubidium) was extracted at a higher level than 1-2 %.
Table 7

Cesium decontamination factors obtained during transport experiments

<table>
<thead>
<tr>
<th>Calixarenes</th>
<th>Time (h)</th>
<th>$^{106}$Ru</th>
<th>$^{125}$Sb</th>
<th>$^{134}$Ce</th>
<th>$^{134}$Eu</th>
<th>Mo</th>
<th>Zr</th>
<th>Fe</th>
<th>Nd</th>
<th>Ce</th>
<th>$\alpha$ tot</th>
<th>Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound 1</td>
<td>13</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>compound 2</td>
<td>8.7</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>compound 3</td>
<td>9</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;50</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

Permeability coefficient and membrane fluxes were calculated. The results are indicated in the Tables 8 and 9.

According to Danesi's model, flux of cations were calculated from experiments carried out with the real waste and simulated waste for different nitric acid concentrations (2-6 M). A decrease of cation flux was observed with an increase of the acidity due to an higher transport of HNO$_3$. At a HNO$_3$ 4 M concentration, the cesium flux was 10 % lowered real waste, this flux was included within the range of reproducibility of fluxes.

Table 8

Permeability coefficients obtained for Cs during transport experiments

<table>
<thead>
<tr>
<th>Calixarenes</th>
<th>$S_{\text{eff}}$ (cm$^2$)</th>
<th>time (h)</th>
<th>Cesium permeability (cm.$^{-1}$.h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed compartment</td>
</tr>
<tr>
<td>compound 1</td>
<td>12.6</td>
<td>13</td>
<td>0.66</td>
</tr>
<tr>
<td>compound 2</td>
<td>12.2</td>
<td>8.7</td>
<td>2.39</td>
</tr>
<tr>
<td>compound 3</td>
<td>12</td>
<td>9</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Table 9

Membrane fluxes obtained for Cs during the transport experiments

<table>
<thead>
<tr>
<th>Calixarenes</th>
<th>$S_{\text{eff}}$ (cm$^2$)</th>
<th>time (h)</th>
<th>Membrane flux (mol.cm$^{-2}$.h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed compartment</td>
</tr>
<tr>
<td>compound 1</td>
<td>12.6</td>
<td>13</td>
<td>$2.6 \times 10^6$</td>
</tr>
<tr>
<td>compound 2</td>
<td>12.2</td>
<td>8.7</td>
<td>$6.7 \times 10^6$</td>
</tr>
<tr>
<td>compound 3</td>
<td>12</td>
<td>9</td>
<td>$6 \times 10^6$</td>
</tr>
</tbody>
</table>

1,3-diisopropoxy-2,4 crown-6-calix[4]arene and 1,3-di(2-nitrophenoxy octyloxy)-2,4 crown-6-calix[4]arene gave better results than bis-crown-6-calix[4]arene (less lipophilic).

1,3-di (n octyloxy)-2,4 crown-6-calix[4]arene was diluted in 1,2 nitrophenyl hexyl ether ($5.10^2$ M) for the distribution coefficient measurements and transport experiments. The composition of the concentrate is given in Table 10.
Distribution coefficients of cesium exhibited 1,3-di-n-octyloxy-2,4- crown-6-calix[4]arene (Table 11) high affinity. The extraction and back-extraction percentages agreed with those obtained the high level liquid waste was decontaminated and were fairly satisfactory.

Table 11

Chemical and radiochemical composition of the real raffinate to reprocess [1]

<table>
<thead>
<tr>
<th>Cations</th>
<th>g.L⁻¹</th>
<th>M</th>
<th>Anions</th>
<th>g.L⁻¹</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>60</td>
<td>2.61</td>
<td>NO₃⁻</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>4.5</td>
<td>0.117</td>
<td>PO₄³⁻</td>
<td>1.7×10⁻³</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>14.9</td>
<td>0.620</td>
<td>Cl⁻</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.38</td>
<td>0.0095</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.5</td>
<td>0.0137</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>0.000693</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.98</td>
<td>0.0175</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>1.3</td>
<td>0.00546</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.02</td>
<td>&lt;2.1×10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.07</td>
<td>1.07×10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;0.01</td>
<td>&lt;1.1×10⁻⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Acidity : 1.05 M

Radioelements | Mbq.L⁻¹ | mCi.L⁻¹ |
--- | --- | --- |
Pu 239 to 242 | 1.7 | 0.046 |
Pu 238 + Am 241 | 8.14 | 0.22 |
Cm 244 | 1.33 | 0.036 |
Cm 242 | 6.66 | 0.18 |
Sr 89 + 90 | 648 | 17.5 |
Co 60 | 3 | 0.1 |
Ru 106 | 720 | 19.5 |
Sb 125 | 40 | 1.1 |
Cs 134 | 180 | 4.9 |
Cs 137 | 3200 | 86.5 |
Ce 144 | 350 | 9.5 |
Pr 144 | 350 | 9.5 |
Eu 154 | 9 | 0.2 |

Table 11

Cs decontamination of the real effluent by liquid-liquid extraction

<table>
<thead>
<tr>
<th></th>
<th>Extraction</th>
<th>Back-extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D Cs</td>
<td>% Extraction</td>
</tr>
<tr>
<td>134Cs</td>
<td>15.8</td>
<td>91.1</td>
</tr>
<tr>
<td>137Cs</td>
<td>14.3</td>
<td>89.2</td>
</tr>
</tbody>
</table>

feed solution : TBP washed effluent, organic solution : calixarene octyl 5.10⁻² M/NPHE, back-extraction : demineralized water.

Only residual plutonium after TBP washing and potassium are noticeably co-extracted. Sodium is not extracted at all and the Cs/Na selectivity is confirmed. Potassium is co-extracted but does not prevent Cs extraction.
The real effluent was introduced after TBP washing and acidification to 1 M HNO₃ in the central compartment of the double membrane system. (The 2 membranes contain the calixarene octyl 5.10⁻² M diluted in NPHE). This two membrane device was used to reduce the duration of transport.

After 9 hours, practically all the cesium was transferred. Other elements were left in the feed solution. The tremendous selectivity of crown 6 calix[4]arenes was demonstrated by the decontamination factors higher than 50 or 100 (Table 12), except in the case of residual plutonium. The symmetric behaviour of feed and strip concentrations confirmed that there was no cesium retention inside the membranes.

Permeabilities, reported in the Table 13, pointed out the transport's efficiency.

**Table 12**

Real effluent Cs decontamination by SLM. Solutions after 9 hours contact.

<table>
<thead>
<tr>
<th>Element X</th>
<th>D.F</th>
</tr>
</thead>
<tbody>
<tr>
<td>239-242Pu</td>
<td>2.5</td>
</tr>
<tr>
<td>238Pu + 241Am</td>
<td>148 ≥ 100</td>
</tr>
<tr>
<td>244Cm</td>
<td>154 ≥ 100</td>
</tr>
<tr>
<td>242Cm</td>
<td>803 ≥ 100</td>
</tr>
<tr>
<td>134Cs</td>
<td>-</td>
</tr>
<tr>
<td>137Cs</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>&gt;100</td>
</tr>
<tr>
<td>K</td>
<td>&gt;105 ≥ 100</td>
</tr>
<tr>
<td>Mg</td>
<td>380 ≥ 100</td>
</tr>
<tr>
<td>Ca</td>
<td>58.7</td>
</tr>
<tr>
<td>Al</td>
<td>40.7</td>
</tr>
<tr>
<td>Fe</td>
<td>&gt;1750 ≥ 100</td>
</tr>
<tr>
<td>Zn</td>
<td>&gt;302 ≥ 100</td>
</tr>
</tbody>
</table>

**Feed solution**: real effluent after TBP washing and acidified to 1 M (HNO₃), organic solution: crown calixarenes 5.10⁻² M/NPHE, back-extraction solution: demineralized water, double membrane system.

**Table 13**

Cs transport from a real effluent. Permeabilities according to Danesi
(calculated for the 4 first hours of the transport)

<table>
<thead>
<tr>
<th></th>
<th>Cs 137</th>
<th>Cs 134</th>
</tr>
</thead>
<tbody>
<tr>
<td>Right</td>
<td>1.65</td>
<td>1.70</td>
</tr>
<tr>
<td>Left</td>
<td>1.62</td>
<td>1.71</td>
</tr>
<tr>
<td>Right + Left</td>
<td>3.27</td>
<td>3.41</td>
</tr>
</tbody>
</table>

**Feed solution**: real effluent after TBP washing and acidified to 1 M (HNO₃), organic solution: crown calixarene 5.10⁻² M/NPHE, back-extraction solution: demineralized water, double membrane system.
CONCLUSION

Studies carried out with several calixarenes display the interest of using calix[4]crowns. These compounds are much more efficient than crown ether for the extraction of cesium from acidic medium and exhibit a tremendous selectivity cesium/sodium, moreover the extraction is reversible, cesium can be recovered in demineralized water, this property allows volume of waste to be strongly decreased. Some preliminary tests indicating a good stability towards irradiation of calix[4]arene crown 6 must be confirmed. Calix[4]arenes seem very promising for the removal of $^{137}$Cs from liquid containing sodium salts at high concentration and also for the selective separation of $^{135}$Cs before transmutation or disposal in a specific matrix.

ACKNOWLEDGMENTS

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BIBLIOGRAPHIE


PARTITIONING OF MINOR ACTINIDES FROM RARE EARTHS BY SOLVENT EXTRACTION WITH DI(2-ETHYL HEXYL) PHOSPHORIC ACID

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P. O. Box 105, Taejon, 305-600, Korea

ABSTRACT

A flowsheet of the solvent extraction process to separate minor actinides (MA) from rare earths (RE) was devised and experimentally tested. The process is based on the high extractabilities of minor actinides and rare earths by di(2-ethyl hexyl) phosphoric acid at low nitric acid concentrations. The extraction process, composed of one extraction and three selective stripings in series, was installed with four miniature mixer-settler banks of a total of 44 stages in a glove box. The operation was performed by using a simulated waste solution containing 15 inactive compounds as the stands-in for rare earths and other fission products, and 241Am and 237Np as radioactive tracers for the minor actinides. For each element fed to the extraction bank, more than 99% of Am, Np, and rare earths were extracted by 1M HDEHP/n-dodecane. Then each of the Am, Np, and RE was selectively back extracted into the aqueous phase by 0.05M DTPA, 6M HNO₃, and 0.5M H₂C₂O₄, respectively, in consecutive stripping processes. In these steps, 99.8% of Am, 97–99% of rare earths elements and 99.4% of Np were separated from one another. The Am and Np products, however, may require further purifications because of other impurities accompanied these elements into their respective product streams.
BACKGROUND ON PARTITIONING & TRANSMUTATION STUDIES IN KOREA

In Korea, 11 nuclear reactors (10 PWRs and 1 CANDU) are currently in operation with total generating capacity of 9.6 GWe. In addition, 7 reactor units are under construction which will be completed in the years from 1997~2002. Accordingly, the total nuclear generating capacity will reach 15.7 GWe in the year 2002. The amount of spent nuclear fuels annually arising from the current operating reactors accounts for 280 MTHM and the cumulative amount reaches about 2800 MTHM (PWR 1600, CANDU 1200 MTHM). The spent fuels are now in storage at each reactor site. However, they are to be stored at a central interim storage facility for the time being before they are reprocessed or disposed of. This program addresses the national policy of just “wait & see” because the procedure for a back-end fuel cycle has not been established yet.

Reactor wastes, namely, low-level wastes are also in storage at each reactor site. They will be disposed of in a final repository in the future. For the last 10 years, lots of effort has been devoted to find a candidate repository site in the midst of strong anti-nuclear movement throughout the country. As a result, a tiny island in the west sea was determined as the candidate site in 1995. However, it was immediately canceled because an active fault was discovered near the island in the survey of geological characteristics. Consequently, the national program on radwaste disposal has changed in that the project should be transferred to the Korea Electric Power Corporation from the Korea Atomic Energy Research Institute (KAERI).

At present, we have no high-level wastes in Korea because we do not have any fuel recycling activities. However, it might be necessary in the future to complete the nuclear fuel cycle in view of the Korean situation, that is, it depends not only on import for almost all of its energy resources, but also on nuclear energy for the major part of its electricity generation. In addition, the amount of spent fuels accumulated will increase year by year. Moreover, it might become more and more difficult to get public acceptance for the direct disposal of the spent fuels in the Korean peninsula. An alternative prospective solution for this might be the transmutation of long-lived radionuclides.

Though several countries are planning to dispose of vitrified high-level wastes at a deep underground repository, there are no countries yet in the world which have put it into action. In fact, even the environmental impact of high-level wastes disposal has not been fully elucidated yet. Actually, there is lots of concern as to whether they can be sustained without the release of radioactive material to the biosphere for hundreds of thousands of years when buried in the geologic repository. In this
respect, it would be attractive to convert the long-lived radionuclides into short-lived or stable nuclides. Residual waste management after transmutation could result in the reduction in the final disposal cost at hand, as well as in the possible contamination of the environment in the future.

With this background in Korea, both partitioning and transmutation studies are being carried out in preparation for future application. In parallel with this, the development of high-level wastes disposal technology is also being performed in KAERI. The future objective facilities for transmutation in Korea include a liquid metal reactor, and an accelerator-driven subcritical reactor (the same as a few other countries). A research project on the former is being carried out with the target of prototype reactor completion by 2011. As to the latter, a new research program is under planning in order to establish a concept of the reactor.

A study on partitioning is also being conducted with simulated waste solutions in KAERI focused on the development of MA, Cs, Sr and Pt-group metals separation methods. It is also considered to include such research area in the near future as thorium fuel cycle with pyroprocessing which is known as an alternative fuel cycle favorably applicable to the subcritical reactor.

INTRODUCTION

Most of minor actinides contained in the typical high-level liquid waste (HLLW) from reprocessing of spent nuclear fuels are composed of long-lived radionuclides. These radionuclides, if they are intended to be transmuted, must be separated from HLLW and then made into the form of target for transmutation.

One of the prospective methods to recover MA from HLLW is the extraction of them at low nitric acid concentrations using di(2-ethyl hexyl) phosphoric acid (HDEHP) as an extractant [1 ~ 6]. In this process, however, most of RE and MA have similar properties in their extractability and thus RE elements are accompanied with MA in the organic phase. Another process for the mutual separation of MA and RE is, therefore, necessary to recover the MA alone. A representative process to separate Am and Cm from RE is the reverse-TALSPEAK process [1, 6] where Am and Cm can be selectively stripped from the organic phase of HDEHP by di-ethylenetriamine pentaacetic acid (DTPA). As for Np, it exists in the state of Np(IV), Np(V), and Np(VI) in nitric acid solution by the disproportionation. The extractability of Np(IV) or Np(VI) with HDEHP is high without regard to the nitric acid concentration, whereas that of Np(V) is much lower. These properties lead to the possibility of separation of Np from either Am or RE. However, Np tends to have

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TABLE 1. CHEMICAL COMPOSITION OF THE SIMULATED WASTE SOLUTION

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRU</td>
<td></td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>$5.90 \times 10^4$ Bq/ℓ</td>
</tr>
<tr>
<td>$^{237}$Np</td>
<td>$1.66 \times 10^6$ Bq/ℓ</td>
</tr>
<tr>
<td>RE</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>$1.05 \times 10^{-3}$ M</td>
</tr>
<tr>
<td>La</td>
<td>$2.96 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Ce</td>
<td>$3.47 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Nd</td>
<td>$5.07 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Y</td>
<td>$7.90 \times 10^{-3}$ M</td>
</tr>
<tr>
<td>FP</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>$3.48 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Ba</td>
<td>$2.37 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Rb</td>
<td>$7.72 \times 10^{-3}$ M</td>
</tr>
<tr>
<td>Pd</td>
<td>$6.58 \times 10^{-3}$ M</td>
</tr>
<tr>
<td>Fe</td>
<td>$2.02 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Ni</td>
<td>$4.09 \times 10^{-3}$ M</td>
</tr>
<tr>
<td>Mo</td>
<td>$1.36 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Sr</td>
<td>$2.08 \times 10^{-2}$ M</td>
</tr>
<tr>
<td>Zr</td>
<td>$4.82 \times 10^{-5}$ M</td>
</tr>
<tr>
<td>Rh</td>
<td>$4.66 \times 10^{-3}$ M</td>
</tr>
<tr>
<td>Media</td>
<td></td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>0.1 M</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1.0 M</td>
</tr>
</tbody>
</table>

**Apparatus for Extraction and Stripping**

Four banks of miniature mixer-settler made of acrylic plastic were used for extraction and selective strips. The volume of each mixer, same with that of settler, was 13 ml. Like conventional mixer-settlers, this apparatus was also fabricated so that the aqueous and organic phase move in counter-current flow. Air pulsation produced by a membrane type pulse generator and distributed to each mixer through a pulse header was used to mix aqueous and organic phases. All the four banks of mixer-settler, as shown in Fig. 1, were installed inside an α-tight glove box in order to shield the α activities of $^{237}$Np and $^{241}$Am. Whenever they are started to run, blank-operation was carried out for over 4 hours by feeding 0.1 M HNO$_3$ instead of the simulated solution and by adjusting the interface level in the settlers so that they can reach an optimal hydraulic condition in advance. Then the regular operation was started by switching the feed to the simulated solution.
more stable form of Np(V) in larger proportion at lower concentration of nitric acid and thus it is necessary to reduce it to the state of Np(IV) or to oxidize to Np(VI) in order to extract it into the organic phase. These characteristics make it possible to combine a few unit processes to a probable process for the partitioning of Am, Cm group, RE group and Np one another. On the basis of the above concept, a partitioning process constituted of one extraction and three selective stripping was drawn out and its validity was experimentally tested in this study. The experiments were conducted with a simulated waste solution containing 17 metal elements. The simulated solution was prepared with 15 inactive compounds as the stands-in for RE and other fission products, and with tracers of $^{241}$Am and $^{237}$Np as the stands-in for Am and Np, respectively. Four banks of miniature mixer-settler with a total of 44 stages were used for extraction as well as selective stripping apparatus. The stripping agents, DTPA, HNO$_3$ and H$_2$C$_2$O$_4$ were respectively employed for back extraction of Am, RE and Np.

**EXPERIMENTAL**

**Preparation of a Simulated Waste Solution**

A simulated waste solution was prepared to contain major metal components of the typical high-level liquid waste from the reprocessing of spent fuels. Inactive compounds of rare earths, Fe, Ni, Mo, Sr, Zr, Cs, Ba, Rb, Pd and Rh were dissolved in the medium, 0.1 M HNO$_3$, in order that they have similar concentrations to those of the high-level liquid waste. Trace amounts of $^{241}$Am and $^{237}$Np were also added to the solution as stands-in for minor actinides, to track the behaviors of Np, Am and Cm in the partitioning process. Hydrogen peroxide [7, 8] was added to the stock solution to control the oxidation valence of Np as Np(IV) because it has higher extractability with HDEHP. Chemical composition of the simulated waste stock solution is illustrated in Table 1.
Extraction of TRU and RE

A 14-stage bank (A1) as shown in Fig. 1 was used for extraction. The simulated solution (aqueous feed), 0.1 M HNO₃ (scrub) and 1M HDEHP/ n-dodecane (extractant) were respectively injected into the 10th, 14th and 1st stage. The operation conditions of the banks are listed in Table 2.

<table>
<thead>
<tr>
<th>Bank No.</th>
<th>Feed Description</th>
<th>Feeding stage</th>
<th>Flow rate (mL/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1: simulated waste</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>2: 0.1 M HNO₃</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>3: 1M HDEHP</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>A2</td>
<td>4: loaded HDEHP</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>5: 1M HDEHP</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>6: 0.05M DTPA in 1.5M Lactic acid</td>
<td>14</td>
<td>95</td>
</tr>
<tr>
<td>A3</td>
<td>6: loaded HDEHP</td>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>7: 6M HNO₃</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>A4</td>
<td>8: loaded HDEHP</td>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>9: 0.5M H₂C₂O₄</td>
<td>8</td>
<td>95</td>
</tr>
</tbody>
</table>

Stripping of Am

A 14-stage bank (A2) was used to strip Am from the organic phase. 0.05M DTPA and 1.5M lactic acid mixture (pH : 3.1) [9] was fed to the 14th stage as a stripping agent while the organic feed containing MA and RE was supplied to the 5th stage. 1M HDEHP/n-dodecane, injected to the 1st stage, served as the scrubber of aqueous stream by extracting Np and RE again to the organic phase.

Stripping of RE

RE elements were stripped from the organic phase by 6 M HNO₃ in the 8-stage bank A3. In this bank, only RE were selectively washed out to the aqueous phase leaving Np still in the organic phase.
**Stripping of Np**

Finally Np was stripped from the organic phase by 0.5 M H₂C₂O₄ [10] through the 8 stages of the bank A4. The Np-loaded solvent was injected into the 1st stage while oxalic acid was fed into the 8th stage.

**Chemical Analyses**

Radioactivities of ²³⁷Np and ²⁴¹Am were measured using a multichannel analyzer (Afora Model LP-4900B) with Ge(Li) detector. Since the elements Ba, Sr, Eu, La, Zr, Ce, Nd and Y are inactive, their concentrations were obtained by an Inductive Coupled Plasma Spectrophotometer. The concentrations of Cs, Rb, Fe, Ni, Pd, Mo and Rh were measured with an Atomic Absorption Spectrophotometer (Hitachi Model 180.80).

**Solvent Regeneration**

The used solvent, containing Fe and mono-ethylhexyl phosphoric acid (H₂MEHP) as the major degradation components, was washed with the mixture of 5% (NH₄)₂CO₃ and 2M manitol.

**Definition of Relative Concentration**

In order to evaluate the state of extraction or stripping of a metal component, the relative concentration (C*) of the metal component concerned was defined as follows:

\[
C^* = \frac{M_i \cdot F_i}{M_f \cdot F_f}
\]

where the subscripts f and i denote feed stream to the bank A1 and internal stream in the corresponding bank, respectively.
RESULTS AND DISCUSSION

Extraction of TRU and RE

Over 99% of Am and Np were found to be extracted by 1M HDEHP/n-dodecane in the bank A1. The contents of Np and Am released to the raffinate were less than 50 Bq/l which were the measurable limits of radioactivity. Fig. 2 shows the steady state concentration profiles of Am, Np, and Eu for the relative concentrations as defined in Equation (1). The high extractability of Np was due to the valency control of Np (Np(V) → Np(IV)) by means of H₂O₂.

Among the impurities contained in the stream of Np and Am, the major ones were found to be RE, Zr, Mo and Fe because 99% of RE, Zr and Fe and 97.8% of Mo were extracted into the organic phase together with Np and Am. Though Ba, Ni, Sr, Cs, Rh, Pd and Rb were also accompanied into the organic phase, their contents lay within the range of only 1 ~ 4% out of the quantities in the feed. Since these impurities tend to cause the forming of the third phase, it would be quite desirable to remove them prior to the solvent extraction.

Selective Stripping of Am

Experimental results show that 99% of Am was selectively stripped from the organic phase in the bank A2. Fig. 3 shows the steady state aqueous concentration profiles of Am, Np, and Eu in the aqueous phase of the bank A2. Np content in the aqueous outlet stream was measured as less than 50 Bq/l assuring that Am and Np can be mutually separated by this selective strip. However, 2.3% of RE, 7% of Fe, 85% of Mo and 0.01~2% of Ba, Ni, Sr, Cs, Rh, Pd and Rb were accompanied with Am into the aqueous outlet stream. Among the RE elements, Eu showed the largest portion of stripping by displaying 2% of the original amount in the feed was liberated to the aqueous phase, which is over 100 times higher than those of other RE elements. These experimental results show that additional purification procedures must be introduced if pure Am product is required.

Selective Stripping of RE

Since the distributions of all RE elements by 1 M HDEHP/n-dodecane are very low at high nitric acid concentrations, the loaded RE could be stripped with 6 M HNO₃. Experimental results show that over 98% of RE were stripped whereas other elements, Np, Ba, Ni, Sr, Cs, Rh, Pd and Rb, were washed out by only 0.01 ~ 2%. Fig. 4 shows the steady state aqueous concentration profiles of La, Nd, Y, and Np in the bank A3. When the aqueous concentration profiles of La, Nd and Y are compared.
one another, as shown in Fig. 4, they represent almost same pattern of profiles meaning that RE elements have very similar behaviors in the extraction and the strippings.

**Stripping of Np**

The Np loaded in the organic phase was finally stripped with 0.5 M H$_2$C$_2$O$_4$. More than 99.4% of Np was stripped back into the aqueous phase accompanying 6.6% of Fe whereas other elements were back extracted from the organic phase by less than 0.1%. The steady state aqueous concentration profile of Np in the bank A4 was illustrated in Fig. 5.

**Composition in the Aqueous Outlet Stream of Each Bank**

The aqueous outlet streams of the bank A1 and A3 correspond to raffinates while those of A2 and A4 correspond to products. The compositions of these outlet streams, expressed as relative concentrations of the unit of percentage (C' x 100), are given in Table 3. The Am product stream of the bank A2 shows that 99.8% of Am was recovered from the original simulated waste. However, it contains appreciable amounts of impurities such as 86.4% of Mo and 7.3% of Fe. The Np product stream of the bank A4 also shows that 99.4% of Np was recovered, however, containing 6.6% of Fe as the only considerable amount of impurity.

**Solvent Regeneration**

The Fe still left in the organic phase was favorably removed by treating with the washing agent mentioned earlier. However, the H$_2$MEHP, one of the degradation products of HDEHP, was removed only in part from the used solvent.
### TABLE 3. THE RELATIVE CONTENTS OF THE VARIOUS ELEMENTS IN THE AQUEOUS OUTLET STREAM OF EACH BANK (Unit: %)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Am</td>
<td>0.03</td>
<td>99.83</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Np</td>
<td>&lt;0.31</td>
<td>&lt;0.31</td>
<td>0.34</td>
<td>99.37</td>
</tr>
<tr>
<td>La</td>
<td>0.01</td>
<td>trace</td>
<td>98.1</td>
<td>trace</td>
</tr>
<tr>
<td>Ce</td>
<td>trace</td>
<td>0.08</td>
<td>99.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>Nd</td>
<td>&quot;</td>
<td>0.03</td>
<td>99.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>Y</td>
<td>0.02</td>
<td>0.03</td>
<td>99.4</td>
<td>0.01</td>
</tr>
<tr>
<td>Eu</td>
<td>0.08</td>
<td>2.32</td>
<td>97.5</td>
<td>0.09</td>
</tr>
<tr>
<td>Cs</td>
<td>98.75</td>
<td>1.05</td>
<td>0.09</td>
<td>trace</td>
</tr>
<tr>
<td>Rb</td>
<td>98.18</td>
<td>0.32</td>
<td>0.11</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ba</td>
<td>98.65</td>
<td>0.05</td>
<td>0.03</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sr</td>
<td>98.24</td>
<td>0.16</td>
<td>0.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pd</td>
<td>99.43</td>
<td>0.43</td>
<td>0.86</td>
<td>&quot;</td>
</tr>
<tr>
<td>Rh</td>
<td>97.5</td>
<td>0.48</td>
<td>0.77</td>
<td>&quot;</td>
</tr>
<tr>
<td>Fe</td>
<td>0.51</td>
<td>7.26</td>
<td>0.08</td>
<td>6.58</td>
</tr>
<tr>
<td>Ni</td>
<td>96.2</td>
<td>1.73</td>
<td>1.11</td>
<td>trace</td>
</tr>
<tr>
<td>Mo</td>
<td>2.2</td>
<td>84.61</td>
<td>0.77</td>
<td>0.01</td>
</tr>
</tbody>
</table>

trace : < 0.01

### CONCLUSIONS

It was shown that the Am and Np, can be effectively recovered from the simulated waste solution by extraction with HDEHP followed by selective strippings. In addition, Am, Np, and RE could be independently separated from each other. As a result, the recovery ratios of Am and Np were found to be 99.8% and 99.4%, respectively. However, the Am and Np products were carrying some amounts of impurities, that is, 7.3% Fe and 84.6% Mo in the former, and 6.6% Fe in the latter, with respect to the original quantities contained in the feed. 97.5 ~ 99.7% of rare earth elements were removed into the RE outlet stream of the bank A3.
REFERENCES

Part 1. Extraction of Am, RE, and Np

1. 1M HDEHP
2. 80 ml/hr
3. HLLW
4. 0.1M HNO₃
5. Raffinate

Part 2. Selective strippings of Am, RE, and Np

1. 1M HDEHP
2. 15 ml/hr
3. 80 ml/hr
4. 0.05M DTPA in 1.5M Lactic Acid
5. 95 ml/hr
6. 6M HNO₃
7. 30 ml/hr
8. 5M H₂C₂O₄
9. 95 ml/hr
10. 1M HDEHP
11. 10 ml/hr
12. 80 ml/hr
13. 15 ml/hr

Figure 1. Flowsheet for respective partitioning of Am, RE and Np by extraction with HDEHP and selective strippings
Figure 2. Concentration profiles of Am, Np, and Eu in the organic and aqueous phases of the bank Al
Figure 3. Concentration profiles of Am, Np, and RE in the aqueous phase of the bank A2
Figure 4. Concentration profiles of RE(La, Nd, Y), and Np in the aqueous phase of the bank A3
Figure 5. Concentration profile of Np in the aqueous phase of the bank A4
ABSTRACT
Current status of development of pyrometallurgical reprocessing technology by CRIEPI was summarized. As for the electrorefining process, three different electrodes were developed for getting higher process efficiency. The prismatic anode basket which rotates during electrorefining was found to accelerate the fuel dissolution. Collection efficiency and morphology of electrodeposited uranium on steel mandrel cathode was found to vary with anode/cathode area ratio. Paddle-shaped stirrer was developed for liquid cadmium cathode which collects TRUs and uranium simultaneously. Optimal operational conditions such as cathode current density and Reynolds number of stirring were determined for collecting uranium without forming dendrite. As one of the promising way to immobilize the water-soluble salt waste, to synthesize natural occurring mineral which contain halide salt in three dimensional cage structure was proposed. Measured leachability from synthesized mineral which contained FP simulating elements was as low as those from vitrified waste form.

I. INTRODUCTION
As the most promising way to reconcile safety and economy, Central Research Institute of Electric Power Industry (CRIEPI) have been focusing on the metal fuel cycle (MFC) that originally developed by Argonne National Laboratory. Pyrometallurgical reprocessing combined with injection fuel casting gives the key features such as compactness, economy and diversion resistance to the MFC. CRIEPI has been studying MFC technology since 1986 in order to establish the technical basis of MFC. Presently, applicability of pyrometallurgical technology is extended around the fuel cycle, as shown in Fig. 1. In this presentation, current status of technological development of the pyrometallurgical processing shown in Fig. 2 was summarized with emphasis on the molten salt electrorefining and waste salt immobilization.

II. ELECTROREFINING PROCESS
An operational sequence of electrorefining step is schematically shown in Fig. 3. The chopped spent metal fuels or reduced oxide fuels are loaded into an anode basket, and actinides are anodically dissolved. They are reduced and collected at two types of cathodes. One is a solid cathode which collects essentially pure uranium, and another is a liquid cadmium cathode where all of the actinides (uranium, plutonium, neptunium, americium and curium) are recovered. Chemically more active FPs such as cesium, barium, cerium, etc. accumulate in the electrolyte salt in the forms of their chlorides. Less active FPs such as ruthenium and
molybdenum remain in anode basket or fall into liquid cadmium layer at the bottom of the electrorefiner. Development of each electrode in the electrorefiner is described below.

A. Anodic Basket for Fuel Dissolution

Anode basket should offer good contact between chopped fuel pins and fresh bulk electrolyte to prevent accumulation of oxidized actinides in the electrolyte around fuels and to facilitate transport of them(7). Hence, two types of anode baskets with different configuration of perforated stainless steel panels were tested. Fig. 4 shows the dissolution rate of uranium segments, 10 mm in diameter and 20 mm in length, charged in these baskets. The higher anode current efficiency was obtained for the prismatic baskets arranged at right angles. It was also found that the dissolution rate is increased with faster rotation of anode baskets.

B. Solid iron cathode for uranium recovery

Due to the highest redox potential among actinides and chemically active FPs(8), uranium predominantly deposits on solid (steel) cathodes. Uranium electrotransport tests were carried out with various concentration of uranium in the electrolyte salt by using the steel cathodes in three different diameters. No deposit was collected on any cathodes at lower concentration (about 0.5 wt%), while dendritic deposits were obtained for any cathodes at higher concentration (about 2.0 wt%). Fig. 5 shows the photographs and the collection efficiency of these deposits. With using the cathode of 15 mm dia. where anode to cathode area ratio was 10.8, needles of the dendritic deposit were thin, long and likely to be broken off from the cathode. That seems to be why the collection efficiency was extremely low in this case. In the case of 30 mm dia. cathode where anode to cathode area ratio was 5.4, the dendrite was much more adherent so that the collection efficiency was quite better. When cathode area was increased further to diameter of 70 mm where anode to cathode ratio was 2.3, concentration polarization was arose at the liquid cadmium anode and the transport of uranium was interrupted, although collection efficiency was fairly good.

C. Liquid cadmium cathode for TRUs recovery

When liquid cadmium cathode is used, TRUs are collected together with uranium because of their significantly reduced chemical activities in liquid cadmium(8). One of the problems regarding to the liquid cadmium cathode is the formation of dendritic uranium(9). When uranium deposits faster than it is taken into the bulk cadmium, uranium dendrite forms at the surface of the cathode as shown in Fig. 6. Once the dendrite grows up, current is concentrated on it and liquid cadmium cathode works as a solid cathode where only uranium continues to deposit.

In order to avoid this problem, stirring of cathode cadmium was considered to facilitate the transport of uranium in cathode cadmium from surface to the bulk. Suitable conditions for depositing uranium on stirred liquid cadmium cathode have been studied by using the puddle shaped stirrer. Fig. 7 shows the effect of stirring with different cathode current density on dendrite formation. The height of each bar indicates how much uranium can be collected without liquid cadmium cathode before dendrite begins to grow up. It shows much
more uranium can be collected without forming dendrite with more impetuous stirring. In these tests, uranium was collected up to 10 wt% into the cathode with current efficiency of approximately 100%.

D. Computer code development for design optimization

(i) simulation of electrochemical behavior

Practically, conditions for electrorefining operation such as composition of the spent fuel and of electrolyte salt cannot be kept constant. Hence, a computational code, TRAIL, was developed for analyses and prediction of the electrotransport behavior of elements in various condition. This code employs diffusion-limited electrochemical reaction model described in Fig. 8. A comparison between actual result of the electrotransport test of uranium and plutonium reported by ANL and calculation is shown in Fig. 9. Good agreement between composition of the cathode products in both cases indicates that the behavior of each element in electrorefining step can be predicted by this code.

(ii) potential distribution calculation of specific electrorefiner

Decrease of the cell resistance is necessary for developing high throughput electrorefiner. Cell resistance strongly dependent on the geometrical configuration of the electrodes in the electrorefiner. Hence, a computational code, CAMBRIA, was developed for analyses of the cell resistance of the electrorefiner with various electrode configuration. This code enables to calculate the 2-dimensional potential distribution and current distribution in the electrolyte by solving the Laplace equation with using Finite Element Method. It should be noted that this code calculates the configuration resistance without polarization. As shown in Fig. 10, however, it works well for rough prediction of the cell resistance.

III. IMMOBILIZATION of SALT WASTE

Salt waste generated at electrorefining step contains much amount of chemically active FPs such as alkali, alkaline earths, and iodine in the form of halides. Because these halides are highly soluble into water, this salt has to be converted into a stable chemical form for disposal. Alkali halides and alkaline halides are, however, hard to be converted directly into oxides, and to be dissolved into bolosilicate glass in high concentration. Hence, method to immobilize waste salt has to be developed. At present, two different immobilization methods are under study in CRIEPI. One is an electrolysis of waste salt into metal and chlorine gas followed by vitrification. It is found that the use of different cathode materials made it possible to separate the radioactive elements from nonradioactive base salt. The detail of the experimental results of this method will be reported in this conference. Another method is to synthesize natural occurring mineral that contains halide salt stably in its structure from the waste salt. The three dimensional sodalite structure (Fig. 11) was found to be synthesized according to the following dry reaction,

\[ 6\text{NaAlO}_2 + 2\text{NaCl} + 6\text{SiO}_2 \rightarrow \text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6]\text{Cl}_2, \]
where a mixture of NaA102, SiO2 and simulated waste salt were pressed at 200 MPa and heated at a
temperature of 973 - 1173 K for 50 - 100h. Products were identified as of sodalite structure by X-ray
diffraction. Leachability was measured for the synthesized sodalite specimen before or after irradiation by γ-
ray. As shown in Table 1, measured leachability of the relevant elements are as low as the values reported for
vitrified waste form or zeolite form[16].

V. SUMMARY

Major progress and present status were summarized on electrorefining process and waste salt
immobilization process. Although it is still in an early stage of development comparing to the conventional
PUREX process, any problems regarding to actual application of pyrometallurgical processing technology was
not found, yet. This technology was originally developed in the United States, however, CRIEPI is now
planning to continue research and development activities to establish its practicability as an advanced
reprocessing technology.

ACKNOWLEDGMENT

The authors wish to acknowledge the contributions from the joint study with Toshiba Corp. for
electrorefining and Hitachi Ltd. for waste salt treatment. They also acknowledge the information exchange with
Argonne National Laboratory about pyroprocess technology.

REFERENCES

Fig. 1 CRIEPI's PYRO program in fuel cycle.

Fig. 2 Pyrometallurgical reprocessing process.
Fig. 3 Sequence of electrorefining process.

Fig. 4 U dissolution rate with different anode baskets.

Fig. 5 Deposits on solid cathodes of different diameter.

Fig. 6 Uranium dendrite on liquid cadmium cathode.

Fig. 7 Deposited U amount before dendrite formation.
Fig. 8 Model for electrorefining simulation code.

Fig. 9 Electrorefining behavior reported by ANL.

Fig. 10 Cell resistance of electrorefiner.

Table 1 Leachability (g/cm²d) from sodalite, zeolite and glass.

<table>
<thead>
<tr>
<th></th>
<th>sodalite</th>
<th>zeolite</th>
<th>bolo-silicate glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.0047</td>
<td>0.12</td>
<td>0.29</td>
</tr>
<tr>
<td>K</td>
<td>0.0061</td>
<td>0.031</td>
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</tr>
<tr>
<td>Na</td>
<td>0.0023</td>
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<td>Al</td>
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<tr>
<td>I</td>
<td>0.0029</td>
<td>NM</td>
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</tr>
</tbody>
</table>

NM: not measured

Fig. 11 Sodalite structure with 3-D cage.
MINOR ACTINIDE SEPARATION
RECENT ADVANCES AT THE CEA

Alain LEUDET, Bernard BOULLIS and Charles MADIC

Commissariat à l’Energie Atomique
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ABSTRACT

In the frame of the french SPIN programme, R&D work has been undertaken at the CEA in order to develop minor actinides separation. The main route concerns solvent extraction processes, and in particular:
- PUREX process adjustment for Np selective recovery;
- DIAMEX process development for Am and Cm extraction from PUREX raffinate.

Important advances have been recently achieved, especially in the field of Am and Cm separation:
- optimization of diamide formula,
- flowsheet improvement to prevent FP extraction,
- progress in An(III)/Ln(III) separation using new extractants.

Main R&D results are presented and discussed.
1. INTRODUCTION

In December 1991, the French Parliament passed a law on research into radioactive waste management. One of its Articles required the “finding of solutions for the separation and transmutation of long-lived radionuclides present in high-level long-lived wastes”. The law set a time limit of fifteen years.

This request is connected with the chemical separation of certain elements and radionuclides of spent fuels to transmute some of their long-lived radioactive isotopes liable to incur long-term hazards. The target elements of this strategy are primarily the so-called minor actinides (neptunium, americium and curium), due to their large contribution to the waste radiotoxic inventory after 1000 years.

Given the large amounts of irradiated fuels to be reprocessed, any valid separation process must be industrial, implying processes as reliable as possible, and always striving to minimize the doses to the personnel and the production of effluents and secondary wastes.

The field is hence limited by these restrictions. The CEA accordingly decided to develop original processes, by relying on considerable basic research conducted for a better understanding of the separation mechanisms. This paper reviews the methods selected and sheds light on recent developments.

2. PROBLEMATICS OF THE SEPARATION OF MINOR ACTINIDES

Irradiated fuel reprocessing by the PUREX process generates a high-level effluent containing all the soluble fission products and minor actinides. This effluent is concentrated today, and then, after interim storage of about one year, the elements it contains are encapsulated in a glass matrix which guarantees high-quality conditioning.

Table 1 lists the quantities of minor actinides contained in one ton of reference UOX fuel, irradiated to 33 GWD/t and cooled for three years.

<table>
<thead>
<tr>
<th>element</th>
<th>isotope</th>
<th>half-life (years)</th>
<th>mass (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np</td>
<td>237</td>
<td>$2.1 \times 10^6$</td>
<td>430</td>
</tr>
<tr>
<td>Am</td>
<td>241</td>
<td>430</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>7400</td>
<td>100</td>
</tr>
<tr>
<td>Cm</td>
<td>245</td>
<td>28</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>244</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>8500</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1: Minor actinides contained in reference UOX fuel

It is important to develop separation processes whose feasibility can be proved before 2006, the deadline set by the law. It was decided to assign priority to developing liquid/liquid extraction processes, which are extremely efficient and could be integrated with the present PUREX process.

The separation of minor actinides raises two very different technical problems according to the element concerned.

- In some conditions, neptunium can be extracted in tri-n-butylphosphate (TBP), the solvent used in the PUREX process. In the operating conditions of the standard PUREX process, it is estimated that about 3/4 of the neptunium is extracted by the TBP in the first extraction cycle, and then separated in the second uranium purification cycle. To guarantee more complete separation of this element, the PUREX process conditions must therefore be adjusted to achieve the desired performance.
• Americium and curium are not extractable by TBP and remain in the aqueous phase produced by the PUREX process. The separation of these elements will require finding new classes of extractants, or the development of different separation techniques. It goes without saying that the latter problem is far more complex than the former.

3. SEPARATION OF NEPTUNIUM

Neptunium, whose stable oxidation state in nitric medium is (V), is relatively inextractable as this species by TBP. However, the dissolution liquors fed to the first extraction cycle of the PUREX process contains significant amounts of nitrous acid, which oxidizes a portion of the Np(V) to Np(VI), a form in which neptunium can be extracted in the organic phase.

Once the neptunium is extracted by the TBP, it follows the uranium stream, and can be separated easily from this stream in the second uranium purification cycle, by changing its oxidation state.

\[
\begin{align*}
\text{U, Np} & \rightarrow 1 \text{CUPu} \\
\text{Pu} & \rightarrow 2 \text{CU} \\
\text{FP, Am, Cm} & \rightarrow \text{Np(V)} \\
\text{reducing agent} & \rightarrow \text{U}
\end{align*}
\]

The basic principle of intensive neptunium separation consists in privileging its oxidation to the hexavalent state by the following reaction:

\[
\text{NpO}_2^+ + 0.5 \text{NO}_3^- + 1.5 \text{H}^+ \rightleftharpoons \text{NpO}_2^{2+} + 0.5 \text{HNO}_2 + 0.5 \text{H}_2\text{O}
\]

This reaction is reversible and catalysed by the nitrous acid produced by the reaction.

To develop this process, two types of investigation were conducted:

• Consolidation of the PAREX code used to predict the behavior of neptunium in the PUREX process. Backup laboratory tests were also performed to consolidate know-how on the redox mechanisms of the Np(V)/Np(VI) system in the presence of the pair HNO_3/HNO_2.

• Comparison of the results of the model with experiments performed in a laboratory-scale installation of α pulsed columns.

These studies revealed that relatively simple changes to the standard PUREX process should significantly improve the neptunium extraction yield. The overall target is a yield of 99.9% (99% in the PUREX process and complementary 0.9% in the DIAMEX process).

If the separation performance is insufficient in terms of the objective assigned, the oxidation of neptunium would have to be intensified by using a specific oxidant of the element, such as vanadium (V). This method has not undergone any development at the CEA for the time being.
4. SEPARATION OF AMERICIUM AND CURIUM

The high-level raffinate from the first extraction cycle of the PUREX process contains the whole americium and curium inventory, and most of the fission products from the irradiated fuel. The CEA is developing two types of process to extract and separate these minor actinides from the fission products. The first is based on extracting the actinides at their stable degree of oxidation in nitric medium, An(III), and the second process chiefly relies on the selective oxidation of americium in degree (IV) or (VI), followed by its selective separation by extraction or nanofiltration. This process, named SESAME, is not dealt with here.

In developing the extraction process for actinides in oxidation degree (III), two requirements were decided from the outset.

- To perform the extraction of An(III) without adjusting the nitric acidity of the high-level raffinate, to eliminate any risk of undesirable precipitation of fission products.

- To minimize the production of secondary wastes by only using totally degradable organic compounds (extractants or reagents). This principle was named the CHON principle, by reference to the substances used, which exclusively contain the atoms C, H, O and N.

The diamide extractants and especially those of the malonamide family (in which the two amide functions are separated by a single carbon atom) can extract An(III) while meeting the above two requirements. This process was named DIAMEX (DIAMide Extraction).

Like the other compounds developed to extract An(III), diamide extractants display no selectivity for all trivalent elements. In particular, the elements of the lanthanide family which have external electron structures and dimensions comparable to those of Am$^{3+}$ and Cm$^{3+}$ ions, are extracted jointly. This entails the need for a supplementary step to separate the two families.

In brief, the separation process for americium and curium is a two-step process:

- An(III)-Ln(III) co-extraction by the DIAMEX process,
- An(III)/Ln(III) partition.

A detailed description of this process is given below.

4.1. DIAMEX process

The extraction of trivalent cations from strongly acidic nitric medium is a difficult operation due to the weak extraction ability of An(III) nitrates and the strong competition which occurs between the extraction of nitric acid and that of the An(III) nitrates.

Diamides, which have two donor oxygen atoms, react with the metallic ion to form a six-apex chelation ring, which is extremely stable. This property considerably increases the affinity of the extractant for trivalent cations.

A first compound was selected in 1991 for the development of the DIAMEX process, dimethyl-dibutyltetradecylmalonamide (DMDBTDMA), with the following semi-developed formula :
This substance was used for the first tests performed on real active solutions in 1993. These tests confirmed the possibility of quantitatively extracting americium and curium (a yield in excess of 99.5% was obtained with only six extraction stages), and then to strip them using a weakly acidic aqueous solution.

However, many flaws were identified at the time:

- a very limited operating range due to a low threshold of third phase appearance,
- undesirable extraction of some fission products, such as Zr, Mo and Ru.

Two research directions were pursued in parallel to solve these problems:

- optimization of the formula of the diamide extractant to improve its properties related to third-phase formation,
- the development of a flowsheet designed to increase the extraction selectivity.

**Extractant optimization**

The properties of diamide extractants can be adjusted by selecting the types of radical carried by the nitrogen atoms of the amide functions and by the central methylene bridge.

Third-phase formation in an extraction process is due to exceeding the solubility of the ligand/cation complex in the organic phase, and results in separation of the organic phase into two phases.

Increasing the length of the alkyl groups helps to increase the lipophilic property of the extractant and of its solvates, increasing the solubility of these products in the organic phase. However, this elongation may have two harmful effects:

- it increases the size of the molecule and, in some situations, decreases the accessibility of the amide functions, to the detriment of the extractive properties,
- it increases the risk of the formation of long-chain degradation products, which may have undesirable surfactant properties, and are difficult to remove from the degraded solvent by aqueous washing because of their insolubility in water.

Hence, optimization of the extractant involves finding the best compromise between the foregoing antagonistic effects. A new compound is currently being identified. It will be synthesized and tested to check that the improvements anticipated are effectively achieved.

**Increasing extraction selectivity**

The alternatives considered to minimize the undesirable extraction of Zr and Mo are based on the formation of inextractable complexes. Several processes have been envisaged, including:

- a separate complexation of the two elements (ketomalonic acid for Zr and hydrogen peroxide for Mo), which necessarily demands two distinct steps because these two compounds interact with each other,
- a combined complexation of both elements by oxalic acid.

It is also necessary to control the behavior and extraction of ruthenium. This is a much more difficult problem, because this fission product has an extremely complex and still virtually unknown chemistry within the DIAMEX process conditions.

**4.2 Actinide(III)/lanthanide(III) partition**

When they leave the DIAMEX process, the actinides(III) are in dilute nitric acid solution, mixed with lanthanides(III). The latter are much more abundant because the molar ratio \( R = \text{number of moles Ln/number number} \)
of moles An is close to 50 for standard UOX fuel. It was decided to assign priority to developing processes for the extractive selection of An(III), leaving the most abundant elements in the initial aqueous solution. This helps to limit the solvent inventory and the size of the extraction units.

Actinide(III)/lanthanide(III) partition is certainly the most difficult step to design in a separation process for minor actinides. This is because very selective compounds have to be found, capable of recognizing elements with very similar properties, and which also have sufficient extraction properties.

All known processes for the separation of the actinide/lanthanide group in oxidation state (III) use the selective properties of ligands containing 'soft' donor atoms. These form stronger complexes with An(III) than with Ln(III).

The most common explanation for this is the existence of a stronger degree of covalence in bonds with actinides, due to a larger spatial extension of the 5f orbitals (actinides) in comparison with the 4f orbitals (lanthanides).

Since trivalent actinides and lanthanides are 'hard' cations in the HSAB (Hard Soft Acid Base) classification, the bonds with 'hard' ligands, such as those which have oxygen donor atoms, are essentially electrostatic, and this partial covalence can only occur with less electro-negative donor atoms than oxygen, i.e. nitrogen or sulfur.

The CEA pursues the following basic objective:

- Selective extraction of An(III) which account for the minority portion of the elements present, by developing an extractant compound which has 'soft' donor atoms.
- Use of an extractant which raises no new problems in waste management and preferably complies with the CHON principle. This limitation reduces the choice to nitrogen molecules and excludes the use of sulfur atoms.
- Direct operation on the aqueous solutions produced by the DIAMEX process, without intermediate acidity adjustment. This implies the presence of an extractant system which operates at relatively high acidity (0.5 to 1 mol/L).

The approach adopted is to design an extractant compound based on a selective complexant for the actinides, made lipophilic by the addition of organic groups.

Two nitrogen complexants were selected:

TPTZ (tripyridyltriazine)

This compound has a coordination site with three nitrogen atoms, which favors good selectivity for An(III) versus Ln(III).

Pyridine 2 carboxamide (picolinamide)

also capable of selective complexation of the actinides, probably via the nitrogen/oxygen site.
Nevertheless, this type of ligand forms weaker bonds with metallic cations than those obtained with oxygenated ligands. This factor underlies the chief difficulty in the application of the processes: competition with oxygenated ligands (e.g. molecules of solvation water), during the extraction process, in which the total or partial dehydration of the metallic ion is required.

The grafting of alkyl groups on these complexing molecules has not made it possible so far to guarantee the intrinsic lipophilic property of the complex to obtain its extraction in the organic phase in the desired acidity range.

This problem is being dealt with by examining the possibility of associating a more lipophilic anion with the extraction process than the nitrate anion, such as the conjugate base of an organic acid:

\[
\text{An}^{3+} + \text{3HA + L} \leftrightarrow \text{AnA}_3\text{L} + \text{3H}^+
\]

HA is the organic acid and L the nitrogen ligand.

The nitrogen complexant/acid exchanger pair forms a synergistic mixture whose extraction efficiency is increased in comparison with that of the two constituents considered separately. The nitrogen complexant cannot extract the actinide nitrates from the aqueous solution by itself, because of the insufficient lipophilic property of the complex formed. Conversely, the acid exchanger cannot distinguish the actinides from the lanthanides because it only has ‘hard’ donor atoms.

To be effective in relatively acidic medium, the organic acid must be sufficiently strong to ensure the lability of the H\(^+\) proton in this medium. Synergistic systems including \(\alpha\)-bromodecanoic acid and TPTZ or TtBPTZ (tri-tertiobutylpyridyltriazine) were studied.

The following results were obtained:

- americium is extracted better than europium with a separation factor of around 10,
- TtBPTZ offers better metal ions distribution coefficients than TPTZ, demonstrating the influence of the lipophilic property of the nitrogen agent on the extracting power of the synergistic mixture.

The entire challenge of this approach is thus contingent on finding strong organic acids, which comply with the CHON principle. Investigations so far have focused on carboxylic acids with an electron attractor group in the \(\alpha\) position, such as -CN and -OH.

### 5. CONCLUSIONS

Major breakthroughs have been achieved in research under way at the CEA on the development of separation processes for the minor actinides.

The intensive separation of neptunium appears feasible if a limited change is made to the PUREX extraction flowsheet. This theory will have to be corroborated in a perfectly representative situation.

The development of actinide(III)/lanthanide(III) co-extraction is highly advanced. It remains to be optimized, by examining the behavior of ruthenium, which appears as an undesirable element.

Work on separating actinides and lanthanides appears to be making headway thanks to the use of synergistic extraction systems. Conditions will have to be found in which these systems comply with the CHON principle and remain effective in slightly more acidic media than today.

These investigations are in the laboratory stage for the time being, and much obviously remains to be done before they can be applied industrially.
ACKNOWLEDGEMENTS

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THE STATE OF THE ART ON NUCLIDES SEPARATION IN HIGH LEVEL LIQUID WASTES BY TRUEX PROCESS

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ABSTRACT

For the advancement of the back-end of nuclear fuel cycle, novel CMPO–TRUEX process was studied for separating minor actinides from fission products in high level liquid waste using real radioactive solutions from PUREX experiments, so as to support PNC's actinides recycling program using fast reactor. The present PUREX process was also studied to improve the separation of $^{237}$Np, $^{106}$Ru and $^{99}$Tc, the most interfering-natured nuclides in both PUREX and TRUEX processes, by utilizing electrochemistry-based salt-free methods which can eliminate the secondary radioactive waste.

The state of the art of separation technologies are described by summarizing the extraction behaviors of nuclides in recent hot counter-current runs using CMPO–TRUEX process with mild salt-free stripping reagents. The degradation and regeneration characteristics of CMPO/TBP/n-dodecane mixture solvent were also simulated by semi-hot experiments. Several experiments to separate minor actinides and lanthanides from the TRUEX mixture product using aqueous aminopolycarboxylate complexant, DTPA, resulted in reasonable MA/Ln separation profiles in multiple mixer-settler stages and allowed a unique separation flowsheet adaptable to the TRUEX process to be proposed.

Application of electrochemistry to assist both solvent extraction processes, e.g., "anodic oxidation" to destroy PUREX and TRUEX solvent waste in the presence of electron transfer mediator $\text{Ag}^{2+}$ or "cathodic reduction" for electrolytic extraction of $\text{Pu}^{4+}$, $\text{RuO}_4^{2-}$ and $^{99}$TcO$_4^-$ from 3 M nitric acid medium is under study.
1. Introduction

Radioactive waste, especially high level liquid waste (HLLW) containing α emitters, have become a central issue from the interest in decreasing long lived toxicity on their long term storage and reducing the cost of the nuclear fuel cycle. Minor actinides (MA), usually lower than 1% by weight, will sustain major toxicity of vitrified HLLW; actinides practically account for ca. 45% of the total initial toxicity (one year after storage), but their contribution will increase up to ca. 70% over 100 years for the case of LWR-HLLW. Such α toxicities of HLLW lie in MA, $^{241}$Am, $^{244}$Cm, $^{237}$Np, and also $^{238}$, $^{241}$Pr derived from the PUREX process. The researches regarding α- and salt-free HLLW will become a key for a new reprocessing system.

Characteristics such as excellent extractability from highly acidic solutions, sufficiently fast kinetics for mass transfer, high radiolytic/hydrolytic stabilities and biological safety of extractants are essential for the process design of any novel solvent extraction system. An extraction process using neutral bifunctional organophosphorus Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (OBD(iB)CMPO or simply CMPO) is a candidate to satisfy such requirements.

The first questions about the TRUEX process are its efficiency as a separation tool in a highly acidic and very complicated solution mixture for producing α-free HLLW, and the second is the quality of the recovered actinides if they are recycled in a reactor. For this evaluation, both optimization of the main TRUEX chemical flowsheet and introduction of a complexant to separate lanthanides (Ln) from MA were carried out by countercurrent experiments. This paper describes the state of the art on TRUEX process development at PNC. The first part deals with some flowsheet improvements of the TRUEX process for actinides separation in a real highly active raffinate (HAR) solution, the second part describes the application of a chelating reagent, diethylenetriaminepentaacetic acid (DTPA) to a TRUEX flowsheet for MA/Ln separation. Auxiliary electrochemical process to assist both PUREX and TRUEX processes are thirdly described. All information is abstracted in attached summary tables.

2. TRUEX as a Tool for α-free Radioactive Wastes

2.1 Fundamental distribution properties of actinides and fission products

Fundamental distribution ratios (Ds) of 4f, 5f elements and fission products were verified in 0.2 M CMPO/1.0–1.4 M TBP/n-dodecane using not only real FR–HAR but also concentrated LWR–HLLW. Element compositions and concentrations of HAR and HLLW are shown in Figure 1, where a HLLW was obtained by commercial LWR spent fuel (less than 33000 MWD/T) reprocessed in the Tokai Reprocessing Plant (TRP) and HAR was originated in reprocessing experiments of FR Joyo spent fuel (burn up at ca. 55000 MWD/T, cooled for ca. 4 years). Relationships between various parameters such Ds and nitric acid concentration have already been given in other papers. The distribution characteristics of trivalent f-elements: $^{241}$Am, $^{244}$Cm and Lns are moderate, suggesting that they will be well extracted and recovered very simply by changing aqueous nitric acid...
Concentration from ca. 5 M to 0.01 M in the general TRUEX flowsheet.

Especially, the increase of nitric acid concentration causes desirable effects in decreasing the extractability of Ru and increasing that of Np. Distribution ratio of Np was confirmed at each acidity by equilibrating both phases over 24 h. At high acidities disproportionation of Np$^{5+}$ into Np$^{4+}$ and Np$^{6+}$ might shift the valency of Np to Np$^{6+}$, which is easily extracted. An opposite tendency of Ru against Np was found either in batch experiments using trinitratonitrosyl ruthenium, RuNO$_3^*$, and in counter-current tests using real HAR containing $^{106}$Ru. These results suggested that different kinds of extraction mechanisms were operative for Ru and Np, and specific variation in distribution tendencies of Ru seemed to be attributed to the diversity of ruthenium species that were affected by even slight differences in extraction conditions. Since Ru behaved similar in batch and counter-current experiments, we concluded that Ru behaved in the form of RuNO$_3^*$ in counter-current runs. Simple adjustment of the feed solution higher than 5 M nitric acid concentration was therefore recommended as an effective method to handle these two key nuclides. Neutral bidentate organophosphorus CMPO alone could make this procedure possible.

The Ds of all other major elements were measured for diluted LWR-HLLW using normal TRUEX solvent (0.2 M CMPO/1.0 M TBP/n-dodecane). Dilution was necessary for preventing third phase formation. It was confirmed that there was little difference in Ds of trivalent f-elements and Ru for HAR or HLLW in the range 0.5~4 M nitric acid. Third phase limit concentrations almost agreed with the predictions from mono element solution system. This suggested that there were probably no mutual interactions among these elements in HLLW and also among the extracted species.

Although tetra- and hexavalent elements needed no special treatment for their forward extraction, perfect back extraction of these might require either strong complexants or higher pH reagents, such as salt-free hydrazine oxalate or hydrazine carbonate as previously reported. The suitable concentrations are different for each reagent; recommended concentrations of these salt-free reagents are for example 0.5 M (at least higher than 0.2 M) to obtain 90% stripping of RuNO$_3^*$ and Zr$^{4+}$ at trace level in a single contact with TRUEX solvent, even with irradiated solvent by $10^7$ R.

2.2 Improved TRUEX flowsheet based on "Salt-Free" concept

Several TRUEX counter-current runs employed to partition actinides in real HAR led to the flowsheet "TRUEX PNC Salt-Free Version". Its block flow and typical material balance are shown in Figure 2. The feed composition of HAR is indicated in Figure 1. The higher acidity (ca. 5 M) was selected for the feed HAR due to the aforementioned reasons and the dual scrubbing was employed to decrease extraction of both RuNO$_3^*$ and free nitric acid. Addition of oxalic acid was minimized to eliminate oxalate precipitation of f-elements, in spite of concerns of lowering decontamination factor of fission products (DF$_{fp}$) and causing accumulation of extractable species. Expecting complete fractional stripping, we prepared 3 banks composed of 51 stages in total, despite having only 6 stages for extraction in this case. Material balance was made based on the flow rates and $\alpha$, $\gamma$ and element concentration. Experimentally, steady state operation had been confirmed within 4-5 hours from the start. Each sample was taken from the settlers after ten hours operation.
Although there was some experimental fractiousness, it was confirmed that most of the f-elements were extracted within the 6 extraction stages, and they were quantitatively recovered again in the aqueous phase. Extractability of Np from highly acidified HAR was sufficiently high in the presence of oxalic acid in the aqueous phase as confirmed by no leakage in the raffinates. Stripping of Np however unexpectedly occurred with dilute nitric acid prior to the contact with HAN. The neighboring transition elements, $\text{Zr}^{4+}$, $\text{Nb}^{5+}$, $\text{Mo}^{6+}$ and $\text{TcO}_4^-$, were also extracted in this condition. Once extracted in the solvent phase, $\text{Zr}$ and $\text{Mo}$ were retained until strip-III, the scrubbing of hydrazine oxalate. Therefore more sensible management is necessary for both elements because of their abundance in spent fuel.

The typical stripping profile for major nuclides indicates that the organic concentrations of $^{238}$Pu, $^{239}$Pu and $^{240}$Pu and $^{106}$Ru were peculiarly high in the stripping banks until strip-III. In normal TRUEX process Pu and Ru used to be retained in the spent organic phase at ca. 20 – 95 % and ca. 2 – 8 % respectively after stripping with dilute nitric acid. For Ru, however, hydration seemed to transform extractable trinitrato nitrosyl species into less extractable mono- or dinitrato nitrosyl species in the alkali scrubbing stages (strip-III and IV) \(^8\). Consequently, high decontamination of $^{106}$Ru could be attained by high pH scrubbing with hydrazine carbonate at the end of solvent regeneration step, offering $\text{DF}_{\text{Ru}-106} > \text{ca. 10}$, by combining high acidity scrubbing at scrub-1 banks with $\text{DF}_{\text{Ru}-106} > 10^3$. The stripping behavior of Pu was similar to that of $^{106}$Ru; namely, $\text{DF}_\text{Pu}$ was ca. 10 with hydrazine oxalate and ca. 20 with hydrazine carbonate. These steps were also capable of removing $\text{UO}_2^{2+}$, HDBP and other acidic degraded species. Scrubbing efficiency of HDBP was tentatively ca. 60 % in the two steps of solvent regeneration.

In this modified TRUEX flowsheet, where complex ions composed of hydrazine oxalate and hydrazine carbonate worked well under high pH conditions, the final amounts of remaining Pu and Ru were respectively reduced to 0.5 % and 0.25 % of their initial concentrations. They are, then, no longer troublesome nuclides in this salt-free TRUEX flowsheet and the final two steps of solvent regeneration become an effective "plutonium/ruthenium barrier". Generally, while the addition of complexants will have trade off the elements between precipitation and third phase formation, the elimination of precipitates highly helped to improve the recovery rates of the elements in this case. The actinide concentrations in the raffinate were usually lower than the detection limits (around $10^4 \text{Bq/mL}$), giving a $\text{DF}_\text{a}$ of $\geq 10^3$, a few more stages would be necessary to absorb process fluctuations.

### 2.3 Stability and safety of CMPO

Solvent degradation of CMPO/TBP by $\gamma$ radiolysis/hydrolysis and its effects on the stripping of the extracted elements were studied. Irradiation experiments using a $^{60}$Co source (ca. 7x$10^4 \text{Ci}$) on pure CMPO and on 0.2 M CMPO/1.0 M TBP/n-dodecane mixed solvent preequilibrated with 3 or 5 M HNO$_3$ showed that two major peaks, assigned to neutral methyl(n-octyl)(phenyl)phosphine oxide (MO$_2$PO) and n-octyl(phenyl)isobutylcarbamoylmethylphosphine oxide (O$_2$(iB)CMPO), were distinct and such radiolytical damage became dominant over $10^7 \text{R}$. For irradiations higher than $10^7 \text{R}$, the practical radiation bounds in partitioning process, TBP's damage was more substantial than CMPO's. Alkali scrubbing with sodium carbonate, tetramethyl ammonium
hydroxide (TMAH) and hydrazine oxalate offered quantitative scrubbing effects only for the former degradation species (probably in the form of octyl(phenyl)phosphinic acid) as well as for Ru, Zr and HDBP. The slow kinetics of each scrubbing treatment necessitated sufficient contact time (> ca. 10 min.) and concentration for each reagent (> 0.2 M). Neutral degradation species are generally very lipophilic, therefore some solid absorbents such as magnesium silicate or activated alumina are recommended as a secondary clean up system.

Thermochemical data of OOD(iB)CMPO, obtained by thermogravimetric analysis and differential thermogravimetry (TG-DTA), indicated that its degradation exothermally proceeded in two steps at least, around 260 °C and 294 °C, and was completed at 300 °C even in the form of amorphous of it with TBP and Ru. The flash and combustion temperatures of CMPO were also quite a bit higher than those of TBP. These results indicate that CMPO is thermochemically stable in the usual operation.

The biochemical data represented by 50% lethal dose, LD50, also suggest that OOD(iB)CMPO should be categorized neither as a poison nor as a toxin, and that it is as safe as TBP whose LD50 for rats has been reported to be 3000 mg/kg. Furthermore, negative results in reverse mutation assay for Salmonella Typhimurium and DNA molecular repair assay for Bacillus subtilis indicated that CMPO is neither a chemical carcinogen nor a hereditary toxicant.

3. Actinide (III) and Ln Separation in CMPO Mixed Solvent System

3.1 Criteria for Am and Cm recovery

In our "Advanced Fuel Recycle System" which is based on MOX fuel, Am is recycled in fast reactors, and Cm is stored for several decades, waiting for 244Cm decay. The incineration of Am needs to separate Cm and lanthanides from Am. On the other hand, contamination with Ln would be allowed in Cm recovery.

It is considered that there is quite a large difficulty in Am/Cm separation by solvent extraction. Thus, TRUEX process must be coupled with some Am/Cm/Ln separation methods. If light lanthanides which are major fission products were removed, the scale of Am/Cm separation process could be reduced. For totally process simplification, it is favorable to add a function of lanthanides rejection to the TRUEX process.

3.2 Utilization of DTPA

A chelating reagent diethylenetriaminepentaacetic acid (DTPA) has been utilized in An(III)/Ln separation based on cation exchange and solvent extraction such as the TALSPEAK process. In a neutral extractant TBP system, DTPA is used with high concentration of nitrate as a salting out reagent.

Light lanthanide elements are less selectively extracted by CMPO than heavy lanthanides from nitric acid solution, and tend to make strong complexes with DTPA. Therefore it is expected that light lanthanides could be rejected in CMPO extraction system, utilizing DTPA complexation. In the studied process, the nitrate concentration was lowered and a higher pH than in the TBP system was used in the extraction experiment.

In order to realize the process using DTPA, stabilization and/or control of pH in the separation process is essential. Certainly, basic distribution data for CMPO–TBP mixed solvent / DTPA–nitrate solution are
3.3 Control of pH

One of the advantages of CMPO is the extraction ability from high acidity solution. However, as the loaded solvent which is contacted with highly acidic waste solution contains considerable amount of nitric acid, it would interfere DTPA–metal complexation. Therefore, it is needed to reduce the acid concentration in the organic phase. Fortunately, the extent of distributions of metal and acid differ using nitrate salt at low acidity. It is considered that the selective stripping of acid from the loaded solvent can be conducted by using proper concentration of nitrate solution.

DTPA has carboxyl groups. Since the first and second dissociation constants are around two, buffering effect could be expected in the acidity range near 0.01 M which is appropriate for separation.

3.4 Basic data on lanthanide distribution

Since the separation system is rather complicated, many factors affect the distribution of trivalent metals. The acidity of the aqueous phase is the most important parameter. In Figure 3, the distribution ratios of four lanthanide elements are plotted as a function of pH. As pH become higher, dissociation of DTPA proceeds, resulting in a decrease of the distribution ratios. And the effect of metal complexation emerges as the difference of the values. As the stability constants of Dy is near that of Am, it is expected that Am could be stripped while major light lanthanides such as Ce and Nd would be kept in the organic phase. The separation factors are almost consistent with the ratio of stability constants of metals. Then it is considered that the separation is mainly governed by selectivity of DTPA complexation.

The higher nitrate and lower DTPA concentration enhance the extraction of metal. Higher temperatures lower the distribution ratios. And the kinetics of stripping of metal from loaded solvent are rapid enough for the use of mixer-settlers as contactors.

3.5 Concept of flowsheet

We made a basic flowsheet for An(III) recovery with lanthanides rejection using DTPA–nitrate solutions. The process is composed of four sections; namely, extraction–scrubbing, acid stripping, An(III) stripping and Ln stripping as shown in Figure 4.

In the first extraction–scrubbing section, the trivalent metals are extracted from acidic solutions. The operation procedure is basically the same as the original TRUEX. The acid in the loaded solvent is removed in the second acid stripping section using a nitrate solution of low acidity. The aqueous waste solution will contain only little activity. Trivalent actinides are back extracted in the third An(III) stripping section with a DTPA–nitrate mixed solution, the pH of which is adjusted around two. It is anticipated that mid lanthanides such as Sm and Eu would be simultaneously recovered with Am and Cm in a certain extent. As the product solution contains a high concentration of nitrate, further treatment will be required to obtain nitric acid solution as product. With dilute nitric acid, retained lanthanides in the organic phase are stripped in the fourth Ln stripping
section. (Recently, we call this process flowsheet as SETFICS * for convenient.)

* Acronym of "Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO–complexant System"

3.6 Results of counter-current experiment

Based on the conceptual flowsheet as stated before, we conducted counter-current hot experiments using a TRUEX product which was previously obtained in the hot tests and acidified to 2 M HNO₃ for extraction. The trivalent metals were well extracted in the first section. In the second stripping section, 0.5 M NaNO₃ solution (pH 2.0) was used. Since re-extraction was not conducted from experimental restriction, approximately 10% of the metals were streamed into aqueous waste. The acid concentration of discharged solvent was lower than 0.01 M.

In Figure 5, the profiles of concentrations and distribution ratios of major nuclides are plotted. The composition of the An(III) stripping solution was 0.05 M DTPA–4 M NaNO₃ solution (pH 2.0). Americium-241 and ²⁴⁴Cm were stripped into product solution while ¹⁵⁵Ce was retained in the organic phase. As the behavior of ¹⁵⁵Eu was similar to that of ²⁴¹Am, the greater part of ¹⁵⁵Eu was recovered with An(III) product. The distribution ratio was varied with acidity of aqueous phase. The pH value became higher in the upper stream of solvent feed point. This tendency resulted in a decrease of distribution ratios and an increase of An(III) recovery.

Table 1 Material balance and decontamination factor

<table>
<thead>
<tr>
<th></th>
<th>¹⁵⁴Ce</th>
<th>¹⁵⁵Eu</th>
<th>¹⁵⁵Eu</th>
<th>²⁴⁴Am</th>
<th>²⁴⁴Cm</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid waste</td>
<td>9.0</td>
<td>8.9</td>
<td>9.5</td>
<td>6.2</td>
<td>6.4</td>
<td>8.6</td>
<td>10*</td>
<td>10*</td>
<td>10*</td>
<td>10*</td>
</tr>
<tr>
<td>An(III) product</td>
<td>0.89</td>
<td>45</td>
<td>46</td>
<td>64</td>
<td>56</td>
<td>67</td>
<td>1.2</td>
<td>&lt;6.1</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Ln waste</td>
<td>85</td>
<td>15</td>
<td>15</td>
<td>5.6</td>
<td>1.6</td>
<td>0.75</td>
<td>52</td>
<td>97</td>
<td>69</td>
<td>71</td>
</tr>
<tr>
<td>Total</td>
<td>94</td>
<td>68</td>
<td>70</td>
<td>76</td>
<td>64</td>
<td>77</td>
<td>63</td>
<td>&lt;110</td>
<td>81</td>
<td>82</td>
</tr>
</tbody>
</table>

* Evaluated values equal to those of radionuclides

Decontamination factors to ²⁴¹Am:

<table>
<thead>
<tr>
<th></th>
<th>¹⁵⁴Ce</th>
<th>¹⁵⁵Eu</th>
<th>¹⁵⁵Eu</th>
<th>²⁴⁴Am</th>
<th>²⁴⁴Cm</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>72</td>
<td>1.4</td>
<td>1.1</td>
<td>1.1</td>
<td>0.95</td>
<td>52</td>
<td>&gt;10</td>
<td>28</td>
<td>46</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The material balance and decontamination factors are summarized in Table 1. Because of the short operation time, the steady state was not attained. Especially, the sum of the output of An(III) and Eu was quite
low. The decontamination factors of light lanthanides were obtained in several tens, and, at least, 80% of lanthanide were removed from An(III) product solution. Therefore, the main contaminants of An(III) were Sm and Eu.

3.7 Further subjects

It has been found that CMPO mixed solvent / DTPA-nitrate solution system has a potential for light lanthanides removal. It is considered that the improvement of An(III) recovery and the reduction of nitrate in stripping solution should further be studied.

4. Supporting Electrochemical Technique for Separation Process

4.1 Electrolytic extraction of platinum group elements and technetium

Precious metals such as Ru, Pd, Rh, Ag and Tc amount to several kilograms per ton of ordinary spent fuel. The ionic state of these elements, especially extractable RuNO$_3^+$ and TcO$_4^-$, behave in a rather complicated manner and eventually dominate the final decontamination factors of the PUREX and successive TRUEX processes. In that sense, their separation prior to both solvent extraction processes is meaningful and worthy to improve decontamination in a limited number of extraction stages and cycles as well as to prepare future multiple usage of precious metals from spent fuel.

Pure cathodic deposition behaviors of Ru$^{3+}$ and Pd$^{2+}$ in 3 M nitric acid were studied using Pt-Ti cathode (20 cm$^2$) in an electrolysis cell equipped with cation exchange membranes. The volume of catholyte and anolyte was 100 ml each, temperature was set at 50 °C, and Ru$^{3+}$ and Pd$^{2+}$ were mixed together at 100 ppm each. In accordance with electrolysis time, both metals were deposited dendritically together. A yield $\geq$ 90% was obtained for both Ru and Pd in a few cases employing high cathodic current density $\geq$ 100 mA/cm$^2$ during 3 hours. In the case of low 10 mA/cm$^2$ electrolysis with less amount of hydrogen evolution, only Pd was deposited with the same high yield. Low deposition yield of Ru (less than 30%) suggests that its redissolution might occur at such a cathodic density. The reported value of $E^0$ for the amorphous TcO$_2$/TcO$_4^-$ electrode is 0.746 V (vs. SHE) $^{13}$, TcO$_4^- + 4H^+ + 3e^- \leftrightarrow TcO_2^{2-} \cdot xH_2O + (2-x)H_2O$

thereby suggesting electrochemical deposition of Tc in nitric acid. The further electrochemical tests by cyclic voltammogram (CV) measurement and galvanostatic electrolysis are in progress for Pd$^{2+}$, RuNO$_3^+$, $^{99}$TcO$_4^-$ and ReO$_4^-$ with 3 M nitric acid.

4.2 Mediated electrochemical destruction of solvent waste

Electrolysis tests were carried out to search for the possibility of electrochemical destruction of PUREX and TRUEX solvent waste $^{12}$. Cyclic voltammogram measurements suggested that adsorption and the direct oxidation of emulsified CMPO (and also TBP) by Pt anode in nitric acid (3 M) was easier than that of n-dodecane.

About 90% of CMPO was decomposed within 3 hours electrolysis with much excess of Ag$^{2+}$ (initial
Ag⁺/CMPO/decalin molar ratio was 1500 : 1 : 30), 500 mA/cm², 50 °C in 3 M nitric acid. Mainly phosphoric acid (ca. 80 %) and carbon mono-, dioxide (ca. 10 % in total) were detected in the aqueous phase and in gas phase, respectively. The presence of Ag⁺ mediator in the electrolysis system considerably accelerated oxidation kinetics by ca. 5 times and improved current efficiencies as compared to that from the direct electrode reaction. Nevertheless, still lower individual current efficiency calculated on the basis of gaseous compositions with the following assumed reactions suggests that electrolysis conditions can furthermore be improved.

Anodic reactions;
\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2e^- \\
\text{Ag}^+ & \rightarrow \text{Ag}^{2+} + e^-
\end{align*}
\]
\[
\begin{align*}
\text{CMPO} + 51\text{H}_2\text{O} & \rightarrow 24\text{CO}_2 + 1/2\text{N}_2\text{O}_5 + 1/2\text{P}_2\text{O}_5 + 144\text{H}^+ + 144e^- \\
\text{CMPO} + 27\text{H}_2\text{O} & \rightarrow 24\text{CO} + 1/2\text{N}_2\text{O}_5 + 1/2\text{P}_2\text{O}_5 + 96\text{H}^+ + 96e^-
\end{align*}
\]

Bulk reactions;
\[
\begin{align*}
2\text{Ag}^{2+} + \text{H}_2\text{O} & \rightarrow 2\text{Ag}^+ + 2\text{H}^+ + \text{O}_2^- \\
\text{Ag}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Ag}^+ + \text{H}^+ + \text{OH}^- \\
\text{CMPO} + 72\text{O}^- & \rightarrow 24\text{CO} + 21\text{H}_2\text{O} + 1/2\text{N}_2\text{O}_5 + 1/2\text{P}_2\text{O}_5 \\
\text{CMPO} + 48\text{O}^- & \rightarrow 24\text{CO} + 21\text{H}_2\text{O} + 1/2\text{N}_2\text{O}_5 + 1/2\text{P}_2\text{O}_5
\end{align*}
\]

The formation of O⁻ and OH⁻ radicals was essential in this mechanism (i.e., double mediatory system), and cation exchange property of diaphragm was very important to prevent consumption of Ag⁺ mediator in the anolyte. Mediation effect of Co³⁺ was lower than Ag⁺, and addition of Ni²⁺ or Ce⁴⁺ unexpectedly brought only negative effects.

Direct and/or mediated electroredox technique can push out separation function and provide new waste minimizing system in the solvent extraction process.

5. CONCLUSION

Basic distribution studies of actinides and FP as well as several TRUEX counter-current runs using real HAR from PUREX experiments successfully led to an original flowsheet "TRUEX PNC Salt-Free Version". With this flowsheet, an α- and salt-free HLLW was obtained, ensuring a DF α > 10³. The DTPA has been successfully adapted with a reasonable separation of MA from light lanthanide in counter-current runs using TRUEX product solution. General process safety on the TRUEX process were preliminarily verified by original experiments. Electroredox methods for separating precious metals and destroying solvent waste have been studied in the frame of salt-free concept.

REFERENCES


Figure 1 Typical Composition of HAW

- HAR by FR reprocessing, volume: ca. 15 L/kg*SF
- HLLW by LWR reprocessing, volume: ca. 1 m³/t*SF
Figure 2(a) Improved TRUEX Flowsheet: PNC TRUEX Salt-Free Version
Figure 2(b) Typical Distribution of Elements
(TRUEX : PNC TRUEX Salt-Free Version)
Figure 3  Lanthanide distribution between CMPO mixed solvent and DTPA–nitrate solution

Organic solvent: 0.2 M CMPO-1.0 M TBP-n-dodecane
Aqueous solution: 0.05 M DTPA-3 M NaNO₃

Figure 4  Conceptual flowsheet for An(III)/Ln separation
Figure 5 Profiles of concentration and distribution ratio of major nuclides in An(III) stripping Section
APPENDIX

Summary Table

<table>
<thead>
<tr>
<th>Extractant</th>
<th>TRUEX</th>
<th>Others (reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Synthesis</strong></td>
<td>OØD(IB)CMPO</td>
<td>40$/kg=3kYen (diamide)</td>
</tr>
<tr>
<td>- Method (synthesis &amp; purification)</td>
<td>established</td>
<td></td>
</tr>
<tr>
<td>- Cost (as a mixed solvt.)</td>
<td>500$/kg=41kYen/L</td>
<td>40$/kg=3kYen</td>
</tr>
<tr>
<td><strong>Stability</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- $^6$Co</td>
<td>highly stable up to $10^7$R</td>
<td>(Over $10^7$R, TBP as well as CMPO will be significantly degraded)</td>
</tr>
<tr>
<td>- Nitric Acid</td>
<td>(acceptable up to 7 M HNO$_3$ in process)</td>
<td></td>
</tr>
<tr>
<td>- Thermal decomposition temp.</td>
<td>272.3–313.2 °C</td>
<td></td>
</tr>
<tr>
<td><strong>Solubility</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Into$\Theta_\omega$(at 0.01–3 M HNO$_3$)</td>
<td>TBP ≤ 300ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CMPO ≤ 10ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Mortality(LD$_{50}$) for</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 mice (male): oral</td>
<td>&gt; 3000 mg/kg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3000 mg/kg (for TBP)</td>
<td></td>
</tr>
<tr>
<td>5 mice (male): dermal</td>
<td>&gt; 2000mg/kg</td>
<td></td>
</tr>
<tr>
<td>- Reverse mutation assay</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td>- DNA repair assay</td>
<td>negative</td>
<td></td>
</tr>
<tr>
<td><strong>Burnability</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Flash point</td>
<td>243.6 °C</td>
<td>perfect (diamide)</td>
</tr>
<tr>
<td><strong>Incinerability</strong></td>
<td>imperfect</td>
<td>(e.g., Ag$^{2+}$ process is under investigation)</td>
</tr>
<tr>
<td><strong>Process Flowsheet</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>0.2 M CMPO/1.0～1.4 M TBP</td>
<td></td>
</tr>
<tr>
<td>Diluents</td>
<td>n-dodecane</td>
<td></td>
</tr>
<tr>
<td>Target waste solutions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Highly active raffinate</td>
<td>applicable</td>
<td></td>
</tr>
<tr>
<td>- HLLW</td>
<td>needs more investigations</td>
<td></td>
</tr>
<tr>
<td>Feed adjustment</td>
<td>ca. 5 M HNO$_3$ with H$_2$C$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>Process sensibility for extraction</td>
<td>durable for acidity changes</td>
<td></td>
</tr>
</tbody>
</table>
Typical mass transfer time

**Forward ext. at C\textsubscript{H} 3 M**

**Strip at C\textsubscript{H} 0.2 M**

FPs scrubbing

Selective stripping method

\[ \rightarrow 1\text{st Step} \quad \rightarrow 2\text{nd Step} \quad \rightarrow 3\text{rd Step} \quad \rightarrow 4\text{th Step} \]

Separability of actinides from FP

- DF for actinides from HAR
- SF for Am/Cs
  - for Am/Tc, Mo, Zr
  - for MA/Ln

Separation of MA from Ln

Third phase formation

- Constituents (confirmed)
- Limit concentration (at
  0.2 M CMPO/1.2 M TBP/nDD,
  C\textsubscript{H} 3 ~ 6 M, 25 °C)

Solvent clean up

- Major degraded material identified at 10\textsuperscript{3}R
- Mass transfer rate of FPs during salt-free scrubbing for irradiated solvent at 10\textsuperscript{3}R.
  - **Scrub at C\textsubscript{HYD-CARBO}**
  - **Scrub at C\textsubscript{HYD-OXAL}**

\[ \rightarrow 1\text{st Clean up method} \quad \rightarrow 2\text{nd Clean up method} \]

**TRUEX**

- “dual” scrubbing with a H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}

- dilute HNO\textsubscript{3}: 0.01 M HNO\textsubscript{3}
  - \textsuperscript{*} An\textsuperscript{3+}, Ln\textsuperscript{3+}, TcO\textsubscript{4}\textsuperscript{-}, Zr\textsuperscript{4+} and Mo\textsuperscript{6+} were separated
  - reducing reagent: 0.01 M HAN
  - \textsuperscript{*} Pu\textsuperscript{4+} was separated
  - complexant: 0.2~0.5 M (N\textsubscript{3}H\textsubscript{3})\textsubscript{2}C\textsubscript{2}O\textsubscript{4}
  - \textsuperscript{*} Pu\textsuperscript{4+}, Zr\textsuperscript{4+}, Mo\textsuperscript{6+}, RuNO\textsubscript{2}\textsuperscript{2+} were separated
  - high pH complexant: 0.2~0.5 M (N\textsubscript{3}H\textsubscript{3})\textsubscript{2}CO\textsubscript{3}
  - \textsuperscript{*} Pu\textsuperscript{4+}, UO\textsubscript{2}\textsuperscript{2+}, RuNO\textsubscript{2}\textsuperscript{2+} were separated

- \textsuperscript{> 10\textsuperscript{3}}
- \textsuperscript{> 10\textsuperscript{4}}

- to be improved

- Applicability of DTPA is under investigation

- in the case of 1.0 M TBP

- H\textsuperscript{+}, Ln\textsuperscript{3+}, Fe\textsuperscript{3+}, UO\textsubscript{2}\textsuperscript{2+}
- Nd\textsuperscript{3+}: 0.04~0.045 M (0.02 M *)
- Pu\textsuperscript{4+}: 0.03 M
- UO\textsubscript{2}\textsuperscript{2+}: 0.025~0.03 M (0.012 M*)

- methyl(n-octyl)(\Theta)phosphine oxide
- n-octyl(\Theta)isobutylcarbamoylmethylenephosphine oxide

- HDBP

- active Al\textsubscript{2}O\textsubscript{3} or floridine

(see Step 3rd and 4th)
Methods of recovery long-lived radionuclides from HLLW with the purpose more safe isolation from environment and transmutation the most toxic radionuclides, are considered.

For separation of minor actinoids and fission products are offered extraction, membrane extraction, ion-exchange chromatographic, precipitation and pyrometallurgical methods with use neutral monodentate and polydentate compounds including carbonyl, amide and phosphoryl groups, phosphorus-organic acids and their salts, cobalt chlorinated dicarbollyde.

The basic problems, arising by use of phosphorus-organic acids (POA) for isolate of pure fractions of minor actinoids from HLW, are discussed.

Opportunity of use new extractant on a basis of acid zirconium compounds salts (ZCS) of POA for partitioning HLW is shown.

Acid zirconium compounds salts (ZCS) of HDEHP and n-alkil(C₈-C₁₀) phenyl-phosphonic acid may be used for deep extraction of TPE and other α-nuclides from HLW with concentration up to 2 mol/l HNO₃. The extraction process of long-lived radionuclides from the solutions, characterized by complex salt composition and high radiactivity level, can be fulfilled by two successive stages. In case ZCS of HDEHP on first stages we separated light REE and TPE, on the two stages REE yttrium group. Scheme of TPE, Ln and ⁹⁰Sr extraction with simultaneous removal of other α-nuclides from HLW includes TPE and Ln extraction with 0.9 mol/l n-alkil(C₈-C₁₀)phenylphosphonic acid solution in n-paraffin dissolvent and ⁹⁰Sr extraction with 0.15 mol/l solution of zirconium salt of the indicated acid.

The perspective approach by choice of technology partitioning consists in combined extraction, sorbtion and precipitation methods for preparation radionuclides to transmutation. The minimization of secondary waste of partitioning is connected with development of new selective reagents, methods of multistage processes organization and also physical methods separation.
Partitioning HLW - the separation long-lived radionuclides from salts, is expedient for reduction of volume the most toxic wastes and for recovery of fractions radionuclides with the purpose transmutation [1]. Both purposes assume deep removal long-lived radionuclides from HLW, and recovery of fractions radionuclides in the form, necessary for inclusion in a matrix with the purpose of reliable disposal or transmutation.

In Russia a number of technologies on partitioning HLW of a working radiochemical plant RT-1 (Mayak) is developed. First of all it concerns to technology partitioning HLW, developed in ARSRIIM after A. A. Bochvar (Moscow) as the part of complex technology of reprocessing spent fuel VVER, based on use HDEHP for extraction of transplutonium (TPE), rare earths elements (REE) and strontium-90 [2]; technologies of removal cesium-137 and strontium -90 extraction CCD, developed in Khlopin Radium institute (St. Petersburg) [3] and sption cesium -137 on ferrocyanide FC-10, developed in the Institute of Physical chemistry (Moscow) [4].

To new development on partitioning HLW use bidentate extractants for removal a-nuclides from HLW (ARSRIIM, Khlopin Radium Institute, Vernadsky Institute of Geochemistry and Analytical chemistry of RAS) [5-9], use of acidic zirconium compounds salts of phosphorus-organic acids(ZC POA) for extraction α-nuclides and strontium-90 from nitric acid solutions (ARSRIIM) [10]; of extraction system on basis of crown-ethers for extraction strontium-90 and cesium-137 (ARSRI Chemical Technology) [1, 11]; A number of processes of separation radionuclides: use cationic chromatography for separation TPE and REE [12,13], extraction and precipitation TPE [14, 15], can be directly used in technology partitioning HLW, in particular for partition more short lived curium. Methods partitioning HLW by use of heavy water blanket [16] and molten fuel [17,18] for transmutation radionuclides are developed.

At the moment on a plant on reprocessing spent fuel RT-1 total losses U, Pu and Np with raffinate of the first and second cycle make accordingly 0,01; 0,025 and 0,5 %. Practically whole Pu and Np through oxalic precipitation are transformed in dioxides and are directed on storage ( part Np is used for reception $^{238}$Pu ) [19]. Work on partition Tc will be carried out at processing spent fuel, thus more than 95 % the localization Tc [20] is expected. Generation of Ru from Tc will potentially allow to pay back a part of expenses on transmutation[21].

HLW concentrate by evaporation and direct on temporary storage and solidification [22]. At evaporation of acidic HLW it is possible remove practically the whole nitric acid, thus rate of evaporation is determined solubility of nitrate HLW [23]. At the given stage there is the basic opportunity of physical partition of HLW in view of various solubility of nitrate radionuclides .

The flow sheet of complex reprocessing spent fuel VVER, developed in ARSRIIM included operations evaporation raffinate after extraction U, Pu and Np for removal of a nitric acid (final acidity - 0,2 - 0,3 mol/l establishments pH 4-4,5 for maintenance of conditions extraction strontium-90 by introduction sodium acetate and citric-ion in quantit 120 % from stoichiometry for linkage Fe, Cr and Ni; joint extraction REE, TPE and strontium-90 by a solution 0,6 mol/l HDEHP in paraffine diluent; stripping strontium-90 0,1 mol/l by a solution of a nitric acid; selective stripping TPE by a solution, containing 0,8 mol/l of lactic acid and 0,05 mol/l of DTPA; stripping REE 3 mol/l by a nitric acid; carbonate regeneration of extractant [2].

By extraction of α-nuclides the aforesaid complexone it is not required. In such variant the process ARSRIIM can be used for partitioning evaporated raffinate of Purex-process at concentration HNO3 0,2 - 0,3 mol/l.

In spite of the fact that the purposes of reprocessing HLW and the requirements to parameters of process of separation long-lived radionuclides have at the moment changed, extractants on a basis of phosphorus-organic acids remain the most effective for group separation of transplutonium and rare earth elements.

For deep extraction TPE and other α-nuclides from HLW with concentration up to 2 mol/l HNO3 can be used of ZCD HDEHP and of a n-alkyl(C$_8$C$_{10}$)phenylphosphonic acid (n-APPhonK).

By use ZCD HDEHP the technological flow sheet includes [10]:- evaporation HLW up to final concentration [HNO3] 1,5 - 2 mol/l; extraction of a sum α-nuclides and REE from HLW; stripping of a sum REE and TPE 6 mol/l HNO3; regeneration extractant with removal of the rests α-nuclides.

The flow sheet of separation TPE, REE, $^{90}$Sr by simultaneous removal from HLW other α-nuclides includes extraction REE and TPE 0,9 mol/l; by a n-APPhonK in n-paraffine diluent and extraction $^{90}$Sr 0,15 mol/l by a solution ZCD of the specified acid [24].
The salts of POA with polyvalent cations as Zr and Hf are effective extractants for alkaline earth elements (AEE), REE and TPE from nitric acid solutions. In a complex \( \text{H}_2\text{ZrA}_6 \), where A - anion POA, under influence central cation there is the strengthening of extraction properties of coordinated molecules HA in relation to one elements and suppression extraction of other elements. Extraction of metals proceeds on the cation exchange mechanism. The solutions ZCS POA in n-paraffine diluents are characterized by significant radiating and chemical stability, keep high extraction ability and capacity on taken metals after boiling (5-6 hours) with 3 mol/l nitric acid and practically do not change of extraction properties up to a doze of absorbed energy \( 4 \times 10^5 \) Gr. The water solutions for reprocessing spent fuel have complex radiochemical and chemical composition. At transition from POA to ZCS POA there is the suppression extraction number salt cations HLW in particular of products of corrosion (Ni, Cr) and some radionuclides, that increases selectivity of separation TPE and \(^{90}\text{Sr}\) from HLW. The essential increase of extraction properties POA by linkage them in the form of zirconium salts at simultaneous increase of selectivity of partitioning long-lived radionuclides from HLW opens prospect of wider use extractants of the given class in practice of reprocessing HLW [25].

For removal \( \alpha\)-nuclides from HLW are offered extractants on a basis carbamoylphosphine oxides and diphosphine dioxides [5-6]. The effect anomalous aryl strengthening of the complexes of actinides provides high extraction ability diphosphine dioxides at clearing HLW from actinides [6].

On experienced laboratory plants an opportunity of deep removal (factor of distribution on one step membrane extraction is \( \text{BO-20} \)) and concentration actinides membrane extraction ditolyldibutylcarbamoylphosphine oxide the house is shown: from 0,01 mg/l up to 80 mg/l on Pu [7].

With the purpose of minimization secondary wastes, formed at partitioning HLW, enhanced explosion- and fire-safety of process in Khlopin Radium institute in quality diluents of neutral bidentate pyrophosphorganic compounds. are offered fluorcontained ethers. At partitioning offered extractants 3-8-divisible reduction of volume HLW is received at a degree of clearing from \( \alpha\)-nuclides \( \times 10^4 \) [8].

Essential lack bidentate extractants, offered for partitioning \( \alpha\)-nuclides from HLW, is low selectivity. For separation REE and partition actinides on a fraction search selective reactants and new ways of realization of multistep processes will be carried out. Is shown, that by use 1,2,4,-tris-(diphenylphosphinmetyl)benzene at extraction from 3 mol/l of a nitric acid factor of separation Am/Eu is equal 7 [9]. The selectivity extractants of the given class is determined by a mutual stereosequence of diphosphate groups. For selective separation radionuclides bidentate extractants engineering extraction chromatography with the purpose of increase of steps of separation can be used, however is more perspectiv, in our opinion, development of engineering liquid chromatography with a free liquid phase [26].

In Khlopin Radium institute partitioning of HLW is developed by use a solution chlorinated cobalt dicarbollide (CCD): \( \text{H}^+ (\{p\text{-}(3)-1,2-\text{B}_2\text{H}_4\text{H}_2\text{C}_2\text{H}_2\text{C}_2\text{H}_2\text{Co}) \) and polyethylene glycol in a mix polar nitroorganic and nonpolar solvents [3, 27 - 29]. The most effective extractant can be used for removal Cs and Sr. At extraction directly from raffinate of Purex-process removal Cs and Sr is achieved more than 99 % with a degree of clearing from impurity \( 10^3 - 10^4 \). With increase of cation charge the efficiency extraction falls, therefore a sum TPE and REE CCD takes from solutions with \( \text{HNO}_3 \) no more than 0,5 mol/l, and the extraction actinides with higher charge is problematic.

The complex flow sheet partitioning HLW of extraction CCD includes operation evaporation HLW, decrease of concentration nitric acid (no more than 0,5 mol/l) with subsequent extraction and fraction stripping REE, TPE, \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\).

The Institute of Physical chemistry (Moscow) has developed the sorption partitioning of \(^{137}\text{Cs}\) from spent fuel solutions. Copper ferrocyanide-based sorbent (FC-10) used is delivered by the Perm State University manufacturing department.

When sorbing from the PUREX raffinate, the FC-10 capacity is 100±5 mg/g at 0.3 mole/l HNO\(_3\) and 5±0.5 mg/g at 3 mole/l HNO\(_3\). With hydrazine addend for combining with nitrous acid, the sorbent capacity is much higher in acidic solutions. Table 1 lists data on the Cs sorption from imitated solutions having 0.05 N\(_2\)H\(_4\) as a function of the HNO\(_3\) concentration.
As can be seen, the gilds good results at 4 mole/l HNO₃. When desorbing ¹³⁷Cs by 6-10 mole/l, no less than 95 % of sorbed is are washed out with the first fire column volumes of eluate.

The sorbent can be regenerated (to convert Fe(III) to Fe(II)) by the following solution, g/l: sodium nitrite, 18; potassium nitrate, 40; (pH 6-8).

Average sorbent losses during 20 successive sorption - desorption - regeneration cycles amount 0.3-0.5 % per cycle.

Major stages of the ¹³⁷Cs recovery are: pH adjustment; hydrazine addition; ¹³⁷Cs sorption by FC-10; ¹³⁷Cs desorption by HNO₃; sorbent regeneration; ¹³⁷Cs desorbate evaporation to cerium nitrate.

Within 1988-93 about 8-10⁶ m³ of diverse process solutions was reprocessed to yield 4-10⁶ ¹³⁷Cs.

In Scientific Research Institute Nuclear Reactors (SRINR) extraction HDEHP is used for separation individual TPE from irradiated targets [13].

The clearing TPE from Al, Fe, Zr will be carried out extraction 0.5 mole/l HDEHP in n-paraffine diluent from citric solutions. For separation TPE and REE is used similar extraction system, but in addition in 0.3 molar/n citric solution (pH 3-3.5) is entered 0.015 mole/l DTPA. The separation Bk, Cf and Es will be also carried out extraction 0.5 mole/l by a solution HDEHP, and separation Am and Cm precipitation double carbonate K and Am after oxidation Am of ammonium persulfate. The basic characteristics of separation TPE and REE are resulted in tab. 2.

Table 2
Parameters of separation TPE and REE at processing irradiated targets

<table>
<thead>
<tr>
<th>Element</th>
<th>D</th>
<th>Ce/TPE</th>
<th>Pm/TPE</th>
<th>Eu/TPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm</td>
<td>0.05</td>
<td>120</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>Cf</td>
<td>0.20</td>
<td>30</td>
<td>10</td>
<td>7</td>
</tr>
</tbody>
</table>

For separation Am and Cm in SRINR is investigated a carbonate method. Process of preparations of fractions Am and Cm with the contents Cm in a fraction of Am up to 0.1 % and Am in a preparation of Cm up to 0.3 - 0.5 % is developed [15].

For recovery individual radionuclides are offered of extraction system on a basis dicyclohexane-18-crown-6 for ⁹⁰Sr and dibenzo-21-crown-7 for ¹³⁷Cs [30]. The technological flow sheet with use of crown-ethers differ by simplicity; from concentrate Sr and Cs desired products can be received by precipitation radionuclides or evaporation of solutions.

Pyrometallurgical (dry) methods of the reprocessing HLW for transmutation radionuclides in blanket molten fluoric salts are developed at the moment in SRINR [18]. The basic flow sheet provides removal of noble fission products from a flow and plant of electrochemical processing of molten fuel. The electrochemical processing of molten fuel includes electrolyzer for separation Zr and minor actinides, electrolyzer for clearing fuel salt from REE and unit of updating of composition of fuel salt.

From considered methods of recovery and the separations long-lived radionuclides at the moment for practical application in Russia are the most fulfilled water extraction and sorption processes. For reprocessing HLW, formed on working radiochemical plants RT-1, in Russia three methods with use POA, CCD and bidentate extractants for removal α-nuclides are offered. Use POA allows thus also to take and ⁹⁰Sr, and in a case CCD to them radionuclides is added and цезий-137.
Despite essential advantages bidentate extractants, first of all an opportunity of removal α-nuclides directly from raffinate Purex-process and simplicity stripping, POA, in our opinion can quite compete at economic comparison of the given technologies. It is connected to expediency evaporation HLW for reduction of their volume. In process evaporation acidity HLW can be lowered up to value, at which can be used POA or them zirconium compounds. The important advantage POA in comparison with bidentate extractants is high selectivity $\Phi$ at group separation TPE and REE. For regeneration POA - strong extractants heavy REE, Fe, Zr and similar cations, phosphoric acid by analogy to processes in a uranium industry [30] can be used. The formed product can be directed on vitrification.

Use CCD as universal extractants for partitioning HLW is limited first of all by its difficulty extraction fourthvalent actinides.

For recovery from raffinate of Purex-process Sr and Cs crown-ethers, however the published losses given not enough for an estimation extractants can be used at processing HLW.

For recovery Cs is well fulfilled copper ferrocyanide-based sorbent (FC-10). Essential advantage given sorbent is an opportunity of its long-duration use in cycles sorption-desorption, that allows to minimize accumulation ferrocyanide waste at partitioning HLW.

For separation TPE and REE are used Talspeak-process and its updatings. But the capacitance of extractants used to REE and supplementary recovery of TRE from complexing agent-bearing solutions set a limit on the process. The TPE recovery could be excluded by allowing the TRE concentrate to stand until organic constituents are completely decomposed.

The basic diagram of the Talspeak-process is unaffected by one or other type of POA.

Extraction chromatography and TVEX processes are useful for selective partitioning of TPE and REE but extractant capacity limitations are much more dramatic in this case.

The solvent chromatography involving a free liquid phase has the advantage of combining a complete exhaustion of extractants with efficient chromatographic partition.

Cation chromatography has its greatest impact in partitioning individual constituents.

Use of dry methods partitioning HLW is of interest for use of physical methods separation - electrolysis, distillation, not requiring introduction chemical reactants. In too time at the stage of gas cleaning there is the essential accumulation secondary waste of processing. An opportunity of use of physical methods partitioning HLW is unsufficiently investigated at processing raffinate of Purex-process. First of all it concerns to an opportunity fractional crystallization in process evaporation HLW at modify of concentration of a nitric acid and salts.

The inclusion of processes partitioning HLW and transmutation actinides and fission products in the nuclear fuel cycle requires accent on problems of safety, protection of an environment and non-distribution [32]. Processing the most active products (up to 1000 KU/l), containing extremely toxic radionuclides, requires as much as possible reliable technology.

The perfection of processes partitioning HLW is connected to development new selective reactants and methods of organization of multistep processes:

- Perfection of existing processes with the purpose of minimization secondary waste and increase of safety of processing HLW;
- seeking for stereoselective polydentate compounds containing carbonyl, amid and phosphoryl groups for selective partitioning of TPE and REE;
- development of the equipment for realization of multistep processes of separation radionuclides, in particular liquid chromatography with a free liquid phase.

Use of physical methods of recovery and separation radionuclides for minimization total accumulation HLW.

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STATUS OF THE PNC HIGH POWER ELECTRON ACCELERATOR

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Design and construction of a high power CW (Continuous Wave) electron linac for studying feasibility of nuclear waste transmutation was started in 1989 at PNC. The PNC linac is the 10 MeV, 20 mA (average current, 20% duty) accelerator with eight normal conducting TWRR (Traveling Wave Resonant Ring) disk loaded accelerating tubes. Various methods have been proposed to transmute long-lived fission products using accelerators. The transmutation by photonuclear reaction using a electron accelerator has advantages of the small production for secondary radioactive waste and broad base of accelerator technology.

The PNC high power CW electron accelerator has been pre-commissioned with the injector and the first accelerating tube. By December 1995, the accelerator was partially built and the injector pre-commissioning began. Then 3.1 MeV beam had coasted though the beam dump. We have been very successful to produce 1 ms pulse width electron beam with 100 mA peak and energy about 3.1 MeV at present.

The whole facility will be completed in March 1997.
INTRODUCTION

Many research efforts have been spent in PNC to establish technologies for safety disposal of radioactive waste. The high level radioactive waste produced from the reprocessing of spent fuel is essential for the completion of nuclear fuel cycle. Current national policy in Japan is to solidify the high level radioactive waste into a stable form and to dispose it in a deep geological repository after 30 to 50 years of storage for decay heat reduction. However, the Japanese Atomic Energy Commission approved the long-term program for research and development on nuclide partitioning and transmutation in October 1988 beside solidification disposal mentioned above. The objective of the program (called OMEGA) is to explore a possibility to utilize the high level radioactive waste as useful resources and make the geological disposal more efficient.

The program is composed of two major area. One is the nuclear partitioning from the high level radioactive waste based on its potential value for utilization. The other is the transmutation of minor actinides and long-lived fission products into short-lived or stable nuclide. It is usually difficult to transmute long-lived fission products in reactors because of small neutron capture cross section. Various methods have been proposed to transmute long-lived fission products using accelerators. The transmutation by photonuclear reaction using an electron accelerator has advantages of the small production for secondary radioactive waste and broad base of accelerator technology. A high power electron accelerator will be required in future transmutation system.

Upon this projection, design and construction of a high power CW electron linac to study feasibility of nuclear waste transmutation was started in 1989 at PNC. Until now, a high power L-band klystron and a prototype high power TWRR accelerating tube were built and successfully validated many of design concepts until end of 1992. By December 1995, the accelerator was partially built and the injector pre-commissioning began. Then 3.1 MeV beam had coasted though the beam dump. The whole facility will be completed in March 1997.

THE LINAC DESIGN

The parameters of the beam produced by the linac are summarized in Table 1. These are very unique specifications for among the existing electron linear accelerators. The long pulse, 4 msec, is used for the beam stability studies of CW linac. The RF source parameters are summarized in Table 2.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Beam parameters for the linac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>10 MeV</td>
</tr>
<tr>
<td>Max. Beam Current</td>
<td>100 mA</td>
</tr>
<tr>
<td>Average Beam Current</td>
<td>20 mA</td>
</tr>
<tr>
<td>Pulse Length</td>
<td>0.1 ~ 4 ms</td>
</tr>
<tr>
<td>Pulse Repetition</td>
<td>0.1Hz ~ 50 Hz</td>
</tr>
<tr>
<td>Duty Factor</td>
<td>0.001 ~ 20 %</td>
</tr>
<tr>
<td>Norm. Emittance</td>
<td>50 ( \pi ) mm mrad*</td>
</tr>
<tr>
<td>Energy spread</td>
<td>0.5 %*</td>
</tr>
</tbody>
</table>

* estimated value by simulation

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Parameters of the RF source.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating Frequency</td>
<td>1249.135 MHz</td>
</tr>
<tr>
<td>Accelerating Mode</td>
<td>2(\pi/3) mode</td>
</tr>
<tr>
<td>Number of Klystron</td>
<td>2</td>
</tr>
<tr>
<td>Klystron Power</td>
<td>1.2 MW</td>
</tr>
</tbody>
</table>

Injector

The injector consists of a 200kV DC gun, magnetic lens, a RF chopper, chopper slits, a prebuncher, and a buncher. Solenoid coils cover these elements from the exit of the gun to the first accelerating tube except
between the RF chopper and chopper slits. Fig. 1 shows these injector components and schematic with the solenoid magnetic fields.

**Electron Gun**

The pulse characteristics of the accelerator beam are initially determined by the electron gun system. The accelerator requires a range of pulse widths from 100 µsec to 20 msec, rise and fall times of ~1 µsec.

As average beam current is very high (20 mA), a grid (intercepting wire mesh) cannot be used for current control because of exceeding electron beam energy deposit to the grid wire. A non-intercepting aperture grid is only capable of high beam current control. The two aperture grids configuration is necessary to control a greater range of beam current according to numerical simulation. The gun electrode configuration was designed using a computer code EGUN [2] calculated the electron trajectories through the gun in the presence of space charge.

**RF Chopper**

The RF chopper [4] consists of a RF chopping cavity and a slit. The RF chopping cavity is a rectangular cavity driven at $f_0$ (fundamental frequency: 1.249135 MHz) with $TM_{010}$ mode and 2$f_0$ with $TM_{0n0}$ mode. There are three field mixed together in the chopper cavity. First one is a fundamental ($f_0$) magnetic field, second one is second harmonic (2$f_0$) magnetic field, and third one is a DC magnetic field bias. Adjusting RF field amplitude and phase, a superposed magnetic field can be equal to zero on the beam center line in 120 degree phase length. The wave form from the chopper cavity is shown in Fig. 2. This chopper provide small transverse emittance and bigger acceptance for phase angle.

**Buncher**

The buncher is a $TM_{010}$ room-temperature cavity at same frequency (1.249135 GHz) as the fundamental of the accelerating tubes. Bunching in the PNC injector occurs in two components: the prebuncher and the 1.2 m long, traveling-wave resonant ring buncher.

The beam current from the DC gun is 300 mA and one third of RF periodic (120 degree) beam passes through the chopper slits. In the buncher the wave phase velocity varies linearly from 0.695 to 1.0 of light velocity. The bunch width becomes about 10 degree at prebuncher exit and 5 degree at buncher exit. The injector has been modeled with the code PARMELA [5], which simulates the beam trajectory from the exit of the electron gun to the accelerating tube.

**Accelerator Section**

The accelerator proper is a traveling-wave accelerator with TWRR excited with microwave power at a frequency of 1249.135 MHz. The accelerating tube has a cylindrical, disk-loaded shape made by OFHC (Oxygen Free High-purity Copper). The structure is designed to produce a constant axial electric field over the length of each independently fed. The number of the accelerating sections is seven and one injector section. Each of the accelerating section whose length is 1.2 meters contains 13 of 2/3n mode cavities and two coupling cavities.

All accelerating sections are designed to have constant gradient structure under the condition of 100mA beam loading. The regenerative type and the cumulative type of BBU (Beam Break Up) will be suppressed partially in the constant accelerator structure because the one accelerator sections of each cavity are designed with the same frequencies of $TM_{40}$ mode and with very different frequencies of $TM_{1n}$-like mode. According to the progressive stop-band technique, the iris diameters in the initial region of the accelerator section are smaller than those in any preceding ones but larger than those in subsequently located ones. The choice of short accelerating section and low attenuation constant structures made possible increase the threshold BBU current and liberate the tolerance of the TWRR resonate frequency, temperature stability, and fabrication. A detail TWRR with accelerating section is described else where [6].

**Beam Dump and Vacuum System**

The conceptual design of the beam dump is based on the following design criteria: (1) to disperse the beam by magnet in front of the beam entry, (2) to stop the beam part by part in spatially separated
blocks, (3) to minimize the induction of radioactivity.

The first criteria is for making the power density smaller by defocusing/spreading the beam. It is also assuring to avoid mishaps of the pin point beam hitting the component. The second criteria makes also a reduction of power deposition in a small region of the beam dump. The third criteria eliminates the use of water to stop the beam. Liquid target does increase the total inventory of the activated materials.

The concept of the present design is, as shown in Fig. 3, Ring and Disk (RD) system. The part where energy is deposited consists of 17 rings and 5 disks (thickness of 5 cm). Each plate is made from OFHC (Oxygen Free High-purity Copper). All the rings have different inside diameters (the beam runs inside this ring.). The frontmost ring has the inside diameter of 19.6 cm and other rings have smaller diameter with increment of 1.2 cm from upstream to downstream. In a module a cooling water flows in series from ring to ring. In order to reduce radiolysis of cooling water and to eliminate the vacuum window between the beam dump (target) and the accelerating tube, cooling water is not exposed to direct incident electron beam. These modules form a total target block and it also electrically insulated from the main body of the beam dump. The problem of connecting between the beam dump and the accelerator (the pressure difference between $1	imes10^{5}$ torr and $1\times10^{7}$ torr in the accelerating tube) was solved by using a differential pumping stations and a low conductance beam transport tube.

RF modulator and Klystron

The klystron is able to operate complete CW (1.2MW CW). But the facility power station could not supply such large power (~5MW), which made the klystron operate 20% duty. Modulation of the klystron pulse voltage is accomplished by controlling the anode voltage for 90kV operation. For 147kV, the beam voltage modulation is employed, using pulse transformers and solid-state switch.

The klystrons used on the PNC accelerator were developed specifically to operate in CW and pulse with good efficiency (> 65%). Extensive window development was necessary to achieve continuous power of 1.2MW at L-band. The output window was designed and tested for pill-box type windows with using TWRR unit replaced the accelerating tube. The test results agree the characteristic of field decrease and reduction of VSWR in the pill-box by the design and suggests that the klystron will be able to produce more than 1.2MW RF with this new window [9].

Control and Data Acquisition Systems

A control system consists of two major parts: (1) computer control and monitor system, (2) an interlock system for use of the machine protection that shuts off the accelerator equipment and to protect personnel.

The computer control and monitor system is consisted of three network layers, which are Ethernet layer, VME-bus layer (SCRAM-net), and high speed communication layer. The beam control contains controls and status displays for each individual linac equipment. These systems are connected Ethernet layer (Ethernet with TCP/IP protocol). The communication network is supervised by the system control work stations which also manage the whole linac operation. These processors are not responsible for crucial operations such as interlock system.

The VME-bus layer (served as the beam control and some of them contained PIOP (Parallel Input/Output Processor) system) is interfaced with the linac equipment and each VME-bus systems connected with Ethernet and SCRAM-net (15MB/sec). Each PIOP node is connected with high speed communication lines as horizontally (or hypercube shape connection), which makes each node communicate with another node a short time as compared with shared bus system. A combination with high speed communication layer and DSP (Digital Signal Processor as node processor) makes fast data processing for large number input events simultaneously. This concept of data processing could not be achieved in conventional system.

The interlock system employs hard wire programmable sequencer system connected crucial equipments, which is completely independent from computer assist system because of more redundancy for safety aspect.

COMMISSIONING

Pre-Commissioning

The commissioning was carried out with partially build accelerator. The injector, the first accelerator section, the beam dump, and RF source was completed in December 1995. The RF conditioning was made in site using
own RF source. Within a few days after the RF conditioning, the buncher and accelerating section was able to store about 1 MW RF peak power in the resonant ring. The unique aspect of this power RF conditioning is burst-pulse operation, which is nine short pulse(100\mu sec) within 4 msec period. The 4 msec pulse power and the CW klystron allow to this kind operation.

**Beam-Commissioning**

Beam commissioning began and 3.1MeV beam had coasted though the linac to the beam dump. By March 22, 50mA of 1 msec beam was achieved. The resonant ring of the buncher and first accelerating section were tuned to the maximum resonated RF power. The RF chopper and the chopper slits were adjusted by the RF power to apply the cavity with a fundamental (\(f_0\)) RF power, then DC magnetic baisses, finally second harmonic (2\(f_0\)) RF power. Fig. 4 shows the beam current in each beam current monitor. The beam current after the chopper shows one third current from the electron gun exit. The energy spectrum measured by bending magnet are shown in Fig. 5. After using the RF chopper, the energy resolution ($\Delta E/E$) is about 5%. This is rough adjustment because the bunch monitors have not been prepared and all phase and bunch length have not be tuned yet. Until now ~100 mA beam with pulse width 1 msec repetition 0.5 Hz has been accelerated. Studies continued at design goal of 100 mA beam with 4 msec and repetition 50Hz, including the resonant rings control with high power operation. The temperature control of resonant rings and accelerating tubes is getting critical with high duty operations.

**CONCLUSION**

The PNC high power CW linac injector and first accelerating section was installed and pre-commissioned during the beginning of 1996. This pre-commissioning shows important results that the accelerator with the traveling wave resonant ring under 100 mA beam loading is easily handled and verified the acceleration of long pulse beam such as 1 msec. Studies continued at design goal of 100 mA beam with 4 msec repetition 50Hz. The rest of accelerating section will be installed by March 1997, then 10MeV high power CW(average 20mA 20%duty) electron linac commissioning will be ready.

**ACKNOWLEDGMENTS**

We would like to strongly our deep appreciation to the professors at National Laboratory for High Energy Physics (KEK) for their incalculably guidance and helpful contributions from beginning of this project. Professors are: I. Sato, H. Kobayashi, and A. Enomoto. Our appreciation goes to Dr. Y. Takeda at Paul Scherrer Institut (PSI) especially for the beam bump design.

**REFERENCES**

[5] "Phase and Radial Motion in Electron Linear Accelerator" code modified by many contributors.
Fig. 1 Injector components and schematic.
Fig. 2  Waveform in chopper cavity.
Fig. 3. A cross section view of the beamdump.
CT1 (after gun) 260mA
CT2 (after tunnel) Fig. 1 position A 88mA
CT3 (after chopper) Fig. 1 position B 88mA
CT4 (after acc. tube) Fig. 1 position C 88mA

Fig. 4 The beam current in each current monitor.
Fig. 5 Energy spectrum.
STATUS OF THE HIGH INTENSITY PROTON LINEAR ACCELERATOR DEVELOPMENT IN JAERI

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Abstract

JAERI has been proposed a high intensity proton linear accelerator to be utilized in future accelerator-driven Partitioning and Transmutation (P&T) system. The R&D of the high intensity proton accelerator was started in 1991 as one of the approaches for the OMEGA program in Japan. The first phase of the R&D has been made successfully on the components of the front-end part of the accelerator i.e., an ion source and RFQ, resulting in the peak current of 70 mA with duty factor of 7–10% operation was obtained at the energy of 2MeV after the RFQ acceleration.

In these years, JAERI has been planned the Neutron Science Research Program (NSRP) for exploring basic researches and nuclear waste transmutation technology based on a next generation spallation neutron source driven by the high intensity proton linac. The conceptual design of the high intensity proton accelerator is rearranged slightly to achieve various operation modes in the NSRP. The second phase R&D has been started for the study of whole accelerator system with 1.5GeV and 10mA, beam power of about 15 MW. This report describes the summary of the first phase R&D and the present status of the second phase development of the high intensity proton linear accelerator.
Introduction

A progress of the technology in the field of charged particle accelerator gave a possibility of high intensity neutron source by nuclear spallation reaction. In 1980's research activities have been made for high intensity proton linacs to be applied to the nuclear fuel breeding and high-level long-lived radioactive waste transmutation. One of the approaches for the OMEGA program in Japan, JAERI has been carrying out the design study of an accelerator-driven nuclear transmutation system of minor actinides. The required beam current to drive a subcritical nuclear reactor for Partitioning and Transmutation (P&T) system is more than 40mA by preliminary evaluation. The initial concept of the high intensity proton accelerator to be used for the OMEGA program is a pulsed linear accelerator with an energy of 1.5GeV and an average current of 10mA (peak current of 100mA with 10% duty factor).

The average proton beam current of 10mA with the energy of above 600MeV is much higher than those for the present operating machines in the world. Most important issue in the proton accelerator is the handling of an intense beam with lower beam loss rate. The velocity of the accelerated proton is changed along with the beam energy. When the energy reaches at 1.5GeV, the velocity still does not get to the light speed. Acceleration method and accelerator structure must be changes to match an effective acceleration and in particular to keep low beam loss rate. In addition, the beam current and the beam quality of the high intensity accelerator are mainly determined by the low energy part of the accelerator because of the space charge effect. The stepwise development for the high intensity proton accelerator has been planned in JAERI. The first phase development was assigned to develop a low energy part components such as a high current and a low emittance ion source, a high peak current RFQ, a DTL hot test model and a high power RF source with a frequency of 200MHz.

To make the best use of the high intensity proton accelerator, JAERI has been proposing the Neutron Science Research Program (NSRP) in these years aiming at the exploring basic researches and nuclear waste transmutation technology by means of the proton accelerator application. The second phase R&D of the high intensity proton accelerator has been started to associate the accelerator design and the NSRP issues[1]. The various proton beam conditions are required such as high peak current, variable intensity, short pulse (less than \( \mu s \)), long pulse (2-3 ms) or continuous wave (CW) beam to realize the experiments in the NSRP. Figure 1 shows a conceptual layout of the accelerator for the NSRP.

The conceptual profiles of the accelerator are; 1) energy and current of the accelerator are 1.5GeV and about 10mA respectively, 2) positive and negative ion beam are simultaneously accelerated with a peak currents of 30mA,
3) main option of the high energy accelerating structure above 100 MeV region is a superconducting cavity system,
4) a beam storage ring is used to make an intense short pulse neutron and 5) the development for CW proton
accelerator is kept in mind to apply a driver of future transmutation system. Preliminary parameters for the NSRP
accelerator are given in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>1.5 GeV</td>
</tr>
<tr>
<td>Accelerated particle</td>
<td>Negative and positive hydrogen ion</td>
</tr>
<tr>
<td>Average current</td>
<td>1st stage: 1 mA</td>
</tr>
<tr>
<td></td>
<td>2nd stage: 10 mA maximum</td>
</tr>
<tr>
<td>Peak current</td>
<td>Nominal 30 mA</td>
</tr>
<tr>
<td>Low energy part</td>
<td>Normalconducting linac / 200 MHz</td>
</tr>
<tr>
<td>High energy part</td>
<td>Superconducting linac / 600 MHz</td>
</tr>
<tr>
<td>Beam operation mode</td>
<td>1st stage: Pulse mode operation</td>
</tr>
<tr>
<td></td>
<td>2nd stage: CW / Pulse mode operation</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>50 Hz maximum</td>
</tr>
<tr>
<td>Macro-pulse width</td>
<td>2 ms (at 1 mA operation) to CW maximum</td>
</tr>
<tr>
<td>Intermediate pulse width</td>
<td>400 ns (interval 270 ns)</td>
</tr>
<tr>
<td>Chopping factor</td>
<td>60 %</td>
</tr>
</tbody>
</table>

The development of the technologies for the nuclear waste transmutation system is one of the major subjects
of the NSRP. In the scale of the NSRP, the R&D experiment for a P&T target system, cross section measurement
of minor actinide (MA) nucleus and basic reactor physics experiments with MA fuel subcritical reactor will be
made by using the high intensity proton accelerator.

**General Aspects of the R&D**

The low energy accelerator components have been developed since 1991 for the R&D to study the front end
of the accelerator. An ion source, an RFQ, and an RF source for 10% duty factor operation were fabricated and
2MeV beam tests have been performed[2]. The characteristics of the RFQ such as beam current, energy spectra
and emittance have been studied. The layout of the RFQ beam test is illustrated in Fig 2. To demonstrate the RF
characteristics and the cooling capability at the high duty factor operation, a DTL hot test model with 9 cells was
fabricated and high power tests were carried out.

The present activity of the second phase R&D attempts a high current negative hydrogen
ion source development, high duty factor (up to CW mode) component development in the
low energy portion (for RFQ and DTL), superconducting accelerating cavity development
and evaluation of high current proton beam dynamics for the conceptual accelerator design.

Fig. 2 A Schematic Layout of 2 MeV RFQ Beam Test Line
Ion Source

A multicusp type hydrogen ion source with two-stage extractor has been developed to obtain a high brightness proton beam. The ion source has been operated successfully with more than the designed current of 140 mA at 100 keV[3]. Normally, the ion source is operated by pulsed mode with a duty factor of 10 % to inject into the R&D 2MeV RFQ. Fundamental capability of the ion source allows an operation with a CW mode. This work was carried out in collaboration with the JT-60 NBI group of JAERI. A typical beam extraction characteristic of the ion source is shown in Fig. 3.

To inject the beam into a beam storage ring at a beam energy of 1.5 GeV for applications of the basic researches, a high brightness negative hydrogen ion source is required. The development of the negative ion source has been started[4]. The structure of the negative ion source is based upon the multicusp type hydrogen ion source and the first beam test of the negative ion source coupled with the R&D RFQ is scheduled at the beginning of 1997.

RFQ

The R&D RFQ is a four-vane type and its frequency is 201.25 MHz. It is designed to accelerate 100 mA (peak) of protons to 2 MeV with a duty factor of 10 %. After the low power tuning and the high power conditioning, the beam tests have been made at JAERI since November 1994. The maximum RFQ output current was 80 mA at the ion source extraction current of 155 mA. The energy of the proton beam from the RFQ was measured by a compact magnetic energy analyzer installed in the Medium Energy Beam Transport (MEBT). The energy resolution is assumed to be 5 % for 2 MeV proton beam. The RFQ beam emittance has been measured by the conventional double-slit type monitor. Typical value of the normalized rms emittance for the RFQ beam were $X - X' = 0.62 \, \text{mm-mrad}$ and $Y - Y' = 0.76 \, \text{mm-mrad}$ at 80 cm downstream of the RFQ.

At the beginning of the beam test in JAERI, the maximum duty factor was limited to less than 2 % due to the partial burn out of the RF contact at the RFQ. A silver plated spiral type RF contact, which is made of beryllium copper alloy, was used between the tank and the vane. The diameter of the contact was 3.2 mm and the thicknesses of the base beryllium copper alloy and the silver plate were 100μm and 30 μm, respectively. To improve the heat transfer properties, the RF contact was replaced by a 100μm thickness silver-plated type. In addition to the contact replacement, copper blocks were installed to cover the open space between the vane and the tank to reduce the heat dissipation at the vane end region. As a result of these modifications, steady operations with 7 % duty factor, and short-duration operation at 10 % duty factor can be achieved at the beam current of 70 mA.

A high power test model of CW-RFQ of 50cm in length is fabricated and tested in 1996 to demonstrate the manufacturing technique and the RF characteristics.
RF Power Source System

A 201.25 MHz RF system was designed and manufactured for the RFQ beam tests and the DTL high power tests. A tetrode, 4CM2500KG (EIMAC), is used in a final-stage amplifier[5]. Dummy load tests were completed resulting in a peak RF power output of 1 MW was achieved at a duty factor of 0.6 % and high duty operation of 12 % with an RF power of 830 kW was generated, which satisfied the requirement for the tests in the R&D. The power efficiency was 60 %, which is in good agreement with the designed value of 62 %.

The voltage and the phase stability during the beam acceleration should be controlled within ± 0.5 % and ±1 degree, respectively. To satisfy these specifications, the RF control system has a feedforward-circuit combined with a feedback-circuit. The performance of the feedback-circuit was examined in the RFQ beam tests. The amplitude and the phase errors were on the order of 0.5 % and 5 degree, respectively, during 100μs period after the beam injection when the beam loading was 110 kW.

DTL

A high power test model of DTL with 9 cells, which is a mock-up of the low energy portion of the DTL, has been fabricated to study the RF characteristics and the cooling requirements. A DC excited electromagnetic quadrupole using a hollow conductor (5 mm x 5 mm) was developed successfully for the focusing magnet, of which field gradient is 80 T/m with 5.5 turns at 780 amperes. The high power tests were carried out with the RF power source[6]. Fig. 4 shows the schematic layout of the test. At first, the duty factor had been limited to less than several percent due to the RF contact problem at the end plate. After an improvement of the RF contact structure, RF power of 128 kW with a duty factor of 20 % was fed to the model without any troubles, this power corresponds to the average axial field of 2 MeV/m. The gap voltage was estimated to be 195 kV at an RF power of 128 kW by a spectrum measurement of Bremsstrahlung X-ray from the model, which was in good agreement with the calculated value of 197 kV by the SUPERFISH code. The measured RF power dissipation in each drift tube and the end plates was in good agreement with the calculation. The calculations were performed with the combination of the thermal deformation from the ABAQUS FEM code and the frequency shift from the SUPERFISH code. These high power test results have confirmed the heat dissipation calculation and the cooling design of the DTL.

To extend the capability of CW operation based upon the previous DTL design parameters, a cold model of CW-DTL will be fabricated in 1996 to examine RF characteristics. Accelerating gradient of the CW-DTL may be lowered to be 1.5 MeV/m in order to reduce the RF consumption and the RF heating. The end point energy for the DTL is 100 MeV which will be determined from the beam dynamics and mechanical consideration of the high energy structure.
Superconducting Cavity

Superconducting (SC) cavity is a main option for high energy portion of the accelerator. Resulting with basic studies for the structure of high energy part of the accelerator, several favorable characteristics were pointed out with SC option in comparison with normal conducting cavity option. There are a high electrical field gradient for beam acceleration of 10 to 25 MeV/m, high quality factor of \( \sim 10^9 \) and acceptable wide beam tube aperture of 100 to 180 mm.

In the CW electron accelerator, technologies of SC accelerators are established. The experiences of design, manufacturing and operation for the electron SC accelerator are accumulated for years such as KEK-TRISTAN and other many laboratories[7], [8]. The high energy part of these electron SC accelerator operates single velocity of light speed. This condition leads uniform cavity shape and uniform cryomodule design for all accelerating cavity structure. In the proton accelerator, however, velocity varies sequentially from 100MeV to 1.5GeV. Fig. 5 illustrates the velocity changes in accelerating electron and proton. Accordingly, the length of the cavity also changes. Main concern is the mechanical strength of the cavity under the vacuum load for the energy range of 100 to 200MeV because of the more flatter shape than electron accelerator's one.

The R&D work for SC accelerator has been started since 1995 in collaboration with KEK SC group[9]. The mechanical structure calculations with the ABAQUS code have been done to determine the cavity shape parameters as well as electromagnetic ones with the SUPERFISH code. The schematic drawing of the JAERI SC accelerator cryomodule is shown in Fig. 6. Niobium superconducting test cavity for the 150MeV region will be fabricated and

![Fig. 5 Accelerating Particle Velocity](image)

![Fig. 6 A Conceptual Drawing of the Proton Accelerator Superconducting Cavity and Cryomodule](image)
examined in 1996 according to the preliminary design. A test stand for the vertical tests of 600MHz cavities has been installed at JAERI with a cryostat of 80 cm in diameter and 350 cm in depth.

The temperature of the vertical test for SC cavity experiments can be adjusted at 2 °K or 4 °K by evacuating the liquid helium vessel. A clean room of class 10 to prepare the clean surface of a test SC cavity with an ultra pure water of 18 MQ-cm generating system, a high pressure of 8.5 MPa water rinsing system and an oil-free ultra high vacuum of 10^-9 Pa pumping system was installed. An image view of the SC cavity preparation work and the vertical test set-up are shown in Fig. 7.

**Summary**

The first phase R&D with the design and the fabrication of the prototype accelerator structures (ion source, RFQ, RF source and DTL) have been carried out. The good performance of the components has been confirmed. In the RFQ beam tests, acceleration current of 70 mA with a duty factor of 7 to 10 % has been achieved.

Since 1995, the basic specification for the accelerator has been changed to match the NSRP in JAERI such as negative and positive ion simultaneous acceleration, variable beam intensity, SC cavity option and storage ring. The second phase R&D work has been started. For the injector of the SC cavities, much longer duty factor or CW beam operation will be required. Design work on the RFQ and DTL for the CW operation is being performed. Negative hydrogen ion source beam acceleration test coupled with 2MeV RFQ beam line is planned in 1997. SC cavity development has been started to establish mechanical property and electromagnetic performance for energy range of 100 MeV to 1.5 GeV with a frequency of 600MHz.
Acknowledgment

The authors would like to thank Drs. S. Noguchi, K. Saito, E. Kako and M. Ono of KEK for discussion and help on the SC cavity development. They also thank Drs. T. Kato, Y. Yamazaki of KEK and Dr. R. A. Jameson of LANL for valuable suggestion about the beam dynamics calculations and accelerator system optimization.

References

Abstract

The calculation models in the cascade code NMTC/JAERI have been improved on bases of the new nuclear theory and new measured data. The intranuclear nucleon-nucleon scattering process calculation has been modified taking into accounts the effects of reflection and refraction of nucleon in nucleus and nucleon-nucleus scattering cross section. The preequilibrium process model was adopted to improve the prediction about nucleon back scattering. Adjustment was made for parameters in the high energy fission model and the adoption of total reaction cross section estimated systematically. Some benchmark calculations were carried out to verify the prediction capability of the modified cascade code. The ACCEL code system for designing an accelerator-driven system has recently been upgraded as the ATRAS system. The Sn transport code TWOTRAN2 and Monte Carlo transport code MORSE have been replaced by new codes TWODANT with faster computation time and MCNP4A with the continuous Monte Carlo method respectively. The 73 groupwise cross sections up to 20 MeV have newly been produced to be used with the TWODANT code. The burnup code BURNER linked with TWODANT was also prepared well.

The conceptual design study on proton accelerator-driven transmutation systems with nitride fuel and new molten salt of minor actinides were carried out as another promising options. The solid fuel system consists of a sodium-cooled subcritical core with pin-bundle type assemblies of actinide nitride fuel and a multi-layer type spallation target of tungsten. It is expected to have the better thermal characteristics than metal fuel system. When the system is driven by several tens mA proton beam with an energy of 1 GeV, amounts of minor actinides transmuted per year and the power generation were given respectively. The burnup calculations up to 300 days and the preliminary dynamics analysis were performed to examine the transmutation capability and the nuclear safety in this system. The nuclear characteristics of the system with MA-PbCl₃ type chloride molten salt fuel was examined and compared with MA-NaCl type one researched already.
1. Introduction

According to the national research and development program OMEGA on partitioning and transmutation, the research activities on the accelerator-based transmutation technologies are being promoted at JAERI in the following items,

1. Development of simulation code system including the spallation cascade code,
2. Design study on accelerator-based transmutation system,
3. Spallation experiment with high energy proton beams,
4. Development of an intense proton linac (1.5 GeV, 10 mA).

In the present paper the recent works on the conceptual design study of the transmutation system and the development of the code system are reported. Descriptions on the items (3) to (4) are given at other sessions in this meeting.

As well known, the calculation for designing the accelerator-driven transmutation system must treat the nuclear processes in the wide range from ~eV to a few GeV. Unfortunately there is not yet the single code that covers all reaction and transport in the energy range because of few available nuclear data in the high energy range. For the sake the hadron cascade code simulates the nuclear reaction and particle transport in the energy range higher than 20 MeV. Its prediction accuracy affects heavily on estimation of ability of accelerator-based transmutation system. So the cascade code NMTC/JAERI7,8 has been recently upgraded, taking into account new experiment data and calculational model, and the new version code named NMTC/JAERI94. In order to calculate the nuclear process in the accelerator-based system, the code system ACCEL9 had been originally developed at JAERI before ~1985 and includes the NMTC/JAERI and the neutron transport codes corresponding to ENDF-B4. To calculate more accurately and efficiently the nuclear reaction and particle transport process in the accelerator transmutation system over the energy range, the "ATRAS"(code system) has been recently developed at JAERI by adopting more powerful codes and the nuclear data library upgraded for higher actinides.

The radioactive nuclides to be transmuted in the JAERI transmutation research program are MAs such as 

\[
\begin{align*}
^{237}\text{Np}, & \quad ^{241}\text{Am}, \quad ^{243}\text{Am}, \\
^{244}\text{Cm}, & \quad ^{245}\text{Cm} \quad \text{and Long-Lived Fission Product (LLFP) such as} \quad ^{99}\text{Tc}, \quad ^{129}\text{I}
\end{align*}
\]

with half lives between a few hundred years and several million years. MA should be transmuted through fission reactions because the transmutation of MA by neutron capture has the possibility of increasing higher actinides. For designing the accelerator transmutation system at JAERI, we adopted the design guide lines as

1. application of spallation neutrons to transmutation system,
2. exclusive system for MA and long-lived FP burning,
3. self-supporting system in energy,
4. transmutation rate of MA (260 kg/y) from ten units of 1 GWe LWRs.

Fissioning of MA, which is a non-fissile material for thermal neutrons, occurs dominantly to neutron capture above the threshold energy of about 500 keV. So JAERI selected the transmutation method of MA by fast fission reactions controlled by spallation neutron source although it requires the large initial MA inventory. LLFP can be transmuted only through thermal neutron capture to stable nuclides because of small capture cross sections for fast neutron. From the reason the thermalized neutron region may be set up around fast subcritical target/core to transmute MA and LLFP simultaneously in one system.

The design studies for two different types of accelerator-driven transmutation system, that is, solid fuel type and liquid fuel type, are being carried out at JAERI. The solid MA (alloy, nitride) fuelled system is composed of tungsten target and solid fuel subassemblies like fast reactor for MA burning. Its R&D works are considered to be the relatively short term project, except an intense proton accelerator, since most of technologies and know-hows already obtained in the fast reactor development can be effectively applied to perform the design study of this type system. The system with the liquid fuels will be developed in the long term project. The molten salt system is expected to be the more promising transmutation system with possibility of online fuel reprocessing but of containing more problems to be resolved than the solid fuel one. The liquid alloy fuel system has a graphite moderator blanket to transmute LLFP by using thermalized neutrons. Both liquid fuel systems have the active, subcritical core region with the hard neutron energy spectra.

For the proton beam-controlled core operated in the subcritical mode, some advantages are considered in the following,

1. No control rod, no safety rod, simple core configuration,
2. Large flexibility in the core design due to less severe requirement to reactivity coefficient,
3. Operation stop by shutting down the proton beam,
4. Less limitation to the burnup time of fuel,
5. Mild requirement to the fine adjustment of fuel composition.
2. Development of code system for designing the accelerator-driven transmutation

In the intranuclear cascade calculation in the NMTC/JAERI code, the nuclear medium effect for nucleon (N) scattering in a nucleus was studied and the accuracy of predictions of reactions induced by lower energy protons was improved. For the OECD/NEA code intercomparison task force, the benchmark calculations on the proton-induced nuclide production cross sections in some targets at the energy of 20 MeV to 5 GeV were carried out using the HETC/3STEP code. The calculated cross sections for heavier resultants had good agreements with experimental one except the accuracy of producing lighter nuclides. Neutronic calculations below 20 MeV in the transmutation system are carried out using the well-prepared transport code connected with the cascade code. Here informations about spallation neutrons with energies below 20 MeV is transfered from the cascade code to the neutron transport code as source neutron terms. For the calculation in the entire energy region, more excellent new code system ATRAS, including the new version cascade code and the 73 groupwised cross sections below 20 MeV extending the JAERI-fast set corresponding to the JENDL3.2, has been newly developed.

2.1 Improvement of cascade codes

For the energy region above 20 MeV, the spallation reaction with many reaction channels occurs dominantly as shown in Fig.1. However there is few nuclear reaction data in this range for various nuclides. At present the best way to analyze these high energy processes is to use the cascade simulation codes. JAERI is using the NMTC/JAERI (High Energy Nuclear Reaction and Nucleon-Meson Transport Code) and NUCLEUS (only intranuclear cascade). The Bertini model in the cascade code had successfully had treated the intranuclear cascade (INC) above 200 MeV of incident particles, using two-bodies collision approximation between nucleons. Since the nucleons with the energy of 20 MeV to 200 MeV in a nucleus have gradually more wave-like nature, the disagreement between experimental data and predictions calculated by the INC model becomes larger. Some of calculation models and collision cross sections in the simulation code were installed before ~1975.

They have been improved and upgraded by the newly developed nuclear theory and the data measured on the recent high energy experiments in the following items,

a) adoption of the in-medium nucleon-nucleon scattering cross section,
b) the effects of reflection and refraction of nucleon in nucleus,
c) addition of preequilibrium process based on the exiton model,
d) modification of high energy fission model (Nakahara model),
e) replacement of original total cross section by Parlstein's systematics one,
f) adoption of level density parameter $a_0$ by Baba and new mass formulas.

In the original INC calculation the mean free path (mfp) for nucleon collision in a nucleus was approximated by the nucleon(N)-nucleon(N) scattering cross section in free space. The influence of nuclear matter mean field (nucleon-nucleon collision) becomes larger for an incident nucleon with less than ~200 MeV. So the parameterized in-medium N-N cross sections dependent on nucleon energy have been installed through the subcode ISOBAR into NUCLEUS to compare more accurate calculation data with recent experimental ones. Figure 2 shows the in-medium total neutron-proton cross sections in the energy range of 50 to 300 MeV calculated by taking into accounts the nucleon-nucleon pairing effect. The use of upgraded cross sections result in prolongation of mfp of nucleon in a nucleus. In Fig.3 the calculated angular distributions of emitted protons with 60 MeV are compared with experiment one in the Au thin foil bombarded by 100 MeV protons. The lines except solid line represent the contribution from each step in multiple scattering. As seen in these figures the distribution calculated by ISOBAR code with free space N-N cross section gives about a half experimental one, whereas the calculated distribution with in-medium N-N cross section agrees well with experimental one, in particular, in the backward direction. Figure 4 compared the calculated neutron production differential cross sections (DXX) with the experimental data by Amian et al. for the reaction Al(p,xn) induced by 800 MeV proton irradiations. There are some differences between both data in the energy range of a few MeV and a few tens MeV when the free space NN cross sections are used, while the result calculated with the in-medium cross sections shows good agreement in each direction.

For the cross section of $(p,n)$ and $(n,p)$ reactions the threshold value has been adopted to treat the quasi-elastic collision properly as many researchers suggested. The refraction and reflection effect has been also taken into account at boundaries assumed in a nucleus according nuclear matter density. Then a moving nucleon with a lower energy changes its direction even when crossing the boundaries. The exiton model was inserted in the Bertini INC model to consider the nucleon emission at the preequilibrium state. The calculated data using this improved version code were compared with ones measured in thin and thick (stopping
also agree well with the experimental ones of the Ir production. Even for the other nuclides in the mass range of 190 production by the spallation reaction of a heavy nuclide. It is observed in Fig. 13 that HETC-3STEP's results indicate that the present fission model is applicable to the estimation of the medium-mass nuclide. Although the high energy fission of sub-actinide nuclides is taken into account in HETC-3STEP, the calculated targets. For the Zr production, the HETC-3STEP reproduces the experimental result quite well in Fig. 12. because of lack of the fragmentation process model. The similar discrepancies are observed for all the other results of the cross sections calculated with HETC-3STEP are compared with the experimental results for the productions of 0, 25, 000 for 197 Au, and 50,000 for 60 Co, respectively. In Figs. 11 to 13 the cross sections calculated with HETC-3STEP are compared with the experimental results for the productions of 7 Be, 90 Zr, 190 Ir and 197 Hg in the 197 Au target. As seen in Fig. 11, this code cannot estimate the 7 Be production because of lack of the fragmentation process model. The similar discrepancies are observed for all the other targets. For the 89 Zr production, the HETC-3STEP reproduces the experimental result quite well in Fig. 12. Although the high energy fission of sub-actinide nuclides is taken into account in HETC-3STEP, the calculated result indicates that the present fission model is applicable to the estimation of the medium-mass nuclide production by the spallation reaction of a heavy nuclide. It is observed in Fig. 13 that HETC-3STEP's results also agree well with the experimental ones of the 197 Ir production. Even for the other nuclides in the mass range of 190.
of 177 to 197, a fairly good agreement with a factor of two to three is obtained between the calculated and experimental results. For the other target, however, lighter the mass of produced nuclides become, worse the agreement between the calculated and experimental results becomes. Therefore the accuracy in the HETC-3STEP calculation for the other targets is poorer than that of $^{197}$Au even in the production of a nuclide with mass number close to the target one.

As the present intranuclear cascade/evaporation model calculates the nuclear reaction in a very classical manner, the accuracy of a factor of two to three for resultant production seems to be acceptable. In order to improve the accuracy of the nuclide production cross section in the framework of the intranuclear cascade/evaporation model, the following physical aspects should be taken into account: (i) the accurate treatment of the threshold energy of the nuclear reaction, (ii) the inclusion of the fragmentation reaction, (iii) more accurate estimation of the charged particle emission in both the INC and preequilibrium processes, (iv) more precise simulation of the statistical decay process by the use of the Hauser Feshbach model.

There are many light nuclei such as Cl in active fluid targets in the JAERI-type liquid transmutation system as described later. In the target region the spallation reaction of MA and light nuclei occur simultaneously in addition of fast fission transmutation of MA. So cascade calculations for the high energy hadron nuclear reaction in a light nucleus and the transport process in the dilute fluid target/core should be analyzed with the higher precision.

2.3 Development of the entire code system ATRAS

The design code system ATRAS (Accelerator-based Transmutation Reactor Analysis System) has been developed to carry out the accelerator transmutation calculation more accurately and effectively. This system consists of the cascade code NMTC/JAERI94, Sn transport code TWODANT, Monte Carlo one MCNP4A, and the burnup code BURNER linked with TWODANT as seen in Fig. 14. The 73 groupwised cross section set below 20 MeV was newly developed on base of the JFS-3-J2 set from the cross section library JENDL-3.2, where the connecting energy between cascade and transport codes was changed from 15 MeV to 20 MeV corresponding to the available energy in the JENDL 3.2.

The ACCEL has been revised and named the ATRAS, which is the integrated code system which can perform following calculations

1) spallation, evaporation and high energy fission processes above 20 MeV,
2) neutron transport process below 20 MeV and
3) core burnup process below 20 MeV.

The first process was calculated with the NMTC/JAERI4 code in which many modifications were applied as described above. For the calculation of the neutron transport below 20 MeV, the two-dimensional Sn transport code TWODANT and the three-dimensional Monte Carlo transport code MCNP-4A were selected. Both codes were modified to apply the non-isotropic volume source of spallation neutrons emitted from the target for the fixed source calculation. The effective microscopic and macroscopic cross sections needed for the transport calculation can be generated by the CSASI module from the SCAL-4 code system. For the third burnup process the ATRAS code is capable for the burnup analysis of the accelerator-based transmutation systems. The BURNER code, burnup calculation module in the VENTURE code system, was used for this purpose. The code was used, linking with TWODANT code to include the effect of the changes of core-averaged neutron spectrum corresponding to each burnup step.

The new file of groupwised cross sections was also prepared for the ATRAS code from the latest JENDL-3.2 library. Structure of this groupwised cross section file is almost the same as the fast reactor group constants set JFS-3-J2. Three groups were added to the energy range from 10 MeV to 20 MeV to connect smoothly the transport code with the NMTC/JAERI code. About 30 nuclides, which are necessary to calculate the JAERI-proposed accelerator-based transmutation systems, were selected from the JENDL-3.2 library. Higher actinides such as Bk and Cf and long-lived fission products (Tc-99, I-129) were also selected for this groupwised cross section file.

By using these codes we could calculate the nuclear characteristics about the accelerator driven transmutation systems in the whole energy range more efficiently and accurately. The ATRAS will be opened for outside use in the near future.

3. Design Studies on accelerator-driven transmutation system

The design studies for two different types of accelerator-driven transmutation system, that is, solid fuel type and liquid fuel type, are being carried out at JAERI. In the present paper the MA nitride fuelled core and the Pb-type chrolide molten salt core were researched respectively as the another promising option.
3.1 Nitride fuel system

The JAERI system concept with TRU-nitride fuel is now under study to take full advantage of the excellent thermal performance of nitride fuel. Neutronics analysis of the accelerator-based transmutation system with solid disk tungsten target and TRU-nitride fuel was performed using the ATRAS codes. This core is a cylinder in dimensions of 80 cm height and 40 cm radius, surrounded by the stainless steel reflector with thickness of 50 cm. The fuels with composition of TRU (90(Np, Am, Cm):10Pu) - 15N are arranged as pin-bundle type assemblies around tungsten target in the core and cooled by sodium flow. Specifications of the core are listed in Table 1. The target was divided into the thin-disk part and thick-part to flatten the released neutron distribution from the side surface of the target. Results of neutronics calculation are summarized in Table 2. The calculation results showed that this system with $k_{\text{eff}}$ of 0.927 and average neutron fluxes of $2.67 \times 10^{14}$ n/cm²/μA can transmute about 5.18 kg/μA of TRU per year and generate a thermal power of 15.7 MW/μA in operation with the 1 GeV proton beam. TRU inventory in the core is about three times lower than the metallic fuel system because of higher density of heavy metal in the nitride fuel. Much higher power density, enough transmutation ratio and neutron spectrum as hard as in the metallic fuel system have been gotten also. The specification of the system was proposed for a benchmark problem in the "OECD/NEA/NSC Benchmark on Physics Aspects of Different Transmutation Concepts".

3.2 Molten salt system

The system with the liquid fuel such as the molten salt is being developed as the long term project in the OMEGA plan. In the liquid target/core transmutation system using MA molten salts, there are no limitations for preventing the melt down accident of fuel and target due to local power peaking. The minor actinides (MA) concentration in molten salt fuel is lower than one in solid fuel. The power peaking around the beam-irradiated zone is not a critical factor because of the relaxed heat condition due to liquid fuel. So the high energy proton beam can be injected directly on the center of the MA fuelled zone where there is no target region with the definite boundary. The concept of an advanced MA molten-salt system has been studied to apply the advantages of a simple fluid target/core to the transmutation system. The flowing MA molten salt forms the subcritical core and itself acts also as spallation target and primary coolant circulating between target/core and heat exchanger in the calculational model in Fig. 15. This system has the reaction vessel with 170 cm in height and 105 cm in radius and the stainless steel reflector with thickness of 20~40 cm. The compact heat exchanger and molten salt pump are installed inside the vessel to reduce TRU molten salt inventory. Nuclear characteristics in the subcritical core filled by the promising chloride molten salt 70PbCl₂-30TRUCI₃, with hard neutron spectrum, has been examined for the same configuration in reaction vessel to one with 64NaCl-36TRUCI₃ which was already studied as the previous case. The fluoride molten salt NaBF₃-NaF was selected as the secondary coolant. The plotting curves in Fig. 16 (a) and (b) represent the neutron hard energy spectra in both molten salt target/core irradiated by 1.5 GeV protons and the outer torus region where the primary cooling system (heat exchangers and pumps) is installed. These regions are separated by an inner cylindrical reflector to protect the heat exchangers and pumps against high neutron flux. The neutron flux in the outer region is kept to be lower by about two orders of magnitude than one in target/core. The power density distribution in the target/core region irradiated with 1.5 GeV protons is shown in Fig.17, where the maximum power density is about 70 MW/m³ at proton current of 1 mA. This system with $k_{\text{eff}}$ of 0.93 and 1.5 GeV-20 mA proton beam can transmute 238 kg of MA per year and produce the electricity of 228 MW sufficient to power up the accelerator. The operating condition is compared with one in the case of 64NaCl-36TRUCI₃ fuel salt in Table 3.

As reported already, the molten salt transmutation system is expected to have the possibility of removing reaction products from the system through He purge method, Cd metal extraction method, cold trapping method and oxidation method respectively.

3.3 Burnup calculations of the JAERI accelerator-driven transmuter

To examine the transmutation capability and the nuclear safety the burnup calculations were carried out in the energy region below 20 MeV for the accelerator-driven MA transmutation systems composed of tungsten target and solid nitride-fuelled core, using the BURNER-TWODANT code in the ATRAS. The one group cross sections were made by averaging the microscopic cross sections produced from JENDL 3.2 with the neutron spectrum calculated by the TWODANT and with the decay data library. From the burnup calculation, it revealed that the transmuted amount is about 300 kg of TRU annually at the constant thermal output of 800 MW through the burning period by adjusting the proton beam current. The evolution of actinide compositions with burnup
time was calculated up to 300 days. Figure 18 represents the dependences of the minor actinide compositions. It is apparent that main minor actinide $^{237}$Np is reduced to about three fifth of initial inventory at 300 burning days. The fact implies the transmutation ability of about 200 kg per year. The BURNER code in the latest version has been improved to include the fission product effects, based on the lumped FP method. Figure 19 shows the comparison of dependences of $k_{\text{eff}}$ on the burnup time calculated by the BURNER without and with the fission product effects. The $k_{\text{eff}}$ was recalculated by the code TWODANT for the renewed compositions of actinides on each step. It has been recognized that the system for both cases always keeps the subcritical state with sufficient margin ($k_{\text{eff}} < 0.96$) although $k_{\text{eff}}$ swings to the positive side over this stage. It seems that the FPs produced in core due to actinide burning makes the good role to suppress the reactivity swing for this short burning period.

3.4 Dynamics calculations of the JAERI accelerator-driven transmuter

The dynamic analysis on the proton beam-driven subcritical transmutation system is very important from a point of view of nuclear safety at normal operation and accidental situation. The preliminary dynamic calculations were done for the metal fuelled fast reactor at subcritical state simulating the proton beam-driven subcritical core, using the EXKARS code. The transient process of the fast reactor with the effective neutron multiplication factor $k_{\text{eff}}$ of 0.96~0.99 and neutron source was calculated by solving the standard dynamic equation including only Doppler and coolant's temperature reactivity coefficients for some reactivity insertions.

4. Summary

The ACCEL code system calculating the nuclear process in the accelerator-driven transmutation system in the wide energy range of eV to GeV has recently been upgraded as ATRAS. For the energy region above 20 MeV the cascade codes NEMT/JAERI and NUCLEUS have been upgraded by taking into accounts the in-medium nucleon-nucleon cross sections, the effects of reflection and refraction of nucleon in nucleus, the pre-equilibrium process, modification of high energy fission model and Baba's level density parameter. These improvements have increased the accuracy of prediction of main parameters estimating the transmutation ability. For Neutronic calculations below 20 MeV in the transmutation system more excellent transport code such as Sn code TWODANT and Monte Carlo code MCNP 4A have newly been prepared respectively. The 73 groupwised cross sections below 20 MeV were produced for the TWODANT calculation from the JENDL3.2 library to calculate effectively the nuclear process of system with spallation neutron spectrum harder than fission neutron one. To examine the transmutation capability and the nuclear safety the burnup code BURNER linked with the TWODANT code was prepared well. By using these excellent and powerful codes we could calculate more efficiently the nuclear characteristics about the accelerator-driven transmutation system in the whole energy range.

The conceptual design studies were also carried out on two promising transmutation systems, MA nitride fuelled and MA Pb-type chloride molten salt cores, using the ATRAS codes. The proposed prototype nitride fuel accelerator transmutation system with $k_{\text{eff}} = 0.927$ can transmute 5.18 kg/MA of MA per one year and generates the thermal power of 16 MW/MA when operated by the proton beam with the energy of 1 GeV. From the burnup calculation, it was shown that the TRU amount transmuted in the nitride fuel system is about 300 kg annually at the constant thermal output of 800 MW. The evolution of actinide compositions with burnup time was calculated up to 300 days. It was also recognized, from the calculation considering the FP production in the core, that the system always keeps the subcritical state with sufficient margin ($k_{\text{eff}} < 0.96$) up to 300 days. The Pb-type chloride molten salt has been chosen due to better nuclear characteristics for studying the new MA molten salt transmutation system. This system with $k_{\text{eff}} = 0.93$ can transmute about 238 kg/y of actinides and generates the electric power of 228 MW in operation with a 20 mA proton beam with an energy of 1.5 GeV. The preliminary dynamic calculations was started for the subcritical fast reactor simulating the proton beam-driven subcritical core.

Acknowledgement
Authors express the great appreciation for helpful discussions with for Dr.s M. Mizumoto, T. Mukaiyama, Y. Nakahara, H. Katsuta, Y. Kato, O. Sato and Mrs. S. Meigo, N. Yoshizawa.

References
Table 1 Design specifications for the nitride fuel transmutation system

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Proton beam</td>
<td>1.0 GeV</td>
</tr>
<tr>
<td>Proton beam radius</td>
<td>15 cm</td>
</tr>
<tr>
<td>Proton beam profile</td>
<td>uniform</td>
</tr>
<tr>
<td>Beam duct radius</td>
<td>15 cm</td>
</tr>
<tr>
<td>Target/Core Radii</td>
<td>concentric cylinders with a height of 1 m / 40 cm</td>
</tr>
<tr>
<td>Target</td>
<td>tungsten (disk layer type)</td>
</tr>
<tr>
<td>Upper target</td>
<td>height 26 cm, disk thickness 1.5 cm</td>
</tr>
<tr>
<td>Lower target</td>
<td>height 54 cm, disk thickness 13 cm</td>
</tr>
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<td>Fuel (90MA-10Pu)N (MA:Np, Am, Cm)</td>
<td></td>
</tr>
<tr>
<td>Fuel pin outside diam.</td>
<td>7.3 mm</td>
</tr>
<tr>
<td>Pin pitch</td>
<td>9.9 mm</td>
</tr>
<tr>
<td>Effective fuel height</td>
<td>80 cm</td>
</tr>
<tr>
<td>Fuel pellet diam.</td>
<td>6 mm</td>
</tr>
<tr>
<td>Sodium bond thickness</td>
<td>0.35 mm</td>
</tr>
<tr>
<td>Cladding thickness</td>
<td>0.3 mm (HT-9 SS)</td>
</tr>
<tr>
<td>Reflector</td>
<td>stainless steel</td>
</tr>
<tr>
<td>Sodium Volume Fraction</td>
<td></td>
</tr>
<tr>
<td>Upper target</td>
<td>86 %</td>
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<tr>
<td>Lower target</td>
<td>37 %</td>
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<tr>
<td>Core</td>
<td>62 %</td>
</tr>
<tr>
<td>Reflector</td>
<td>41 %</td>
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<tr>
<td>TRU initial inventory</td>
<td>1150 kg</td>
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Table 2 Neutronics characteristics in the nitride fuel transmutation system

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
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<tr>
<td>k-effective</td>
<td>0.927</td>
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<tr>
<td>Thermal output</td>
<td>15.7 MW/mA</td>
</tr>
<tr>
<td>TRU disappearance</td>
<td></td>
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<tr>
<td>Np</td>
<td>1.93 kg/mA/year</td>
</tr>
<tr>
<td>Pu</td>
<td>1.00 kg/mA/year</td>
</tr>
<tr>
<td>Am</td>
<td>1.96 kg/mA/year</td>
</tr>
<tr>
<td>Cm</td>
<td>0.29 kg/mA/year</td>
</tr>
<tr>
<td>Average neutron energy</td>
<td>840 keV</td>
</tr>
<tr>
<td>Neutron fraction above 1 MeV</td>
<td>24.6 %</td>
</tr>
<tr>
<td>Average neutron flux</td>
<td>2.67x10^14 (n/cm²/mA)</td>
</tr>
<tr>
<td>Maximum reactivity swing</td>
<td>+ 6.7 % delta-k/k at 210 days</td>
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</table>

Table 3 Comparison of operating conditions for both molten salt system

<table>
<thead>
<tr>
<th>Specification</th>
<th>PbCl₂ type</th>
<th>NaCl type</th>
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</thead>
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<tr>
<td>Target/Fuel/Primary coolant</td>
<td>Chloride molten salt</td>
<td>Fluoride molten salt</td>
</tr>
<tr>
<td>(composition)</td>
<td>70PbCl₂-30(Pu+MA)Cl₃</td>
<td>64NaCl-36(Pu+MA)Cl₃</td>
</tr>
<tr>
<td>Secondary coolant</td>
<td>Fluoride molten salt</td>
<td>92NaBF₅-8NaF</td>
</tr>
<tr>
<td>(composition)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actinide inventory</td>
<td>4932 kg</td>
<td>5435 kg</td>
</tr>
<tr>
<td>k_f</td>
<td>0.92</td>
<td>0.91</td>
</tr>
<tr>
<td>Proton beam</td>
<td>1.5 GeV-28 mA</td>
<td>1.5 GeV-25 mA</td>
</tr>
<tr>
<td>Thermal power</td>
<td>800 MW</td>
<td>800 MW</td>
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<tr>
<td>Transmutation</td>
<td>250 kg/y (5.1 %/y)</td>
<td>250 kg/y (4.6 %/y)</td>
</tr>
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Fig. 1 Schematic illustration of spallation & cascade and neutron transport

Fig. 2 Comparison between the free nucleon-nucleon cross section and in-medium ones parameterized by Li, Machleidt and Zhuo

Fig. 3 Angular distributions of protons emitted with 60 MeV in the Au (p,xp') reaction for 100 MeV proton incidence

The open circle indicates the experimental data. The solid, dashed, dot-dashed and dotted lines represent the total, 1st step, 2nd step and 3rd step contributions of multi scattering in the calculation with ISOBAR respectively.
Fig. 4 Calculated neutron production DDX in thin Al target bombarded by 800 MeV protons are compared with the experimental data. The solid lines stand for the calculated values with statistical error ± σ (a) free space NN cross sections and (b) in-medium cross section. The open symbols show the experimental data by Amian.

Fig. 5 Experimental and calculated yields of $^{59}$Co in $^{60}$Ni samples in the tungsten target-installed lead assembly for 500 MeV proton bombardment.

Fig. 6 Experimental and calculated neutron yield from the stopping length Au target bombarded by 68 MeV protons.

Fig. 7 Experimental fission cross sections for $^{238}$U(p, fission) from 10 MeV to 10 GeV and ones predicted by both cascade codes of NUCLEUS and HETC/KFA2.

Fig. 8 Adjustment of width in the FP yield curve in Nakahara's HEF model to be fitted to experimental data for $^{235}$U(p, fission) reaction with proton energy of 300 MeV.
Fig. 9 Comparison of the mass distribution of products calculated by the modified Nakahara model with experimental data for $^{235}$U(p, fission) reaction with proton energy of 2.9 GeV.

Fig. 10 Experimental fission cross sections from 1 MeV to 10 GeV for $^{235}$U(a, fission) and ones predicted by the NUCLEUS with Baba's data and Ignatyuk formula.

Fig. 11 Cross sections of the $^{197}$Au(p, x)$^7$Be reaction. The marks indicate the experimental results. The solid line stands for the calculated results of HETC/3STEP.

Fig. 12 Cross sections of the $^{197}$Au(p, x)$^{90}$Zr reaction.

Fig. 13 Cross sections of the $^{197}$Au(p, x)$^{190}$Ir reaction.

Fig. 14 Flow chart of the ATRAS code system.
Fig. 15 Calculational model of MA molten salt target/core transmutation system

Fig. 16 Calculated neutron energy spectra in the target/core filled with TRU chloride molten salt and the outer porous region for heat removal

Fig. 17 Power density distribution in the target/core region
Fig. 18 Variation of minor actinides in the nitride fuel core upon burnup

Fig. 19 Comparison of dependences of $k_{\text{eff}}$ on the burnup time without and with the fission product effects.
ANALYSIS OF REACTION RATE DISTRIBUTIONS ON A THICK TUNGSTEN TARGET
BOMBARDED WITH PROTONS OF 0.8 TO 1.2 GEV

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Abstract

In order to estimate the accuracy of the NMTC/JAERI-MCNP-4A code system, an analytical study is performed for the distributions of reaction rates of various activation samples on the surface of a cylindrical thick tungsten target bombarded with 0.8 and 1.2 GeV protons. It is found through the comparison between the experiment and calculation that the NMTC/JAERI-MCNP-4A code system can represent the reaction rates of the activation detectors which are sensitive to the sub-10 MeV neutrons with an accuracy of 10 to 15%. As the threshold energy of the activation detector increases, however, the agreement becomes worse. The calculated results are 50 to 75% in the C/E ratios for the activation detectors sensitive to the neutrons with tens of MeV. The disagreement suggests that the NMTC/JAERI estimates too low the production of neutrons with energies of several tens of MeV in the thick target.
1. Introduction

An accelerator-driven subcritical system is proposed as one of options for the transmutation of long-lived transuranic (TRU) nuclides. Various concepts[1-5] have been proposed for the accelerator-driven transmutation systems. Many of them adopt the design concept that the subcritical core consists of a spallation neutron target surrounded with a blanket including TRU fuels. The target is bombarded with intermediate energy protons of 0.8 to 1.6 GeV with a current of several tens of mA. A heavy metal such as tungsten and lead has been generally selected as target material in design studies because it has high neutron yield of a couple of tens of neutrons per incident proton and can suppress the power density distribution within an acceptable level.

The neutron yield and source neutron energy spectra are important factors to characterize not only the neutronic performance of the subcritical core but for the shielding design. The neutronic calculation of accelerator-based transmutation systems has been carried out with a Monte Carlo simulation code system combining the nucleon-meson transport code such as LAHET[6], HETC-KFA[7] and NMTC/JAERI[8] with the neutron transport code of MORSE[9] and MCNP[10]. Since there are few available nuclear data covering the energy region up to a few GeV yet, it is necessary to enhance the accuracy of the nucleon-meson transport code for detailed neutronic design studies.

It is known that the nucleon-meson transport codes can describe the spallation reaction qualitatively well. However, there still remains some points to be improved in the code. Those aspects were recently confirmed through a code intercomparison conducted by OECD/NEA[11-13]. In JAERI, we have also been estimating the accuracy of the NMTC/JAERI code in comparison with our own experimental data[14-18] in the intermediate energy region of 40 MeV to 3.0 GeV.

As an extension of the study, a reaction rate distribution measurement on a thick tungsten target was carried out using protons of 0.8, 1.0 and 1.2 GeV as a cooperative work between JAERI and Institute of Theoretical and Experimental Physics under the contract of International Science and Technology Center project #157. Analytical study has just started using the NMTC/JAERI-MCNP-4A code system. This paper presents the comparison of the calculated results with experimental ones for the reaction rates of some activation detectors for 0.8 and 1.2 GeV proton incidence.

2. Experiments

The experiment was carried out at the booster beam line of Institute of High Energy Physics in Russia. In the experiment, 0.8, 1.0 and 1.2 GeV protons were injected into a cylindrical tungsten target having the size of 20 cm in diameter and 60 cm in length. The purity and density of the tungsten target was 19.1 g/cc and 99.95%, respectively. Reaction rate distributions on the cylindrical side surface of the target were measured using various kinds of activation detectors. For the 0.8 and 1.2 GeV proton incidence, the high purity foils of $^{27}\text{Al}$, $^{12}\text{C}$, $^{31}\text{P}$, $^{32}\text{S}$, $^{103}\text{Rh}$, $^{115}\text{In}$, $^{197}\text{Au}$ and $^{209}\text{Bi}$ were put on the side surface at the distances of 2, 8, 12, 17, 30 and 55 cm from the beam incident surface. In this study, the reaction rates of the $^{27}\text{Al}$, $^{31}\text{P}$, $^{32}\text{S}$ and $^{209}\text{Bi}$ samples were analyzed. The physical and nuclear characteristics of the activation detectors are summarized in Tables 1 and 2, respectively.

During the irradiation period, proton beam intensity was monitored using an induction current sensor with an accuracy of about 3%. The profile of the beam was the Gaussian distribution with a FWHM of 2.4 cm. The number of protons injected in the target was $1.3 \times 10^{14}$ to $4.3 \times 10^{15}$. The $\gamma$ and $\beta$ rays from the activation detectors were measured using Ge-detectors and polystyrene scintillation counters, respectively. The error in determining the activities of the activation samples were less than 3% at 0.95 confidence level for the $\gamma$-ray measurement, while less than 22% at 0.95 confidence level for the $\beta$-ray measurement.

3. Calculation

The calculation was carried out using the nucleon meson transport code NMTC/JAERI and the continuous energy Monte Carlo code MCNP-4A. The flow of the calculational procedure is shown in Fig. 1. NMTC/JAERI calculated the nuclear reactions on the basis of the intranuclear cascade[19] evaporation[20] model including the high energy fission process[21] and also simulated the particle transport in a thick medium. The parametrized in-medium nucleon-nucleon (NN) cross sections[22] similar to those of Cugnon[23] were employed instead of the free NN ones in the intranuclear cascade calculation. The level density parameter derived by Ignatyuk[24] with the parameters proposed by Mengoni et al.[25] was selected in the evaporation calculation.
the particle transport calculation, the cutoff energy was set to be 5 MeV for charged particles and 20 MeV for neutron. The nucleon-nucleus collision cross sections based on the systematics derived by Pearlstein[26] were employed in the energy region below 1 GeV, while the geometric cross sections were used in the energy region above 1 GeV. The transport of neutrons in the energy region below 20 MeV was calculated with MCNP-4A using a continuous energy cross section library, FSXLIB-J3R2[27], which was processed from the nuclear data file JENDL-3.2[28]. Here, the neutron induced nuclear reactions below 20 MeV are taken into account as the cross section data in FSXLIB-J3R2.

Reaction rate of the activation detector, \( j \), on the cylindrical surface of the tungsten target is obtained as

\[
R_j = \int_{E_h}^{E_{\text{max}}} \sigma_j(E)\phi(E)dE,
\]

where \( \sigma_j(E) \) represents the nuclide production cross section and \( \phi(E) \) stands for the neutron or proton flux. In this calculation, the energy group structure defined in the HILO-86R library[29] was employed up to 400 MeV. In order to cover the higher energy region, supplemental energy groups of 50 MeV interval were added up to 800 MeV and then those of 100 MeV one were given between 800 and 1200 MeV.

As for the nuclide production cross section, the data of JENDL Dosimetry file[30] were used in the MCNP-4A code in the energy region below 20 MeV. In the energy region above 20 MeV, on the other hand, the nuclide production cross sections were calculated with the ALICE-F code[31] at the energy boundary of the energy group structure. The cross section in each energy group was obtained by the weighted average of the calculated values with \( 1/E \) spectrum.

The neutron or proton flux was calculated with the NMTC-JAERI-MCNP-4A code system for the incident protons of 400,000 with the revised data and parameters described above. The profile of proton beam was selected as the gaussian distribution of 2.4 cm in FWHM. In the error estimation, the statistical error of the neutrons counted in each energy group was only taken into account. The ambiguity of the nuclide production cross section was not included. For the C/E ratios, the error was obtained from the experimental error and the statistical error in the calculation based on the propagation theory.

The contribution of leakage protons to the reaction rates was estimated with the nuclide production cross sections calculated with ALICE-F. It was found that the contribution of the proton induced reactions was so small as a few percent of the total reaction rate even in the most sensitive case. In consequence, the calculated results of the neutron induced reaction are compared with the experimental ones in the following discussion.

4. Results and Discussion

The calculated reaction rates are compared with the experimental ones in Figs. 2 to 5. The C/E ratios of the reactions are shown in Fig. 6. The sensitivity of the reaction rates to the neutron energy are shown in Fig. 7 for the activation detectors whose threshold energies are lower than 20 MeV. It is observed in Fig. 2 that the calculated reaction rate distributions agree well with those of experimental ones for all the reactions at incident energy of 0.8 GeV. Judging from the results of C/E ratios, good agreement is obtained between the calculated and experimental reaction rates of \(^{32}\)S(n,p)\(^{32}\)P and \(^{27}\)Al(n,p)\(^{27}\)Mg. A large difference appears between the calculated and experimental results of the \(^{31}\)P(n,p)\(^{31}\)Si reaction in the region from 2 to 12 cm. For the \(^{27}\)Al(n,p)\(^{24}\)Na reaction, the calculated reaction rates are constantly lower than the experimental ones about 25 to 30% at all the positions. The most sensitive neutron energy is between 8 and 25 MeV for this reaction as seen in Fig. 7. Since the ambiguity of the cross section data of the \(^{27}\)Al(n,p)\(^{24}\)Na reaction is not so large as 30% in that energy region, the disagreement indicates that the NMTC/JAERI-MCNP-4A code system estimates the leakage neutron in that energy region as low as about 25 to 30%.

As shown in Fig. 3, the agreement between the calculated and experimental reaction rates is poor for the activation detectors with higher threshold energy. It is observed in Fig. 6 that the calculated results are about 25 to 30% lower than the experimental ones for \(^{209}\)Bi(n,4n)\(^{206}\)Bi, \(^{209}\)Bi(n,5n)\(^{205}\)Bi, and \(^{209}\)Bi(n,7n)\(^{203}\)Bi. As far as the \(^{209}\)Bi(n,6n)\(^{204}\)Bi reaction is concerned, a significant disagreement of a factor of 2 or more is observed between the calculated and experimental results. The sensitivity of the reaction rates to the neutron energy are shown in Fig. 8 for the \(^{209}\)Bi(n,xn) reactions. The \(^{209}\)Bi(n,6n)\(^{204}\)Bi reaction is dominant in the energy range of 45 to 90 MeV. Figures 9 to 12 compare the calculated nuclide production cross sections of the \(^{209}\)Bi(n, xn) reactions with
recent experimental results[32]. It is observed that the calculated nuclide cross sections are in fairly good agreement with the experiment ones and never deviate from those more than a factor of 2 in the sensitive energy region of 45 to 90 MeV. Therefore, the disagreement in the $^{209}$Bi(n, xn) reactions seems to mainly come from the underestimation of the amount of leakage neutron by the NMTC/JAERI calculation.

For the 1.2 GeV proton incidence, it is observed in Figs. 4 and 6 that the calculated results are in good agreement with the experimental ones for the $^{32}$S(n,p)$^{32}$P reaction except at the distance of 55 cm. The fairly good agreement is obtained in the results of the $^{31}$P(n,p)$^{31}$Si reaction although the calculated results are slightly higher than the experimental ones. The calculated reaction rates of the $^{27}$Al(n,p)$^{27}$Mg reaction are lower than the experimental results by 15 to 20% near the front surface, while they agree well with the experimental results between 12 and 30 cm. A significant underestimation of 21 to 34% is observed in the results of the $^{27}$Al(n,p)$^{24}$Na reaction except for the position of 55 cm. This is the same tendency as for the analysis of the 0.8 GeV proton incidence.

In Fig. 4, it should be noted that the experimental reaction rates decrease rapidly from 30 cm to 55 cm. Such phenomena, on the other hand, do not appear in the calculated results. This leads to the significantly large C/E ratios at 55 cm for those reactions although they are not shown in Fig. 6. The neutron production at the deep position seems to be estimated too large by the reason that the mean free path of high energy neutron or proton is overestimated by NMTC/JAERI. This problem is, however, not resolved for the time being.

As far as the $^{209}$Bi(n,xn) reactions are concerned, the NMTC/JAERI calculation again gives lower reaction rates than the experimental ones as seen in Fig. 5. Judging from the C/E ratios shown in Fig. 6, the degree of agreement is almost the same as for the case of the 0.8 GeV proton incidence. The C/E ratios of the $^{209}$Bi(n,4n) $^{206}$Bi reaction are poorer than that for the 0.8 GeV proton incidence. These results indicate that the present NMTC/JAERI code estimates the production of neutrons with energies of several tens of MeV too low even for the 1.2 GeV proton incidence. At the position of 55 cm, the phenomena mentioned above does not appear for the $^{209}$Bi(n,xn) reactions.

The present NMTC/JAERI code has already been employed in the analysis[16] of the neutron spectra of a thick lead target bombarded with the 0.5 and 1.5 GeV protons. It was pointed out in Ref. 16 that the code gave lower neutron yield than the experimental results especially in the energy region between 20 and 80 MeV. The present analysis points out the same feature of NMTC/JAERI as for the previous one. Since various microscopic factors are mixed in the results of integral experiment, the cause of the problem is not attributed only to the treatment of the nuclear reaction process. It is also necessary to investigate the accuracy of the nucleon-nucleus cross sections employed in the energy region above 20 MeV.

At last, a large fluctuation is observed in the C/E ratios of a part of the reaction rates, e.g. $^{209}$Bi(n,4n) $^{206}$Bi and $^{209}$Bi(n,7n)$^{203}$Bi at the distance of 30 cm for the 0.8 GeV proton incidence. Some additional error may be included in those experimental results.

5. Concluding Remarks

The reaction rate distributions of various activation detectors on the cylindrical surface of a tungsten target bombarded with 0.8 and 1.2 GeV protons were analyzed with the NMTC/JAERI-MCNP-4A code system. It was found through the comparison with the experimental results that the code system predicted the reaction rates induced by the sub-10 MeV neutrons with an accuracy of 10 to 15%. Considering that some approximations are included in both the nuclear reaction and particle transport calculation parts of NMTC/JAERI, the accuracy of the code is reasonable.

For the activation detectors sensitive to the neutrons with tens of MeV, however, the agreement between the calculated and experimental results reduced and the C/E ratio was in the level of 50 to 75%. These results suggested that NMTC/JAERI estimated the neutrons in tens of MeV region too low. This feature of NMTC/JAERI was consistent with the conclusion obtained from the other work on neutron spectra measurement and should be improved by further studies from both the microscopic and macroscopic point of view.

References


Table 1. Physical characteristics of activation detectors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (mm)</th>
<th>Density (g/cc)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>20x3</td>
<td>2.20</td>
<td>100</td>
</tr>
<tr>
<td>S</td>
<td>20x3</td>
<td>2.07</td>
<td>95.02</td>
</tr>
<tr>
<td>Al</td>
<td>25x25x1.6</td>
<td>2.699</td>
<td>100</td>
</tr>
<tr>
<td>Bi</td>
<td>20x1</td>
<td>9.747</td>
<td>99.99</td>
</tr>
</tbody>
</table>

Table 2. Nuclear characteristics of activation detectors.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Half-Life</th>
<th>γ-β-ray Energy</th>
<th>Emission Rate</th>
<th>Threshold Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>32S(n,p)32P</td>
<td>14.3 days</td>
<td>694.7 keV (β)</td>
<td>1.0</td>
<td>0.96 MeV</td>
</tr>
<tr>
<td>31P(n,p)31Si</td>
<td>157.3 min</td>
<td>595.7 keV (β)</td>
<td>0.999</td>
<td>0.73 MeV</td>
</tr>
<tr>
<td>27Al(n,p)27Mg</td>
<td>9.45 min</td>
<td>843 keV (γ)</td>
<td>0.7</td>
<td>1.9 MeV</td>
</tr>
<tr>
<td>27Al(n,α)24Na</td>
<td>15.0 hours</td>
<td>1369 keV (γ)</td>
<td>1.0</td>
<td>3.27 MeV</td>
</tr>
<tr>
<td>209Bi(n,4n)206Bi</td>
<td>6.243 days</td>
<td>803.1 keV (γ)</td>
<td>0.989</td>
<td>22.56 MeV</td>
</tr>
<tr>
<td>209Bi(n,5n)205Bi</td>
<td>15.31 days</td>
<td>703.4 keV (γ)</td>
<td>0.311</td>
<td>29.63 MeV</td>
</tr>
<tr>
<td>209Bi(n,6n)204Bi</td>
<td>11.22 hours</td>
<td>374.7 keV (γ)</td>
<td>0.737</td>
<td>37.99 MeV</td>
</tr>
<tr>
<td>209Bi(n,7n)203Bi</td>
<td>11.76 hours</td>
<td>820.2 keV (γ)</td>
<td>0.296</td>
<td>45.31 MeV</td>
</tr>
</tbody>
</table>
Fig. 1. Calculation flow of the NMTC/JAERI-MCNP-4A code system.
Fig. 2 Experimental and calculated reaction rates of S(n,p)$^{32}$P, P(n,p)$^{30}$Si, Al(n,p)$^{27}$Mg and Al(n,α)$^{24}$Na for the 0.8 GeV proton incidence on the thick tungsten target. The open and solid marks indicate the experimental and calculated results of NMTC/JAERI-MCNP-4A, respectively. The lines are for eye-guide.

Fig. 3. Experimental and calculated reaction rates of Bi(n,4n)$^{209}$Bi, Bi(n,5n)$^{208}$Bi, Bi(n,6n)$^{208}$Bi and Bi(n,6n)$^{208}$Bi for the 0.8 GeV proton incidence on the thick tungsten target. The notes to the marks and lines are the same as for Fig. 2.

Fig. 4. Experimental and calculated reaction rates of S(n,p)$^{32}$P, P(n,p)$^{30}$Si, Al(n,p)$^{27}$Mg and Al(n,α)$^{24}$Na for the 1.2 GeV proton incidence on the thick tungsten target. The notes to the marks and lines are the same as for Fig. 2.

Fig. 5. Experimental and calculated reaction rates of Bi(n,4n)$^{209}$Bi, Bi(n,5n)$^{208}$Bi, Bi(n,6n)$^{208}$Bi and Bi(n,6n)$^{208}$Bi for the 1.2 GeV proton incidence on the thick tungsten target. The notes to the marks and lines are the same as for Fig. 2.
Fig. 6. C/E ratios between the calculated and experimental reaction rates of the activation detectors:
(a) $^{32}\text{S}(n, p)^{32}\text{P}$ reaction, (b) $^{31}\text{P}(n, p)^{31}\text{Si}$ reaction, (c) $^{27}\text{Al}(n, p)^{27}\text{Mg}$ reaction, (d) $^{27}\text{Al}(\alpha, n)^{24}\text{Na}$ reaction,
(e) $^{209}\text{Bi}(n, 4n)^{206}\text{Bi}$ reaction, (f) $^{209}\text{Bi}(n, 5n)^{206}\text{Bi}$ reaction, (g) $^{209}\text{Bi}(n, 6n)^{206}\text{Bi}$ reaction, (h) $^{209}\text{Bi}(n, 7n)^{206}\text{Bi}$ reaction. The solid and open marks indicate the results of the 0.8 and 1.2 GeV proton incidence, respectively. The lines are for eyeguide.
Fig. 7. Sensitivity of the reaction rates to the neutron energy for $S(p,p)^{32}P$, $P(n,p)^{31}Si$, $Al(n,p)^{27}Mg$ and $Al(n,\alpha)^{24}Na$ at the distance of 12 cm from front surface.

Fig. 8. Sensitivity of the reaction rates to the neutron energy for $Bi(n,4n)^{209}Bi$, $Bi(n,5n)^{208}Bi$, $Bi(n,6n)^{207}Bi$ and $Bi(n,7n)^{206}Bi$ at the distance of 12 cm from front surface.

Fig. 9. Experimental and calculated cross section of $^{209}Bi(n,4n)^{209}Bi$. The open marks indicate the experimental data[32]. The solid lined represents the calculated results of ALICE-F.

Fig. 10. Experimental and calculated cross section of $^{209}Bi(n,5n)^{209}Bi$. The notes to the marks and lines are the same as for Fig. 9.
Fig. 11. Experimental and calculated cross section of $^{209}\text{Bi}(n,6n)^{204}\text{Bi}$. The notes to the marks and lines are the same as for Fig. 9.

Fig. 12. Experimental and calculated cross section of $^{209}\text{Bi}(n,7n)^{203}\text{Bi}$. The notes to the marks and lines are the same as for Fig. 9.
NUCLEAR MEASUREMENT ACTIVITIES OF PNC
FOR TRANSMUTATION OF FISSION PRODUCTS

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Abstract. This paper reviews the PNC's activity on nuclear data measurements for the study of the transmutation of fission products. Thermal neutron capture cross sections and resonance integrals of $^{137}$Cs, $^{90}$Sr, $^{99}$Tc, and $^{129}$I were measured for the study of the transmutation method using thermal neutrons. High resolution measurements of photonuclear reaction cross section are also in progress for the study of the transmutation method using monocromatic photons.
INTRODUCTION

To investigate the system transmuting fission products (FP), accurate nuclear reaction cross sections are required for FP. What kind of nuclear reactions should be used for FP transmutation depends on how large is the cross section utilized. For the study of the transmutation methods using a high flux fission reactor, a high intensity proton accelerator, and also a high flux fusion reactor, thermal neutron cross sections ($\sigma_0$) and resonance integrals ($I_0$) are especially important. However, these data are old and sometimes reported values differ each other. Therefore, we have measured these cross sections first for $^{137}$Cs, $^{90}$Sr, $^{99}$Tc, and $^{129}$I. As a results, we have found out that the $\sigma_0$ and $I_0$ of $^{90}$Sr and $^{137}$Cs are too small to be transmuted by using thermal neutrons.

As an alternative method transmuting $^{90}$Sr and $^{137}$Cs, we started the study of a monochromatic photon method; a high energy photon can transmute a nucleus via photonuclear reaction. If there is a sharp and intense resonance peak in the photonuclear reaction cross section, the monochromatic photon of the same energy with the resonance can effectively transmute a nucleus. However, very little is known about the precise photon energy dependence of the photonuclear reaction cross section. To obtain the intrinsic resonance peak width and intensity, we proposed a new experimental method.

The results of the experiments and the simulations are briefly described below.

THERMAL NEUTRON CAPTURE CROSS SECTIONS AND RESONANCE INTEGRALS

Accurate data of neutron cross sections are required for the research of the transmutation method of nuclear waste. Data reported, however, show discrepancies between them. Therefore, we designed experiments to obtain more accurate data of neutron cross sections of important long-lived fission products, $^{137}$Cs[1,2], $^{90}$Sr[3], $^{99}$Tc[4] and $^{129}$I[5]. Standardized solution of each radioactive nuclide was irradiated at a thermal neutron reactor of Japan Atomic Energy Research Institute (JAERI) or Rikkyo University. Samples were irradiated with or without a Cd shield. The number of nuclei in the target to be irradiated was determined by an isotope ratio method (IRM) or an efficiency tracing technique (ETT) which meets the nuclear property of each nuclide. The amount of reaction products, $^{138}$Cs, $^{91}$Sr, $^{100}$Tc and $^{130}$I, by neutron capture were obtained by measuring gamma-ray intensities from these nuclei. The reaction rates obtained were analyzed, and thermal neutron cross sections and resonance integrals were deduced. The results were compared with the data reported by others[6-13]. Some data of cross sections were revised from the data by others and some data of resonance integrals were newly obtained[1-5]. Measurements of neutron capture cross section of $^{135}$Cs are in progress.

The targets of $^{137}$Cs and $^{90}$Sr were irradiated at the swimming pool type reactor JRR-4 of JAERI with or without a Cd shield by using a pneumatic tube system. The reactor has a 1/E neutron spectrum in the resonance neutron region. The irradiation position was characterized as having a thermal neutron spectrum of $4 \times 10^{13}$ n/(cm$^2$•s) and an epithermal index in the Westcott's convention[14] of 0.03. After the irradiation, a chemical procedure for purification of the irradiated target was carried out[2,3]. The impurity activities such as $^{24}$Na and $^{38}$Cl were removed from the target. The targets of $^{99}$Tc and $^{129}$I were irradiated in the rotary specimen rack (RSR) of the TRIGA MARK II reactor of Rikkyo University. The
thermal neutron flux of this irradiation position was $5 \times 10^{11}$ $n/(\text{cm}^2 \cdot \text{s})$ and the epithermal index 0.03. The chemical procedure was not applied to the targets of $^{99}\text{Tc}$ and $^{129}\text{I}$ since half-lives of these are short.

![Gamma-ray spectrum obtained from neutron-irradiated and chemically purified $^{137}\text{Cs}$ sample in 10-min measurement](image)

**Fig. 1** Gamma-ray spectrum obtained from neutron-irradiated and chemically purified $^{137}\text{Cs}$ sample in 10-min measurement

| Table I. Results of the neutron capture cross section and resonance integrals |
|---------------------------------|-----------------|-----------------|-----------------|
| Nuclides | present results(b) | previous data(b) | Authors |
| $^{137}\text{Cs}$ | $\sigma_0 = 0.25 \pm 0.02$[2] | $\sigma_0 = 0.110 \pm 0.033$ | Stupegia[6] |
| | $I_0 = 0.36 \pm 0.07$[2] | | |
| $^{90}\text{Sr}$ | $\sigma_0 = 0.0153 \pm 0.0013$[3] | $\sigma_0 = 0.0140 \pm 0.0024$ | McVey et al.[7] |
| | $-0.0042$ | $0.8 \pm 0.5$ | Zeisel[8] |
| | $I_0 \leq 0.16$[3] | | |
| $^{99}\text{Tc}$ | $\sigma_0 = 22.9 \pm 1.3$[2] | $\sigma_0 = 20 \pm 2$ | Lucas[9] |
| | $I_0 = 398 \pm 38$[2] | $I_0' = 186 \pm 16$ | Lucas[9] |
| $^{129}\text{I}$ | $\sigma_0^{2+} = 17.4 \pm 1.7$[2] | $\sigma_0 = 26.7 \pm 2.0$ | Roy[10] |
| | $I_0^{2+} = 17.8 \pm 2.0$[2] | | Block[12] |
| | $\sigma_0^{5+} = 12.6 \pm 2.2$[2] | | Roy[10] |
| | $I_0^{5+} = 15.5 \pm 2.9$[2] | | |
| | $\sigma_0$ (total) = $30.0 \pm 1.4$ | | |
| | $I_0$ (total) = $33.2 \pm 1.5$ | | |

The radioactivity of the irradiated targets were measured by using a high purity Ge-detector system of 90% relative efficiency combined with a fast data acquisition system. For example, weak gamma-rays from $^{138}\text{Cs}$ were measured together with strong gamma-
rays from $^{137}$Cs simultaneously (see Fig. 1). Details of the experiments and the analysis were published in ref. [1-5]. Results obtained are summarized in Table I.

The results show that the cross section of $^{137}$Cs obtained is about twice of the previous one[6] and an experimental data of the resonance integral was newly obtained. Our results for $^{137}$Cs are more reliable than that by Stupegia[6], since our method (IRM) could remove various sources of uncertainty as mentioned in ref. [1-3]. The cross section obtained for $^{90}$Sr is in agreement with the value by McVey et al.[7] but not with that by Zeisel[8]. The resonance integral of $^{90}$Sr was also obtained. The cross section of $^{90}$Tc is almost equal to the previous data[9], and an experimental resonance integral is about twice of the value reported previously. The cross sections of $^{129}$I were obtained for formation of the ground state and the isomeric state of $^{130}$I separately. Previous data[10-13] show only a cross section of formation of the ground states. The resonance integrals were also obtained for formation of two states $^{130}$I separately.

**FINE STRUCTURE OF PHOTONUCLEAR REACTION CROSS SECTION**

Fine structure of photonuclear reaction cross section in the giant resonance (GR) region can provide important information about the excitation mechanism of the GR and also for the study of the nuclear transmutation process using monochromatic photons[15]. In particular, the intrinsic width of fine peak in the GR is important because it determines the peak value of the cross section. However, very little is known about the width at present. The energy resolution for the cross section measurement using tagged photons[16,17] or monochromatic photons[18] was typically 100-500keV. Therefore, peak widths observed for some nuclei were almost determined by the experimental resolution. To obtain the intrinsic peak width, we proposed an experimental method that measures transmitted photons using a high resolution and high energy photon spectrometer (HHS)[19].

Figure 2 shows the conceptual setup of the experiment. The incident white photons should cover the energy range of interest. The photons are obtained by electron induced bremsstrahlung or more effectively by laser Compton scattering[20,21]. The transmitted photons from a thick target is measured by the HHS composed of two large germanium (Ge) detectors surrounded by a Bi$_3$Ge$_3$O$_6$ (BGO) anti-coincidence spectrometer. The energy resolution of the experiment in the GR region should be improved to 10-20keV because the Ge detector has an energy resolution of about 0.1%[22] for high energy photons. The design of the HHS is shown in Fig.3. To obtain the large photopeak efficiency for high energy photons, two large N-type Ge detectors (relative efficiency of each crystal was 90% at 1.33MeV) were arranged like twins along a beam axis. To improve their peak/background (=total-peak) ratio, the twins were surrounded by thick BGO crystals that were used as an anti-coincidence spectrometer. Figure 4 shows the response function of the HHS for a collimated 15MeV photon beam of 2cmΦ. This was the result simulated by a Monte Carlo electron-gamma-shower code EGS4[23]. The response functions of the single Ge detector and the twin Ge detectors are also shown in the figure. The photopeak counts in the three spectra were normalized to be the same number, and the spectra were broaden with the energy resolution ($\Delta E\gamma/E\gamma$) $10^3$ of the Ge detector.

To simulate the photonuclear cross section measurement with the HHS, the flux distribution of transmitted photons from a thick water target was calculated as an example. The size of the target was 5cm in diameter and 60cm in length. The density of the water
Target
High resolution and
2ph energy photon
spectrometer

Incident white photons
Transmitted photons

Fig. 2 Schematic setup of high resolution measurement of photonuclear cross section using HHS

Fig. 3 Cross section of the HHS

Fig. 4 Response functions of three type spectrometer for 15 MeV photon

Fig. 5 (a) Assumed photonuclear absorption cross section of $^{14}O$, (b) Incident white photon flux (upper) and transmitted photon flux (lower), and (c) Transmission photon spectrum observed by a single germanium detector (lower) and the HHS (upper)
target was assumed to be $1.0g/cm^3$. The simulation code EGS4 was modified\cite{24} to include the photonuclear cross section of $^{16}O$ as a part of photon-material interaction. Two narrow photon absorption cross section peaks of $^{16}O$ were artificially included in the code to simulate narrow dips in the transmission spectrum. The artificial cross section of the Breit-Wigner shape is shown in Fig. 5(a). The width and height of the peak at 14.9MeV are 10keV and 100mb, and those at 15.0MeV were 50keV and 30mb, respectively. An incident photon flux was assumed to be white with an energy range of 14.8 to 15.1MeV. Figure 5(b) shows the incident white photon flux and the transmitted photon flux. Two dips can be clearly seen in the transmitted photon flux.

Figure 5(c) shows the transmission spectra observed by the single Ge detector(lower spectrum) and the HHS (upper spectrum). These were obtained by folding the transmitted photon flux(Fig. 5(b)) using the response function of each detector. The dips are not clear in the spectrum observed by the single Ge detector because of its low peak/background ratio. On the other hand, the dips are clearly shown in the spectrum observed by the HHS. The FWHM of the dip observed at 14.9MeV is about 20keV. Therefore, widths of fine peaks in the GR region can be measured with the energy resolution of $10^{-3}$ by observing transmitted photons using the HHS, and correcting the detector energy resolution. Details of the simulation were described in ref. \cite{19}.

Fine structure of the photonuclear reaction in the GR energy region was shown to be observable using the specially designed high resolution and high energy photon spectrometer, HHS with an energy resolution of 10-20keV. The measurements using the HHS are in progress to supply data for nuclear transmutation studies using monochromatic photons.

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References

RECENT MEASUREMENTS OF FISSION NEUTRON YIELD DATA OF MINOR ACTINIDES

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ABSTRACT

An experimental study of the fission neutron yield data for Np-237, Am-241, and Am-243 is under way for both prompt and delayed neutrons. Preliminary results of this experimental program are discussed in this paper.

The fission neutron yields, \( \nu \), of Np-237 and Am-243, as well as U-235, were measured for 144 keV silicon-filtered neutron beam at University of Missouri Research Reactor. The measured values were as follows:

\[
\begin{align*}
\nu : & \quad \text{Np-237} : 3.13 \pm 0.12 \quad \text{Am-243} : 4.00 \pm 0.35 \quad \text{U-235} : 2.54 \pm 0.06.
\end{align*}
\]

These values for minor actinides were about 20% larger than those of ENDF/B-VI and JENDL-3.2, while that for U-235 was 4% larger than the data files.

The delayed neutron data for Np-237, Am-241, and Am-243 were measured using fast pneumatic transfer system in Texas A&M University TRIGA reactor. The measured delayed neutron yields, \( \nu_d \) per 100 fissions in the thermal neutron spectrum were as follows:

\[
\begin{align*}
\nu_d \text{ (per 100 fissions)} : & \quad \text{Np-237} : 1.29 \pm 0.04 \quad \text{Am-241} : 0.49 \pm 0.02 \quad \text{Am-243} : 0.84 \pm 0.04.
\end{align*}
\]

The ratios of the present values to those of the evaluated data files were 1.19, 1.14, and 1.05 for ENDF/B-VI, and 1.06, 1.09, and 0.88 for JENDL-3.2.

The 6-group data for the delayed neutron, \( \lambda \), and \( \beta \), were also obtained from the experiment and compared with ENDF/B-VI. The measured decay constant, \( \lambda \), agreed well with the data file. Large discrepancies were, however, found in the group fraction, \( \beta \), especially for Am-243.

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1. INTRODUCTION

Fission neutron yield data of Np-237, Am-241, and Am-243 play important roles in a minor actinide (MA) burning reactor in which MA's are the major part of the nuclear fuel. The reliability of these data, however, seems insufficient for the design and the safety analysis of such a reactor. At present, new measurements\(^{1,2}\) are under way for both prompt and delayed neutron yield data of these nuclei. Preliminary results of this experimental program are to be discussed in this paper.

The accuracy of fission neutron yield, \(\nu\), greatly influences the criticality of the nuclear reactor. For Am isotopes, however, there was no experimental work on \(\nu\), while some experimental values are available for Np-237. In the present work, the neutron yields of Np-237 and Am-243 were measured for 144 keV silicon-filtered neutron beam at University of Missouri Research Reactor. The measurement for Am-241 was also attempted, but the reliable result can not be obtained because of the strong \(\gamma\) -ray emission from the sample.

The accuracy of delayed neutron yield and 6-group data, \(\nu_d\), \(\rho\), and \(\lambda\), greatly influences the reactor dynamics. For Np-237 and Am-241, Waldo et al.\(^{3}\) and Benedetti et al.\(^{4}\) measured these data in thermal and fast neutron spectra, respectively, while there was no experiment for Am-243. Waldo et al. tried to make measurements for Am-243, but the Am-241 impurity of their sample prevented them. In the present work, the delayed neutron data for Np-237, Am-241, and Am-243 were measured by using fast pneumatic transfer system in Texas A&M University TRIGA reactor. Measurement in the fast neutron spectrum is in progress and is to be reported elsewhere.\(^{5}\)

In the next section, the experimental methods are described for both the fission neutron yield measurement and the delayed neutron measurement. Then, the measured values are compared with those form the evaluated nuclear data files, ENDF/B-VI and JENDL-3.2.

2. EXPERIMENT

2.1 Fission neutron yield measurements

Experimental technique adopted here was newly developed to overcome the restriction of the amount of actinide samples. Proton recoil counters were used as the neutron detector, which can discriminate high energy fission neutrons from numerous scattered ones of 144 keV. The absolute fission rate was estimated by solid state track detectors. Both the proton recoil detectors and the track detectors were calibrated by Cf-252 fission source. The experimental arrangement is shown in Fig. 1. Details of the measurement were as follows.

Samples

Two kinds of samples were used in the measurement. One is the neutron emission sample for the fission neutron measurement, which had the dimension of \(12.7\text{mm} \times 1.02\text{mm}\) and \(100 \sim 300\) mg of the oxide of the target actinide covered by titanium metal of 0.05mm\(^2\). The other is the fission rate sample, where the actinide was electroplated on platinum backing disk and covered by a gold or nickel layer. The samples contain the actinide of 0.08 \sim 2.3 mg.

The isotopic purity of both samples were 97.7 % for U-235, 99.999 % for Np-237 and 99.997 % for Am-243, respectively.
In addition to above actinide samples, blank samples and Cf-252 samples were also prepared for the background subtraction and the detection efficiency calibration, respectively.

**Fission neutron measurement**
A silicon-filtered beam from Missouri University Research Reactor was used as the neutron source. To eliminate the affect of thermal neutrons, a cadmium sheet of 2 mm was put between the beam outlet and the sample. The neutron beam was collimated to 16 mm.

Fission neutrons from the neutron emission sample were counted by three proton recoil detectors. To cut the 144 keV neutrons scattered by the sample, the discrimination level of the recoiled proton energy was set to 200 keV for U-235 and Np-237 and to 440 keV for Am-243. The higher discrimination level for Am-243 aimed to prevent signals due to the pile up of the strong γ-ray from the sample affecting the background counts. For the same reason, a lead sheet was placed between the sample and the detectors for the measurement of Am-243.

The detection efficiency was calibrated by using Cf-252 neutron source under the same experimental condition as the measurement of the actinide samples.

To obtain the number of the fission neutrons from the actinide, the background subtraction and the correction for the scattering of the actinide itself were done by using the count rate from the blank sample.

**Fission rate measurement**
A solid state track detector was attached to the fission rate sample and irradiated in the silicon-filtered beam simultaneously with the fission neutron measurement. The fission reaction was detected by the tracks of the fission fragments which penetrate the gold or nickel cover of the sample and go into the detector.

To obtain clear image of tracks, various detector material and various chemical etching processes were examined, and consequently, polycarbonate was chosen as the material and the optimum process was determined.

The detection efficiency was calibrated by Cf-252 sample covered by gold or nickel which has the same thickness as the fission rate sample.

**Determination of ν**
The ratio of the neutron emission rate to the fission rate, which were both calibrated to the absolute values, yields the number of the neutron emission per fission, ν.

2.2 Delayed neutron measurement
Experimental technique adopted here was similar to Keepin's. The actinide samples used in the delayed neutron measurements were identical to those for the measurement of ν. The isotopic purity of Am-241 was essentially 100%.

**Delayed neutron measurement**
A TRIGA-type research reactor at the Texas A&M University Nuclear Science Center was used as the irradiation field. An existing

Fig.2 Sample receiver and detectors for delayed neutron measurement
pneumatic transfer system was revised to get enough speed to measure the delayed neutrons belonging to 1 ~ 5th. precursor groups ($T_{1/2} = 0.7 ~ 55\text{sec}$).

Three BF$_3$ proportional counters were used for the detection of the delayed neutron emission. The actinide sample contained in a polyethylene vial was irradiated at the core receiver in the reactor and then transmitted to the sample receiver outside the reactor by the pneumatic system. The sample receiver and the BF$_3$ counters were surrounded by paraffin as shown in Fig. 2 to enhance the neutron detection efficiency. Three irradiation times were chosen to put emphasis on different precursor groups.

The efficiency of the detection system was calibrated by the delayed neutron emission from irradiated U-235 samples whose fission properties were considered to be well known.

**Fission rate measurement**

After the irradiation of each sample, $\gamma$ -ray spectroscopy was performed to determine the absolute fission rate. The activities of Ba-140, La-140, Ru-103, I-131, and Mo-99 were measured. The detection efficiency of gamma-rays was calibrated by Eu-152 source depending on the energy of $\gamma$ -ray. The cumulative fission yields quoted from ENDF/B-VI were used to convert the activities of FP's to absolute fission rates.

**Determination of $\beta, \lambda, \nu$ and $\nu_d$**

To obtain the relative fraction and the decay constant of each precursor group, a least squares analysis was performed for the measured time attenuation curves of the delayed neutrons. Moreover, by combining the absolute neutron emission rate and the absolute fission rate, the number of delayed neutrons per fission was deduced. Calculated data was used for the 6th. group based upon Tuttle's empirical expression and group-wise parameters given by Benedetti.

3. DISCUSSION

3.1 Fission neutron yield

The experimental results of fission neutron yields are shown in Table 1 together with those of the evaluated nuclear data files.

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>ENDF/B-VI</th>
<th>JENDL-3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-235</td>
<td>2.54 ±0.06</td>
<td>2.44</td>
<td>2.45</td>
</tr>
<tr>
<td>Np-237</td>
<td>3.13 ±0.12</td>
<td>2.66</td>
<td>2.56</td>
</tr>
<tr>
<td>Am-243</td>
<td>4.00 ±0.35</td>
<td>3.30</td>
<td>3.23</td>
</tr>
</tbody>
</table>

It can be observed that present work gives larger values than both files; 4% for U-235, about 20% for Np-237 and Am-243. The relatively good agreement for U-235 indicates the validity of the present experimental method. For Np-237, however, large discrepancy was observed, though better agreement had been expected since the nuclear data files were evaluated on the basis of previous experimental work. Therefore, some experimental bias may exist in the present measurement.

On the other hand, there has been no experimental data available for Am-243. Hence, if the bias in Np-237 is settled, the present measurement will become invaluable in the evaluation of the minor actinide nuclear data.

3.2 Delayed neutron data

The experimental results of absolute delayed neutron yields are compared with those of the previous measurements and the evaluated nuclear data files in Table 2.
Table 2 Results of delayed neutron yields $\nu_d$ (per 100 fission)

<table>
<thead>
<tr>
<th>Energy range</th>
<th>Present</th>
<th>Waldo et al.</th>
<th>Benedetti et al.</th>
<th>ENDF/B-VI</th>
<th>JENDL-3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np-237</td>
<td></td>
<td>Thermal</td>
<td>Thermal - 4MeV</td>
<td>Thermal - 6MeV</td>
<td></td>
</tr>
<tr>
<td>Thermal</td>
<td>1.29 ± 0.04</td>
<td>1.07 ± 0.10</td>
<td>1.22 ± 0.03</td>
<td>1.08</td>
<td>1.22</td>
</tr>
<tr>
<td>Am-241</td>
<td>0.49 ± 0.02</td>
<td>0.51 ± 0.07</td>
<td>0.39 ± 0.02</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td>Am-243</td>
<td>0.84 ± 0.04</td>
<td>—</td>
<td>—</td>
<td>0.80</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Since $\nu_d$ is considered to be constant below several MeV, the experimental values and those of the data files in Table 2 are comparable in spite of the different energy range.

For Np-237, the present work shows better agreement with JENDL-3.2 and Benedetti than ENDF/B-VI and Waldo. For Am-241, however, the present work agrees with Waldo's measurement very well. On the other hand, for Am-243, there has been no experimental work, and JENDL-3.2 gives 13% larger value than the present work, while ENDF/B-VI agrees with the present value within the experimental error.

Table 3 Results of 6-group data for delayed neutron from Np-237

<table>
<thead>
<tr>
<th>Group</th>
<th>Decay constant $\lambda_i$ (s$^{-1}$)</th>
<th>Relative yields $\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td>ENDF/B-VI</td>
</tr>
<tr>
<td>1</td>
<td>0.0129 ± 0.0006</td>
<td>0.0133</td>
</tr>
<tr>
<td>2</td>
<td>0.0324 ± 0.0010</td>
<td>0.0316</td>
</tr>
<tr>
<td>3</td>
<td>0.1048 ± 0.0019</td>
<td>0.1168</td>
</tr>
<tr>
<td>4</td>
<td>0.341 ± 0.013</td>
<td>0.301</td>
</tr>
<tr>
<td>5</td>
<td>0.85 ± 0.06</td>
<td>0.867</td>
</tr>
<tr>
<td>6</td>
<td>2.76</td>
<td>0.021&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

a) calculated

Table 4 Results of 6-group data for delayed neutron from Am-241

<table>
<thead>
<tr>
<th>Group</th>
<th>Decay constant $\lambda_i$ (s$^{-1}$)</th>
<th>Relative yields $\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td>ENDF/B-VI</td>
</tr>
<tr>
<td>1</td>
<td>0.0122 ± 0.0005</td>
<td>0.0133</td>
</tr>
<tr>
<td>2</td>
<td>0.0318 ± 0.0016</td>
<td>0.0308</td>
</tr>
<tr>
<td>3</td>
<td>0.111 ± 0.007</td>
<td>0.1131</td>
</tr>
<tr>
<td>4</td>
<td>0.300 ± 0.017</td>
<td>0.287</td>
</tr>
<tr>
<td>5</td>
<td>0.890 ± 0.023</td>
<td>0.865</td>
</tr>
<tr>
<td>6</td>
<td>2.64</td>
<td>0.018&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

a) calculated
Table 5 Results of 6-group data for delayed neutron from Am-243

<table>
<thead>
<tr>
<th>Group</th>
<th>Decay constant $\lambda_1$ ($s^{-1}$)</th>
<th>Relative yields $\beta_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work</td>
<td>ENDF/B-VI</td>
</tr>
<tr>
<td>1</td>
<td>0.0131 ±0.0002</td>
<td>0.0135</td>
</tr>
<tr>
<td>2</td>
<td>0.0311 ±0.0009</td>
<td>0.0298</td>
</tr>
<tr>
<td>3</td>
<td>0.107 ±0.007</td>
<td>0.1138</td>
</tr>
<tr>
<td>4</td>
<td>0.324 ±0.021</td>
<td>0.299</td>
</tr>
<tr>
<td>5</td>
<td>0.914 ±0.031</td>
<td>0.882</td>
</tr>
<tr>
<td>6</td>
<td>0.029 a)</td>
<td>2.81</td>
</tr>
</tbody>
</table>

a) calculated

4. CONCLUSION

Preliminary results of the experimental program on fission neutron data for minor actinides are reported. The fission neutron yields, $v$, of Np-237 and Am-243 were measured using a 144 keV silicon-filtered neutron beam at University of Missouri Research Reactor. The measured values were about 20% larger than ENDF/B-VI and JENDL-3.2. The result for U-235 by the same experimental method shows 4% larger value than the data files.

The delayed neutron data for Np-237, Am-241, and Am-243 were measured by using a fast pneumatic transfer system at the Texas A&M University TRIGA reactor. The measured delayed neutron yields per 100 fissions in the thermal neutron spectrum were 1.29 ±0.04, 0.49 ±0.02, and 0.84 ±0.04. The ratios of the present values to those of the evaluated data files were 1.19, 1.14, and 1.05 for ENDF/B-VI, and 1.06, 1.09, and 0.88 for JENDL-3.2.

The 6-group constants, $\beta_1$, and $\lambda_1$, were also deduced from the experiment. The measured decay constant, $\lambda_1$, agreed well with the data file. Large discrepancies were, however, found in the group fraction $\beta_1$, especially for Am-243.

REFERENCES

Properties of neptunium-plutonium mixed nitride solid solutions were investigated. The solid solutions covering the whole range of composition were prepared by heating the mixtures of NpN and PuN in nitrogen-hydrogen mixed gas stream at 2023 K. Formation of high-purity solid solution with a single phase was confirmed by X-ray diffraction and chemical analyses and composition dependence of the lattice parameters was examined. Vaporization behavior over the solid solutions was investigated by Knudsen-mass spectrometry and temperature dependence of the partial pressures of Np(g) and Pu(g) was examined. Furthermore, the thermal conductivities were determined from the thermal diffusivities measured and specific heat capacities estimated. The thermal conductivities of the solid solutions lay between those of NpN and PuN.
1. Introduction

Feasibility studies for transmuting minor actinides in fast reactors have been conducted in many countries from the viewpoint of a better management of the high level nuclear waste [1,2]. One of the incentives to using nitride fuel for transmutation is the probable formation of solid solution among actinide mononitrides with an extensive composition besides the superior thermal and neutronic properties. At present, however, the information on the mononitride solid solutions has been quite scarce except that of uranium-plutonium mixed nitride which has been developed as an advanced fuel for fast reactors. So it is significant to prepare the mononitride solid solutions containing minor actinides and determine their properties for the application of nitride fuel to transmutation. This report concerns the preparation and a few properties of neptunium-plutonium mixed nitride solid solutions including their lattice parameters, vaporization behavior and thermal conductivities estimated from thermal diffusivities.

2. Sample preparation

Neptunium-plutonium mixed nitride solid solutions (Np,Pu)N were prepared by heating the mixtures of NpN and PuN synthesized by carbothermic reduction from their oxides. Powders of NpO₂, PuO₂ and graphite were obtained from Harwell Laboratory, British Nuclear Fuels Ltd. and Graphitwerk Kropmlühl GmbH, respectively, and their characteristics were described in earlier papers [3,4]. The mixing molar ratios of graphite to the dioxides, C/NpO₂ and C/PuO₂, for carbothermic reduction were chosen at 2.2. The reduction was carried out at 1823 K in N₂ gas stream for 43 ks, followed by decarbonization at 1723 K in N₂-8%H₂ mixed gas stream for 86 ks. The products, NpN and PuN, were mixed at the molar ratios PuN/(NpN+PuN) of 0, 0.25, 0.50, 0.75 and 1.0 for the measurement of lattice parameter and vapor pressures and at 0.33 and 0.67 for the thermal diffusivity measurement. The mixed powders were pressed into green pellets under a pressure of ~300 MPa and heated again for the formation of solid solution at 2023 K in N₂-8%H₂ mixed gas stream for 90-180 ks. Then the pellets were subjected to X-ray diffraction and chemical analyses for characterizing the products.

The typical results of characterization were summarized in Table 1. According to the X-ray diffraction pattern, the formation of solid solution (Np,Pu)N with a single phase of fcc was confirmed for all the composition investigated. Namely, no other phases than NaCl-type mononitride were identified and the separation of the diffraction lines into Kα₁ and Kα₂ at high angles was fairly good. The results of chemical analysis indicated that both the oxygen and carbon contents in the samples, which are considered as principal impurities in nitride fuel prepared by carbothermic reduction, were lower than 0.05 wt.% On the other hand, the nitrogen contents almost corresponded to the stoichiometric composition. The manner of the characterization mentioned above was described in detail elsewhere [5]. Although the chemical analyses of neptunium and plutonium were not conducted in this study, it was considered that the nominal composition kept unchanged since no significant loss of actinides by vaporization was observed during the sample preparation stage. In this study, the preparation of samples was carried out in the gloveboxes with high-purity argon gas atmosphere.

3. Results and discussion

3.1 Lattice parameter

Five X-ray diffraction lines of (600/442), (531), (440), (511/333) and (422) were used to calculate the lattice parameter of (Np,Pu)N solid solutions. The composition dependence of the lattice parameter was shown in Fig. 1. Lattice parameters of NpN and PuN were 0.4897±0.00003 and 0.49501±0.00002 nm, respectively, which agreed well with the reported values [6,7]. The lattice parameter increased with PuN content in the solid solution as was anticipated. However, the change in the lattice parameter deviated positively from the Vegard's law between NpN and PuN as shown in the figure. It is well known that the dissolution of carbon and oxygen in actinide mononitride lattice results in the increase of the lattice parameter [8,9]. However, the present carbon and oxygen contents, lower than
500 ppm, were considered to be too low to influence the lattice parameter significantly. It was also considered from the experimental results that the incompleteness of the formation of solid solution or the heterogeneity of the sample could not affect the lattice parameter measured. On the other hand, the self irradiation damage had been almost recovered since the X-ray diffraction analysis was conducted on the next day of the heat treatment at 2023 K. From the speculation mentioned above, we now consider that the deviation of the lattice parameter from the Vegard's law has some relation with the bonding characteristics of (Np,Pu)N solid solutions.

Furthermore, we have observed the similar results for (U,Pu)N solid solutions, where the lattice parameter deviated positively from the Vegard's law especially in PuN rich region as shown in Fig. 2 [7,10]. The present lattice parameter of NpN just corresponded to halfway between those of UN and PuN. As the atomic number of the elements in the compound increases, the total number of electrons increases with the change of composition. In actinide mononitrides including their solid solutions, part of the electrons outside Rn shell are thought to be localized to the atom, and part of them itinerant and participating in bonding. Since the change in the lattice parameter reflects the nature of electron population in the solid solutions, we consider that the present and previous results may be related with occupancy states in the unfilled 5f-6d hybridized band near the Fermi level.

3.2 Vaporization behavior

Vaporization behavior of (Np,Pu)N solid solutions was investigated by use of Knudsen-effusion mass spectrometry with a tungsten cell having an orifice of 1 mm in diameter. Three kind of solid solutions, (Np0.75Pu0.25)N, (Np0.5Pu0.5)N and (Np0.25Pu0.75)N, were subjected to the measurements. The apparatus used was described in detail elsewhere [11] and an ionization potential was chosen at 10 eV throughout this study. The actinide bearing species observed in gaseous phase were Np(g), NpO(g), Pu(g) and PuO(g). Among them the pressures of NpO(g) and PuO(g) were much smaller than those of Np(g) and Pu(g) except in the initial heating stage. The absolute pressure was calculated from the ion intensity by use of a modified integral method.

Temperature dependence of the pressures of Np(g) and Pu(g) over the solid solutions was shown in Fig. 3. The pressures of Np(g) over the solid solutions showed the similar temperature dependence with that over Np(l) as in the case of NpN [12], which strongly suggested the precipitation of liquid neptunium during the measurements. On the other hand, temperature dependence of Pu(g) over the solid solutions was rather complicated. At temperatures higher than 1773 K, the slope of the logarithmic pressures of Pu(g) versus the reciprocal temperature was similar with the pressure over PuN [13] and there found a composition dependence of the solid solutions. At temperatures lower than 1473 K, however, the temperature dependence approached that over Pu(l) and the composition dependence became indefinite. At intermediate temperatures between 1443 and 1773 K, the transition stage was observed as shown in the figure. It was considered that the pressures of Pu(g) observed at high temperatures reflected the vapor pressure of Pu(g) over (Np,Pu)N being influenced by the Pu/(Np+Pu) ratio in solid phase, while the pressures of Pu(g) observed at lower temperatures the pressure over Pu(l) precipitated during the measurement.

It is well known that UN(s) vaporizes incongruently precipitating liquid uranium on account of the lower pressure of U(g), while PuN(s) vaporizes congruently into Pu(g)+0.5N2(g) [14,15]. Recent study on the vaporization behavior of NpN(s) revealed that the precipitation of liquid neptunium occurred during the measurement [12]. Although further study is needed hereafter, the vaporization behavior of (Np,Pu)N solid solutions seems to have both characteristics of those of NpN and PuN. Qualitative and quantitative thermodynamic analyses are under way in this respect.

3.3 Thermal conductivity

Thermal diffusivities of two kind of solid solutions, (Np0.67Pu0.33)N and (Np0.33Pu0.67)N, were measured from 750 to 1630 K by laser flash method. The apparatus used was described in detail elsewhere [16]. The samples for the measurement, discs of ~8 mm in diameter and ~1.4 mm thickness, were obtained by slicing the sintered solid solution pellets by a diamond wheel cutter. The results of the thermal diffusivity measurements are shown in Fig. 4. It was seen that the thermal diffusivities gradually increased with temperature and decreased with PuN content in the solid solution over the temperature range investigated, although the exact comparison was difficult on account of...
the difference of density between the two samples. The origin of the difference in sintered density is not clear for the moment.

Thermal conductivity could be calculated by the product of thermal diffusivity, specific heat capacity and bulk density of the sample. The specific heat capacities of the (Np,Pu)N solid solutions were unknown unfortunately, and they were evaluated by the Kopp's law as a first approximation. The specific heat capacity of PuN was quoted from the report of Spear and Leitnaker [17] and the value for NpN was estimated from an empirical equation by the authors [18]. The thermal conductivities of two kind of the solid solutions obtained are shown in Fig. 5, in which they are corrected for porosity to the theoretical density by Maxwell-Eucken equation and the results for NpN [18] and PuN [19] are included for comparison.

It was seen from the figure that the thermal conductivities of the present solid solutions lay between those of NpN and PuN and showed almost the similar temperature dependence with them. The thermal conductivities also decreased with PuN content in the solid solutions, especially in NpN rich region. However, we must bear in mind that the results mentioned above have several uncertainties derived from the estimation of specific heat capacity and the correction for porosity besides the experimental error itself. The measurement of the specific heat capacity is planned in near future by use of differential scanning calorimeter.

4. Summary

The solid solutions of neptunium-plutonium mixed nitride (Np,Pu)N were prepared and some properties were examined in this study. The results are summarized as follows.
(1) Formation of the (Np,Pu)N solid solutions with a single phase of fcc was confirmed over the whole range of composition.
(2) Change in the lattice parameter of the solid solutions deviated positively from the Vegard's law as was reported in the case of (U,Pu)N solid solutions.
(3) Vapor pressures of Np(g) over the solid solutions suggested the precipitation of liquid neptunium during the measurements, while that of Pu(g) showed a rather complicated temperature dependence.
(4) Thermal conductivities of the solid solution, which were determined from thermal diffusivities measured and specific heat capacities estimated, lay between those of NpN and PuN and decreased with PuN over the temperature range investigated.

Acknowledgement

The authors wish to express their thanks to Drs. M. Hoshi and T. Muromura for the interest in this study.

References

Table 1  Typical characteristics of the samples after the heat treatment in N\textsubscript{2}-8\%H\textsubscript{2} mixed gas stream

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat-treatment period (ks)</td>
<td>43</td>
<td>43</td>
<td>86</td>
<td>43</td>
<td>86</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>Phases</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>N content (wt.%)</td>
<td>5.65</td>
<td>n.d.</td>
<td>5.64</td>
<td>n.d.</td>
<td>5.60</td>
<td>n.d.</td>
<td>5.57</td>
</tr>
<tr>
<td>O content (wt.%)</td>
<td>0.03</td>
<td>n.d.</td>
<td>0.04</td>
<td>n.d.</td>
<td>0.04</td>
<td>n.d.</td>
<td>0.04</td>
</tr>
<tr>
<td>C content (wt.%)</td>
<td>0.05</td>
<td>n.d.</td>
<td>0.02</td>
<td>n.d.</td>
<td>0.03</td>
<td>n.d.</td>
<td>0.03</td>
</tr>
</tbody>
</table>

n.d. = Not determined
Fig. 1 Lattice parameter of (Np,Pu)N solid solutions
Fig. 2 Lattice parameter of (U,Pu)N solid solutions
Fig. 3  Vaporization behavior of (Np,Pu)N
Fig. 4 Thermal diffusivity of (Np,Pu)N solid solutions
Fig. 5 Thermal conductivity of (Np, Pu)N solid solutions corrected to 100% T.D. compared with those of NpN [18] and PuN [19].
NITRIDE-FORMING BEHAVIOR IN LIQUID CADMIUM-URANIUM-LANTHANIDES ALLOYS

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Abstract

The nitride formation reaction of liquid 2wt% U-1wt% Gd-1wt% Ce-Cd alloys has been studied over the temperature range of 773~873 K using graphite and molybdenum crucibles. The Cd-U alloys were contacted with nitrogen gas or Li$_3$N. Uranium in the liquid Cd alloy was preferentially nitrided to form U$_2$N$_3$, which were produced at nitrogen gas-liquid alloy interface. A little gadolinium precipitated as nitrides, GdN or (U,Gd)N phase. The rest of gadolinium and almost all of cerium remained in the Cd phase as MCd$_n$ (M: Gd and Ce) intermetallic compounds. Resistance of Ce to nitridation is due to the lower activity coefficient in Cd-rich solution at the temperatures.
1. Introduction

The nitride-forming reaction in liquid alloys containing actinide and lanthanide elements is of interest for both technological and fundamental science. Actinide nitride has been extensively studied as a candidate fuel for actinide burning systems. In the proposed pyrochemical processing [1], nitride fuels are recovered as metals or alloys by electrorefining in a LiCl-KCl eutectic salt. The recovered metallic fuels are then converted to the nitrides in liquid Cd-An (An:actinides) alloys. In this process, actinides can be separated from lanthanides as a result of activity coefficient differences between actinides and lanthanides. The further removal of lanthanides from actinides may be achieved if necessary [2]. The use of Cd-An alloys is superior in some points such as high vapor pressure of Cd to other liquid-metal processes, for example, the liquid tin process [3,4]. In the liquid tin process, it is difficult to remove Sn by distillation after nitriding because of its high boiling point. Li$_3$N may be also used in the liquid Cd process as a nitriding agent, instead of nitrogen gas, because the nitrogen evolved during electrolysis of the nitrides in the salt is trapped by lithium to form Li$_3$N.

The purpose of this study is to understand the basic behavior of nitriding in liquid Cd containing uranium and lanthanides and to determine if lanthanides could be separated by nitride precipitation techniques in Cd-U alloys.

2. Experimental

Nitriding of liquid Cd-U-Gd-Ce alloys was performed in closed quartz ampoules using nitrogen gas or Li$_3$N. Reaction temperatures used were 773 and/or 873 K. Graphite and/or molybdenum crucibles were used to contain the liquid Cd alloys and they were degassed in a high vacuum at 1023 K before alloying. Molybdenum is considered to be the best material as a container for liquid Cd alloys because the solubility of Mo in liquid Cd is very small at the present temperatures (about $10^{-7}$-$10^{-6}$ wt%) [5,6].

Approximately 7 g Cd-2wt%U-1wt%Gd-1wt%Ce alloys were prepared in an inert atmosphere. Uranium, gadolinium, cerium, and cadmium metals of 99.9% purities were weighed and placed in quartz tubes together with graphite or molybdenum crucibles in an argon-atmosphere glove box. The samples in the quartz ampoules were sealed in high-purity helium gas and then melted for 20-50 h at 873 K to obtain the homogenized Cd-U-Gd-Ce alloys.

Nitridings were performed in nitrogen gas of 99.995wt% purity. About 250 Torr nitrogen was contained in the quartz ampoule of 20~50cc in volume at room temperature. The nitrogen pressure increased up to about 600~700 Torr at the reaction temperatures of 773 and 873 K, where nitriding times were 100-170 h. For the Mo crucibles, the liquid Cd alloys were often stirred during nitriding using Mo rods which were placed in the Mo crucible. To terminate the nitriding, the quartz ampoules were water-cooled. The amounts of nitrogen absorbed in the liquid alloys were measured by fracturing the quartz ampoules in water after nitriding and correcting the rest of nitrogen gas.

In the case of nitriding with Li$_3$N, the Cd-U alloy containing Gd and Ce was sealed with Li$_3$N under vacuum in a quartz ampoule using a graphite crucible and then heated to 773 K. The amount of Li$_3$N added was ~25mg, which was determined from a condition that an increase of inner pressure in the quartz ampoule due to decomposition of Li$_3$N to N$_2$ is not in excess of 760 Torr at 773 K.

In addition, a simple technique was employed to measure the time dependences of the amounts and pressures of nitrogen reacted with the Cd-U alloy. The Cd-U alloy containing Ce and Gd was held in a long glassy carbon crucible in order to prevent loss of Cd due to vaporization during nitriding. The crucible was then placed in a quartz tubing, which is connected with a pressure gauge for measuring the pressure in the system. The dead volume of the system was measured with pure helium. Nitriding of the alloy with nitrogen was performed at 873 K without stirring.

After nitriding, the samples were cut to half together with the crucibles and products in the Cd alloys were examined. Electron-probe micro-analysis (EPMA) was used to identify phases in the Cd alloys, in particular, the stoichiometry of nitride precipitates of uranium or lanthanides. The acceleration voltage and beam size were 20 KV and ~1μm in diameter, respectively. The X-ray intensities were converted into compositions using the pure
elements, UN and U$_2$N$_3$ standards. The detection limits of the EPMA analysis are about 0.1, 0.1, 0.2, 0.2, 0.5 and 1.0 wt% for Cd, U, Gd, Ce, N and C, respectively.

3. Results

3.1 Reaction with nitrogen gas

3.1.1 Products for the graphite crucibles

Fig. 1 shows the results when the Cd-2wt%U-1wt%Gd-1wt%Ce alloys were nitrided for 100 and 170 h at 873 and 773 K, respectively, in the graphite crucibles. The compositions of precipitates found in the alloy solidified from 873 K are summarized in table 1, where the concentration of nitrogen in stoichiometric U$_2$N$_3$ is about 8.1 wt%.

The EPMA analysis of the Cd alloys solidified from 773 and 873 K clearly indicated that uranium precipitates in the Cd alloys were mainly U$_2$N$_3$ and U(C,N) phases. The U$_2$N$_3$ phase was found only at the surface of the Cd alloy, that is, the interface between the liquid alloy and nitrogen gas, as shown in figs.1(a) and (d). This suggests that the U$_2$N$_3$ phase was formed by a direct reaction between the dissolved uranium in the Cd melt and nitrogen gas in atmosphere. The formation reaction of the U$_2$N$_3$ can be described by the equation,

$$2U(\text{dissolved}) + \frac{3}{2} N_2(g) = U_2N_3(s).$$

The reaction appears to be rapid at 873 K, producing porous reaction layers, accompanied by considerable amounts of spalled fragments. From the EPMA analysis of the U$_2$N$_3$ precipitates, they contained a little gadolinium and cadmium of 0.4 and 0.5 wt%, respectively. However it was not obvious whether the chemical form of Gd is nitride or metallic. As a result of the high density of U$_2$N$_3$ compared with Cd, the U$_2$N$_3$ precipitates formed at the alloy surface were expected to sink to the bottom of the graphite crucible. However the U$_2$N$_3$ did not sink and increased its thickness at the alloy surface through nitriding. This is mainly due to formation of the layered nitride at the liquid alloy surface as a result of static nitriding reaction without stirring, as clearly shown in fig. 1(d), where formation and growth of very thin adherent U$_2$N$_3$ layer at the alloy surface solidified from 773 K can be observed. The U$_2$N$_3$ layer formed on the overall surface of the liquid alloy would depress further nitridation of uranium dissolved in the Cd alloy. In a deed, the amount of nitrogen absorbed in the liquid alloy nitrided for 170 h at 773 K was below about 1 ccSTP, which correspond to about 10% in conversion rate of U dissolved in the Cd alloy to U$_2$N$_3$.

By contrast, the U(C,N) phase concentrated at the near bottom of the crucible, as shown in fig. 1(c).

Precipitates of uranium carbide, probably, UC, were also observed around the bottom of the Cd alloy homogenized in a helium atmosphere at 873 K before nitriding. This means that the UC precipitates were produced by a reaction between uranium and free carbon in the liquid Cd. Therefore, formation of the U(C,N) precipitates in the nitrided alloy was due to nitridation of the UC precipitates formed during alloying with atomic nitrogen dissolved in the Cd melt. On the other hand, the concentration of U in the Cd phase nitrided at 873 K was below about 0.1 wt% which corresponds to the detection limit of the EPMA analysis. However, a small fragment of pure uranium was found at the near bottom of the Cd alloy nitrided at 773 K, suggesting that 2 wt%U may be in excess of the solubility of U in the Cd alloy at 773 K. From the U-Cd binary phase diagram [5], the solubilities of U in Cd are 2.35 and 2.14 wt% at 773 and 873 K, respectively.

The lanthanides, in particular, cerium, were quite different in their precipitation behavior from uranium. Cerium nitride, probably CeN, or Ce-contained U-N phases cannot be found in the Cd alloys nitrided at 773 and 873 K. Almost all the lanthanide elements precipitated in the Cd alloy as a M(Gd,Ce)-Cd intermetallic compound. From the EPMA analysis, the M-Cd intermetallic compound was estimated to be (Gd,Ce)Cd$_{11}$ phase, where the concentrations of Gd and Ce were a little scattered among the precipitates, as shown in table 1. The intermetallic compound MCd$_{11}$ formed on water-cooling after nitriding and remained in suspension in the Cd melt. The result that unlike U, the lanthanides, in particular, cerium, did not form the nitrides can be explained by the very low activity coefficients of lanthanides in cadmium, compared with that of uranium. The activity coefficients of U, Gd and Ce in Cd are 75, 6.3E-7 and 1.3E-8 at 773 K, respectively [6] and indicate that the Cd-Ce, Gd alloys are very stable and the much larger concentrations are necessary to equal the chemical activity of U.

3.1.2 Products for the Mo crucibles

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The appearance of nitride precipitates for the Mo crucible was significantly different from that for the graphite crucible. Table 2 indicates the compositions of precipitates found in the alloy nitrided for 100 h at 873 K. Fig. 2 shows typical sections of the near bottom and near surface regions of the Cd alloys nitrided for 100 h at 873 and 773 K, respectively. From the EPMA analysis, both the precipitates appear to consist of U$_2$N$_2$ and U-N phases containing gadolinium. The formation of the nitride layer on the alloy surface found at 773 K is also very similar to those for the graphite crucible without stirring. The nitride precipitates found on the near bottom region are likely to have a very thin layer structure, suggesting that the precipitates were formed at the alloy surface. Sinking of the nitride precipitates to the bottom can be explained by fragmentation of the nitride layer formed at the surface due to mechanical stirring during nitriding.

As shown in table 2, the EPMA analysis of the thin layered U-N precipitates found at 873 K, which contained a little gadolinium, showed that the precipitates have low nitrogen contents, 6.4–7.2 wt%, compared with that of U$_2$N$_2$ phase (8.1 wt%), and 0.3–2.4 wt% Gd was present in the precipitates. This result suggests the product to be the mixture phase of uranium and gadolinium nitrides. The formation of U$_2$N$_2$ occurs initially and a decrease in concentration of U in the liquid Cd promotes formation of gadolinium nitride, GdN or (U,Gd)N. The amounts of nitrogen absorbed in the liquid alloys during nitriding are summarized in table 3. For the nitriding at 873 K, the conversion of U to U$_2$N$_2$ attained to about 92%. At this stage where the concentration of U in Cd is very low, the chemical activity of U would be greatly reduced to approximately that of Gd and Gd is likely to form the nitride, probably GdN or (U,Gd)N, because the activity coefficient of Gd in Cd is higher than that of Ce. The formation of (U,Gd)N at the alloy surface means coprecipitation of U and Gd. Moreover, decomposition of U$_2$N$_2$ to UN in the liquid Cd could occur, because the solubility of nitrogen in liquid Cd is expected to be very low. The nitride layer formed on the alloy surface at 773 K, as shown in fig. 2(b) also contained 0.9 wt% Gd, suggesting that both U$_2$N$_2$ and GdN or (U,Gd)N could be formed simultaneously.

On the other hand, all of Ce precipitated in MCd$_n$ intermetallic phases together with Gd in the Cd alloys solidified from both 773 and 873 K. As mentioned before, the strong resistance of Ce to nitride forming, compared with U and Gd, can be explained by its lower activity coefficient in Cd, that is, its greater stability of Cd-Ce alloys. The composition of the MCd$_n$ seems to be scattered among the precipitates, as shown in table 2. This tendency was very similar to that for the graphite crucible. Some of the MCd$_n$ precipitates found in the alloy nitrided at 773 K contained a little uranium and the conversion of U to U$_2$N$_2$ was low, compared with that at 873 K. This indicates that uranium in the Cd alloy would be not completely nitrided at 773 K.

3.1.3 Time dependence of nitriding reaction

Fig. 3 shows the time dependences of nitrogen pressure in the quartz ampoule and conversion of uranium in the Cd-U alloy to U$_2$N$_2$ during nitriding at 873 K. The conversion was calculated from the amount of nitrogen absorbed in the Cd alloy. The equilibrium amount of U$_2$N$_2$ formed was about 45%. Therefore, the nitriding of uranium dissolved in the Cd alloy was not completed. The time dependence of conversion demonstrates that the reaction rate increases rapidly at early stage, attains the maximum at ~5 hours and then decreases gradually. This tendency means that U$_2$N$_2$ layer formed at the alloy surface prevented further progress of nitriding reaction. From the EPMA analysis, the formation of U$_2$N$_2$ layer at the alloy surface was also observed. As mentioned before, it is likely that mechanical stirring is an effective technique for enhancing or completing the conversion of uranium to nitride.

3.2 Reaction with Li$_2$N

Fig. 4 shows typical cross sections of surface regions for the Li$_2$N contained Cd alloy annealed at 773 K. From the EPMA analysis, it was found that the reaction of the liquid Cd-U alloy with Li$_2$N yields the uranium sesquinitride, U$_2$N$_3$. The formation of U$_2$N$_3$ occurred at both the surface of the liquid Cd alloy and the interface between Cd-Li phase and the liquid Cd alloys. The U$_2$N$_3$ precipitates contained a little Gd. U(C,N) phase also precipitated at the near bottom of the alloy. Lanthanides, Ce and Gd, concentrated in the MCd$_n$ intermetallic phase. The nitriding behavior of Cd-U-lanthanides alloy with Li$_2$N appears to be very similar to those with nitrogen gas. On the other hand, the Cd-Li precipitates floated to the alloy surface, suggesting that the reaction between Cd and Li$_2$N yields a low density Cd-Li intermetallic compound. The composition of the Cd-Li alloy lies in the range of CdLi$_2$–CdLi$_3$; the phase diagram of Cd-Li system suggests the product to be CdLi$_3$ [5].

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About 7 cc nitrogen remained in the quartz ampoule after nitriding. The amount of nitrogen evolved by complete decomposition of Li$_3$N is estimated to be ~8 cc. This suggests that almost all of Li$_3$N was decomposed by the reaction with Cd to evolve nitrogen gas and ~1 cc of the evolved nitrogen contributed the nitriding of uranium in the Cd alloy. The conversion of uranium to U$_2$N$_3$ was no more than ~10%. This conversion rate is significantly lower than those for the nitriding with stirring.

The results of the present experiment described above indicate that the nitride precipitation technique using liquid Cd alloy could be a useful technique in separating lanthanides, in particular, light elements such as La ~ Nd from actinides. The Li$_3$N can be also used as a nitriding agent in this process, instead of nitrogen.

Acknowledgments

The authors are grateful to Drs. Hoshi and Muromura at the Japan Atomic Energy Research Institute for support of this study. We want to express thanks to F.Kobayashi for providing some experimental materials.

References

### Table 1
The composition of products in the Cd alloy at 873 K for the graphite crucible

<table>
<thead>
<tr>
<th>Phases</th>
<th>Concentrations (wt%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Cd matrix</td>
<td>99.9</td>
</tr>
<tr>
<td>( \text{U}_2\text{N}_3 )</td>
<td>0.5</td>
</tr>
<tr>
<td>((\text{Gd,Ce})\text{Cd}_n)</td>
<td>88.1–88.3</td>
</tr>
<tr>
<td>( \text{U}[(\text{C},\text{N})] )</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

### Table 2
The composition of products in the Cd alloy at 873 K for the Mo crucible

<table>
<thead>
<tr>
<th>Phases</th>
<th>Concentrations (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Cd matrix</td>
<td>100</td>
</tr>
<tr>
<td>( \text{U}_2\text{N}_3 )</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>((\text{Gd,Ce})\text{Cd}_n)</td>
<td>89.12–88.4</td>
</tr>
<tr>
<td>( \text{U}2\text{N}_3 \cdot \text{Gd} )</td>
<td>1–0.9</td>
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### Table 3
The amounts of nitrogen absorbed into the Cd alloys in the Mo crucibles

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Time (h)</th>
<th>Initial volume (cc at STP/g U)</th>
<th>Absorbed volume (cc at STP/g U)</th>
<th>Conversion to ( \text{U}_2\text{N}_3 ) (%)</th>
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</thead>
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<tr>
<td>773</td>
<td>100</td>
<td>100.2</td>
<td>55.3</td>
<td>78.3</td>
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<tr>
<td>873</td>
<td>100</td>
<td>89.8</td>
<td>64.6</td>
<td>91.5</td>
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</table>
Figure 1  Backscattered electron micrographs of the Cd alloys in graphite crucibles: Micrographs a), b) and c) were taken of the near surface, center and near bottom regions of the alloy solidified from 873 K, respectively. Micrograph d) was taken of the near surface region of the alloy solidified from 773 K.

Figure 2  Backscattered electron micrographs of the Cd alloys in Mo crucibles: Micrographs a) and b) were taken of the near bottom and the near surface regions of the alloys solidified from 873 and 773 K, respectively. Both the precipitates are $U_2N_3$ containing GdN or (U,Gd)N.
Figure 3  Time dependences of nitrogen pressure and conversion of uranium to $U_2N_3$ for the Cd-U alloy nitrided at 873 K.

Figure 4  Backscattered electron micrographs of the Cd alloy nitrided with Li$_3$N: Micrographs a) and b) were taken of the near surface regions of the alloy solidified from 773 K. Gd-contained $U_2N_3$ precipitates were found at the alloy surface and the interface between the Cd-Li intermetallic compound (CdLi$_3$) and the Cd alloy.
RECOVERY OF VALUABLE METALS 
FROM HIGH-LEVEL RADIOACTIVE WASTE

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Processing steps of the recovery of valuable metals from spent nuclear fuel are studied by means of experiments of lead extraction from high level radioactive waste (HLW) and selective separation of noble metals from simulated waste. Lead extraction and cupallation are found to be effective to recover valuable metals from the actual insoluble residue in dissolver solution of spent fuel. As for refining processes of noble metals extracted in lead, selective separation of ruthenium by ozone oxidation method and mutual separation of rhodium and palladium by solvent extraction method, precipitation method and ion exchange method are examined. These methods are found to have high efficiency for refining these three metals. An optimum conceptual flow sheet for recovery of valuable metals from HLW is derived from these experimental studies.
1. Introduction

Spent nuclear fuels contain significant quantities of valuable metals - the platinum-group metals and technetium. The recovery of the platinum-group metals, palladium, rhodium and ruthenium, leads to a new source of these three metals which have uncertainty in supply because of world's limited producers and are increasing in demand because of the growth of high-technology industry. Spent nuclear fuels also contain technetium which is nearly absent in nature and promising in some kinds of fields of material application. Thus there is considerable incentive to recover the platinum group metals from spent nuclear fuel and various processes to recover them have been evaluated on a laboratory scale[1].

Power Reactor and Nuclear Fuel Development Corporation (PNC) began in 1986 to study and has been developing the technologies to recover and utilize three of the platinum-group metals and technetium from spent nuclear fuel as a part of the partitioning program of HLW (OMEGA project) in cooperation with private companies and universities. All the experimental and bibliographic studies were performed under advice of a special committee - The Technical Committee of Recovery and Utilization of Valuable Metals in Spent Nuclear Fuel sponsored by PNC. The committee had prepared the R&D's program after evaluation of possible flows for recovery and utilization of the valuable metals, which had resulted an optimum flow for the recovery.

Some parts of the platinum-group metals exist as the main constituent of the insoluble residue from dissolution stage of spent fuel in Purex process. The recovery of the platinum-group metals from the insoluble residue is simpler and easier than that from HLLW since the residue consists of metallic alloy containing the metals. Thus we have been developing mainly the processes to recover the noble metals from the insoluble residue.

Fig.1 shows the processing steps for recovery and purification of the platinum-group metals from HLW. In this paper we describe the experimental results on each stage in Fig.1, and discuss a conceptual flow sheet for recovery of the platinum-group metals from HLW.

2. Lead extraction

Lead metal was selected as a scavenger in the first stage of separation of the platinum group metals from other fission products and TRU elements. Sodium borate was used as a glass-forming material to fix other constituents of insoluble residue and calcination.

The actual insoluble residue was obtained from the dissolution stage of FBR spent fuel with burn-up 88000 MWd/t. The majority of particle size of the residue was less than 2 \( \mu m \) in diameter. The residue had the composition of 30% Ru, 7.8% Rh, 8.7% Pd, 12% Tc, 23% Mo, 10% Pu and 2.3% U. The irradiated fuel was dissolved under the mild condition so that some part of plutonium and uranium oxide remained to be undissolved. This enabled to estimate the decontamination factor of TRU elements. The residue of 0.45g was mixed with granular lead metal and sodium borate powder in weight ratio of 50 to 1 and 20 to 1 respectively. Table 1 shows the condition of the lead extraction. The mixture was placed in a mullite crucible and then melted at 800°C for 3hr in the air. Another extraction temperature, 1100°C was used in order to examine influence of temperature on phase separation. After melting the mixture was cooled in the furnace and the lead metal called Pb button was separated from the glass. All the operation of lead extraction test was performed in a hot cell.

The distribution of the platinum-group metals in the Pb button was determined by electron probe microanalysis. Rhodium and lead existed in the Pb button uniformly while ruthenium segregated in the upper part of the Pb button close to the boundary between lead and glass. In some extraction conditions a Pb button was not formed and rather small metal phases were dispersed in the glass. Rhodium and lead seem to be alloy with lead. Technetium existed in the same area where ruthenium segregated in the Pb button. On the other hand, ruthenium, rhodium and palladium were not detected in the glass as if the Pb button formation was not perfect. The volatile fraction of ruthenium was not determined in the hot test, however the cold test gave no indication of volatilization of ruthenium while lead extraction at the same condition.

Radioactivities of the glass as well as the lead were measured to determine the decontamination factors of TRU elements. As shown in Table 1 the decontamination factors for Pu, Am and Cm were more than 200.
3. Cupellation

As the platinum-group metals are contained in a Pb button, Pb separation at early stage may be effective to make the following processes easier. Cupellation method is applied to roughly remove lead from lead-platinum group elements alloy to obtain noble metal bead.

Lead button containing the platinum metals were heated on a magnesia crucible or a calcium phosphate crucible (cupel) at 850-1050°C in the air, and then a metal bead were obtained. The main constituent of the bead was platinum group metals, therefore this method was proved to be available for Pb separation process from Pb button. This treatment is optional and not essential for the following separation processes, so that it possible to dissolve Pb button directly without cupellation.

4. Ruthenium separation

The Pb button, containing the platinum group metals (Ru, Rh, Pd), Tc and Mo, is obtained at the Pb extraction stage as before. After that, the Pb button is dissolved with nitric acid solution and Ru is separated selectively from this solution by ozone oxidation method. Ruthenium is purified by taking advantage of volatility of RuO₄. Ozone gas oxidation process is applied for purification of ruthenium in the sludge from the dissolution treatment. Ozone gas bubbling in nitric acid solution is also effective to remove very small quantity of ruthenium in it. This treatment makes it possible to operate the following processes for mutual separation of rhodium and palladium in a glove box owing to decrease of the activity mainly caused by ¹⁰⁶Ru.

The quaternary Mo-Ru-Rh-Pd alloy was prepared as the simulated insoluble residue based on the method reported by Naito et al. [2]. The composition of the alloy is that of fission produced noble metal alloys and has the ε phase structure. Appropriate amounts of Mo, Ru, Rh and Pd metal powders, all with high purity (99.9%), were mixed and pressed into pellet and then sintered at 1723K in vacuum for 3hours. The pellets were pulverized to fine powder. The particle size of the powder was adjusted to be 3 μ m in average using a vibration mill and a membrane filter.

The Pb metal called Pb button of 5g was separated after the lead extraction of the simulated insoluble residue. The Pb button was dissolved with boiling 3M nitric acid (100ml) for 3hours, using a flask with a reflux condenser. After dissolution the nitric acid solution was filtrated with a 0.45 μ m membrane filter to remove the undissolved powder.

The experimental apparatus employed for Ru separation system is shown diagrammatically in Fig.2. The sample, which was 50mg of the undissolved powder or 50ml of the dissolution fraction after Pb button dissolution process, was transferred to the oxidation reactor at 298K. And then ozone was supplied to the reactor from the reservoir by nitrogen carrier for 4 hours. The operation for the oxidation reaction was repeated 3 times for the undissolved powder and 2 times for the dissolution fraction with every one batch. The chemical compositions of each stage were determined with ICP-AES and ICP-masspectrometry. The distribution of the platinum-group metals in the powder samples was analyzed by electron probe microanalysis.

Fourteen experiments for the undissolved powder were performed and the average value of the results is shown in Fig.3. The recovery of Ru which was converted into RuO₄ and collected in the absorption bottle, was more than 98% in this procedure. Only 2% of Ru was remained in the undissolved powder after the ozone oxidation process. Through this operation nearly all of Rh, Pd and Mo were remained in the undissolved powder and less than 0.1% of those were found respectively in the Ru fraction recovered. The remainder of Ru which is not reacted in this procedure seems to be existed as alloy powder based on the EPMA observation. So a sample for re-extraction with lead was prepared by collecting the remainder of fourteen experiments and a recovery experiment of Ru was performed all over again. The recovery of Ru including a loss due to the lead extraction was higher than 93%. Thus total recovery efficiency of Ru from the undissolved powder was more than 99.8% through the ozone oxidation process coupled with the re-extraction by lead.

The separation of Ru in the solution was also performed by ozone gas bubbling into the dissolution fraction. The recovery of Ru was more than 93% in this procedure. Finally it was found that the transference rate of Ru from the insoluble residue into the dissolution fraction could be decreased less than 1.5 X 10⁻⁵ using the ozone oxidation.
5. Mutual separation of rhodium and palladium

Various techniques, which are precipitation, solvent extraction, ion exchange and so on, had been studied or used in the platinum group metals refining industry. Among these techniques, solvent extraction of Pd by amine or sulfide extraction is considered to be promising for Pd separation from the nitric acid solution. Some tests for these extractants, therefore, have been carried out. On the other hand, mutual separation of other elements (Rh, Mo, Pb) by solvent extraction or ion exchange method was considered not to be suitable because a good extractant or an ion exchanger had not been found. On this study, precipitation separation method by adding chemical agents were, therefore, has been studied as refining process of Rh, because Rh is most promising element to be used in common industry.

Tri-n-octylamine (TNOA) is one of amine extractants promising for Pd extraction. The mixture of 10% TNOA and CCl₄ or n-dodecane was used for the present study. Extraction experiments were carried out under the condition of O/A=1 for 30 minutes mixing at room temperature. Distribution ratio are almost coincident whether CCl₄ was used for diluent or n-dodecane, however the third phase formation is observed on either solvent. Dodecyl alcohol (5%) addition to either solvent is enough to prevent formation of third phase, and settling time is rather short (1-2 minutes). Nitric acid concentration dependence on distribution ratios of metals by 10% TOA/n-dodecane extractions is shown in Fig 4. It is seen that distribution ratio of Pb decreases with increasing acidity, and the values are not so high that Pd is extracted effectively at over 3N nitric acid concentration.

Table 2 shows the results of Pd back extraction from 10% TNOA/n-dodecane by various aqueous solutions under the condition of O/A=1 for 5 minutes mixing at room temperature. Palladium is back extracted to 1 wt% thiourea (CS(NH₂)₂) solution, though it is not done to each other solution. Especially, when ammonia is used, precipitates are formed so that phase separation is difficult. And more than 99% of Pd is stripped by reduction with a hydride solution from the thiourea solution. Chemical form of Pd recovered is powder metal. Thiourea solution, therefore, would be suitable back extraction reagent.

Furthermore the back extraction efficiency was not changed even if thiourea content was changed from 0.1 Wt% to 5wt%. Thiourea is less than 3N nitric acid solution is also available for back extraction and it is useful to promote phase separation, but it is decomposed in 6N nitric acid.

Recently DHS (di-hexyl sulfide) has been studied as a promising extractant of Pd. While most of sulfide extractants are chemically unstable, DHS is rather stable for practical use. Pd extraction study of DHS were hence carried out. Shellsol AB (aromatic solvent) and n-dodecane were selected as diluents. The extraction conditions were those same as TNOA experiments, and DHS content was 10%. Fig.5 shows nitric acid content dependence on distribution ratios of metals by 10% DHS/n-dodecane, which are almost same values as those when shillsol AB is used for a diluent instead of n-dodecane. From this figure, it is seen that the distribution ratios of Pd are extremely high and they are not dependent on nitric acid concentration.

Some reagents for Pd back extraction from 10% DHS/n-dodecane were tested it as TNOA experiments. As shown in table 3, ammonia solution and thiourea solution are effective reagents. To recover Pd from ammonia solution, however, is difficult, though it is easy from thiourea solution by reduction with a hydride solution. Consequently thiourea solution is suitable back extraction reagent from DHS same as TNOA.

Rhodium, Mo and Pb would be contained in the raffinate of Pd extraction process. Neutralization precipitation method was adopted for the Pb separation process. If acetic acid is added to the raffinate before neutralization, Pb would remain in the solution and other elements would be precipitated. This is because Pb acetate is not decomposed by neutralization, though the others are precipitated by hydrolysis with neutralization. pH dependence on the Pb separation was investigated. After adding 20wt% acetic acid, precipitation reaction was executed for 1 hour at room temperature, where pH of the solution was prepared by adding ammonia (pH10) and sodium hydroxide (pH 10-12). The results are shown in Fig 6. It is seen that more than 90% of Rh and Mo are precipitated as hydroxide at pH8-10 and Mo is dissolved again as molibdate at pH 12, while more than 80% of Pb remains in the solution. More than 99% of Pb is recovered as Pb(CO₃)₂ form the neutralized solution by adding carbonate to the solution. The chemical form of recovered Pb may be suitable to be returned to the lead extraction process, because Pb(CO₃)₂ is decomposed easily by heating. The recovery of Pb precipitate would be higher if these procedures are repeated, so that the neutralization method at pH 8-10 would be suitable for Pb separation.
The precipitate recovered on neutralization of the raffinate would contain Rh, Mo and small amount of Pb. As can be seen from Fig.6 mentioned above, more than 80% of Mo is not precipitated in the solution prepared at pH 12 by adding sodium hydroxide but more than 90% of Rh is precipitated. Mutual separation of Rh and Mo, therefore, would be achieved roughly using the precipitation separation method for the precipitate recovered on the Pb separation. As the precipitation separation, it may be appropriate method to dissolve Mo selectively from the precipitate by washing it with ammonia or sodium hydoxide of over pH12. Although Mo is dissolved selectively actually by this method, a small amount of Mo and Pb remain in the Rh precipitate.

Some resin were tested for Rh purification by means of batchwise adsorption. From this test, it is found that chelate resin CS-346 (Sumichelate), amideoxime type, has good performance for Rh purification. The adsorption behavior of CS-346 is shown in Fig.7. It is seen from this figure that Rh would be purified by passing the solution through a column of CS-346 after dissolution of the Rh precipitate with acid solution. On the other hand, coprecipitation method with selenium (Se) or tellurium (Te) was also studied for Rh separation, as this method had been used as analytical method. It was experimentally evaluated that the coprecipitation method was not suitable for practical process because of its long reaction time.

The results presented above indicate that a flow sheet shown in Fig.8 is desirable for a mutual separation process of palladium and rhodium in nitric acid solution. The starting solution of this process flow is the nitric acid solution containing Pb, Pd, Rh and Mo. Palladium is separated selectively from the solution using DHS extraction process, and it is back extracted to thiourea solution, so that it is recovered as metal by reduction agents. On the other hand, the raffinate is added with acetic acid and ammonia solution, so that Pb is recovered to be returned to the former process. The precipitate is treated with sodium hydroxide solution to be separated to Mo and Rh fractions. Rh would be refined finally using chelate resin.

6. Conceptual flow sheet

Based on the results described above, the flow sheet for recovery of noble metals from HLW has been established, that is shown in Fig.9. Lead extraction method is chosen for the first step to separate the noble metals from other fission products because of compatibility with vitrification of HLLW for geologic disposal. After the lead extraction, the cupellation method is applied to roughly remove lead from lead-platinum group elements alloy to obtain noble metal bead. Then the bead is dissolved in nitric acid. Ruthenium in the bead is almost not dissolved in nitric acid, therefore sludge mainly containing ruthenium is separated by filtration. After the separation of ruthenium, aqueous processes are applied for mutual separation of rhodium and palladium.

7. Conclusion

We have determined the conceptual flow sheet as for platinum group metals containing in the insoluble residue. Each separation method used in the flow sheet shown in Fig.9 has high separation factor enough for practical use. It is required to perform the recovery steps continuously and determine the final recovery efficiencies of platinum group metals in order to confirm the effectivity of the flow sheet. The objective of this study is to establish a flow sheet for recovery of the valuable metals from HLW. We are planning to modify the flow sheet for recovery of other valuable metals, especially technetium.

References
Table 1 Decontamination factors of lead extraction for some TRU nuclides

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity in Lead (A) [kBq/g]</th>
<th>Activity in Glass (B) [kBq/g]</th>
<th>DF (B/A)</th>
</tr>
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<tbody>
<tr>
<td>$^{239}$Pu + $^{240}$Pu</td>
<td>$1.1 \times 10^3$</td>
<td>$1.5 \times 10^3$</td>
<td>140</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>$2.0 \times 10^2$</td>
<td>$5.9 \times 10^4$</td>
<td>300</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>$5.1$</td>
<td>$1.2 \times 10^3$</td>
<td>240</td>
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<tr>
<td>$^{244}$Cm</td>
<td>$1.7 \times 10^2$</td>
<td>$4.4 \times 10^4$</td>
<td>260</td>
</tr>
</tbody>
</table>

Fig. 1 Processing steps for recovery and purification of the platinum group metals from HLW

Fig. 2 Apparatus for ruthenium oxidation recovery

Fig. 3 Total efficiency of Ru recovery by ozone oxidation method
Figu. 4 Distribution ratios of metals by 10% TNOA in n-dodecane as a function of nitric acid concentration.

Figu. 5 Distribution ratios of metals by 10% DHS in n-dodecane as a function of nitric acid concentration.

Figu. 6 Lead separation from metals precipitate rate of Pb, Rh, Mo as a function of pH by precipitation method (neutralization).

Figu. 7 Adsorption rate of metals as a function of nitric acid concentration by chelata resin CS-346.

Simulated Nitric Acid Solution: Rh:Pd:Mo:Pb = 20:50:20:4000 mg/l

Solvent Extraction: DHS/n-dodecane, TOA/n-dodecane

O/A = 1, batch shaker, 30 min

Back Extraction: thiourea

Stripping: NaBH₄

Precipitation Method: NaOH

Solution: carbonate

Precipitate: Pb(CO₃)₂

Fig. 8 Flow sheet for mutual separation of platinum group metals.
Table 2 Palladium back extraction from TNOA/n-dodecane by various aqueous solution

<table>
<thead>
<tr>
<th>Back Extraction Agent</th>
<th>Back Extraction Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td></td>
</tr>
<tr>
<td>0.1N HNO₃</td>
<td>7</td>
</tr>
<tr>
<td>6.0N HNO₃</td>
<td>25</td>
</tr>
<tr>
<td>0.1N HClO₄</td>
<td>26</td>
</tr>
<tr>
<td>3.0N HClO₄</td>
<td>18</td>
</tr>
<tr>
<td>Alkali</td>
<td></td>
</tr>
<tr>
<td>6.0M NH₄OH</td>
<td>&gt;99</td>
</tr>
<tr>
<td>0.5M NaOH</td>
<td>8</td>
</tr>
<tr>
<td>4.0M NaOH</td>
<td>23</td>
</tr>
<tr>
<td>0.5M Na₂CO₃</td>
<td>2</td>
</tr>
<tr>
<td>Others</td>
<td></td>
</tr>
<tr>
<td>1.0wt% (NaH₂)CS</td>
<td>&gt;99</td>
</tr>
<tr>
<td>20wt% Na₂S₂O₃</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 3 Palladium back extraction from DHS/n-dodecane by various aqueous solution

<table>
<thead>
<tr>
<th>Back Extraction Agent</th>
<th>Back Extraction Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td></td>
</tr>
<tr>
<td>0.1N HNO₃</td>
<td>N.D.</td>
</tr>
<tr>
<td>6.0N HNO₃</td>
<td>N.D.</td>
</tr>
<tr>
<td>0.1N HClO₄</td>
<td>N.D.</td>
</tr>
<tr>
<td>3.0N HClO₄</td>
<td>N.D.</td>
</tr>
<tr>
<td>Alkali</td>
<td></td>
</tr>
<tr>
<td>6.0M NH₄OH</td>
<td>&gt;99</td>
</tr>
<tr>
<td>0.5M NaOH</td>
<td>9</td>
</tr>
<tr>
<td>4.0M NaOH</td>
<td>25</td>
</tr>
<tr>
<td>0.5M Na₂CO₃</td>
<td>27</td>
</tr>
<tr>
<td>Others</td>
<td></td>
</tr>
<tr>
<td>1.0wt% (NaH₂)CS</td>
<td>&gt;99</td>
</tr>
<tr>
<td>20wt% Na₂S₂O₃</td>
<td>73</td>
</tr>
</tbody>
</table>

N.D.: not detected

Fig. 9 Conceptual flow sheet for recovery of noble metals from insoluble residue
PARTITIONING TEST FACILITY CONSTRUCTED IN NUCEF

Y. Morita, I. Yamaguchi, T. Fujiwara, K. Mizoguchi, M. Kubota

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Department of Chemistry and Fuel Research
Japan Atomic Energy Research Institute

Partitioning Test Facility was constructed in NUCEF (Nuclear Fuel Cycle Safety Engineering Research Facility) at JAERI, Tokai, in order to demonstrate the 4-group partitioning process developed in JAERI using real high-level liquid waste (HLLW). The present paper shows the purpose of the facility, the equipments in the facility and the preliminary results of the partitioning tests with simulated HLLW.

In the partitioning facility, 2 to 20 L of HLLW (5000 Ci at maximum) can be treated per experiment. Main components in the facility are a vessel for denitrification, a filter unit, extractors (two 16-stage mixer-settler units), adsorption columns and the related equipments.

Partitioning tests with simulated HLLW are now in progress. The results will be compared with those of the tests with real HLLW. In the latest test, lanthanides were almost completely extracted with DIDPA and well back-extracted with 4 M HNO₃.
1. Purpose of the facility

The main purpose of the facility is to demonstrate the 4-group partitioning process developed in JAERI using real high-level liquid waste (HLLW). The results of the partitioning tests with real HLLW are compared with those of the tests with simulated HLLW. The comparison and the further examination on the properties of real HLLW and on the influence of radiation would give validity and limitation of the experiments with simulated HLLW, which have been carried out before and will be performed in the future from the viewpoints of basic chemistry and chemical engineering.

The facility will be used also for the test of the optimized or advanced process and a new partitioning process to which new extractants, new adsorbents and new methods are applied. The facility has enough flexibility.

2. The 4-group partitioning process

The flow scheme of the 4-group partitioning process is shown in Fig. 1. In this process, elements in HLLW are separated into four groups: transuranium elements (TRU), Tc - platinum group metals (PGM), Sr - Cs and the other elements. For the TRU separation, extraction with diisodecylphosphoric acid (DIDPA) has been studied. One of the extraction process established is shown in Fig. 2, which includes the separation of Am, Cm from lanthanides by selective stripping with diethylenetriaminepentaacetic acid (DTPA). For the separation of Tc and PGM, two methods were studied; one is the precipitation by denitration and the other is the adsorption with active carbon. An adsorption method with inorganic ion exchangers (titanic acid and zeolite) was developed for the separation of Sr and Cs.

3. Outline of the facility

In the partitioning facility, 2 to 20 L of HLLW (5000 Ci at maximum) can be treated per experiment. The reprocessing facility, which was installed in the same hot cell in NUCEF, will provide real HLLW. The partitioning facility can also accept HLLW from other reprocessing plants.

Main components in the facility are Denitration and Concentration Vessel, Filter Unit, Extractors, Adsorption Columns and the related equipments. In the Denitration and Concentration Vessel, 6 L of HLLW can be concentrated and 2 - 3 L of HLLW can be denitrated. Precipitates formed in this vessel are separated by sintered-metal filter in the Filter Unit. Two 16-stage mixer-settler units are installed for the separation of TRU from HLLW. The process to be tested with these extractor units is composed of the following three steps: extraction with DIDPA, back-extraction with 4 M HNO₃ and back-extraction with H₂C₂O₄, steps surrounded by broken lines in Fig. 2. Other steps of extraction and back-extraction can also be tested by changing the reagents and by changing the mixer-settlers if required. Particularly, the separation of Am, Cm from lanthanides by selective stripping with DTPA is one of the most important items to be tested in the future. The Adsorption Columns can be used in two adsorption processes; one is adsorption of Tc and PGM with active carbon and the other is adsorption of Sr and Cs with inorganic ion exchangers. Precipitation of Tc and PGM by denitration is also examined using the Denitration and Concentration Vessel.

The flow sheet of the partitioning test facility is shown in Fig. 3. The facility is also equipped with a vessel for oxalate precipitation.

4. Partitioning tests with simulated HLLW

Partitioning tests with simulated HLLW are now in progress. The results will be compared with those of the tests with real HLLW, as mentioned above. The tests with simulated HLLW showed that all the components in the facility could be operated safely and remotely.

In the latest test, phosphoric acid was added to HLLW before denitrification as pre-treatment for the DIDPA extraction in order to completely remove Zr, which sometimes disturbs the DIDPA extraction. About 99.5 % of Zr were removed from the simulated HLLW as a precipitate in this pre-treatment step. In the DIDPA extraction step, lanthanides were almost completely extracted with DIDPA and well back-extracted with 4 M HNO₃. Table 1 shows fractional distribution of each element. The ratio of Nd extracted was more than 99.99 %. Since the extraction behavior of Am is very similar to that of Nd, Am would also be extracted with the high yield in this step. The back-extraction of lanthanides was not complete but would be improved by
adding one more stage (presently 5 stages) and/or by raising temperature. Other elements except Fe were not extracted and therefore well separated from lanthanides. Fe was stripped from the solvent in the second back-extraction step with H$_2$C$_2$O$_4$ with a yield of 99.8 %.

Element behavior at the following steps in the 4-group partitioning process will be investigated in the next test.

5. Future plan

In 1996 - 97, tests with some tracers ($^{237}$Np, $^{99}$Tc, etc.) in simulated HLLW will be performed to examine the behaviors of the elements that are not contained in the simulated HLLW. Partitioning tests with real HLLW are scheduled in 1998. The separation of Am and Cm from lanthanides will be included in the test with real HLLW. Further, the facility will be used for the test of a new partitioning process with real HLLW.

<table>
<thead>
<tr>
<th>Element</th>
<th>Raffinate</th>
<th>Back-extracted with 4M HNO$_3$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>&lt; 0.002</td>
<td>5.6</td>
<td>94.4</td>
</tr>
<tr>
<td>La</td>
<td>&lt; 0.06</td>
<td>&gt; 99.93</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Nd</td>
<td>&lt; 0.01</td>
<td>98.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Gd</td>
<td>&lt; 0.04</td>
<td>97.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe</td>
<td>4.64</td>
<td>0.52</td>
<td>94.84</td>
</tr>
<tr>
<td>Ru</td>
<td>98.7</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Rh</td>
<td>&gt; 99.0</td>
<td>0.9</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Pd</td>
<td>98.2</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Sr</td>
<td>&gt; 99.98</td>
<td>0.02</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Ba</td>
<td>&gt; 99.99</td>
<td>0.01</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Rb</td>
<td>&gt; 99.96</td>
<td>&lt; 0.03</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Cs</td>
<td>&gt; 99.90</td>
<td>&lt; 0.07</td>
<td>&lt; 0.03</td>
</tr>
</tbody>
</table>
Fig. 1 The 4-Group Partitioning Process to be tested in NUCEF using real high-level liquid waste.
Fig. 2 DIDPA Extraction Process including the Separation of Am and Cm from Lanthanides. - Two-Cycle Process -
Fig. 3 Flow Sheet of the Partitioning Test Facility in NUCEF
ENHANCEMENT OF CONFINEMENT CAPABILITY OF LONG-LIVED NUCLIDES
IN A SIMPLIFIED FUEL CYCLE

Sachio FUJINE, Gunzo UCHIYAMA, Takehiro KIHARA, Toshihide ASAKURA,
Tsutomu SAKURAI and Mitsuru MAEDA
Japan Atomic Energy Research Institute(JAERI)

ABSTRACT

Study on PARC(Partitioning Comumdrum Key) process concept is under way using Back-End Cycle Key Elements Research Facility(BECKY) in NUCEF. Reprocessing should be performed economically and safely. Process simplification will be effective to improve economical competitiveness. And enhancement of confinement capability of long-lived nuclides will be effective to improve the safety standard and to ease the people's anxiety about reprocessing wastes. Those two measures are apparently contradictory each other. However, both measures are closely linked and interdependent in some cases. We are studying simplified reprocessing concept PARC which is expected to reduce risks due to long-lived nuclides in the reprocessing waste management, not only in the geological disposal but also in the environmental releases.
1. Introduction

It is important that the application of separation and transmutation functions of long-lived nuclides does not pose a substantial increase of economical burden on actual nuclear fuel cycle. According to the study until now, neptunium(\(^{237}\)Np), technetium(\(^{99}\)Tc), plutonium, americium and iodine(\(^{129}\)I) are assessed to take relatively significant role on potential hazard as long-lived elements in HLW.

\[\text{Spent fuel} \rightarrow \text{Controlled Dissolution (Control of species)} \rightarrow \text{Collection of C-14/I-129} \rightarrow \text{I-129}\]

\[\text{Simplified Coextraction (One Cycle)} \rightarrow \text{Separation of Am/Cm (Extraction, Others)} \rightarrow \text{Cm} \rightarrow \text{Cooling Storage}\]

\[\text{Separation of Np and Tc (Selective reduction)} \rightarrow \text{Am} \rightarrow \text{Np} \rightarrow \text{Tc} \rightarrow \text{Am}\]

\[\text{U/Pu Partitioning (High Pu recovery rate)} \rightarrow \text{Target for Transmutation} \rightarrow \text{Transmutation}\]

\[\text{U} \rightarrow \text{Pu} \rightarrow \text{Molten Salt} \rightarrow \text{Sphere, Vipac (Nitride, Metal)} \rightarrow \text{Accelerator} \rightarrow \text{Fission Reactor}\]

Fig. 1 Advanced nuclear fuel cycle applied PARC process concept

Np and Tc are special elements which easily diffuse into products in reprocessing and migrate fast in geological matrix, too. This characteristic property makes those elements assessed as highly potentially
hazardous. Although Pu and the daughter Am do not migrate fast in geological matrix, the influences of these elements are estimated to be significant because of the increased amount recycled in the future fuel cycle. I-129 and C-14, the latter has been assessed from long ago to have a significant influence on the public health, are volatile and easy to be released into the environment. Those nuclides, alike Kr-83, are assessed to be relatively influential on the effective dose of inhabitants near reprocessing facility. Technologies for economical and effective separation of the above-mentioned long-lived nuclides are expected to be useful for enhancement of radioactivity confinement capability in reprocessing. Particularly, enhancement of separation efficiency for the elements which are susceptible of diffusing into products, such as Np and Tc, improves the performance of separation step. From these points of view, we are studying PARC concept of reprocessing incorporated with transmutation function of long-lived nuclides. Figure 1 shows our concept of fuel cycle in the future.

2. Back-End Cycle Key Elements Research Facility BECKY for Chemical Process Study

A research facility, NUCEF-BECKY, has been utilized in JAERI at 1995 to study nuclide behaviors in chemical processes and to study feasibility of advanced processes. Miniature scale experimental equipment has been installed in a small-scale α γ cell of BECKY with a capacity of 3kg/y of highly radioactive spent fuel. Main flow sheet of equipment for reprocessing study is shown in Fig.2.

Fig.2 Schematic diagram of experimental equipment for reprocessing in α γ cell of BECKY-NUCEF

Experiments started with uranium mixed with simulated fission products for preparing actual hot test
with spent fuel around 1997. Data of dissolution, iodine distribution and extraction have been collected so far. Distribution profiles of iodine in the head-end process were measured using I-131 as a radioactive tracer. Concentration of nitrous acid were measured in continuous dissolver and pulsed columns. Chemical process study program consists of five subjects: (1) Kinetics study of spent fuel dissolution, (2) Feasibility of simplified extraction process, which separates Np and Tc as well as U and Pu, (3) Assessment of capability of minor radioactive nuclides confinement in the process, (4) Development and verification of process simulation code, (5) Adsorption technique of iodine and carbon-14 from dissolver off-gas.

Fig.3 PARC process concept; Advanced Purex incorporated with partitioning function
3. Simplified Chemical Processing

We have proposed "PARC (Partitioning Conundrum Key) process\(^{(23)}\), as shown in Fig. 3. This is a challenging program to enhance confinement capability of long-lived nuclides in a simplified reprocessing. This process is designed to separate long-lived nuclides; diffusing Np-237 and Tc-99 in extraction, volatile C-14 and I-129 in head-end, and minor actinide Am from acidic raffinate. Used acid and organic solvent are recycled in the process. Principal features are as follows,

- Simplifying the chemical process
- Enhancement of separation efficiency of the extractable Np and Tc as well as Pu and U.
- Removal of C-14 and I-129 from the off-gas in head-end.
- Recovery of the inextractable minor actinides Am as much as possible
- Recycle use the used reagent at the maximum.

![Graph showing separation of Np and Tc in one-cycle extraction flow sheet](image-url)
4. Separation Technique of Np-237 and Tc-99

Extraction flow sheet of PARC is designed as one-cycle process based on Purex technology as the primary option, since extractant TBP exhibits sufficiently high separation ability on the major elements; uranium and plutonium. Neptunium and technetium are separated from U and Pu before U/Pu separation step in one-cycle extraction by applying innovative valence control technique (4). Figure 4 shows concentration profiles obtained in a flow sheet experiment using mixer-settlers. Very high recovery rate of Np, over 99.9%, has been demonstrated by conducting selective Np reduction with a decomposable reagent butyraldehyde for a Np-Tc and U solution system. 99.98% of Np, extracted together with U in the co-decontamination step, was reduced by n-butyraldehyde and separated from U in Np separation step. More than 99.8% of Tc was separated from U in Tc separation step using 5.5M nitric acid scrub solution. In a separately conducted experiment, Pu was separated from U using iso-butyraldehyde effectively without applying hydrazine for a Np, U and Pu solution system. Decomposition of butyraldehyde has been studied in order to get rid of side effect on the separation efficiencies in the down streams. Decomposition fraction calculated from measured concentrations of total organic carbon in aqueous solution is shown in Fig. 5. It was found that more than 99% of n-butyraldehyde was decomposed within 50 minutes with silver catalyzed electrochemical oxidation. Air bubbling without electrochemical oxidation decomposed app. 90% of n-butyraldehyde in 1 hr.

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Fig. 5 Decomposition of selective organic reagent, n-butyraldehyde

As the basis of one-cycle extraction process development, have been collected data of Np and Tc
behaviors under a standard flow sheet condition of a large scale Purex type reprocessing plant. It was found that approx. 99% of Tc was extracted with U and Zr by TBP and only 1% of Tc was transferred into the raffinate of co-decontamination step. Approximately 30% of Np was transferred into the raffinate.

5. Technique for capturing I-129 and C-14

Iodine-129 is controlled to be released to dissolver off-gas (DOG) completely and removed by AgS (Silver impregnated Silica-gel). In order to assess confinement capability of volatile long-lived iodine I-129, iodine distribution in BECKY experimental equipment of head-end process (shown in Fig.2) was measured under continuous dissolution of unirradiated simulated spent fuel(5). Pellets of the simulated spent fuel consist of uranium and non-radioactive fission product elements. A trace amount of radioactive iodine I-131 was added as KI to dissolver under operation. Nitrous acid concentration was high at approx. 3x10^-3 mol/l as shown in Fig.6. Most of iodine was released to DOG and captured completely by iodine adsorbent columns under condition of linear off-gas velocity up to 22 cm/s and adsorbent temperature at 150°C. Amount of iodine captured in columns is estimated to be approx. 74% iodine loaded in dissolver. Less than 1% of iodine loaded was remained in fuel solution. The other iodine was distributed in HEPA filter by 11%, inside surface of pipes by 2%, insoluble residue and others by 12%, respectively. Colloidal formation with fission products such as AgI or PdI_2 is considered to be predominant retention mechanism under iodine concentration less than 10^-6 mol/l in solution(6).

![Graph showing Uranium and nitrous acid concentrations in continuous dissolver](image-url)
Major chemical form of C-14 is carbon dioxide (CO$_2$). CO$_2$ is released to DOG under dissolution of spent fuel. As an adsorbent, hydrogenated mordenite, which is capable of reversible adsorption-desorption of CO$_2$, has been selected after screening test of various kinds of adsorbents. Breakthrough curves of CO$_2$ show adsorption capacity of hydrogenated mordenite is improved under lower temperature.

6. Development of Simulation Codes

Process simulation code system ARECS (Fig. 7), associated with fundamental reprocessing data-base, has been developed to simulate chemical process system composed of dissolution, off-gas treatment and extraction process. This code system is capable of simulating the behaviors of not only U and Pu but also long-lived minor nuclides such as I-129, C-14, Np-237, Tc-99 which are important in the development of nuclear fuel cycle technology. And, a computer code has been developed to simulate generation and migration of very short-lived volatile nuclide such as I-131 by spontaneous fission of TRU nuclides. TRU nuclides such as Cm-244 generate various very short-lived volatile nuclide by spontaneous fission.
8. Conclusion

Development of chemical process technology for PARC concept is under way using Back-End Cycle Key Elements Research Facility (BECKY) in JAERI. High efficiency was demonstrated for separation of Np-237, Tc-99, I-129 and C-14 under a simulated condition. It is expected that technologies for enhancing confinement capability of long-lived nuclides improve the safety standard and to ease the people's anxiety about reprocessing wastes.

REFERENCES

Summary

Research and development of a simplest process of disposing of high-level radioactive waste, Super High Temperature Method, has been carried out. Batch pouring process of continually supplied fused and molten raw material of calcinated waste has been investigated. This process has successfully delivered two good products of platinum group element alloys and solidified HAW of highly reduced volume which may contain actinide elements.

1. Introduction

Two lines of research and development have been carried out as to HLLW Management. One way is to obtain solidification of HLLW to store it for several tens of years and then bring it to underground disposal. A second is that by transmutation. Namely, partitioning long-lived nuclides out of HLLW and transmuting them into nuclides of shorter lives. Research and development of retrieving useful elements out of HLLW has also been carried out and put to practical use too. Effective utilization of elements contained in HLLW is acknowledged to be an important subject. It will, however, be left out of this paper, because the principal subject here is to present the trend of HLLW management simply and clearly.

There have often been disputes between two lines of research and development. Selection of the nuclides to be put to transmutation was one of subjects of disputes. Prof. Pigford has pointed out, "Minor actinides that are thought to be highly toxic will be stably maintained under the environment of the underground disposal. In selecting the objects of transmutation, they should be fission product nuclides of relatively high mobility." There has been no true technical discussion as regards this suggestion.

Another subject of a dispute is that about the accountability. A transmutation facility will have to be operated in order to carry out transmutation of the nuclides. Operation of the facility will require energy. This energy will be supplied by nuclear power generation. Nuclear fission products will be produced by operating nuclear power plant. The total amount of toxicity of the nuclear fission products is required to be less than the amount of nuclides that is put to transmutation. Furthermore, there is another problem of the total amount of wastes generated in the whole nuclear fuel cycle mainly involved in nuclear power generation for operating the facility. Also the facilities and the installations will become wastes. The facilities to be used for transmutation of specific kinds of nuclides are bound to be contaminated. This issue either has not been put to relevant discussion. Other concerns are related to social acceptability of the underground disposal and realizability of transmutation. Political and generic measures to cope with these problems are being investigated in France.[1]

Apart from these discussions, technology aiming at reasonable HLLW management is subjected to research and development recently.

It is the concept of "Reprocessing-Separation-Conditioning-Disposal" together with research and development of industrial technology that makes the concept feasible. Super High Temperature Method by Japan, Partitioning-solidification technology by former USSR, proposal of Separation-Conditioning (S-C) concept.
by France, SYNROC Solidification of partitioned actinides by Australia are included. Waste Minimization by U.S. also may be in the same line.[2]

The method by former USSR is in partitioning HLLW into several groups of fission products by means of extraction or ion exchange and solidifying each group separately. In one of these processes HLLW is partitioned into fission products and transition metal elements (Zr, Mo,Pd etc.). FPs are vitrified. Transition metals are cemented. Other than vitrification, Synroc Solidification by melting has also been developed. Cold crucible method has been developed as for solidification technique. 1996, the First Committee of Nuclear Ministry of Russia(MINATOM) decided to extend this method further.

France established a law in order to proceed research and development concerning High Level Waste Management with centralized concern about waste management including P/T. An annual report of each organization which checks and reviews the research and development activities is published in accordance with this law. The first report in 1995 describes the concept of Separation-Conditioning(S-C). France considers the reprocessing process a unified process of reprocessing and waste management. (They are not necessarily treated in the same way in other countries. Reprocessing plants are closed in those countries and management of HLLW in hand is a subject of concern). France is making an effort to reduce the output of radioactive wastes to an utmost limit in reprocessing process based on the above mentioned concept.

Development of a cold crucible is being carried out in order to cope with obsolescence of the melting furnace. This technique is in the stage of technical completion.

In Australia, Research of Synroc solidification of actinides separated from HLLW is being carried out. Development of the above mentioned solidification technique by Russia and development of the oxide solidification technique by Super High Temperature Processing Method by Japan that will be described later are both in the line leading toward the method of solidification unexpectedly similar to Synroc Concept created by Prof. Ringwood.

In the United States research and development is being carried out based on the idea of minimizing the waste generated in the reprocessing plant for military purposes. However, this idea is not carried through HLLW management. A huge vitrification plant is being brought into operation. At INEL, on the other hand, research and development of Separation-Conditioning is just being carried out. Structuring of the overall concept of Waste Minimization of HLLW may be required.

As to S-C in Japan, partitioning by wet method and solidification of each group was proposed by JAERI. Development of partitioning technique is being mainly carried out at JAERI, while development of vitrification technique is not being carried out.

Super High Temperature Method in Japan is a new S-C technique by metallurgical procedure. In the beginning, this method was started aiming at solidification of HLLW without addition of matrix material like glass. It was discovered in the stage of research that highly exothermic FP, cesium, is vaporized and separated, that elements of the platinum group are reduced by adding reducing agents and separated as alloys, and that other FP oxides (including actinides) are melted and solidified.

Selection of the reductant is an important subject in Super High Temperature Method. Platinum group elements are those which can be easily reduced among HLLW FPs. Insoluble materials in spent fuels are small particles of alloys formed by the platinum group elements in FP under the condition of oxygen shortage.

Platinum group elements are reduced when the calcine is heated in the inactive atmosphere, and small
particles of alloys are formed. Small particles of alloys are dispersed in the calcine of oxides of FP elements which are not reduced under this condition. When the calcine is heated with addition of reductant, the whole system is melted and the metal and the oxide phases are separated into upper and lower layers. The principal action of the reductant consists of reduction of the transition metal elements included in FP. As the results of reaction, the transition metal elements including platinum group elements form alloys of relatively low melting points. And also, the reductant produced by reaction is an oxide itself. This oxide forms a composite oxide of relatively low melting point.

The reductants are selected from elements with intermediate value of the standard free energy of oxide phase formation and that of metal phase formation. Also, it is chosen to be one of elements which bring about the phenomenon of lowering of melting point. Results of selection of favorable candidate elements are boron, aluminum, silicon, and titanium.

When boron is adopted the oxide phase is of poor water resistance. When aluminum is adopted lowering phenomenon of melting point is relatively weak, thus the temperature of treatment is required to be brought up. When silicon is used, the oxide phase becomes glassy. Namely, vitrification is attained within Super High Temperature Method. When titanium is used, separation of two phases is effective, and the oxide phase is water resistant also. Therefore, at this time, silicon and titanium are favorable as reductant.

Processing with titanium compounds were adopted for current experiments. Titanium alloys, titanium carbide, and titanium nitride are applicable as reductant of titanium compounds. Since titanium alloys in the form of particle, it is feared that homogeneity of mixing with calcine might be insufficient. Since titanium carbide and titanium nitride are in stable powder form, mixing with calcine will be easy. Titanium nitride has been chosen this time.

Reductants are titanium or reducing titanium compounds. Titanium is turned into titanium oxide as the result of reaction and introduced into the oxide phase. Titanium constitutes composite oxides with rare earths, alkaline earths, zirconium, etc. that constitutes oxide phase. By this method, separation of cesium, retrieval of elements of the platinum group, and high volume reduction and solidification are achieved through simple procedures.

In this report, results of experiments concerning continuous supply of simulated calcine-retrieval of the platinum group elements by batch flow down process-preparation of solidification of highly reduced volume will be presented.

2. Process of Super High Temperature Method

The Process of Super High Temperature Method is as follows:

HLLW → Calcination → Sublimation → Reduction → Melting → Pouring → Separation → Storage

High level liquid waste is brought into composite oxides of fission products through calcining process. Cs etc. are separated through vaporization of the calcine.

Oxides of platinum group elements are reduced into metallic phase and partitioned from the oxide phase of rare earth elements and other elements by processing at 1000 C with the reductant of titanium nitride. The system is then processed by melting at 1600 C in order to be partitioned into two phases of metal and oxide.

3. Objectives of the experiments

Up to this stage, experiments have been carried out using 20 g of simulated calcine and a crucible of 30 ml in order to determine the conditions of reduction and fusion-separation of the platinum group elements. Next stage will be developing the technological facilities. A cold crucible technology is presumed for the melting
facility. As a preliminary experiment for this process, a method of heating the crucible for melting by high frequency induction and subsequently melting the calcine by conduction heating from it has been investigated. In the process of melting, the calcine is continually supplied. As to crucibles, there are two ways of methods one of which is using the same crucible for melting and also for solidifying, and another is to provide these two sorts of crucibles separately. By the former method the surface portion of the solidification will not be melted homogeneously. It is required to establish a method of obtaining a satisfactory solidification by the latter. Two procedures were examined in comparison.

4. Experiments

Sample material:
Calcine of equivalent composition to that after sublimation was prepared by blending commercially available oxides of reagent grade. The amount of the reagent is several hundreds of grams.

Heating:
The melting temperature is 1600°C. The apparatus is shown in Fig. 1.
Three ways of heating were carried out.
1. A carbon crucible was heated by high frequency induction method.
2. A boron nitride crucible placed in a carbon crucible which was heated by high frequency induction was in turn heated by conduction method.
3. A method to pour the melt from the nitride crucible as above into the receptacle installed underneath (Fig.2).

Melting:
The sample material was melted by continuously feeding it into the crucible in terms of a vibration feeder.

Pouring:
In the three methods as mentioned above, molten sample material was poured into the receiving crucibles (kept at protection temperature) through a bottom hole of the melting crucible.

Solidification:
Sample material was released to be solidified by deenergizing the protective heating of the melting crucible or the receiving crucible.

5. Results and discussion

(1). The method of high frequency induction heating the carbon crucible.
In this case the metal and the oxide phases are separated into the upper and the lower layers. However, the state of separation is not clear-cut. Also there are voids in the oxide phase. This is thought to be attributed to the reduction reaction caused by the crucible material, carbon.

(2). The method of conduction heating the nitride crucible which is placed in a carbon crucible heated by high frequency induction.
In this case the metal phase and the oxide phase are separated into upper and lower phases. Separation of the metal ingot is appreciable also. No void is observed in the oxide phase. It is thought because the crucible material, boron nitride does not generate reduction reaction that gives out bubbling action. However, the surface of the oxide phase is not clean.

(3). The method of pouring down into the receiving crucible installed underneath from the boron nitride crucible in the procedure (2).
In this procedure, the metal phase and the oxide phase are separated cleanly. The metal ingot is also separated well. There is no void observed in the oxide phase. The surface of the oxide phase is clean (Fig.3).
I has been confirmed that normal metal and oxide layers can be constituted by the process of continuous feed and batch pouring. Feasibility of formation of normal products has been demonstrated by making it possible to melt the calcine at high temperature in terms of the cold crucible process, although the melting in this experiment was carried out by thermal conduction method.

References:
Fig. 1 The experimental apparatus

Fig. 3 Oxide and Metal obtained by the method of pouring down
Fig. 2 Crucibles of the method of pouring down
BASIC STUDY OF PHOTOCHEMISTRY FOR APPLICATION TO NUCLEAR FUEL CYCLE TECHNOLOGY

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Abstract

In this study, we have accomplished for the first time the photochemical valence adjustment of Pu and Np for the separation and coextraction of these elements in a nitric acid solution using UV light irradiation. Also, the separation and coextraction of Pu and Np were substantiated in principle by the photochemical and solvent extraction operations. The separation and coextraction of Pu and Np by solvent extraction using 30% TBP/n-dodecane were carried out during and after the photochemical valence adjustment. By only one photochemical separation operation, about 86% of Pu and about 99% of Np were distributed into the organic phase and the aqueous phase, respectively, and then by only one photochemical coextraction operation, about 86% of Pu was distributed together with about 99% of Np into the same organic phase. Based on these experimental data, we determined that the photochemical oxidation reaction was due to the photoexcited nitric acid species, \( *\text{NO}_3^- \). Using the strong oxidative ability of this species, the photochemical dissolution of UO\(_2\) powder in a nitric acid solution by UV light irradiation was also accomplished for the first time at room temperature (20 °C). Photochemical dissolution tests of UO\(_2\) powder ranging 1 mg to 100 mg suspended in 2 ml of 1-6M HNO\(_3\) solutions were carried out at room temperature using a Hg lamp. From the results of the tests, 10 mg of UO\(_2\) powder was completely dissolved in 2 ml of a 3M HNO\(_3\) solution at 20°C under an irradiation rate of 1.3 W/cm\(^2\) for 40 min.
1. Introduction

Most nuclear fuel reprocessing plants have been adopting the PUREX process technologies. Uranium(U) and plutonium(Pu) in spent nuclear fuel are recovered and refined using these technologies with a high recovery efficiency.

Neptunium(Np), however, is distributed on both sides of the nuclear fuel production and also in highly radioactive aqueous waste. This phenomenon is caused because of the difficulty in valence adjustment of Np using various chemical reagents in nitric acid solution$^{(1)}$-$^{(3)}$.

It is generally supposed that photochemical techniques offer a potential for selectivity in systems where chemical methods offer little selectivity. From that point of view, photochemical studies of U, Pu and neptunium(Np) have been carried out for separation and reprocessing techniques mainly in the USA. These studies can be divided into several categories which are the studies for the photochemical behavior of nuclear fuel$^{(4)}$-$^{(8)}$, Np$^{(9)}$-$^{(12)}$ and photochemical reprocessing technologies$^{(13)}$-$^{(15)}$. These studies, however, only describe the fundamental photochemical behavior of these elements' valences and did not carry out quantitative valence adjustment for the separation and coextraction of Np with experimental data. They did not then discuss the mechanism of the photochemical redox reaction such as our suggestion involving a photoexcited nitric acid species$^{(6)}$, we report the results of the quantitative photochemical separation and coextraction experiments of Pu and Np and then we have considered that the photoexcited nitric acid species, *NO$_3^-$*, contributed most effectively to the oxidation reactions of Pu and Np. These reactions are caused by a higher redox electrode potential of the photoexcited species than that of the ground state species, NO$_3^-$.$^{(17)}$-$^{(19)}$. Based on the results, we have also attempted to use the strong oxidative ability of *NO$_3^-$* for the dissolution reaction of UO$_2$ powder at room temperature.$^{(20)}$.

2. Experimental

2.1 Apparatus and analysis

As the light source, a super high-pressure Hg lamp (WACOM Co., Ltd. BMO-250DI) was used in the wavelength range of 250 nm to 600 nm. The maximum output intensity was 1.5 W/cm$^2$. The homogeneity and temperature of the test solution were kept constant using an electric temperature stabilizer and a magnetic stirrer during the tests.

The valences of Pu and Np in nitric acid solutions were analyzed using an spectrophotometer (Shimazu UV-1200).

2.2 Preparation of test solution and UO$_2$

The Pu stock solution was previously refined using an anion exchange column americium(Am) was removed from the solution. The concentration of Pu in the solution was calculated using its specific $\alpha$-radioactivity obtained by mass spectrometric analysis and the data obtained by the $\alpha$-ray counting method. The analyzed isotopic composition is shown in Table 1.

The $\alpha$-radioactive purity of Np-237 in the Np stock solution was 100.0% and the concentration of Np in the solution was also determined by the $\alpha$-counting method.

The test solutions of Pu and Np mixed solution containing additional reagents such as hydroxylamine nitrate(HAN) and hydrazine(HDZ) or urea, which were all reagent grade, were prepared by mixing their stock solution and additional reagents for about 10 mins. before the start of the irradiation test.

The specific properties of the UO$_2$ powder used for the tests are shown in Table 2.
Table 1 Isotopic composition of Pu used in test

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Pu-238</th>
<th>Pu-239</th>
<th>Pu-240</th>
<th>Pu-241</th>
<th>Pu-242</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abundance (Wt%)*</td>
<td>0.148</td>
<td>75.79</td>
<td>21.51</td>
<td>1.855</td>
<td>0.697</td>
</tr>
</tbody>
</table>

*: Analyzed on Feb. 10, 1993

Table 2 Specific properties of UO₂ Powder used in tests

<table>
<thead>
<tr>
<th>U content (%)</th>
<th>O / U</th>
<th>Ave. par. size (μm)</th>
<th>Density (g/cm³)</th>
<th>Spec. surf. area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.73</td>
<td>2.06</td>
<td>0.68</td>
<td>1.96</td>
<td>4.28*</td>
</tr>
</tbody>
</table>

*: BET method
2.3 Experimental procedure

The photochemical valence adjustment and solvent extraction test experiments were carried out as follows.

(1) Photochemical valence adjustment
For Pu and Np in a nitric acid solution, the extractable valences are Pu(IV and VI) and Np(IV and VI), while the inextractable valences are Pu(III) and Np(V) with 30 % TBP/n-dodecane. It is the purpose of this study to determine whether the photochemical technique can adjust the valences of Pu and Np to suitable valences for their separation or coextraction.

For the separation experiments, the initial valences in the test solutions of Pu and Np were previously adjusted to Pu(III) and Np(V) using HAN and HDZ before the light irradiation. It was then evaluated whether Pu(III) could be photooxidized to Pu(IV) and Pu(VI) (extractable valences) by the irradiation, and Np(V) (inextractable valence) remained at the same valence during the light irradiation. On the other hand, during the coextraction experiments, the initial valences in the test solutions containing urea were Pu(IV, VI) and Np(V). It was then evaluated whether the light irradiation could completely adjust them to Pu(IV, VI) and Np(VI) (all of these valences being extractable). Furthermore, their valence behavior was also examined under no light irradiation (dark reaction) for the comparison to that under the light irradiation.

Two ml of the test solution was placed in a 1cm square quartz cell generally used for photospectrometry. The cell was then irradiated using the Hg lamp for an appropriate time. The changes in the Pu and Np valences were measured by the photospectrometer at specified intervals using the quartz cell containing the test solution. In these tests, the experimental variables included the irradiation rate (0, 0.05, 0.15 and 1.45 W/cm²) and the concentration of HNO₃ (0.4, 1, 2 and 3 M).

(2) Solvent extraction
First, for the separation of Np from the Pu and Np mixed solution, 1 ml of the 2M HNO₃ solution containing Pu (1.0x10⁻³ M), Np (1.0x10⁻³ M) and HAN+HDZ (8.0x10⁻² M each), and 1 ml of 30 % TBP/n-dodecane were placed in the quartz cell. The cell was set into the cell holder which contained the temperature stabilizer and stirrer, and the light irradiation and the solvent extraction were then started simultaneously.

In the case of the coextraction operation, 1 ml of the 3 M HNO₃ solution containing Pu (1.0x10⁻³ M), Np (1x10⁻³ M) and urea (8.0x10⁻² M), and 1 ml of 30 % TBP/n-dodecane were used. In one case, the light irradiation and the solvent extraction were simultaneously carried out. In the other case, the solvent extraction operation was done after the photochemical valence adjustment.

After specified intervals of the solvent extraction operation, aliquots of both phases were taken out of the other cell and analyzed using the spectrophotometer.

(3) Photochemical dissolution
1-100mg of UO₂ powder are weighed precisely and are placed in a quartz cell, normally used in photospectrometry, containing 2ml of a nitric acid solution. The solution is then irradiated using the Hg lamp, and the absorption spectrum of the solution is measured at the appropriate irradiation time.

The photochemical dissolution fraction of the UO₂ powder is calculated by the ratio between the absorbances Ai and At of UO₂²⁺ at 425nm and an arbitrary time i and t, which is the complete dissolution time at t, as follows.
Dissolution fraction(%) = \( \frac{A_i}{A_t} \times 100 \) (1)

\( A_i \) : Absorbance at time \( i \).
\( A_t \) : Absorbance at time \( t \) of the complete dissolution time.

The concentration of nitrous acid, HNO\(_2\), a by-product of the UO\(_2\) dissolution reaction, is also determined by the absorbance of the test solution at 370nm and a calibration curve which is obtained by analysis of standard concentrations of HNO\(_2\) from 1.0X10\(^{-3}\) to 5.0X10\(^{-2}\) M.

The temperature and the homogeneity of the solution are kept constant with a temperature stabilizer and a magnetic stirrer during an irradiation test.

The experimental variables are the irradiation rate whose levels are 0, 0.7 and 1.3W/cm\(^2\), the concentration of HNO\(_3\) whose levels are 1, 3 and 6M and the weight of the UO\(_2\) powder whose levels are 1, 10 and 100mg.

3. Results and discussion
3.1 Photochemical valence adjustment
For the photoreaction tests, three kinds of experimental conditions for the Pu and Np mixed solution were adopted.

1. the examination of the photochemical behavior of Pu and Np valences in the nitric acid solution without the addition reagent,
2. the valence adjustment for the separation of Np from Pu, and
3. the valence adjustment for the coextraction of Np with Pu.

(1) Photochemical reaction of Pu and Np without addition reagent
Figure 1 shows the results of the photochemical reaction of Pu and Np in 3 M HNO\(_3\) solution containing no additional reagent under the conditions of 1.40 W/cm\(^2\) irradiation rate and 20 °C.

![Fig.1 Change in absorption spectra by photochemical reaction in Pu, Np mixed 3M HNO\(_3\) solution containing no additional reagent vs. irradiation time](image-url)
As seen in this figure, around 85% of Np(V) decreased and was photooxidized to Np(VI) within 15 mins. After that, the reverse reaction of Np(VI)→Np(V) progressed predominantly, and then Np(V) gradually increased. This phenomenon is caused by the relationship between the oxidation reaction of the photoexcited nitric acid species\(^\text{(16)}\), \(*\text{NO}_3^-\), and the redox reaction by nitrous acid\(^\text{(22)}\), \(\text{NO}_2^-\) of the photolysis product as follows.

- The oxidation reaction of Np(V)→Np(VI) by \(*\text{NO}_3^-\)

\[
\begin{align*}
&\text{\(*\text{NO}_3^-\cdot 3\text{H}^+ + 2\text{e}^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O},\)}

&\begin{array}{c}
\text{NpO}_2^{2+} + \text{e}^- \rightarrow \text{NpO}_2^{+},
\end{array}

\downarrow

&\text{\(*k_{5-6}\)}

&\text{\(*\text{NO}_3^-\cdot 2\text{NpO}_2^{2+} + 3\text{H}^+ \rightarrow 2\text{NpO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O}\)}

\end{align*}
\]

where \(*k_{5-6}\) : photochemical reaction rate constant.

- The reduction reaction of Np(VI)→Np(V) by \(\text{HNO}_2\)

\[
\begin{align*}
&\text{\text{NpO}_2^{2+} + \text{e}^- \rightarrow \text{NpO}_2^{+},}\n
&\text{\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O},}\n
\downarrow

&\text{\(k_{6-5}\)}

&\text{2\text{NpO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NpO}_2^{2+} + \text{NO}_3^- + 3\text{H}^+  \quad (3)}

\end{align*}
\]

where \(k_{6-5}\) : reaction rate constant.

Pu(IV) is also photooxidized to Pu(VI) by the photoexcited nitric acid species and a part of the Pu(VI) is reduced to Pu(IV) by nitrous acid\(^\text{(22)}\).

As seen in Figure 1, if the decomposition reagents such as HDZ\(^\text{(24)}\) or urea\(^\text{(25)}\) were not contained in the Pu and Np mixed solution, the complete valence adjustment for their separation or coextraction would not be attained using the Hg lamp irradiation.

(2) Photochemical valence adjustment for separation

1. Effect of concentration of \(\text{HNO}_3\)

Mixed solutions of 1×10⁻³ M Pu and Np containing reductants, 1×10⁻² M of \(\text{HAN}\) and HDZ, were prepared by changing the \(\text{HNO}_3\) concentration to 0.4 M, 1 M, 2 M and 3 M. These solutions were then examined at the irradiation rate of 0.15 W/cm². Figures 2 and 3 show the results of the irradiation tests at concentrations of 2 M and 3 M \(\text{HNO}_3\), respectively. All of the results under the condition of each acidity are shown in Table 3. These data are calculated as the average reaction rate as follows.

Average photochemical reaction = \[
\frac{\text{Variation value (mol)}}{\text{Average photochemical reaction (M/min)}} \quad \text{Reaction time (min)} \quad (4)
\]
Fig. 2 Change in Pu and Np valences by photochemical reaction in 2M HNO₃ containing HAN and HDZ vs. irradiation time.

Fig. 3 Change in Pu and Np valences by photochemical reaction in 3M HNO₃ solution containing HAN and HDZ vs. irradiation time.

(a) Change in absorption spectra.

(b) Change in abundance of valences.
Table 3  Change in photochemical reaction rate according to increase in acidity

<table>
<thead>
<tr>
<th>Acidity($\text{HNO}_3$) (M)</th>
<th>Average photochemical reaction rate (mol/min)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pu(III)$\rightarrow$Pu(IV) Pu(IV)$\rightarrow$Pu(VI) Np(V)$\rightarrow$Np(IV) Np(V)$\rightarrow$Np(VI)</td>
</tr>
<tr>
<td>0.4</td>
<td>$1.07 \times 10^{-6}$ $6.76 \times 10^{-7}$ - -</td>
</tr>
<tr>
<td>1</td>
<td>$5.78 \times 10^{-6}$ $6.10 \times 10^{-6}$ - -</td>
</tr>
<tr>
<td>2</td>
<td>$1.27 \times 10^{-5}$ $1.07 \times 10^{-6}$ - -</td>
</tr>
<tr>
<td>3</td>
<td>$1.29 \times 10^{-5}$ $1.87 \times 10^{-6}$ $2.06 \times 10^{-6}$ -</td>
</tr>
</tbody>
</table>

* : Average photochemical reaction rate was calculated as ratio of change value in concentration of Pu or Np per reaction time.

$[\text{Pu}]$ and $[\text{Np}] = 1 \times 10^{-3}$ mol/dm$^3$. $[\text{HAN}]$ and $[\text{HDZ}] = 1 \times 10^{-2}$ M, Irra. rate = 0.15 W/cm$^2$.

- : Can not be observed.

As shown in this table, the higher the acidity, the faster the photochemical reaction rate except only for the data of Pu(IV)$\rightarrow$Pu(VI) at 3 M $\text{HNO}_3$. In the case of Np, all of the results at lower than 2 M $\text{HNO}_3$ did not change at all in both cases of the oxidation and reduction reaction of Np(V). This is because an exception occurred due to the strong reducing ability of HAN and HDZ only at the highest acidity of 3 M $\text{HNO}_3$ even though the test solution was irradiated at the rate of 0.15 W/cm$^2$. On the other hand, Np(V) was continuously reduced to Np(IV) even after Pu(III) had completely disappeared after 40 mins. irradiation as shown Fig. 3-(b). This phenomenon indicates that Np(V) was not reduced by Pu(III) only, which is different from the results reported by Koltunov et al. (26). After about 40 mins. irradiation, the reductants are only HAN and HDZ. Therefore, it can be considered that these reductants reduce Np(V) to Np(IV). However, we do not understand why Np(V) was not reduced to Np(IV) under the same condition of only Np(V) 3 M nitric acid solution as previously mentioned. This reason has to be clarified by future experiments.

2. Effect of light irradiation rate

The results of the irradiation tests using the Pu and Np mixed 3 M $\text{HNO}_3$ solution containing $1 \times 10^{-2}$ M of HAN and HDZ and changing the irradiation rates to 0.05, 0.15, and 1.45 W/cm$^2$ are shown in Table 4. These results are shown as the values of the average photochemical reaction rate. As seen in this table, the increase in the irradiation rate hastened the reaction rate of the photochemical oxidation of Pu and Np.

The reducing reaction of Np(V)$\rightarrow$Np(IV) and the oxidation reaction of Np(V)$\rightarrow$Np(VI) are shown in Eqs.(5), (6) and (7), respectively.
Table 4. Change in photochemical reaction rate according to increase in irradiation rate

<table>
<thead>
<tr>
<th>Irradiation rate (W/cm²)</th>
<th>Average photochemical reaction rate (mol/min)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pu(III)→Pu(VI)</td>
</tr>
<tr>
<td>0.05</td>
<td>7.33×10⁻⁶</td>
</tr>
<tr>
<td>0.15</td>
<td>1.29×10⁻⁵</td>
</tr>
<tr>
<td>1.45</td>
<td>5.52×10⁻⁵</td>
</tr>
</tbody>
</table>

*: Average photochemical reaction rate was calculated as ratio of change value in concentration of Pu or Np per reaction time. [Pu] and [Np] = 1×10⁻³ mol/dm³, [HAN] and [HDZ] = 1×10⁻² M, Irra. rate = 0.15 W/cm².
- : Can not be observed.

- Reducing reaction of Np(V) by reductants
  4NpO₂⁺ + 10H⁺ + 2NH₂OH⁺ → 4Np⁴⁺ + H₂N₂O₂ + 8H₂O
  4NpO₂⁺ + 11H⁺ + N₂H₅⁺ → 4Np⁴⁺ + N₂ + 8H₂O

- Oxidation reaction of Np(V) by the photoexcited nitric acid species, *NO₃⁻:
  *NO₃⁻ + 2Np⁴⁺ + 3H₂O → 2NpO₂⁺ + HNO₂ + 5H⁺

From the comparison among each variable level in Table 4, it was found that the photooxidation rates of Pu(III)→Pu(VI) and Pu(IV)→Pu(VI) became faster, and then the reducing reaction of Np(V)→Np(IV) became inferior compared to the photooxidation reaction of Np(V)→Np(VI) based on Eq. (7) according to the increase in the irradiation rate.

As shown in these results, the most suitable irradiation rate condition was 0.15 W/cm² for the separation of Np from Pu in the 2 M HNO₃ solution, which contains 1×10⁻³ M Pu and Np and also contains 1×10⁻² M HAN and HDZ.

(3) Photochemical valence adjustment for coextraction

The experiments on the photochemical valence adjustment for the coextraction of Pu and Np were carried out using the Pu, Np mixed solution containing the additional reagent of 8×10⁻² M urea and 1×10⁻³ M of Pu and Np in 3 M HNO₃. The irradiation rate was 1.45 W/cm². The results are shown in Figs. 4-(a) and (b). As seen in Fig. 4-(a), the absorption spectrum of Np(V) at 980 nm disappeared up to 10 mins. irradiation, and only the minor absorption spectrum of Pu(VI) at 980 nm remained. Np(V) was completely photochemically oxidized to Np(VI). Pu(IV) was also photochemically oxidized to Pu(VI) and decreased according to the irradiation time. These results indicate that all valences of Pu and Np were photochemically adjusted to the coextractable valences for 30 % TBP/n-dodecane under the experimental conditions shown in this study.
(a) Change in absorption spectra

(b) Change in abundance of valences

Fig. 4 Change in absorption spectra by photochemical reaction in Pu, Np mixed 3M HNO\textsubscript{3} solution containing urea vs. irradiation time

(4) Dark reaction after valence adjustment

In general, there is at least an interval of several hours between the valence adjustment and the solvent extraction operation during an actual process. If the adjusted valences change during this interval, the efficiency of the separation or coextraction becomes low. Therefore, it is important to determine the stabilities of the adjusted valences in a nitric acid solution.

Figure 5 shows the results of the dark reaction, the stabilities of the adjusted valences after stopping the light irradiation of the Pu and Np mixed solution containing HAN and HDZ in 3 M HNO\textsubscript{3}. As seen in this figure, Pu(VI) was rapidly reduced to Pu(IV), and then part of the Pu(IV) was further reduced to Pu(III) after stopping the light irradiation. Np(V) was also rapidly reduced to Np(IV). As shown by these results, the adjusted valences of Pu and Np in the 3 M HNO\textsubscript{3} solution containing HAN and HDZ were not stable. Therefore, in the case of the separation, the solvent extraction has to be immediately carried out after the operation of the photochemical valence adjustment or be simultaneously carried out during the light irradiation.

Figure 6 shows the results of the dark reaction after stopping the light irradiation of the Pu and Np mixed solution containing urea in the 3 M HNO\textsubscript{3}. As seen in this figure, all of the photochemically adjusted valences were entirely stable after stopping the light irradiation for more than 4 hours. Based on these results, there is no problem for the solvent extraction operation even several hours after the valence adjustment in the case of coextraction.

3.2 Solvent extraction for separation and coextraction of Np from/with Pu

During or after the light irradiation, the solvent extraction operation was examined using 30 % TBP/n-dodecane to confirm whether Pu and Np can be separated or coextracted.
Fig. 5 Stability of valences of Pu and Np in 3M HNO₃ solution containing HAN and HDZ after stopping light irradiation

Fig. 6 Stability of valences of Pu and Np in 3M HNO₃ solution containing urea after stopping light irradiation
(1) Separation

The results of the separation by the simultaneous operations of irradiation and solvent extraction are shown in Table 5. As seen in this Table, Pu(III) in the aqueous phase completely disappeared after 15 mins. operation. Pu(III) was photochemically oxidized to Pu(IV) and Pu(VI) like the results when only the operation of the valence adjustment was carried out, and Pu having these valences was then simultaneously extracted into the organic phase. In the case of Np, most of the initial Np(V) in the aqueous phase did not change and remained in the aqueous phase depending upon its specific distribution coefficient in the solvent. About 98 % of the initial Pu(III) was photooxidized to Pu(IV) or Pu(VI) and 86.2 % of Pu was extracted into the organic phase during 30 mins. During the irradiation and extraction, Pu(IV) in the organic phase gradually decreased, and Pu(VI) inversely increased. This oxidation reaction of Pu(IV) to Pu(VI) in the organic phase may be due to the photoexcited nitric acid species in the aqueous phase being in contact with both phases. The clear reason for this phenomenon must be defined by detailed data obtained in the future.

Consequently, 87.1% of Pu was extracted into the organic phase and 99.8% of Np remained in the aqueous phase only using one operation of the simultaneous irradiation and extraction.

Table 5 Results of simultaneous operation of irradiation and solvent extraction for separation of Np from Pu

(a) Abundances of Pu valences in both phases vs. operation time

<table>
<thead>
<tr>
<th>Valence</th>
<th>Just before operation</th>
<th>Time of simultaneous ope. of irra. and ext.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15min</td>
</tr>
<tr>
<td>Aq.</td>
<td>Pu(III)</td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>Pu(IV)</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>Pu(VI)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Org.</td>
<td>Pu(III)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td></td>
<td>Pu(IV)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pu(VI)</td>
<td>12.2</td>
</tr>
<tr>
<td>Gross Pu in Org.</td>
<td>&lt;0.1</td>
<td>83.7</td>
</tr>
<tr>
<td></td>
<td>in Aq.</td>
<td>100.0</td>
</tr>
<tr>
<td>Org. / Aq.</td>
<td></td>
<td>5.13</td>
</tr>
</tbody>
</table>

(b) Abundances of Np valences in both phases vs. operation time

<table>
<thead>
<tr>
<th>Valence</th>
<th>Just before operation</th>
<th>Time of simultaneous ope. of irra. and ext.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15min</td>
</tr>
<tr>
<td>Aq.</td>
<td>Np(IV)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td></td>
<td>Np(V)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>Np(VI)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Org.</td>
<td>Np(IV)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td></td>
<td>Np(V)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Np(VI)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Gross Np in Org.</td>
<td>&lt;0.1</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>in Aq.</td>
<td>100.0</td>
</tr>
<tr>
<td>Org. / Aq.</td>
<td></td>
<td>0.009</td>
</tr>
</tbody>
</table>

Pu : 1.0×10⁻³ M
Np : 1.0×10⁻³ M
HAN : 1.0×10⁻² M
HDZ : 1.0×10⁻² M
HNO₃ : 2.0M
Temp. : 20°C
Irra. rate : 0.15 W/cm²
Coextraction

1. Solvent extraction operation after photochemical valence adjustment

As shown in chapter 3.3, Np(vi), Pu(iv) and Pu(vi), which were photochemically adjusted in 3 M HNO$_3$ solution containing urea, were very stable for more than 4 hours even though the light irradiation stopped. The solvent extraction test was then carried out after the valence adjustment with the irradiation rate at 1.45 W/cm$^2$, using the 1x10$^{-3}$ M of Pu and Np mixed solution containing 8x10$^{-2}$ M of urea in 3 M HNO$_3$ and 30 % TBP/n-dodecane. The results are shown in Table 6. This table shows the changes in the abundance(%) of each valence in both the aqueous and organic phases at the appropriate operation time of the light irradiation and of the solvent extraction without light irradiation.

### Table 6 Results of extraction operation after photochemical valence adjustment for coextraction of Pu and Np

<table>
<thead>
<tr>
<th>Valence</th>
<th>Abundance(%)</th>
<th>Photochemical val. adj. time</th>
<th>Solv. ext. time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 min</td>
<td>10 min</td>
</tr>
<tr>
<td>Pu(III)</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>82.3</td>
<td>65.3</td>
<td>58.9</td>
</tr>
<tr>
<td>Pu(VI)</td>
<td>17.7</td>
<td>34.7</td>
<td>41.1</td>
</tr>
<tr>
<td>Pu(III)</td>
<td></td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Pu(IV)</td>
<td></td>
<td>36.1</td>
<td></td>
</tr>
<tr>
<td>Pu(VI)</td>
<td></td>
<td>52.5</td>
<td></td>
</tr>
<tr>
<td>Gross Pu in Org.</td>
<td>88.6</td>
<td>88.3</td>
<td></td>
</tr>
<tr>
<td>in Aq.</td>
<td></td>
<td>11.4</td>
<td>11.7</td>
</tr>
<tr>
<td>Org. / Aq.</td>
<td></td>
<td>7.77</td>
<td>7.55</td>
</tr>
</tbody>
</table>

### (b) Abundances of Np valences in both phases vs. operation time

<table>
<thead>
<tr>
<th>Valence</th>
<th>Abundance(%)</th>
<th>Photochemical val. adj. time</th>
<th>Solv. ext. time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 min</td>
<td>10 min</td>
</tr>
<tr>
<td>Np(IV)</td>
<td></td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Np(V)</td>
<td>100.0</td>
<td>7.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>&lt;0.1</td>
<td>93.0</td>
<td>99.7</td>
</tr>
<tr>
<td>Np(IV)</td>
<td></td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Np(V)</td>
<td></td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Np(VI)</td>
<td></td>
<td>92.3</td>
<td></td>
</tr>
<tr>
<td>Gross Np in Org.</td>
<td>92.3</td>
<td>92.3</td>
<td></td>
</tr>
<tr>
<td>in Aq.</td>
<td></td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Org. / Aq.</td>
<td></td>
<td>12.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Pu : 1.0x10$^{-3}$ M, Np : 1.0x10$^{-3}$ M, Urea : 1.0x10$^{-2}$ M, HNO$_3$ : 3.0M, Temp. : 20°C, Irra. rate : 1.45 W/cm$^2$
As seen in this table, Pu(IV) was gradually photooxidized to Pu(VI) and nearly 100% of the Np(V) was photooxidized to Np(VI) after 20 mins. On the other hand, during the extraction operation, 92.3% of Np was extracted in the organic phase, and 7.7% of Np remained in the aqueous phase after 10 mins. The Np valence remaining in the aqueous phase was Np(V), in spite of the complete adjustment to 100% of Np(VI) being achieved. This indicates that part (about 8%) of Np photooxidized to about 100% of Np(VI) was reduced to Np(V) during the mixing operation with 30% TBP/n-dodecane. The remaining Np(V) in the aqueous phase would be completely extracted into the organic phase by the recycling operation of the photochemical oxidation and the extraction.

Based on these data, it was shown that Pu and Np in a nitric acid solution were efficiently coextracted in 30% TBP/n-dodecane using this photochemical technique.

2. Simultaneous operation for coextraction

A simultaneous operation test of light irradiation and solvent extraction for the coextraction of Pu and Np was carried out using a Pu and Np mixed solution containing urea. The results of this test are shown in Table 7.

<table>
<thead>
<tr>
<th>Table 7 Results of simultaneous operation of irradiation and solvent extraction for coextraction of Pu and Np</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Abundances of Pu valences in both phases vs. operation time</td>
</tr>
<tr>
<td>Valence</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Aq. Pu(III)</td>
</tr>
<tr>
<td>Pu(IV)</td>
</tr>
<tr>
<td>Pu(VI)</td>
</tr>
<tr>
<td>Org. Pu(III)</td>
</tr>
<tr>
<td>Pu(IV)</td>
</tr>
<tr>
<td>Pu(VI)</td>
</tr>
<tr>
<td>Gross Pu in Org.</td>
</tr>
<tr>
<td>in Aq.</td>
</tr>
<tr>
<td>Org./Aq.</td>
</tr>
</tbody>
</table>

(a) Abundances of Np valences in both phases vs. operation time

<table>
<thead>
<tr>
<th>Valence</th>
<th>Just before operation</th>
<th>Time of simultaneous ope. of irra. and ext.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15min</td>
</tr>
<tr>
<td>Aq. Np(IV)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Np(V)</td>
<td>100</td>
<td>97.2</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Org. Np(IV)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Np(V)</td>
<td>–</td>
<td>0.9</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>1.9</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Gross Np in Org.</td>
<td>&lt;0.1</td>
<td>2.8</td>
</tr>
<tr>
<td>in Aq.</td>
<td>100.0</td>
<td>97.2</td>
</tr>
<tr>
<td>Org./Aq.</td>
<td>–</td>
<td>0.03</td>
</tr>
</tbody>
</table>
As seen in this table, the initial valences, Pu(IV) and Pu(VI), were extracted into the organic phase depending upon their specific distribution coefficients, and Pu(IV) in the organic phase decreased as Pu(VI) increased according to the irradiation time similar to the data shown in Tables 5-(a) and 7-(a). On the other hand, regarding Np, part of the Np(V) was photooxidized and was extracted into the organic phase. However, the extracted Np(VI) was gradually reduced to Np(V) and was then reversely extracted into the aqueous phase despite light irradiation. Therefore, Np(V) in the aqueous phase gradually increased. This result indicates that Np(V) was not photochemically oxidized to Np(VI) at all in the case of the simultaneous operation. It is quite different from the result shown in Table 6-(b) despite the same light irradiation.

This phenomenon also indicates that Pu and Np can be mutually separated using the Pu and Np mixed nitric acid solution containing not only HAN and HDZ but also urea in 3 M HNO₃ by the simultaneous operation of light irradiation and solvent extraction. This simultaneous operation is, however, not suitable for the purpose of the coextraction of Pu and Np with 30 % TBP/n-dodecane.

3.3 Photochemical dissolution
(1) Dissolution curve
Ten mg of UO₂ powder was placed in a quartz cell containing 2ml of a 3M HNO₃ solution. The solution was then irradiated using the Hg lamp at an irradiation rate of 1.3W/cm² while maintaining both the temperature of the solution (at 20 ± 1°C) and the homogeneity. Figure 7-(a) shows the results of the changes in the absorption spectrum of the solution according to the irradiation time. As shown in this figure, the absorption bands of UO₂⁺⁺ from 410 to 430nm and those of HNO₂ as a by-product of the UO₂ dissolution reaction from 360 to 390nm appeared after only 10 minutes of irradiation. These increases in the absorbances at these absorption bands show the increase in the dissolution fraction of UO₂ powder. Figure 7-(b) shows the changes in the UO₂ dissolution fractions which are calculated by Eq. (1) based on the data of Fig. 7-(a). The changes in the concentrations of HNO₂ according to the irradiation times are also shown in Fig.7-(b).

Fig.7 Photochemical dissolution of UO₂ powder in 3M HNO₃ solution at 20°C
As shown in this figure, the UO$_2$ powders were completely dissolved after 40 mins. of irradiation even at 20°C, with the same amount of HNO$_2$ as compared to that of the dissolved UO$_2$ powder which was produced after 15 mins. of irradiation. Then, after 30 mins. of irradiation, the amount gradually decreased.

Figure 8 shows the difference in the dissolution curves, the relationship between the UO$_2$ dissolution fraction and the irradiation time, for the different irradiation rates 0(dark reaction), 0.7 and 1.3W/cm$^2$. As shown in this figure, the photochemical dissolution reaction of 10 mg UO$_2$ powder at 20°C was completed at about 40 mins. and 80 mins. under the irradiation rates of 1.3 and 0.7W/cm$^2$, respectively. Under the dark condition, the dissolution fraction was 45% after 90 mins. of irradiation.

Judging from these data, the irradiation rate significantly affects the photochemical dissolution reaction.

Figure 9 shows the results of the dissolution reaction of 10 mg UO$_2$ which were obtained with a 0.7W/cm$^2$ irradiation rate at 20°C while varying the concentration of HNO$_3$ to 1, 3 and 6M.

The photochemical dissolution reaction in the 6M HNO$_3$ solution was completed after only 14 mins. at a 0.7W/cm$^2$ irradiation rate. The complete dissolution time is about 1/5 of that in 3M HNO$_3$ solution. As for the 1M solution, the photochemical dissolution reaction hardly progressed, and the fraction being only 2-3% even after 90 mins. of irradiation.

The concentration of HNO$_3$ significantly affects the photochemical dissolution rate of UO$_2$ powder as seen above.
Figure 10 shows the results of the photochemical dissolution reaction obtained by changing the weight of the dissolved UO\(_2\) powder from 1, 10 and 100mg. As shown in this figure, the dissolution rate become faster in the order of 100, 10 and 1 mg, and the complete dissolution time become shorter in the same order.

![Graph](image)

**Fig. 9** Photochemical dissolution of UO\(_2\) powder in various concentration of HNO\(_3\) at 20°C

![Graph](image)

**Fig.10** Photochemical dissolution of UO\(_2\) powder 1mg, 10mg and 100mg in 2ml of 3M HNO\(_3\) solution
The dissolution reaction mechanism of UO$_2$ powder in nitric acid solution has been studied by Y. Ikeda and H. Tomiyasu et al.\(^{(27)}\) using a UO$_2$ powder enriched with $^{17}$O. Additionally, X. Machuron-Mandard and C. Madic\(^{(28)}\) studied the dissolution reaction mechanism of PuO$_2$ powder using $^{18}$O-enriched water. In these studies, they concluded that the UO$_2$ and PuO$_2$ powders were dissolved through a one or two electron transfer reaction based on the data from NMR analysis. These experiments indicate that the dissolution mechanism is by the redox reaction of electron transfer between a solvent such as nitric acid and UO$_2$ or PuO$_2$ powder.

Therefore, the standard electrode potentials are important in evaluating the dissolution reaction. The standard redox electrode potentials of nitric acid, nitrous acid, UO$_2$, PuO$_2$ and related ion species based on several references\(^{(29),(30),(31)}\) are shown in Fig.11.

![Figure 11: Standard redox electrode potentials of various reactions related to this study](image_url)
In general, if the difference between two electrode potentials of a pair of half reactions, $E_o$, is larger than 0.4V, the redox reaction between the pair might easily progress. For example, in the case of the dissolution reaction of $\text{UO}_2$ in a nitric acid solution, the difference, $E_o$, between the two half redox reactions of $\text{NO}_3^-$ and $\text{UO}_2$ is about 0.5V. Therefore, the reaction will easily progress. However, in the case of the dissolution reaction of $\text{PuO}_2$ in a nitric acid solution, the difference in the electrode potentials, $E_o$, is a negative value between these half reactions, Eqs.(8) and (9).

$$\text{NO}_3^- + 3\text{H}_2\text{O} + 2\text{e} = \text{HNO}_2 + \text{H}_2\text{O} \quad (E_o = +0.94) \quad \text{(8)}$$

and

$$\text{PuO}_2^{2+} + 2\text{e} = \text{PuO}_2 \quad (E_o = +1.22). \quad \text{(9)}$$

Therefore, in general, we have to heat the nitric acid solution to activate the potential of Eq. (8). On the other hand, in the case of the oxidation reaction of $\text{Np( V)}$ to $\text{Np( VI)}$ by nitric acid ion, the difference between two of the half reactions, Eqs. (8) and (10) is also a negative value.

$$\text{NpO}_2^{2+} + \text{e} = \text{NpO}_2^{2+} \quad (E_o = +1.15V) \quad \text{(10)}$$

Therefore, the oxidation reaction of $\text{Np( V)}$ to $\text{Np( VI)}$ hardly progresses at room temperature in nitric acid solution. However, Figure 12 obtained in our previous study indicates that the oxidation reaction of $\text{Np( V)}$ using the photochemical technique easily progresses. This oxidation reaction is thought to be caused by the photoexcited nitric acid ion, $^*\text{NO}_3^-$, shown in Eq.(11) below.

![Graph of Oxidation reaction of Np(V) to Np(VI) by photoexcited nitric acid](image)

**Fig.12 Oxidation reaction of Np(V) to Np(VI) by photoexcited nitric acid**
Fig. 13 Relative spectral energy distribution curve of mercury lamp

Fig. 14 Absorption spectrum of HNO₃
\[ \text{\textit{NO}_3^- + 3\textit{H}^+ + 2\text{e}^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}} \]

\[ \text{NpO}_2^{2+} + \text{e}^- \rightarrow \text{NpO}_2^+ \]

\[ \downarrow \]

\[ \text{\textit{NO}_3^- + 3\textit{H}^+ + 2\text{NpO}_2^{2+} \rightarrow 2\text{NpO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O}} \] (11)

In general, a photoexcited species formed by the absorption of photon energy is more active and has a short-lived redox potential in proportion to the photon energy absorbed by the species (32).

Figure 13 shows the relative spectral energy distribution curve of the Hg lamp used in our study. Figure 14 shows the absorption spectrum of a HNO\(_3\) solution from 0.1 to 3M HNO\(_3\). Judging from both figures, it is ascertained that the Hg lamp light below 350nm photoexcites a nitric acid ion species, NO\(_3^-\). Based on the above-mentioned photoexcited nitric acid, \("\text{NO}_3^-\)", the results of the photochemical dissolution reaction of the UO\(_2\) powder in nitric acid solution can be explained as follows.

Ikeda, Y. et al. (27) explained the UO\(_2\) dissolution reaction with nitric acid as follows:

\[ \text{UO}_2 + 2\text{NO}_3^- + 4\textit{H}^+ = \text{UO}_2^{2+} + 2\text{NO}_2(aq) + 2\text{H}_2\text{O} \] (12)

\[ 2\text{NO}_2(aq) + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2 \] (13)

From Equations (12) and (13), Eq. (14) is derived.

\[ \text{UO}_2 + \text{NO}_3^- + 3\textit{H}^+ = \text{UO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O} \] (14)

Equation (14) proves the production of UO\(_2^{2+}\) and HNO\(_2\) as shown in Fig. 1-(a).

This nitrous acid then dissolves UO\(_2^{2+}\) as shown in Fig.1-(a).

\[ \text{UO}_2 + 2\text{HNO}_2 + 2\textit{H}^+ = \text{UO}_2^{2+} + 2\text{NO} + 2\text{H}_2\text{O} \] (15)

Under the Hg lamp irradiation, the irradiation rate and the concentration of nitric acid significantly affected for the dissolution rate. This is brought about by the increase in the concentration of the photoexcited nitric acid, \("\text{NO}_3^-\)". The dissolution reaction of the photoexcited nitric acid is shown in Eq. (14)' as related to Eq. (14).

\[ \text{UO}_2 + \text{NO}_3^- + 3\textit{H}^+ = \text{UO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O} \] (14)'

Nitrous acid is regenerated by the catalyzing reaction (33),(34) after the dissolution reaction according to Eqs. (9) and (10).

\[ 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O} = 3\text{HNO}_2 \] (16)

As shown in Figure 7-(b), the concentration of the dissolved UO\(_2\) and the generated HNO\(_2\) were equal up to 20 mins. of irradiation time. This is due to the relationship among Eqs. (14)', (15) and (16).
Results similar to those of Fig. 7-(b) were reported by T. Fukasawa et al. [35]. After 20 mins. of irradiation time, the concentration of HNO₂ gradually decreases mainly due to the decomposition reaction of HNO₂ by the light as follows.

\[ 2\text{HNO}_2 \xrightarrow{\text{hv}} \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \] (17)

(3) Effect of irradiation rate on photochemical dissolution rate

Based on the results of Figures 8 and 10 obtained by the tests changing the variable level of the irradiation rate, the coefficient of the dissolution rates \( V(\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}) \) for 10mg UO₂ and 100mg UO₂ were calculated by the following Eq. (18) and are shown in Tables 8-(a) and -(b), respectively.

Table 8 Change in photochemical Dissolution rate depending on irradiation rate

(a) Weight of UO₂ : 10mg

<table>
<thead>
<tr>
<th>Irra. rate (W/cm²)</th>
<th>Disso. rate coef. (mol · cm⁻² · min⁻¹)</th>
<th>Ratio to dark rate coef.</th>
<th>Time for complete disso. (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>3.50 × 10⁻⁶</td>
<td>14.4</td>
<td>40</td>
</tr>
<tr>
<td>0.7</td>
<td>1.05 × 10⁻⁶</td>
<td>4.3</td>
<td>78</td>
</tr>
<tr>
<td>0.0</td>
<td>2.43 × 10⁻⁷</td>
<td>-</td>
<td>350</td>
</tr>
</tbody>
</table>

Acidity : 3M HNO₃, Temp. of sol. : 20°C

(a) Weight of UO₂ : 100mg

<table>
<thead>
<tr>
<th>Irra. rate (W/cm²)</th>
<th>Disso. rate coef. (mol · cm⁻² · min⁻¹)</th>
<th>Ratio to dark rate coef.</th>
<th>Time for complete disso. (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>9.35 × 10⁻⁶</td>
<td>8.9</td>
<td>14</td>
</tr>
<tr>
<td>0.5</td>
<td>3.00 × 10⁻⁶</td>
<td>2.9</td>
<td>40</td>
</tr>
<tr>
<td>0.0</td>
<td>1.05 × 10⁻⁶</td>
<td>-</td>
<td>60</td>
</tr>
</tbody>
</table>

Acidity : 3M HNO₃, Temp of sol. : 20°C
\[
V = \frac{\Delta D_0}{S_0 \times 10^4 \times w/1000}
\]

where \( V \): Coefficient of dissolution rate \((\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1})\)

\( \Delta D_0 \): Slope of dissolution curve obtained in tests at the beginning of dissolution reaction \((\text{mol} \cdot \text{min}^{-1})\)

\( S_0 \): Specific surface area \((\text{m}^2/\text{g})\) of UO\(_2\) powder used in test shown in table 2

\( w \): Weight of UO\(_2\) powder used \((\text{mg})\).

In the case of 10mg UO\(_2\), the ratio of the coefficients of the dissolution rate, \( V_{1.3} \) and \( V_0 \), and the complete dissolution times between the irradiation rates of 1.3W/cm\(^2\) and 0W/cm\(^2\) (dark) was 14.4 and 8.75, respectively. The ratio of the rate coefficients between \( V_{1.3} \) and \( V_{0.7} \) under 1.3W/cm\(^2\) and 0.7W/cm\(^2\) was 3.3, though the ratio of the irradiation rate was 1.9. In the case of 100mg of UO\(_2\), the ratio of the coefficients of the dissolution rate between \( V_{1.3} \) and \( V_0 \) was 8.9. The ratio of the rate coefficients between \( V_{1.3} \) and \( V_{0.5} \) was 3.1 though the ratio of the irradiation rates was 2.6.

Thus, the increase in the irradiation rate of the Hg lamp significantly accelerated the photochemical dissolution rate of UO\(_2\) powder in 2ml of a 3M HNO\(_3\) solution at 20 °C, although the effect of the difference in the irradiation rate for 100mg of UO\(_2\) dissolution was smaller than that for 10mg.

(4) Effect of concentration of HNO\(_3\) on photochemical dissolution rate.

Based on the results of Figure 9, obtained by the tests changing the level of the HNO\(_3\) concentration from 6M, 3M to 1M under an irradiation rate of 0.7W/cm\(^2\), the coefficients of the photochemical dissolution rate were calculated and are shown in Table 9.

<table>
<thead>
<tr>
<th>Conc. of HNO(_3) (M)</th>
<th>Disso. rate coef. ((\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}))</th>
<th>Ratio to dark rate coef.</th>
<th>Time for complete disso. (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>(4.20 \times 10^{-5})</td>
<td>3.0</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>(1.05 \times 10^{-6})</td>
<td>4.3</td>
<td>75</td>
</tr>
<tr>
<td>1</td>
<td>(1.17 \times 10^{-8})</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Weight of UO\(_2\): 10mg, Irra. rate: 0.7W/cm\(^2\), Temp. of sol.: 20, – : No mea.
As shown in this table, the ratio of the rate efficiencies between 6M and 3M HNO₃ is 40.0 though the ratio of the acidity is only 2.0. The ratio of the rate coefficients between the photochemical dissolution reaction at 0.7W/cm² and the dark reaction under 6M HNO₃ is 3.0. The ratio of the coefficients of the photochemical dissolution rate at 6M and 1M HNO₃ is 3590. Thus, the effect of the concentration of HNO₃ on the photochemical dissolution reaction is clearly more significant than the effect of a change in the irradiation rate.

(5) Change in photochemical dissolution rate depending on weight of UO₂ dissolved

How much UO₂ powder can be photochemically dissolved in a definite volume of nitric acid solution is an important point for evaluating the applicability of this technology. Especially, as the penetration ability of the light is weak, and the transmittance of the Hg lamp light into the 1cm square spectrophotometric quartz cell containing 100mg UO₂ powder in 3M HNO₃ solution is only 1%.

At the beginning of this study, we doubted whether a weight of as much as 100mg of UO₂ powders can be photochemically dissolved in an amount as small as 2ml of 3M HNO₃ was in fact possible.

We, therefore, examined the photochemical dissolving ability by changing the weight of the UO₂ powder. Figure 10 shows the results when 1, 10 and 100mg of the UO₂ powder were photochemically dissolved in 2ml of 3M HNO₃ solution under the conditions of an irradiation rate of 1.3W/cm² and a solution temperature of 20°C.

Based on the results of Figure 10, each coefficient of the dissolution rate, the time for complete dissolution and the ratio of the rate coefficient to the dark reaction are shown in Table 10. As shown in this table, the dissolution rate for 100mg UO₂ in 2ml of 3M HNO₃ solution, which is a suspension rather like a concentrated mud solution, is the fastest of the three variable levels. The ratio of the coefficient of the dissolution rate between 100mg and 10mg UO₂ is 2.7.

Furthermore, the ratio of the time for the complete dissolution of 100 and 10 mg of UO₂ is 0.35.

### Table 10 Change in photochemical Dissolution rate depending on weight of UO₂ powder dissolved

<table>
<thead>
<tr>
<th>Weight of UO₂ (mg)</th>
<th>Disso. rate coef. (mol · cm⁻² · min⁻¹)</th>
<th>Ratio to dark rate coef.</th>
<th>Time for complete disso. (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9.35 × 10⁻⁶</td>
<td>8.9</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
<td>3.50 × 10⁻⁶</td>
<td>14.4</td>
<td>40</td>
</tr>
<tr>
<td>1</td>
<td>6.78 × 10⁻⁷</td>
<td>-</td>
<td>105</td>
</tr>
</tbody>
</table>

Irra. rate : 1.3W/cm², Acidity : 3M HNO₃, Temp. of sol. : 20, - : No mea.
Thus, in the range of 1 to 100 mg, it is concluded that the larger the amount of UO$_2$ powder, the faster the UO$_2$ powder dissolves. Although more detailed experiments and evaluations are required hereafter for more precise and quantitative estimations, the reasons for this phenomenon are considered nevertheless to be as follows:

- The larger the amount of UO$_2$ powder suspended in the nitric acid solution, the greater the probability of a collision between the photoexcited nitric acid species and the UO$_2$ powder is during the photoexciting state, the faster the UO$_2$ powder dissolves.
- The larger the amount of UO$_2$ powder suspended in the solution, the higher the concentration of nitrous acid generated due to the dissolution reaction is and also the faster the UO$_2$ is dissolved by the generated nitrous acid.
- The catalytic effect of UO$_2^{2+}$ promotes the dissolution reaction of UO$_2$ powder.

4. Conclusion

As advanced Purex technologies, separation and coextraction of Np from/with Pu in a mixed nitric acid solution and effective dissolution are needed in a new nuclear fuel cycle technology in the future. The results of this study indicate that photochemical techniques for the separation and coextraction of Np from/with Pu, which involve the valence adjustment followed by solvent extraction, and the dissolution at room temperature have much potential for the above-mentioned purpose in principle.
References

Summary of Session 1

Co-Chairman: Dr. T. Mukaiyama

Professor Y. Fuji-ie, Commissioner of the Atomic Energy Commission (AEC), welcomed the participants. During his welcome address, he stressed the important role of nuclear energy for the future, and highlighted the Japanese position in carrying forward R&D efforts towards commercial implementation of the nuclear fuel cycle. One of the most important tasks for the mature nuclear fuel cycle, he said, was the establishment of the HLW management scheme. He noted that P&T type of work should continue at all times, because policy changes may occur in the future, and because basic research had rather long lead times. Such basic studies may provide insight into better and novel methods in solving HLW problems.

Mr. G. Stevens, Head of the Nuclear Development Division of the OECD Nuclear Energy Agency (NEA), opened the meeting and welcomed the participants on behalf of the NEA. He summarised the history of the NEA P&T programme and explained how it stimulated international collaborations for better understanding of the technical issues involved, and better orientation of future work. He was very pleased to see that so many participants from all around the globe were able to participate in the meeting and underlined that substantial benefits could be achieved from wider international co-operation. He thanked the Japanese Government for the generous support it provided in this field.

Mr. T. Arimoto, Director of the Radioactive Waste Policy Division, Science and Technology Agency (STA) of Japan, described the important position of geological disposal of HLW in the "Long-Term Programme for R&D, and Utilization of Nuclear Energy" issued by the AEC of Japan in 1994. In 1995, the AEC set up two committees for addressing the disposal of HLW, and the policy for the back-end of the nuclear fuel cycle. A wide range of studies for obtaining public understanding and for approving the implementation of HLW disposal would be performed. Other studies would consider technological issues concerning disposal. P&T was considered to be a future technology in the Long-Term Programme.

Mr. M. Hugon, European Commission (EC), reported on the EC-funded research activities on new fuel cycle concepts. These included three work areas, namely: strategic studies; partitioning techniques; and transmutation techniques. The strategic studies covered four projects: evaluation of possible P&T strategies; nuclear data for advanced MOX fuels; thorium cycles as nuclear waste management options; and impacts of accelerator-based technologies on nuclear fission safety. Experimental work on partitioning was carried out under two projects: new partitioning technologies, and extraction and selective separation of long-lived nuclides by functionalised macrocycles. Transmutation techniques studies were covered under two projects: the joint EFTTRA experiment on Am transmutation, with irradiation experiments performed in the HFR at Petten, and neutron driven transmutation by adiabatic resonance crossing. About forty European research institutions had participated to the projects since 1996, aiming at having a clearer picture in efficiently reducing the radiotoxicity of nuclear wastes.

Dr. A. Grigoriev, IAEA, reported on the IAEA activity on partitioning and transmutation. The IAEA first started a Co-ordinated Research Programme (CRP) in 1976 and its results were published in 1982. The conclusion of that report was rather negative for P&T. In 1990, the former Soviet Union requested the IAEA to re-active its P&T programme. Since then, the IAEA organized two consultant meetings and one technical committee meeting on this subject. The IAEA had also initiated two CRPs, one on the safety, environmental and non-proliferation aspects of P&T, and another on benchmark calculations of a PWR-cell loaded with (Pu-Th)O_2 fuel and Th-cycle accelerator-driven systems. Two status reports
were in preparation, one on transmutation activities in non-OECD countries, and another on accelerator-driven hybrid systems. These IAEA activities which were complementary to other international programmes, especially to those of the OECD/NEA, were not expected to address possible proliferation issues regarding partitioning.

Mr. J.-F. Babelot of the JRC ITU reported on the EFTTRA irradiation experiments in Phenix and in the HFR. The objective of the European collaboration for Experimental Feasibility of Targets for Transmutation was conducting joint experiments for studying various materials for transmutation. Tc metal rods were irradiated in the HFR up to 6.4 per cent burn-up, and no swelling of the rods was observed. Based on the examination of the irradiated iodine containing capsules, NaI was concluded to be better than CeI₃ or PbI₃. Inert matrices, namely oxide and nitride, were evaluated for MA transmutation both in a PWR and in a fast reactor, and the irradiation behaviour experiments of the candidate matrices were planned. The irradiation of Am oxide embedded in a spinel matrix was under preparation.

The international meetings organized by the NEA and the IAEA for exchange of information were seen as one of the most effective ways in obtaining a clearer picture of P&T aspects, which were both technically very complex and politically sensitive.

In Europe, as was reported by Messrs. Hugon and Babelot, well oriented and well organized collaborative P&T studies, including strategic studies, evaluations and experiments, were performed. The experimental data obtained by those joint efforts, especially irradiation data, would be very valuable for the international community in performing future work.

Following the introductory remarks and the reports on international activities, two invited key-note presentations were made: one by Dr. L. H. Baestle of SCK-CEN on a systems analysis approach for P&T issues and another by Professor M. Salvatores of CEA on the physics and strategies of transmutation.

Dr. Baestle was the Chairman of the NEA Expert Group on P&T System Studies which was preparing a report on that subject. His presentation focused on the general scope and the work of the NEA expert group. Professor Salvatores discussed the reactor physics approach for comparing different transmutation systems, namely, a fast reactor, a PWR, an accelerator-driven system, heterogeneous recycling and homogeneous recycling. One of the conclusions of his analysis was that transmutation in PWRs was less attractive, and therefore, the role of Superphenix was very important for the development of targets for Am irradiation.
Summary of Session 2

Chairman: Professor M. Salvatores

In session 2, mostly national programmes had been presented (in Japan: the JAERI and PNC programmes; the activities in the Netherlands; the IPPE and ITEP activities in Russia; and in France the national programme and related scenarios studies).

In Japan, the framework was provided by the Long-Term Programme for Research, Development and Utilisation of Nuclear Energy. A new initiative had been taken by JAERI -- the Neutron Science Project. Accelerator-based transmutation was part (or would be part) of this project. In France, the framework was the 1991 Parliament Law for radioactive waste management, which required that work was performed during a fifteen year period, in order to gather the necessary elements for selecting appropriate options by the year 2006. In Russia, the role of the ISTC had been mentioned, since certain major programmes were performed there under funding of that Institute. Basic physics activities had also been highlighted.

The "double strata" concept by JAERI (presented by Dr. Mukaiyama) had the merit of conceptually confining the new P&T technologies to some specialised installations. This seemed to be a worthwhile approach to be further studied. In a somewhat opposite attitude (but also very valuable), the PNC approach (presented by Dr. Nakajima) favoured the optimisation of the standard fuel and fuel cycle technology, in order to reduce costs and increase competitiveness.

The French programmes (presented by Mrs Viala) illustrated priorities, in chemistry, for assessing, at the industrial level, the separation capability of trivalent actinides/lanthanides and, in fuel fabrication (Am targets), for realistic scenarios assessment.

In the scenarios presented by the CEA, MA were recycled in a fast reactor core: homogeneous recycling was preferred for Np, while heterogeneous recycling, by means of targets, was preferred for Am, in particular in a once-through option (this "hybrid" mode of recycling had also been considered by PNC in Japan).

The relevance of plutonium recycling characteristics was highlighted, both in the presentation of Dr. Rabotnov and in that of Dr. Delpech. In particular, the latter presentation gave quantified indications of mass flows in a reactor park recycling both plutonium and MA, and the related needs in fuel fabrication and fuel reprocessing plants; and this was a matter for discussion during the session.

From the presentations, it had been possible to recognise the wide network of international collaborations in all the fields of P&T (chemistry, physics, accelerator-based technologies). A significant example was the presentation of the Dutch programme by Mr. Kloosterman. Their programme was deeply embedded in European Commission activities and benefited from them.

In summary, constant progress had been reported by the major laboratories involved in the field. Perspectives seemed to be based on a relatively constant funding for these laboratories. The major challenge was still finding an appropriate measure for cost/benefit analyses.
Summary of Session 3

Chairman: Dr. P. Wydler

The contributions to this session covered studies of different transmutation systems (PNC, JAERI, KAERI), investigations relating to the P&T fuel cycle (JAERI, Belgonucléaire/EdF), and a target irradiation experiment with Tc-99 carried out in the Petten thermal High Flux Reactor (HFR) in the framework of the EFTTRA co-operation. Most of the important issues and options were addressed in the session including critical and accelerator-driven fast reactors with different types of fuel (oxide, nitride, molten salt) and wet or pyrometallurgical reprocessing, as well as different recycling modes (homogeneous, heterogeneous with inert matrices).

An option which relied primarily on proven reactor technology was to recycle the nuclides to be transmuted in a normal fast reactor. A comparison of different recycling modes for MAs and Tc-99 in a fast reactor was presented by PNC. Relatively high transmutation rates were reported for a case where Np was dispersed homogeneously in the core and Am, Cm and rare earths were recycled heterogeneously in target subassemblies in the blanket region. However, to preserve the safety characteristics of the core, the fraction of MAs in the fuel had to be restricted to about 5 wt%. For the transmutation of Tc-99 a new target subassembly concept using "duplex pellets" with zirconium hydride moderator was proposed.

Accelerator-based systems had the advantage that the deterioration of the core safety characteristics with increased MA concentrations can be compensated by the subcriticality of the core. Three accelerator-based systems for burning MAs were mentioned. In the framework of the OMEGA programme, JAERI investigates a solid system based on fast reactor technology (nitride fuel / sodium coolant) as also a "fast" molten salt system (molten chloride target / fuel) as a more advanced option, both systems being optimised for a high support ratio in the double stratum fuel cycle. An overview of the systems and the supporting R&D was presented, and a lead-based chloride salt was proposed as an alternative fuel for the molten salt system. The system studied by KAERI incorporated features of the Los Alamos ATW system (lead target, molten fluoride salt) and had an intermediate neutron spectrum in the core. A graphite reflector with a softer neutron spectrum was provided, but was found to be unsuitable for burning FPs at an interesting rate.

The current R&D status for the nitride fuel cycle at JAERI was summarised in an overview paper. Pellet-type mixed nitride fuel, fabricated by a conventional route, had been characterised and irradiation-tested in JMTR to a burnup of more than 5 per cent FIMA with good results (no pin failures, low FP releases), an alternative fabrication route for nitride fuel particles by the sol-gel method had been investigated, and the pyroprocess for reprocessing the fuel had been further evaluated; reprocessing experiments with NpN and PuN using laboratory-scale electrorefiners were about to begin.

The fabrication of target pins for the heterogeneous recycling of Am would be associated with higher radiation levels than the current MOX fabrication. In a joint study, Belgonucléaire and EdF had estimated the resulting dose rate increases and impact on the shielding for the different fabrication stages. Dose rate increases up to a factor of 2800 in the case of a transfer canister were predicted. Validation experiments were performed to assess the uncertainties of the calculations.
The EFTTRA co-operation aimed to investigate the behaviour of MA and FP targets during irradiation experimentally. In an irradiation of six metallic Tc-99 rods in the Petten HFR, more than 6 per cent of the Tc-99 was transmuted to stable Ru-100. ECN Petten performed the PIE for one of these rods and obtained reasonable agreement between measured and predicted ruthenium profiles provided that a Monte Carlo code with a point cross-section library was used in the analysis. A new measurement of the thermal absorption cross section of Tc-99 in the HFR may help to resolve remaining small discrepancies.

Regarding the evolution of the reported activities since the Cadarache P&T meeting in 1994, one could notice a move from the innovative to a stable development phase. Efforts in the fuel and target development area had been strengthened, and the concept of the double stratum fuel cycle, including accelerator-based MA burners, had found wider acceptance. Evaluations of the radioprotection implications had been initiated and filled an important gap. Considering the still not very clear incentive and goals for transmuting the fission products, the analytical and experimental effort devoted to studies of the Tc-99 transmutation was noticeable.
Considering the overall perspective for P&T, the first task to be tackled was partitioning, because otherwise transmutation would be an unrealistic endeavour. Partitioning was seen as an extension of the closed fuel cycle to those nuclides which constitute a potential and/or an intrinsic hazard. The obvious starting point of partitioning was the source term, where hazardous and long-lived nuclides were brought together with less toxic and short-lived nuclides; and that was the high-level waste solution.

If an analysis was attempted from that viewpoint, methods which had been developed especially for that purpose should be considered. Three papers dealt with that subject directly:

- Products and wastes from 4-group partitioning process developed in JAERI (DIDPA process), by M. Kubota and Y. Morita of JAERI.
- Minor actinide separations: recent advances at the CEA (DIAMEX process), by A. Leudet, B. Boullis, C. Madic of CEA.
- The state of the art on nuclides separation in HLLW by TRUEX process, by M. Ozawa, Y. Koma, Y. Tanaka and S. Shikakura of PNC.

These methods were already under development during the previous NEA information exchange meeting. The highlights of these papers were as follows:

For the JAERI DIDPA process, the flowsheet was fully integrated and was capable of partitioning the HLLW nuclides into the following groups:

- TRU group
  - Am-Cm
  - Lanthanides
  - Np-Pu
  - U
- Platinum group metals (PGM) and Tc
- Cs-Sr

The process had only one drawback, that was the HLLW had to be partially de-acidified. Impressive separation and recovery yields had been reported (99.9, 99.5). The process produces only moderate amounts of secondary wastes (128 kg NaNO₃/tHM).

The DIAMEX process (CEA), permitted the quantitative extraction of MA from HLLW by the use of malonanide molecules (DMDBTDMa). However, continuous progress had been reported in the synthesis of new extractants with even better properties. The separation of An-Ln had not yet been demonstrated unequivocally and further progress was needed, but the prospects were good that a fully "saltfree — high acid" process would become operational.

Concerning the TRUEX process (PNC), the flowsheet was a solid improvement of the original ANL flowsheet, since a number of "salt free" re-agents had been introduced and were successful. The flowsheet looked complicated but was, in fact, an integrated series of liquid extraction and strip operations providing: An-Ln fraction; plutonium; and Mo-Zr-Ru (contaminants recycled).
A major point to be noted was the direct use of HLLW solutions without dilution or de-acidification.

Closely associated with these "encompassing" partitioning methods, some very specific advances had been reported:

- Selective extraction and transport of cesium with CALI[4]ARENES crown CRWN from radioactive liquid wastes, by J.F. Dozol et al. from CEA.

These new molecules, with very complex structure, were capable of extracting selectively Cs-137 from a variety of active solutions, including HLLW. Currently, the kinetics were slow, but progress may be expected (contact phase, temperature, etc.):

- Partitioning of minor actinides from rare earths by solvent extraction with D 2 EHPA, by J.-H. Yoo et al.

This technologic development was a necessary step in the mastering of more elaborate partitioning methods.

A very special type of partitioning technique was the pyrometallurgical partitioning approach. This technology needed to be considered as a step in the future, when very highly irradiated targets and fuels would be produced in fast reactors and, possibly, in ADT facilities, to the extent that multi-recycling of such targets was required. Three papers from CRIEPI and associates dealt with this subject:

- Molten salt electrorefining to separate TRUs from rare earth elements, by T. Hijikata et al.
- Pyrometallurgical processing technology development, by T. Koyama et al.
- Development of pyrometallurgical partitioning technology of long-lived nuclides -- development of salt wastes treatment technology, by Y. Sakamura et al.

Pyrometallurgical techniques were difficult to implement, because of the "moisture" and, sometimes, the "oxygen" interference in the processes. But they had a fundamental merit that radiation damage and decay heat emission did not play a significant role, and that criticality risks were minimal.

The technological requirements were, however, much more severe than those for aqueous methods:

- HLLW must be denitrated and chlorinated.
- Electrochemical processes were complex.
- Separation factors were, generally, smaller.
- An important technological effort had been accomplished in the electrorefining, but much needed still to be done.
- Waste issues had been studied — in particular, how to treat unrecyclable residues (NaCl, Cd, etc.). Questions regarding immobilization processes of salt residues were given tentatively acceptable answers (sodalite solidification of NaCl; Pb-Cd embedment).

In summary, great technological efforts needed to be made in order to consider pyrometallurgy as a viable option for multi-recycling of fuel and target materials.

An overview was also provided, by I.V. Mukhin, of the R&D work going on in Russia in the partitioning field. This would certainly lead to improve contacts with Russian colleagues.
Concerning international co-operation, task distribution should be performed according to available means and resources in order to avoid duplication. It would be worth trying to recontact colleagues in the United states to resume collaboration.

The future tasks could be summarised as follows:

- Investigate the link between spent LWR-MOX and P&T operations.
- Bridge the gap between the waste management and P&T communities.
- Further investigate the recycling technologies of very hot fuels and targets. Study the limits of the aqueous processing.
- Start performing strategic studies of P&T in the general context of nuclear development.
In this session, posters were presented with a large variety of subjects and scopes ranging from short-term to long-term research.

The presentation started with the poster of Dr. Emoto (PNC) about the status of the electron accelerator, which could be used to transmute radioactive fission products with a small neutron capture cross section. Possible candidates of such fission products were Sr-90 and Cs-137.

The next three posters by Drs. Kusano, Nishida and Takada gave a coherent overview of work done at JAERI on Accelerator Driven Systems. The second poster dealt with the status of the R&D on the proton linac with energy of 1.5 GeV and an average current of 5 mA. This was already a big step towards an accelerator with a current of 40 mA needed for ADS. The third poster focused on the improvement and benchmarking of the NMTI cascade code and its inclusion in the ATRAS code system. This code can now be used to model the spallation reaction and high-energy fission processes, the neutron transport, and the core burn-up. It had been used to design two types of reactor systems: a nitride-fueled reactor for the short term and a molten salt fueled reactor for the longer term. Both systems were capable of transmuting the minor actinide production of ten units of 1 GWe LWRs. The benchmarking of the new ATRAS code system with experimental data was described in the fourth poster of this session by Dr. Takada.

Some interesting measurements were presented in the fifth and sixth poster presentations by Dr. Harada of PNC and Dr. Oigawa of JAERI. In the fifth poster, the measurements of thermal cross sections and resonance integrals of some important fission products were described. Interestingly, the cross section of Tc-99 was much larger than that assumed until now. For Sr-90 and Cs-137, the measurement of the photonuclear cross sections was in progress. In the sixth poster, the neutron fission yields and the delayed neutron data of some minor actinides were presented. Both fields were very important for the future development of burner reactors loaded with large amounts of minor actinides and fission products.

The last two posters dealt with the development of nitride fuels for future fast reactors. In the seventh poster, by Y. Arai, the lattice parameter, vapour pressure and thermal conductivity were presented for solid solutions of neptunium-plutonium mixed nitrides. Given that thermodynamic data on nitride compounds of minor actinides were not well known, that paper constituted a valuable contribution. Much work remained to be done, even on oxide compounds of minor actinides. The eighth paper, by M. Akabori, provided a better insight on nitride forming reactions in liquid alloys, which was of interest for the conversion of metallic fuels to nitrides.

In general, it was very positive that measurements of cross sections, neutron fission yields, and thermodynamic data had been performed, because the importance of such data cannot be easily underestimated. Also the validation and benchmarking of codes being used for new applications like accelerator driven systems were quite important. Future work on those subjects would further advance P&T research.

The non-technical aspects of the session concerned mainly the economics of accelerator driven systems. Since every stage of the nuclear fuel cycle was expected to become more expensive in the long term, the design of an accelerator driven system, which may consume up to 40 per cent of its own generated electricity, should be carefully investigated in order to make such systems as cheap as possible. Additionally, issues related to licensing should not be forgotten.
Summary of Session 5B
Chairman: Mr. M. Hugon

Five posters were presented by Japanese research institutions in this session. Three subjects were treated: (i) liquid-liquid extraction, by JAERI (two posters); (ii) dry reprocessing, by PNC (two posters); and (iii) photochemistry, by PNC (one poster).

JAERI presented the PARC (Partitioning Conundrum Key) process concept. This concept was developed by using the Back-End Cycle Key Elements Research Facility (BECKY) in NUCEF. Simplification of the chemical process and enhancement of the separation efficiency and of the confinement capability of long-lived nuclides were key parameters in improving economical competitiveness and safety standards.

The subject of the second poster was a presentation of the Partitioning Test Facility built in NUCEF in order to test the 4-group partitioning process developed by JAERI with real HLLW. Two to twenty liters of HLLW (5 000 Ci at maximum) can be treated during each experiment. Partitioning tests with simulated HLLW had already been started.

Recovery of valuable metals from spent nuclear fuel by lead extraction from high-level radioactive waste was investigated by PNC. Ruthenium was selectively separated by ozone oxidation. Different methods such as solvent extraction, precipitation and ion exchange were studied for the selective separation of rhodium and palladium. A process to recover technetium would be developed at a later stage.

A very high temperature method was being developed by PNC to separate platinum group metals from the actinide and rare earth elements. Titanium nitride was mixed with calcinated HLLW. The oxides of the platinum group elements were reduced into a metallic phase and partitioned from the oxide phase containing the actinides and rare earths at 1 600 degrees C.

In the last poster, PNC presented an application of photochemical techniques for the separation and co-extraction of neptunium from/with plutonium in a mixed nitric acid solution. The solution was irradiated by a high-pressure mercury lamp, which leaded to a valence adjustment of neptunium and plutonium, and, then, to a substantial improvement of their co-extraction in the organic phase. The photochemical dissolution of UO₂ powder in a nitric acid solution, at room temperature, appeared also to have much potential.
Summary of the Meeting

Mr. J. Lefèvre

Following the Mito City P&T Information Exchange meeting, related issues seemed to be better understood for the following reasons:

1. Goals were more clear:
   - P&T would not replace geological disposal.
   - Potential hazard reduction was mainly associated with TRU elements (Pu > Am >> Np, perhaps Cm).
   - Reduction of the dose impact to man would come from mobile fission product radionuclides (I-129, Cs-135 > Tc-99).

2. The main motivations for P&T were:
   - Ethical reasons for the future generations.
   - Public claims concerning geological waste disposal sites (for example, in France).

3. There was, however, a need to better define the following:
   - Performance to be coupled with which type of criteria (feasibility, credibility or safety gains) ?
   - Which time limits should be considered (1 000, 10 000, 100 000 years or even more) ?
   - Which were the best ways for industrial implementation (existing processes and facilities adaptation, new processes and new technologies or a step by step approach) ?
   - What would constitute a reasonable level of extra costs ?
   - Which were the safeguards aspects to be taken into account ?

Although P&T was seen as a rather long-term research programme, immediate and continuous answers were always needed by decision-makers and politicians. In this regard, it would be necessary: to continue performing technical studies; to continue evaluating the results obtained; to continue with systems and strategic studies; and to continue with the necessary economical evaluations.

Although several disparate approaches were under way, it should be recognised that two large programmes were currently leading P&T efforts: OMEGA in Japan and SPIN in France. Both were in good progress. Partitioning can be performed by both aqueous, and by dry and pyrometallurgical processes, while transmutation could be accomplished by reactor concepts (thermal and fast), fuels and targets, and by accelerators. Concerning partitioning and conditioning two new facilities were in operation: ATALANTE and NUCEF.

Given that P&T programmes constituted long-term activities, there was clearly a role for international organisations in order to disseminate results and ensure proper co-ordination of resources.
Session 6 (Closing Remarks)

Chairman: Mr. G.H. Stevens

It was very positive that so many knowledgeable people from all over the globe participated in the meeting. Warmest thanks were due to the organisers for having hosted an excellent meeting and for their hospitality.

Although some ideas presented were radical in the extreme, over the last few years more filtering of concepts was done and more experiments were performed. Issues concerning benefits for future generations vis-a-vis the risks for facility workers were becoming more prevalent.

Despite the widespread effects of privatisation and the introduction of greater competition into electricity production, resulting in reduction of energy R&D budgets, it was encouraging to see that stable funding was generally ensured for work on the P&T option.

The NEA would go ahead with its P&T systems studies activity and, given the ever increasing number of meetings in this area, would carefully evaluate the future continuation, scope and type of P&T Information Exchange meetings at appropriate intervals.
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