Nuclear Science Committee

Actinide and Fission Product Partitioning and Transmutation

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Foreword

The benefits of partitioning and transmutation (P&T) have now been established worldwide and, as a result, many countries are pursuing R&D programmes to advance the technologies associated with P&T. In this context, the OECD Nuclear Energy Agency (NEA) has organised a series of biennial information exchange meetings to provide experts with a forum to present and discuss state-of-the-art developments in the field of partitioning and transmutation since 1990.

Previous meetings were held in Mito (Japan) in 1990, at ANL (United States) in 1992, in Cadarache (France) in 1994, in Mito (Japan) in 1996, in Mol (Belgium) in 1998, in Madrid (Spain) in 2000, in Jeju (Korea) in 2002, in Las Vegas (United States) in 2004, in Nîmes (France) in 2006, in Mito (Japan) in 2008, in San Francisco (United States) in 2010, in Prague (Czech Republic) in 2012 and were co-sponsored by the European Commission (EC) and the International Atomic Energy Agency (IAEA).

The 13th Information Exchange Meeting was held in Seoul (Republic of Korea) on 23-26 September 2014, hosted by Seoul National University. The workshop comprised a plenary session on national and international programmes followed by technical sessions and a poster session covering various aspects of P&T. The information exchange meetings on P&T form a part of the NEA programme of work in the field of advanced nuclear fuel cycles. These proceedings include papers presented at the 13th Information Exchange Meeting. The opinions expressed are those of the authors only and do not necessarily reflect the NEA views or its member countries.
Acknowledgements

The OECD Nuclear Energy Agency (NEA) wishes to thank the Nuclear Transmutation Research Centre of Korea (NUTRECK) at Seoul National University, for hosting the 13th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation. The NEA would also like to express its gratitude to all the scientists who participated in this workshop and contributed to the improvement of international co-operation in the field of partitioning and transmutation. Special thanks are due to Professor I-S. Hwang and his students for their invaluable assistance and support in organising this conference. We would also like to thank members of the Scientific Advisory Committee for devoting time to organising this workshop and in particular to reviewing the abstracts.

The NEA also extends its gratitude to the European Commission and the International Atomic Energy Agency for their co-operation.
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Executive Summary

The OECD Nuclear Energy Agency Information Exchange Meeting on Actinides and Fission Products Partitioning and Transmutation, organised since 1990, is a forum for experts to present and discuss the state-of-the-art development in the field of P&T. Thirteen meetings have been organised so far and held in Japan, the United States, France, Belgium, Spain, the Republic of Korea and the Czech Republic. This 13th meeting was hosted by Seoul National University (Seoul, Republic of Korea) and was organised in co-operation with the International Atomic Energy Agency (IAEA) and the European Community (EC).

The meeting covered strategic and scientific developments in the field of P&T such as: fuel cycle strategies and transition scenarios, the role of P&T in the potential evolution of nuclear energy as part of the future energy mix; radioactive waste management strategies; transmutation fuels and targets; advances in pyro and aqueous separation processes; P&T specific technology requirements (materials, spallation targets, coolants, etc.); transmutation systems: design, performance and safety; impact of P&T on the fuel cycle; fabrication, handling and transportation of transmutation fuels.

A total of 103 presentations (39 oral and 64 posters) were discussed among the 110 participants from 19 countries and 2 international organisations. The meeting consisted of one plenary session where national and international programmes were presented followed by 5 technical sessions:

- Fuel Cycle Strategies and Transition Scenarios.
- Transmutation Systems and Infrastructures.
- Waste Management for P&T Scenarios.
- Transmutation Fuels and Targets.

Opening Session

The meeting opened with a welcome address by Professor Il-Soon Hwang from Seoul National University and Jim Gulliford, Head of the NEA Division of Nuclear Science followed by the Honourable Dr Han-Py Kim, member of the National Assembly, Committee on Trade, Industry and Energy of Korea.

**D. Warin** (CEA, France) gave an introductory lecture on the benefits and challenges of P&T for a sustainable nuclear energy. P&T can help reduce the burden of long-term waste management and improve related public acceptance. As a result, many countries are increasing R&D efforts on P&T technologies for a wide range of fuel cycle concepts.

Session 1: National and International Programmes

**J. Gulliford** (NEA) summarised the on-going activities of NEA related to P&T. Most work is carried out within the Nuclear Science programme of work. Current activities involve MA bearing fuel performance benchmark studies, an international review of separation processes, minor actinides management and recycling.
An overview of the IAEA activities on P&T was given by U. Basak (IAEA) and S. Monti (IAEA). The framework of the IAEA activities is carried out by several Nuclear Energy sections and technical working groups (TWG) and is implemented through co-ordinated research projects (CRP). An assessment of partitioning processes was performed and the trends in advanced pyroprocessing were reviewed. Transmutation activities focus on fast neutron systems such as fast reactors (FR) and accelerator-driven systems (ADS).

J-H. Lee (ROK) presented the status of the back-end of the nuclear fuel cycle in Korea. No decision has yet been made regarding spent fuel management strategy in Korea. A public engagement commission (PECOS) was set up to survey public opinion. Currently the spent fuel is kept in an interim storage. In the meantime, R&D programmes on pyroprocessing and SFR are on-going with the objective of operating a close fuel cycle in the near-term. For partitioning, the PRIDE facility (PyRoprocessing Integrated inactive DEmonstration facility) is in operation and engineering scale demonstration on surrogates is expected. A prototype SFR was designed for transmutation. Current R&D activities focus on the 3S (safety, safeguards and security) requirements.

P. Paviet (US) gave an overview of actinide partitioning research in the US. The US is currently operating a once-through nuclear fuel cycle but is evaluating advanced (closed) fuel cycle for potential deployment around mid-century. A comprehensive Nuclear Fuel Cycle Evaluation and Screening Study has been completed and showed that continuous recycle of U/Pu or U/TRU (transuranic) is among the most promising fuel cycle. The US Fuel Cycles Technologies programme is performing R&D on advanced partitioning technologies for potential fuel cycles. Investigations support both homogeneous and heterogeneous approaches and focus on more robust and simpler processes. Both aqueous and electrochemical technologies are being developed.

Z. Hodgson (UK) outlined the status of nuclear energy development in the United Kingdom. The current UK policy is to operate an open fuel cycle and reprocessing plants are planned to be shut down in the near future. The UK roadmap focuses on keeping scenario options open and training the next generation of nuclear scientists. Importance is given to actinide separation processes in particular advanced reprocessing and MA partitioning.

D. Warin (France) illustrated the R&D programmes for the management of Pu and minor actinides in France. Sustainability of the fuel cycle will be reached by operating a closed fuel cycle through systematic recycle and fast reactors. Minor actinides recycling in fast reactors will provide a solution to waste management. The 2013-2023 R&D programmes focus on (1) Pu multirecycling; (2) partitioning Am and (3) transmuting Am. The sodium cooled prototype reactor ASTRID aims at demonstrating MA transmutation.

M. Alyapykev (Russian Federation) summarised the R&D programmes on partitioning in the Russian Federation. Primary programmes concentrated on the separation of Cs and Sr but the current priority is given to Am. New ligands and modification of existing aqueous processes are being investigated to optimise the separation of Am from spent fuel.

H. Oigawa (Japan) highlighted the new energy plan issued after the review of the Japan R&D programme carried out by the government. Two fuel cycle options are considered for P&T: homogeneous recycle in FBR and transmutation in ADS. Transmutation of minor actinides (MA) is the main focus and will be conducted in Monju. A transmutation experimental facility (TEF) will be built in J-PARC. Future R&D plan involves partitioning of MA and transmutation in ADS. The importance of international collaboration (i.e. MYRHHA) was mentioned.
Session 2: Fuel Cycle Strategies and Transition Scenarios

**F. Alvarez-Velarde** (on behalf of NEA/EG AFCS) presented the results of a benchmark study on uncertainties analysis of input parameters on nuclear fuel cycle scenario carried out within the NEA Expert Group on Advanced Fuel Cycle Scenarios (EGAFCS). The objectives of the international study were to provide guidance on which input parameters are important to be investigated thoroughly, and which components can be less well-known, given the objectives of a particular study. Twenty-two magnitudes were estimated by the codes and 17 sensitivity studies were calculated. A first estimation on which input parameters impact significantly (given the objectives of a particular study) was obtained. These results and conclusions will be included in an NEA report expected to be published in 2015.

The results of the study of the environmental impact of different nuclear fuel cycle were explained by **S. Bourg** (France). The simulation tool NELCAS was developed and a twice-through fuel cycle and a once-through fuel cycle were studied. Comparison to other sources of energy showed the low impact of nuclear energy. Simulations also demonstrated the significant contribution of the front-end activities on the global impact. In addition, the beneficial effects on the overall footprint of recycling processes were demonstrated.

**T. Kim** (US) described the Evaluation and Screening study (E&S) carried out in the United States in order to strengthen the basis for the implementation of a nuclear energy R&D programme. This presentation focused on the comparison of mass flow data analysis for different fuel cycles options. The conclusions of this study showed that natural resource utilisation is generally lower than 2% for fuel cycle options that require enriched uranium fuel, but could be improved by avoiding enriched uranium fuel support. The mass of spent nuclear fuel and high level waste (SNF+HLW) can be reduced by continuously recycling nuclear fuel. Mass of DU (depleted uranium) is a major fraction of the DU+RU+RTh mass for fuel cycle options that require enriched uranium.

The decision to phase out electric energy production in nuclear power plants in Germany has led to a number of questions regarding the future of P&T research. The Federal Ministry for Economic Affairs and Energy and the Federal Ministry of Education and Research have launched a study managed by the National Academy of Science and Engineering to answer these questions on a broad scientific basis. The objective was to evaluate scientific and technological as well as socio-economic challenges and opportunities of the P&T technology with a view to the phase-out decision, both in a national and an international context. The scientific and technological aspects of P&T were analysed with respect to a possible contribution to the management of nuclear waste. The outcomes of the study and recommendations were presented by **B. Merck** (Germany).

Session 3: Transmutation Systems and Infrastructures

**H. Aït Abderrahim** (Belgium) gave an invited presentation on the MYRRHA project (Multipurpose hYbrid Research Reactor for High-tech Application) and explained its role in the European strategy for P&T. One option to solve the issue of treatment of High Level Waste (HLW) is the transmutation of waste in accelerator driven systems such as MYRRHA. This reactor initiative is part of the European Sustainable Nuclear Industrial Initiative (ESNII) and is supported through international and bilateral collaborations. This reactor should replace the currently operating material test reactor BR2 and is planned to be fully operational by 2026. MYRRHA would be used for testing Gen-IV, for demonstrating P&T technology, and for the production of radioisotopes.

**A. Saturnin** (France) presented the studies carried out on minor actinide transmutation scenarios. The recycling of minor actinides in sodium-cooled fast neutron reactors has been studied, in homogeneous or heterogeneous modes or in a dedicated ADS stratum (Accelerator-Driven System). The transport of minor
actinides loaded elements is one of the technical issues under analysis: the feasibility of this operation was examined, pointing out all associated difficulties and uncertainties and the annual transport requirements in routine conditions were evaluated.

**T. Taiwo** (United States) summarised the US Nuclear Fuel Cycle Evaluation and Screening study. This study covered all aspects of the nuclear fuel cycle from mining to disposal. Different fuel cycle options were listed in order to identify the potential challenges and benefits as well as the most promising options. It also allowed ascertaining R&D needs.

**T. Sasa** (Japan) described the J-PARC Transmutation Experimental Facility (TEF) designed to support ADS design and technology. This new facility will consist of two buildings, an ADS target test facility (TEF-T) and a transmutation physics experimental facility (TEF-P). The work carried out at TEF will be part of a joint roadmap with MYRRHA.

**V. Ignatiev** (Russian Federation) summarised the progress made on molten salt reactor technology for transmutation. The results of a benchmark study involving codes and experimental data on MOSART and MSFR were presented.

Fuel cycle options for on-going/regional and phasing out scenario with ASTRID-like burners were investigated. **B. Vezzoni** (Germany) discussed the performances of both types of burners and explained that the results of the study showed that the burners allowed the use of all TRU compositions foreseen in the fuel cycle with a proper choice of the MAs/Pu ratios and of the U/TRU fractions.

**J. Lim** (Belgium) gave an overview of the experimental facility MEXICO designed to support the engineering and licensing of MYRRHA. The main purpose of MEXICO is to study LBE coolant chemistry, specifically, to develop oxygen control systems and purification technology. Highly accurate oxygen control was achieved by both oxygen control systems during the first experimental campaign.

### Session 4: Waste management for P&T scenarios

**J. Cobos** (Spain) presented the solubility studies carried out at CIEMAT on ThO₂(cr) and irradiated Th-MOX fuels. The fabrication and characterisation of the fuel pellets was described as well as the experimental results of leaching tests in different conditions.

**H. Ju** (Republic of Korea) presented some studies on the impact of potential inadvertent human intrusion on geological repository. Seven scenarios were considered to see the impact of partitioning ratio and loading of the waste in term of safety and radiation dose.

### Session 5: Advanced Nuclear Fuel Recycling

On behalf of members of the OECD Nuclear Energy Agency Expert Group on Fuel Recycling Chemistry, **S. Cornet** (NEA) summarised the state-of-the-art report on progress in separation chemistry, minor actinide separation and perspective for future R&D currently in preparation. This report reviews the status of separation processes related to current and future nuclear fuel cycles. Technological readiness of various reprocessing techniques was described.

#### 5a: Aqueous Processes

**S. Bourg** (France) described the ExAm process developed at CEA for the recovery of americium. This process was demonstrated in a hot lab in April 2010 and, since then experiments have been performed to improve several aspects of the process and define an optimised process flowsheet using the PAREX code.
Activities on minor actinide partitioning and lanthanide-actinide separation at the Indira Gandhi Centre for Atomic Research were summarised by R. Kumaresan (India). Different extractants are being considered and two-cycle process involving TRUEX solvent and HDEHDGA was demonstrated. Research is currently focusing on the development of a single cycle approach.

M. Nilsson (United States) presented some of the main results from an on-going project studying the connection between extraction synergy and micro-emulsions. The study investigated synergistic extraction of trivalent lanthanides and uranyl combining TBP and HDBP. Data obtained from EXAFS, XANES and thermodynamic studies of the metal extraction point towards the existence of two different metal-ligand complexes. The aggregates might not participate directly in the metal ion extraction, although it is quite possible that it strongly affects system behaviour.

T. Matsamura (Japan) mentioned the MA separation process currently being investigated. This process consists of a two-step extraction, the first one being the co-extraction of An(III)/Ln(III) with N,N,N’,N’-tetradecyldiglycolamide (TDdDGA). The second step separates An from Ln. New extractants are being explored.

A. Wilden (Germany) presented the results of the development of two innovative partitioning processes i-SANEX and 1-cycle SANEX. These separation processes are based on solvent extraction studies which benefit from the experience gained over the last 15 years in European collaborative projects. Both spiked processes showed excellent performance for the recovery of An (III) from simulated HAR solution. The 1-cycle SANEX and innovative SANEX processes demonstrated the possibility of separating An(III) directly from HAR solution in a single cycle.

5b: Pyrochemical Processes

S. Bourg (France) gave an overview of the work carried out at CEA on the Direct Oxide Solubilisation (DOS) process, an optimised process for head-end steps and liquid/liquid extraction. This study investigated the capability of fluoride salts for direct oxide dissolution preventing the use of HF gas. A theoretical approach coupled with experimental data was carried out on several simulated fission product and actinide oxides with promising results. The process was validated on an oxide mixture representative of irradiated fuel.

The use of Laser Induced Breakdown Spectroscopy (LIBS) to carry out quantitative measurement of molten salt composition was described by S-H. Kim (ROK).

S-M. Woo (United States) presented the development of a model for Pu mass accountancy in Pyroprocessing. A method to quantitatively evaluate the probability of error in the determination of Pu to Cm-244 ratio was proposed. As a first step, numerical recipes were developed for the deterministic evaluation of spent fuel composition. Uncertainties associated with the spent fuel composition were then quantitatively evaluated by a random-sampling approach.

J-H Jang (Republic of Korea) summarised the study of the separation of adhered salt in uranium deposits generated from an electrorefiner. Salt distillation with multilayer porous crucibles were tested and proved to be effective.

Session 6: Transmutation fuels and targets

V. Royet (France) gave an overview of the recent outcomes on the development of AmBB (Americium bearing blankets) fuels. Promising results were achieved for the conversion and fabrication of these types of fuel at laboratory scale. In addition, collaborative irradiation programmes and PIE examination are on-going. A database on MABB is planned to be generated by 2020.
M. Kato (Japan) described the relationship between mechanical and thermal properties in MA bearing fuels. The heat capacity and thermal conductivity were analysed in order to contribute to the development of Pu-burning MOX fuels.

An innovative route called calcined resin microsphere pelletisation (CRMP) for the development of mixed oxide fuel pellets was mentioned by M. Caisso (France). The main goal of this study was to point out and interpret the key-steps of weak acid resin (WAR) spherical precursor mineralisation into oxide through structural in-situ characterisations.

R. Kennedy (United States) reported the progress of R&D programmes carried out at Idaho National Laboratory (INL) regarding the development of actinides bearing alloy metallic fuels. In particular, demonstration of the fabrication of fuels under remote (hot cell) conditions; the chemical sequestration of lanthanide fission products to mitigate fuel-cladding-chemical-interaction (FCCI); and transmission electron microscopy (TEM) and atom probe tomography (APT) studies on the as-cast microstructure of the metallic fuel alloys were mentioned.

M. Ohta (Japan) discussed the results of irradiation tests of minor actinide bearing metal fuels with different burn-ups. Based on the chemical analysis results, the burn-ups were evaluated. The MA transmutation performance of U-Pu-Zr-MA alloys with medium burn-up was mentioned.

F. Delage (on behalf of GIF) presented the progress status of the Sodium Fast Reactor Advanced Fuel Project within the Generation IV International Forum. The project includes research on remote fuel fabrication & material manufacturing techniques as well as performance under irradiation.

Poster Session

64 posters were presented covering all areas of P&T. Among them, 10 posters were related to ADS and 21 to reprocessing.
Opening Session
Welcome address

J. Gulliford
OECD Nuclear Energy Agency

On behalf of the OECD Nuclear Energy Agency, I am very pleased to welcome you all to the 13th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation.

Let me start by expressing my sincere appreciation to our hosts, the Nuclear Transmutation Research Centre of Korea (NUTRECK) at Seoul National University, and in particular Professor Il Soon Hwang from the organisation.

This year is the 24th anniversary of the series of meetings initiated in 1990. Since then, the event has been held every second year at locations in Europe, Asia and North America. And of course, this time, I am very pleased to be able to join you here in Seoul.

This is my first visit to Seoul, so before I came, I did a little bit of research on the history of the city and how it is developing now. Well, it did not take me long to find out a few interesting facts. One of the first was that it was recently ranked joint leader in a review of technical readiness in a study of the world’s top 30 global cities. It seems that this determination to be at the forefront of technical innovation is not just a modern phenomenon. I also discovered that, in the late 19th century, Seoul became the first city in East Asia to introduce electricity (initially in the Royal Palace) before going on to implement electric street lighting a decade later. Today, the city is widely reputed to have the fastest internet connections with state of the art fibre optic network. So, in a city at the forefront of technical innovation and with a world class communications infrastructure, how appropriate should it be to host an information exchange meeting in a research area as technically challenging as partitioning and transmutation.

At the time of the last IEMPT event in Prague, the nuclear research community was still in the process of assessing how the events at Fukushima might shift the emphasis of our programmes of work. While it is true that significant resources have being brought to bear on safety issues related to the current fleet of nuclear power plant, it is also very clear that there remains a high level of interest (perhaps even higher than before Fukushima) in the continued development of advanced nuclear systems, as I am sure will be made very apparent through the presentations and discussions that we will share here this week.

So, as well as addressing some of the specific lessons learned from Fukushima, I see clear signs of continued international support for the general aims of energy policies that will be sustainable in the long term. In the shorter term, we are also seeing more to start the process of testing and improving innovative fuel designs and new fuel cycle options which offer the prospect of reduced levels of radioactive waste and which may ultimately significantly reduce the burden on disposal systems.

The OECD Nuclear Energy Agency is happy to offer its support to these developments and I can confirm our continued interest in helping to organise future IEMPT events.

Ladies and Gentlemen, welcome to the 13th IEMPT here in Seoul. I am sure we will have a successful and stimulating meeting.

Thank you for your attention
Welcome address

Honourable Dr. Han-Pyo KIM
Member of National Assembly
Committee on Trade, Industry and Energy
Republic of Korea

Mr. Gulliford of the OECD Nuclear Energy Agency, Mr. Hwang of Seoul National University, Mr. Basak of the IAEA, Mr. Warin of the French CEA, distinguished scientists and engineers, ladies and gentlemen, I am highly honoured to speak before many of world’s brightest people who gathered here at the 13th Information Exchange Meeting on Partitioning and Transmutation.

As a member of the National Assembly, I came here today to learn how to partition and transmute some Korean politicians who have high toxicity. I also came to pay my tribute to all of you who have come a long way to share knowledge and pride to solve one of mankind’s most challenging problems, called spent nuclear fuels and high-level wastes.

I was intrigued when I learned about the worldwide impasse of spent nuclear fuel management. I was scared by learning that terrorists can make dirty bombs out of insecure radioactive wastes. I was saddened by learning that many politicians and bureaucrats are trying to turn their attention away from this difficult problem.

Spent nuclear fuels at some of oldest Korean nuclear power plant will fill up their storage pools in as early as 2016. The Korean President Park has promised the nation that she will have her administration solve the problem through a consent-based process in order to keep one third of national electricity from nuclear power.

She made a wake-up call to politician and bureaucrats who have been hibernating under the roof of “wait-and-see” policy. We just began Korea’s first public debate on spent nuclear fuel management policy with a goal to find interim storage solutions.

While studying nuclear industry, I learned that the traditional approach called “deep geologic disposal” for spent nuclear fuels is under fire from public as well as some of world class experts. This was manifested by the evaporation of US Yucca Mountain Project, after thirty years of effort with 20 billion dollars of spending.

The US Blue Ribbon Commission asked by the U.S. President Obama recommended spent nuclear fuel interim storage to buy time for exploring game-changing innovation while searching for the first burying ground. This implies that geologic disposal will be very difficult to build even in US where there are a large number of empty land spaces.

Ladies and gentlemen, if a large country like the United States faces difficulties, what can be the choice for smaller countries with high population densities? I am fully convinced that P&T is the right solution to the spent nuclear fuel problem for all the densely-populated countries.
However, it would be necessary for several smaller countries to assemble an international consortium to solve this problem. The international consortium can be essential to avoiding fumbles in safety, security and safeguards. On this ground, I would like to express my sincere thanks to the leadership of OECD Nuclear Energy Agency, European Commission and International Atomic Energy Agency for their foresight in promoting this international collaboration on P&T.

Ladies and gentlemen, there will be rough water ahead of you as you are sailing to change the course of the world for the safety of future generations. We must not forget that there were messy oppositions to every great idea in the history of innovation. Some would try to discourage your good motivation just to defend their old-fashion business.

Believe or not, many selfish stakeholders tried to kill monumental inventions such as telephone, Apollo spacecraft, X-ray, automobiles, trains and even PC! We must not forget the history that all those great innovations won the war at the end, without exception.

As a law-maker, I am committed to serve you by developing legislations for the future. I have a great respect for the Member of French Parliament, Mr. Christian Bataille (who helped French P&T community fly by legislating the Law of 1991). I am impressed by the European Commission’s directive asking all the member states to follow the Bataille model. I have agreed to work with the IAEA to extend the models for the future of P&T technology.

Ladies and gentlemen, you have assembled here in Korea for this NEA meeting at the best season of a year. I hope you could take time out to partition and transmute yourselves from being serious scientists or engineers to Gangnam-style dancers during or after this conference.

At every step of your stride, I wish you – ladies and gentlemen – all the best and the brightest success as your endeavour will save our future generations and precious biosphere on this beautiful planet.

Thanks you very much for your attention.
Partitioning and transmutation for a sustainable nuclear energy

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Abstract

One major point for societal acceptance of nuclear energy is the management of nuclear waste, to minimise their quantity, their radio toxicity, and to optimise their final storage.

Reprocessing allows having a fuel cycle, where the plutonium is no more a waste. In this case, only 4% of the burned fuel becomes final waste and the final radio toxicity is also drastically reduced. This plutonium recycling in reactor is clearly the more efficient way to minimise the waste quantity and radio toxicity. Only fast breeder reactors allow a multi recycling of the Plutonium and the Uranium obtained, by reprocessing.

But three minor actinides remain with a lot of other fission products, in these 4% of burned fuel. Their partitioning operation was tested in laboratory and seems achievable. For their transmutation, an international campaign was made between 2003 and 2009, in the Phenix French sodium fast breeder reactor and also in some experimental reactors as HFR, to optimize the transmutation possibilities. The main results are the interest of fast breeder reactor for this job, and the demonstration of several technological and practical possibilities. The more interesting actinide to suppress, if we want jointly decrease the waste radio toxicity and his residual power in the final storage, is the Americium. Subsequently the studies on the ASTRID project are mainly oriented today on the Americium transmutation possibilities, in a future FBR.

Other ways to reduce nuclear waste quantity and radio toxicity, are studied in the world, as for example the ADS, or the better use of LWR reactors. A review of these options is made with some comparisons with the FBR possibilities.
Session 1:
International and National Programmes

Chair: I.-S. Hwang (Republic of Korea)
On-going P&T activities at the OECD Nuclear Energy Agency

S. Cornet and J. Gulliford
OECD Nuclear Energy Agency, France

Abstract

Partitioning and transmutation is considered as a potential route for improved management of spent nuclear fuel through the reduction of long lived radionuclides. Many countries are conducting R&D programmes dedicated to developing the necessary technologies.

Through international collaboration, the OECD Nuclear Energy Agency is coordinating a series of projects related to transmutation and partitioning covering both strategic and scientific issues. The activity is carried out by expert groups of the NSC Working Party on Scientific Issues of the Fuel Cycle (WPFC) whose programme of work covers existing and advanced nuclear fuel cycles, including fuel cycle scenarios, separation chemistry, innovative fuels and materials, and waste management. Outputs include reports on the advances and progresses of R&D in P&T which help identify gaps and needs in this field.

Introduction

Partitioning and transmutation (P&T) is considered as a potential route for the long-term management of spent nuclear fuel (SNF), to help reduce the radiological hazard, decrease the decay heat load in waste and reduce the quantities of fissile/fertile radionuclides that pose proliferation concerns [1]. Several countries have now recognised the need for investigating P&T strategies as part of advanced fuel cycles to address waste management and economic issues.

The NEA is involved in a number of activities related to P&T covering both strategic and scientific issues. These are mainly conducted under the guidance of the Nuclear Science Committee (NSC). The work is carried out by expert groups of the NSC Working Party on Scientific Issues of the Fuel Cycle (WPFC) who deal with issues arising from various existing and advanced nuclear fuel cycles, including fuel cycle scenarios, separation chemistry and flowsheets, innovative fuels and materials, and waste management. The WPFC also interacts with other relevant NSC Working Parties and NEA Standing Technical Committees, to ensure that the respective work programmes are complementary and to support common work where appropriate.

A series of reports covering these topics have been published or are in the process of being finalised. This paper describes the latest NEA activities, developments and findings in the field of partitioning and transmutation.

Minor actinides separation chemistry

Recycling is recognised as an important step to minimise the quantity and residual heat of long-lived nuclear waste and alleviate the burden on future deep geological repositories. The first step in recycling technology considers the separation of actinides through chemical separation methods based on either solvent extraction or pyroprocessing. An efficient and selective recovery of key elements from spent nuclear fuel (SNF) is essential for a successful sustainable fuel cycle concept.
The Expert Group on Fuel Recycling Chemistry is currently preparing a state-of-the-art report to assess the status of current technologies for the separation of minor actinides (MA). It mainly reviews current and advanced processes using aqueous (PUREX, advanced PUREX, GANEX, NEXT, etc.) or pyroprocessing technology to achieve either recovery of U and Pu alone or co-processing of U, Pu, Np. Processes for separation of Am and Cu are also reviewed. Comparison of chemical process and technical maturity is achieved through Technology Readiness Levels (TRL). As of today, only the PUREX process is well-established and used at commercial scale. Other aqueous processes technologies are established but need to be industrially demonstrated. Pyroprocessing, however, is still at an early stage of development but appears as a promising technology to treat advanced spent fuels such as metal, nitride, etc.

Recycling transuranics

A general international consensus shows that recycling of transuranics (TRU) through their transmutation in fast reactors is necessary to ensure the sustainable development of nuclear energy. Generally, two different route are being explored: homogeneous mode (recycling of grouped TRU) and heterogeneous (separation of MA from U and Pu) modes. A comparison of different studies performed in several international laboratories was carried out where the criteria for a choice between both recycling modes was defined and compared [2]. The specific scenarios for implementation, potential non-proliferation issues, and strategies for Cm management were considered. In this study, the impact on fuels fabrication and behaviour under irradiation as well as on both the reactor core and the power plant was highlighted. The multi-criteria analysis showed no large discrepancies between the two modes of minor actinides transmutation. Both are feasible and the final choice will depend on the importance given by decision-makers to different criteria.

Minor actinides burning in LWRs

Although fast reactors are considered as the preferred option for TRU transmutation, studies have nevertheless demonstrated that it was possible to achieve MA transmutation in thermal reactors. The Expert Group on Reactor Physics and Advanced Nuclear Systems (EGRPANS) (under the guidance of the Working Party on Scientific Issues of Reactor Systems) has prepared a report [3] to determine if thermal reactors could be a viable alternative to fast reactors by reviewing past experiments published in the literature. The outcomes of this study are that thermal reactors can burn MA and could play a role in reducing radiotoxicity of waste awaiting the deployment of fast reactors. In addition, they could be used to demonstrate technologies on existing reactors. MA burning R&D is however, still at a conceptual stage and design, fuel performance and waste management need further development to be demonstrated at commercial scales.

Minor actinides bearing fuels

Over the last decade, minor actinides fuels have been the subjects of numerous studies through different national and international R&D programmes. The Expert Group on Innovative Fuels has initiated a review of those programmes to assess the most recent advancements in the field in the form of a State-of-the-art report on Innovative Fuels [4] focusing, in particular, on fuel containing minor actinides (MA) to be irradiated in advanced nuclear systems.

Different fuel types were reviewed (metal, oxide, nitrides, dispersions fuels and special mechanical fuel forms) mainly for fast neutron reactors examining different technical issues associated with their fabrication, characterisation, irradiation performance, design and safety criteria. The technical maturity of each fuel was also assessed.

Metal and oxide fuels containing minor actinides have been widely investigated and irradiations tests and PIE have been performed. Additional results, however, are needed to gain further insights on He gas release and fuel cladding chemical interactions (FCCI). Nitrides fuels have numerous advantages for use in
ADS compared to other types of fuels due to their higher density. However, more fundamental research is needed to determine their safety performance.

On the other hand, dispersion fuels and special mechanical fuel forms (particles, namely Vipac and Spherepac) are new concepts. The first irradiation tests on inert matrix fuel containing MA started in the mid-90s. Three types of dispersion fuel have now been subjected to safety tests. Some irradiation experiments have marked important milestones in the R&D of transmutation fuels. However, the examination of the behaviour and safety issues of transuranic bearing fuels are limited to laboratory scale (grams quantities of TRU) and irradiation tests have been limited to small samples or rodlets. More experimental data coupled to modelling are needed to gain better understanding of fuel behaviour under operating conditions.

**Advanced fuel cycle scenarios**

Through the development of computer codes, many countries are currently evaluating potential future nuclear energy, employing fuel cycle scenario studies as a mechanism to inform decisions on future reactor types, fuel types, and other fuel cycle facilities. To meet the demand from member countries, the NEA is conducting various projects related to fuel cycle transition scenarios in particular through the Expert Group on Advanced Fuel Cycle Scenarios.

After reviewing national, regional and worldwide transition scenarios,[5] the Expert Group performed a benchmark study on different selected scenarios to compare existing codes in term of capabilities, modeling and results [6]. A study to evaluate the effects of the uncertainties of input parameters on the outcomes of fuel cycle scenario studies is currently ongoing with the objectives to provide guidance on the importance of each input parameters. A reference fuel cycle scenario (transition from a fleet of UOX fuelled PWRs to a fleet of MOX fuelled FRs under a constant nuclear energy demand) was employed to ensure that all codes performed comparable analyses of the scenario, and to identify any differences attributable to the modeling approaches between the codes. The results showed that difference between codes can be considered as acceptable.

The sensitivities of output metrics such as resource consumption, enrichment requirements, plutonium and spent fuel inventories, and reprocessing capacity to the various parameters are being evaluated. Varied input parameters include: nuclear energy demand and energy demand profile, spent nuclear fuel cooling time, fresh fuel fabrication time, date and rate of introduction of the fast reactors, fuel burnup, fuel composition (including the minor actinide content of the fast reactor fuel in case of MA transmutation), fast reactor breeding ratio, reactor lifetime, and introduction date, capacity, and losses of the reprocessing plant. The results show the relative impact of each parameter on each output metric.

**Waste management**

Separation of the actinides americium and curium is an important concept in advanced nuclear fuel cycles to reduce the amount of transuranic in waste. However, their similar chemistry makes their separation quite challenging. In this context, some countries have investigated the best ways to manage these isotopes. A recent report reviewed the methods used in France, Japan and the US to control the production and handling of curium [7]. Three different way are possible: 1) the separation of curium from americium and the storage of curium to allow decay to $^{240}$Pu; 2) recycling curium and americium without separation; 3) waiting several decades before reprocessing to allow minimisation of curium decay emissions and to reduce the specific requirements for its separation from americium. French studies compare the recycle of all minor actinides with the recycle of only neptunium and americium for sodium-cooled fast reactors. In the latter, after being separated from americium, $^{244}$Cm is stored for a long period to allow decay to $^{240}$Pu which can then be recycled. In Japan, scenarios compare the production of MA using different fuels or reactors: low enriched uranium in LWR used fuel, U-Pu MOX used fuel, FBR MOX used fuel and FBR U-transuranium (TRU) used MOX fuel. Studies have shown the effects of increasing decay
time following irradiation on decay heat generation from both fission products and actinide isotopes. Research in the US compared curium inventories in LWR used fuel as a function of decay time and its impact on reprocessing technologies.

**Minor actinide management**

Due to the difficulties in material handling, sample preparation and post-treatment, integral experiments for MA have been limited resulting in a lack of accuracy of nuclear data. In this context, an Expert Group on Integral Experiment for Minor Actinide Management (EGIEMAM) was established to review integral experiments for validating MA nuclear data, as well as to recommend additional integral experiments needed for validating MA nuclear data and to investigate the possibility to establish an international framework to facilitate integral experiments for MA management. The report “Review on existing integral data” [8] reviews the state of the art of nuclear data, relevant activities in international organisations, and existing integral data for MA. It concluded that further integral measurements are needed for $^{237}$Np, $^{241}$Am, $^{242m}$Am, $^{243}$Am, $^{242}$Cm, $^{243}$Cm, $^{244}$Cm, $^{245}$Cm. In addition, international collaboration such as joint design of reactor physics MA measurements in selected facilities and an international collaboration of irradiation programme for MA were suggested.

**Conclusions**

While P&T will never replace the need for waste repositories, it has the potential to reduce the level of radiotoxicity and residual heat in the waste streams. For this reason, P&T is active at national level in many countries and through international collaboration. The current focus of several R&D programmes is the separation of americium and its transmutation in fast reactors or ADS systems.

Through the work conducted within its numerous expert groups, the OECD Nuclear Energy Agency supports various activities related partitioning and transmutation covering all areas of the fuel cycle (fuel fabrications, systems and infrastructures, reprocessing and waste disposal and continues to help its member countries consolidating international knowledge. In addition the biennial Information Exchange meeting on Actinide and Fission Product Partitioning and Transmutation give experts the opportunity to present, share and discuss state-of-the-art developments in the field of P&T.

**References**

Partitioning and Transmutation: IAEA Activities

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Abstract

The importance of partitioning and transmutation (P&T) processes for sustaining nuclear energy growth in the world has been realized in several countries across the world. P&T processes aim at separation and recycling of actinides including minor actinides (MAs) from the spent fuel or high-level liquid waste. The objective of these processes include reuse of separated fissile materials from spent nuclear fuels to obtain energy, enhance resource utilisation, reduce the disposal of toxic radio-nuclides and improve long-term performance of geological repositories. R&D programmes have been launched in many of the Member States to develop advanced partitioning process based on either aqueous or pyro to recover MAs along with other actinides as well as automated and remote techniques for manufacturing fuels containing MAs for the purpose of transmuting them either in fast reactors or accelerator driven hybrids. A number of Member States have been also developing such transmutation systems with the aim to construct and operate demo plants and prototypes in the next decade.

The International Atomic Energy Agency has a high priority for the activities on partitioning and transmutation and regularly organises conferences, workshops, seminars and technical meetings in the areas of P&T as a part of information exchange and knowledge sharing at the international level. In the recent past, the Agency organised two technical meetings on advanced partitioning processes and actinide recycle technologies with the objective of providing a common platform for the scientists and engineers working in the areas of separation of actinides along with MAs from spent nuclear fuels and manufacturing of advanced fuels containing MAs in order to bridge the technological gap between them. In 2010, the Agency concluded a Coordinated Research Project (CRP) related to Assessment of Partitioning Processes. The Agency also conducted a first CRP on Studies of Advanced Reactor Technology Options for Effective Incineration of Radioactive Waste between 2002 and 2007 which was followed in the years 2005-2010 by a more specific CRP on Analytical and Experimental Benchmark Analyses of Accelerator Driven Systems. In parallel the status of the ADS technology for high level waste transmutation has been the focus of a study carried out by all the national and international organizations with an active programme on ADS, under the guidance of the IAEA Technical Working Group on Fast Reactors and ADS (TWG-FR). Finally, the benchmark analysis of two BN-600 reactor cores loaded with MOX fuel containing weapons-grade Pu and MOX fuel containing Pu and minor actinides from spent LWR fuel have been recently published. This paper will present the main results of these P&T activities as well as some new initiatives which have been discussed in recent meetings of the Technical Working Group on Nuclear Fuel Cycle Options (TWG-NFCO) and TWG-FR.
An Overview of Actinide Partitioning Research in the U.S. Fuel Cycle Research and Development Programme

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Abstract

The United States Department of Energy’s Fuel Cycle Research and Development program is investigating a number of technologies to support development of fuel cycle options for possible future implementation. One of the areas under development is the partitioning of actinide elements to enhance geologic disposal by transmutation in fast reactors. The Fuel Cycle Research and Development programme is researching both aqueous separation methods (primarily focused on oxide fuels) and pyrochemical methods (primarily focused on recycle of metal fast reactor fuel). An overview of the potential benefits of this type of fuel cycle in the United States will be provided, along with a description of the major research efforts underway to develop and demonstrate cost-effective partitioning technologies.
Status of Nuclear Energy Research and Development and Progress on Advanced Reprocess Technologies in the United Kingdom

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Abstract

In March 2013, the UK Government published the results of a major review of Nuclear Industry Strategy (NIS) which set out the approach needed to realise the vibrant, diverse and strategically cohesive sector that Government and industry wishes to see develop. In the field of nuclear R&D, the UK Government recognised the need for a national Nuclear Energy R&D Programme and it has established the Nuclear Innovation and Research Advisory Board (NIRAB) and future pathways for a Nuclear Energy R&D Roadmap for the United Kingdom. Additionally, a strategic review of the National Nuclear Laboratory (NNL) has led to the NNL reverting to being a Government-owned company from October 2013; with key remits to support the United Kingdom’s strategic nuclear research and development requirements, to operate supporting facilities, and to provide advice to Government in support of nuclear policy.

Whilst current reprocessing programmes in the United Kingdom are close to completion (~2018), and with this the pursuit by the United Kingdom for the time being of an open nuclear fuel cycle, there is a commitment to safeguard and enhance key nuclear scientific skills and facilities in the field of advanced systems, including advanced reprocessing and recycle technologies. Importantly, this approach allows the United Kingdom to revert to a closed fuel cycle under certain scenarios, as stated in the UK’s Nuclear Energy R&D Roadmap for pathways that indicate up to 75 GW of installed nuclear energy capacity by the mid-21st century. Building on the United Kingdom’s long track record in spent fuel reprocessing, continued investments have been made and recent research highlights include the development of a new grouped actinide extraction (GANEX) process with European framework partners, and Advanced PUREX flowsheets through the Department of Energy and Climate Change (DECC) programme.
Plutonium and Minor Actinides Management in France: Future Possible Scenarios

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Abstract

Plutonium management options are key for the development of sustainable nuclear fission systems. Several reasons for this: (i) plutonium efficient burning can open the way to the valorisation of huge natural energy resources ($^{238}$U, the plutonium precursor, is the most abundant fossil energy source); (ii) and plutonium is also, to several respects, a sensitive element (plutonium handling and/or disposal raise important issues).

This gives the guidelines for French fuel cycle back-end policy: used (enriched uranium oxide) nuclear fuel is currently reprocessed, and recovered plutonium is re-loaded as MOX fuel in LWRs. This allows uranium savings (about 10% of French electricity come from burning MOX fuels), and final waste without plutonium (nuclear glasses for fission products and minor actinides confinement); the recovered plutonium is systematically recycled (no Pu build-up increase) and used MOX fuels are stored in pools, as a resource for future nuclear systems. This can be seen as the first step toward sustainability.

Next step of sustainability would be the deployment, in the French fleet, of Generation IV fast neutron reactors which could allow, in the future, a complete and recurrent recycle of both uranium and plutonium, drastically extending (about two orders of magnitude) the natural uranium use, and possibly eradicating any TRU content in the final waste.

Such options are currently investigated in the frame of a specific Act, voted by the French Parliament “for sustainable management of radioactive materials and waste”. Different scenarios have been drafted and will be assessed (taking into account the diverse criteria and appropriate attributes), as a joint work embedding research and industrial bodies.

A dedicated research programme, the ASTRID programme, has been launched by CEA: it aims at designing of a generation IV sodium cooled demonstrator (both reactor and related fuel cycle facilities), which could be operated from around 2025.

Fuel cycle technologies are focusing important means, concerning both fuel fabrication and used fuel processing: the main goals are, keeping a progressive (step by step) approach, to improve current technologies (simplify, even increase compactness, safety, safeguardability), to adapt them to the specific features of fast reactor future fuels (higher Pu content, higher burnup,…), and, in a longer perspective, to complete them to allow in addition TRU recycle (Am recovery in used fuel and Am-bearing fuels manufacturing). The presentation will give, for these respective routes, the main guidelines and recent advances.
R&D on HLW Partitioning in Russia

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Abstract

Results of more than thirty years investigations on high level radioactive waste (HLW) partitioning in Russia are described. The objectives of research and development is to assess HLW partitioning technical feasibility and its advantages compared to direct vitrification of long-lived radionuclides. Many technological flowsheets for long-lived nuclides (caesium, strontium and minor actinides) separation were developed and tested with simulated and actual HLW. Different classes of extractants, including carbamoylphosphine oxides, dialkylphosphoric acids, crown ethers and diamides of heterocyclic acids were studied. Some of these processes were tested at PA “Mayak” and MCC. Many extraction systems based on chlorinated cobalt dicarbollide (CCD), including UNEX-extractant and its modifications, were also observed. Diamides of diglycolic acid and diamides of heterocyclic acids in polar diluents have shown promising properties for minor actinide-lanthanide extraction and separation. Comparison of different solvents and possible ways of implementing new flowsheets in radiochemical technology are also discussed.

Introduction

In the Russian Federation, the concept of closed nuclear fuel cycle (NFC) involving spent nuclear fuel (SNF) reprocessing is accepted. It is known that one of the advantages of closed NFC is the possibility for radical resolution of problem on long-term safe management of long-lived radionuclides, because the SNF reprocessing enables to recover and handle them separately.

An efficient method for the management of long-lived radionuclides is transmutation. The long-term radiotoxicity of the remaining waste could be significantly decreased by additional recovery of the MAs and their transmutation into short-lived radionuclides in advanced nuclear reactors or accelerator driven systems. The resulting waste could reach the radiotoxicity level of natural uranium ores in a few centuries instead of more than 100 000 years. This is the goal pursued by the global strategy of partitioning and transmutation developed in several European research projects of the Euratom programme [1].

Another promising way is to create extra strong matrices being disposed into geological formations. In the case of transmutation, or in the synthesis of highly strong matrices for geological disposal, there is a need for the selective recovery of long-lived radionuclides contained in SNF. This may be achieved by the availability of reprocessing plants with special facilities for recovery of long-lived radionuclides in the NFC infrastructure.

The goals set to partitioning were different and changed overtime. Up to 1985, the main goal was to separate individual isotopes for their subsequent use. Today, the main goal is to get several fractions or individual radionuclides for their following storage or transmutation. One of the options is the separation of Am and creation of new fuel with minor actinides.
This paper summarises the results of R&D on HLW partitioning in Russia.

**Cs and Sr recovery**

Strontium-90 is the major generator of heat and caesium-137 is the major generator of gamma radiation in HLW after 3-year storage. One of the tasks that were set for partitioning at an early period was the selective separation of Sr. In the United States, the high selective SREX-process was developed for this purpose [2]. This process is based on the use of 4,4'(5')-di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6) dissolved in PUREX-process solvent (TBP in Isopar-L).

In Russia, the modification of this process was performed. Fluorinated alcohols instead of TBP-kerosene mixture were proposed as a diluent. This allowed the use of cheaper compound – dicyclohexano-18-crown-6 (DCH18C6) [3]. This system (DCH18C6 in fluorinated alcohols) was tested many times including hot test with real HLW at PA “Mayak”.

The next step of this work was the creation of the process for simultaneous extraction of Cs and Sr by a mixture of different crown-ethers [4]. DCH18C6 was chosen for Sr extraction and dibenzo-21-crown-7 (DB21C7) – for Cs recovery. As a diluent, polar fluorinated diluent (H(CF₂)₅CH₂OH) with addition of higher alcohols was used. The test in laboratory scale showed that more than 99.5% Cs and Sr could be recovered from acidic wastes.

![Figure 1: Structures of crown ethers](image)

For simultaneous separation of Cs and Sr the greatest success was achieved by using CCD-process [5]. Chlorinated cobalt dicarbollide (CCD) was proposed for extraction by Czech scientist [6]. It was shown that the solvent including CCD and polyethylene glycol (PEG) in polar fluorinated diluent – meta-nitrobenzotrifluoride (F-3) [7] is acceptable for use in technology. The structures of the mentioned compounds are presented in Figure 2. The proposed flowsheet provides a separation of 99% of Cs and Sr and less than 0.15% remain in raffinate. This process was used at industrial scale. More than 1 179 m³ of HLW was processed; more than 50 million Ci of Cs and Sr were recovered at PA “Mayak”.

![Figure 2: Structures of CCD, PEG and fluorinated diluents](image)
UNEX-process

An example of complex approach to partitioning is the UNEX-process. It was developed as a result of cooperation between Idaho National Laboratory (United States) and Khlopin Radium Institute (Russia) for treatment of highly salted solutions. UNEX-process uses a solution of chlorinated cobalt dicarbosside, carbamoylphosphine oxide (CMPO) and polyethylene glycol (PEG) in polar fluorinated diluent as a solvent. The classical solvent composition of UNEX-solvent is 0.08 M CCD + 0.01 M PEG + 0.02 M CMPO in polar diluent. In the United States, phenyltrifluoromethylsulphon (FS-13) was chosen whereas in Russia, meta-nitrobensotrifluoride (F-3) as a diluent was tested. This process extracts actinides, lanthanides, Cs and Sr from acidic wastes and their separation in Cs-Sr and An-Ln flows at the stripping stage. Different variations of UNEX-process were tested many times in the USA and in Russia. Also several hot tests were carried out [8].

To achieve partitioning of solutions with high concentration of lanthanides the composition of UNEX-process solvent was modified. Instead of CMPO, tetrabutyldiamide of dipicolinic acid (TBuDPA) was proposed [9]. The new UNEX-solvent composition was 0.08 M CCD + 0.01 M PEG-400 + 0.05-0.06 M TBuDPA in polar diluent [10]. The dynamic test with simulated HLW was carried out at PA “Mayak” and confirmed that new solvent can be used for treatment of wastes with high concentration of fission products.

A system based on bis-tetrazolyl-pyridines with CCD was studied. CCD-NATP mixtures selectively extract Am with a Am/Eu separation factor of more than 90 [11.] This ligand possesses high stability in acidic solutions. The flowsheet for separation of minor actinides was calculated and will be tested.

Minor actinides recovery

Processes on the base of “hard” donor ligands

One of the difficult tasks in radiochemistry is the separation of minor actinides from lanthanides as these groups of metals have a very similar chemical behaviour. A lot of different ligands and processes on their base for separation of minor actinides from nitric acid solutions were proposed and tested. The most powerful and well known compounds for extraction of actinides are “hard” donor ligands: carbamoylphosphine oxides, diamides of carboxylic acids, phosphine oxides etc. All these compounds extract both actinides and lanthanides from acidic solutions.

Figure 3: Structures of “hard” donor extractants
Neutral bifunctional extractants have been studied in Russia for several years. These studies have been carried out in parallel with investigations in the USA, Europe and India. Classical TRUEX-process uses CMPO dissolved in PUREX-process solvent. Some modifications of TRUEX process were developed in Russia. All modification was aimed to increase the loading capacity of the extraction system by changing the paraffinic diluent to a polar one. First of all, the so-called “Russian TRUEX-process” should be mentioned. In this process CMPO dissolved in polar fluorinated diluent F-3 was used [12]. In addition, some modifications of SETFICS-process were made. One of them proposed a solvent based on CMPO dissolved in the mixture of TBP and F-3 [13]. The proposed flowsheets were tested many times including tests with real HLW.

Recently, a new modification of the SETFICS-process was made. A new non-toxic fluorinated inflammable diluent Formal-N2 was proposed [14]. A dynamic test of new solvent using model solutions was carried out. The results of the test showed good extraction and hydrodynamic properties of new solvent. It was shown that Am can be fully separated from La and partially recovered from Ce, Pr and Nd.

It is known that salts of dialkylphosphoric acids can extract metals from acidic solutions. Solution of zirconium salt of dibutylphosphoric acid (Zr-DBP) in TBP-Isopar L was proposed for the processing of radioactive wastes. The authors state that the advantages of this solvent were its compatibility with the PUREX solvent and the low price of the extractant. This system provides separation of TPE, lanthanides and also Sr. It was tested in different conditions and also a hot test with real HLW was carried out. 0.4M Zr-DBP solution in 30% TBP + isopar-L was used as a solvent. Thirty liters of HLW were treated [15].

Diamides of diglycolic acid of different structure were studied in Russia. Polar fluorinated diluents allow the use of short-length diamides without third phase formation during extraction [16]. A new flowsheet for minor actinides separation was tested at PA “Mayak” using simulated waste with high concentration of fission products. 0.2 M TODGA in F-3 was used as a solvent. It was shown that this system allows recovering of minor actinides with lanthanides. The flowsheet was then modified and a new test is now planned.

“Mixed” donor ligands

Another class of ligands studied in Russia as potential extractants for minor actinides separation is diamides of heterocyclic dicarboxylic acids. These ligands belong to mixed donor ligands: they possess “soft” donors – nitrogens of pyridine ring and “hard” donors – carboxylic oxygens. Such combination provides high extraction ability to f-elements and a better affinity to actinides. The main advantages of this class of products are their high solubility in polar diluents and easiness of synthesis. Three classes of diamides of heterocyclic dicarboxylic acids are now under investigation in Russia.

Diamides of dipicolinic acid (DPA) are promising ligands for the separation of actinides from HLW. These ligands extract both actinides and lanthanides from nitric acid solutions. The separation factor for Am/Eu recovery is moderate and do not enhance the value of 6. At the same time, minor actinides can be separated from REE at the stage of stripping. The flowsheet for separation of minor actinides from HLW with high concentration of lanthanides was developed. This flowsheet was calculated for recovering of 99.5% of Am from simulated solution.

Figure 4: Structures of “mixed” donor extractants
Diamides of 2,2’-dipyridyl-6,6’-dicarboxylic acid have an additional pyridine ring in their structure and selectively extract minor actinides from nitric acid solutions. Lanthanides are not extracted. A Am/Ln separation factor more than 10 was achieved [17]. All lanthanides can be separated from fission products on the stage of extraction. The flowsheet for separation of minor actinides from HLW with high concentration of lanthanides was calculated and tested at laboratory scale using simulated solutions.

The latest class of diamides is diamides of 1,10-phenanthroline-2,9-dicarboxylic acid. These ligands seem very promising for the separation of actinides from HLW and are now actively studied not only in Italia and China, but also in Russia.

Conclusion

Partitioning is a traditional direction of R&D in Russia. The original target of partitioning was the separation of radionuclides for use. Nowadays the main priority is the separation of radionuclides, particularly of Am, for burning in new reactors-types. To find the appropriate extraction system for Am separation from HLW, new ligands are being developed and investigated and well-known processes modified. The most promising ligands are diamides of dicarboxylic heterocyclic acids. The use of polar fluorinated diluents, as an alternative to traditional hydrocarbon diluents, is the specifics for partitioning in Russia. Russia was the pioneer in the use of fluorinated diluents, but they are now being studied in other countries.

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References


Review of ADS and P&T Programme in Japan

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Abstract

The partitioning and transmutation (P&T) technology to reduce the burden of high-level radioactive waste management is recently receiving more public attention than ever before in Japan. In this context, the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan launched a Working Party to review research and development (R&D) on P&T using an Accelerator Driven System (ADS), and issued an interim report of the Working Party in November 2013. Although P&T concept with ADS, called “Double-strata Fuel Cycle”, had been regarded as a backup option of that with a Fast Breeder Reactor, the Working Party recommended to change the R&D phase of this technology from a fundamental stage to a principle demonstration stage. For ADS, the Working Party recommended to promote the R&D toward the Transmutation Experimental Facility of J-PARC, though further technical evaluation was requested to start its construction. The Working Party also recommended to consistently facilitate various R&D for other technical areas than ADS in parallel. Such technical areas include partitioning process for minor actinides and fission products, and dedicated transmutation fuel and its cycle. A consolidated roadmap toward the realisation of this technology was also discussed in the Working Party.

Introduction

In Japan, research and development (R&D) on the partitioning and transmutation (P&T) technology has been energetically promoted under the OMEGA program since 1988 [1]. The Atomic Energy Commission (AEC) of Japan held two checks and reviews (C&Rs) so far: one was from 1999 to 2000 [2], and the other was from 2008 to 2009 [3]. In the C&R in 1999, it was recommended to facilitate R&D for two types of P&T technology in parallel, i.e., the homogeneous MA recycle by commercial fast breeder reactor (FBR) cycle and so-called Double-strata fuel cycle concept where the dedicated transmutation by accelerator driven system (ADS) is adopted. In the C&R in 2008, the report said that the activities for the R&D of P&T technologies should be undertaken as a part of the activities for the R&D of FBR and its fuel cycle technologies. ADS was considered as a backup option when FBR with homogeneous MA recycling would confront difficulty.

Since the accident of Fukushima Daiichi Nuclear Power Plant in March 2011, the nuclear power in Japan has been facing various difficulties. Although the problem of radioactive waste management was not a newly emerging one, it has been emphasised as one of fatal defects to continue the use of nuclear power. The scheme to find candidate sites for the disposal of high-level radioactive waste (HLW) had been unsuccessful in Japan for these 10 years. Based on these contexts, technology to reduce the volume and harmfulness of HLW is gathering lots of attention from public.

The Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, launched two technical working parties (WPs) to discuss the way forward to facilitating the R&D on P&T. One of two WPs is the WP on Monju Research Plan (hereinafter called as WP-Monju), and the other is the WP to Review P&T Technology (hereinafter called as WP-PT). The WP-Monju was established in October 2012,
and issued its report in September, 2013 [4]. The scope of this WP was not limited to the waste management aspect, but it covered general technical aspects for FBRs including safety research.

The WP-PT was established in July, 2013, and issued its interim report in November, 2013 [5]. Because discussion by WP-Monju had started, the scope of the WP-PT was limited to the P&T technology using ADS. The WP-PT restarted the discussion in July 2014, and will issue its view in September.

In parallel, the Ministry of Economy, Trade and Industries (METI) of Japan had conducted the discussion about the energy policy, and eventually the Cabinet decided to approve the new Strategic Energy Plan in April, 2014 [6]. This new Strategic Energy Plan includes some mentions concerning the promotion of P&T technology.

According to these movements, R&D on P&T is being accelerated in Japan. In this work, the outline of these political movements is reviewed, putting an emphasis on the R&D for ADS. Moreover, recent R&D activities based on these policies are briefly shown.

**WP-Monju**

Because of the sodium leakage accident in 1995 and other troubles so far, including the adaptation to the new regulation after the accident of Fukushima Daiichi Nuclear Power Plant, the prototype fast breeder reactor Monju has not yet been able to restart. In this period of time, the circumstances around FBR changed largely in Japan. The ability to deal with plutonium and MA flexibly has been emphasised rather than the saving of uranium resource.

In the context of this situation, MEXT established WP-Monju to re-define the meaning of the fast reactor development and to make the role of Monju clear.

After about one-year discussion, WP issued the Monju Research Plan, where Monju is positioned as a core field of R&D for three items: (1) Compilation of R&D results including verification of technical feasibility for FBR plants, (2) R&D aiming at reduction of volume and radiological toxicity of wastes using FBR/FR system, and (3) R&D aiming at establishment of safety technology system for FBR/FR as a nuclear power plant.

**WP-PT**

As mentioned in the above, the Double-strata fuel cycle concept including a dedicated transmutation system such as ADS has been recognised as the backup of the homogeneous MA recycling in commercial FBR cycle. Considering the present situation around nuclear power in Japan, however, the incentive to promote R&D on ADS has been increasing because it is meaningful to secure flexible options for the future. This was a motivation to launch this WP. The discussion in the WP-PT included the current P&T research activities, construction of the Transmutation Experimental Facility (TEF) in J-PARC, and collaboration with the MYRRHA project proposed by the Belgian Nuclear Research Centre(SCK•CEN).

TEF consists of two facilities [7]: the ADS Target Test Facility (TEF-T) and the Transmutation Physics Experimental Facility (TEF-P). TEF-T is a material irradiation facility with a 400-MeV 250-kW proton beam delivered by a proton LINAC of J-PARC. A lead-bismuth spallation target will be installed, and various candidate materials for beam window of ADS will be irradiated with protons and spallation neutrons. TEF-P is a critical / subcritical facility where a 400-MeV 10-W proton beam is available to conduct subcritical experiment. A certain amount of minor actinides will be used as well as the nuclear fuel to simulate transmutation systems.
The Interim Report summarised the evaluation results on the progress of R&D issues and the future plans as:

- **TEF-T** is being proposed under J-PARC to verify the feasibility of the beam window which is a big challenge for ADS. It is appropriate to shift the R&D of the facility to the next stage. It is required to make a detailed plan of irradiation and test including the maintenance and improvement of infrastructure for post irradiation tests.
- **TEF-P** is being proposed under J-PARC to overcome difficulties in reactor physics issues such as for a subcritical core and an MA-loaded one. Since this facility is proposed as a nuclear reactor, the safety review based on the new regulation is to be applied. With taking care of this point, it is appropriate to shift the R&D of the facility to the next stage. Since TEF-P is required to assure the safety, non-proliferation, physical protection, and nuclear security as a nuclear reactor facility, the R&D plan, the facility plan and the management system of TEF-P should be established so as to meet these conditions.
- Before the construction of TEF, review is required on the status of the achievement for R&D subjects.
- For MYRRHA Programme, it is appropriate to proceed with negotiation about JAEA’s participation at a reasonable level and mutual collaboration with Belgium and other relevant countries.
- The evaluation of technical readiness levels of the technical fields (partitioning, ADS, fuel cycle, and fuel) showed that we are approximately on the stage to move up R&D from “conceptual study” to “principle demonstration”, and it is appropriate to shift the R&D to the next stage of engineering scale.

As for the Roadmap to realise this technology:

- It is important to promote the R&D of P&T technology with keeping consistency among various fields of technology. The roadmap proposed by JAEA (Figures 1 and 2) is regarded as appropriate.
- The plan of further future in the roadmap should be reviewed in appropriate timing, taking account of the re-consideration of the nuclear policy and progress of R&D including other types of P&T such as the FBR cycle.
- Issues to be continuously discussed were verified as: Although it is considered appropriate to promote J-PARC TEF to the next stage, further check and review is required on the status of the achievement for underlying R&D, technical feasibility including operation and maintenance, consistency to regulations, etc.

**New strategic energy plan**

The Government of Japan periodically formulates the Basic Energy Plan in accordance with an article in the Basic Act on Energy Policy that entered into force in 2002. So far, three versions were issued in 2003, 2007 and 2010, respectively, and the fourth one, called the Strategic Energy Plan, was issued in April 2014.

Drastic change of domestic and international circumstances around the energy was taken into account to formulate this Plan. The largest change must be the accident of the Fukushima Daiichi Nuclear Power Plant. In spite of the accident, the Plan defines the nuclear power as an important base-load power source as a low carbon and quasi-domestic energy source, contributing to stability of energy supply-demand structure, on major premise of ensuring of its safety. This issue to its superiority in stability of energy supply and efficiency, its low and stable operational cost, and is free from green-house effect gas emission during operation.
Figure 1: Roadmap for partitioning and ADS fuel cycle

MA separation
- Separation process
- Waste treatment
- Plant design
  - Innovative extraction
  - Tracer tests
  - MA/RE recovery
  - MARS separation
  - Treatment of products and secondary wastes
  - Solvent recovery process
  - Design of separation equipment & plant

Fuel fabrication for MA transmutation
- Fuel fabrication process / plant
- Conceptual study of the process
- Waste estimation
- Flowsheet design

Pyroprocessing of MA fuel
- Fuel performance
- Preliminary assessment of the fuel property
- Preconditioning
- Chopping tests of surrogate fuel rods
- Basic data measurements

Electrical reprocessing / MA recovery
- Waste treatment
- Waste treatment tests with surrogates
- Zeolite column tests
- Flow sheet design

Engineering-scale chopping tests with surrogates
- MA fuel sample irradiation tests
- Design & optimization of the equipment system
- Unit operation tests of actual scale equipment
- BENCH scale tests with irradiated fuels
- Engineering-scale tests with surrogates

Actual fabrication plant
- (Supply of MA products for ADS fuel fabrication)
- Item completed
- Item in progress (red) and to be focused on (black)
- Item in the future: An item requiring new facility is shown by “@” (10gMA) and “©” (kgMA-6MA)

Note: Time axis does not represent exact periods of development
- Flow of technology
- Flow of MA

Figure 2: Roadmap for ADS plant

Reactor physics
- Code development
- Physics of sub-critical
- Basic experiment of spallation reaction
- Simulation of core element, sub-critically measured quantity

MA nuclear data
- Nuclear data measurement
- Consistency data
- ENDF / elsewhere

Plant
- Conceptual design of plant
- Safety concept
- Conceptual design of safety instrument
- Control method of accelerator
- Validation of small instrument

LBE thermal hydraulics
- Conceptual study of element technology
- Prototypical study of target
- Property, etc.

Spallation target
- Conceptual study of target
- Basic data acquisition for corrosion and irradiation effect

Material for LBE
- Conceptual study
- Lab-scale test of element technology

Accelerator
- J-PARC accelerator
- Full-scale development
- Improvement of reliability
- Development of superconducting accelerator
- Development of superconducting accelerator for the 1st ADS

Construction of the 1st ADS (800MWe, MOX fuel partially containing MA)
- R&D on MA fuel manufacturing and reprocessing

Plant design and instrument development for the 1st ADS
- Flow of technology
- Flow of MA

Output
- Item almost completed
- Item in progress (red) and to be focused on (black)
- Item to be promoted based on the evaluation
- Item in the future: An item requiring new facility is shown by “©”.
The Plan puts emphasis on the importance of activities to resolve the challenge of how to manage and dispose of spent fuel, as well as the Fukushima restoration, safety operation of nuclear plants, and public acceptance.

As for the P&T technology, the Government will promote technology development on volume reduction and mitigation of degree of harmfulness of radioactive waste. Specifically, development of technologies for decreasing the radiation dose remaining in radioactive waste over a long period of time and enhancing the safety of processing and disposal of radioactive waste, including nuclear transmutation technology using fast reactors and accelerators, will be promoted by utilising global networks for cooperation. Also, while the Government examines the situation of study and progress in terms of final disposal, it studies the feasibility of integrated implementation of the R&D for final disposal and reduction of volume, international research cooperation and a researcher resource development related to them.

Based on this new Strategic Energy Plan, a subcommittee to discuss the specific actions for the nuclear policy was launched in June, 2014, and wide range of discussion is being conducted.

**Recent R&D on ADS and its fuel cycle**

Based on the descriptions in the interim report of WP-PT, the R&D on ADS and its related fuel cycle technology have been promoted.

For ADS, preparation to construct TEF is being conducted [7]. Considering the increased regulation after the accident of the Fukushima Daiichi Nuclear Power Plant, it will take longer time to obtain the licence of TEF-P which is defined as a nuclear reactor facility. We, therefore, intend to start construction of TEF-T at first around the fiscal year of 2016.

Before the construction of TEF-T, various developments are necessary. One of those is the technology for a lead-bismuth spallation target. We are installing loop facilities to verify the oxygen control technique, a flow meter, and so on. Another is the remote handling technique to deal with irradiated target vessel and activated samples.

For TEF-P, safety analysis under the new nuclear regulation is being conducted. The feasibility to deal with MA-bearing fuel in the facility is also to be verified.

International collaboration is also very important. Figure 3 shows the relation of TEF with the MYRRHA Programme. TEF-T will contribute to the upgrade of MYRRHA from a viewpoint of the material of the beam window. TEF-P will provide valuable information for the physics of MA transmutation system using a certain amount of minor actinides. On the other hand MYRRHA is a rather demonstrative facility where a high-power subcritical reactor is driven by a proton accelerator. MYRRHA is also relevant for the accumulation of experiences on lead-bismuth coolant system. Both projects, therefore, complement each other to realise the ADS for MA transmutation.

R&D for partitioning of high-level liquid waste (HLLW) is also being conducted. A new separation process to separate minor actinides and lanthanides together from HLLW using the extractant called TDDGDA was developed and its satisfactory performance was verified [8]. The process to separate minor actinides from lanthanides is, however, still under investigation.

For the MA-bearing fuel for ADS and its fuel cycle are also being developed. The first candidate of the ADS fuel is uranium-free nitride with inert matrix of ZrN. The dry process will be applied for the reprocessing of this nitride fuel. Fuel property database is being prepared, and an analysis code for fuel behaviour simulation is to be developed. The fabrication method of nitride fuel is also under investigation. For the dry process, a method to enhance the recovery ratio of actinides from spent ADS fuel is being developed.
This is being carried out at the existing facilities in JAEA. In order to proceed to the next step of the demonstrative stage, a new hot-cell facility should be built where kg-order of minor actinide handled.

Conclusion

Recently in Japan, P&T technology is getting more public attention than ever before. In this context, national review activities for Monju and ADS were conducted. Moreover, the Government of Japan determined the new Strategic Energy Plan, where the importance of the R&D on P&T is clearly pointed out. Based on these recent situations, various R&D on ADS and its fuel cycle are being promoted. The technical development for TEF of J-PARC is also being conducted to start its construction from the fiscal year of 2016.

References


Session 2:
Fuel Cycle Strategies and Transition Scenarios

*Chairs: H. Oigawa (Japan) and J. Law (United States)*
The Effects of the Uncertainty of Input Parameters on Nuclear Fuel Cycle Scenario Studies


Abstract

Decisions taken in the near term can have large consequences on the eventual outcomes of a chosen fuel cycle due to the long-time frames involved in the development, construction, operation and decommissioning of nuclear facilities, and the storage of nuclear waste. Numerous elements of future fuel cycles, such as the future nuclear energy demand and costs associated with future fuel cycle facilities that are not available commercially today, are not currently known, or not well-known. Due to these uncertainties, many countries are currently evaluating potential future nuclear energy scenarios, employing fuel cycle scenario studies as a mechanism to inform decisions on future reactor types, fuel types, and other fuel cycle facilities.

Fuel cycle scenario studies are complex, involving many interconnecting components. Many of the input parameters have large uncertainties. However, not all uncertainties will have a significant impact on each of the evaluation metrics of the fuel cycle. Certain evaluation metrics will be more sensitive to different input parameters. The Nuclear Energy Agency’s Expert Group on Advanced Fuel Cycle Scenarios has undertaken a study to evaluate the effects of the uncertainties of input parameters on the outcomes of fuel cycle scenario studies. The goal of this work is to provide guidance on which input parameters it is important to investigate thoroughly and know well, and which components can be less well-known, given the objectives of a particular study.

Each participating member chose their own scenario code, the choices of which include: VISION, COSI, FAMILY, COSAC and EVOLCODE. A simplified nuclear fuel cycle scenario was employed as a reference case to first ensure that all codes performed comparable analyses of the scenario, to identify any differences attributable to the modeling approaches between the codes, and to provide a baseline against which to evaluate sensitivities. The reference scenario involves the transition from a fleet of UOX fuelled PWRs to a fleet of MOX fuelled FRs under a constant nuclear energy demand.

The sensitivities of output metrics such as resource consumption, enrichment requirements, plutonium and spent fuel inventories, and reprocessing capacity to the varied parameters were evaluated. Varied input parameters include: nuclear energy demand and energy demand profile, spent nuclear fuel cooling time, fresh fuel fabrication time, date and rate of introduction of the fast reactors, fuel burnup, fuel composition (including the minor actinide content of the fast reactor fuel in case of MA transmutation), fast reactor breeding ratio, reactor lifetime, and introduction date, capacity, and losses of the reprocessing plant.

The results show how the output metrics are affected by the choice of scenario code, with an explanation of which assumptions underlie these effects. The results also show the relative impact of each parameter on each output metric. If the feasibility of the scenario in terms of fissile materials availability is threatened, possible adjustments of input parameters are explored.
Comparison of the Overall Environmental Footprint between Current and Future Nuclear Fuel Cycles

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Abstract

Nuclear energy is anticipated to be one of the possible energy sources which can allow the production of energy at high load with a high level of reliability without significant impact on the environment. Nowadays, most of the countries have chosen an open fuel cycle which basically considers spent nuclear fuel as a waste, whereas others like France, the United Kingdom, Japan and soon China reprocess their spent fuel to recover the plutonium (and partially U) to produce mixed oxide fuel to be irradiated in a second cycle. In a second step, considering the possibility of fertilising $^{238}\text{U}$ to $^{239}\text{Pu}$ in fast reactors, recycling major actinides is thought to be a major improvement towards the global sustainability of the nuclear energy: It will indeed allow the natural resource efficiency to be increased by orders of magnitude by consuming quantitatively the natural uranium resource involved. Driven by the Fukushima accident, nuclear energy is currently questioned about its overall environmental impact and footprint. However, very little information is available on the actual footprint of current and future nuclear systems. In order to bring insights on this issue, a life cycle assessment simulation tool NELCAS was developed based on the French nuclear closed fuel cycle. It allows the calculation of representative key environmental indicators and potential impact indicators for the whole nuclear systems. The very good consistency of the results with the literature data confirms the relevance and robustness of NELCAS. It was subsequently used to derive representative indicators for open and future potential fuel cycles, i.e. mixed GEN3 and GEN4 reactors fleet and full GEN4 reactors fleet. The results demonstrate the very significant improvement brought by the actinides recycling and the future fuel cycle. Most of the indicators are very significantly decreased with the implementation of long-term recycling strategies. This paper will present in the details the figures of merit of the different fuel cycles options and assess their respective sustainability.
Mass Flow Data Comparison for Comprehensive Fuel Cycle Options

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Abstract

One of the key objectives stated in the United States Department of Energy, Nuclear Energy R&D Roadmap is the development of sustainable nuclear fuel cycles that improve natural resource utilisation and provide adequate capability and capacity to manage wastes produced by the fuel cycle. In order to inform this objective, an evaluation and screening of nuclear fuel cycle options has been conducted. As part of that effort, the entire fuel cycle options space was represented by 40 Evaluation Groups (EGs), and mass flow information for each of the EGs was provided by using an Analysis Example (AE).

In this paper, the mass flow data of the 40 AEs are compared to inform on trends in the natural resource utilisation and nuclear waste generation. For the AEs that need enriched uranium support, the natural uranium required is high and the natural resource utilisation is generally lower than 2% regardless of the fuel cycle strategy (i.e., once-through, limited recycle, or continuous recycle). However, the utilisation could be improved by avoiding enriched uranium fuel support. The natural resource utilisation increases to more than 80% by recycling the nuclear fuel continuously without enriched uranium support.

The combined mass of spent nuclear fuel (SNF) and high-level waste (HLW), i.e., SNF+HLW mass, is lower by using a continuous recycle option compared to a once-through fuel cycle option, because SNF mass is converted to mass of recycled products and only fission products and other process losses need to be disposed. The combined disposed mass of depleted uranium (DU), recovered uranium (RU) and thorium (RTh), i.e. DU+RU+RTh mass, has a similar trend to the uranium utilisation. For the AEs that need enriched uranium fuel, the DU and RU are the major fraction by mass of the DU+RU+RTh, which are two orders of magnitude higher in mass compared to those for the AEs that do not need enriched uranium fuel.

Introduction

The United States Department of Energy’s Office of Nuclear Energy (DOE-NE) developed a roadmap for its research, development and demonstration activities to ensure that nuclear energy remains a compelling and viable energy option for the United States, based on its ability to provide abundant and stable electricity supply while helping to meet clean air and carbon reduction goals. One of the key objectives stated in this Nuclear Energy Research and Development (R&D) Roadmap [1] is to develop sustainable nuclear fuel cycles, where the nuclear fuel cycle is the progression of nuclear fuel from mining and enrichment to power generation to ultimate disposal of the used nuclear fuel or derived waste products.
To achieve this objective and enable prioritisation of future activities, an Evaluation and Screening (E&S) study [2,3] of nuclear fuel cycle options has been conducted to inform the potential benefits and challenges of nuclear fuel cycle options and to identify a relatively small number of promising fuel cycle options with the potential for achieving substantial improvements compared to the current nuclear fuel cycle in the United States. The study was required to consider the complete nuclear energy system extending from mining to disposal.

As the entire space of potential fuel cycle options is quite large, there was a need to ensure that an adequate set of fuel cycle options was evaluated in order to inform comprehensively on potential fuel cycle performance. It was determined that the study could be conducted at a physics-based functional level, where each part of fuel cycle was represented only by the physics characteristics of that part, such as the use of thermal neutron irradiation or fast neutron irradiation. Using this approach, it was possible to develop a comprehensive set of fuel cycle option groups that were subsequently collected into 40 Evaluation Groups (EGs) based on the similarity of physics-based performance. In addition, an Analysis Example (AE) was identified for each EG. The fuel cycle performance parameters of the AEs were evaluated in order to generate data needed for the development of metrics data that were used to inform the high-level fuel cycle evaluation criteria utilised in the E&S study. The mass flow information is one of the evaluated fuel cycle performance data.

In this paper, the 40 EGs are introduced, along with a sample AE for a specific EG. The mass flow data of the AEs are then compared to inform on trends in the natural resource utilisation and nuclear waste generation. It is noted that a similar comparison had been conducted in Ref. 4 using a limited set of Analysis Examples. That earlier comparison has now been extended in this paper using data for the 40 AEs.

Nuclear fuel cycle evaluation groups

In principle, an almost endless variety of nuclear fuel cycles may be possible reflecting the specific nuclear technologies that could be available. This made it necessary to develop an approach for informing on the entire space of fuel cycle options, and the E&S study was conducted using the following key steps:

- Development of a comprehensive set of fuel cycle option groups that represent the performance of all possible fuel cycle options for generating and using nuclear power based on fundamental reactor physics principles.
- Collection of the set of fuel cycle option groups into so-called Evaluation Groups (EGs) based on similarities in physics-based performance, and confirmation that these groups are appropriate when all high-level criteria are considered.

This process resulted in the 40 distinct EGs that were determined to be sufficient to comprehensively represent all fuel cycle options to inform on their potential for providing substantial improvement with respect to the specified high-level fuel cycle evaluation criteria [3]. The high-level descriptions of the 40 EGs are provided in Table 1, which includes 8 once-through EGs, 10 limited recycle EGs, and 22 continuous recycle EGs. The detailed procedures for developing the evaluation groups are described in Refs. [2,3].

In Table 1, the EGs in yellow highlight require enriched uranium fuels. Each evaluation group contains one or more fuel cycle option groups. For instance, the once-through fuel cycle option with the current state-of-the-art commercial Pressurised Water Reactors (PWRs) utilising low enriched uranium (LEU) nuclear fuel is in EG01. On the other hand, one with CANDU reactors utilising natural uranium fuel is in EG03.
the fuel cycle performance parameters were evaluated for it. As example, Figure 1 and Table 2, respectively, show the material flow diagram and mass flow data of the AE for EG32. It is noted that an online Fuel Cycle Catalog [6] has been developed as a repository of information on fuel cycle options and associated technologies.

Table 1: Key description of forty evaluation groups

<table>
<thead>
<tr>
<th>EG</th>
<th>Key Description Indicative of Fuel Cycles in Evaluation Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Once-through</strong></td>
</tr>
<tr>
<td>EG01</td>
<td>Once-through using enriched-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG02</td>
<td>Once-through using enriched-U fuel to high burnup in thermal or fast critical reactors</td>
</tr>
<tr>
<td>EG03</td>
<td>Once-through using natural-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG04</td>
<td>Once-through using natural-U fuel to very high burnup in fast critical reactors</td>
</tr>
<tr>
<td>EG05</td>
<td>Once-through using enriched-U/Th fuel in thermal or fast critical reactors</td>
</tr>
<tr>
<td>EG06</td>
<td>Once-through using Th fuel to very high burnup in thermal EDS</td>
</tr>
<tr>
<td>EG07</td>
<td>Once-through using natural-U fuel to very high burnup in thermal or fast EDS</td>
</tr>
<tr>
<td>EG08</td>
<td>Once-through using Th fuel to very high burnup in fast EDS</td>
</tr>
<tr>
<td></td>
<td><strong>Limited Recycle</strong></td>
</tr>
<tr>
<td>EG09</td>
<td>Limited recycle of U/TRU with new natural-U fuel to very high burnup in fast critical reactors</td>
</tr>
<tr>
<td>EG10</td>
<td>Limited recycle of 233U/Th with new Th fuel in fast and/or thermal critical reactors</td>
</tr>
<tr>
<td>EG11</td>
<td>Limited recycle of 233U/Th with new enriched-U/Th fuel in fast or thermal critical reactors</td>
</tr>
<tr>
<td>EG12</td>
<td>Limited recycle of U/Pu with new natural-U fuel in fast and/or thermal critical reactors</td>
</tr>
<tr>
<td>EG13</td>
<td>Limited recycle of U/Pu with new enriched-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG14</td>
<td>Limited recycle of U/Pu with new natural-U fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG15</td>
<td>Limited recycle of U/Pu with new enriched-U fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG16</td>
<td>Limited recycle of U/Pu with new enriched-U fuel in thermal critical reactors and fast EDS</td>
</tr>
<tr>
<td>EG17</td>
<td>Limited recycle of Pu/Th with new enriched-U/Th fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG18</td>
<td>Limited recycle of 233U/Th with new enriched-U/Th fuel in thermal critical reactors</td>
</tr>
<tr>
<td></td>
<td><strong>Continuous Recycle</strong></td>
</tr>
<tr>
<td>EG19</td>
<td>Continuous recycle of U/Pu with new natural-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG20</td>
<td>Continuous recycle of U/TRU with new natural-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG21</td>
<td>Continuous recycle of U/Pu with new enriched-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG22</td>
<td>Continuous recycle of U/TRU with new enriched-U fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG23</td>
<td>Continuous recycle of U/Pu with new natural-U fuel in fast critical reactors</td>
</tr>
<tr>
<td>EG24</td>
<td>Continuous recycle of U/TRU with new natural-U fuel in fast critical reactors</td>
</tr>
<tr>
<td>EG25</td>
<td>Continuous recycle of 233U/Th with new enriched-U/Th fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG26</td>
<td>Continuous recycle of 233U/Th with new Th fuel in thermal critical reactors</td>
</tr>
<tr>
<td>EG27</td>
<td>Continuous recycle of 233U/Th with new enriched-U/Th fuel in fast critical reactors</td>
</tr>
<tr>
<td>EG28</td>
<td>Continuous recycle of 233U/Th with new Th fuel in fast critical reactors</td>
</tr>
<tr>
<td>EG29</td>
<td>Continuous recycle of U/Pu with new natural-U fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG30</td>
<td>Continuous recycle of U/TRU with new natural-U fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG31</td>
<td>Continuous recycle of U/Pu with new enriched-U fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG32</td>
<td>Continuous recycle of U/TRU with new enriched-U fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG33</td>
<td>Continuous recycle of U/Pu with new natural-U fuel in both fast EDS and thermal critical reactors</td>
</tr>
<tr>
<td>EG34</td>
<td>Continuous recycle of U/TRU with new natural-U fuel in both fast EDS and thermal critical reactors</td>
</tr>
<tr>
<td>EG35</td>
<td>Continuous recycle of U/Pu with new enriched-U fuel in both thermal critical reactors and fast EDS</td>
</tr>
<tr>
<td>EG36</td>
<td>Continuous recycle of U/TRU with new enriched-U fuel in both thermal critical reactors and fast EDS</td>
</tr>
<tr>
<td>EG37</td>
<td>Continuous recycle of 233U/Th with new enriched-U/Th fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG38</td>
<td>Continuous recycle of 233U/Th with new Th fuel in both fast and thermal critical reactors</td>
</tr>
<tr>
<td>EG39</td>
<td>Continuous recycle of 233U/Th with new enriched-U fuel in both thermal critical reactors and fast EDS</td>
</tr>
<tr>
<td>EG40</td>
<td>Continuous recycle of 233U/Th with new Th fuel in fast EDS and thermal critical reactors</td>
</tr>
</tbody>
</table>

For the purpose of performing reactor physics-based analyses and to generate data needed for the metrics associated with the high-level criteria, an Analysis Example (AE) was identified for each EG and the fuel cycle performance parameters were evaluated for it. As example, Figure 1 and Table 2, respectively, show the material flow diagram and mass flow data of the AE for EG32. It is noted that an online Fuel Cycle Catalog [6] has been developed as a repository of information on fuel cycle options and associated technologies.
Table 2: Mass flow data of analysis example of EG32

<table>
<thead>
<tr>
<th>Stage</th>
<th>1</th>
<th>2</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology</td>
<td>Fuel</td>
<td>NPPT</td>
<td>Rep/Sep</td>
</tr>
<tr>
<td>Electricity (GWe-year)</td>
<td>63.4</td>
<td>36.6</td>
<td>100.0</td>
</tr>
<tr>
<td>Feed or product of nuclear materials (metric ton)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural resource</td>
<td>NU</td>
<td>-12 027.2</td>
<td></td>
</tr>
<tr>
<td>Products from fuel or NPPT technology</td>
<td>DU</td>
<td>+10 634.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LEU</td>
<td>+1 389.6</td>
<td>-1 389.6</td>
</tr>
<tr>
<td></td>
<td>RU</td>
<td></td>
<td>+169.0</td>
</tr>
<tr>
<td></td>
<td>TRU</td>
<td></td>
<td>+84.2</td>
</tr>
<tr>
<td></td>
<td>DF</td>
<td>+1 389.6</td>
<td>-1 389.6</td>
</tr>
<tr>
<td>Products from Rep/Sep technology</td>
<td>RU</td>
<td>+1 287.2</td>
<td>-169.4</td>
</tr>
<tr>
<td></td>
<td>TRU</td>
<td></td>
<td>+17.6</td>
</tr>
<tr>
<td></td>
<td>FP</td>
<td>+70.8</td>
<td></td>
</tr>
<tr>
<td>Loss</td>
<td></td>
<td>+2.8</td>
<td>+13.9</td>
</tr>
</tbody>
</table>

All the mass data in Table 2 were evaluated for the fuel cycle equilibrium state with the assumption of nuclear material loss rate of 0.2% during fresh fuel fabrication and 1.0% during discharge fuel (DF) reprocessing/separation (Rep/Sep) processes. The masses were normalised to 100 GWe-year of electricity for the whole nuclear fleet, which is about the current electricity capacity of the nuclear fleet in the United States. The signs (-) and (+) indicate the feed and product to or from each fuel cycle technology category, respectively. In this particular fuel cycle option, the PWR and SFR provide electricity shares of 63.4% and 36.6%, respectively, in the equilibrium state.

Masses in each column indicate the mass flow per each fuel cycle function to support each stage, while the masses in the last column indicate the total feed and final products from the AE. For instance, in order to generate 100 GWe-year of electricity, this particular AE requires 12 027 tons of natural uranium (NU) and produces 10 635 tons of depleted uranium (DU), 1 266 tons of non-used recovered uranium (RU), etc.
(RU), and 107 tons of fission products (FPs). It also has 20 tons of material losses in the fuel fabrication and discharge fuel Rep/Sep processes. Similarly to the information for EG32, the mass flow data of all AEs of the 40 EGs were evaluated.

Comparison of mass flow data

In this section, using the mass flow data of all AEs of the 40 EGs, the required natural resource masses, natural resource utilisation, disposed masses of spent nuclear fuel (SNF), high-level waste (HLW), DU, RU, and recovered thorium (RTh) are compared. For consistent comparison, the mass flow data for each AE was renormalised to unit electricity generation (i.e., metric ton per GWe-year), done with common fuel cycle assumptions such as material loss rates of 0.2% and 1.0% during fuel fabrication and Rep/Sep process, respectively, and 5-year post-irradiation cooling, 1-year fuel fabrication times, and uniform thermal efficiency of 33%. Exceptions were for the thermal efficiency of the EDS which was adjusted accounting for the electricity consumption to support the system components: e.g., the accelerator in an EDS, and when an MSR is adopted as the AE of a specific EG, the material loss fraction was assumed to be lower than that of the common assumption because the molten-salt fuel is continuously reprocessed in an online mode.

Natural uranium and/or thorium requirement and utilisation

The required natural resource (t/GWe-year) and its utilisation (%) for all AEs of the 40 EGs are plotted in Figure 2, in which the EGs are re-ordered by the required natural resources. In this study, the natural resource utilisation (%) was defined as the ratio of the natural resource mass consumption to the required natural resource mass. It is noted that the total mass of the FPs is equivalent to the natural resource consumption by fission. The total FP masses are comparable regardless of the fuel cycle options because of the similar fission rate per unit energy generation. Thus, the natural resource utilisation is inversely proportional to the required natural resource mass, as the trend shown in Figure 2.

![Figure 2: Required natural resource and utilisation](image)

The natural resource utilisation is generally lower than 2% for the AEs regardless of the fuel cycle strategy (i.e., once-through, limited recycle, or continuous recycle) when enriched uranium fuel is required. This is because the major portion of natural uranium is converted into DU in the enrichment process. The EGs that need enriched uranium are highlighted in yellow in Table 1.

The once-through fuel cycle using PWRs, which is the AE of EG01 and currently utilised in the United States, has a natural resource utilisation of about 0.6%. On the other hand, the once-through fuel
cycle using High Temperature Gas-cooled Reactors (HTGRs), which is the AE of EG02, has the lowest utilisation because of its high uranium enrichment, which is required to achieve high burnup. It is noted that, although enriched uranium fuel is used, the natural resource utilisation of the continuous recycle option of the AE of EG37 increases to ~5% because the ratio of the PWRs with enriched uranium fuel to the entire nuclear fleet is small in this particular AE.

For the fuel cycle options that do not need enriched uranium support, the natural resource utilisation is high and the maximum achievable resource utilisation is dependent on the fuel cycle strategy. Compared to the once-through fuel cycle strategy, the resource utilisation can be increased up to 30% (AE of EG04) by irradiating the natural uranium to a very high burnup in a fast reactor. The utilisation can be increased further by recycling the used nuclear fuel (UNF): 50% by recycling it limited times (AE of EG09) and more than 80% by recycling it continuously (AE of EG24).

It is noted that the natural resource utilisation of a continuous recycle option could be close to 100%, which is the theoretical maximum value when there are no material losses during the Rep/Sep and fuel fabrication process. However, as shown in Figure 2, the natural resource utilisation values of the continuous recycle options are lower than the theoretical maximum value due to the material losses in the fuel fabrication and DF Rep/Sep processes. The impact of the material losses on the resource utilisation is described in [4]. Even though uniform assumptions for losses were used, the exception of having to specify losses for an MSR differently (0.2% rather than 1.0%) caused the AE of EG26 to have the highest utilisation because the exception resulted in the lowest material losses being assumed for the MSR that was utilised as the AE of EG26. If the material losses of the AE for EG26 were increased to ~5.1%, based on the Molten-Salt Breeder Reactor (MSBR) study in the 1970s [7], Reference 4 indicates that the natural resource utilisation of EG26 would be lower than 70%.

Mass of spent nuclear fuel and high-level waste

The mass of SNF+HLW disposed per energy generated for all AEs of the 40 EGs are plotted in Figure 3, where the mass is for the heavy-metal and fission products only, and does not include cladding or structure for SNF or any waste form matrix for HLW. The mass varies from 1.3 t/GWe-yr to 147.6 t/GWe-yr. Figure 3 shows that in general (but with a few exceptions), the mass of SNF+HLW disposed per energy generated decreases from the once-through fuel cycle options to those of continuous recycle fuel cycle options. The SNF is the dominant contribution to the SNF+HLW mass for the once-through fuel cycle options, while the SNF mass is zero for the continuous recycle options. For the once-through fuel cycle options, the SNF mass is inversely proportional to the average discharge burnup. Thus, the AE of EG03, which is a once-through fuel cycle using Heavy Water Reactors (HWRs) with natural uranium feed, has the highest SNF+HLW mass because the discharge burnup from the HWRs is smallest amongst the 40 AEs. The relatively low SNF+HLW mass for the once-through strategy EG08 is due to the fact that the associated AE utilised only natural uranium as fuel and that fuel is irradiated to a very high burnup (~75%) in a Fission-Fusion Hybrid (FFH) system.

The total SNF+HLW masses are comparable for the continuous recycle options, which consist of the mass of fission products (FPs) and other waste products and material losses from used fuel reprocessing and fresh fuel fabrication. The FPs are the dominant contributors to the SNF+HLW mass of the continuous recycle options and the FP mass is comparable in all AEs of the 40 EGs because about the same mass of heavy metal is destroyed during fission to generate the same amount of electricity. The minor difference is due to the corrections of thermal efficiencies for EDS that are necessary because a portion of their fission energy is used for driving auxiliary systems. Thus, the material losses from reprocessing govern the minimum bounding value of the SNF+HLW mass for the continuous recycle options. Due to the low loss fraction assumed for the MSRs as noted above, the AE for EG26 has the lowest SNF+HLW mass value.
The mass of DU+RU+RTh disposed per energy generated for all the AEs of the 40 EGs are plotted in Figure 4. Regardless of the fuel cycle, a sizeable amount of DU is produced for fuel cycles that need enriched uranium fuel. The AE of EG01 produces 167 metric tons of DU to generate one GWe-yr of electricity. Another once-through fuel cycle AE with HTGRs that represents EG02 gives the highest DU mass of 296 t/GWe-yr because it requires a large amount of uranium with higher enrichment on a per unit energy generation basis. The DU mass is zero for the fuel cycle options that do not need enriched uranium support and the fuel cycle options that are fed thorium fuel only.

Figure 4 shows that the AE of EG12 gives the highest RU mass. This is a two-stage limited recycle example in which the recovered plutonium (Pu) is recycled in a thermal spectrum system without enriched uranium support. The first stage of the AE of EG12 uses HWRs, which breed Pu without enriched uranium support, and the recovered Pu from the stage is burnt once in the second stage utilising PWR technology. As a result, the AE of EG12 does not produce DU, but produces significant amount of RU from the initial NU fuel. The RU mass is zero for all once-through fuel cycle options. In addition, the RU mass is zero for the fuel cycle options that recycle the RU entirely or the fuel cycle options that are fed thorium fuel only.

Some fuel cycle options produce both DU and RU. For instance, the AE of EG13 is a two stage-limited recycle example in which the recovered Pu from the first stage that uses enriched uranium fuel is recycled in the thermal reactors of the second stage. Consequently, the option produces both DU and RU.

Among all AEs of the 40 EGs, fifteen AEs require thorium feed along with or without uranium feed. There is no RTh mass in all the AEs because the recovered thorium is entirely recycled in all of them.
Conclusions

In this paper, mass flow data have been compared for the Analysis Examples of the 40 evaluation groups (EGs) used in an Evaluation and Screening study of fuel cycles for the United States Department of Energy, Office of Nuclear Energy. The mass flow data were evaluated for the equilibrium state and normalised to unit electricity generation. The comparisons were for the required natural uranium and thorium masses, natural resource utilisation (%), and disposed masses of spent nuclear fuel (SNF), high-level waste (HLW), depleted uranium (DU), recovered uranium (RU) and thorium (RTh).

The study indicated that for the AEs that need enriched uranium support, the required natural uranium is high and as a result, the natural resource utilisation is generally lower than 2% regardless of the fuel cycle strategy. However, the natural resource utilisation could be improved if the enriched uranium fuel support is avoided. For the fuel cycle options that do not need enriched uranium support, the natural resource utilisation is as high as ~30% for the once-through options, ~50% for the limited recycle options, and more than 80% for the continuous recycle options.

In general, the mass of SNF+HLW is lower by using a continuous recycle option relative to a once-through fuel cycle because SNF mass is converted to mass of recycled products and only fission products and other process losses need to be disposed. For the once-through fuel cycle options, the SNF+HLW mass was found to vary from 2 t/GWe-year to ~150 t/GWe-year, depending on the discharge burnup. However, the SNF+HLW masses are comparable for the continuous recycle options, which are about 1.3 t/GWe-year, and fission products are the dominant contributors to the mass. It is noted that the SNF+HLW mass is for the heavy-metal and fission products only, and does not include cladding or structure for SNF or any waste form matrix for HLW.
The mass of DU+RU+RTh varies from 0 t/GWe-year to ~300 t/GWe-year. For the AEs that need enriched uranium fuels, the non-used DU and RU are the major fraction of the DU+RU+RTh mass. Generally, DU is the dominant contributor and RU is the second leading contributor. There is no RTh in any AEs because of either no Th feed or complete recycle of the recovered Th. The DU+RU+RTh masses are about two orders of magnitude different between fuel cycles that need enriched uranium fuels and those that do not.

Acknowledgements

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The German P&T Study: Results and Conclusions
in the View of the Contributing Helmholtz Research Centres

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Abstract

The decision to phase out electric energy production in nuclear power plants in Germany has put some questions on the future of P&T research. The Federal Ministry for Economic Affairs and Energy and the Federal Ministry of Education and Research have launched a study managed by the National Academy of Science and Engineering to answer these questions on a broad scientific basis. The major mandate was to evaluate scientific and technological as well as socio-economic challenges and opportunities of the P&T technology in the view of the phase out decision, both in a national and an international context. The scientific and technological aspects of P&T are analysed with respect to a possible contribution to the management of nuclear waste, using the following structure:

- Starting point and boundary conditions – waste amounts and final disposal strategies.
- Definition and description of scenarios – possible ways for transmutation; European vs. national.
- Technology challenges of P&T – description of the major challenges to be solved on the way to a possible industrial application.
- Safety aspects – dedicated safety aspects including all steps of the P&T cycle.
- International projects & competences in Germany – what is going on around the world and which support could come from the German industry?

In parallel, the socio-scientific, the ecologic and the economic aspects have been analysed using expert interviews, group Delphi and independent expert opinions on economic, legal and environmental aspects. An overview of the study’s results will be given from the viewpoint of the contributing Helmholtz research centres at Jülich (FZJ), Dresden-Rossendorf (HZDR) and Karlsruhe (KIT), with a focus on the research-political recommendations and the developed research strategy proposed to the ministries.

Introduction

As a result of the Fukushima event, the German government has decided to shut down 8 nuclear power plants (NPPs) immediately. In June 2011, the German government announced the Energiewende. This decision prepared the way for the phase out of the electric energy production in nuclear power plants in Germany. The process was fixed in the 13th Amendment of the Atomgesetz in August 2011. It was decided that the remaining 9 German NPPs will be shut down by 2022 [1].

However, no decision has been made regarding the final disposal of highly radioactive (heat generating) nuclear waste in Germany. No site for the final disposal of this kind of waste is available and a previous site
The political decision to phase out electric energy production in nuclear power plants in Germany has put some important and urgent questions on the future of P&T research in Germany. To answer these questions on a broad scientific basis, the Federal Ministry for Economic Affairs and Energy and the Federal Ministry of Education and Research have launched a study managed by the National Academy of Science and Engineering (acatech). The major objective was to evaluate scientific and technological as well as socio-economic challenges and opportunities of the P&T technology in the view of the phase out decision. The results are published as an acatech STUDIE, a 300-page report giving a comprehensive view on the situation of P&T in Germany [3]. Based on the STUDIE, an acatech POSITION [4] was prepared by acatech. The POSITION’s text was agreed upon by all participants to the STUDIE. The POSITION gives acatech’s conclusions and political recommendations regarding the future of P&T research in Germany. This manuscript summarises the major results of the POSITION. The POSITION should provide the scientific basis for the urgently required political decision on the future of P&T. This may have an important impact on the question of radioactive waste storage to be answered by the above-mentioned commission.

The amount and properties of the nuclear waste to be disposed of is highly important for its management and for the decision on a possible final disposal site. The technology of P&T could provide an opportunity to reduce the long term risk potential of the heat generating nuclear waste by transmuting the long lived transuranium (TRU) isotopes (plutonium and the minor actinides, i.e. neptunium, americium and curium) into short lived ones. In the partitioning step uranium and the TRU are separated while the fission products remain in the waste stream to be vitrified. Thus, only the vitrified fission products as well as the activated structural materials would have to be disposed of as heat generating waste. Low activity liquid wastes such as decontamination and rinsing solutions accumulated as secondary waste streams must be sent to a low-level waste repository. The fission products generated by the transmutation of the actinides also have to be sent to the final repository for high level nuclear waste.

Four possible social development scenarios have been designed as a reference for the STUDIE; they are based on the German nuclear phase out decision:

- **Abstinence**
  Germany operates no transmutation facility; no research on P&T is institutionally funded.

- **Participation to research**
  Germany carries out national research to maintain an influence on international bodies and participates to European and international research programmes.

- **Participation to European Systems:**
  Germany carries out national research and actively participates to international research programmes and to European initiatives towards the construction of P&T facilities.

- **Application in Germany**
  Both P&T research and the construction of P&T facilities are actively carried out as part of a national waste management strategy.

The consequences of these scenarios have been evaluated and compared based on a broad choice of methods, providing a specific chances-to-risk estimation.
Chances of P&T (compare [4])

- If successfully applied on industrial level, P&T offers the benefit of significantly reducing the volume of the highly radioactive heat generating waste. The volume required for storage is expected to be reduced to approximately one third, mainly due to the separation of uranium. Simultaneously, the volume of low-level waste would increase by one third.

- P&T reduces the long-term radioactivity and radiotoxicity after several hundred years and thus the hazard potential. After 1 000 years, the radioactivity level would be comparable to the level after one million years without P&T. However, based on the currently available experience and the results of the preliminary safety analysis for the Gorleben final disposal site, the release potential would not be reduced.

- The threat of diversion and misuse of plutonium from a final disposal is eliminated. Separated plutonium will be transmuted, thus only marginal amounts (i.e. processing losses) will go to the final disposal.

- Partitioning opens the way for improved conditioning of mobile fission and activation products. This eliminates the instant release from directly disposed fuel assemblies, thus reducing the long term risk of a release into the biosphere.

- P&T reduces the heat generation after 70 to 100 years due to the separation of plutonium and americium. Placing the waste into the final disposal after this time period offers the possibility of reducing the spacing between disposal drifts.

Risks of P&T (compare [4])

- P&T facilities carry a potential environmental risk. This risk is comparable to be one arising from the operation of future facilities for reprocessing and conditioning and of nuclear reactors of the 4th generation.

- The risk of misuse of radioactive materials is increased during the period of the operation of the P&T facilities (approx. 150 years). Depending on the separation processes, plutonium and minor actinides may be present in pure or in mixed form. These materials could be diverted during transport or storage. The same can be claimed for other radioactive materials due to the required prolonged opening period of the final disposal sites.

- The cost of P&T per ton of waste will be high due to the limited waste amounts in Germany. Construction and operation of P&T facilities is not expected to be efficient from an economic point of view, compared to direct disposal.

- The majority of the German public is opposed to any kind of nuclear facility. Construction and operation of P&T facilities is expected to lead to public protests.

- Negative media coverage may be expected on planning, construction, and operation of P&T facilities, as has been the case with other nuclear facilities in the past.

Limitations

Some benefits of P&T will have small or no effect due to the specific situation in Germany. This situation is defined by the fact that part of the German spent fuel has already been reprocessed and the waste has been vitrified, and by the phase out decision. Furthermore, the amount of secondary low and intermediate level waste will increase by approx. 30%. Additional storage and disposal capacity has to be created for this waste.
Some recommendations as given by acatech (compare [4])

On the one hand, constructing and operating P&T facilities in Germany – independently of other countries – is not advisable from an economic, ecotoxicologic and societal point of view. On the other hand, stopping the R&D activities and disembarking from all P&T options seems premature from the current point of view. Both fundamental and applied research should be continued in a European framework. This will keep open all options for a period of time required to answer the open questions on P&T technology. Furthermore, competence and jobs in nuclear research as well as participation in international committees and panels can be maintained.

1. P&T research in a European context as well as the evaluation of a future German contribution to P&T in Europe is recommended.
2. The participation to research should not lead to any dependency regarding investments into future application of P&T.
3. An interdisciplinary, comprehensive study should be worked out as basis for a decision on a possible contribution to P&T in Europe. Processes involving the general public should be planned in time for a decision to be expected in 10 to 15 years.
4. Germany should follow the European perspective as well as national research activities related to the phase out decision.
5. The German industry should consider a possible implementation of P&T as a chance.
6. Research should focus on key topics:
   - Efficient partitioning.
   - Efficient transmutation of the TRUs.
   - Safety evaluation of the facilities.
   - Societal implications of all options.
7. An interdisciplinary approach must be followed to evaluate and communicate scientific and technological development to the public.
8. A research alliance should be established.

Recommendations regarding science (compare [4])

R&D should focus on essential topics. Further to scientific and engineering challenges, societal, environmental and economical implications need to be addressed within the P&T context. Safety research, influencing all areas of P&T, is of utmost importance. acatech recommends focusing on the following major R&D topics:

- **Efficient partitioning** of the long-lived, highly radioactive and heat generating TRUs from the waste stream. The challenges are: minimising the TRU losses and the secondary waste streams; developing safe, environmentally acceptable and proliferation resistant processes; improving the conditioning of the waste streams.
- **Efficient transmutation** of the separated TRUs in tailored systems. The requirements are: safe operation of facilities, high transmutation rate to minimise the number of recycling steps and transports, and consequently reduced environmental impact. Additionally, economic analysis and optimisation of the proposed concepts should be provided.
• **Enhancing methods for evaluating the safety** of P&T facilities. The safety assessment of all P&T process steps (partitioning, fuel fabrication, transmutation, transport) requires developing and providing an adequate safety approach. This has to be backed with models and the required software tools.

• **Determination and evaluation of the social implications** of all possible options. Technical solutions have to be implemented in an economic, political and societal environment. This is not only a matter of acceptance, but also a matter of integration into the democratically authorised energy policy and the increasingly democratic culture of planning large infrastructural investments.

A more detailed view on the key technologies identifies the following central challenges for the technological research on P&T:

• **Partitioning**
  The research topics range from basic research in radiochemistry (development of highly efficient extraction processes) to scale-up studies towards an industrial facility. The objective is the separation of TRU from irradiated LWR fuel and the production of dedicated transmutation fuel. An optimised conditioning of the partitioning waste streams is a further issue.

• **Transmutation systems**
  System dependent research has to be based on the evaluation of the strengths and weaknesses of different transmutation systems (critical vs. sub-critical systems, solid vs. liquid fuelled systems) to fulfil the objectives of the phase out decision and the strategy given by politics. Following the evaluation, dedicated R&D has to be promoted, e.g.
  - **ADS**: development of the fast neutron source (proton accelerator and spallation neutron source)
    Development of a super conducting linear accelerator is an important goal. The objective is a significant improvement in continuous operation mode reliability, combined with an economic optimisation. Another aim is the improvement of the classical external spallation target. The expected result is a high power external neutron source located in the centre of the reactor core: design, coupling to the accelerator, safety, structural materials, thermodynamics, neutronics and nuclear data. The fertile free fuel option should be further developed; this avoids additional TRU built up, resulting in a highly efficient transmutation.
  - **Liquid fuelled reactors**: safety approach and fuel cycle
    A safety approach for the evaluation of the design of a reactor system with liquid fuel and integrated fuel processing (salt cleaning) is to be developed. The continuous removal of fission products from the fuel and the handling of the fission products need to be improved and optimised.

• **Nuclear data and reactor physics**
  Uncertainty in the nuclear database – both in general and with respect to the minor actinides – has to be reduced by suitable experiments and improved modelling. Zero power experiments in a fast reactor environment have to be performed for ADS to study the safety parameters both experimentally and on the basis of validated simulations. Simulation tools for the modelling of the moving fuel, the continuous feeding of fuel and the fission product removal and release are required for liquid fuelled reactors.

• **Transmutation**
  Research is focused on all aspects relevant to safety and to the optimisation of transmutation efficiency. Thermodynamics, fuel behaviour, material research and technological development (models, laboratory scale experiments and full scale component tests) are required for the safe operation of the coolant/fuel of a transmutation facility. Extensive R&D is required and has to be backed with irradiation tests of both fuel and structural materials.
Conclusions from the contributing Helmholtz centres’ point of view

The centres of the Helmholtz Association expect that the ministries consider the recommendations given by acatech in order to scientifically contribute to the decision on how to proceed with the national P&T research in Germany.

The transformation of the recommendations given by acatech shall be realised with the budgets for the third programme oriented research period, starting in January 2015. This also includes the global budget for the programme “Nuclear Waste Management and Safety as well as Radiation Research” (NUSAFE) and the institutionally funded part of the P&T research.

Based on the expected budget, the continuation of the research cooperation within both European and international networks is planned to be continued as previously has been the case within several European framework programmes. A focus will remain on major challenges to be solved for a safe and reliable operation of P&T facilities such as advanced separation technologies, liquid metal technologies, advanced components and structural materials and development and application of simulation tools.

acatech concludes that additional funding may be required to contribute to European initiatives or investigations in line with German phase out decision [4]. European initiatives are mainly driven by the MYRRHA project; however, the scope could be broadened. acatech recommends additional funding for creating dedicated European infrastructures for P&T.

This is well recognised by the Helmholtz centres, which are highly interested and willing to participate to European initiatives. The Helmholtz centres are willing to continue their work in the European and international context as recommended by acatech (Recommendation 1). Additional funding would allow work with focus on the specific situation given by the phase out decision. The work should be started on a comparison of different P&T systems and how they comply with the phase out decision, i.e. using as few facilities as possible for an operating period as possible, generating as little TRU losses as possible. Based on the results, a system should be selected and developed to demonstrate the feasibility of P&T under the objectives of the phase out decision. Finally, a system optimised for TRU burning could be an attractive option for many countries operating a fleet of LWR only, not willing to switch to a fast reactor fleet of significant size.

Acknowledgements

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Session 3:
Transmutation Systems and Infrastructures

Chairs: T. Taiwo and P. Paviet (United States)
Contribution of the European Commission to a European Strategy for HLW Management through Partitioning and Transmutation: Presentation of MYRRHA and its Role in the European P&T Strategy

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Abstract

To be able to answer the world’s increasing demand for energy, nuclear energy must be part of the energy mix. As a consequence of the nuclear electricity generation, high-level nuclear waste (HLW) is produced. The HLW is presently considered to be managed through its burying in geological storage. Partitioning and transmutation (P&T) has been pointed out as the strategy to reduce the radiological impact of HLW. Transmutation can be achieved in an efficient way in fast neutron spectrum facilities, both in critical fast reactors as well as in accelerator driven systems (ADSs).

For more than two decades, the European Commission has been co-funding various research and development projects conducted in many European research organisations and industries related to P&T as a complementary strategy for high-level waste management to the geological disposal. In 2005, a European strategy for the implementation of P&T for a large part of the HLW in Europe indicated the need for the demonstration of its feasibility at an ‘engineering’ level. The R&D activities of this strategy were arranged in four ‘building blocks’:

1. Demonstration of the capability to process a sizable amount of spent fuel from commercial light water reactors (LWRs) in order to separate plutonium, uranium and minor actinides.
2. Demonstration of the capability to fabricate at a semi-industrial level the dedicated fuel needed as load in a dedicated transmuter.
3. Design and construction of one or more dedicated transmuters.
4. Provision of a specific installation for processing of the dedicated fuel unloaded from the transmuter, which can be of a different type than the one used to process the original spent fuel unloaded from the commercial power plants, together with the fabrication of new dedicated fuel.

MYRRHA contributes to the third building block. MYRRHA is an ADS under development at SCK•CEN in collaboration with a large number of European partners. One of the objectives of the new MYRRHA facility is to address the technical feasibility of transmutation of HLW. Within this paper the development of the MYRRHA project and its role as transmutation facility are described briefly.

Introduction

Presently, the EU relies on 30% of its electric power production from Generation II and III nuclear fission reactors leading to the annual production of 2 500 t/y of used fuel, containing 25 t of plutonium, and HLW such as 3.5 t of MAs, namely neptunium (Np), americium (Am) and curium (Cm), and 3 t of long-lived fission products (LLFPs). These MA and LLFP stocks need to be managed in an appropriate way. The used fuel reprocessing (closed fuel cycle) followed by the geological disposal or the direct geological disposal (open fuel cycle) are today the envisaged solutions, depending on national fuel cycle options and waste
management policies. The required time scale for geological disposal exceeds our accumulated technological knowledge and this remains the main concern of the public. P&T has been pointed out in numerous studies as the strategy that can relax constraints on geological disposal, and reduce the monitoring period to technological and manageable time scales. Therefore, a special effort has to be made to integrate P&T in advanced fuel cycles and advanced options for HLW management. Transmutation based on critical or sub-critical fast spectrum transmuters should be evaluated in order to assess the technical and economic feasibility of this waste management option, which could ease the development of a deep geological storage.

Despite diverse strategies and policies pursued by European Member States concerning nuclear power generation and envisaged fuel cycle policy ranging from the once-through without reprocessing to the double-strata fuel cycle ending with the ADS as the ultimate burner or Generation IV fast critical reactors multi-recycling all transuranic materials, P&T requires an integrated effort at the European and even worldwide levels. Even when considering phasing out of nuclear energy, the combination of P&T and a dedicated burner such as ADS technologies, at a European scale, would allow meeting the objectives of both types of countries: the ones phasing out nuclear energy and countries favouring the continuation of nuclear energy development towards the deployment of new fast spectrum reactors.

After nearly 20 years of basic research funded by national programmes and Euratom Framework Programmes (FPs), the research community needs to reach a position of being able to quantify indicators for decision makers, such as the proportion of waste to be channelled to this mode of management, but also issues related to safety, radiation protection, transport, secondary waste streams, costs and scheduling. These elements must be delivered by the EU organisations working on P&T research, all largely involved in the various FP projects related to high-level waste management via P&T and acting from FP4 to FP7. A summary table (Table 1) indicates European Commission investment in P&T research through the Euratom FP. The funding of P&T projects highlighted does not always represent a full financial contribution to the P&T activity area and in itself shows the effort provided through the co-funding of P&T research activities by Euratom.

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From 2005, the research community on P&T within the EU started structuring its research towards a more integrated approach. This resulted during the FP6 in two large integrated projects, namely EUROPART dealing with partitioning, and EUROTRANS dealing with ADS design for transmutation, development of advanced fuel for transmutation, R&D activities related to heavy liquid metal (HLM) technology, innovative structural materials and nuclear data measurement. This approach resulted in a European strategy based on the so-called four building blocks at engineering level for P&T:

1. Demonstration of the capability to process a sizable amount of spent fuel from commercial LWRs in order to separate plutonium (Pu), uranium (U) and minor actinides (MA).
2. Demonstration of the capability to fabricate at a semi-industrial level the dedicated fuel needed to load in a dedicated transmuter.
3. Design and construction of one or more dedicated transmuters.
4. Provision of a specific installation for processing of the dedicated fuel unloaded from the transmuter, which can be of a different type than the one used to process the original spent fuel unloaded from the commercial power plants, together with the fabrication of new dedicated fuel.
This approach will result in the identification of the costs and the benefits of P&T for European society.

The MYRRHA project contributes heavily to the third building block of this European strategy and in this paper we will focus on the ADS programme in the EU through the MYRRHA project and the associated FP7 projects contributing to the progress of ADSs in Europe, namely:

- ARCAS project [1]: aiming at a technical and economical comparison of FRs and ADSs for transmutation of Mas.
- CDT project [2]: aiming at setting up a centralised multidisciplinary team based at the Belgian Mol site to obtain an advanced design of a flexible fast spectrum irradiation facility working in sub-critical mode (ADS) and critical mode by building up on what has been accomplished during the FP5 and FP6 projects related to ADS design and national programmes’ projects related to MYRRHA.
- MARISA project: aiming at bringing the MYRRHA project to a level of maturity required to start the construction phase of the MYRRHA facility.
- MAX project [3]: aiming at consolidating the conceptual design of the superconducting linear accelerator for MYRRHA (MLA) with its reliability target as the principal focus, and at initiating the engineering design of selected components, preparing for adequate prototyping activities.
- FREYA [4] project: aiming at validating the methodology of online reactivity monitoring initiated within the GUINEVERE project [5] in FP6 and planned to be used in MYRRHA. The project is also intended to support the development of the core design and operation of MYRRHA.
- MAXSIMA project [6]: aiming at contributing to the safety assessment studies of MYRRHA.

Partitioning and transmutation

The concept of P&T has three main goals: the reduction of the radiological hazard associated with spent fuel by reducing the inventory of MAs, the reduction of the time interval required to reach the radiotoxicity of natural uranium, and the reduction of the heat load of the HLW packages to be stored through geological disposal leading to its efficient use.

Partitioning is the separation of the radiotoxic elements out of spent fuel. Within the concept of P&T, one can distinguish the following possible fuel cycles, as seen in Figure 1:

- in the “once-through” nuclear fuel cycle (a), there is no reprocessing of the spent fuel;
- within a simple recycle programme, a part of the plutonium is reused, together with fresh uranium, to produce mixed oxide (MOX) fuel (b);
- in a next step, the unprocessed actinides can be ‘burned’ in an ADS (c);
- in the double strata concept (d), fuels with a high content of MAs can be “burned” in ADSs or dedicated FRs.
Transmutation of minor actinides (like americium, neptunium and to a less extent curium) present in the nuclear waste reduces the radiological impact of the HLW and the needed legal monitoring periods to human periods to mitigate human ingress. The time scale needed for the radiotoxicity of the waste to drop to the level of natural uranium will be reduced from a “geological” value (500 000 to 1 million years) to a value that is comparable to that of human activities (several hundreds of years) [7-9]. During transmutation, the nuclei of the actinides are fissioned into shorter-lived fission products (Figure 2).

**Figure 1: Schematic overview of partitioning**

In order to transmute the MAs in an efficient way, high-intensity and high-energy neutron fluxes are necessary. Therefore, only nuclear fast fission reactors being critical or sub-critical can be utilised.

If the aim is to transmute large amounts of MAs in the dedicated transmuter then it is necessary to use an ADS. The sub-criticality is mandatory due to the smaller delayed neutron fraction within the MAs (0.01 to 0.1%) compared to uranium-235 (0.7%) to allow the criticality variation control when considering large inventory of MAs in the core (< 10%).

The implementation of P&T on a large part of the HLW in Europe needs the demonstration of its feasibility at an engineering level. MYRRHA will contribute to the demonstration for the engineering feasibility of the ADS concept and to the efficient demonstration of the transmutation within this concept. Nevertheless, MYRRHA has been conceived as a multi-purpose irradiation facility.
MYRRHA – A flexible fast spectrum irradiation facility

MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) is the flexible experimental ADS in development at SCK•CEN. MYRRHA is able to work both in sub-critical (ADS) and in critical mode. In this way, MYRRHA should target the following applications:

- To demonstrate the ADS full concept by coupling the three components (accelerator, spallation target and sub-critical reactor) at reasonable power level to allow operation feedback, scalable to an industrial demonstrator.
- To allow the study of the efficient technological transmutation of HLW.
- To be operated as a flexible fast spectrum irradiation facility allowing for:
  - Fuel developments for innovative reactor systems.
  - Material developments for Gen IV systems and fusion reactors.
  - Radioisotope production for medical and industrial applications.
  - Industrial applications, such as Si-doping.

In ADS mode, the linear accelerator is the driver of MYRRHA while it provides the high energy protons that are used in the spallation target to create primary neutrons which in turn feed the subcritical core. The accelerator must be able to provide a proton beam with energy of 600 MeV and a maximum current of 4 mA, which will be delivered to the core in continuous wave mode. The beam is delivered to the core from above through a window-target design.

MYRRHA is a pool-type ADS; the reactor vessel houses all the primary systems. In the current design (Figure 3), the reactor pit implements the function of secondary containment in case the reactor vessel leaks or breaks, improving the capabilities of the reactor vault air cooling system. The vessel is closed by the reactor cover, which supports all the in-vessel components. A diaphragm inside the vessel functions to separate the hot and cold lead–bismuth eutectic (LBE), to support the in-vessel fuel storage and to provide a pressure separation. The core is held in place by the core support structure consisting of a core barrel and a core support plate.

**Figure 3: Section of the MYRRHA reactor**

In the present state of the design, the reactor core (Figure 4) consists of MOX fuel pins, typical for FRs. The central hexagonal position of the MYRRHA core houses a windowed beam tube-type spallation target. Thirty-seven positions can be occupied by in-pile sections (IPSs), or by the spallation target (the central one...
of the core in sub-critical configuration), or by control and shutdown rods (in the core critical configuration). This gives large flexibility in the choice of a more suitable position (neutron flux) for each experiment.

Figure 4: Section of the MYRRHA core

In sub-critical mode, the spallation target assembly, located in the central position of the core, brings the proton beam via the beam tube into the central core region. The assembly evacuates the spallation heat deposit, guarantees the barrier between the LBE and the reactor hall, and assures optimal conditions for the spallation reaction. The assembly is conceived as an IPS and is easily removable or replaceable.

Differently from the critical layout, in ADS mode the six control rods (buoyancy-driven in LBE) and the three scram rods (gravity-driven in LBE) will be replaced by absorbing devices to be adopted only during refuelling. Thanks to the (aimed and reached) flexibility, such absorbing devices will be implemented by adopting the control rods, but they will be controlled manually only by the operator.

A detailed description of the MYRRHA facility is given in a companion paper of this conference [11].

Updated planning for MYRRHA

The duration of the preparation phase of the MYRRHA project has been updated with about 2-year extension with respect to previous publications. This preliminary extension has been caused by several factors:

- The choice of the FEED contractor has been made in conformity with a European open call for tenders that is very time-demanding.
- The licensing scheme of the project has been, subdivided into two phases: a pre-licensing phase that will last at least 4 years followed by a licensing phase to come later.
- The research activities, which run in parallel to the design, have been deeply evaluated and their planning has been adapted and this induces also some delays.

The project will be undergoing a full evaluation at the end of 2014 with the Belgian government financing authorities to assess the next stages of the project.

Conclusion

The strategy of the European Commission for preparing the implementation of P&T as a high-level waste management approach complementing geological disposal is reaching an interesting stage of pilot-scale demonstration. The first building block, advanced reprocessing of spent fuel at ATALANTE in France, is progressing and delivering very promising results. The second building block has made a major
step compared to few years ago thanks to the Institute for Transuranium Elements (ITU) of the Joint Research Centre (JRC) of the European Commission in Karlsruhe, Germany, which is upgrading the MALAB (Minor Actinides LAB) capabilities up to 250 kg (Pu+MA) transuranic materials. The third building block of dedicated burners is addressed through two projects in development in Europe: the ASTRID SFR prototype in France and the MYRRHA ADS project in Belgium, which is discussed in this paper. The fourth block presently not heavily addressed in Europe; this is a mandatory step in the future for all programmes of advanced reprocessing such as pyro-reprocessing.

MYRRHA is foreseen to be operated in both sub-critical and critical modes. In sub-critical mode, it will demonstrate the ADS technology and the efficient transmutation of MAs in sub-critical mode. As a fast spectrum irradiation facility, it will address fuel research for innovative reactor systems, material research for Gen IV systems and for fusion reactors, radioisotope production for medical and industrial applications such as Si-doping.

References

Impact of Transmutation Scenarios on Fuel Transportation

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Abstract

Minor actinides transmutation scenarios have been studied in the frame of the French Sustainable Radioactive Waste Management Act of 28 June 2006. Transmutation scenarios supposed the introduction of a sodium-cooled fast reactor fleet using homogeneous or heterogeneous recycling modes for the minor actinides. Americium, neptunium and curium (MA) or americium alone (Am) can be transmuted together in a homogeneous way embedded in FR-MOX fuel or incorporated in MA or Am-Bearing radial Blankets (MABB or AmBB). MA transmutation in Accelerator Driven System has also been studied while plutonium is being recycled in SFR.

Assessments and comparisons of these advanced cycles have been performed considering technical and economic criteria. Transportation needs for fresh and used transmutation fuels is one of these criteria. Transmutation fuels have specific characteristics in terms of thermal load and neutron emissions. Thermal, radiation and criticality constraints have been taken into account in this study to suggest cask concepts for routine conditions of transport, to estimate the number of assemblies to be transported in a cask and the number of annual transports. Comparison with the no transmutation option, i.e. management of uranium and plutonium in SFRs, is also presented.

Regarding these matters, no high difficulties appear for assemblies with limited content of Am (homogeneous or heterogeneous recycling modes). When fuels contain curium, technical transport uncertainties increase because of the important heat release requiring dividing fresh fuels and technological innovations development (MABB and ADS).

Introduction

Studies have been carried out on minor actinides transmutation scenarios under the French law of 2006 relating to the sustainable management of radioactive materials and waste. The recycling of minor actinides in a base of sodium-cooled fast neutron reactors has been studied, in homogeneous or heterogeneous modes or in a dedicated ADS stratum (Accelerator Driven System). The transport of minor actinides loaded elements is one of the technical issues under analysis: the feasibility of this operation shall be examined, pointing out all associated difficulties and uncertainties [1].

The first section provides a description of several minor actinides transmutation scenarios that have been defined. The following three sections deal with thermal stresses, the exposure to ionizing radiation as well as transport criticality. The last section provides a first evaluation of the annual transport requirements in routine conditions. The impact of the minor actinides transmutation has been assessed for the case without transmutation with the single uranium and plutonium recycling in fast neutron reactors.
Study approach and assumptions

Study scenarios

The scenarios only consider a French context, assuming a constant annual power production of 430 TW.h/year. After a first phase in which the reactors were partially replaced by EPR™ reactors, two deployment phases of the Generation IV fast reactors are considered, the first of 20 GWe from 2040 to 2050 and the second of 40 GWe from 2080 to 2100. The electrical potential of the fast neutron reactors under study is of each 1 450 MWe (core SFR V2B) and 154 MWe for the ADS (concept ADS Pb-EFIT for the European EUROTRANS project) [2,3]. The evolution of the nuclear power basis is simulated through the COSI code, in which the associated cycle plants capacities are also assessed [2]. The impact of the transmutation scenarios on the fuel manufacturing and spent fuel processing plants is also shown in [4].

Several minor actinides transmutation scenarios (MA) are considered. The homogeneous transmutation of americium, neptunium and curium is studied in fuel cores of the MOX type (option is called “Core Fuels Recycling”, Figure 1). The minor actinides content varies in the course of the scenario between 3.9 and 1.2% in equilibrium, where in this case the need exists for the manufacturing and recycling of 450 tons/year (2 760 assemblies yearly). The case of recycling americium alone is also considered with a maximum americium content of 2.9% during the scenario and 0.9% in equilibrium.

Another transmutation option consists in the recycling of minor actinides (MA) (or americium) in radial blankets («Bearing Radial Blankets», Figure 2). The bulk minor actinides (or americium) content is 20% with an irradiation time of 10 cycles of 410 Effective Full Power Days (or 10% with 5 cycles of 410 EFPD) requiring 29 tons/year or 244 assemblies yearly (or 75 tons/year and 522 assemblies yearly).

The minor actinides transmutation in ADS has also been studied, whereby plutonium was recycled in fast neutron reactors (Figure 3). The ADS fuel consists of plutonium and minor actinides oxides on an inert MgO type matrix (magnesium oxide). The manufacturing and recycling of 20 tons per year is required, which consists in 688 assemblies yearly with mean plutonium and minor actinides oxides contents of respectively 33% and 40%.

Characteristics of fuels/blankets

The emission characteristics, whether thermal or neutron, of minor actinides fuels can be much more important than those of standard fast neutron reactor fuels, and even than those of pressurised water reactor fuels (UOX and MOX) which are currently manipulated. The characteristics of the fresh objects are shown in Table 1 and the characteristics of spent objects in Table 2. In the latter case, the cooling time of the assemblies may vary according to the sustained assumptions in the scenarios: this can be 5 years (a) but also reduced to 3.4 years in some cases (b). This reduction is considered necessary for certain scenarios, with the alternative to develop the reactor concept in order to have the required plutonium available for the deployment of the second fast neutron reactor phase (e.g. by using radial blankets) [1].
The most disadvantageous assemblies are those with high curium concentrations (MABB and ADS fuels). This is also valid for spent americium loaded blankets due to the great presence of curium generated by the americium transmutation.

Table 1: Characteristics of fresh fuels/blankets in equilibrium (circa 2130)

<table>
<thead>
<tr>
<th>No transmutation</th>
<th>Homog. Mode Core Fuels Recycling</th>
<th>Heterog. Mode Bearing Blankets Recycling</th>
<th>ADS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Load (kW/ass.)</td>
<td>0.3</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Neutronic Emissions (neutrons/s/ass.)</td>
<td>2.0E+07</td>
<td>3.4E+07</td>
<td>3.8E+09</td>
</tr>
<tr>
<td></td>
<td>7.1E+07</td>
<td>3.2E+10</td>
<td>1.6E+10</td>
</tr>
</tbody>
</table>

Table 2: Characteristics of spent fuels/blankets in equilibrium (circa 2130)

<table>
<thead>
<tr>
<th>No transmutation</th>
<th>Homog. Mode Core Fuels Recycling</th>
<th>Heterog. Mode Bearing Blankets Rec.</th>
<th>ADS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Load (kW/ass.)</td>
<td>1.3 (b)</td>
<td>1.8 (b)</td>
<td>2.2 (b)</td>
</tr>
<tr>
<td>Neutronic Emissions (neutrons/s/ass.)</td>
<td>0.5E+09 (b)</td>
<td>1.6E+09 (b)</td>
<td>2.8E+09 (b)</td>
</tr>
<tr>
<td></td>
<td>5.3E+09 (a)</td>
<td>2.7E+10 (a)</td>
<td>1.5E+10 (a)</td>
</tr>
</tbody>
</table>

Study principles for transport

The feasibility of fresh and spent fuel assemblies transportation required for each transmutation scenario was studied based on the same approach. For each fuel transport a packaging type is suggested based on current concepts whereby thermal stresses, radiation protection and criticality are considered. Our study approach has not included other issues in this stage, such as mechanical resistance (assemblies’ deformation), handling, containment, regulations (circulation, physical protection ...). In general, only the routine transport conditions are considered (undamaged fuel assemblies and no drop, fire, immersion or other accidental conditions). Conclusions of the study (number of fuel assembly transported per cask) would be different if these additional constraints were taken into account.

A packaging model has been defined which is used for the following calculations. This consists in a multi-layer packaging with an outer diameter of 2.13 m and a centre basket enclosing the assemblies (basket diameter of 1.21 m), and surrounded by a steel layer with a thickness of 30 cm (ensuring radiation protection), whereby this layer is covered by a 14 cm thick neutron absorbing resin layer. There is mechanical gap, especially between each assembly and the basket, as well as between the basket and the cylindrical shell: these parameters shall be discussed later as these have an impact on heat removal. Several transport capacities are considered, between one and twelve assemblies per packaging (Figure 4). Any eventual locking systems likely to reduce the number of assemblies per packaging are not considered in this analysis.
Thermal studies

The thermal study is aimed at defining the maximum thermal power to be removed for a fixed packaging configuration, with the restriction of not surpassing an established fuel clad temperature in order not to damage the assemblies. A modelling was performed for conductive and radiative thermal exchanges within the packaging, based on calculations with the ANSYS™ tool. In the case of multi-assemblies packaging, the same have not been modelled pin by pin due to the great amount of fuel pins, but an equivalent thermal conductivity in the assembly was considered [5]. This approach allows for the execution of parametric calculations while the most important parameters were highlighted.

It is assumed that the packaging is passively cooled by means of helium. This gas is an excellent option due to its high thermal conductivity. Sodium, in spite of its higher preference, was not opted for because of safety reasons. Also, the analysis includes the assumption that the operations to be performed in the transport are feasible, e.g. the fuel assembling in the manufacturing plant or the handling of spent fuel at the outlet of the reactor, in spite of the associated uncertainties.

An analysis was made of the impact of important parameters, such as the maximum allowed temperature for the fuel cladding, gap and material emissivity. The accepted maximum temperature for the fuel cladding depends on the material and its condition (fresh, irradiated). This is still unknown today, but the assumed range is between 450°C and 650°C for fresh assemblies and 650°C for spent assemblies, whereas the latter value is of the same magnitude as the thermal handling criteria out of sodium considered in the Phenix and Superphenix reactors [6]. This characteristic shall be determined by the chosen material of the cladding.

The mechanical gap standards for the packaging have been determined in analogy with the current transport packagings, with a 2mm gap between the hexagonal tube and the basket, and a gap of 5 mm between the basket and the shell. On the contrary, a gap reduced to zero is considered in order to identify its impact: a very significant reduced gap seems feasible and is patent-pending [7]. For the assessment of the accepted thermal power it is important to know the emissivity of the fuel cladding and hexagonal tube. Based on current knowledge of the assemblies’ structures, emissivities of the hexagonal tube equivalent to 0.35 and of the fuel cladding equivalent to 0.45 are considered. Due to the importance of these properties, emissivity measurements of structure materials shall be required for optimal results.

The results show that at a maximum fuel clad temperature of 450°C, the transportation of 12 assemblies with a thermal power of 2.5 kW each and with standard gap is feasible. If this value reaches 650°C, the 12 fuels must have a maximum power of 4.6 kW each. A decreased gap improves significantly the thermal constraints (respectively 3.5 and 6.6 kW). In case of one assembly transportation, thermal limit is 3.3 kW (450°C and standard gap) and can increase as far as 8.8 kW (450°C and reduced gap).

Radiation protection studies

Fuel transport must comply with regulatory dispositions with regards to ionising radiation exposure [8]. For each packaging configuration in the study, ambient dose equivalent rates were considered with regards to the fissile column and compared according to the following values: 2mSv/hr at contact and 0.1 mSv/hr at 2m from the packaging surface. Calculations were made by means of the TRIPOLI-4® code [9], in which each assembly was represented by the fissile column alone (Figure 5).

By successively considering different load types in the cask, radiation protection studies have defined the maximum number of assemblies for transportation in a packaging for each of the examined scenarios. The same have also demonstrated the impact of the basket type enclosing the fuels, as well as of the neutron absorbing resin.
The basket of the study is made of aluminium with natural boron, although it should be evaluated whether this is feasible. With regards to the resins, the current materials may be renewed, but in view of an identical radiation protection efficiency, a material shall be selected which fits best with regards to thermal constraints due to the temperature level reached according to the transported fuels or blankets (approximately between 50 and 110°C).

**Criticality study**

Criticality studies have been performed in the case of fresh core fuel and ADS fuel transport, because, in a first approach it was considered that these cases would be more disadvantageous than the spent cores with regards to criticality risks. Calculations were made based upon the calculation package CRISTAL v1.2, during routine transport conditions.

The first results demonstrate that the transportation of 12 assemblies is only feasible with a guaranteed absolute absence of water in the assemblies and in the packaging, whereby this result is obtained for plutonium contents of 22% or 18%. In order to overcome such constraints (absence of water), a transport per lot of 8 with an assemblies distribution in circle is allowed (Figure 6). Also a study was performed on the transport of ADS assemblies, strongly loaded with plutonium and minor actinides, whereby a single assembly per packaging was considered. The first results show no specific constraints with regards to the presence of water or the number of fuel pins, apart from the compliance with the dimensional and media requirements.

**Figure 6: Sectional view of a packaging with eight cavities**
Transport results

Selected transport packaging

For each of the scenarios in the study, the selection of the transport packages was based on an iterative approach considering thermal constraints, ionising radiation exposure and criticality. The study assumed a maximum temperature of 450°C for new fuel clad, whereby the maximum temperature for fuel clad in the case of a spent blanket or assembly was not to surpass 650°C.

In the case of non-recycled minor actinides, the fresh SFR-MOX assemblies can be transported by groups of 8, in routine transport conditions. Transport with greater assemblies’ number is constrained subject to criticality risk prevention.

The transportation of fresh americium loaded fuel assemblies (AmCF) used in the scenario of homogeneous americium transmutation is feasible by groups of 8. After irradiation the produced curium-244 content at 0.1% in equilibrium or 0.2% in transient phase becomes a limiting factor. The packaging capacity should be reduced to 7 in compliance with the regulatory limits for radiation exposure.

The minor actinides transmutation scenario leads to the presence of curium in the fresh assemblies (AMCF) which has a great impact on their transport. Actually, a curium content of 0.2% in a fresh assembly sets a limit due to the radiation protection criteria, resulting in the required reduction of 7 fresh assemblies in a packaging. After the passage in the reactor the objects also have to be transported by groups of 7, due to the high neutron emission.

The transport of americium AmBB loaded blankets in the heterogeneous transmutation scenario of americium alone is limited for the spent blankets, due to the exposure to ionising radiation. The transport by groups of 3 blankets is feasible.

As the curium content increases, technical difficulties become more complex. For the transport of fresh objects with a curium content of between 1.9 and 2.5% in the AMBB or with a curium and plutonium content of between 3 and 5% in the ADS fuels, the thermal emission is even prohibitive for a unit transport. The transport must be fractioned in three parts, if the maximum temperature for a fresh object cannot exceed 450°C (the fractioning level of the assembly varies according to the assumption made for the fuel clad temperature).

For AMBB blankets and spent ADS fuels the thermal emission is very high after 5 years of cooling as pointed out in Table 2. This is in excess of the value of 7.5 kW which is the threshold considered for the handling of the fuels in the reactor (the maximum allowed power for handling the assemblies is 2.5 kW, whereas research is made to increase this limit to 7.5 kW [1]). With regards to this handling constraint, an increased cooling time is thus essential: a period of 15 years would be necessary for the AMBB.

In the case of ADS fuels, a relatively low supplementary period should be considered as at the end of the scenario, the residual power is evaluated at 7.9 kW after 5 years of cooling. Even at 7.5 kW, the thermal emission remains high, imposing a unitary transport of each of the objects which requires important technological innovations for the packaging transport concept aimed at the reduction of mechanical gaps. In the absence of innovative technologies, it would be necessary to disassemble the spent fuels on each reactor into a specific cell with the implied consequences (exploitation constraints, increased costs and higher number of annual transports).
Impact of the transmutation on the number of annual transports

The analysis aims at the evaluation of the number of annual transports required for each transmutation scenario, based on the one hand, on the annual fresh fuels flux between the manufacturing plant and the reactors, and on the other hand, on the annual fuels flux between the reactors and the processing plant. It is assumed that the manufacturing and processing operations take place at the same site.

Figure 7 shows the number of annual transports assessment in equilibrium in the fast neutron reactors for each of the transmutation scenarios compared to the case without transmutation. In the latter case, the number of annual transports is 700 (fresh and spent fuels). As a comparison, today’s fuel cycle balance is approximately 200 transports per year of spent fuel (with a similar type of cask, class B). The homogeneous americium or minor actinides transmutation has nearly no impact on the annual transport quantity with a ratio of 1.1 or 1.3. The heterogeneous americium transmutation only results in a minor increase of the transport compared to the case without transmutation (ratio of 1.5). The impact of the transmutation on the transport item is clearly more significant with the increase of the curium content: the annual transport flux increases three-fold in the case of heterogeneous minor actinides transmutation and five-fold for ADS fuels.

Figure 7: Assessment of number of annual transports

<table>
<thead>
<tr>
<th>no MA transmutation</th>
<th>Am Core Fuels / Bearing-Blankets Recycling</th>
<th>MA Core Fuels / Bearing-Blankets Recycling</th>
<th>ADS Recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.1</td>
</tr>
</tbody>
</table>

While there were no technical difficulties in the americium transmutation scenarios (homogeneous and heterogeneous), this is no longer true for the fuel assemblies or blankets containing curium. It becomes more uncertain due to the quite significant thermal emission requiring either the fractioning of the fresh objects or the development of innovative packaging technologies related to thermal exchanges (MABB and ADS fuels). For each scenario in the study, the annual number of transports has been considered for the cost assessment in this item, which, although of little importance, has been integrated into the cost assessment of the transmutation. [1,10].

Conclusions

This study constitutes a first analysis of the transportation of assemblies in the case of minor actinides transmutation scenarios. Although only routine transport conditions have been considered, this study provides quantitative elements with regards to the feasibility of fresh and spent assemblies transport within the framework of minor actinides transmutation scenarios.
In the case of curium containing fuels, transport uncertainties exist with regards to the significant thermal emission requiring the fractioning of fresh assemblies and the development of innovative technologies (in the case of MABB and ADS). Compared with fuels containing curium, there are no high difficulties with regards to assemblies with limited americium content in the case of homogeneous and heterogeneous recycling. Studies on americium contained fuels, however, should be detailed so as to guarantee the industrial feasibility of their transportation.

References


Nuclear Fuel Cycle Evaluation and Screening Findings on Partitioning and Transmutation

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Abstract

A Nuclear Fuel Cycle Evaluation and Screening (E&S) study has recently been completed in the United States. The study considered the entire fuel cycle, included considerations for both once-through and recycle fuel cycle options, evaluated a set of 40 fuel cycles that allowed a comprehensive assessment of fuel cycle performance, identified a relatively small number of promising fuel cycle options that have the potential for achieving substantial improvements compared to the current nuclear fuel cycle in the United States, and allowed the identification of research and development (R&D) activities needed to support the development of the promising fuel cycle options. Nine high-level criteria (Nuclear Waste Management, Proliferation Risk, Nuclear Material Security Risk, Safety, Environmental Impact, Resource Utilisation, Development and Deployment Risk, Institutional Issues, and Financial Risk and Economics) and associated metrics were used in the study to compare the performance of nuclear fuel cycle options to that of the current fuel cycle practiced in the United States.

The study also evaluated a number of fuel cycle characteristics that may have the potential to impact future R&D directions. These included for example:

1) The fuel resources used, i.e., uranium and/or thorium.
2) Impact of extremely high burnup fuels.
3) Minor actinide recycle.
4) The impact of losses during separations (partitioning).
5) Critical versus subcritical (externally-driven) systems for material irradiation.
6) Impact of spectrum of irradiation system, i.e., fast, thermal or intermediate.
7) Waste generation reduction, all of which were quantified in the study.

The E&S study has implemented a framework that can be used now and in the future to objectively inform on the potential of alternative nuclear fuel cycles, providing decision-makers and others with perspective on fuel cycle capabilities.

Introduction

An Evaluation and Screening (E&S) study [1] of nuclear fuel cycle options has been conducted for the U.S. Department of Energy (DOE) Office of Nuclear Energy to provide information about the potential benefits and challenges of nuclear fuel cycle options and to identify a relatively small number of promising fuel cycle options with the potential for achieving substantial improvements compared to the current nuclear fuel cycle in the United States. The study was required to consider the complete nuclear energy
system extending from mining to disposal. The set of fuel cycle options was to be as comprehensive as possible with respect to potential fuel cycle performance.

The E&S study used an objective and independently reviewed evaluation process to provide information about the potential benefits and challenges that could strengthen the basis and provide guidance for the research and development (R&D) activities undertaken by the DOE Fuel Cycle Technologies Programme Office (Figure 1). Using the nine Evaluation Criteria specified in the Charter and associated evaluation metrics and processes developed during the E&S study, a screening was conducted of fuel cycle options to provide answers to the questions:

1. Which nuclear fuel cycle system options have the potential for substantial beneficial improvements in nuclear fuel cycle performance, and what aspects of the options make these improvements possible?
2. Which nuclear material management approaches can favourably impact the performance of fuel cycle options?
3. What R&D investments are needed to support the set of promising fuel cycle system options and nuclear material management approaches, and what are the technical objectives of associated technologies?

This paper summarises the framework developed for the E&S study of fuel cycle options and the results obtained from the study.

Figure 1: Nuclear fuel cycle evaluation and screening informing the doe decision-making process

Study approach

Logical framework

A systematic logical framework was developed to provide an objective comparative assessment of the fuel cycle options, relative to the Basis of Comparison, which is the current fuel cycle being used in the United States (once-through fuel cycle approach using enriched uranium fuel in light water reactors). However, it was recognized that the current U.S. fuel cycle is not yet complete since disposal of spent fuel
has not yet been implemented. For the purposes of conducting the E&S study where the performance of the complete fuel cycle was to be compared, it was assumed that spent fuel disposal was available, without assessing or otherwise commenting on the time and effort required to implement such disposal capabilities.

The general approach for the study consisted of three major steps:

- **Background preparations.**
  - Develop evaluation metrics for each criterion.
  - Create a comprehensive set of fuel cycle options.
  - Generate the metric data.

- **Evaluation.**
  - Define a range of value judgments to represent various perspectives on what constitutes a substantial improvement and on the relative importance of changes in each Metric and Criterion.
  - Apply these value judgments to rank fuel cycle performance with respect to the evaluation metrics, evaluation criteria, and for combinations of evaluation criteria.

- **Screening.**
  - Conditionally identify any promising fuel cycle options for each evaluation metric, evaluation criterion, and for combinations of evaluation criteria based on the level of improvement that can be obtained.
  - Provide the corresponding R&D directions
  - Document the results.

These steps, presented in Figure 2, were developed and conducted by an evaluation and screening team (EST), comprised of experts knowledgeable in fuel cycle, decision analysis and financial issues. Stakeholders from industry, universities, and the government provided input to the options and metrics development processes. A DOE-established independent review team (IRT) conducted review of the process, interim deliverables, and final report.

Figure 2: Nuclear fuel cycle evaluation and screening process

All of the evaluation and screening analyses were performed with an interactive software tool specially developed for this purpose. The tool provides the capability for a user to explore any value judgment desired.
Evaluation criteria and metrics

Nine evaluation criteria were specified by the DOE Office of Nuclear Energy as shown in Table 1. For each of the evaluation criteria, one or more metrics were developed to allow comparison of fuel cycle performance. The E&S study determined that the first six of the criteria inform on the potential for an alternative fuel cycle to provide benefits compared to the current U.S. fuel cycle while the last three inform on challenges associated with these alternative fuel cycles.

Table 1: Evaluation and screening criteria

<table>
<thead>
<tr>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear waste management.</td>
</tr>
<tr>
<td>Proliferation risk.</td>
</tr>
<tr>
<td>Nuclear material security risk.</td>
</tr>
<tr>
<td>Safety</td>
</tr>
<tr>
<td>Environmental impact.</td>
</tr>
<tr>
<td>Resource utilisation.</td>
</tr>
<tr>
<td>Development and deployment risk.</td>
</tr>
<tr>
<td>Institutional issues.</td>
</tr>
<tr>
<td>Financial risk and economics.</td>
</tr>
</tbody>
</table>

The metric data provided the information required to evaluate and subsequently screen the fuel cycle options to identify the most promising alternatives based on the potential for improvement with respect to the evaluation metrics. Relevant stakeholders from industry, universities, and the government provided input to the metric development process. The metric descriptions included justification for each metric and the associated calculation or estimation methodology.

For criteria with multiple evaluation metrics, the sensitivity of the results to the relative importance of each metric was investigated. Similarly, when multiple criteria were considered simultaneously, the relative importance of the evaluation criteria was varied.

Fuel cycle options for comprehensive evaluation

As the set of fuel cycle options was required to be comprehensive with respect to potential fuel cycle performance, an approach was developed based on the fundamental physics-based functional characteristics of nuclear fuel cycles rather than on specific fuel cycle technologies. The major functional characteristics used in the study were:

- “Once-Through” or “Recycle”, where recycle includes limited recycle and continuous recycle.
- Irradiation system, which could be self-sustaining (critical reactor) or externally-driven (sub-critical reactor).
- Neutron spectrum such as thermal or intermediate or fast.
- Nuclear fuel for the potential sources available naturally, i.e., uranium or thorium or thorium/uranium.
- Isotopic Enrichment, indicating whether uranium enrichment is required.

Using these characteristics, over four thousand fuel cycle options were identified at the physics-based functional level.

Part of the process was to group fuel cycle options with similar physics-based characteristics and performance. This step resulted in the forty (40) distinct Evaluation Groups that were determined to be sufficient to comprehensively represent all fuel cycle options to inform on their potential for providing substantial improvement with respect to the specified Evaluation Criteria. The set of 40 Evaluation Groups included: 8 once-through Evaluation Groups; 10 limited recycle Evaluation Groups; and 22 continuous recycle Evaluation Groups.
**Metric data**

Each metric required either quantitative or qualitative information. As a result, for many of the metrics, it was necessary to define an Analysis Example for each Evaluation Group that was typical of members of each group for the purposes of providing the information needed for the metric data. The data range for each metric was divided into a small number of bins, with each bin covering a range of value. The quantitative and qualitative metric information for the evaluation groups were then placed into the appropriate metric data bin for each metric. The use of bins across the data range for each metric accommodated both the variation in performance within the Evaluation Group and the uncertainty associated with the data.

**Value judgments and ranking**

In general, the value of an improvement is a subjective judgment as is the amount of improvement that would be considered substantial, or "significant". In the E&S study, a range of value judgments was used to explore the sensitivity of the identification of promising Evaluation Groups. For the individual evaluation metrics, these value judgments took the form of conditional statements concerning the level of improvement, i.e., if a given level of improvement was considered significant, then these Evaluation Groups would be considered "promising" for that evaluation metric. When multiple metrics needed to be combined to inform on an evaluation criterion, the value judgments took the form of (1) functions indicating the relative importance of a change in the metric over a data range of interest and (2) sets of metric tradeoff factors for combining the evaluation metrics to inform on each evaluation criterion.

Additionally, criteria tradeoff factors were used for exploring the effects of the relative importance of criteria when multiple criteria were being considered, where each set of criteria tradeoff factors defines what was called a "scenario" in the study. The result of applying the value functions was a utility indicating the relative merit of the Evaluation Group performance.

**Results of the E&S study**

The performance improvement of the Evaluation Groups with respect to the basis of comparison was used to identify those Evaluation Groups that could be considered as promising. An additional step was used to correlate the potential improvement in performance for the “benefit” criteria with the risk of developing and deploying the fuel cycle representing the “challenge” criteria, resulting in two-dimensional plots of utility of the benefit versus the utility of the challenge. This allowed identification of promising options along with consideration of the corresponding risk of development and a relative indication of the costs of such development.

**Promising fuel cycle options**

Among all options, three groups of fuel cycles consistently provided the highest improvements compared to the current fuel cycle in the United States, regardless of the perspective on the relative importance of the six benefit criteria, with the following descriptions indicative of the fuel cycles in these three groups:

- Continuous recycle of U/Pu with new natural-U fuel in fast critical reactors.
- Continuous recycle of U/TRU with new natural-U fuel in fast critical reactors.
- Continuous recycle of U/TRU with new natural-U fuel in both fast and thermal critical reactors.

When the benefit and challenge criteria were jointly considered, another group was added:

- Continuous recycle of U/Pu with new natural-U fuel in both fast and thermal critical reactors.

These groups were designated the most promising options if the amount of reduction in the waste generated and the fuel resources needed was considered to be both important and substantial.
Fourteen other promising groups were identified in the study. These groups focused on the continuous recycle of thorium fuel and/or use of externally-driven systems in both once-through and continuous recycle strategies.

None of the most promising fuel cycles are ready to be deployed today, and R&D is required to develop the appropriate implementing technologies. The study examined the current state of knowledge and experience to identify the R&D needs for each part of the fuel cycle. A general finding is that the R&D needs for the most promising options are sometimes pertinent to the needs of other less performing options. [1] These included R&D on fast critical reactors because these reactors facilitate effective consumption of actinide elements and efficient use of uranium fuel resources; R&D on separation of U/Pu or U/TRU from irradiated fuel to make them available for recycle; and R&D on recycle fuel development to facilitate use of separated U/Pu or U/TRU as fuel, with the fuel having irradiation capability (e.g., fuel burnup, cladding integrity) comparable to or greater than today’s nuclear fuel.

Insights from E&S study

The study concluded that of the six benefit criteria, only the Nuclear Waste Management and Resource Utilisation criteria show the potential for the choice of fuel cycle to offer the possibility for substantial improvement compared to the current U.S. fuel cycle (assumed to be completed by implementation of spent fuel disposal). Continuous recycle of actinide elements is key to providing the performance improvement. Modest changes were observed for the Environmental Impact criteria. The most promising fuel cycles were also found to be capable of safe deployment, with safety challenges comparable to the current U.S. fuel cycle. The study noted that many promising options have common R&D needs, reducing the need to make early decisions on specific fuel cycle choices, but time is required to develop the pertinent technologies.

It was found that it would be more challenging to use thorium than uranium in a self-sustaining fuel cycle. The potential benefits with thorium use in thermal or fast reactors were not quite as great as for uranium use in fast reactors.

R&D to mature technologies to the point where they are ready for industrialisation can be several billion dollars when major engineering demonstration facilities are included. Any new fuel cycle option faces institutional issues related to the lack of regulations/licensing experience and the lack of supporting infrastructure.

The study indicated that any transition to a new fuel cycle from the current U.S. fuel cycle would take decades to complete, however, some benefits may accrue much more quickly. It also indicated that many fuel cycle options may be expected to have electricity production costs that are similar to, or close to, the estimated production costs for continuing the current U.S. fuel cycle.

Acknowledgements

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References

Abstract

Since the Fukushima accident, nuclear transmutation is considered as an option for waste management. Japan Atomic Energy Agency proposes the transmutation of minor actinides (MA) in accelerator-driven system (ADS) using lead-bismuth eutectic alloy (LBE) as a spallation target and a coolant of subcritical core. To obtain the data required for ADS design, we plan the building of a transmutation experimental facility (TEF) is planned within the J-PARC project. TEF consists of an ADS target test facility (TEF-T), which will be installed 400 MeV-250 kW LBE spallation target for material irradiations, and a transmutation physics experimental facility (TEF-P), which set up a fast critical/subcritical assembly driven by low power proton beam with MA fuel to study ADS neutronics. At TEF-T, various research plans to use emitted neutrons from LBE target are discussed. The paper summarises a roadmap to establish the ADS transmutor and latest design activities for TEF construction.

Introduction

After to the great East Japan Earthquake and ensuing tsunami, the Fukushima-Daiichi nuclear power plant was seriously damaged and many nearby residents are still forced to be evacuated. Following the accident, the public interest in nuclear waste management has increased. The Cabinet of Japan decided on a new strategic energy policy in April 2014 to promote “a decreasing the radiation dose remaining in radioactive waste over a long period of time and enhancing the safety of processing and disposal of radioactive waste, including nuclear transmutation technology using fast reactors and accelerators”.

Japan Atomic Energy Agency (JAEA) precedes R&Ds to reduce the radiological hazard of HLWs by partitioning and transmutation (P&T) technology [1]. As for the transmutation of radiological waste, the accelerator-driven system (ADS), which combines a high intensity proton accelerator and a fast subcritical core, is discussed from a viewpoint of transmutation efficiency and compatibility with a power generation cycle. Within the framework of the J-PARC project, JAEA is preparing to construct the transmutation experimental facility (TEF) to study minor actinides (MA) transmutation in both MA-loaded fast reactors and ADS [2]. TEF is located at the end of LINAC, which is also important components to be developed for future ADS, and shares the proton beam with other experimental facilities in J-PARC. R&Ds for important technologies required to build the TEF are also performed, such as application methods of MA bearing fuel in the critical/subcritical assembly, spallation product removal method especially for the polonium, and so on. The objectives, the latest design concept, and key technologies to construct TEF are described in this paper.

JAEA proposed ADS

JAEA’s reference design of ADS is a tank-type subcritical reactor, where lead-bismuth eutectic (LBE) alloy is used as both the primary coolant and the spallation target (Figure 1). The spallation target region is located at a central part of the core. In the target region, LBE is flowing from the core bottom along to the dedicated wrapper tube and flow guide. A proton beam with about 1.5 GeV-30 MW proton beam is
supplied from the accelerator to operate the ADS. The rated power, which is controlled by adjusting the injected proton beam current of the accelerator, is 800 MWth.

**Figure 1: ADS for transmutation of MA proposed by JAEA**

A tank-type system is adopted to eliminate the necessity of heavy primary piping. All primary components, including two primary pumps and four steam generators, are set up in the reactor vessel. The heat generated in the target and the core is removed by forced convection of the primary LBE, and transferred through the steam generators to a secondary water/steam system for power conversion. The inlet and outlet coolant temperatures were set to 300 and 407°C respectively, which are low enough to prevent material corrosion by LBE.

Nitride fuel was selected as a fuel for dedicated MA transmutation, suitable for reprocessing for ADS. To minimise the burnup reactivity change and the power peaking, the fuel region is divided into several zones with a different fuel composition. About 2 500 kg of MA is loaded in the core and 10% of them can be transmuted annually. The maximum $k_{eff}$ during whole burnup cycles was set to 0.97. The burnup swing in whole cycles is about 3% $\Delta k/k$.

**Transmutation experimental facility**

As shown in Figure 2, TEF consists of two individual buildings: ADS target test facility (TEF-T) [3] and transmutation physics experimental facility (TEF-P) [4].

The two buildings are connected by a beam transport line with a low power beam extraction mechanism using a laser beam. TEF-T is planned as a material irradiation facility which can accept a maximum 400 MeV-250 kW proton beam on a LBE spallation target. It can also be used for various purposes such as measurement of the reaction cross-sections of MA and structural materials, semiconductor development, etc. TEF-P is a facility with critical/subcritical assembly to study neutronics and controllability of ADS. Using these two facilities, basic physical properties of subcritical system and engineering tests of spallation target will be studied. R&Ds for several important technologies required to build the facilities are also performed, such as laser charge exchange technique to extract a very low power
beam for reactor physics experiments, a remote handling method to load MA bearing fuel into the critical/subcritical assembly, the spallation and activation product removal method especially for the polonium, and so on.

Figure 2: Transmutation experimental facility

Design studies for TEF-T

The main purpose of TEF-T is to obtain the data to evaluate the actual lifetime of beam window. TEF-T mainly consists of a spallation target, a cooling circuit, and hot cells to handle the spent target and irradiation test pieces. A proton beam current density of 20 μA/cm², which is almost the same as the future ADS design, was adopted as a reference. The irradiation performance of the reference case was evaluated around 8 DPA/yr by 400 MeV-250 kW beam irradiation. This value is about 20% of DPA considered in the beam window of JAEA-ADS. Further optimisation of the target design to increase DPA is underway.

To operate LBE loop with high temperature condition above 400°C, the mockup of the primary circuit is under manufacturing and will be operated to develop the technology for target loop maintenance. The measurement and operation devices of the oxygen concentration in LBE are attached to suppress the corrosion by LBE. Remote handling techniques for maintenance of irradiated LBE loop is also under development including replacement of spent target and other loop components with preheating systems.

When LBE is irradiated by high-energy protons or neutrons, polonium isotopes will be accumulated and they should be carefully controlled. The removal method of polonium was studied for the design of exhaust circuit of TEF-T. An equilibrium vapourisation test of polonium from liquid Pb-Bi was performed and equilibrium vapourisation characteristics were measured by transpiration method with LBE, which was irradiated at the JAEA/JMTR [5]. It was shown that at the low temperature around 450°C, considered as a standard operational condition of TEF-T and future ADS, most accumulated polonium remained in LBE as a chemical compound with Pb or Bi which is much harder to evaporate than elemental polonium. Another experiment to recover evaporated polonium in the exhaust circuit was performed [6]. LBE samples were irradiated at the JAEA/JRR-4 and were heated in a special vacuum vessel up to 690°C. By adopting the multi-layered filter, which consists of the stainless steel meshes with two different finenesses, escaping polonium can be decreased to 1/400.
Design of high power spallation target for TEF-T

A high power spallation target, which will be mainly used for material irradiation of candidate materials for a beam window of full-scale ADS, is an essential issue to realise a TEF-T. To set up the beam parameters, future ADS concepts are taken into account. In the reference case of the target, proton beam current density of 20 μA/cm², which equals to the maximum beam current density of JAEA proposed 800 MWt ADS, was assumed.

To evaluate a feasibility of a designed beam window of TEF target, numerical analysis with a 3D model was performed. The analysis was done by considering a current density and shape of the incident proton beam into the target, and the thermal-fluid behaviour of LBE around the beam window as a function of flow rate and inlet temperature of LBE. The thickness of the beam window is also considered parametrically. After the temperature distribution analysis, structural strength of the beam window is determined to evaluate a soundness of the target.

A concave shape beam window was used for this analysis. The prototype design of the beam window for TEF target system was shown in Figure 3.

![Figure 3: Prototype LBE spallation target for TEF-T](image)

The material of beam window would be a type 316 stainless steel as a primary candidate for operation temperature below 450°C. The concave section in the centre part of the target was connected to the convex section in the terminal part, and finally, it was connected to the straight tube. In the analysis, the thickness of beam window was parametrically set from 3 to 2 mm. A straight tube part has coaxially arranged annular and tube type channels. The inner diameters of the outside tube and inside tube were set to 150 mm and 105 mm, respectively. The total length of the analysis region was 600 mm, which corresponds to an effective target depth for 400 MeV proton injection and primary beam suppression. An irradiation sample holder, which was installed in the inner tube, holds irradiation specimens. The size of each specimen was set to 40×145×2 mm, tentatively. The rectification lattice having the aperture of the plural squares type was installed at the front-end of the sample holder. A slit of 2 mm in width was arranged along the side of the rectification lattice to cool off the sample holder by flowing LBE.

The thermal-fluid behaviour of the target was calculated by the STAR-CD with a detailed three-dimensional model. The quarter-part model was set to tetra metric type and the divided face was set to a reflected image condition in the CFD analysis. In this calculation model, a hexahedral element was used and the total number of the elements was about 220 000. At first, LBE flowed through the annular region...
and it joined in the centre of the beam window, and then, turned over and flowed in the inner tube after having passed a rectification lattice and an irradiation sample. In a default condition, the flow rate at the inlet of annulus region was 1 litre/sec, and this was equivalent to the flow velocity of 0.125 m/sec. LBE flow is easy to form a complicated turbulent flow. Therefore, the standard k-ε model for high Re number type was used for a turbulence model. A heat deposition given by the incident proton beam, which was analysed by the hadronic cascade code PHITS [7], was used for CFD analysis. The internal pressure to the inside of the beam window was set to 0.3 MPa in consideration of the flowing LBE and the cover gas. On the outer wall of the beam window and the border of the atmosphere, release of the radiant heat was considered. In this analysis, the embrittlement of the structural materials by the irradiation was not considered. Based on the results provided by CFD analysis, the analysis to verify the feasibility of the beam window was performed by ABAQUS code, the computational code for the finite element method. The operating conditions for the first stage of material irradiation in TEF were decided by a result of the analysis on each condition.

The CFD analyses were performed by changing flow rates. The maximum velocity of LBE was confirmed at the rectification lattice part and was approximately 1.2 m/sec in the case of the inlet flow rate of 1 litre/sec. When the inlet flow rate increases much higher value, the maximum velocity in the target increases more and cannot be applied because the fluid vibration by LBE was concerned as well as the acceleration of erosion and/or corrosion of the material. So, the design limitation of this target is set to 2 m/sec.

The temperature profile on the beam window, by changing the thickness of the window, was performed with 1 litre/sec of LBE flow. The maximum temperature is 544ºC in the case of 3mm thick stainless steel window. In the case of 2 mm thick window, the peak temperature decreases to 477ºC. The temperature differences between outside and inside, at the centre of the window were 65ºC and 37ºC in the case of 3 mm thick window and 2 mm thick window, respectively. From these results, it was disclosed that a condition of 2 mm was desirable for design parameter.

The temperature and thermal stress for the steady state was estimated using ABAQUS code. In the ABAQUS code, only a beam window was modelled as the cylinder-slab geometry. The model consisted of 1 896 4-node axial-symmetric elements. For the analysis, results by STAR-CD were converted to the temperature of each node. From the analysis result, the stress strength reached the maximum value of 190 MPa on the outer surface of the beam window. When the maximum temperature of the beam window is adapted to 470ºC from the result of STAR-CD, these stresses were lower than the tolerance level of the stress strength of the materials for a fast reactor, which sets less than 294 MPa, and hence, the feasibility of a designed beam window was confirmed.

Outline of TEF-P

Several neutronic experiments for ADS have been performed in both Europe [8,9] and Japan. In Japan, subcritical experiments were performed at the Fast Critical Assembly (FCA) in JAEE/Tokai with a $^{252}$Cf neutron source and a DT neutron source. Subcritical experiments with a thermal subcritical core driven by 100 MeV protons are being performed at Kyoto University Research Reactor Institute. There have been, however, no subcritical experiments combined with a spallation source installed inside the subcritical fast-neutron core. The purposes to build TEF-P are (1) Study on reactor physics aspects of the subcritical core driven by a spallation source, (2) Demonstration of the controllability of the subcritical core including a power control by the proton beam power adjustment, and (3) Investigation of the transmutation performance of the subcritical core using certain amount of MA and LLFP.

TEF-P is designed with referring to FCA as shown in Figure 5, the horizontal table-split type critical assembly with a rectangular lattice matrix, to utilise operation experiences and existing experimental data of FCA. In this concept, the plate-type fuel for FCA with various simulation materials such as lead and
sodium for coolant, tungsten for solid target, ZrH for moderator, B$_4$C for absorber, and AlN for simulating nitride fuel, can be commonly used at TEF-P. The proton beam will be introduced horizontally at the centre of the fixed half assembly and various kinds of spallation targets can be installed at various axial position of the radial centre of the subcritical core.

Figure 5: TEF-P critical/subcritical assembly with Pin-type MA fuel

In the experiment with a proton beam, the effective multiplication factor ($k_{\text{eff}}$) of the assembly will be kept less than 0.98. One proton with energy of 400 MeV produces tens of neutrons by the spallation reaction with a heavy metal target such as lead. The 10 W proton beam corresponds to the source strength of $10^{12}$ neutrons/sec, which have enough strength to measure the neutronic characteristics.

From the viewpoint of the neutronic analyses for subcritical systems, it is desirable to make the core critical in order to ensure the quality of experimental data of the subcriticality and the reactivity worth. So, the subcritical core can make critical condition when the proton beam is suppressed.

As for the transmutation characteristics of MA and LLFP, fission chambers and activation foils are used to measure the transmutation rates. The cross section data of MA and LLFP for high energy region (up to several hundreds MeV) can be measured by the Time of Flight (TOF) technique with the proton beam of about 1ns pulse width which can be delivered by a special beam extraction device using an Nd:YAG laser source [10]. Several kinds of MA and LLFP samples are also prepared to measure their reactivity worth, which is important for the integral validation of cross section data.

One of the main purposes of TEF-P is to perform integral experiments using MA because the present accuracy of nuclear data is not sufficient for ADS design [11]. To improve the accuracy of the nuclear data especially for MA, both the differential experiments and the integral experiments are necessary, while the integral experiments on MA are more difficult than those on the major actinides. The effectiveness of MA-loaded experiments with a certain amount of MA was discussed [12]. In the procedure, data of virtual experiments using TEF-P are determined to estimate the reduction of the errors in the effective cross sections. The data by TEF-P was assumed to be equal to the calculation result, and experimental error was taken from the past experiments in FCA. By using a certain amount of MA, which is about order of kg, typical improvement was observed.

When the highly MA contained fuel is used with critical assembly, remote handling operation and constant heat removal should be required. The development of the technologies to handle the high MA contained fuel with effective heat removal, during storage, transport, and loading of the MA fuel, is underway.
Conclusion

JAEA has been promoting various R&Ds on ADS to reduce the burden of spent nuclear fuels and high-level radioactive wastes. For the basic experimental studies necessary for future ADS design and construction, a plan to build Transmutation Experimental Facility has been proposed. The design optimisation of TEF-T to improve irradiation performance, including R&D for polonium management, was carried out. The effectiveness of TEF-P experiments using a certain amount of MA was assessed quantitatively.

References

MARS: Story on Molten Salt Actinide Recycler and Transmuter Development by Rosatom in Co-operation with Euratom

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Abstract

New design options of MOSART and MSFR systems without and with U-Th support fuelled with different compositions of transuranic elements trifluorides from spent LWR fuel both based on homogeneous cores and used fuel salts with high enough solubility for transuranic elements trifluorides are being examined within MARS (Rosatom) and EVOL (Euratom) parallel coordinated projects. The paper has the main objective of presenting the fuel cycle flexibility of the mentioned above systems while accounting technical constrains and experimental data received in this study. A brief description is given of the calculation core neutronics properties and fuel cycle scenarios as well as experimental results on key fuel salt properties, salt chemistry control and combined materials compatibility to satisfy MOSART and MSFR systems requirements. Measurements described mainly concern phase behaviour and transport properties data for selected fuel salts. As for fuel salt clean up operations in MOSART and MSFR fuel cycles, the most uncertain its part concerning rare earth removal is discussed. Last section is focused on the compatibility of special Ni-based alloys with fuel salt selected at temperatures required for MOSART and MSFR operation. The major achievements are: (1) ability to produce and maintain a high level of purity in fuel salt, (2) effective control of the Redox potential of the salt medium in order to minimize corrosion, (3) understanding of basic corrosion mechanisms in MOSART and MSFR systems. HN80MTY alloy can be recommended for further consideration as the main container material for the fuel circuit with operating temperature up to 1 023 K required for MOSART and MSFR designs.

1. Introduction

Many countries worldwide contributed to molten salt reactor (MSR) technology, among which the United States, the Russian Federation, the European Union, France, Japan, India and for the past few years China and Korea have also contributed. The European Union, France and the Russia Federation are focusing on the development of a fast spectrum MSR capable of either breeding or transmutation of actinides from spent nuclear fuel. In 2010, as result of the coordinated call two projects on MSR were selected funded by the European and Russian Agencies: (1) Russian Project: “Minor Actinides Recycling in molten salts” (MARS)-; (2) European Project: “Evaluation and Viability Of Liquid fuel fast reactor systems”(EVOL). A three-years Euratom – Rosatom collaboration, through parallel co-ordinated projects (MARS-EVOL) on molten salt reactors included the following work packages:

(1) Core design analyses using coupled neutronics and thermal-hydraulics numerical simulations.
(2) Neutronic benchmark, static and transient calculations of criticality, neutron spectrum, delayed neutron fraction, feedback coefficients, heavy nuclei inventories.
(3) Thermodynamic, physical and chemical data acquisition (experimental and modelling) on molten salt.
(4) Materials compatibility and salt chemistry control.
The European and Russian partners have carried out theoretical and experimental studies to verify the feasibility of the MOSART [1] and MSFR [2] systems to reduce long-lived waste toxicity and produce electricity simultaneously. The common objective of the MOSART and MSFR projects is to develop a conceptual design for intermediate/fast spectrum MSRs with an effective system configuration resulting from physical, chemical and material studies, for the reactor core, the processing unit and waste conditioning.

These studies led to the design of two fast spectrum concepts: MOSART and MSFR. The first concept aims to be used as an efficient burner of TRU waste from spent LWR fuel with MA/TRU ratio up to 0.45 without any uranium and thorium support [1]. The second concept has a good breeding capability when using the thorium fuel cycle but high power densities would be required to avoid excessive fissile inventories (300 MW/m³). The objective of this paper is to present the fuel cycle flexibility of the MSR designs while accounting technical constrains based on the experimental data received within MARS project for MOSART and MSFR systems.

Section 2 examines core neutronics properties and fuel cycle scenarios for different MOSART and MSFR configurations. Note that, for both systems, system minimal temperature in primary circuit of fuel salt determines not only its melting point, but also the solubility of TRU trifluorides in the solvent for this particular temperature [3].

In Section 3, experimental results on key physical and chemical properties of selected MOSART and MSFR fuel salts, which determine the main fuel salt parameters (e.g. inlet / outlet temperatures, critical loadings and temperature reactivity coefficient of the fuel salt, etc) are presented. The measurements described, mainly concern phase behaviour and transport properties data for selected fuel salts. As for fuel salt clean up operations in MOSART fuel cycles, the most uncertain its part concerned rare earth removal [3] is discussed. Maximum temperature of the fuel salt of the MSR primary circuit made of special Ni-base alloy is mainly limited by tellurium intergranular corrosion (IGC) under strain depending on salt Redox potential [3].

Section 4 focuses on the compatibility of special Ni-based alloys with fuel salt selected at temperatures required for MOSART and MSFR operation. The major achievements are:

1. Ability to produce and maintain a high level of purity in fuel salt.
2. Effective control of the Redox potential of the salt medium in order to minimise corrosion.
3. Understanding of basic corrosion mechanisms in MOSART and MSFR systems.

2. Core neutronics and fuel cycle properties

This section briefly describes the core and fuel circuit parameters for MOSART and MSFR systems with single- and two-fluid homogeneous cores. Characteristics of MOSART and MSFR systems under investigation are given in Table 1. MCNP-4B+ORIGEN2.1 complex adapted for specificity of MOSART and MSFR was used as the calculation tool at all stages of MARS study. EVOL partners (CNRS/IN2P3/LPSC and Politecnico di Milano) used for the neutronic benchmark in evolution calculations of the MSFR design, respectively the following codes: (1) probabilistic code MCNP with a homemade materials evolution code REM; extraction of nucleus i with a specific removal constants λchem; fissile and fertile composition adjusted to control the reactivity and (2) ERANOS-based EQL3D procedure and extension for the MSFR: ERANOS 2.2-N code system for core calculation (33-group energy); fission products removal and refuelling adjustment simulated; SERPENT-2 extension for on-line fuel salt processing. SERPENT is a three-dimensional Monte Carlo code; developed extension of SERPENT-2 code takes into account online fuel processing and features a reactivity control algorithm.
2.1. Transmuter mode

A promising single fluid configuration for the 2.4 GWt MOSART is the homogeneous cylindrical core (3.6 m high and 3.4 m in diameter) with 0.2 m graphite reflector filled with 100% of 73LiF-27BeF$_2$ salt mixture. It is feasible to design a critical homogeneous core fueled only by TRU trifluorides from UOX or MOX LWR used fuel while equilibrium concentration for trifluorides of actinides (0.4 mole% for Li,Be/F core, with the rare earth removal cycle 1 EFPY) is truly below solubility limit (about 2 mole%) at minimal fuel salt temperature in primary circuit 873-900 K (Figure 1). The effective flux of such system is near $1 \times 10^{15}$ n cm$^{-2}$ s$^{-1}$. The main attractive features of MOSART system [1] deals with the use of (1) simple configuration of the homogeneous core (no solid moderator or construction materials under high flux irradiation); (2) proliferation resistant multiple recycling of actinides (separation coefficients between TRU and lanthanide groups are high, but within the TRU group are very low); (3) the proven container materials (special Ni-Mo alloys) and system components (pump, heat exchanger etc.) operating in the fuel circuit at temperatures below 1 000 K, (4) core inherent safety due to large negative temperature reactivity coefficient (-3.7 pcm/K), (5) long period (1-3 EFPY) for soluble fission products removal.

Figure 1: Molar concentrations of TRU vs. time for different solvents and feedings (MA/TRU ratios) for single fluid system (1- MA/TRU=0.1 in Li,Be/F; 2 – MA / TRU = 0.1 in Na,Li,Be/F; 3 – MA / TRU = 0.35 in Li,Be/F) and two fluid system with 233U recycling from blanket to fuel stream (4 – MA / TRU =0.45 in Li,Be/F); actinides trifluorides solubility in fuel salt at 923K (5) [1]

It is possible to expand even more possibilities of single fluid MOSART transmuter mode of operation and to increase the rate of minor actinides burning, surrounding its core by thorium-containing blanket with molar composition 75LiF-5BeF$_2$-20ThF$_4$ or 78LiF$_2$-22ThF$_4$ (50-60 cm thickness). From blanket uranium (80-100 kg/yr) processed by the volatility process is recycled to fuel stream of two-fluid system, but the thorium-bearing salt is returned to the blanket. The use of produced $^{233}$U as additional source of neutrons in fuel salt permits to decrease equilibrium TRU concentration, and thus to widen the
range of possible fuel make up compositions to MA bearing ones. Taking in to account constrains on the solubility of TRUF$_3$ for 73LiF-27BeF$_2$ solvent (mole %) the limit on MA/TRU ratio in the fuel feeding for this mode of operation may be near 0.5 (Figure 1) and the rate of MA burning 315 kg/yr. Such composition of feeding leads to the further increase of total loading of the primary circuit (up to 23 t) and to the complication of the design due to the use of two-fluid configuration.

2.2. Self-sustainable mode

Interesting possibilities may be demonstrated by the use of MOSART with the reduced dimensions as self-sustainable system with CR=1. For transition to this mode of operation a strategy of gradual increase of thorium concentration in the fuel salt is required. Single fluid 2.4 GWt Li,Be/F MOSART core (radius - 1.4 m, height – 2.8 m) containing as initial loading 2 mole % of ThF$_4$ and 1.2 mole % of TRUF$_3$ with the rare earth removal time 1 EFPY after 12 years can operate without any TRUF$_3$ make up basing only on Th support as a self-sustainable system (Figure 2). The maximum concentration of TRUF$_3$ during this transition does not exceed 1.7 mole %. At equilibrium molar fraction of ThF$_4$ in the fuel salt is near 6% and it is enough to provide the system with CR = 1 up to 50 years of the reactor operation. The reactivity temperature coefficient of the homogeneous core is not only essentially negative, but also practically has no inerterion. In the case of self-sustainable MOSART its value on equilibrium is $-6.7$ pcm/K. The use of the Th – containing blanket permits to reduce the transition to self-sustainable mode of operation period down to 3-4 EFPY, but of course makes the system as whole more complicated from a technical point of view. Any moment of self-sustainable mode system can be used for transition to breeder mode with CR > 1 due to increasing thorium concentration in the fuel salt. So self-sustainable mode demonstrates the MOSART abilities as transforming system and can be used for starting U-Th fuel cycle on the base of first TRU loading from LWR SNF.

Figure 2: Transition to equilibrium of ThF$_4$ (1), TRUF$_3$ (2), UF$_4$ (3) in single fluid 2.4 GWt MOSART (self-sustainable mode) with Li,Be,Th/F core (CR=1) gradual increase of thorium [1]

2.3. Breeder mode

Reference MSFR is a 3 GWt reactor with a total fuel salt volume of 18 m$^3$, operated at a maximum fuel salt temperature of 1 023 K. The fuel salt is composed of lithium fluoride and thorium fluoride and the proportion of heavy nuclei is fixed at 22.5 mole%. The preliminary design of the primary circuit of the MSFR is a single compact cylinder (2.25 m high and 2.25 m diameter) where the nuclear reactions occur within the liquid fluoride fuel salt acting also as the coolant. The fuel salt flows in the central part of the core freely from the bottom to the top without any solid moderator. The return path of the salt is divided into 16 sets of pumps and heat exchangers located around the core. Bubbles are injected in the fuel salt circulation after the exchangers and separated from the liquid at the core outlet. The fuel salt runs through the primary circuit in 3-4 s. The total fuel salt volume is distributed half in the core and half in the external
fuel circuit (salt collectors, salt bubble separators, fuel heat exchangers, pumps, salt injectors and pipes). As in MOSART the lower neutronic reflector of the MSFR is connected to a drain system enabling the reactor core to be drained for planned shutdowns or in case of incidents that lead to a temperature increase in the core. Thus the entire fuel inventory can be passively drained by gravity into subcritical, passively cooled tanks. MSFR configurations corresponding to various starting modes of the reactor are all characterised by excellent safety coefficients and have the same very good deployment capabilities. Methods for fission product removal, actinides recycling and waste management in MOSART and MSFR are very similar and described in details elsewhere [1,2]. In Figures 3 and 4, the results of neutronics benchmark for evolution calculation of MSFR loading and breeding gain are presented. Very good agreement between the different simulation tools used in MARS and EVOL projects with the same nuclear database should be emphasised (Figure 3). Higher sensibility on the data basis choice than on the tool also was found (Figure 4).

**Figure 3: Evolution calculation: Different tools, same data basis – ENDF-B6 [2]**

![Graph showing evolution calculation](image)

**Figure 4: Evolution calculation: Breeding gain [2]**

![Graph showing breeding gain](image)

### 3. Key properties of fuel salt

When substantiating any MSR concept it is necessary to have detailed information on physical and chemical properties of candidate fuel salts as well as fission products behaviour for the system nominal operating and accidental conditions. MSR flowsheet development, first of all, requires reliable data on a phase diagram of the selected salt mixtures, on solubility of the fuel components in it, as well as fuel salt thermophysical properties: thermal conductivity, heat capacity, density, viscosity [3]. Due to the solubility limit, the main concerns for MSR designs are to be expected with actinides and lanthanides dissolved as trifluorides [1,2]. Below are listed the key thermal physical and chemical properties of molten binary LiF-BeF$_2$ and LiF-ThF$_4$ as well as ternary LiF-NaF-BeF$_2$ and LiF-BeF$_2$-ThF$_4$ mixtures important for the MOSART and MSFR design calculation.
3.1. Phase equilibria and TRU trifluorides solubility

The melting points (solidification temperature) determined in this study for selected eutectic mixtures 73LiF-27BeF₂, 78LiF-22ThF₄, and 77LiF-17BeF₂-6ThF₄ (Table 2a) by the method of differential scanning calorimetry agree with the data obtained by the method of differential thermal analysis in the limits of experimental error (±2 K). Actinides and lanthanides fluorides solubility in the melts were measured by techniques of local γ-spectrometry, isothermal saturation and reflectance spectroscopy. The apparatus and general techniques have been described elsewhere [1]. The techniques developed provide reliable determination of equilibrium in the system melt-solid state and measurement with relative error less than 10%. The data on solubility in molten salt fluorides appear to follow a linear relationship within the experimental accuracy of the measurements when plotted as logarithm of molar concentration of actinide trifluoride vs. 1/T(K). For molten LiF-BeF₂, LiF-ThF₄, LiF-NaF-BeF₂ and LiF-BeF₂-ThF₄ salt mixtures the equations are given in Table 2b. Particularly, it was found that two beryllium fluoride containing solutions LiF-BeF₂ and LiF-NaF-BeF₂ with BeF₂ concentration 27 mole % provide close values for solubility of PuF₃ in the temperature range of 825-1000 K (Table 2a). The solubility of some other actinide fluorides, including AmF₃ in the molten LiF-BeF₂ salt mixtures was also measured. In our tests for two beryllium fluoride containing solutions ranging in BeF₂ concentration from 27 to 34 mole % the ²⁴¹Am analysis showed that behaviour of americium was almost identical to that of plutonium. For 78LiF-7ThF₄-15UF₄ and 72,5LiF-7ThF₄-20,5UF₄ melts the joint solubility of PuF₃ and CeF₃ in the temperature range 873-1023 K was measured (Table 2c) [4]. In this case logarithms of the molar concentration for CeF₃, PuF₃ as well as (CeF₃+PuF₃) vs. 1 / T (K) in the studied ternary melts LiF-UF₄-ThF₄ are not linear. Near the liquidus temperature for 78LiF-7ThF₄-15UF₄ and 72,5LiF-7ThF₄-20,5UF₄ salts the CeF₃ significantly displace plutonium trifluoride at their joint dissolution. This suggests that the use of CeF₃ additives in the fuel LiF-ThF₄-UF₄-PuF₃ salt can provide effective removal for PuF₃.

Table 2a: Melting temperatures ($T_{melt}$) and solubility of PuF₃ ($S$) for selected fuel salts at minimal temperatures in the primary circuit of MOSART and MSFR systems [1]

<table>
<thead>
<tr>
<th>LiF</th>
<th>BeF₂</th>
<th>ThF₄</th>
<th>$T_{melt}$ (K)</th>
<th>S (mole%)</th>
<th>Mode of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td>27</td>
<td>0</td>
<td>853</td>
<td>2.1</td>
<td>3.1</td>
</tr>
<tr>
<td>78</td>
<td>0</td>
<td>22</td>
<td>843</td>
<td>4.0</td>
<td>5.2</td>
</tr>
<tr>
<td>77</td>
<td>17</td>
<td>6</td>
<td>870</td>
<td>3.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 2b: Solubility of PuF₃ in molten salt fluoride mixtures: log $S$, mole% = $A + B/T,K$ [1]

<table>
<thead>
<tr>
<th>LiF</th>
<th>BeF₂</th>
<th>ThF₄</th>
<th>$T$, K</th>
<th>$A$</th>
<th>$-B*10^{-3}$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>73</td>
<td>27</td>
<td>0</td>
<td>825-1000</td>
<td>3.927</td>
<td>3.099</td>
<td>Isothermal saturation</td>
</tr>
<tr>
<td>66</td>
<td>34</td>
<td>0</td>
<td>800-900</td>
<td>3.231</td>
<td>3.096</td>
<td>γ-spectrometry</td>
</tr>
<tr>
<td>78</td>
<td>0</td>
<td>22</td>
<td>873-973</td>
<td>2.58</td>
<td>1.73</td>
<td>γ-spectrometry</td>
</tr>
<tr>
<td>75</td>
<td>5</td>
<td>20</td>
<td>873-1023</td>
<td>2.06</td>
<td>1.34</td>
<td>γ-spectrometry</td>
</tr>
<tr>
<td>77</td>
<td>17</td>
<td>6</td>
<td>848-998</td>
<td>3.61</td>
<td>2.91</td>
<td>γ-spectrometry</td>
</tr>
</tbody>
</table>

Table 2c: Joint solubility of PuF₃ and CeF₃ in fuel salts, mole % [4]

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>72,5LiF-7ThF₄-20,5UF₄</th>
<th>78LiF-7ThF₄-15UF₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PuF₃</td>
<td>CeF₃</td>
</tr>
<tr>
<td>873</td>
<td>0,35±0,02</td>
<td>1,5±0,1</td>
</tr>
<tr>
<td>923</td>
<td>4,5±0,2</td>
<td>2,5±0,1</td>
</tr>
<tr>
<td>973</td>
<td>8,4±0,4</td>
<td>3,7±0,2</td>
</tr>
<tr>
<td>1023</td>
<td>9,4±0,5</td>
<td>3,9±0,2</td>
</tr>
</tbody>
</table>
3.2. Density

The density of molten $78\text{LiF}-22\text{ThF}_4$ and $71\text{LiF}-2\text{BeF}_2-27\text{ThF}_4$ salt mixtures (mole %) have been measured by method of hydrostatic weighing from the liquidus temperatures up to ~ 1073K. Measurement error is estimated as 0.9%. For the $78\text{LiF}-22\text{ThF}_4$ and $71\text{LiF}-2\text{BeF}_2-27\text{ThF}_4$ (mole%) melts, respectively, correlation dependences for the density ($\rho$, kg/m$^3$) vs. temperature (T, K) were obtained, respectively:

$$\rho = 4742.3 - 8.82 \times 10^{-1} T$$

and

$$\rho = 4992.0 - 7.40 \times 10^{-1} T \ [1].$$

3.3. Thermal conductivity

The thermal conductivity of molten salt fluoride mixtures have been measured by steady state method of coaxial cylinders with temperature gradient in the salt gap about 1 K in order to minimise the contribution of radiation heat transfer. As compared to the transient methods, it also enables simpler and more accurate account of systematic and random errors, especially during absolute measurements. The apparatus device, precision adjustment of the cylinders as well as the use of the protection heaters, standard thermocouples, automatic recording thermoelectric power with high precision ($\pm 0.0001$ mV) have allowed the exact measuring thermal conductivity ($\pm 5\%$). The thermal conductivity ($\lambda$) of molten $78\text{LiF}-22\text{ThF}_4$ and $70\text{LiF}-8\text{CaF}_2-22\text{ThF}_4$ salt mixtures (mole %) was measured at several temperatures in the range of 891 K to 1 020 K. The values found (W·m$^{-1}$·K$^{-1}$) are plotted in Figure 5. The reasonable trends have been found towards an increase of thermal conductivity $\lambda$ (W·m$^{-1}$·K$^{-1}$) of salt mixtures studied with temperature T (K) which can be described by linear equations for molten $78\text{LiF}-22\text{ThF}_4$ and $70\text{LiF}-8\text{CaF}_2-22\text{ThF}_4$ salt mixtures (mole%), respectively:

$$\lambda = 0.93 + 8.40 \times 10^{-5} T$$

and

$$\lambda = 0.84 + 8.06 \times 10^{-5} T.$$  

3.4. Heat capacity

The studies on thermochemical properties of molten salts mixtures were performed with the STA 449C Jupiter® synchronous thermal analyser. This analyser allows making measurements simultaneously by the methods of differential scanning calorimetry and thermogravimetry in a wide range of temperatures and obtaining information on thermal stability, evaporation, melting points, and enthalpy of fusion and heat capacity of solid and liquid salts. The experimental procedure is described elsewhere [1,5]. The temperature dependence of the heat capacity ($c_p$) of molten $78\text{LiF}-22\text{ThF}_4$ eutectic mixture measured in the range from 867 K to 907 K is described, within the experimental error, by a linear equation (in J·g$^{-1}$·K$^{-1}$):

$$c_p = -1.111 + 0.00278 \cdot T.$$  

It has been found that the heat capacity of $70\text{LiF}-8\text{CaF}_2-22\text{ThF}_4$ melt in the range from 837 K to 873 KK is constant with temperature: 1.222 J·g$^{-1}$·K$^{-1}$. The heat capacity of molten $78\text{LiF}-22\text{ThF}_4$ mixture extrapolated to the melting point (839 K) is 1.221 J·g$^{-1}$·K$^{-1}$. 

Figure 5: Thermal conductivity of molten $78\text{LiF}-22\text{ThF}_4$ (1) and $70\text{LiF}-8\text{CaF}_2-22\text{ThF}_4$ (2) salt mixtures vs. temperature [1]
3.5. Viscosity

The viscosity of the different molten salt mixtures has been measured at the temperature ranging from liquidus up to 1 160 K by the method of torsional oscillations attenuation of the cylinder with the melt under study. The apparatus and general technique have been described elsewhere [6]. The dependences of kinematic viscosity ($\nu$, $10^{-6}$ m$^2$/s) vs. temperature (T, K) for molten salt mixtures are given in Table 3. In the temperature range where the melts behave like normal (single phase) liquids, the experimental viscosity values were approximated by the expression: $\nu = A \cdot \exp \left(\frac{B}{T}\right)$. The parameters of model were obtained by least squares method. The kinematic viscosity root mean square (RMS) estimated in the assumption about dispersion homoscedasticity is $(0.04÷0.20) \times 10^{-6}$ m$^2$/s. Effect of CeF$_3$ and BeF$_2$ addition on viscosity of mentioned above eutectics was also studied. In most cases the presence of CeF$_3$ (from 1 to 10 mole%) or BeF$_2$ (from 2 to 5 mole%) in the eutectic mixtures decreased its viscosity at the cold leg of the measured temperature range. Differ from other molten salt mixtures under study the addition of 3 mole% of CeF$_3$ to the 75LiF-20ThF$_4$-5BeF$_2$ melt significantly increased its liquidus temperature.

<table>
<thead>
<tr>
<th>Composition (mole %)</th>
<th>T (K)</th>
<th>$\nu \cdot 10^6$ (m$^2$/s)</th>
<th>RMS$\cdot 10^6$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78LiF–22ThF$_4$</td>
<td>898-1 119</td>
<td>1.980 exp{3 689*(1/T - 0.9698E-3)}</td>
<td>0.042</td>
</tr>
<tr>
<td>71LiF–27ThF$_4$–2BeF$_2$</td>
<td>866-1 073</td>
<td>2.075 exp{3 093*(1/T – 1.033E-3)}</td>
<td>0.10</td>
</tr>
<tr>
<td>75LiF–20ThF$_4$–5BeF$_2$ with 3 mole% CeF$_3$</td>
<td>851-1 093</td>
<td>2.1905 exp{1 8774*(1/T – 1.013E-3)}</td>
<td>0.12</td>
</tr>
<tr>
<td>966-1 115</td>
<td>2.037 exp{1 465*(1/T – 0.9627E-3)}</td>
<td>0.053</td>
<td></td>
</tr>
<tr>
<td>75LiF–20BeF$_2$–5ThF$_4$</td>
<td>924-1 158</td>
<td>1.996 exp{3 159*(1/T – 0.9593E-3)}</td>
<td>0.038</td>
</tr>
<tr>
<td>723-1 070</td>
<td>3.267 exp{3 042*(1/T – 1.086E-3)}</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>15LiF–58NaF–27BeF$_2$ with 1 mole % CeF$_3$</td>
<td>723-1 063</td>
<td>2.6375 exp{1 870*(1/T – 1.084E-3)}</td>
<td>0.116</td>
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</tbody>
</table>

3.6 Equilibrium distribution of lanthanide and actinide elements between molten fluoride/chloride salts and liquid bismuth solutions

The extraction of lanthanum, neodymium, samarium, europium and thorium from 73LiF-27BeF$_2$, 78LiF-22ThF$_4$, 75LiF–5BeF$_2$–20ThF$_4$, 15LiF–58NaF–27BeF$_2$, and 60LiF–40NaF (mole %) fluoride salt melts into liquid bismuth with admixtures of lithium as a reducing agent was studied at 853–1 023 K [1]. Equilibrium values of their distribution coefficients D were measured. In Figures 6 and 7, straight lines in logarithmic coordinates (lgD(Nd,La,Sm,Eu,Th) vs. lgD Li) describe our experimental data. Data from the experiments with the above mentioned molten salt mixtures yielded a valence very close to 2 for samarium and europium, to 3 for the lanthanum and neodymium, as well as to 4 for thorium. The extraction of Nd and La as well as in less extent Sm and Eu from molten 73LiF-27BeF$_2$ salt is quite efficient. A decrease in the mole fraction of LiF in LiF–BeF$_2$ melts substantially increased the effectiveness of its separation from lanthanides. The distribution coefficients obtained for LiF-ThF$_4$ and LiFBeF$_2$-ThF$_4$ salts cannot provide the effective separation between thorium and lanthanides in the fluoride salt/bismuth solutions. For molten 78LiF-22ThF$_4$ and 7474LiF-22BeF$_2$-4ThF$_4$ salt mixtures (mole%) the measured values of $\alpha = D(Nd,La)/D(Th)$ are 1 and 3 respectively at lgD(Li) $\approx$ -2.5. Excellent separation of thorium from lanthanides and alkaline-earth elements can be made by use of LiCl. It was found that small additions (<1 mole%) of free fluoride ions have an influence on the distribution coefficient of thorium in LiCl/Bi system (Figure 8).
Figure 6: Distribution of neodymium, lanthanum (left), samarium and europium (right) between molten 73LiF-27BeF$_2$ salt (mole%) and liquid bismuth at 923 K

Figure 7: Distribution data between molten LiCl salt and liquid Bi at 923 K for Nd$^{3+}$ (curve I, this work), Ln$^{3+}$ (curve II, this work), Th$^{4+}$ (curve III, this work with 0.5 mole % ThF$_4$ in LiCl) and Th$^{4+}$ (curve IV without ThF$_4$ in LiCl, [7])

Figure 8: Microstructure of surface layer for Hastelloy N specimens without loading after 250 hrs exposure in Li,Be,U/F fuel salt for U(IV)/U(III) ratios:

a) - 30 (at 1 033 K), b) - 60 (at 1 033 K) and c) - 90 (at 1 073 K)

<table>
<thead>
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<th>No.</th>
<th>K $\times 10^3$ pc $\times$ μm/cm</th>
<th>l (μm)</th>
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</thead>
<tbody>
<tr>
<td>a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b)</td>
<td>3.500</td>
<td>69</td>
</tr>
<tr>
<td>c)</td>
<td>4.490</td>
<td>148</td>
</tr>
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</table>
4. Materials compatibility and salt chemistry control

Current study with molten LiF-BeF$_2$ and LiF-BeF$_2$-ThF$_4$ salt mixtures (mole %) fuelled by 2 mole% of UF$_4$ and containing additives of metallic Te or Cr$_3$Te$_4$, include five 250 hrs tests with exposure of Ni-based alloys specimens at temperatures from 993K to 1073K and under mechanical loading from 0 to 50 MPa. The Ni-based alloys selected for testing had the following compositions (in mass %): original Hastelloy N (Mo–16.28, Cr–7.52, Fe – 3.97, Ti – 0.26, Si -0.5), HN80M-VI (Mo–12, Cr–7.6, Nb–1.5), HN80MTY (Mo–13, Cr–6.8, Al–1.1, Ti–0.9), HN80MTW (Mo-9.4, Cr-7.0, Ti-1.7, W-5.5) and EM-721 (Cr-5.7, Ti-0.17, W-25.2). The corrosion facility described elsewhere [1] allows to test the alloy specimens in the nonisothermal dynamic conditions with difference of the fuel salt temperature in the upper and near-bottom parts of test section about 40K. Chemical analysis determined by ICP–AES in a typical frozen sample of melt before corrosion test showed the content of the major impurities (in mass %) as follows: Ni-0.005; Fe-0.024; Cu<0.001; Cr -0.001; oxygen<0.05 In our tests, the [U(IV)]/[U(III)] ratios in the fuel salt were changed in the range from 0.7 up to 500. On the basis of the testing results (Figures 9 to 11), some general regularities can be emphasised, concerning behaviour of the multicomponent heterophase system consisted of the alloys specimens submerged in the molten 73LiF-27BeF$_2$ and 75LiF-5BeF$_2$-20ThF$_4$ salts with addition of 2 mole % (UF$_4$+UF$_3$) mixture and Cr$_3$Te$_4$. In the fuel salt with [U(IV)]/[U(III)] ratio in the range of 4÷20 any tellurium IGC of the selected alloys does not occur. As shown in Figure 9, after Hastelloy N [3] exposure without stress at 1023 K in Li,Be,U/F at [U(IV)]/[U(III)]=60 the significant Te IGC was found. In the molten salt mixture with [U(IV)]/[U(III)] ratio < 100 any traces of Te IGC on the HN80MTY and H80M-VI alloys specimens are not found (Figure 10). Certain signs of incipient IGC in the form of Te presence on the grain boundaries in the HN80MTB and EM-721 alloys surface layer and formation of not too deep cracks on HN80MTB alloy surface were revealed at [U(IV)]/[U(III)] =100. In the melt with [U(IV)]/[U(III)] ratio equal 500 in all of the alloys tested the tellurium IGC took place (Figure 11). The tellurium IGC for the HN80MTY alloy (the $k$ parameter) is by 3÷5 times lower as compared to other alloys. The EM-721 alloy has the minimal resistance to tellurium IGC ($k = 9 \times 200$ pc·μm/cm, the depth of cracks is up to 434 μm). The studies have shown, that the Ni based alloys IGC is controlled by the [U(IV)]/[U(III)] ratio, and its dependence on this parameter is of threshold character. Providing control the of [U(IV)]/[U(III)] ratio, it is possible to eliminate completely or to minimize Te IGC. It does not undergo tellurium IGC in the molten 73LiF-27BeF$_2$ and 75LiF–5BeF$_2$–20ThF$_4$ solvent with addition 2 mole % of (UF$_4$+UF$_3$) mixture at [U(IV)]/[U(III)] ≤100. HN80MTY alloy has the best corrosion and mechanical properties even at 1 073K and [U(IV)]/[U(III)]=500.
Figure 9: Microstructure of surface layer for E-721 (a,b,c) and HN80MTY (d,e,f) specimens after 250 hrs exposure in Li,Be,U/F fuel salt without loading: a,d - for U(IV)/U(III) ratios: a - 30 (at 1033 K); b,e - 60 (at 1033 K) and 90 (c,f - at 1073 K)

a) no IGC

b) $K = 3.38 \times 10^3$ pc/μm/cm

c) $K = 5.83 \times 10^3$ pc/μm/cm

d) no IGC

e) no IGC

f) $K = 5.30 \times 10^3$ pc/μm/cm
Figure 10: Surface layer of Ni-based alloy specimens after 250 hrs exposure under strain 25 MPa at 1013K in fuel salt with [U(IV)]/[U(III)] ratios 100 (left) and 500 (right): (a and b) HN80M-VI, (c and d) HN80MTY, (e and f) HN80MTW, (g and h) EM-721; enlargement $\times50$ [1]

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References

Innovative TRU Burners and Fuel Cycles Options for Phase-Out and Regional Scenarios

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Karlsruhe Institute of Technology, KIT, Germany

Abstract

Partitioning and transmutation (P&T) technologies may be considered either for minor actinides (MAs) inventory stabilisation (typical for on-going/regional scenarios) or for a drastic reduction of the transuranics inventory (as in phasing-out scenarios). In this paper, two sodium-cooled fast reactor cores, based on the French ASTRID design and characterised by different amounts of MAs in the fuel, are proposed. Attention focuses on the safety and on the burning performances of the systems. The behaviour of the systems under dynamic conditions has been investigated considering phasing-out and on-going fuel cycle scenarios. The results demonstrate the flexibility of such systems when employed in different kinds of fuel cycles. The impact of different parameters, such as the initial isotopic vector (and Cm content) and the cooling time before reprocessing, on the simulation results is investigated as well.

Introduction

The adoption of partitioning and transmutation (P&T) technologies may be considered either for stabilising the minor actinides (MAs) inventory keeping plutonium (Pu) as a resource (on-going/regional scenarios) or for significantly reducing the accumulated transuranics (TRU) inventory and minimising the burden associated with their disposal (phasing-out conditions) [1].

Whatever is the considered objective, the development of innovative nuclear reactors able to efficiently burn MAs or TRU is an important pre-requisite. In particular, Fast Reactors (FR) may allow fulfilling different goals such as breeding fissile material or burning TRU elements or MAs for practically any Pu vector, MAs content, or MAs to Pu ratio. Therefore, they allow envisaging flexible options for P&T use for any kind of fuel cycles [2-5].

In this paper, we propose two 1 200 MWth sodium-cooled FR cores with a conversion ratio (CR) lower than one for incinerating either all TRU or mainly MAs.

The systems are based on the available French ASTRID sodium-cooled FR core design [6]. The so-called Pu burner is mainly devoted to a phase-out strategy and aims at reducing at first the Pu mass in the cycle (Pu is the dominant component of the TRU inventory). The MA burner is more oriented to on-going and regional nuclear energy options and it aims reducing the MAs mass in the cycle and keeping Pu mass rather stable. In developing the systems, considerable attention has been focused on safety aspects [2]. The deterioration of safety parameters expected by the use of large Pu content (more than 20%) and different amounts (2-12%) of MAs into driver fuel has been compensated by modifying the initial ASTRID design. The reduction by 20% of the active core height and the total power, together with the elimination of the internal fertile blanket and the reduction of the lower axial blanket allow obtaining a negative coolant void effect (if both the core and the plenum above it are voided) for both systems.

1. The CR is defined here as the ratio of the TRU production (from U) to the destruction rates (mainly due to TRU fission).
In order to investigate the behaviour of the Pu and MAs fast reactor burners under dynamic fuel cycle conditions, two scenarios with different objectives have been considered. For the phasing-out case, it is assumed that the German accumulated TRU inventory (175 tons of TRU, produced by 19 German LWRs, scheduled to be gradually shut-down before the end of 2022) should be burned within about 150 years [7-9]. A first step to scenario optimisation is presented here by analysing the impact of the introduction of a single burner reactor (unit) into the fuel cycle. With respect to this case, several assumptions as the initial isotopic vector (including initial Cm content in the fuel) and the cooling time before reprocessing and reloading, are investigated. The results obtained allow to find appropriate boundary conditions for future optimisations that includes iterations between neutronics investigations and scenario studies.

As a first step to regional scenario studies, MA burner systems are introduced in a simplified ongoing scenario for stabilising the MAs inventory. The scenario is characterised by a constant nuclear energy production, where the transition from LWRs to FRs fleet is achieved by using the Pu available in the cycle. The results obtained are compared with previous studies based on the employment of the European Sodium-cooled Fast Reactor (ESFR) [10,11].

**Computational methods**

The 3D (HEX-Z) models of the Pu and MA FR burners have been assessed by means of the ERANOS2.2 code [12]. Effective neutron-cross sections at 33 energy-groups have been processed by means of the ECCO code [13], using the JEFF3.1 nuclear data library [14], and neutron transport calculations, have been performed by means of the VARIANT code [15].

Scenario analyses have been carried out by using the COSI6 (v6.0.8) code [16]. For each of the systems considered in the study, dedicated COSI6 libraries have been generated at KIT on the basis of the ERANOS calculations.

**Assessment of the ASTRID-like models**

The Pu and MAs burner models are based on the French ASTRID CFV² concept developed by CEA with support of AREVA and EdF [6,17]. The models (1 200 MWth) have been assessed for achieving a CR of 0.5-0.7 (by increasing the TRU content in fuel) without a significant power reduction as compared to the ASTRID original design (1 500 MWth and CR=1).

In order to compensate the reactivity increase due to the use of large Pu content and partly the deterioration of safety parameters, the core height has been reduced by about 20% (50/70 cm height for the inner/outer core regions, respectively) and the internal blanket in the inner core has been removed. The thermal power has been reduced to 1 200 MWth in order to keep the same power density as in the French ASTRID design. In addition, the height of the lower axial blanket has been reduced to 2 cm in order to decrease the breeding capability). The RZ layout is shown in Figure 1.

The TRU vector considered in both cases (Table 1) corresponds to one used in the past in European studies associated to the inert matrix fuel in the design of the European Facility for Industrial Transmutation (EFIT), i.e. a typical MOX Spent Nuclear Fuel (SNF) reprocessed 30 years after its irradiation in a PWR with a burnup rate of about 45 MWd/kg [18]. This vector, if compared with the composition evaluated for the German SNF inventory by GRS [9] or the one corresponding to 400 TWhe PWR park with a 60 GWd/t burnup after 50 years cooling [19], shows the worst Pu quality and the larger Am-241 and Cm-244 contents, making the choice very conservative for the aim of the study. Such a vector, indeed, can be assumed as a reasonable estimation of the average fuel composition during the fuel

2. CVF means « Cœur à Faible effet de Vide » i.e. low sodium void core.
3. The vectors indicated in Table 1 are used in scenario simulations as well. In the figures they are recalled in agreement with Table 1: Ref.: GRS and IAEA.
cycle taking into account the disappearance of Pu-239 and the formation of Am-241 during the cycle. The main characteristics of the burners are given in Table 2. The Pu enrichment has been set to get the required CR under the condition that the systems are critical after they are loaded with fresh fuel and operate for 3 irradiation cycles, i.e. at the end of cycle 3, EOC3).4

![Figure 1: burner 2D (RZ) model (dimension in cm) [2]](image)

Table 1: Pu and MA vectors: Reference composition and alternatives

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Pu vector (wt. %)</td>
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<td></td>
</tr>
<tr>
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<td>3.7</td>
<td>2.45</td>
<td>4.45</td>
</tr>
<tr>
<td>Pu239</td>
<td>46.4</td>
<td>52.49</td>
<td>57.17</td>
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<tr>
<td>Pu240</td>
<td>34.1</td>
<td>32.19</td>
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</tr>
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<td>Pu241</td>
<td>3.8</td>
<td>0.9</td>
<td>0.6</td>
</tr>
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<td>Pu242</td>
<td>11.9</td>
<td>11.97</td>
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</tr>
<tr>
<td></td>
<td>MAs vector (wt. %)</td>
<td></td>
<td></td>
</tr>
<tr>
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</tbody>
</table>

Keeping the geometry fixed, different Pu to MAs ratios have been employed in the two burners in order to achieve the desired objective, i.e. burning of Pu or of MAs. In both cases, homogeneous TRU loading (mixed U-TRU oxide fuel) has been assumed. MAs (ca. 10% wt.) are homogeneously mixed with depleted U in the lower axial blanket to further improve the safety performance, as in earlier studies performed within the CP-ESFR project [10,11].

4. For the burner models, the loading scheme assumed is of 5 cycles of 365 effective full power days (efpd). Therefore, EOC3 is considered the condition of equilibrium for FR systems with a batch scheme of 5 irradiation cycles.
Transmutation and safety performances

As indicated in Table 2, the Pu burner works quite well, i.e. it only burns Pu since CR(Pu)=CR(TRU). The MA burner mainly transmutes MAs (CR(TRU)=0.55) but a small amount of Pu is burned as well (CR(Pu)=0.9). The same results appear in the analysis of isotope-wise transmutation performances indicated in table 3. For the Pu burner, Pu consumption comes from Pu-239, Pu-240 and Pu-242 and MAs consumption mainly comes from Am-241, while Am-243 and Cm-244 are produced leading to a net MAs balance (-0.2 kg/TWhth). For the MA burner, the total consumption of MAs is -14.5 kg/TWhth (mainly Am-241 and Am-243) while Cm is generated. The total amount of Pu is almost conserved but the vector is deteriorated (Pu-239 consumption and build-up of Pu-238), an important aspect that impacts the scenario studies.

Table 2: Main parameters of the ASTRID-like burners

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pu burner</th>
<th>MA burner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (MWth), Cycle length (efpd)</td>
<td>1200/365(5)</td>
<td>1:2</td>
</tr>
<tr>
<td>MAs/Pu</td>
<td>1:20</td>
<td>1:2</td>
</tr>
<tr>
<td>U inventory at BOL (tons)</td>
<td>6.8³/5.9³/0.3³/0.2³</td>
<td>6.1³/5.2³/0.3³/0.2³</td>
</tr>
<tr>
<td>MAs inventory at BOL (tons)</td>
<td>0.12³/0.12³/0.03³/0.02³</td>
<td>1.1³/1.1³/0.03³/0.02³</td>
</tr>
<tr>
<td>Pu inventory at BOL (tons)</td>
<td>2.4³/2.4³/0.0³/0.0³</td>
<td>2.2³/2.2³/0.0³/0.0³</td>
</tr>
<tr>
<td>Pu enrich. (wt.%)</td>
<td>25³/27³</td>
<td>22.5³/24.5³</td>
</tr>
<tr>
<td>Conversion ratio</td>
<td>0.68(Pu)/0.68(TRU)</td>
<td>0.9(Pu)/0.55(TRU)</td>
</tr>
<tr>
<td>Average discharge burnup (MWd/kg)</td>
<td>100/137</td>
<td>100/133</td>
</tr>
<tr>
<td>Reactivity loss (pcm/efpd)</td>
<td>7.8</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 3: Isotope-wise TRU consumption (core + blanket) in kg/TWhth

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Pu burner</th>
<th>MA burner</th>
<th>Isotope</th>
<th>Pu burner</th>
<th>MA burner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu238</td>
<td>-0.63</td>
<td>5.22</td>
<td>Am2343</td>
<td>0.76</td>
<td>-1.92</td>
</tr>
<tr>
<td>Pu239</td>
<td>-8.21</td>
<td>-6.80</td>
<td>Np237</td>
<td>-0.09</td>
<td>-0.63</td>
</tr>
<tr>
<td>Pu240</td>
<td>-2.82</td>
<td>-2.56</td>
<td>Np239</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Pu241</td>
<td>0.26</td>
<td>0.07</td>
<td>Cm242</td>
<td>0.18</td>
<td>1.01</td>
</tr>
<tr>
<td>Pu242</td>
<td>-1.83</td>
<td>-0.15</td>
<td>Cm243</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>Am241</td>
<td>-1.79</td>
<td>-15.60</td>
<td>Cm244</td>
<td>0.54</td>
<td>1.56</td>
</tr>
<tr>
<td>Am242m</td>
<td>0.12</td>
<td>0.72</td>
<td>Cm245</td>
<td>0.05</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The safety performances of the Pu and MA burners have been investigated in [2]. The main kinetics and safety parameters have been evaluated at Beginning of Life (BOL) and at EOC3. As shown in Table 4, no significant degradation of the kinetics parameters ($\beta_{eff}$ and $\Lambda$) occurs during the irradiation. The same behaviour is observed for the Doppler constant ($K_D$). Concerning the coolant void effects, if the core is voided, both systems show a positive reactivity effect at BOL. However, if the upper Na plenum is voided too, the coolant void worth is negative in both systems at both BOL and EOC3. A detailed investigation of the space-wise and cell-wise coolant void reactivity distributions can be found in [2]. For such analyses exact perturbation calculations have been performed in the 3D (HEX-Z) models by using the KIN3D [20] kinetics module of the VARIANT code.

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### Table 4: Kinetics parameters and main safety parameters at BOL and EOC3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pu burner BOL</th>
<th>Pu burner EOC3</th>
<th>MA burner BOL</th>
<th>MA burner EOC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{\text{eff}}$ (pcm)</td>
<td>331</td>
<td>328</td>
<td>275</td>
<td>272</td>
</tr>
<tr>
<td>$\Lambda$ (µs)</td>
<td>0.661</td>
<td>0.632</td>
<td>0.420</td>
<td>0.470</td>
</tr>
<tr>
<td>$K_D$ (pcm)</td>
<td>-571</td>
<td>-540</td>
<td>-275</td>
<td>-272</td>
</tr>
<tr>
<td>Reactor condition</td>
<td>$\Delta\rho$ (S)</td>
<td>$\Delta\rho$ (S)</td>
<td>$\Delta\rho$ (S)</td>
<td>$\Delta\rho$ (S)</td>
</tr>
<tr>
<td>Voided core</td>
<td>3.1</td>
<td>4.0</td>
<td>5.9</td>
<td>6.1</td>
</tr>
<tr>
<td>Voided core + plenum</td>
<td>-3.4</td>
<td>-2.6</td>
<td>-0.3</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

### Fuel cycle options

In order to investigate the systems behaviour under dynamic fuel cycle conditions, two scenarios with different objectives have been considered: a phasing-out scenario and an on-going scenario. In the phasing-out case, it is assumed that the German accumulated TRU inventory (175 tons of TRU with 137 tons of Pu and 38 tons of MAs) should be burned in about 150 years [9]. The introduction of three generations of single units of 1 200 MWth each and 50 years lifetime starting from 2075 (this initial deployment date has been chosen arbitrarily) has been considered. This simplification helps to illustrate the impact on the scenario analyses of modelling assumptions like the initial isotopic vector. In the reference case, the isotopic vector of the TRU legacy stock is the same as the one used for modelling the burners (Table 1), in order to have the same burning rates between COSI and ERANOS simulations. Concerning reprocessing and fabrication options, it has been assumed that the TRU from LWR are reprocessed and burned at first and, only after having consumed the accumulated stock, the TRU coming from FR SNF starts to be reprocessed. For a single unit, the accumulated LWR Pu (137 tons) is enough to fabricate the fuel for the entire operation period. This implies that the Pu vector remains practically unchanged. Under these conditions the impact of the cooling time before reprocessing is not visible, therefore an alternative case, where four units work in parallel, has been considered.

For the ongoing scenario, the produced energy is kept fixed to ca. 70 TWh/y,
and a transition from LWR, after 60 years of operation, to FR fleet is considered [21]. In the study it was assumed that one ESFR unit (3 600 MWth) is replaced by three 1 200 MWth MA burner units (Figure 2). MAs are loaded only in the MA burner cores while Pu feeds both systems.

**Figure 2: On-going scenario: (a) LWR and FR share; b) fast fleet composition**

5. Both the Pu burner and the MA burner system have been considered in the study. The adoption of two extreme cases allows assessing the boundary conditions for further optimization of systems and scenario.

6. 70 TWh/y corresponds to the energy produced by ca. 6 ESFR units (3 600 MWth each).
Some assumptions (used in the past, e.g. [1]) are quite challenging from a technical point of view: six months for fabrication and reprocessing, 85% load factor, 40% thermal efficiency, 99.9% separation efficiency for all TRU. These assumptions impact the results of the scenario studies. In order to quantify the impact of the initial TRU vector (including the initial Cm content) and the cooling time before FR SNF reprocessing\(^8\) a parametric study has been carried out for the phasing-out case. Similar studies, for the on-going scenario, have been carried out in [21].

**Results: phasing-out scenario**

In Figure 3a, the total Pu mass (considering all facilities in the cycle including repository) is shown. The introduction of one unit allows a reduction of Pu initial mass between 10% (ca. 16 tons) and 20% (29.5 tons) for the MA burner and Pu burner, respectively. These values are affected by the choice of the initial TRU vector assumed for the LWR SNF as indicated by Figure 3b. In particular, using a better quality Pu (Table 1) implies a lower enrichment of the fuel, a lower CR(Pu) and therefore a lower Pu reduction in cycle (the Pu mass in the cycle after 150 y for both cases is ca. 4% higher).

![Figure 3: Pu total mass evolution (case: one unit)](image)

The MAs mass evolution is shown in Figure 4a. The adoption of the MA burner leads to a reduction of 46% (18 tons) while the use of the Pu burner results in an increase of 4.6 tons (ca. 12%), mainly due to the decay of Pu-241 to Am-241 in the LWR SNF storages (in agreement with the burning rates of Table 3). The effect of the initial TRU vector is shown in Figure 4b. A smaller amount of Pu-241 in stock (Table 1) leads to the formation of less Am-241 (by decay) for the Pu burner case (differences of the order of 5-8%). For the MA burner case, the MA mass reduction becomes larger (up to ca. 56% in the case of IAEA vector).

![Figure 4: MAs total mass evolution (case: one unit)](image)

---

7. Vector associated to the LWR accumulated SNF.
8. Considering 2 years cooling time for the reference case as in [9].
Concerning the Cm in the cycle (Figure 5a), the Cm inventories in both systems during the first 80 years are dominated by the Cm-244 decay (Ref. vector cases), dominant contribution also in the case of fuel with large Am content (MA burner) where an accumulation of Cm was expected (see burning rates in Table 3). The accumulation happens (MA burner case) after year 80 when MAs from FR SNF are recycled. Changing the initial vector (Figure 5b), i.e. using vectors in which the Cm-244 contribution is low (0.3% vs. 3% wt., Table 1), the Cm inventory in the cycle at time 0 is ca. 50% of the inventory of the Ref. case and the expected behaviour of Cm accumulation is visible since the beginning of the scenario (Figure 5b). Further investigations considering the Cm strategy and the assessment of the impact on quantities like decay heat at fabrication and reprocessing plants, are planned.

Figure 5: Cm total mass evolution (case: one unit)

After introduction of a single unit working for 150 years, a large residual mass of TRU remains in the cycle. According to the trends shown above, we can consider that the complete TRU burning may be achieved by a fleet of about four to five Pu burners and two MA burners (or 6-7 systems with intermediate characteristics), working in average for 150 years, which corresponds to an “effective CR” of about 0.62-0.65. Effort are ongoing at KIT for optimising the scenario including this aspect and the issue of the “last transmutation core” (critical burner or a subcritical machine) able to deal with the residual TRU inventory at the end of the cycle. The results presented here form the basis for fixing the boundary conditions during the optimisation process.

A case in which four Pu burner units work in parallel has been studied to determine the effect of SNF multi-recycling (in that case, FR Pu is recycled from year 30) and of a different cooling time before reprocessing. With 4 units in operation (Figure 6-a), the Pu mass in the cycle is reduced by almost 67% (3 times compared to the single unit10) and the MAs mass increase remains almost the same (15% vs. 12%). The Pu mass is not affected by different cooling times (5 or 10 y instead of the 2 y used as reference) before reprocessing, while MAs mass shows variations of ca. 2-4% (Figure 6b). Investigations of the impact on the decay heat at fabrication and reprocessing are planned.

9. All LWR MAs are used for fuel fabrication before year 80 in the MA burner case scenario, while for the Pu burner case scenario, characterised by lower MA content, LWR MAs continue to be used up to the end of the scenario.
10. The Pu reduction is not fully proportional to the number of units. In fact, the reprocessed Pu has a “poorer quality” than the initial one, i.e. the Pu-239 fraction of 43% instead of 47% due to the assumed characteristics of the fuel cycle. A lower Pu-239 fraction impacts the Pu content (increase by ca. 1–2%) needed for maintaining the core criticality resulting in different Pu burning rates and Pu balance in the cycle.
As first step to regional scenario studies, the adoption of the MA burner has been tested with respect to a simplified ongoing scenario used in the past at KIT [10]. The impact of a mixed fleet (ESFR & MA burners in Figures 7 and 8) has been compared with several cases: (a) LWR: reference case where only LWR are operated; (b) ESFR: fast fleet composed only of ESFR systems loaded with MOX fuel (all MAs are sent to the repository); (c) ESFR-5%MA: fast fleet composed only by ESFR systems with 5%wt. of MAs homogeneously loaded in core (strong effects on safety parameters); and (d) CONF2-10%MABB: fast fleet composed only of ESFR optimised cores, including lower axial blanket made of depleted U with 10% MA (in this case the driver fuel is normal MOX fuel with less influence on reactivity effect deterioration).

As indicated in Figure 7a, the adoption of only three units of MA burners (ESFR & MA burners case) is sufficient to reduce the MAs in the cycle to the same level as in the case of a full fleet loaded homogeneously with 5% MAs in the core. The Pu mass evolution in the cycle is comparable to ESFR cases (Figure 7b).

The use of the mixed fleet (i.e. with MA burners) case is more favourable from the safety point of view due to a lower Na void reactivity effect in burner systems with MA-bearing fuels compared to larger ESFR-like ones. In fact it is possible to obtain a design with a negative total coolant void reactivity effect (-$0.3, Table 4) while for the ESFR reference case, the void effect was systematically positive (more than $4, [10]). Preliminary results concerning the impact on cycle facilities (i.e. fabrication and reprocessing plants) are presented here. The specific activity\textsuperscript{11} (TBq/t) of the material in input to the fabrication plants is shown in Figure 8a. The behaviour obtained for the mixed fleet (ESFR & MA burners case) remains

\textsuperscript{11} Averaged values evaluated considering the mass of different types of batches that are fabricated.
comparable with the case of a full fleet loaded homogeneously with 5% MAs in the core. A similar behaviour for the specific decay power (W/t) is evident in Figure 8b. The results are encouraging and more investigations (using also different codes) are planned to confirm these trends.

**Figure 8:** Specific activity a) and power b) of the material in input to fabrication plant (on-going scenario)

![Graphs showing specific activity and power](image)

**Conclusions**

Two FR critical core models for burning Pu and MAs have been assessed for on-going/regional and phasing-out scenario analyses. The models are based on the original French ASTRID design. Considerable attention on assessing the models has been devoted to the burning and to the safety performances of the systems. Results show that the main safety parameters of the two systems seems reasonable and do not significantly deteriorate during the irradiation. The Doppler constant is relatively large in magnitude for the Pu burner and smaller, but still not negligible and strictly negative for the MA burner. The coolant void reactivity effects are also negative, if the core and upper plenum are voided, being closer to zero for MA burner. Both systems show good burning performances: the Pu burner burns mainly Pu (98.5% of the total TRU burned) and the MA burner mainly MAs (77.8% of the total TRU burned). Results show that the burners allow the use of all TRU compositions foreseen in the fuel cycle with a proper choice of the MAs/Pu ratios and of the U/TRU fractions.

Additional studies are needed to confirm the safety of both designs, in particular for the MA burner. Note that the Pu and MA burners are established as extreme cases; depending on the objective (burning all TRUs or only MAs) and safety constraints, intermediate fuel compositions with intermediate burnup performances can be chosen.

These core performance evaluations based on the core burnup simulation results are confirmed by fuel cycle studies performed with the COSI6 code for phasing-out and on-going scenarios. The analysis of a single unit deployed in three successive generations for 150 years in the phasing-out scenario represents the first step for future optimisation activities at KIT. Results obtained for two extreme cases form a basis for neutronics model improvements (as concerns e.g. possible fuel isotopic composition) and scenario optimisation. For this purpose, investigations about the impact of the initial TRU vector (including initial Cm content) and cooling time before reprocessing on the trend have been carried out. Future activities on phasing-out scenario optimisation, including the issue of the “last transmutation core”, are planned at KIT on the basis of the presented results.

The simplified on-going scenario has been studied also in view of regional scenario investigations. Preliminary results concerning the impact on fabrication have been presented. The results are rather consistent, showing the potential of appropriate FR designs to reduce significantly TRU or MAs inventories within a reasonable timeframe.
Acknowledgments

The authors wish to thank Dr. Edgar Kiefhaber (KIT) for the careful revision of the paper.

References


Session 4:
Waste Management For P&T Scenarios

Chairs: Z. Hodgson (United Kingdom)
(Th,Pu)O₂ Stability under Repository Conditions

CIEMAT, Spain

Abstract

In the current uranium oxide nuclear fuel cycle, some uncertainties remain, mainly due to its radiotoxicity from the fission products (FP), plutonium and minor actinides (MA) as by-products of the fuel irradiation. Recycling Pu in the advanced closed cycles to reduce the Pu inventories is one of the main recommendations of the treaty of non-proliferation of nuclear weapons (NPT). The behaviour of different matrices for Pu incineration and/or conditioning is being studied. Thoria (ThO₂) is one of the candidate materials due to its abundance and chemical stability against irradiation and temperature.

Due to that, it is essential to gain knowledge about the behaviour of this irradiated matrix considered as waste. Therefore, it is required to identify and determine the release rate of radionuclides generated (FP, PA, Pu and U-233). Thorium has only one oxidation state (Th [IV]) hence its aqueous stability is not dependent on the environment, such as oxidising or reducing conditions.

This paper is focused on ThO₂(cr) and irradiated Th-MOX doped with 3% of Pu solubility studies under different nuclear fuel stored conditions. ThO₂ pellets doped with a ~3 wt. % of Pu were fabricated by a SOL-GEL method (in which Pu is mixed, forming a solid solution with the matrix). After characterisation the pellets were irradiated to a burnup of 38.8 MWd/kgTh. Batch leaching tests of both types of materials were carried out at room temperature under anoxic conditions and in leachants with different carbonate concentration, such as: 0, 1.2 and 20 mM carbonated concentration. The results obtained show that the concentration of carbonate in solution has a strong influence on thorium dissolution behaviour. Experimental results of Th concentration were compared to thermodynamic calculations performed using PHREEQC code. The database used for this work was collected from existing literature selected data for pure solid phases (solubility limiting solid phase (SLPS) and control the solubility of each of the elements): ThO₂(s), ThO₂.xH₂O(am), since the hydrated phases will be the dominant aqueous species in the system. The results were compared to the experimental values obtained.
Session 5:
Advanced Nuclear Fuel Recycling

Chairs: D. Warin (France) and V. Ignatiev (Russian Federation)

Part A: Aqueous Processes
Part B: Pyroprocessing
International Assessment of Separation Processes Related to Current and Future Nuclear Fuel Cycles

P. Baron, a E.D. Collins, b G. De Angelis, c J.P. Glatz, d V. Ignatiev, e T. Inoue, f A. Khaperskaya, g I-T. Kim, h T. Koyama, i H.S. Lee, h K. Minato, i Y. Morita, j R. Taylor, j J. Uhlir, k D. Warin, l S.M. Cornet

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c: ENEA, Italy
d: JRC-ITU, European Commission
e: Kurchatov Institute, Russian Federation
f: CRIEPI, Japan
g: Rosatom, Russian Federation
h: KAERI, Republic of Korea
i: JAEA, Japan
j: NNL, United Kingdom
k: Rez, Czech Republic
l: OECD Nuclear Energy Agency

Abstract

The implementation of advanced nuclear systems requires new technologies associated with the back-end of the fuel cycle. Improved or new separation techniques such as advanced head end processes, coprocessing solvent extractions, and pyroprocessing are being investigated in different member countries.

The role of the Expert Group on Fuel Recycling Chemistry [under the guidance of the Nuclear Science Committee and the mandate of the Working Party on Scientific Issues of the Fuel Cycle (WPFC)] is to share up-to-date information on recent developments in the field of recycling and perform technical analyses of advanced processing concepts, including technological maturity in design bases for future spent nuclear fuel recycling plants. A state-of-the-art report on progresses on separation chemistry, minor actinides separation and perspective of future R&D is currently being written by experts. The status of current technologies is detailed depending on the fuel types. Technological readiness of the various reprocessing techniques is also assessed.

Additional activities include studies on the feasibility of reprocessing of molten corium and the potential options for treatment after the Fukushima accident. Information regarding R&D facilities available for international cooperation for advanced fuel cycles and allowing the manipulation of at least 1 gram of TRU and/or SNF is being collected and will be gathered into a database.
EXAM Selective Am Recovery Process: Near Past Results and Near Future Liquid-Liquid Separation Experiments

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Abstract

As americium is the main contributor to the long-term radiotoxicity and to the heat emission of high-activity waste, CEA teams have been involved for several years in the development of liquid-liquid separation processes able to recover americium selectively from PUREX or COEX raffinates. The principle of the EXAM process is to extract americium and some light lanthanides with a mixture of extracting molecules in organic phase and to maintain curium and heavy lanthanides in aqueous solution using a hydrophilic glycolamide molecule TEDGA to complex them among other fission products. The initial concept validated in 2010 has evolved to the so call concentrated Exam process based on the use of a nearly 3 times concentrated raffinate solution in order to improve the compactness of the future plant.

In this scope, experiments were performed to study several aspects of the process such as the concentration step before americium precipitation, the behaviour of molybdenum in the process, the effect of stronger alpha radiolysis. These experimental results were taken into account to define an optimised process flowsheet using the PAREX code. A next run of this process is planned to assess the whole performances of this flowsheet. Firstly, a surrogate solution containing americium and curium traces will be used in the C17 Atalante medium activity hot cell to validate the flowsheet and the behaviour of elements of interest in liquid-liquid representative contactors. Then, the ultimate experiment will be conducted, after a three times concentration of a genuine radioactive raffinate, in the Atalante CBP high shielded cell facility to produce several grams of purified americium solution. This recovered and purified americium, will be used to produce (U, Am)O₂ powder and pellets for a later irradiation in the ATR reactor. This experimental irradiation will be a test for the americium transmutation in fast reactor in heterogeneous mode using BBMA concept (Blanket Bearing Minor Actinide).
Separation of Minor Actinides by a Single Cycle Approach using Unsymmetrical Diglycolamide and Diglycolamic Acid

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Abstract
A new class of CHON-extractants, namely unsymmetrical diglycolamides (UDGA) and diglycolamic acid were developed for the partitioning of minor actinides from high level liquid waste. Group separation of trivalent metal ions (An(III) + Ln(III)) from fast reactor (FR) simulated high-level liquid waste (SHLLW) was demonstrated using UDGA, N,N-didodecyl-N',N'-dioctyl-3-oxapentane-1,5-diamide (D3DODGA) without the addition of organic phase modifier in n-dodecane phase. A single-cycle approach has been explored for the separation of trivalent actinides from FR-SHLLW using the solvent phase composed of D3DODGA and di-2-ethylhexyldiglycolamic acid (HDEHDGA), or tetra-bis(2-ethylhexyl)diglycolamide (TEHDGA) and bis(2-ethylhexyl)phosphoric acid (HDEHP). A procedure was developed to minimise the extraction of unwanted metal ions by using aqueous soluble complexing agents in FR-SHLLW. Based on the optimised conditions, a counter current mixer-settler run was performed to separate Am(III) from FR-SHLLW using a novel ejector based mixer-settler. Quantitative extraction of trivalents (Am(III) + Ln(III)) was observed in both the systems. Am(III) alone was back extracted from loaded organic phase using a solution of diethylenetriaminepentaacetic acid - citric acid. The results showed the possibility of selective separation of trivalent actinides alone from high level liquid waste in a single cycle process.

Introduction
Partitioning and Transmutation (P&T) of trivalent actinides is being considered as a viable strategy for the safe management of high-level liquid waste (HLLW) [1]. The HLLW generated from reprocessing of spent nuclear fuel is composed of a complex mixture of several elements such as the actinides, fission products and corrosion products present in 3-4 M nitric acid medium. Several reagents such as the organophosphorous compounds, malonamides, and diglycolamides have been proposed for partitioning trivalent actinides from HLLW [2,3]. In early stage, the TRUEX process was developed for trivalent actinide partitioning using a bidendate organophosphorous reagent, n-octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) [2]. Later, the extractants made-up of CHON elements have been proposed as they offer the additional advantage of complete incinerability of the spent solvent. In the last decade, diglycolamides (DGAs) (alkyl-3-oxapentane-1,5-diamide derivatives) have emerged as promising candidates [3]. Among the various DGAs, the symmetrical alkyl derivatives containing octyl (TODGA) and bis(2-ethylhexyl) (TEHDGA) substituents are popular. However they also have some limitations. To overcome the limitation of these derivatives the concept of unsymmetry in diglycolamides was introduced. Unlike the symmetrical DGAs, the alkyl group attached in UDGAs are not the same. Thus, we prepared several unsymmetrical diglycolamides and studied the extraction of actinides and fission products from nitric acid medium [4,5]. Our studies revealed that the unsymmetrical diglycolamides are superior reagents as compared to the existing diglycolamides.
The current approach for partitioning of trivalent actinides from HLLW is a two-cycle approach \[2,3\], namely, i) the group separation i.e., the separation of trivalent actinides together with lanthanides, in the first step, which is followed by the ii) lanthanide–actinide separation in the second step. The mutual separation of trivalent actinides and lanthanides is necessary prior to transmutation, since the lanthanides act as neutron poisons during transmutation of actinides that reduce the efficacy of transmutation. Thus, the extractants indicated above such as CMPO, DGA and malonamides are proposed for group separation (i.e. step 1) \[2-5\] and extractants such as HDEHP, bis-triazinylpyridine (BTP) have been proposed for lanthanide-actinide separation (i.e. step 2) \[2\]. However in the recent past, single-cycle methods for the separation of trivalent actinides are receiving increased attention. There are a couple of approaches reported in literature. The first one is the direct separation of trivalent actinides from HLLW \[6-10\]. The methods such as Selective Actinide Extraction (SANEX) concept, Actinide reCycling by SEParation and Transmutation (ACSEPT) and 1-cycle SANEX concept \[6,7\] were developed for direct separation of actinides from HLLW. In contrast to this, the second approach involves the extraction of both the trivalent actinides and lanthanides together in organic phase followed by selective stripping of actinides alone from the loaded organic phase \[8-10\]. Based on this approach, methods such as TRUSPEAK \[8\] and PALADIN \[9\] were developed. However, the studies reported on single-cycle methods indicate that the solvent phase used for extraction was not completely incinerable. Moreover, the methods employed unconventional diluents, other than n-dodecane, for extraction.

Significant efforts have been taken in our laboratory to understand the problems associated with the existing diglycolamides as well as with single-cycle approaches, and to provide technically viable solutions to the challenges posed during trivalent actinide partitioning. The drawbacks of the symmetrical octyl derivatives (TODGA and TEHDGA) of DGAs are the third phase formation and extraction of unwanted metal ions. However, it was realised that the extraction and stripping behaviour of trivalents were strongly dependent on the nature of alkyl group attached to the amidic nitrogen atom. Therefore, the separations achieved using DGAs can be influenced by the nature of alkyl substituents \[3\]. In this context, we synthesised several unsymmetrical diglycolamides (UDGAs) and studied the extraction of actinides and fission products from nitric acid medium \[4,5\]. Our findings have shown that the dodecyl group in conjunction with the octyl group present in the UDGAs, N,N'-didodecyl-N',N'-dioctyl-3-oxapentane-1,5-diamide,(D3DODGA) \[4,5\] not only retained the excellent extraction properties of diglycolamides, but also surmounted the problem of third phase formation during the extraction of trivalent metal ions from 3-4 nitric acid medium. Our studies have shown that D3DODGA does not require any phase modifier during the extraction of trivalent actinides from 3-4 M nitric acid medium since the limiting organic phase concentration of trivalent ion for third phase formation in 0.1 M D3DODGA in n-DD was more than 100 mM \[4,5\].

In this paper we provide the results of mixer-settler studies to demonstrate the feasibility of using a modifier-free organic phase composed of D3DODGA in n-dodecane for the separation of trivalent actinides from fast reactor (FR) simulated HLLW. Using D3DODGA, a novel approach namely Single cycle method for Minor Actinide partitioning using completely incinerable Reagents (SMART) has been developed. This method uses the applications of D3DODGA and di-2-ethylhexyl diglycolamic acid (HDEHDGA) for the single-cycle separation of trivalent actinides from FR-SHLLW. The structures of extractants and stripping reagents are shown in Figure 1. Unlike other systems, the diglycolamide and diglycolamic acid used are made-up of CHON atoms, and thus completely incinerable. Moreover, they are compatible with nuclear diluent, n-dodecane. The counter-current mixer-settler run was performed using a 20-stage mixer-settler. The results obtained from these studies are reported in this paper. It also reports the mixer-settler studies on single-cycle method using mixture of extractants TEHDGA and HDEHP in n-dodecane for comparison.

Experimental

TEHDGA, D3DODGA and HDEHDGA were synthesised by the procedure described elsewhere \[3,4,11\]. The FR-SHLLW was prepared based on the composition shown in Table 1. The composition is based on the HLLW arising from reprocessing of spent fast reactor fuel with a burnup of 80 000 MWd/Te.
and 2-year cooling [12]. Both extraction and stripping of metal ions was performed in a counter-current mode using a 20-stage or 16-stage ejector mixer settler as described elsewhere [10]. The organic and FR-SHLLW (2L each) were passed in a counter-current mode and the mixing of the organic and aqueous phases was achieved by air pulsing in the column by applying vacuum and pressure alternatively with the help of a solenoid valve operated by a cyclic timer. The flow-rate for both extraction and back extraction was maintained at 3 mL/min by means of metering pumps equipped with precise flow control. The stage samples of organic and aqueous phase were collected for analysis, after establishing a steady state. The back extraction of metal ions from the loaded organic phase was carried out in a counter-current mode using the same mixer-settler in a separate run. The radioactivity of $^{152+154}$Eu(III) and $^{241}$Am(III) in various streams was measured by using HPGe detector coupled with a multichannel analyser. Estimation of other metal ions was carried out by ICP-AES.

**Figure 1: Structures of TEHDGA, HDEHP, D$_3$DODGA, HDEHDGA, DTPA, CA and CyDTA**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.342</td>
</tr>
<tr>
<td>Ce</td>
<td>0.684</td>
</tr>
<tr>
<td>Pr</td>
<td>0.339</td>
</tr>
<tr>
<td>Nd</td>
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</tr>
<tr>
<td>Sm</td>
<td>0.306</td>
</tr>
<tr>
<td>Pm</td>
<td>0.053</td>
</tr>
<tr>
<td>Eu</td>
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</tr>
<tr>
<td>Gd</td>
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</tr>
<tr>
<td>Tb</td>
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</tr>
<tr>
<td>Dy</td>
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</tr>
<tr>
<td>Y</td>
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</tr>
<tr>
<td>Fe</td>
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<tr>
<td>Mo</td>
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</tr>
<tr>
<td>Cr</td>
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<tr>
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<td>Cd</td>
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<td>Sn</td>
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<td>Na</td>
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<td>Tc</td>
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<td>Sb</td>
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<tr>
<td>$^{241}$Am</td>
<td>0.218</td>
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<tr>
<td>$^{152+154}$Eu Tracer</td>
<td>[HNO$_3$] $\sim$ 3 M</td>
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</table>
Results and discussion

Studies with unsymmetrical DGA

The extraction behaviour of various metal ions present in the FR-SHLLW containing about 3.2 g/L of trivalent metal ions (Am(III) and Ln(III)) was studied using a solution of 0.1 M D3DODGA/n-DD, by batch equilibration mode. The details are described elsewhere [13]. The extraction of Am(III) was accompanied by the co-extraction of all lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II) from FR-SHLLW. The co-extraction of unwanted metal ions was minimised by adding a suitable aqueous soluble complexing agents to FR-SHLLW, prior to extraction. As a result, trans-1,2-diaminocyclohexane-N,N,N’N’-tetra-acetic acid (CyDTA) was identified as an appropriate reagent for preventing the extraction of zirconium and palladium, that posed problems during recovery of trivalent metal ions from the loaded organic phase.

Mixer-settler studies with unsymmetrical DGA

Based on those primary results, a counter-current mixer-settler run was performed in a 20-stage mixer-settler. The extraction profile of Am(III) and Ln(III) in 0.1 M D3DODGA/n-DD, in a 20-stage mixer-settler is shown in Figure 2a. The extraction was carried out from FR-SHLLW containing 0.05 M CyDTA spiked with (152,154)Eu(III) and 241Am(III) tracer. It is observed from Figure 2a that the percentage of Eu(III) in aqueous phase decreased sharply in the first contact and the percentage of Eu(III) is negligible after 4 contacts. This indicates that more than 90% of Eu(III) is extracted in the first contact itself and within 4 contacts quantitative extraction of Eu(III) from FR-SHLLW is achieved. Similarly, quantitative extraction of Am(III) is achieved 7-8 stages, as shown in Figure 2a. From the mixer-settler run, the preferential extraction of trivalents in 0.1 M D3DODGA/n-DD follows the order Eu(III) > Sm(III) > Am(III) > Nd(III) > Pr(III) > Ce(III) > La(III). The lanthanides the Pr(III), Ce(III) and La(III) remain in aqueous phase even at 8th stage. They are extracted only beyond 10th stages and the extraction of La(III) completes only in 19th stage.

A counter current stripping run was performed using the same mixer-settler in a separate run. The results are shown in Figure 2b. The study revealed that significant amount of trivalents is back extracted into the aqueous phase in the first contact itself, and all the trivalent metal ions are quantitatively back extracted into aqueous phase in 5 stages. Based on this study, a flow-sheet shown in figure 3 could be proposed for the separation of trivalent metal ions from FR-SHLLW using 0.1 M D3DODGA/n-DD. It can be seen that the flow-sheet is simple as compared to other flow-sheets developed for trivalent actinide partitioning. It requires 20 stages for quantitative extraction of trivalents and 3-5 stages for stripping. It is important to note that this method does not demand any scrubbing stages before stripping, which otherwise generates large volume of secondary waste. Perhaps scrubbing was needed in other flow-sheets where the solvent phase extracts significant concentration of unwanted metal ions such as Sr(II). In addition, the presence of phase modifier in organic phase in other systems also extracts substantial amount of nitric acid from aqueous phase leading to the requirement of scrubbing and large number of stages for back extraction of target metal ions. Such requirement does not arise in the present study. The study also indicated that the problems due to curd-formation or precipitation was not observed during the entire run, thus confirming the clean separation of trivalent metal ions from FR-SHLLW using 0.1 M D3DODGA/n-DD. Therefore, D3DODGA is a promising candidate for the separation of Am(III) from FR-SHLLW.

SMART approach

As discussed above, the extractant D3DODGA has advantage over other diglycolamides and therefore a novel approach namely, Single cycle method for Minor Actinide partitioning using completely incinerable ReagenTs (SMART) was explored using D3DODGA and HDEHDGA [10]. The diglycolamic...
Acid is an acid derivative of alkyl-3-oxapentane, emerging as a promising candidate for lanthanide-actinide (Ln-An) separation [11]. Unlike the other reagents in use, the diglycolamic acid is made up of CHON-atoms and are completely miscible with n-dodecane. The distribution ratio of various metal ions present in FR-SHLLW was measured in a solution of 0.1 M D^3DODGA + 0.2 M HDEHDGA/n-DD. The details are described elsewhere [10]. The extraction of Am(III) was accompanied by the co-extraction of lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II). Since it was desirable to retain these troublesome metal ions in aqueous phase, as discussed above, the complexing agent CyDTA, was added to FR-SHLLW and the extraction and stripping conditions were optimised [10].

**Figure 2a:** Extraction profile of Am(III) and Ln(III) in a 20-stage mixer-settler
Organic phase: 0.1 M D^3DODGA /n-DD
Aqueous phase:
FR-SHLLW + 0.05 M CyDTA spiked with ^241^Am(III) & ^152-154^Eu(III) tracer

**Figure 2b:** Stripping Profiles of Am(III) and Ln(III) in a 20-stage mixer-settler
Organic phase: Loaded organic
Aqueous phase: 0.01 M nitric acid

**Figure 3:** Proposed flow-sheet for partitioning of trivalent actinides from FR-HLLW using modifier-free unsymmetrical diglycolamide, 0.1 M D^3DODGA/n-DD. The numbers 1 to 20 represents each mixer and settler.

Based on the optimised conditions, the counter-current mixer-settler run was performed in a 20-stage mixer-settler. The results are shown in figure 4a (only few lanthanides are shown in the figure for clarity).
The mixer-settler profiles show that Am(III) is quantitatively extracted in 4 stages. A similar extraction profile was also obtained for other lanthanides except lanthanum, which required 8-10 stages for complete extraction. Interestingly, Sr(II) exhibiting a distribution ratio of 0.51 was extracted to the extent of 90%. However, it was noted that the troublesome metal ions such as Zr(IV), Mo(VI), Fe(III), Cr(VI), Ni(II), Pd(II), Ru(III), Rh(III) were rejected to raffinate in addition to other elements.

The recovery of Am(III) from the loaded organic phase was carried out using an aqueous formulation, 0.01 M DTPA + 0.5 M CA at pH 1.5. The stripping profile of Am(III) and some lanthanides obtained in a 20-stage mixer-settler is shown in Figure 4b. At the 20th stage, the loaded organic makes a first contact with aqueous stripping formulation and it is expected to recover Am(III) alone from the loaded organic phase during striping. It is observed from Figure 4b that significant amount of Am(III) is back extracted into aqueous phase at this stage and stripping of Am(III) is observed in all 20 stages. About 55% of the Am(III) was recovered after 20 stages (product stream). Figure 4b also shows the stripping behaviour of some lanthanides (only few lanthanides are shown in the figure for clarity). It is important to observe that significant amount of early-lanthanides (from lanthanum to samarium) are stripped to the aqueous phase along with Am(III), whereas the later-lanthanides (beyond samarium) behave similarly to Eu(III). Depending on the nature of lanthanides, the stripping of “early lanthanides” was determined to be 60-85% in 5-10 contacts (from 20 to 10 stages, Figure 2b). It is important to note that the recovery of “early lanthanides” is better than the Am(III) recovery (~55%). In contrast, the cumulative recovery of “later lanthanides” was lower than 5%.

Therefore, the study clearly shows that recovery of Am(III) is accompanied by the stripping of “lighter lanthanides”. Even though, the separation of Am(III) from lanthanides is not clean, as it is envisaged, the study is important from the point of view of single cycle separation, and the lanthanides needs to be retained in organic phase during stripping. This could be achieved by using different solvent formulations as discussed below.
Mixer-settler studies using TEHDGA and HDEHP

As discussed above, the SMART approach yielded significant contamination of lighter lanthanides in the aqueous product. In view of this, we also studied the alternative extractant system composed of TEHDGA and HDEHP. The TALSPEAK process is a well-established method for the mutual separation of Ln(III) and An(III). This method uses HDEHP as an extractant, which is commercially available and studied for the separation of various metal ions in industrial scale. It is well-recognised that the diglycolamide, TEHDGA/n-DD, forms third phase with nitric acid and trivalent metal ions (Ln(III) and An(III)). The formation of a third phase is usually prevented by the addition of phase modifiers such as tri-n-butylphosphate (TBP) and dihexyloctanamide (DHOA) etc. to the organic phase. However, in the present study, it is proposed to use HDEHP in the solvent formulation to separate trivalent actinides from chemically similar lanthanides. The concentration of HDEHP needed in the solution of 0.1 M TEHDGA – HDEHP/n-DD was optimised (to 0.25 M HDEHP) such that the solvent formulation does not lead to the third phase formation during the extraction of trivals (Ln(III) and An(III)) from FR-SHLLW. Batch studies revealed that extraction of Am(III) was accompanied by the co-extraction of lanthanides and unwanted metal ions such as Zr(IV), Mo(VI), Y(III), Fe(III) and Pd(II). Similar to previous case the aqueous complexing agent CyDTA was added in SHLLW to minimise the extraction of unwanted metal ions. The details are described elsewhere [14].

Based on those studies, a counter current mixer-settler run was performed to separate Am(III) from SHLLW as well as from lanthanides, using a 16-stage mixer-settler. The extraction and stripping profiles are shown in Figures 5a and 5b. It is observed that Eu(III) is extracted quantitatively in 4 stages, whereas Am(III) exhibiting lower distribution ratio than Eu(III) requires about 11 stages for complete extraction. A similar extraction profile was observed for the extraction of other lanthanides from SHLLW. It was noted that all lanthanides, Mo(VI) and Y(III) are extracted quantitatively from FR-SHLLW in 0.1 M TEHDGA-0.25 M HDEHP/n-DD, and Fe(III) was extracted to the extent of 80%. Other metal ions were rejected to raffinate. The recovery of Am(III) from the loaded organic phase was carried out by using 0.05 M diethylenetriaminepentaacetic acid-0.5 M citric acid at pH 3 using same mixer settler in a separate run. The stripping profile is shown in figure 5b. The stripping of Am(III) was quantitative. However, the americium product contained about 10%-20% of lighter lanthanides i.e. lanthanum to neodymium, perhaps due to the presence of these lanthanides in high concentration in FR-SHLLW. The contamination of heavier lanthanides was less than 5%. In addition to this Y(III) and Mo(VI) were stripped to the extent of 29% and 100% respectively. However, these elements do not interfere in the transmutation of Am(III) as neutron absorption cross section for these elements is less. Our results, thus confirm the possibility of separating Am(III) directly from FR-SHLLW in a single-cycle processing step, for the facilitating transmutation of americium. The proposed flow-sheet for the selective separation of trivalent actinides from HLLW is presented in Figure 6.
Figure 5a: Extraction profile of Am(III) and Eu(III) in a 16-stage mixer-settler
Organic phase:
0.1 M TEHDGA - 0.25 M HDEHP/n-DD.
Aqueous phase: FR-SHLLW spiked with $^{241}$Am(III) & (152+154)Eu(III) tracer.

Figure 5b: Stripping profile of Am(III) and Eu(III) in a 16-stage mixer-settler
Aqueous phase: 0.05 M DTPA - 0.1 M CA at pH 3.

Figure 6: Proposed flow-sheet for single cycle separation of trivalent actinides from FR-HLLW using 0.1 M TEHDGA + 0.25 M HDEHP/n-DD. The numbers 1 to 20 represents each mixer and settler.

Conclusions

Partitioning of trivalent americium from FR-SHLLW was demonstrated, for the first time, using a modifier-free unsymmetrical diglycolamide, D³DODGA, in n-dodecane. Quantitative extraction of Am(III), Ln(III) and Y(III) from FR-SHLLW in 0.1 M D³DODGA/n-DD was achieved in 20-contacts and the recovery of Am(III) and other trivalents from the loaded organic phase was achieved in 5 contacts using 0.01 M nitric acid. We explored a novel approach, namely SMART, using CHON based completely incinerable reagents D³DODGA and HDEHDGA. The extraction and stripping behaviour of Am(III) and other metal ions present in the FR-SHLLW was studied using a solution of 0.1 M D³DODGA + 0.2 M HDEHDGA/n-DD in 20-stage mixer-settler. About 55% of the Am(III) was recovered in 20 stages (product stream). It was accompanied by the co-stripping of significant amount of lighter lanthanides. To improve the separation factor, a solution of 0.1 M TEHDGA and 0.25 M HDEHP in n-dodecane was employed in a single-cycle process approach. The lanthanides, Y(III) and Mo(VI) exhibited higher distribution ratio than Am(III) were quantitatively extracted in 4 stages, whereas Am(III) required 11 stages for complete extraction. Quantitative recovery of Am(III) was observed in four stages. This was accompanied by the co-stripping of 18% La(III) and about 10% Ce(III), Pr(III), and Nd(III). The stripping
of other lanthanides having very large neutron cross section was 5%. The study, thus, indicated the possibility of separating of Am(III) from SHLLW, which contained chemically similar lanthanides and several other metal ions in a single-cycle processing step.

References

Microemulsions and Aggregation Formation in Extraction Processes for Used Nuclear Fuel

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b: Idaho National Laboratory, United States
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Abstract
Advanced fuel cycles all over the world rely heavily on successful chemical separation of various elements in used nuclear fuel. Numerous solvent extraction processes have been developed for the treatment of this material. Under certain conditions the extraction systems may behave different from classical solvent extraction theory. One chemical interaction of interest is the formation of large aggregates that has been observed during solvent extraction. In our work, we are studying the effect and relationship of extensive aggregate formation with enhanced extraction of metal ions, i.e. synergistic extraction. Our studies so far have shown the importance of combining and comparing several different analytical techniques, such as metal ion extraction, physicochemical measurements, thermodynamics studies and structural investigations. Overall, the results do not disagree with classic understanding of extraction synergy although there appear to be additional chemical interactions that may affect the distribution of metal ions prompting further studies.

Introduction

To meet the current and future demand for energy all available resources are needed. Nuclear energy is good for production of base load power but the downside is the used nuclear fuel that needs to be managed. One option for managing this material is recycling of the used fuel which requires advanced chemical separation processes. Liquid-liquid extraction is a proven technique that is used in industry for separation of uranium and plutonium from the rest of the material in used nuclear fuel in the so-called PUREX (Plutonium URanium EXtraction) process used in France, Japan and the United Kingdom [1]. The PUREX process relies on tributyl phosphate, TBP, to selectively extract U and Pu away from the fission and corrosion products present in the used nuclear fuel as well as other minor actinides, e.g. Np, Am, Cm. The extraction of metal ions using TBP has been studied extensively over the years and the extraction trends of various metal ions from moderately concentrated nitric acid solutions are well characterised [2-4]. TBP coordinates to metal ions through a solvation mechanism, [5] recovering the neutral metal nitrate species via displacement of water molecules from the inner-coordination sphere, favoured by high nitric acid concentrations (Equation 1).

\[
M^{m+} + n\text{NO}_3^- + m\text{TBP} \rightleftharpoons \text{M(NO}_3)_n(\text{TBP})_m + \text{water}
\] (1)

A bar over a species denotes that it is present in the organic phase.

The exact composition of the extracted complex may vary depending on the metal and the diluent. The examples given by Irving and Edgington (1960) for U(VI), i.e. UO$_2^{2+}$, extraction suggest n=2 and m=2[5].
It was observed early on that TBP would extract nitric acid and that extraction processes using TBP would, under certain conditions form a third phase, [6] causing disruptions in the process. In the early 1990s, Osseo-Asare [7] postulated that the third phase formation from TBP was due to reverse micelles in the organic phase that would grow into large aggregates until they formed a separate phase. In the last two decades the nature of these reverse micelles and the third phase have been studied very closely and work from Argonne National Laboratory carried out by Chiarizia et al. [8,9] have shown that the TBP indeed forms reverse micelles in the organic phase, incorporating water and mineral acid. Furthermore, the formation of these reverse micelles and the larger aggregates was studied and a model was presented [10] describing the observed phenomena using neutral organophosphorous ligands, e.g. TBP, TOPO (trioctyl phosphine oxide) or TBPO (tributyl phosphine oxide).

During the extraction of highly radioactive material, as in the PUREX process, the TBP will inevitably degrade by radiolysis and hydrolysis. The primary degradation product of TBP is dibutyl phosphoric acid, HDBP, itself an effective extraction reagent. The appearance of HDBP in a process complicates the scrubbing of certain elements and the stripping of plutonium and uranium, it has also been noticed that HDBP may increase the chance of third phase formation.

The reason for the difficulty of scrubbing and stripping when HDBP is present is partly because HDBP may extract a range of different metal ions by an ion exchange mechanism and the selectivity for U(VI) and Pu(IV,VI) over metal ions of other valence states decreases. Furthermore studies have shown that combining TBP and HDBP will result in an enhanced extraction compared to using each reagent by itself [11-13]. This enhanced extraction effect is commonly referred to as synergistic extraction. This has been observed in several different systems combining neutral phosphorous containing reagents with acidic extractants [5,14,15].

These studies often explain synergism as increased dehydration of the metal ion improving its extraction into the organic phase. Some studies have shown that combining TBP and HDBP results in enhanced extraction of metal ions compared to using each reagent alone [11-13]. Hahn and Vander Wall [11] suggested two possible mechanisms for the extraction of U(VI) using a combination of TBP and HDBP:

\[2\text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{HDBP} + 2\text{TBP} \rightleftharpoons [\text{UO}_2(\text{DBP})_2][\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2] + 2\text{H}^+ \]  
\[2\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2 + (\text{HDBP})_2 \rightleftharpoons [\text{UO}_2(\text{DBP})_2(\text{NO}_3)_2(\text{TBP})_2] + 2\text{HNO}_3 + 2\text{TBP} \]

Other work, pioneered by Osseo-Asare, has taken a different approach and has attempted to explain the synergistic extraction as a reverse micelle enhanced extraction in system containing combinations of reagents where at least one displays surface active tendencies, e.g. combining LIX®63 (5,8-diethyl-7-hydroxydodanen-6-oxime) with DNNSA (di-nonyl-naphthalene sulfonic acid) [16,17]. In these studies the systems are modelled based on the assumption that the formation of the reverse micelles results in an increased solubility of metal ion complexes in the organic phase.

In this work we have chosen to look closer at an extraction system combining TBP and HDBP where synergy has been observed in the past and to investigate if this synergy is truly due to mixed complexes or the possible formation of larger aggregates, i.e. reverse micelles, in the organic phase. The work presented here represents some of the main results from our ongoing project probing the connection between extraction synergy and microemulsions.

**Results of previous studies**

Our collected studies have focused on the combination of TBP and HDBP for the extraction of trivalent lanthanides although some tests have been carried out with uranyl ions as well. Initial extraction studies on this system provided indications that the water uptake was not following the expected trend, as
is shown below. This prompted further studies to examine the possibility of aggregate formation using Small Angle X-ray scattering, SAXS. These studies indeed indicated formation of larger aggregates, as will be shown below, although the role of these aggregates in metal uptake was not clear. Continued studies using X-ray absorption, where the environment directly surrounding the metal ion was probed, provided insight in the TBP and HDBP binding characteristics. The thermodynamics of metal ion extraction in the TBP/HDBP system and the possible heat of formation of microemulsions were studied in order to draw any conclusions of the enthalpic contributions of aggregates to metal ion extraction. Finally, studies have been initiated using molecular dynamic simulations in an attempt to visualise the organic phase interactions. More details for each of these studies are provided below. For details of the experiments and further details of the results we refer to previous publications from our group [18-23].

Extraction studies

Extraction experiments were carried out using combinations of TBP and HDBP in mole ratios of 4:0, 1:3, 2:2, 3:1 and 0:4. Different lanthanides, lanthanum, La, europium, Eu, dysprosium, Dy, and lutetium, Lu at different concentrations have been investigated. Uranyl was investigated as well due to the affinity of TBP towards this cation, compared to the trivalent lanthanides. TBP has low affinity for trivalent lanthanides under the conditions studied here. Two different concentrations of nitric acid were studied, 0.2 M HNO₃ (low acid) and 2 M HNO₃ (high acid) to see what effect this would have. As HDBP is an acidic reagent it is expected to extract less at high acid, while extraction by TBP would be favoured by high acid. Details of the extraction studies can be found in recent papers by Anderson et al. and Braatz et al. [19-21]

Figure 1a shows how the distribution ratios of Dy³⁺, Eu³⁺ and UO₂²⁺ varies with the TBP:HDBP mole ratio. The dashed lines in Figure 1a represent a possible extraction trend for additive behaviour of the two reagents. Figure 1b shows the water uptake in the organic phase at the various mole ratios of TBP/HDBP. For the low acid system, a non-linear trend for both water and metal uptake is observed, indicating a possible synergistic effect between the TBP and HDBP extractants. At high acidity, the trend for metal and water extraction is more linear so that, at this condition, only a weak synergistic effect, if any, is produced by the TBP-HDBP mixture. However, the uranium extraction still shows a non-linear uptake at high acid likely due to the increased affinity of TBP to UO₂²⁺ at these conditions. Figure 1b also shows the concentration of water in the organic phase before contact with an aqueous phase, i.e. blank. It can be seen that the water content in the organic phases is very low before contact.

Figure 1: a. Distribution ratios of dysprosium, europium and uranyl and b. water concentration in organic phase, from contacting 2 M HNO₃ or 0.2 M HNO₃ with organic phases containing varying ratios of TBP and HDBP. Also shown is the water content in blank, non-pre-equilibrated (or “dry”) organic phases. (Figures reproduced from data in [18,21]).
Results show that HDBP does indeed extract lanthanides to a much higher degree than TBP and that there is possible synergy. The increased water uptake is not in line with the classic explanation of synergy as a mixed complex should dehydrate the metal ion. The water uptake is, however, indicative of the formation of reverse micelles.

**X-ray scattering**

To investigate aggregation in the organic phase as a function of TBP:HDBP, and how this might affect metal ion extraction at low and high acid concentrations, SAXS measurements were performed on solutions with and without metal ions. Details of the experimental procedure and analysis can be found in Ellis et al. [18]. The scattering data collected clearly showed that the mixture of TBP and HDBP resulted in increased scattering of the X-rays at low Q compared to when TBP or HDBP were used alone. The data was analysed for radius of gyration and maximum linear extent.

The metrical information about the aggregates observed in the SAXS data is provided in Figure 2 in terms of radius of gyration, Rg values, which are plotted as a function of the mixing ratio of the extractants. For 100% HDBP, the aggregates formed upon extraction of 2 M HNO₃ (12.7 Å) are smaller than those from 0.2 M HNO₃ (15.4 Å), whereas for 100% TBP the trend in Rg is reversed, with the aggregates formed upon extraction of 0.2 M HNO₃ (11.7 Å) being smaller than those formed upon extraction of 2 M HNO₃ (15.6 Å). This trend in aggregate size correlates with organic phase water content (Figure 1b) and is consistent with the formation of reverse micelles.

**Figure 2: Radius of gyration, Rg, (in Å) calculated from the SAXS measurements of organic solutions containing varying ratios of TBP and HDBP.**

The open points indicate the Rg in solutions contacted with aqueous solutions with no dysprosium added and the closed points show the Rg from contact with aqueous solutions containing Dy. Also shown is the Rg for the blank, non-pre-equilibrated organic phases. Figure reproduced from data in [18,19].

The results show that the system ordering with mixed TBP + HDBP extractants is not a simple arithmetic average of the responses for the two end members, TBP and HDBP on their own. That is, the Rg values peak between the two end member solutions. Between the two end points, there are peaks of 19.3-20 and 21.3 Å in Rg values for the 0.2 M and 2 M HNO₃ systems at the extractant molar ratios of 0.25 and 0.50, respectively. The variation in the experimentally-determined Rg values clearly shows that the particle scatterers assemble into larger entities in the mixed extractant phases than in the single component extractant systems. Such behaviour is consistent with the formation of mixed aggregates and micellisation. It is noteworthy that the peak Rg value in the synergistic 0.2 M acid system corresponds to the optimum TBP mole ratio for the combined uptake of lanthanide and water (Figure 1), so that aggregation and synergism may, in this case, be linked. In contrast to this the peak for the Rg values for 2 M HNO₃ are not
as readily linked to a maximum uptake of water, metal or acid. Furthermore, the extraction of dysprosium, as for the data in Figure 2, at a total concentration of $10^{-4}$ M does not appear to be a significant contributor to the uptake of water or the size of the aggregates.

**X-ray absorption**

The X-ray scattering data suggested that aggregates are present but it was unclear what their role was in the metal extraction. To determine the coordination environment around the metal ion, X-ray absorption spectroscopy (XAS) measurements were carried out. The XAS data was used for both EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Spectroscopy).

**EXAFS**

The $k^2\chi(k)$ EXAFS data for the complexes formed by extraction from aqueous phase into an organic phase containing TBP, HDBP or a mix of both was collected. The corresponding FT (Fourier transforms) and fits are shown in Figure 3. The FT data of the organic phases show two peaks of physical significance: an intense peak at 1.8-1.95 Å attributed to the nearest O neighbour, and a medium peak at 3.3-3.45 Å attributed to the distant P atoms. Based on the appearance of the Ln-O and Ln-P interactions in the FT data, all of the Ln $k^2\chi(k)$ EXAFS for the organic phases were fit using a two shell (O and P) backscattering model, with the exception of the 1M TBP samples which showed no distant Ln-P interactions due to the low metal ion concentration in the organic phase.

![Figure 3: EXAFS data after Fourier transform and the fits. Data from the aqueous phase is included. Figure reproduced from data in [22].](image)

The results of the fit indicate that Dy and Lu are six-coordinate with O atoms with organic phases containing any concentration of HDBP, though Lu and Dy do show 8 coordinate with O atoms when extracted by 1M TBP alone from 2M HNO$_3$ and there is an apparent increase in the coordination number as the TBP concentration is increased to its final value of 8 at 1M TBP. A direct indication of the coordination number

**XANES**

A direct indication of the coordination number can be gained by XANES analysis of the X-ray absorption data. The intense L$_3$-edge peaks collected from the XAS experiment are characteristic of Ln(III). The responses across the TBP/HDBP organic systems are essentially equivalent which suggests that the Ln(III) coordination environment changes very little. The peaks in the normalised XANES data were fitted and peak centres and full-with-half-maximum (FWHM) were obtained for each dataset. It was
observed that the FWHM decrease with increasing TBP concentration which may be interpreted as a change in the coordination environment, also be seen with the EXAFS data, suggesting a change from 6 oxygen coordinated to 8 oxygen coordinated as TBP concentration increases.

Further investigation of the XANES region and further evidence of the coordination environments can be obtained by taking the second derivative of the L\(^3\)-edge peak. For the extraction from low nitric acid, there is evidence of two minima in the 2nd derivative of the L\(^3\)-edge peak for all conditions investigated. This double minima is evidence of crystal field splitting and also indicative of an octahedral geometry, namely a complex containing 6 ligands about a metal centre. For the high acid data, an evolution in the crystal field splitting is apparent in the 2nd derivative data as the concentration of TBP increases. This evolution lends some support to the coordination number changing from 6 to 8 in O as the concentration of TBP is increased. The second derivative data for lutetium at high acid at all TBP/HDBP conditions are shown in Figure 4.

**Figure 4: 2\(^{nd}\) derivative of the L3 edge peak for Dy extracted from 2 M HNO\(_3\).**

The y-axis is arbitrary units. Figure reproduced from data in \[22\].

**Thermodynamics of aggregate formation**

In order to gain insight in how aggregates may affect the extraction equilibria, and particularly the thermodynamics and temperature dependence of metal ion extraction reverse micelle formation was studied by isothermal titration calorimetry (ITC). Details of these experiments can be found in Jackson et al. 2014. \[23\] The goal of this study was to find any heat associated with the reverse micelles formed by a combination of TBP and HDBP, as suggested by the SAXS data. To benchmark our calorimetry method two experiments were carried out before any attempts were made on the TBP/HDBP system. The first test was on regular micelle formation using AOT in water. The calorimetric response was typical for aggregate formation and the CMC value obtained was on the same order as that reported in previous literature. However, the heat of reverse micelle formation using AOT in either octane or n-dodecane with different additions of water did not result in any sharp transition in heat generation. Separate experiments using tensiometry and viscometry suggested that reverse micelles should form under the conditions used. This suggested that the heat of reverse micelle formation is very small and/or that no well defined CMC exists for reverse micelles compared to that of regular micelles.

Extractions of dysprosium, similar to those described above, using combinations of TBP and HDBP were carried out at different temperatures. The extraction data is shown below in Figure 5 in the form of a Van’t Hoff plot where the natural logarithm of the distribution ratio is plotted versus the inverse temperature. The slopes of the straight lines fitted to the data are proportional to the enthalpy of the extraction reaction. It can be seen that the slopes using either pure HDBP (0:4 TBP:HDBP) or even just small additions of HDBP to TBP (3:1 TBP:HDBP) resulted in negative slopes that are fairly similar. Pure
TBP (4:0 TBP:HDBP) resulted in a positive slope. The results indicate that dysprosium extraction by pure TBP follows a different extraction mechanism than when combinations of TBP and HDBP or when pure HDBP is used. Furthermore, using combinations of the two reagents shows similar temperature dependence as when pure HDBP is used. This is directly in line with the EXAFS and XANES data suggesting that, for metal ions extracted from 0.2 M HNO₃, any addition of HDBP will cause HDBP to govern the extraction mechanism and the metal ion will be extracted as 6-coordinate by 3 HDBP dimers.

**Figure 5: Van’t Hoff plots for TBP:HDBP ratios.**

Dysprosium was extracted from 0.2 M HNO₃ using a total of 1M extracting reagent in n-dodecane.

**Figure reproduced from data in [23].**

Molecular dynamic simulations

Molecular dynamic simulation studies on systems of TBP/n-dodecane/H₂O/HNO₃ were carried out to investigate if aggregates of TBP would form in these simulations, as have been observed experimentally. Initial studies showed that TBP does indeed cluster during the simulations. However, it was observed that the organic solvent behaved erratic and that the intramolecular forces that govern these simulations were poorly presented by the default model. This has been observed by other research groups attempting similar simulations [24]. Current work has focused on improving the force-fields for these molecules to make the MD simulations produce data that can match more closely the chemical and physical properties of the pure substances before any attempts of high-level simulations are made.

Conclusions

Although previous studies of synergistic extraction of metal cations using combinations of neutral and acidic reagents explain the enhanced extraction by increased dehydration of the metal ion and the formation of mixed extractant complexes, our evidence for the increased water extraction coupled with the aggregate formation suggests a reverse micellar aspect to synergism in the system containing TBP and HDBP. The data from EXAFS, XANES and thermodynamic studies of the metal extraction point towards the existence of two different metal-ligand complexes. One formed with only HDBP when any amount, equal to or above 0.25 M HDBP is present. And one type of complex formed with TBP in systems where only TBP is present as the extracting reagent. The aggregates might not participate directly in the metal ion extraction, although it is quite possible that it strongly affects our system behaviour. This system where we combine an acidic and a neutral phosphoric extractant is commonly encountered in used nuclear fuel treatment and further insight into the extraction behaviour of the TBP-HDBP system with trivalent lanthanides will help us draw conclusions regarding other systems where multiple extraction reagents are used in combination to enhance extraction.
Acknowledgements

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References


Development of Separation Process for Minor Actinides Using TDdDGA and New Extractants

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Abstract

Separation process for minor actinides (MA = Am, Cm and Np) has been developed at Japan Atomic Energy Agency using new innovative extractants to improve the partitioning process from the viewpoints of the economy and the reduction of secondary wastes. Phosphorus-free compounds consisting of carbon, hydrogen, oxygen and nitrogen (CHON principle) were applied to the separation steps for MA. At the first step, MA and lanthanide elements (Ln) are recovered from high-level liquid waste by solvent extraction with N,N,N’,N’-tetradodecyldiglycolamide (TDdDGA). Trivalent actinides Am and Cm, are separated from RE at the next step by solvent extraction using podand type soft-donor extractant such as N,N,N’,N’-tetrakis(pyridin-2-ylmethyl)- decane-1,2-diamine (TPDN) or hybrid type extractant such as N-octyl-N-(p-tolyl)-1,10-phenanthroline-2-carboxamide (OctTolPTA). This paper presents the current status of the research and development programme. This study is carried out under the Innovative Nuclear Research and Development Programme by the Ministry of Education, Culture, Sports, Science and Technology of Japan.
Assessment of the Pyrochemical DOS Process for the Recovery of Actinides from Irradiated Oxide Fuels

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Abstract

Among the various techniques of reprocessing, pyrochemical separation technology using high-temperature molten salts and metal media presents a potential interest for an overall separation and transmutation strategy for long-lived radionuclides. The pyrochemical R&D programme, launched at the CEA Marcoule in the late 90s, aims at demonstrating the feasibility of an innovative grouped separation of actinides with sufficient decontamination of fission products. A reference process route based on two liquid/liquid extraction steps was developed for the reprocessing of oxide type fuels.

The first step consists in a selective reductive extraction of actinides in liquid aluminium from molten fluoride media. This reductive extraction involves a conversion of the oxide fuel species into fluorides prior to the liquid/liquid contact. This conversion was considered until now to be achieved by HF gas fluorination. The second step, so-called actinides back-extraction, consists in a liquid/liquid oxidative extraction of the Ans from aluminum matrix in molten chloride media. The core of this process was already extendedly studied within the last years and lead to an excellent selectivity of the reductive extraction regarding the actinides and a quasi quantitative back-extraction of the Ans in the chloride salt in a single batch.

The present work focuses on an optimisation of the head-end steps and the reductive liquid/liquid extraction. Taking advantage of the physico-chemical properties of fluoride salts, in particular its capability for direct oxides dissolution, the investigations lead to a major improvement of the head-end steps, preventing any use of HF gas for conversion of oxides into fluoride species prior to the reductive extraction. The important parameters, such as AlF₃ enrichment, Al₂O₃ activity in the salt, pO²…, and the feasibility of the reductive extraction from the direct dissolution of oxides into the fluoride melt could be determined by a bibliographic survey and thermodynamic approach. This theoretical approach was completed by experimental data acquisition on the behaviour of several simulated fission products and actinides oxides. Finally, an overall experiment was performed on an oxide mixture as a surrogate of irradiated oxide fuels pellets.
Quantitative Analysis of KF-LiF-ZrF$_4$ Molten Salt by Probe Assisted in-situ LIBS Systems


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e: SNU Nuclear Transmutation Energy Research Centre of Korea, Seoul National University, Republic of Korea

Abstract

Pyroprocessing draws attention as a recycling process of spent nuclear fuel for future nuclear reactor. In the aspect of process control and safeguards of the pyroprocessing, it requires a technology to measure the concentration of molten salt in real-time. The existing technologies measure the concentration by chemical analysis of sampled molten salt in the hot cell but it is disadvantageous in the aspects of cost, safety and time. The LIBS (Laser-Induced Breakdown Spectroscopy) is a form of atomic emission spectroscopy in which a pulsed laser is used as the excitation source. LIBS technology is appropriate to measure sensitive nuclear materials in hot cell because it is capable of measuring specimen quantitatively and qualitatively by exited atom by laser. Spectrum obtained from plasma is largely influenced by laser operation conditions and physical properties of specimens. Also, plasma induction is limited on the surface of specimen, so analysis of composition inside of the molten salt is extremely difficult. Thus, several restrictions should be overcome in order to apply LIBS for the measurement of molten salt (KF-LiF-ZrF$_4$) composition in real-time. In this study probe assisted LIBS system will be introduced with KF-LiF-ZrF$_4$ to quantitatively measure molten salt composition. Echelle spectrometer was used and the measurable wavelength area was 250-400 nm, the range of UV ray. NIST atomic spectra database measured the wavelength for molten salt composition, and each element was selected high signal intensity and wavelength range that is not overlapped by other elements.
Model Development for Pu-Mass Accountancy of Pyrometallurgical Processing with the Pu/Cm-244 Ratio Method

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Abstract

Measurement of Pu mass during operation of the pyrometallurgical processing by using the formula, \( \text{Pu mass} = (\text{Pu/Cm-244}) \times \text{Cm-244 mass} \), has been proposed. Among various errors, potentially significant error is anticipated with the ratio of Pu to Cm-244 because of heterogeneity in spent fuel. The aim of the present study is to establish a method to quantitatively evaluate the probability for Type-I error (false positive) to occur in the pyroprocessing system. The Type-I error probability is considered as the metric of the system performance regarding the safeguardability. Toward this objective, in the present paper, numerical recipes for deterministic depletion simulation of spent fuel are developed to obtain detailed spatial variability in spent fuel compositions. With the developed recipes, uncertainties associated with the spent fuel composition are quantitatively evaluated by a random-sampling approach. Probability density functions are assumed for uncertainties associated with fuel manufacturing parameters. Significant difference in uncertainties is observed for compositions depending on location on the fuel pin and on simulation configurations.

Background, scope and objective

Before starting commercial operation of a large-scale pyrometallurgical processing system for spent fuel management, reliable material accountancy must be established. However, highly corrosive molten salt used at high temperatures prohibits detectors from the accurate measurements of the material composition at the required frequency for timely detection of material diversion. Moreover, assay of the nuclear materials in metal or salt solution through destructive analysis (DA) or non-destructive analysis (NDA) can contain significant uncertainty due to the heterogeneity of the spent fuel and salt solution in a batch-wise process [1]. These difficulties induce less measurement accuracy and reliability, which potentially increases proliferation risk.

A method [2] has been suggested to indirectly measure plutonium (Pu) mass over the whole operation period of the pyrometallurgical processing system, which is based on the following equation:

\[
\text{Pu mass} = \frac{\text{Pu}}{\text{Cm-244}} \times (\text{Cm-244 mass})
\]

In this equation, neutrons from spent fuel materials are mostly generated by the spontaneous fission in Cm-244 and therefore the mass of Cm-244 is directly measurable by measuring neutron count rates at various points in the process [2]. The Pu/Cm-244 ratio, on the other hand, is considered to be indirectly determined by numerical evaluation with a fuel burnup code, for the materials that consist of a batch or a campaign before a series of processes is applied to that batch. Inaccuracy in this method occurs in each term of the right-hand side of Equation (1). For example, existence of minor neutron sources other than Cm-244, such as Pu-240 and Cm-246, affect the accuracy of the Cm-244 mass measurement [2]. Also, accuracy and precision of the Cm tracking is recognised as an important point for feasibility of the method.
Modification of the facility design to improve the material accountancy was suggested [5]. To measure the Cm-244 mass accurately and precisely, DUPIC Safeguards Neutron Counter (DSNC) was developed by the joint research between KAERI and LANL and authorised by IAEA [6]. Borrelli [7] analysed the magnitude of neutron fluxes by spontaneous fission neutron from Cm-244 in the fuel fabrication hot cell. Because the accuracy of the Pu to Cm-244 ratio is determined by fidelity of the depletion simulation model, depletion codes have been tested to check accuracy for various initial fuel enrichments, the neutron emission rate, and the cooling time [8].

The objective of the present study is to establish a method to quantitatively evaluate the probability for Type-I error (false positive) to occur in the pyroprocessing system. The Type-I error probability is considered as the metric of the system performance regarding the safeguardability.

To achieve this goal, the present study consists of multiple steps. Firstly, numerical recipes for deterministic evaluation of spent fuel compositions are developed. Numerical recipes should enable accurate numerical simulation, with which spent fuel compositions are obtained with detailed spatial variability in a fuel-pin as well as in a fuel assembly scale while taking various shuffling schemes into account. With the developed recipes for deterministic depletion simulation, in the following stage, uncertainties associated with the spent fuel composition are quantitatively evaluated by a random-sampling approach. Probability density functions are assumed for parameters with uncertainties. Uncertainties can occur due to (1) uncertainty associated with input data such as cross-section data, thermal hydraulic conditions, and as-built manufacturing uncertainties; (2) uncertainty in modelling due to incomplete knowledge and/or simplification for complex physical processes; and (3) numerical errors due to discretisation applied in a numerical solution [9].

Secondly, the overall uncertainty in Pu mass assay for the entire pyroprocess is quantitatively evaluated. For this purpose, a multi-compartment model has been established for the pyroprocessing system. A probability distribution function for the materials unaccounted for (MUF) is to be obtained by taking into account uncertainties associated with the spent fuel compositions obtained in the previous stage and those associated with system parameters included in the multi-compartment model.

The third step is to develop scenarios for material diversion, based on the observations obtained from the previous steps. For each of those scenarios, type-I error probability and its occurrence probability are evaluated as performance metric for the safeguardability of the pyroprocessing system.

In this paper, the steps included in the first stage are discussed.

**Deterministic simulation for fuel composition**

To begin with, Serpent, the continuous-energy Monte Carlo depletion computer code [10], has been benchmarked by comparing the results reported in [11,12]. Serpent showed better agreement with the measured values than other codes. The reason for this better performance by Serpent would be that while other codes such as MOCUP couple MCNP with ORIGEN2 by the explicit Euler method [13], the coupling scheme for Serpent is the predictor-corrector method [13]. The Euler method has drawbacks when actual values change significantly between the simulation time steps. Such situation is often observed at the beginning of burnup, because fission poison concentrations (e.g. Xe) would significantly change at the beginning of the reaction that would influence on the large change of nuclear reaction rates in the fuel. Better performance by Serpent could also result from difference in solution methods for the depletion calculation. ORIGEN (included in MOCUP) uses the matrix exponential method and assumes the short-lived nuclides decay instantly and secular equilibrium approximations [14]. The default method in Serpent for the depletion and transmutation simulation is Transmutation Trajectory Analysis (TTA) [15], which gives more accurate results than ORIGEN, although it takes longer computational time than ORIGEN. In addition, Serpent has various user-friendly features in terms of a geometrical modeling and the input of operating conditions, etc. Therefore, Serpent was chosen for the simulation code in this study.
To determine appropriate radial resolution, three different models have been compared. The single mesh giving sufficiently good agreement with 10-mesh results, one homogenised mesh was used in the radial direction in a fuel pin. To determine appropriate axial resolution, various mesh sizes ranging between 1 and 5 cm in the axial direction for the fuel pin-cell were tested. 5-cm length has been chosen as the upper bound because the rod-cut process in the head-end process of the pyroprocessing adopts this size [16]. 1-cm length has been chosen as the lower bound by considering a fuel pellet height. The best accuracy for the Pu-239 mass density was observed with a mesh size of 1cm. Therefore, the mesh size of 1cm for the top and bottom regions of the fuel was chosen.

For achieving depletion simulation with high fidelity, simulations must be performed at the assembly scale. The type of reactors and conditions for fuel assemblies were qualitatively considered. Some “extreme” cases were then identified to observe ranges of spent fuel compositions. In South Korea, 23 commercial nuclear reactors are currently operating [17], 19 of which are PWRs. Among 19 PWRs, eleven are Optimized Power Reactor (OPR)-1000. Therefore, OPR-1000 was chosen as the representative reactor for the present analysis. For the OPR-1000 reactor core, 14 different assembly types were identified as shown in Table 1.

### Table 1: Types of assemblies in OPR-1000 [19]

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<tr>
<th>Assembly type</th>
<th>Enrichment [w% 235U]</th>
<th>Burnup [MWd/kgU]</th>
<th># of fuel rods per assembly</th>
<th># of Gd poison rod per assembly</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
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<td></td>
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<td>37.1–39.7</td>
<td>184/52</td>
<td>–</td>
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<td>72</td>
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<td>176/52</td>
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<td></td>
<td></td>
<td>40</td>
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<td>184/52</td>
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<td>F1</td>
<td>4.50/4.01</td>
<td>18.4–22.4</td>
<td>176/52</td>
<td>8</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>F2</td>
<td>4.50/4.01</td>
<td>20.1–22.0</td>
<td>172/52</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>

Two assemblies were selected for detailed depletion simulation as follows. The low burnup assembly is of interest, because the difference between the middle, bottom, and top parts of the fuel pin is expected to become greater [18]. In other word, lower burnup cases show greater heterogeneity of nuclide composition in the axial direction. According to [19], the assembly type with the lowest burnup (11.6 MWd/kgU) is included in Type A0. In contrast, the highest burnup (52.1 MWd/kgU) is in the Type D2 assembly. Because sufficient information assembly was not available for the control rod in the D2, the second highest burnup assembly, D0 (51.2 MWd/kgU) was selected. From these two cases, “bracket” ranges of nuclide compositions that would be observed in the spent fuel from OPR-1000 were determined. For the depletion simulation, a quarter of an assembly was considered due to symmetry.

The mass densities of Pu and Cm-244 for a quarter of each assembly are plotted as a function of the normalised axial location in Figure 1. The red lines indicate the simulation result for the second highest burnup assembly (D0), while the results for the lowest burnup assembly (A0) are represented by the black lines. The flat regions in both figures have occurred because a single mesh is applied for the middle of the fuel region. Significant heterogeneity is observed in Pu and Cm-244 mass density profiles along the axial direction, in the end parts of the assembly.
Uncertainties in the Pu and Cm-244 mass densities due to manufacturing uncertainties

To observe effects of data uncertainty on the nuclide composition in spent fuel, a random-sampling approach was applied, in which numerous realisations are simulated by sampling parameter values based on probability density functions (PDF) for individual parameters with uncertainties. The results for individual realisations are statistically analysed to obtain a PDF for the quantities of interest, i.e., the Pu and Cm-244 mass densities, and the Pu/Cm-244 ratio in a fuel assembly. In this paper, uncertainties have been considered for the fuel pellet radius and the enrichment of uranium, both of which can be categorised as uncertainties that occur during manufacturing of nuclear fuel. Although the burnup simulation should be conducted at the assembly scale, in this paper, the pin-cell scale was adopted in order to save computation time and to make a scoping estimate for the importance of uncertainties of this kind. If it turns out to be important, the assembly scale will be adopted in the future.

The design parameters for a fuel pin-cell are shown in Table 2. These parameters are fixed in the random sampling. The burnup is set at 37.1 MWd/kgU during 4 cycles including burning times, cooling times and the boron concentration as shown in Table 3. Initial fuel and water composition are shown in Table 4. While the inlet and outlet water temperatures are not necessary in the two-dimensional fuel pin-cell simulation, the coolant water temperature is assumed as the average coolant temperature, given in Table 2, for the active fuel region for the three-dimensional simulation. The inlet and outlet temperatures are assumed as 268°C and 300°C, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data</th>
<th>Parameter</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of fuel pellet</td>
<td>UO₂</td>
<td>Fuel diameter [cm]</td>
<td>9,56E-01</td>
</tr>
<tr>
<td>Fuel density [g/cm³]</td>
<td>1,00E+01</td>
<td>Active fuel length [cm]</td>
<td>3,47E+02</td>
</tr>
<tr>
<td>Rod pitch [cm]</td>
<td>1,56E+00</td>
<td>Clad material</td>
<td>Zircaloy-2</td>
</tr>
<tr>
<td>Outer diameter of rod [cm]</td>
<td>1,12E+00</td>
<td>Water temperature [K]</td>
<td>5,58E+02</td>
</tr>
<tr>
<td>Inner diameter of rod [cm]</td>
<td>9,86E-01</td>
<td>Water density [g/cm³]</td>
<td>7,57E-01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating cycle</th>
<th>Specific power [kW/kgU]</th>
<th>Burntime [days]</th>
<th>Downtime [days]</th>
<th>Boron concentration [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,47E+01</td>
<td>3,06E+02</td>
<td>7,10E+01</td>
<td>3,31E+02</td>
</tr>
<tr>
<td>2</td>
<td>2,68E+01</td>
<td>3,82E+02</td>
<td>8,31E+01</td>
<td>4,70E+02</td>
</tr>
<tr>
<td>3</td>
<td>2,28E+01</td>
<td>4,66E+02</td>
<td>8,50E+01</td>
<td>5,04E+02</td>
</tr>
<tr>
<td>4</td>
<td>1,89E+01</td>
<td>4,61E+02</td>
<td>1,87E+03</td>
<td>4,93E+02</td>
</tr>
</tbody>
</table>
Table 4: Initial fuel and coolant water composition and number density [21]

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Number Density [atoms/b-cm]</th>
<th>Nuclide</th>
<th>Number Density [atoms/b-cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U</td>
<td>6.15E-06</td>
<td>$^{14}$N</td>
<td>1.04E-05</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>6.89E-04</td>
<td>$^{16}$O</td>
<td>4.48E-02</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>3.16E-06</td>
<td>$^1$H</td>
<td>5.06E-02</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>2.17E-02</td>
<td>$^{16}$O</td>
<td>2.53E-02</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>9.13E-06</td>
<td>$^{10}$B</td>
<td>2.76E-06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{11}$B</td>
<td>1.12E-05</td>
</tr>
</tbody>
</table>

Due to the fact that the manufacturing uncertainties for the OPR-1000 assembly are not available in open literature, the uncertainty information for Three Mile Island (TMI) Unit-I has been used instead [9]. The uncertainties of fuel pellet radius and fuel enrichment applied in this study were set as shown in Table 5 based on the TMI-I data [9,20]. The normal distribution is assumed for each parameter uncertainty [9] based on the mean and the standard deviation. The random sampling has been done by the MATLAB software to develop the data set for 200 realisations.

Table 5: Manufacturing uncertainties for the fuel pin-cell simulation

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel pellet radius [cm]</td>
<td>4.78E-01</td>
<td>2.20E-03</td>
</tr>
<tr>
<td>Fuel enrichment [U-235 w/o]</td>
<td>3.08E+00</td>
<td>5.00E-04</td>
</tr>
</tbody>
</table>

The mean of Pu and Cm-244 mass densities of 200 realisations are summarised in Table 6. The probability density functions for the Pu and Cm-244 mass densities and the ratio of Pu to Cm-244 by the fuel pellet radius uncertainty are shown in Figure 2. As a representative figure, the only figures plotted by taking into account the pellet radius uncertainty are involved in this paper. There are 12 figures drawn depending on the location and the dimension. Three different locations in the three-dimensional fuel pin-cell are selected. The mass densities of Cm-244 and Pu are greater in the middle of fuel than at the top and bottom of fuel. This is due to a greater burnup generating more Pu and Cm-244 in the middle than in other part of the fuel rod. The relative standard deviations of Pu mass density range from 1.41% to 3.51% for the three-dimensional fuel pin-cell, taking into account different manufacturing uncertainties. The highest value is observed at the top of fuel rod, when the fuel enrichment and pellet radius uncertainties are considered together. The lowest value is found at the middle of fuel rod with just the fuel enrichment uncertainty. Generally, the relative standard deviation of Pu and Cm-244 mass densities at the middle of fuel is smaller than at the top and bottom of the fuel, due to a larger statistical uncertainty of Serpent at the top and bottom of fuel. In the case of two-dimensional simulations, the relative standard deviation is between 5.18E-2 % and 4.09E-1 %. The absolute values of two-dimensional simulation are much smaller than the results from the three-dimensional simulation. The reason would be also due to the low statistical uncertainty of Serpent in the two-dimensional simulation.
Figure 2: PDFs for the Pu and Cm-244 mass densities and the Pu/Cm-244 ratio in the two- and three-dimensions by the fuel pellet radius uncertainty

(a) Pu at the top  (b) Cm-244 at the top  (c) Pu/Cm244 at the top

(d) Pu at the middle  (e) Cm-244 at the middle  (f) Pu/Cm244 at the middle

(g) Pu at the bottom  (h) Cm-244 at the bottom  (i) Pu/Cm-244 at the bottom

(j) Pu in the 2D  (k) Cm-244 in the 2D  (l) Pu/Cm-244 in the 2D
Table 6: Statistical summary for the Pu to Cm-244 mass density by the difference uncertainty sources

<table>
<thead>
<tr>
<th>Uncertainty sources</th>
<th>Cm-244</th>
<th>Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>[g/cm³]</td>
<td>[g/cm³]</td>
</tr>
<tr>
<td>Fuel enrichment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>1.58E-05</td>
<td>5.64E-06</td>
</tr>
<tr>
<td>Middle</td>
<td>1.06E-03</td>
<td>1.29E-04</td>
</tr>
<tr>
<td>Bottom</td>
<td>1.60E-05</td>
<td>5.62E-06</td>
</tr>
<tr>
<td>2D</td>
<td>3.70E-04</td>
<td>1.12E-06</td>
</tr>
<tr>
<td>Fuel pellet radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>1.61E-05</td>
<td>5.19E-06</td>
</tr>
<tr>
<td>Middle</td>
<td>1.08E-03</td>
<td>1.61E-04</td>
</tr>
<tr>
<td>Bottom</td>
<td>1.54E-05</td>
<td>5.16E-06</td>
</tr>
<tr>
<td>2D</td>
<td>3.71E-04</td>
<td>3.18E-06</td>
</tr>
<tr>
<td>Enrichment +Pellet radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>1.66E-05</td>
<td>5.13E-06</td>
</tr>
<tr>
<td>Middle</td>
<td>1.09E-03</td>
<td>1.56E-04</td>
</tr>
<tr>
<td>Bottom</td>
<td>1.57E-05</td>
<td>5.05E-06</td>
</tr>
<tr>
<td>2D</td>
<td>3.71E-04</td>
<td>2.03E-06</td>
</tr>
</tbody>
</table>

Note: ‘Top’ is the location between 346.2 and 347.2 cm high from the bottom of the fuel rod. “Middle” is from 173.1 to 174.1 cm high, and ‘Bottom’ is between 0 and 1 cm. “2D” means results for the two-dimensional fuel pin-cell simulation. “SD” and “RSD” stand for the standard deviation and the relative standard deviation, respectively.

A similar tendency is observed for the Cm-244 mass density; however the magnitude of relative standard deviation is around 10 times greater than the Pu mass density. Cm-244 is generated after several stages of the decay chain from U-238. The uncertainties of Cm-244 mass density through decay chains would be propagated to the final amount. However, Pu-239, which is the dominant isotope in determination of total Pu amount, is mostly generated by the neutron absorption of U-238 and loosed by the fission and absorption reaction. The uncertainty propagation of Pu through the decay chains would be smaller than Cm-244. The effect of fuel pellet radius uncertainty is greater than the fuel enrichment uncertainty by the comparison of two-dimensional results. This can be explained by the fact that the uncertainty of fuel enrichment is smaller than the uncertainty of fuel pellet radius as shown in Table 5.

Table 7 shows the Pu to Cm-244 ratio in two different ways. First, the ratio was calculated for each individual realisation by using the results for Pu and Cm-244 mass densities. Using the 200 ratios, the mean value and standard deviation of the ratio have been obtained (columns 3 to 5). In the other way, the mean and standard deviation of Pu and Cm-244 mass densities shown in Table 6 are substituted into Equation (2) to calculate the mean and standard deviation of the ratio.

The relative standard deviation by the second way is greater than by the first at the middle of fuel, while the smaller values are observed at the top and bottom of fuel. The mean value of the ratios at the middle of fuel is two orders of magnitude different from the ratios at the top and bottom of fuel. The second way would be similar to procedures that would be taken in normal operations, in which materials in an assembly are mixed in one campaign of pyroprocessing, but the results shown in Table 7 indicate that depending on the size of a batch for processing the uncertainty associated with the ratio can be significantly different, which could potentially be a loophole that might lead to material diversion.
Table 7: Statistical summary for the Pu to Cm-244 ratio by the difference uncertainty sources

<table>
<thead>
<tr>
<th>Uncertainty sources</th>
<th>Pu/Cm244 by 200 realisations</th>
<th>Pu/Cm244 by the error propagation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>Fuel enrichmen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>3.38E+03</td>
<td>1.24E+03</td>
</tr>
<tr>
<td>Middle</td>
<td>8.66E+01</td>
<td>8.88E+00</td>
</tr>
<tr>
<td>Bottom</td>
<td>3.33E+03</td>
<td>1.21E+03</td>
</tr>
<tr>
<td>2D</td>
<td>2.22E+02</td>
<td>6.81E-01</td>
</tr>
<tr>
<td>Fuel pellet radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>3.26E+03</td>
<td>1.12E+03</td>
</tr>
<tr>
<td>Middle</td>
<td>8.54E+01</td>
<td>1.03E+01</td>
</tr>
<tr>
<td>Bottom</td>
<td>3.44E+03</td>
<td>1.22E+03</td>
</tr>
<tr>
<td>2D</td>
<td>2.21E+02</td>
<td>9.49E-01</td>
</tr>
<tr>
<td>Enrichment + Pellet radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top</td>
<td>3.15E+03</td>
<td>1.06E+03</td>
</tr>
<tr>
<td>Middle</td>
<td>8.44E+01</td>
<td>1.00E+01</td>
</tr>
<tr>
<td>Bottom</td>
<td>3.30E+03</td>
<td>1.07E+03</td>
</tr>
<tr>
<td>2D</td>
<td>2.22E+02</td>
<td>1.38E+00</td>
</tr>
</tbody>
</table>

\[
\text{Mean of ratio} = \frac{\text{Mean of Pu}}{\text{Mean of Cm-244}}
\]

\[
\text{SD of ratio} = \text{Mean of ratio} \times \sqrt{\left(\text{RSD of Pu}\right)^2 + \left(\text{RSD of Cm-244}\right)^2}
\]

**Conclusion**

First, numerical recipes for deterministic depletion simulation have been established with the Serpent code. With the developed recipes, irradiated fuel compositions of two bounding cases among fuel assemblies in OPR-1000 have been calculated. The results confirm that there is substantial difference in compositions among fuel assemblies in a reactor core and in locations within a fuel pin.

Uncertainties associated with the Pu and Cm-244 mass densities and its ratios have been quantitatively evaluated for manufacturing uncertainties by the random sampling method. The results indicate that there are significant differences in uncertainties associated with the Pu and Cm-244 mass densities and its ratios, depending not only on simulation configurations, such as the two- and three-dimensional fuel pin-cell simulations, but also on locations along the fuel pin. For example, the results for two-dimensional simulation show that the effect of manufacturing uncertainties on the uncertainties of Pu and Cm-244 mass density prediction in spent fuel would be negligible, whereas it would not be a negligible level in the three-dimensions. This suggests that three-dimensional depletion simulation is necessary to obtain correct uncertainty information for spent fuel compositions.

In order to provide a more robust and reliable discussion for the effects of manufacturing uncertainties, further studies are suggested:

- In the present study, only 200 realisations have been made for random sampling. The number of realisations should be increased or better method for sampling should be adopted, such as Latin Hypercube sampling for better statistical results.
- The statistical uncertainty of the Serpent simulation could be decreased by increasing neutron histories, but this requires longer running times.
- Other manufacturing parameters, such as the cladding radius and the fuel density, could be added for consideration.
- An assembly scale analysis should be performed for uncertainties, and compared with the pin-scale results.
NEA/NSC/R(2015)2

Acknowledgements

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References


Salt Separation from Uranium Deposits by Multilayer Porous Crucibles

S.W. Kwon*, K.M. Park, J.G. Kim, I.T. Kim and S.B. Park
Korea Atomic Energy Research Institute, Republic of Korea

Abstract

Pyroprocessing has been developed for the recovery of actinide elements from spent fuel due to its advantages of compactness, proliferation resistance, and reduction of a secondary waste generation. The solid cathode processing is necessary to separate the salt from the cathode, for the preparation of the uranium ingot with a high purity. An increase of the throughput of the salt removal process from uranium deposits, generated on the solid cathode of the electrorefiner in the pyroprocess [1-2] is necessary. In this study, an attempt to enlarge a throughput of the salt distiller with multilayer porous crucibles for the separation of the adhered salt in the uranium deposits generated from the electrorefiner was carried out. The feasibility of the porous crucibles was tested by the salt separation experiments. A two-step weight reduction was observed in the porous crucible. However, the salt weight only decreased at high temperature by distillation in a non porous crucible. The first weight reduction was caused by the liquid salt penetration through the perforated crucible during the temperature elevation until the distillation temperature. The salt weight reduction started at about 450°C. After the liquid salt flew out through the perforated crucible by gravity, the weight was kept constant up to the salt evaporation temperature. The second weight reduction started at about 650°C. Besides the porous crucible, the concept of multiple crucibles (multilayer) was also proposed. Multilayer crucibles have a benefit to expand the evaporation surface area. It could be concluded that the multilayer porous crucible system is an effective way for the achievement of a high throughput performance in the salt separation process because the liquid salt of the uranium deposits can be separated during temperature elevation for the distillation and high surface area for salt evaporation.

References

Session 6:
Transmutation Fuels And Targets

Chairs: N. Chauvin (France) and J.R. Kennedy (United States)
Abstract

In the field of minor actinide transmutation in future Generation IV SFR reactor, CEA investigates in priority the recycling of Americium (Am) in the radial blankets located in the outer core area (AmBB: Americium Bearing Blankets).

This paper gives an overview of the recent outcomes of the R&D programme carried out at CEA in the different fields of research: from powder elaboration to experimental irradiation.

Concerning the powder elaboration, several batches have been produced by the oxalic co-conversion route as well as by the Calcined Resin Microsphere Pelletisation. Different tests have been then performed for the fabrication of pellets according to the current specifications of AmBB.

For these two processes, different additional developments of innovative technologies have been achieved well adapted with the processes constraints and hot cell operating.

Information on irradiation programmes (MARIOS in HFR and ongoing DIAMINO in Osiris) are presented.

The next steps of the programme will then be tackled.

Introduction

In the framework of GEN-IV, the use of U-MA (minor actinides) mixed oxides as fuels for transmutation is a promising route to recycle these elements. Two different modes are envisaged, namely homogeneous and heterogeneous [1]. For heterogeneous transmutation, dedicated assemblies located at the core periphery would be used, including fuels composed of depleted uranium and a larger amount of MA (up to 20 at.% of the actinides). The CEA has focused its research efforts on the second transmutation mode for americium alone because of its relative abundance and high radiotoxicity and with the objective of defining simple and robust processes and technologies to fabricate AmBB\(^1\) pins in the prospect of transmutation experiments in ASTRID.\(^2\) This R&D programme covers numerous fields as for example: processes for the conversion of actinide solution as well as pellets fabrication processes including comprehensive studies, technological development of innovative technologies for hot cell operating at different scales, modelling and simulation of the fuel under irradiation, experimental irradiations and associated characterisations in order to validate the fuel design and to gather experimental feedback. Some of recent outstanding developments are presented hereafter.

Conversion and pellets fabrication

2. ASTRID: Advanced Sodium Technological Reactor for Industrial Demonstration.
Different processes for the fabrication of $\text{U}_{1-x}\text{Am}_x\text{O}_{2+\delta}$ fuels are studied and still under development in order to respect the fuel specifications but also to define simplified routes well adapted for hot cell operating and scale-up. Therefore our research effort recently focused on the use of a solid solution of co-converted mixed oxide powder (from oxalate co-converted powder and spherical co-converted particles on ion exchange resins (WAR)) allowing the reduction of the fabrication steps and a better control of the contamination. The different processes under development are presented schematically below in Figure 4.

Figure 1: Flowchart of the processes for the AmBB fabrication

Conversion

For the heterogeneous mode and the fabrication of mixed oxides for AmBB, research has focused on co-conversion of $(\text{U,Am})\text{O}_2$ following the EXAm enhanced separation process [2,3] by two processes: oxalate co-precipitation and co-immobilisation on ion exchange resins.

In 2012, the oxalate co-precipitation process feasibility at laboratory scale was demonstrated thanks to the production of two 15 g batches of co-converted $(\text{U,Am})\text{O}_2$ and $(U_{0.85}\text{Am}_{0.15})\text{O}_2$ [4]. Oxalate co-precipitation was performed in a vortex reactor by remote operation in shielded cells (Figure 2).

---

3. Weak Acid Resin.
After filtration and drying the precipitate was calcined and the resulting oxide powder analysis revealed a fluorite-structured solid solution without any additional phases. SEM analysis have been performed and showed a powder composed of porous soft agglomerates of several hundred micrometers made of submicronic particles (Figure 3).

Figure 3: SEM micrograph of (U₀.₉,Am₀.₁)O₂ powder

In 2013, a significant batch of 6 g has been produced with the WAR conversion process [5,6]. The WAR conversion process is based on the fixation of U(VI) and Am(III) cations into beads of carboxylic ion exchange resin. The loaded resin microspheres are then heated in air up to 800°C to remove the organic materials and supply the metallic oxides in the form of microsphere. An ultimate reduction step is then necessary to form the solid-solution and to adjust the oxygen stoichiometry of the uranium-americium mixed oxide to a value close to 2. Those different steps are summarised in Figure 4.

Figure 4: Principle of the WAR process

Different characterisations (TIMS, XRD) displayed: a final concentration of Am same as the one in solution, a fluorite-structured solid solution. Morphological analysis revealed a good sphericity and a medium diameter of 300 μm. A density of 24 ±1% was measured indicating an important porosity well adapted for the pressing step (Figure 5).
The first of these processes has the advantages of robustness, reliability, and flexibility, but requires further R&D to control the co-precipitated powder morphology to limit dispersion and allow direct press compaction. The second is intrinsically capable of producing microspheres (or spherical particles) that are directly pelletised with minimal dispersal and excellent flowability, but requires significant R&D to control the synthesis conditions.

**Pellets fabrication**

The first process based on reactive sintering, which consists into mixing two (or more) different oxides before a thermal treatment, was used to produce the dense samples for MARIOS [7]. But in the case of U-Am mixed oxides, such a process only leads to limited densities that barely reach 93%TD (of the theoretical density) [8]. This limitation is due to the principle of a reactive sintering, during which the solid solution formation and the densification have to occur during a single thermal treatment. A competition thus occurs between these two phenomena, which limits the densification: as long as the solid solution is not formed, the densification cannot be complete.

To overcome these limitations, a new process, called UMACS (Uranium-Minor Actinide Conventional Sintering) was developed and used for the fabrication of the samples for DIAMINO irradiation [9,10]. Firstly, a solid state route is employed to synthesise a solid solution: a homogeneous powder is obtained, pelletised and heat treated to favour the formation of the intended $U_{1-x}Am_xO_{2+\delta}$ oxide solid solution. Secondly, a $U_{1-x}Am_xO_{2+\delta}$ powder is produced from those heat-treated pellets by the use of a grinding step. The resulting powder is then again pressed to form pellets, which are sintered during a dedicated cycle at high temperature in controlled atmosphere. At this stage, the americium is already combined with the uranium in a solid solution, which considerably reduces the risk of sublimation.

In 2013, first experiments have been performed for the fabrication of pellets, using the batch of $U_{0.85}Am_{0.15}O_{2+\delta}$ powder synthesised by oxalic co-precipitation, to evaluate the simplified route. The characterisation of the precursor was firstly carried out especially by TIMS to verify the americium concentration (15.8% ± 0.3%). Then a dilatometric study was performed in order to fix the optimal conditions for densification. Two heat treatments were then completed on green pellets pressed at 450 MPa during 5 hours at 1 873 and 1 923 K under Ar/H\textsubscript{2} atmosphere. Obtained densities ranged from 94.7 ± 0.5%TD to 95.7% ± 0.5%TD. Visual inspection of the pellets shown in Figure 2 did not display any macroscopic defects (cracks, shape modification, etc.). The pellet morphology observed by MEB-FEG showed a very dense homogeneous microstructure with only a residual submicronic porosity. The final concentration of americium measured was 15.6 ± 0.3 % proving the lack of americium sublimation during the heat treatment.
More recently pellets fabrication tests have been carried out using $U_{0.9}Am_{0.1}O_{2+x}$ microspheres as precursor produced by the WAR process described above. The same abovementioned method was used allowing the fabrication with CRMP$^3$ process [11,12] of homogeneous and dense pellets (94.9 ± 0.5 % DT) with no structural defects. Final characterisation indicated no loss of americium.

**Conclusion**

These first very promising tests at laboratory scale for simplified route allowed the fabrication of dense pellets with homogeneous microstructure and composition and no defects even with non-optimised sintering conditions. Future studies, to further understand the correlation between the solid solution formation and final sintering, will be carried out to optimise the different steps of the process.

**Technological developments**

Different developments of innovative technologies are carried out in order to improve the fabrication processes performance and also to allow an increase in the production rate. All these developments take of course into account from the beginning the specific constraints of hot cell operating. For example, the improvement of the filtration step performance of the co-precipitated oxalate led us to develop with FLOWERSEP a new filtration technology called LAMINARFLOW (Figure 8). The basic principle is a centrifugal separation with laminar flux thanks to different parts turning at different speeds. This prototype will also provide a continuous draining system of the filtered precipitate. The objective is to have a validated prototype for glove box operating at the end of 2017.
For pellet fabrication currently manually shaped, collaboration has been set up between the CEA and CHAMPALLEALCEN for the definition of an innovative automatic press completely nuclearised [13]. The design has been first controlled thanks to a 3D simulation in order to validate the press assembly, operating, maintenance and dismantling with slave manipulators (Figure 9) before manufacturing.

Main characteristics are: compactness with a maximum height of 1200 mm, 10 tons capacity, electromechanical that is to say oil free and a production rate of 1 to 5 pellets per minute (Figure 10). The first tests in a hot cell mockup will be carried out before the end of 2014 and firstly on surrogates.

Experimental irradiations

The heterogeneous fuel qualification procedure includes four phases as illustrated in Figure 11. The selection phase determines the fuel specification requirements. The concept validation phase involves
analytic or semi-integral irradiation experiments on an individual pellet or cladding segment. Integral experiments on full-scale pins or capsules are performed during the prototype validation phase. The final industrial qualification phase is carried out on a complete assembly.

**Figure 11: qualification phases for heterogeneous fuel concept**

The concept validation phase is currently underway through the MARIOS\(^5\) \([14,15]\), under Post Irradiation Examinations, and ongoing DIAMINO \([16]\) irradiation. The main goal of these experiments is to investigate gaseous release and swelling of Am-bearing UO\(_{2-x}\) fuels as a function of temperature, fuel microstructure and gas production rate. A small pin has been fabricated for each experimental configuration (corresponding to 1 temperature × 1 microstructure × 1 helium production rate). Finally, four and six small pins were irradiated or are under irradiation as part of the MARIOS and DIAMINO experiments, respectively (Table 1). Samples with 15% of \(^{241}\)Am were or are irradiated for about one year in the HFR and the OSIRIS reactor, corresponding to about 300 and 200 EFPD respectively. Samples with 7.5% or \(^{241}\)Am will be irradiated for about twice this duration, i.e. about two years.

**Table 1: MARIOS and DIAMINO irradiation characteristics**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Targeted temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600</td>
</tr>
<tr>
<td><strong>Am(_{BB}) (15% Am)</strong></td>
<td></td>
</tr>
<tr>
<td>Standard microstructure</td>
<td>DIAMINO</td>
</tr>
<tr>
<td><strong>Am(_{BB}) (7.5% Am)</strong></td>
<td></td>
</tr>
<tr>
<td>Standard microstructure</td>
<td></td>
</tr>
<tr>
<td>Optmized microstructure</td>
<td></td>
</tr>
</tbody>
</table>

The next step will tackle semi-integral irradiation first with MARINE\(^6\) (under preparation) \([15,17]\) expected to start in 2015 in HFR. MARINE (stands for “MA heterogeneous Recycle semi-Integral Experiment”) will provide a comparison between sphere-packed and pelletised (\(U_{0.85,Am_{0.15}}\)O\(_2\)) fuel performances at 1 000°C during around 350 EFPD, in two instrumented (on-line pressure measurement) small pins. In the scope of the bilateral collaboration between DOE and CEA, a second irradiation is under discussion and definition to be performed in ATR. This irradiation will provide information on the behaviour of oxide and metal fuels. Around 6 mini-pins could be irradiated at 800°C and 1 000°C during 700 EFPD. Especially two mini-roadlets could be made of (\(U_{0.85,Am_{0.15}}\)O\(_2\)) pellets from oxalic co-converted powder, one with \(^{243}\)Am and \(^{241}\)Am coming from reprocessing of spent fuel via ExAm and one with \(^{241}\)Am. Two others could be made of (\(U_{0.85,Am_{0.15}}\)O\(_2\)) pellets synthetised with the CRMP process described above.

PIE results for MARIOS, DIAMINO and MARINE are expected around 2018.

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5. In the framework of the European program FAIRFUELS AND PELGRIMM projects.
6. In the framework of the European program: PELGRIMM project.
Beside AmBB experimental irradiations, several irradiations completed on IMF (Inert Matrix Fuel), described in Table 2, from PHENIX reactor are available for PIE and proposed for international collaboration (pins are provided by CEA for PI examinations and the results will be shared).

**Table 2: Irradiations characteristics proposed for international collaboration**

<table>
<thead>
<tr>
<th>Inert Matrix Fuels for Am transmutation</th>
<th>COCHIX</th>
<th>CAMIX</th>
<th>ECRIX B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>2 pins</td>
<td>1 pin</td>
<td>1 pin</td>
</tr>
<tr>
<td>Micro and macro-dispersed in MgO</td>
<td>(Am₀.₀₉₁Zr₀.₆₆₂Y₀.₃₃₈)O₂₋ₓ</td>
<td>solid solution (Am₀.₀₆₂Zr₀.₇₈₂Y₀.₉₆₈)O₂₋ₓ</td>
<td>CERCE AmO₁.₆₂ micro-dispersed in MgO</td>
</tr>
<tr>
<td>Irradiation length</td>
<td>178 EFDP</td>
<td>234 EFDP</td>
<td>508 EFDP</td>
</tr>
<tr>
<td>Fission rate</td>
<td>18.5 at%</td>
<td>23 at%</td>
<td>30 at%</td>
</tr>
</tbody>
</table>

**Conclusion**

In the framework of actinides transmutation at CEA, significant results have been achieved for conversion and fabrication at laboratory scale, a comprehensive database for MABB will be available in 2020, thanks to ongoing analytical and future semi-integral irradiations. The decision to go further in the demonstration of AmBB transmutation could be taken at this date: i.e. prototypic experiments in ASTRID sodium fast reactor in 2025.

**References**


Thermal and Mechanical Properties of UO₂ and PuO₂

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\textsuperscript{b}: Kyushu University, Japan

Abstract

It is important to evaluate basic properties of UO₂ and PuO₂ as fundamental aspects of MA-bearing MOX fuel development. In this work, mechanical properties of UO₂ and PuO₂ were investigated by an ultrasound pulse-echo method. Longitudinal and transversal wave velocities were measured in UO₂ and PuO₂ pellets, and Young’s modulus and shear modulus were evaluated, which were 219 MPa and 89 MPa for PuO₂, and 249 MPa and 95 MPa for UO₂ respectively. Poisson’s ratio was 0.32 in both materials. The relationship between mechanical and thermal properties was described by using thermal expansion data which had been reported previously, and the heat capacity and thermal conductivity were analysed.

Introduction

The Cabinet of Japan decided on 11 April 2014 to approve the new Strategic Energy Plan as the basis for the orientation of Japan’s new energy policy. The plan describes that Government of Japan will promote technology development on volume reduction and mitigation of degree of harmfulness of radioactive waste, including nuclear transmutation technology using fast reactors and accelerators [1]. A new project started with the aim to reduce minor actinide (MA) elements in high-level radioactive waste, which is being advanced by using fast reactors and accelerator-driven systems [2]. Within this project, MA-bearing MOX fuels and (Pu,Am)O₂-bearing inert matrix fuels need to be developed.

It is essential to evaluate basic properties of UO₂ and PuO₂ which are base fuel materials as fundamental aspects of MA-bearing fuel development. Especially, heat capacity and thermal conductivity of UO₂ and PuO₂ are important data to analyse dependence of thermal behaviours on the material composition. However, data on PuO₂ are limited, and it is difficult to understand the mechanism of temperature dependence of their properties. It was reported that heat capacity of PuO₂ is about 5 J/mol K higher than that of UO₂ in the temperature range of 800-1 500 K [3]. Regarding thermal conductivity of PuO₂, both lower and higher data have been reported as compared with UO₂ [4-7]. The reasons for these differences are unknown. In this work, mechanical properties of UO₂ and PuO₂ were investigated by an ultrasound pulse-echo method. Bulk modulus \( K \), Debye temperature \( T_D \) and the Grüneisen constant were estimated from the experimental data, and heat capacity and thermal conductivity of UO₂ and PuO₂ were analysed.

Experimental

Powders of UO₂ and (U₀.₉₇Pu₀.₀₃)O₂ were pressed and sintered into cylindrical pellets. Sintering of pellets was carried out at 1 923 K in an atmosphere of Ar/H₂ mixed gas with added moisture. They were 5.5-6.0 mm in diameter and 4.3-7.2 mm long. The sintered pellets were analysed by X-ray diffraction. Lattice parameters, density and porosity are shown in Table 1. Sound velocities of longitudinal and transverse waves in the sintered pellets were measured with an ultrasound pulse-echo instrument (KJTD
Co., Ltd., model HIS-3). The sound velocity in a CeO₂ pellet was measured as a standard before and after the UO₂ and PuO₂ pellet measurements.

### Table 1: Pellet specimens and their properties

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Lattice parameter (nm)</th>
<th>Density (g/cm³)</th>
<th>Theoretical density (%)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>0.5471</td>
<td>10.36</td>
<td>94.61</td>
<td>0.054</td>
</tr>
<tr>
<td>(Pu₀.₉₇Am₀.₀₃)O₂</td>
<td>0.5398</td>
<td>10.77</td>
<td>93.83</td>
<td>0.062</td>
</tr>
</tbody>
</table>

### Results and discussion

#### Mechanical properties and Debye temperature

Sound velocities of waves in UO₂ and (Pu₀.₉₇Am₀.₀₃)O₂ pellets were measured at room temperature, and the measured data were normalised to the full density (100%TD). The shear modulus \( G \), Young’s modulus \( E \), bulk modulus \( K \) and Poisson’s ratio \( \nu \) can be calculated by:

\[
\begin{align*}
G &= \rho V_l^2 \\
E &= G[(3V_t^2 - 4V_l^2)/(V_l^2 - 4V_t^2)] \\
K &= \rho(3V_t^2 - 4V_l^2)/3 \\
\nu &= (V_t^2 - 2V_l^2)/(V_l^2 - V_t^2)/2
\end{align*}
\]

where \( \rho \) is the density of the specimen, \( V_l \) is the longitudinal wave velocity and \( V_t \) is the transverse wave velocity. The calculated data are shown in Table 2. The \( G \), \( E \) and \( K \) of (Pu₀.₉₇Am₀.₀₃)O₂ were greater than those of UO₂. Other data are also shown for comparison [8-11] in the table. The reported data of UO₂ [8,9] were consistent with the current data. The data of PuO₂ reported by Nakamura et al. [11] were in good agreement with those of (Pu₀.₉₇Am₀.₀₃)O₂. The thermal properties in Sections 3.2 and 3.3 were analysed assuming that the data of (Pu₀.₉₇Am₀.₀₃)O₂ equalled those of PuO₂.

### Table 2: Mechanical properties

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( G ) (GPa)</th>
<th>( E ) (GPa)</th>
<th>( K ) (GPa)</th>
<th>( \nu ) (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂ (This work)</td>
<td>83.1</td>
<td>219.3</td>
<td>202.1</td>
<td>0.319</td>
</tr>
<tr>
<td>(Pu₀.₉₇Am₀.₀₃)O₂ (This work)</td>
<td>94.7</td>
<td>249.3</td>
<td>226.7</td>
<td>0.317</td>
</tr>
<tr>
<td>UO₂ [8]</td>
<td>82.0</td>
<td>220.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UO₂ [9]*</td>
<td>81.4</td>
<td>217</td>
<td>–</td>
<td>0.31</td>
</tr>
<tr>
<td>PuO₂ [10] *</td>
<td>–</td>
<td>268</td>
<td>–</td>
<td>0.28</td>
</tr>
<tr>
<td>PuO₂ [11]*</td>
<td>93</td>
<td>247</td>
<td>–</td>
<td>0.322</td>
</tr>
</tbody>
</table>

*: Calculation

#### Heat capacity evaluation

Heat capacity at constant volume \( C_v \) was evaluated by the Debye model. Debye temperature \( T_D \) can be written by:

\[
T_D = (h/k_B)(9N/4\pi a^3)^{1/3}(1/V_l^3 + 2/V_t^3)^{-1/3}
\]

where \( h \) is the Planck constant, \( k_B \) is the Boltzman constant, \( N \) is the number of atoms in the unit cell, and \( a \) is the lattice constant. The Debye temperatures \( T_D \) of UO₂ and (Pu,Am)O₂ were estimated to be 384 K and 406 K, respectively. The \( C_v \) was obtained from \( T_D \) by Equation 6:
\[ C_v = 9nR \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx, \]  
where \( n \) is the number of atoms per molecule and \( R \) is the gas constant. The \( C_v \) was obtained by Equation 6 as a function of \((T/T_D)\).

It was assumed that the heat capacity \( C_p \) at constant pressure was described by:
\[ C_p = C_v + C_d = C_v(1 + \gamma \alpha T), \]  
where \( C_d \) is the dilatational term, \( \gamma \) is the Grüneisen constant and \( \alpha \) is the thermal expansion coefficient.

\[ \gamma = \frac{\alpha V_m}{C_v}, \]  
where \( V_m \) is molecular volume. Recently, Kato et al. [12] measured thermal expansion of \((U,Pu)O_2\) as functions of Pu content and O/M ratio. The \( \alpha \) values of UO\(_2\) and PuO\(_2\) were evaluated from their data as 2.94×10\(^{-5}\) and 2.89×10\(^{-5}\), respectively. It was assumed that the \( \alpha \) of \((Pu,Am)O_2\) equalled that of PuO\(_2\). The \( \gamma \) of UO\(_2\) and \((Pu, Am)O_2\) were 2.13 and 2.22, respectively, by Equation 8. From these analysis results, the temperature dependence of \( C_p \) could be calculated, and the data are shown in Figure 1 together with other reported data [3,13]. The \( C_p \) values of UO\(_2\) and \((Pu, Am)O_2\) which were calculated by Equations 7 and 8 were almost the same, but lower than the data which were obtained in experiments.

Kato et al. [14] analysed the \( C_p \) of PuO\(_2\) by Equation 9.
\[ C_p = C_v + C_d + C_{sch} + C_{exc} \]  

Here, \( C_{sch} \) is the Schottky term and \( C_{exc} \) is the excited term at high temperatures. Kato et al. showed that \( C_{sch} \) and \( C_{exc} \) were important in heat capacity evaluation of PuO\(_2\). \( C_{sch} \) was roughly approximated by the two-level-system model. \( C_{exc} \) was obtained from oxygen Frenkel pair formation which was reported by Konings et al. [15]. \( C_{sch} \) and \( C_{exc} \) are described by Equations 10 and 11 respectively.

\[ C_{sch} = Nk_B \left[ \frac{\varepsilon}{k_BT} \frac{\exp\left( \frac{\varepsilon}{k_BT} \right)}{\exp\left( \frac{\varepsilon}{k_BT} \right) + 1} \right]^2 \exp\left( \frac{\varepsilon}{k_BT} \right) \]  
\[ C_{exc} = \frac{\Delta H_{OFF}}{\sqrt{2RT}} \exp\left( \frac{-\Delta H_{OFF}}{2RT} \right) \exp\left( \frac{\Delta S_{OFF}}{2R} \right) \]  

Here \( \varepsilon \) is the energy between the two levels, \( \Delta H_{OFF} \) and \( \Delta S_{OFF} \) are enthalpy and entropy of oxygen Frenkel pair formation. The \( \varepsilon \) was obtained by fitting the experimental data with Equation 10. The calculated \( C_p \) values are shown in Figure 2. The \( C_p \) values were consistent with experimental data [3,13]. The calculated data of PuO\(_2\) were also in good agreement with experimental data in the temperature region below 1 500 K. The \( C_p \) of PuO\(_2\) is about 5 J/molK higher than that of UO\(_2\). It is considered that the difference of \( C_p \) is caused by \( C_{sch} \). The \( \varepsilon \) values were obtained as 0.08 eV and 0.2 eV, respectively, for UO\(_2\) and PuO\(_2\). However, the data of PuO\(_2\) differed from the experimental data [3,13] in the higher temperature region. In this region, experimental data of PuO\(_2\) are limited. It is needed to carry out more experiments and theoretical analysis.
Figure 1: Temperature dependence of $C_v$, $(C_v+C_d)$ and experimental data [3,13]

Figure 2: Temperature dependence of $C_p$ calculated by Equation 9 and experimental data [3,13]

Thermal conductivity

Thermal conductivity $\lambda$ values of PuO$_2$ are shown in Figure 3. In early studies, Gibby [4] and Fukushima et al. [5] reported lower data compared with UO$_2$ [16]. However, recent studies [6,7] showed that $\lambda$ of PuO$_2$ was significantly higher than that of UO$_2$. It is necessary to resolve the significant differences relating to the $\lambda$ values of PuO$_2$.

Thermal conductivity was analysed by Slack’s equation [17,18] as follows:

$$\lambda_s = \frac{1}{A+B T}$$  \hspace{1cm} (12)

$$\begin{align*}
A &= \left[ (\pi^2 V_m T_D) / (3 \hbar v_p^2) \right] \sum_i \Gamma_i \\
\nu_p &= (2\pi k_B T_D / \hbar) (V_m / 6\pi^2)^{1/3} \\
\sum_i \Gamma_i &= \Gamma_u + \Gamma_O \\
\frac{1}{B} &= 3.04 \times 10^{-7} \frac{\bar{M} T_D^3 \delta}{\gamma^2 n^{2/3}}
\end{align*}$$

Here $\nu_p$ is phonon velocity, $\Gamma_i$ is the cross section, $\bar{M}$ is average mass, $\delta$ is $(V_m)^{1/3}$ and $n$ is the number of atoms per molecule. The calculation results are shown in Figure 4. The $\lambda_s$ value of PuO$_2$ was slightly higher than that of UO$_2$. The $\lambda_s$ obtained by Slack’s equation includes the contribution of the phonon vibration term. So, other contribution terms like the electronic contribution must be taken into account. The thermal conductivity $\lambda$ is experimentally obtained by:

$$\lambda = C_p \cdot \rho \cdot \alpha$$  \hspace{1cm} (13)

where the $\alpha$ is thermal diffusivity. $C_p$ is described by Equation 9. It was considered that the contribution of $(C_{sch} + C_{exc})$ was not contained in $\lambda_s$. Hence, Equation 13 is corrected by:

$$\lambda = \frac{(C_p + C_d + C_{sch} + C_{exc})}{(C_p + C_d)} \cdot \lambda_s$$  \hspace{1cm} (14)
The data calculated by Equation 14 are shown in Figure 5, and they represented the experimental data very well. The results showed that \( \lambda \) of PuO\(_2\) was higher than that of UO\(_2\).

**Conclusions**

The mechanical properties of UO\(_2\) and (Pu,Am)O\(_2\) were measured by the ultrasonic pulse-echo method. Using the data, heat capacity and thermal conductivity were analysed. The heat capacity analysis results of UO\(_2\) and PuO\(_2\) revealed the effect of \( C_{\text{sh}} \) and \( C_{\text{ex}} \) at high temperatures. The contribution of these terms was the cause of the higher \( C_p \) of PuO\(_2\) as compared with UO\(_2\). Thermal conductivity correlation was derived based on Slack’s equation, and the correlation was extended by taking account of \( C_{\text{sh}} \) and \( C_{\text{ex}} \). It was concluded that the \( \lambda \) of PuO\(_2\) was higher than that of UO\(_2\), which was consistent with experimental data. The relationship between mechanical and thermal properties was analysed in UO\(_2\) and PuO\(_2\), and the models represented the experimental data accurately.
Acknowledgement

The authors are pleased to acknowledge Mr. H. Uno for his collaboration for the sample preparation and measurements.

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Dustless Process for Minor Actinide-Bearing Blanket Fabrication

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Abstract

$U_{1-x}Am_xO_{2\pm\delta}$ mixed-oxides are considered promising compounds for americium heterogeneous transmutation in fast neutron reactors. At lab-scale, the fabrication of americium bearing blankets (AmBB) under the form of ceramic pellets, required for irradiation, follows a powder metallurgy route which generates highly contaminant fine particles. Considering scale-up, dustless processes that can avoid particle dispersion in the fabrication lines are thus recommended. With this aim, the development of an innovative route called calcined resin microsphere pelletisation (CRMP) process has been initiated. The general approach consists in synthesising mixed-oxide microsphere precursors from beads of ion exchange resin through an adaptation of the weak acid resin process (WAR), and their pelletisation before sintering. This study focuses on the microsphere synthesis and particularly on the mechanisms implied during the thermal conversion of metal loaded ion exchange resin in porous mixed-oxide microspheres. The results are discussed, in a first time, on the basis of the synthesis of oxide microspheres integrating uranium and americium surrogates (Ce and Gd respectively) before a transposition to the highly active materials in a second time.

Introduction

Minor actinides (MA) are generated in UOX (uranium oxide) and MOX (mixed oxide) fuels during irradiation in nuclear reactors [1]. In the framework of their future management, their transmutation in fast neutron reactors through MABB (Minor Actinide-Bearing Blanket) irradiation represents a major research concern. In this context, due to its relatively high radiotoxicity in ultimate waste (if Pu multi-recycling option is considered), research is currently focused on americium (Am) transmutation through the fabrication of $U_{1-x}Am_xO_{2\pm\delta}$ mixed-oxide pellets. Commonly, these fabrications are based on powder metallurgy processes with ball-milling steps which generate large amounts of fine radioactive particles. Dustless processes are thus mandatory before envisaging an industrial deployment. Answering this need, the development of an innovative route using micrometric spherical precursors is studied. Through an adaptation of the weak acid resin (WAR) process [2,3], the general approach consists in synthesising micrometric and brittle spherical $U_{1-x}Am_xO_{2\pm\delta}$ mixed-oxide precursors. More particularly, oxide microsphere synthesis deals with fixing
americium and uranium ions into ion exchange resin microspheres and then mineralising as-loaded resin to form oxide microspheres. Then, they are shaped and sintered as dense pellets, answering the required AmBB specifications. The spherical geometry was thus chosen to facilitate the filling of the compaction chamber and subsequent pelletisation, as well as to reduce particle dissemination.

**Surrogate in-situ study: characterisation of the oxide synthesis**

This study part is dedicated to the fabrication of (Ce,Gd)O₂ mixed-oxide pellets by the CRMP process. Lanthanide surrogates were used for the demonstration of the process feasibility, such as cerium and gadolinium, for uranium and americium respectively. Indeed, this allows many experiments to be performed at lower cost. As a matter of fact, resin microspheres, loaded with a selected Ce/Gd ratio of 80/20, were prepared from aqueous solution of lanthanides nitrates. Then, characterisations by TGA (thermogravimetric analysis), HT-XRD (high-temperature X-ray diffraction), HT-Raman spectroscopy and HT-XAS (high temperature X-ray absorption spectroscopy) of the metal loaded resin were performed to study the release of carbon from the initial polymeric structure and the oxide formation. Key temperatures were then identified, corresponding to the important steps of the formation of a (Ce,Gd)O₂ solid solution. The organic matter departure occurs around 400 K and was evidenced through weight losses of TGA measurements. Then, the oxidation on-set was identified by HT-XAS and HT-XRD measurements, as the determination of cerium oxidation degree through XANES analysis shows its oxidation from Ce⁺³ to Ce⁺⁴. Thus, it attests the formation of an oxide from 500 K, which also corresponds to the temperature where first HT-XRD peaks appear, identified as a fluorine-type structure of Ce. Finally, the formation of a solid solution was determined by HT-Raman results that show the formation of oxygen vacancies from 600 K to 1 000 K. This result corresponds to the progressive substitution of Gd inside the cerium cubic structure. The whole results thus enable the progressive comprehension of resin microsphere mineralisation coming from WAR process.

**Actinide in-situ study: XAS and XRD measurements**

After this preliminary study, the loading of ion exchange resin with uranium and americium with a U/Am ratio of (90/10) was also studied. Oxide microspheres obtained from loaded resin with uranium and americium were characterised. Two specific calcinations are required to get the oxide microspheres under the solid solution form. More precisely a first thermal treatment under air is necessary for optimal carbon departure and a second thermal treatment has to be done under a reducing atmosphere (Ar-H₂) to form the (U/Am)O₂ solid solution required before pelletisation and sintering steps.

HT-XRD measurements were performed during the reduction part, starting with oxidised microspheres collected after air calcination. The acquisition was done until 2 023 K and reveals two significant results. Firstly, the diagram collected before reduction at room temperature (RT) shows one single monophasic U₃O₈ phase without any crystallised AmO₂ phase. Secondly, during thermal treatment, the formation of a solid solution between 523 K and 873 K is assessed with the progressive disappearance of the initial U₃O₈ peaks in a 100 K-range. Formation of the U₁₋ₓAmₓO₂±δ compound is then followed by crystallite growth until 2 023 K.

HT-XAS measurements were collected at ANKA synchrotron using resin microspheres stocked just after synthesis. XANES spectra were collected at UL₃ and AmL₃ edges during the two specific thermal treatments previously described. Concerning the evolution of the uranium oxidation degree under oxidative thermal treatment, U element is present under the form U⁵⁺/⁶⁺ in the first part of mineralisation. Then an apparent reduction of U with the apparition of U⁴⁺/⁵⁺ is noticed from 850 K. After oxidation under air, spectra are recorded during the gas transition and finally for the temperature increase under reductive atmosphere. From the gas change, it can be remembered that spectra show significant shift on lower energies and change in curve appearance, meaning the reduction of U with Ar-H₂ into U⁴⁺/⁵⁺, reinforced by the temperature elevation. Concerning Am, spectra reveal, at the beginning of the oxidation, the apparition of a
Small quantity of Am\textsuperscript{IV} in a majority of Am\textsuperscript{III}. From 750 K, the sole presence of Am\textsuperscript{III} during the whole mineralisation can be ascertained by spectrum appearance and WL position.

Concerning the first part of the mineralisation, under air, the partial reduction of U element into U\textsuperscript{IV/V} could be for now explained by the following hypothesis, linked to XRD results. Indeed it could correspond to the formation of nano-domains of (U,Am)O\textsubscript{2} inside the structure, involving the participation of Am\textsuperscript{III} and U\textsuperscript{IV/V}. These new structural arrangements would be both compatible with a monophasic U\textsubscript{3}O\textsubscript{8} compound from an XRD point of view, and with the presence of U\textsuperscript{IV/V} added to U\textsuperscript{V/VI}, from 850 K under air, observed through XAS.

The results concerning the second part of the mineralisation step, with solid solution formation, are concordant with previous XAS studies on uranium-americium mixed oxides prepared by solid state reaction, showing a similar cationic charge distribution with the presence of reduced Am\textsuperscript{III} but partially oxidised U\textsuperscript{IV/V} \cite{4,5}. The correlation between these results and literature thus confirms the electronic charge transfer between U and Am in the compounds and their chemical homogeneity.

Conclusion

To conclude, the main goal of this study was to point out and highlight the key-steps of WAR spherical precursor mineralisation into oxide through structural in-situ characterisations. The first part of this study dedicated to mineralisation of surrogate materials has been recently finalised while the second part concerning actinides materials is pursued. The understanding and control of the implied mechanisms during mineralisation is a first step towards the synthesis of well-adjusted precursors for pelletisation and thus the fabrication of dense pellets dedicated to americium transmutation.

Acknowledgements

The authors thank P. Coste and M. Bataille for in-situ XAS measurements; J.-C. Richaud from the LEFCA for in-situ XRD recordings; A. Gauthé, I. Jobelin, P. Grangaud and J.-M. Pomarede for sample synthesis; CEA/MAR/DRCP/SE2A/LAMM for TIMS measurements. We acknowledge the ANKA Synchrotron Light Source for provision of beamtime at the INE beamline and for assistance in setting up the in-situ XAS measurement system. M. Caisso and F. Lebreton are also grateful for Ph.D. fellowship funding by the CEA PACFA programme. XAS in situ experiment developments were funded by the NEEDS programme.

References


Progress on the Application of Metallic Fuels for Actinide Transmutation

J. Rory Kennedy¹, Randall Fielding¹, Dawn Janney¹, Robert Mariani¹, Melissa Teague¹, Gerald Egeland²
¹ Idaho National Laboratory, USA
² University of Nevada, USA

Abstract

Idaho National Laboratory (INL) is developing actinide bearing alloy metallic fuels intended for effecting the transmutation of long-lived isotopes in fast reactor application as part of a partitioning and transmutation strategy. This presentation will report on progress in three areas of this effort: demonstration of the fabrication of fuels under remote (hot cell) conditions directly coupled to the product from the pyroprocessing of spent fuel as part of the Joint Fuel Cycle Studies (JFCS) collaboration with the Korean Atomic Energy Research Institute (KAERI); the chemical sequestration of lanthanide fission products to mitigate fuel-cladding-chemical-interaction (FCCI); and transmission electron microscopy (TEM) and atom probe tomography (APT) studies on the as-cast microstructure of the metallic fuel alloy. For the JFCS efforts, we report on the implementation of the Glove-box Advanced Casting System (GACS) as a prototype casting furnace for eventual installation into the INL Hot Fuel Examination Facility (HFEF) where the recycled fuel will be cast. Results from optimising process parameters with respect to fuel characteristics, americium volatility, materials interaction, and lanthanide fission product carry over distribution will be discussed. With respect to the lanthanide carry over from the pyroprocessing product, encouraging studies on concepts to chemically sequester the FCCI promoting lanthanides within the fuel matrix thus inhibiting migration and interaction with the cladding will be presented. Finally, in relation to advanced modelling and simulation efforts, detailed investigations and interpretation on the nanoscale as-cast microstructure of possible recycle fuel composition containing U, Pu, Am, Np as well as carry-over lanthanide species will be discussed. These studies are important for establishing the initial conditions from which advanced physics based fuel performance codes will run.
Evaluation of Minor Actinide Transmutation Performance in Fast Reactor Metal Fuel Irradiated up to ~6.0 at.% Burnup

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a: Central Research Institute of Electric Power Industry (CRIEPI), Tokyo, Japan
b: Joint Research Centre, Institute for Transuranium (JRC-ITU), Karlsruhe, Germany

Abstract

Uranium-plutonium-zirconium (U-Pu-Zr) alloys with a minor actinide (MA) and rare earth (RE) content of 5 wt% or less were irradiated for 360 equivalent full-power days in the fast reactor Phénix. After cooling, the isotopic compositions of the irradiated alloys were analysed by inductively coupled plasma – mass spectrometry (ICP-MS). The analysis results indicated that the discharged burnups of U-19Pu-10Zr, U-19Pu-10Zr-2MA-2RE, U-19Pu-10Zr-5MA and U-19Pu-10Zr-5MA-5RE alloy samples were 5.4-5.9, 5.8-6.4, 5.3-6.2 and 5.4-5.8 at.%, respectively. The differences in the MA isotopic ratios before and after irradiation were assessed to discuss the transmutation performance of MAs added to U-Pu-Zr fuel. Calculation by the ORIGEN2 code accurately predicted the transmutation performance of MAs irradiated up to ~6.0 at.% burnup.

Introduction

Some isotopes of the minor actinides (MAs) of neptunium (Np), americium (Am) and curium (Cm) generated in spent nuclear fuels have very long half-lives, such as several million years for 237Np and 247Cm. Even in a spent light water reactor (LWR) uranium dioxide (UO2) fuel, where the MA production is low, a major part of the radiotoxicity is caused by MAs over a long period after ~300 years cooling [1]. Furthermore, some other MA nuclides such as 241Am and 244Cm are a major source of heat generation from spent LWR fuels after several decades of cooling [2]. When enriched plutonium (Pu)-containing fuels such as LWR mixed oxide (MOX) fuel or fast reactor (FR) fuel become widely utilised, further MA accumulation will become problematic. For this reason, future fuel cycle technologies are required to recover MAs as well as U and Pu from the spent fuels and recycle them in the FRs to lower the burden of geological repositories through the reduction of the long-term radioactive toxicity and heat generation of radioactive waste [3]. In recent years, various irradiation experiments on MA transmutation, such as AFC [4], ECRIX [5], FUTURIX-FTA [6] and Am-1 [7], have been carried out in several countries. However, few quantitative results have been reported for the MA transmutation performance of U-Pu-Np-Am-Cm fuels.

The Central Research Institute of Electric Power Industry (CRIEPI) has been developing uranium-plutonium-zirconium (U-Pu-Zr) alloy fuels containing MAs in cooperation with the Joint Research Centre, Institute for Transuranium Elements (JRC-ITU). This type of fuel is advantageous for efficiently recovering and transmuting MAs. Our previous characterisation experiment on U-Pu-Zr-MA(-RE) alloys indicated that the mechanical and thermal properties of U-Pu-Zr fuels containing 5 wt% or less MA and RE hardly differ from those of conventional U-Pu-Zr ternary alloys [8].

On the basis of these experimental results, metal fuel pins including MA-containing alloy segments in the fuel stacks were fabricated for an irradiation experiment. These fuel pins were irradiated for 120, 360 or 600 equivalent full-power days (EFPDs) in the fast reactor Phénix with the support of Commissariat à
l’énergie atomique (CEA), France, and the target peak burnups of ~2.5, ~7 and ~10 at.% were attained, respectively. After the irradiation experiment, post-irradiation examinations (PIEs) were started one after another from the low burnup fuels [8]. For the low-burnup fuels, the change in the isotopic composition during the irradiation experiment was consistent with the predicted MA transmutation performance for U-Pu-Zr-MA fuel alloys [9].

In this paper, the actual burnups of fuel samples irradiated for 360 EFPDs are quantified on the basis of mass-spectrometry results. Then, the MA transmutation performance of U-Pu-Zr-MA alloys with medium burnup is discussed.

Irradiation experiment [8]

Four different fuel alloys, U-19Pu-10Zr, U-19Pu-10Zr-2MA-2RE, U-19Pu-10Zr-5MA and U-19Pu-10Zr-5MA-5RE, were prepared by casting, where MA is a mixture of Np, Am and Cm and RE is a mixture of yttrium (Y), cerium (Ce), neodymium (Nd) and gadolinium (Gd). Then, three types of metal fuel pins, which include these fuel alloys in part of the U-19Pu-10Zr fuel stacks, were fabricated for irradiation in the Phénix reactor. Schematic views of the axial profile of the metal fuel pins and the fuel pin arrangement in an irradiation capsule are shown in Figure 1. Three irradiation capsules with an identical configuration were prepared to achieve three different burnups with irradiation periods of 120 EFPDs (METAPHIX-1), 360 EFPDs (METAPHIX-2) and 600 EFPDs (METAPHIX-3).

Table 1 shows the measurement results for the initial compositions of the fuel alloys. The fuel rods contain large variations in the elemental composition with the sample position, presumably due to the heterogeneity of the alloys. That is, the uncertainty in each actinide concentration reaches more than 5% in some samples.

Figure 1: Schematic views of metal fuel pins used in irradiation experiment and pin arrangement in irradiation capsule

(a) Axial profile
(b) Irradiation capsule
### Table 1: Measurement results of initial fuel composition [wt%]

<table>
<thead>
<tr>
<th></th>
<th>U-19Pu-10Zr</th>
<th>U-19Pu-10Zr-2MA-2RE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Target</strong></td>
<td>Measurement*</td>
<td>Target Measurement</td>
</tr>
<tr>
<td>U</td>
<td>71 (78.89)</td>
<td>67 (76.14)</td>
</tr>
<tr>
<td>Pu</td>
<td>19 (21.11)</td>
<td>19 (21.59)</td>
</tr>
<tr>
<td>Np</td>
<td>–</td>
<td>1.2 (1.36)</td>
</tr>
<tr>
<td>Am</td>
<td>–</td>
<td>0.6 (0.68)</td>
</tr>
<tr>
<td>Cm</td>
<td>–</td>
<td>0.2 (0.23)</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
<td>10.75 ±0.07</td>
</tr>
<tr>
<td>Y</td>
<td>–</td>
<td>0.2</td>
</tr>
<tr>
<td>Ce</td>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>Nd</td>
<td>–</td>
<td>1.4</td>
</tr>
<tr>
<td>Gd</td>
<td>–</td>
<td>0.2</td>
</tr>
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</table>

<table>
<thead>
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<th>U-19Pu-10Zr-5MA</th>
<th>U-19Pu-10Zr-5MA-5RE</th>
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<td><strong>Target</strong></td>
<td>Measurement</td>
<td>Target Measurement</td>
</tr>
<tr>
<td>U</td>
<td>66 (73.33)</td>
<td>61 (71.76)</td>
</tr>
<tr>
<td>Pu</td>
<td>19 (21.11)</td>
<td>19 (22.35)</td>
</tr>
<tr>
<td>Np</td>
<td>3.0 (3.33)</td>
<td>3.0 (3.53)</td>
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<tr>
<td>Am</td>
<td>1.6 (1.78)</td>
<td>1.6 (1.88)</td>
</tr>
<tr>
<td>Cm</td>
<td>0.4 (0.44)</td>
<td>0.4 (0.47)</td>
</tr>
<tr>
<td>Zr</td>
<td>10</td>
<td>10.88</td>
</tr>
<tr>
<td>Y</td>
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<td>0.5</td>
</tr>
<tr>
<td>Ce</td>
<td>–</td>
<td>0.5</td>
</tr>
<tr>
<td>Nd</td>
<td>–</td>
<td>3.5</td>
</tr>
<tr>
<td>Gd</td>
<td>–</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Average of 14 samples.

Impurities < 0.4 wt%.
Concentrations of the actinide elements excluding Zr and RE are shown in parentheses.

**Chemical analysis**

The four types of irradiated fuel alloy samples, U-19Pu-10Zr, U-19Pu-10Zr-2MA-2RE, U-19Pu-10Zr-5MA and U-19Pu-10Zr-5MA-5RE, were cut into disks with ~4 mm thickness from the METAPHIX-2 fuel pins, as shown in Figure 2, and individually dissolved with the cladding in a HNO₃-HF mixture at ~100°C.

**Figure 2: Sample of irradiated METAPHIX-2 fuel, U-19Pu-10Zr-5MA-5RE alloy, used for chemical analysis**
The irradiation positions of the respective samples are shown in Figure 1a. The sample solution was collected through a filter with a 1 μm mesh. Although part of the cladding materials remained in some cases, fuel materials including Zr and all the FPs were completely dissolved over several hours. The isotopic compositions of these collected solutions were analysed by inductively coupled plasma – mass spectrometry (ICP-MS).

**Burnup evaluation**

On the basis of the results of chemical analysis, the burnups of the fuel samples were evaluated using lanthanum-139 (139La), ruthenium-102 (102Ru) or ruthenium-104 (104Ru) as the burnup indicator. Note that the conventional burnup evaluation method using neodymium-148 (148Nd) is not applicable in this study because REs including Nd were added to some of the fresh fuel alloys. To examine the validity of an alternative burnup indicator such as 139La, 102Ru or 104Ru, the conventional 148Nd method [10] was also applied to the samples without RE addition, i.e., U-19Pu-10Zr and U-19Pu-10Zr-5MA alloys. The fission yield data were obtained from the ENDF/BVII library provided by the NEA data bank [11].

The evaluated burnups are summarised in Table 2 together with the predicted results based on the irradiation conditions. The variation in the predicted burnup is due to the uncertainty of the initial fuel composition. The results of burnup evaluated using the indicator nuclides are consistent with each other. This suggests that 102Ru and 104Ru can be applied as alternative burnup indicator nuclides for low-decontamination fuels recycled with significant amounts of RE fission products.

Although the burnup of the U-Pu-Zr-5MA-5RE alloy sample was somewhat lower than the predicted value, the target burnups were approximately attained for all samples.

**Table 2: Evaluated and predicted burnups of samples of METAPHIX-2 fuels used for chemical analysis [at. %]**

<table>
<thead>
<tr>
<th>Indicator nuclide</th>
<th>U-Pu-Zr</th>
<th>U-Pu-Zr-2MA-2RE</th>
<th>U-Pu-Zr-5MA</th>
<th>U-Pu-Zr-5MA-5RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>148Nd</td>
<td>5.7</td>
<td>N/A</td>
<td>5.4</td>
<td>N/A</td>
</tr>
<tr>
<td>139La</td>
<td>5.9</td>
<td>5.8</td>
<td>5.3</td>
<td>5.6</td>
</tr>
<tr>
<td>102Ru</td>
<td>5.5</td>
<td>6.4</td>
<td>6.2</td>
<td>5.8</td>
</tr>
<tr>
<td>104Ru</td>
<td>5.4</td>
<td>6.0</td>
<td>5.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Prediction*</td>
<td>5.4-6.5</td>
<td>5.8-7.0</td>
<td>5.7-6.9</td>
<td>6.0-7.2</td>
</tr>
</tbody>
</table>

*: Based on the irradiation power history evaluated by CEA. The variation in the prediction originates from the uncertainty of the initial fuel composition.

**Actinide transmutation**

The actinide element compositions measured by ICP-MS analysis are shown in Table 3. The predictions by the ORIGEN2 code using the ORLIBJ40 library [12] are also shown in parentheses. In the ORIGEN2 calculation, the one-group cross-section data for a prototype MOX fuel fast reactor was employed to simulate the Phénix reactor core. Note that the measurement accuracy for the composition analysis by ICP-MS is about 5% to 15% including the uncertainty in the sample preparation procedure and in the analytical technique. Moreover, the uncertainty of the initial fuel composition shown in Table 1 complicates the evaluation of the change in the elemental composition during the irradiation experiment. On the other hand, the isotope ratio in each actinide element is not expected to vary with the position in the initial fuel rods. For this reason, the change in the isotope ratio in the actinide elements was investigated in this study.
Table 3: Actinide compositions of METAPHIX-2 fuel samples (wt%)

<table>
<thead>
<tr>
<th></th>
<th>U-19Pu-10Zr</th>
<th>U-19Pu-10Zr-2MA-2RE</th>
<th>U-19Pu-10Zr-5MA</th>
<th>U-19Pu-10Zr-5MA-5RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>79.27 (79.50)</td>
<td>74.91 (76.22)</td>
<td>75.84 (74.15)</td>
<td>72.79 (72.95)</td>
</tr>
<tr>
<td>Pu</td>
<td>20.66 (20.41)</td>
<td>22.91 (21.82)</td>
<td>19.79 (21.49)</td>
<td>22.82 (22.38)</td>
</tr>
<tr>
<td>Np</td>
<td>0.04 (0.02)</td>
<td>1.27 (1.11)</td>
<td>2.68 (2.64)</td>
<td>2.65 (2.82)</td>
</tr>
<tr>
<td>Am</td>
<td>0.03 (0.06)</td>
<td>0.67 (0.64)</td>
<td>1.31 (1.33)</td>
<td>1.36 (1.45)</td>
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<tr>
<td>Cm</td>
<td>0.00 (0.00)</td>
<td>0.25 (0.21)</td>
<td>0.37 (0.39)</td>
<td>0.39 (0.39)</td>
</tr>
</tbody>
</table>

*: Results predicted by ORIGEN2 are shown in parentheses.

The measurement results for the actinide isotope ratios are summarised in Tables 4 and 5 along with the predictions by ORIGEN2. As shown in these tables, most measurement results agree well with the ORIGEN2 calculations except for some trace isotopes such as $^{242m}$Am and $^{243}$Am in the U-19Pu-10Zr sample.

Table 4: Isotope ratios of actinide elements in U-19Pu-10Zr and U-19Pu-10Zr-2MA-2RE (wt%)

<table>
<thead>
<tr>
<th></th>
<th>U-19Pu-10Zr</th>
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<th>U-19Pu-10Zr-2MA-2RE</th>
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<td>As-fabricated</td>
<td>METAPHIX-2</td>
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<td>Measurement</td>
<td>Prediction</td>
<td>Measurement</td>
<td>Prediction</td>
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<tr>
<td>U</td>
<td>$^{234}$U</td>
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<td>0.001</td>
<td>0.001</td>
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<tr>
<td></td>
<td>$^{235}$U</td>
<td>0.40</td>
<td>0.33</td>
<td>0.30</td>
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<td></td>
<td>$^{236}$U</td>
<td>0.002</td>
<td>0.04</td>
<td>0.03</td>
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<tr>
<td></td>
<td>$^{238}$U</td>
<td>99.60</td>
<td>99.63</td>
<td>99.67</td>
</tr>
<tr>
<td>Pu</td>
<td>$^{239}$Pu</td>
<td>0.007</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$^{240}$Pu</td>
<td>95.28</td>
<td>88.24</td>
<td>88.08</td>
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<tr>
<td></td>
<td>$^{241}$Pu</td>
<td>4.62</td>
<td>11.16</td>
<td>11.34</td>
</tr>
<tr>
<td></td>
<td>$^{242}$Pu</td>
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<td>0.55</td>
<td>0.51</td>
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<tr>
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<td>$^{243}$Pu</td>
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<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Np</td>
<td>$^{237}$Np</td>
<td>–</td>
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<td>100</td>
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<tr>
<td>Am</td>
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<td>97.81</td>
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<td>$^{242m}$Am</td>
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<td>9.15</td>
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<td>$^{246}$Cm</td>
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<td>–</td>
</tr>
<tr>
<td></td>
<td>$^{247}$Cm</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*: Calculated by ORIGEN2
Table 5: Isotope ratios of actinide elements in U-19Pu-10Zr-5MA and U-19Pu-10Zr-5MA-5RE (wt%)

<table>
<thead>
<tr>
<th></th>
<th>U-19Pu-10Zr-5MA</th>
<th>U-19Pu-10Zr-5MA-5RE</th>
</tr>
</thead>
<tbody>
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<td>METAPHIX-2</td>
</tr>
<tr>
<td></td>
<td>Measurement</td>
<td>Prediction*</td>
</tr>
<tr>
<td>U</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>0.001</td>
<td>0.04</td>
</tr>
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<td>$^{235}$U</td>
<td>0.40</td>
<td>0.27</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>0.002</td>
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<td>$^{238}$U</td>
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<td>$^{237}$Np</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Am</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>40.92</td>
<td>39.83</td>
</tr>
<tr>
<td>$^{242m}$Am</td>
<td>0.29</td>
<td>2.04</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>58.79</td>
<td>58.13</td>
</tr>
<tr>
<td>Cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{242}$Cm</td>
<td>0.0</td>
<td>0.06</td>
</tr>
<tr>
<td>$^{243}$Cm</td>
<td>0.0</td>
<td>0.50</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>85.66</td>
<td>81.78</td>
</tr>
<tr>
<td>$^{245}$Cm</td>
<td>7.78</td>
<td>11.63</td>
</tr>
<tr>
<td>$^{246}$Cm</td>
<td>6.27</td>
<td>5.49</td>
</tr>
<tr>
<td>$^{247}$Cm</td>
<td>0.29</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*: Calculated by ORIGEN2

The change in the isotope ratio up to a given time after fuel fabrication was defined by the following equation;

$$\text{Change in the isotope ratio} = \frac{(\text{Isotope ratio at a given time}) - (\text{Initial}^* \text{ isotope ratio})}{(\text{Initial}^* \text{ isotope ratio})}.$$  

*: Initial = at the time of fuel fabrication

Figures 3 to 6 show the history of the change in the isotope ratio of Pu, Am and Cm in the METAPHIX-2 fuel samples after fuel fabrication. In these figures, the measurement results obtained by chemical analysis are designated by solid circles. In the ORIGEN2 calculation, the experiment history, such as ~9.0 years waiting before irradiation, ~2.7 years irradiation and ~3.5 years cooling, is properly reflected. The ORIGEN2 calculations indicate that the isotope ratio changes markedly during neutron irradiation and also in the waiting period and cooling time owing to radioactive decays. Comparing the results of measurement and ORIGEN2 calculations in these figures reveals that the change in the actinide isotope ratio is reasonably well predicted by the ORIGEN2 code. Even for Cm isotopes, the nuclear data accuracy of which is expected to be relatively low, the calculations are in reasonable agreement with the measurement results. This is because Cm isotopes are hardly affected by isobar overlaps and interference by adjacent broad large peaks in ICP-MS analysis.
These results for the changes in the isotope composition indicate that Pu, Am and Cm nuclides are transmuted as expected in U-Pu-Zr-MA(-RE) alloys irradiated up to ~6.0 at.% burnup in a fast reactor.

Figure 3 History of change in isotope ratio in Pu and Am in U-Pu-Zr alloy fuel relative to initial isotope ratio at the time of fuel fabrication. Irradiation was carried out from 9.0 to 11.7 years after fuel fabrication.

![Figure 3](image)

* Change in the isotope ratio = \( \frac{\text{Isotope ratio at a given time} - \text{Initial isotope ratio}}{\text{Initial isotope ratio}} \)

Figure 4: History of change in isotope ratio in Pu, Am and Cm in U-Pu-Zr-2MA-2RE alloy fuel relative to initial isotope ratio at the time of fuel fabrication. Irradiation was carried out from 9.0 to 11.7 years after fuel fabrication.

![Figure 4](image)

* Change in the isotope ratio = \( \frac{\text{Isotope ratio at a given time} - \text{Initial isotope ratio}}{\text{Initial isotope ratio}} \)
Figure 5: History of change in isotope ratio in Pu, Am and Cm in U-Pu-Zr-5MA alloy fuel relative to initial isotope ratio at the time of fuel fabrication. Irradiation was carried out from 9.0 to 11.7 years after fuel fabrication.

(a) Pu isotopes
(b) Am isotopes
(c) Cm isotopes

* Change in the isotope ratio = \(\frac{\text{Isotope ratio at a given time} - \text{Initial isotope ratio}}{\text{Initial isotope ratio}}\)

Figure 6: History of change in isotope ratio in Pu, Am and Cm in U-Pu-Zr-5MA-5RE alloy fuel relative to initial isotope ratio at the time of fuel fabrication. Irradiation was carried out from 9.0 to 11.7 years after fuel fabrication.

(a) Pu isotopes
(b) Am isotopes
(c) Cm isotopes

* Change in the isotope ratio = \(\frac{\text{Isotope ratio at a given time} - \text{Initial isotope ratio}}{\text{Initial isotope ratio}}\)
**Summary**

The isotopic compositions of four types of irradiated METAPHIX-2 fuel samples, U-19Pu-10Zr, U-19Pu-10Zr-2MA-2RE, U-19Pu-10Zr-5MA and U-19Pu-10Zr-5MA-5RE, were analysed by ICP-MS. On the basis of the results of composition analysis, the burnups of these fuel samples were quantitatively determined using $^{139}$La, $^{102}$Ru or $^{104}$Ru as an alternative burnup indicator to the conventional $^{148}$Nd. The burnups evaluated using these indicator nuclides were consistent with each other. This suggests that $^{102}$Ru and $^{104}$Ru can be used as alternative burnup indicator nuclides applicable to low-decontamination fuels recycled with significant amounts of REs. The evaluated burnups of METAPHIX-2 fuel samples of 5.3 to 6.4 at.% indicate that the medium burnup targets were approximately attained in this irradiation experiment.

The change in isotope ratio in the major nuclides of Pu, Am and Cm after fuel fabrication was evaluated and compared with the results of ORIGEN2 calculations. The change in the isotope ratio due to nuclear transmutation and radioactive decay was reasonably well predicted by ORIGEN2. As a result, it was concluded that Pu, Am and Cm nuclides added to U-Pu-Zr alloy and irradiated up to ~6.0 at.% burnup in a fast reactor are transmuted as expected.

**References**


Poster Session

Chair: M.-H. Kim (Republic of Korea)
Economics Assessments of Nuclear Fuel Cycle Scenarios: Validation of TR_EVOL Code

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CIEMAT, Spain

Abstract

Economic competitiveness is one of the main issues for the development of sustainable nuclear energy, since nuclear fuel cycle choices such as energy policies, fuel diversity, security of supply and associated social and environmental effects could impact the cost of nuclear energy. In this context, CIEMAT has upgraded the fuel cycle code TR_EVOL to include a new module capable of making economic assessments of nuclear fuel cycle scenarios. The aim of this module is the estimation of the levelised cost of electricity, although other indicators can also be estimated, such as the generation cost per technology type, investment profiles, final disposal gallery length, etc.

TR_EVOL uses a series of cost sources strictly related to the generation cost for a nuclear power plant: Investment cost, Fuel cost, Operation and Management cost, and Decommissioning, Dismantling and Disposal costs (waste management costs).

This work has been focused in the validation of the TR_EVOL economic module. This validation has been carried out on the one hand by making use of the ARCAS EU project and its economic assessments for advanced reactors. The Investment cost, the Fuel cost and the O&M costs were assessed and validated using these data (differences smaller than 1%, 3% and 2%, respectively, between ARCAS and TR_EVOL). On the other hand, for the waste management cost, a specific validation was required due to its high sensitivity to the different fuel cycle options. Published data for the final disposal provided by institutions responsible of nuclear waste management were used for this purpose. The assessment showed differences smaller than 7% in case of open cycle scenarios and smaller than 12% for partially closed cycles. These results show that the TR_EVOL economic module has been successfully validated, demonstrating the capability of proper economic predictions.

Introduction

Economic competitiveness is one of the main issues for the development of sustainable nuclear energy, since nuclear fuel cycle choices such as energy policies, fuel diversity, security of supply and the associated social and environmental effects could impact the cost of nuclear energy.

In this context, CIEMAT has upgraded the fuel cycle code TR_EVOL [1]. This code was designed to study different short-, medium- and long-term options for the introduction of various types of nuclear reactors and fuel cycle facilities, and for the usage of associated nuclear material, giving due consideration to the isotopic composition of the material in any stage of the fuel cycle: essentially uranium, plutonium, minor actinides and fission products. Now, the code includes a new module capable of making economic assessments of nuclear fuel cycle scenarios. The aim of this module is the estimation of the levelised cost of electricity (LCOE), although other indicators can also be estimated, such as the generation cost per technology type, investment profiles, final disposal gallery length, etc.
This work has been focused in the validation of the TR_EVOL economic module. This validation has been carried out on the one hand for the three main components of the LCOE (Investment cost, the fuel cost and the O&M cost, according to [2] and [3]) as a cross check of the results of economic analyses of different strategies of Partitioning and Transmutation (P&T) performed in the ARCAS EU project.

On the other hand, for the waste management cost, a specific validation was required due to its high sensitivity to the different fuel cycle options. Since no generic unit costs have been found in the bibliography, the aim of this work has been the development of a model that provides final results compatible with published data provided by institutions responsible of nuclear waste management.

TR_EVOL economic module

The treatment of the economic information applied to the nuclear fuel cycle has been implemented in the TR_EVOL fuel cycle code as an additional module. The economic module treats the information located in the cost input files and applies the models and unit costs to the mass balance output obtained with the main part of the code.

The cost simulation is mainly based on the definitions and subdivisions of the costs given by the Economic Modelling Working Group of the Generation IV International Forum [4]. The description of the model for the four components of the fuel cycle cost and its derived costs are detailed in the following:

- **Investment cost**: It includes the overnight cost and financial costs (financial costs are additionally split in interest during construction and interest for the financing).
- **Fuel cost**: This contribution represents the front-end cost, including structural fuel assembly and required reprocessing in case of MOX and advanced fuel fabrication.
- **Operation and maintenance (O&M)**: Annual cost for the plant, which depends on the installed capacity.
- **Decommissioning, Dismantling and waste Disposal (DDD)**: In addition to reactor plant dismantling, the fuel waste final management associated to the back-end fuel costs is included here; i.e., interim (ID) and final disposal (FD) costs.

**Results**

**Cross checking of the main components of the cost**

**Introduction**

The EU-funded project “ADS and fast reactor comparison study in support of Strategic Research Agenda of SNETP” (ARCAS) [5] embarked on the mission of helping policymakers and governments to decide on the best options to streamline their nuclear facilities for more efficient energy production considering the maturity of the technology and how this could be incorporated into economic analyses. Assessments involved fuel cycle cost and transmutation with maximal minor actinide content involved in core loading, in addition to checking a number of safety parameters. The project successfully analysed existing studies, outlining a legal framework of partitioning and transmutation operations.

The ARCAS economic document [6] (taken as reference for this evaluation) analysed the economics of different strategies for a nuclear fuel cycle scenario, in order to give zero net production of minor actinides (MA) for the whole reactor park. Applying two different economic models and hypotheses (by CNRS and NRG) for the accelerator-driven subcritical system (ADS) system (as EFIT configuration [7]) and two different types of fast reactor (FR, homogeneous and heterogeneous configurations) [8], ARCAS provided the LCOE per reactor type.
In this work, two fuel cycle options (one scenario with ADS and other with FR homogeneous configuration, both considering a fleet of light water reactors, LWR) from the ARCAS reference were chosen to be studied. Their comparison will serve for the demonstration of the capabilities of the TR_EVOL economic module. The economic model and hypotheses provided by NRG have been used here.

**Fuel cycle description**

The comparison has been carried out using the characteristics and parameters for FR and ADS proposed by ARCAS (European Fuel Cycle, where the whole fuel cycle scenario is described including the LWR) and the economic hypotheses used by NRG. Costs related to the investment, fuel and O&M have been evaluated.

The scenarios used in this study are:

- **FR simulation**: the scenario chosen for the assessment of the FR cost has been the homogeneous configuration with 70% of the energy provided by FR and 30% by LWR with 100% UO2. In this scenario, the fast reactors burn both the MA contained in their used fuels and the MA of the LWR strata.

- **ADS simulation**: for the ADS, the model considers 97.4% of the energy production by LWR with 100% UO2 and the other 2.6% is provided by ADS. The ADS is designed to be dedicated to MA burning. As a consequence, it has a large MA burning capacity (estimation about 112.5 kg/TWh). Although the share of electricity produced in ADS is small, the amount of ADS systems in the park is still quite significant, due to the small power per unit, of 400 MWth.

**Cross checking results**

The results, summarised in Table 1, include the estimations for all the items that explain the LCOE (excluding the DDD cost). It can be seen that the results from TR_EVOL code are rather similar to those obtained by the NRG model simulation, with differences smaller than 3%, for both scenarios. This shows that the TR_EVOL economic model works correctly for the three main components of the LCOE: investment costs, fuel cost and O&M cost.

**Table 1: ARCAS and TR_EVOL cost estimation.**

<table>
<thead>
<tr>
<th>Cost</th>
<th>FR scenario</th>
<th>ADS scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NRG model (c€/kWhe)</td>
<td>TR_EVOL model (c€/kWhe)</td>
</tr>
<tr>
<td>Capital</td>
<td>7.35</td>
<td>7.38</td>
</tr>
<tr>
<td>O&amp;M</td>
<td>1.18</td>
<td>1.17</td>
</tr>
<tr>
<td>Fuel</td>
<td>2.14</td>
<td>2.08</td>
</tr>
</tbody>
</table>

**The back-end cost**

**Introduction**

This section aims to find the key parameters needed to create an accurate model (and its corresponding unit costs, given that very limited information is available in bibliography) for the decommissioning, dismantling and disposal (DDD) cost. The objective is to provide the user with generic values for each unit cost required for the construction of the economic model. Additionally, applying those unit costs calculated here, the TR_EVOL model has been validated in each item of the DDD cost by means of the comparison of its results with the published cost data.
To begin with, there is a consensus in the literature about the cost of decommissioning and dismantling, expressed as a percentage depending on the overnight cost of the power plan. Based on the information obtained from reference [9], the percentages to be used range from 10% to 20%. So an average value of 15% seems reasonable.

It is widely known that costs related to the intermediate and final disposal for a nuclear storage have large uncertainties due to the limited data available in case of the ID in operation and the almost inexistent information about FDs. However, TR_EVOL includes a methodology for the estimation of a cost for both ID and FD separately. In order to find reasonable unit costs that work correctly in cases where the information is not available and the disposal parameters are unknown, the model can use standardised costs treated from the available information.

In the following, if it is not specified otherwise, costs are expressed in Euro, 2012 price level.

**Interim disposal cost model**

The model for the ID is divided in a Fixed Cost (FC), which (a priori) does not vary according to the mass to store, and a Variable Cost (VC), depending on the mass to store. Published data for Swedish storage with a 9 470 t capacity [10] and the Spanish ID with a capacity of 6 676 t [11] give enough information to obtain a representative value for both the FC and VC. Several values of the O&M unit cost can be however obtained from references for these IDs.

The published data about the Swedish CLAB (Centralt Lager för Använt Bränsle, interim storage), in operation since 1985, explicitly includes the investment and O&M costs of this facility [12,13,10]. However reference [10] analyses the cost of increasing the capacity of the ID from the period going from 2002 to the end of the fuel cycle scenario (EOC), during which the mass to store is supposed to go from 5 734 t to 9 470 t at EOC for a total of 40 years of operation per reactor. From these references, a fixed cost of 345 MEuro and a decommissioning cost of 65 MEuro can be derived. Nevertheless, for the O&M cost, [12,13] and [10] provide different values, as explained as follows.

It is possible to obtain the unit cost for the O&M required for the model dividing the O&M cost (526 MEuro) by the mass managed (~3736 t). As a result, the O&M unit cost is 0.14 MEuro/tHM. However, the investment cost shown in the reference represents the cost for the expansion of the ID capacity by means of the introduction of new storage canisters. It is clear that a fixed cost definition should not be dependent on the mass to store; thus, this investment should be considered as a variable cost in our model. Therefore, it is necessary to add this cost to the O&M unit cost, giving a unit cost of 0.184 MEuro/tHM. On the other hand, since the older references estimated in 1 606 MEuro the cost of the ID, and considering the abovementioned fixed cost plus the decommissioning cost, the O&M unit cost, in this case, is ~0.151 MEuro/tHM, although this estimation is based on 10 years older data.

Both models give a cost of the ID equal to 2 152 MEuro and 1 840 MEuro, respectively. Despite having these two different unit costs for the O&M of the Swedish ID with a 15% of difference between both results, the newest value of 0.184 MEuro/tHM has been considered as the most representative for the estimation, so that in this case, the total ID cost considered as more reasonable is 2 152 MEuro.

A detailed cost analysis can be also carried out for the Spanish ID thanks to the information published by the Spanish waste management public company ENRESA [11]. Unfortunately this reference does not provide the cost for construction and O&M explicitly. This reference gives a value of 1 596 MEuro (1 388 MEuro at 2006 price level, year of publication) in the total budget for the ID, which is shared into four periods. The first one until year 2005 can be considered for the construction of At-Reactor storages, located in some nuclear power plants, which are not taken into account in this work since they are out of
the ID cost facility. The second and third ones, for year 2006 and from 2007 to 2010, are representative for the ID R&D and construction respectively. Assuming the year 2010 as the commissioning deadline (according to the Spanish law), the cost for these periods is ~503 MEuro (438 MEuro at 2006 price level). Finally, the fourth period, from 2011 to 2070 with a budget of 904 MEuro (785 MEuro at 2006 level price) is probably for O&M and decommissioning of the ID. Thus, the total cost for the ID presented by the reference may be close to 1 407 MEuro, from which 503 MEuro could be considered as a fixed cost.

Additionally, the reference estimates that Spanish ID has been designed for 6 674 tHM generated along the cycle. If the decommissioning cost for the Swedish ID (65 MEuro) is also considered as fixed cost and added to the 503 MEuro, the total O&M cost for the Spanish ID is 838 MEuro and its unit cost becomes 0.126 MEuro/tHM.

About the detailed specifications for the SF storage, another publication by ENRESA [14] gives information about a model to store the fuel assemblies in canisters with around 1.86 t of capacity. Using this model, the VC of the ID can be described in detail as a function of the number of canister instead of the mass to store. This model was implemented in TR_EVOL to give a more accurate estimation due to some special constrains as, for example, the thermal limitation per canister. Thus, the variable cost model for the Spanish ID can be explained as the canister cost times the number of canisters, for both PWR and BWR plants. Considering a mass per assembly of 0.465 t for PWR and 0.180 t for BWR and that one canister can contain 4 PWR assemblies or 12 BWR assemblies, with the previous O&M unit cost it can be obtained that:

- Canister cost (PWR) = 0.234 MEuro/Canister.
- Canister cost (BWR) = 0.272 MEuro/Canister.

The variable cost calculated following the ENRESA specifications is summarised in Table 2. Note that the HLWs are also included in the calculations, although the canister costs are taken into account as a PWR canister. As it can be seen in the table, a value of 868 MEuro is assumed for O&M cost. This value seems different to the value presented before (838 MEuro), due mainly to rounding issues plus 19 MEuro more added from the HLW, which were omitted in the first estimation for simplification. The total cost for the ID, including FC, is around 1 436 MEuro.

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Nº Assemblies</th>
<th>Assemblies per canister [11]</th>
<th>Number of canisters</th>
<th>O&amp;M cost (M€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWR</td>
<td>11311</td>
<td>4</td>
<td>2828</td>
<td>662</td>
</tr>
<tr>
<td>BWR</td>
<td>8260</td>
<td>12</td>
<td>688</td>
<td>187</td>
</tr>
<tr>
<td>HLW</td>
<td>243</td>
<td>3</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>3597</td>
<td>868</td>
</tr>
</tbody>
</table>

The performed analyses are summarised in Table 3, where the main findings are shown in order to give the user some parameters and unit costs to be used for a TR_EVOL ID cost approximation.

<table>
<thead>
<tr>
<th>Item</th>
<th>Swedish ID</th>
<th>Spanish ID</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost</td>
<td>345</td>
<td>503</td>
<td>424</td>
</tr>
<tr>
<td>Decommissioning cost</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Total fixed cost</td>
<td>410</td>
<td>568</td>
<td>489</td>
</tr>
<tr>
<td>O&amp;M unit cost (M€/t)</td>
<td>0.184</td>
<td>0.126</td>
<td>0.155</td>
</tr>
</tbody>
</table>
Final disposal cost approximation

As for the ID, the FD cost can be divided in a fixed cost plus a variable cost. The fixed cost represents the sum of the overnight cost for the FD, the overnight cost for the encapsulation plant (EP), and the decommissioning cost. Additionally, the variable cost is explained by the cost of storing and managing a certain SF mass: O&M cost in the disposal plus O&M cost in the EP.

The following analysis gives the results for FD cost and provides the user with the unit costs necessary to estimate any generic FD cost through TR_EVOL economic module. Although a representative fixed cost for a general FD concept is difficult to obtain due to the lack of information, the values provided here might serve as a gross estimation. To do this analysis, the information published for some IDs has been used, in particular, for Finland [15], Spain [11], Sweden [10], Canada [16], France [17] and Switzerland [18]. This information, about the SF mass generated by each fuel cycle and its estimated FD cost, has been published by the companies engaged in the development and construction of these facilities.

It has to be mentioned that the French and Swiss FD designs are considered for a fuel cycle with reprocessing strategy. Concerning this issue, it has been observed that the material to be stored in the FD, with different fuel types and strategies for encapsulation and management, might need to be treated specifically for each nuclear fuel cycle or, otherwise, to find a common parameter among them that could explain the variable cost. The first option is quite difficult to implement in a TR_EVOL simulation, which is designed for the study and comparison of fuel cycle scenarios and not for a thorough FD cost estimate. The second option, finally chosen for TR_EVOL model, makes use of the concept of gallery length (GL), common parameter to the final disposal for every kind of fuel cycle. As abovementioned, the variable cost consists in the O&M costs for EP and FD. Now, the cost of the gallery has to be included here, as a fixed cost per km of gallery.

For the VC (EP) the cost of the Swedish encapsulation plant can be used [10]. In this case, the cost for the 4 500 canisters (9 500 tHM) is around 915 MEuro, this means 0.203 MEuro per canister. On the other hand, the O&M for the SF in the FD or VC (FD) is ~191 MEuro, which divided by the number of canisters give a value of 0.042 MEuro per canister.

The estimation of the gallery length cost depends obviously on the mass to store, which can be worked out considering the number of canister to store and its dimension. At first, the canister (or packages) number depends on the fuel type and the number of the spent fuel assemblies that can be deposited. For the Spanish case, the number of canister and the gallery length calculated by TR_EVOL model is as follows:

- Mass estimated at EOC: ..............................~6 674 tHM.
- Mass per SFA:......................................0.465 t (PWR assembly); 0.180 t (BWR assembly).
- Numbers of SFA per canisters: .................................4 PWR or 12 BWR.
- Canister length:..............................................4.6 m.
- Separation between canisters taken from [20]: ...............................................2 m.

Using these values, the number of canisters to be stored is equal to 3 588, very close (2% difference) to the value of 3 517 canisters published in [11]. The gallery length required for storing the 3 588 canisters in the Spanish FD is around 24 km and, applying the same reasoning, the gallery length of the Swedish and Finnish FDs is 30 and 18 km, respectively.

Considering the published data for the Finnish, Spanish and Swedish FDs (fixed costs and variable costs) the gallery length cost can be obtained for each case since, with this model, it is the only unknown variable in the cost equation. The final value of the gallery length unit cost can be obtained as an averaged value and is equal to 19.7 MEuro/km.

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Table 4 shows a comparison of the referenced FD costs used for the estimation and the results obtained by TR_EVOL model. The relative errors between both sets of results are quite satisfactory (smaller than 7%), meaning that the model developed here can describe correctly the cost of the FD. In addition to the first three cases, and to explore the model representativeness, the FD cost has also been obtained for the Canadian FD design, which has the biggest capacity of the world with almost 200 000 t of HM. The result also agrees reasonably well with the reference, with an underestimation of only 2.4%. This result is fairly accurate despite that the dimension of the canister was unknown (for different fuel dimension is used in Canadian heavy water reactors). However, a canister length of 4.6 m plus a separation between canisters of 2 m has been used in the gallery length estimation (as for PWR).

**Table 4: FD cost for Once-through nuclear fuel cycle**

<table>
<thead>
<tr>
<th>Country</th>
<th>Reference</th>
<th>Mass (tU)</th>
<th>Reference Cost (M€)</th>
<th>Reference Cost (M€ 2012)</th>
<th>TR_EVOL model (M€)</th>
<th>Relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finland</td>
<td>[15]</td>
<td>5 500</td>
<td>3 330</td>
<td>3 330</td>
<td>3 239</td>
<td>-2.7%</td>
</tr>
<tr>
<td>Spain</td>
<td>[11]</td>
<td>6 765</td>
<td>3 000</td>
<td>3 450</td>
<td>3 475</td>
<td>1.1%</td>
</tr>
<tr>
<td>Sweden</td>
<td>[10]</td>
<td>9 471</td>
<td>2 500</td>
<td>3 575</td>
<td>3 814</td>
<td>6.6%</td>
</tr>
<tr>
<td>Canada</td>
<td>[16]</td>
<td>192 000</td>
<td>9 749</td>
<td>14 167</td>
<td>13 826</td>
<td>-2.4%</td>
</tr>
</tbody>
</table>

Considering that the cost comparison performed for FD in Open cycles validates this model (provided that the correct parameters are used), the main question now is if this model can be also applied for FDs in fuel cycles with reprocessing strategies. For that, two fuel cycle scenarios with partial reprocessing strategies (Switzerland and France) have been assessed. Table 5 shows the mass for storing and the cost estimation given by bibliography and the estimation made by TR_EVOL model.

For Switzerland, which is planning to reprocess one third of its 3 400 t of SF generated, the proposed cost is 3 020 MEuro. Applying the model to the 2 200 t of UO$_2$ SF stored as in the Open cycle case and the 52 t of HLW generated from the 1 200 t of UO$_2$ reprocessed stored in universal canisters vitrified (UC-V), the result is close to the referenced value with a 7.9% difference. On the other hand, for the French FD case the reprocessing assumptions taken from the International Panel of Fissile Materials [17] were assessed. This reference argues that at EOC 17 600 t of UO$_2$ and 4 800 t of MOX will be placed along with 1 550 t of HLW from the reprocessing of 36 100 t of UO$_2$. The result shows that the value calculated by TR_EVOL model underestimates the reference value by an 11%.

**Table 5: FD cost for reprocessing strategies (masses in t)**

<table>
<thead>
<tr>
<th>Country</th>
<th>Reference</th>
<th>UO$_2$ SF</th>
<th>MOX SF</th>
<th>HLW</th>
<th>Reference cost (M€)</th>
<th>Reference cost (M€ 2012)</th>
<th>TR_EVOL model (M€)</th>
<th>Relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switzerland</td>
<td>[18]</td>
<td>2 200</td>
<td>0</td>
<td>52</td>
<td>2 770</td>
<td>3 020</td>
<td>2 780</td>
<td>-7.9%</td>
</tr>
<tr>
<td>France</td>
<td>[17]</td>
<td>17 600</td>
<td>4 800</td>
<td>1 320</td>
<td>12 200</td>
<td>13 981</td>
<td>12 409</td>
<td>-11.2%</td>
</tr>
</tbody>
</table>

It is clear that the differences between the model results and the references data are part of the uncertainty produced by the lack of useful information about the cost of the HLW storage, and also by the intermediate level waste generated by reprocessing and not considered in the model. However, the results show that the model predicts reasonably well the cost of the FD for both open cycle scenarios and scenarios with reprocessing strategies.

**Model improvements**

Even though estimates carried out by ID and FD models can be considered suitable for fuel cycle analyses and studies, TR_EVOL code includes some features that may improve significantly the performance...
of its simulations. The main improvement to be considered is the thermal limit for the FD and ID management. Most studies consider the mass for storing as a material with some years of decay, i.e. 5 years of cooling decay before ID storing or 50 years for FD. However, those cases are strongly dependent on fuel cycle parameters as the fuel cycle strategy, reactor and fuel type, burnup, etc. Modifications of these parameters between fuel cycle scenarios could change the years of cooling time required for the SF to cope with the thermal limitations of the ID and FD designs, deeply impacting the mass to store per canister.

The thermal limit considered for FD design in granite and clay to ensure that the maximum temperature (100°C) in the rock to preserve its integrity is of 1.2 kW per canister in Spain [21] or 1.7 kW in Finland [14]. For instance, for the particular FD designs of Spain, Sweden, Finland and Switzerland, about 4 UO₂ SFA can be stored per canister. However, if the thermal heat of the SFA exceeds the thermal limit, the number of assemblies per canister must be reduced, having an impact in the required gallery length and in the cost.

A different process is carried out for the HLW. According to reference [22] the HLW mass per glass is limited to 56 kg for FP and reprocessing losses. However this mass depends on the fuel type, irradiation condition, etc. Consequently, the mass per glass varies along the fuel cycle scenario and by source. Thus, the thermal limit is required as a condition for the HLW loading process. The importance lies in that HLW from cooler SF allows loading more material into the glass, reducing the associated cost of storing and encapsulation processes.

These improvements have already been implemented in the code, although their results have not been used for the validation of the economic model, hence they are considered to be beyond the scope of this work.

Conclusions

In this work, the validation of the TR_EVOL economic module has been carried out. On the one hand, the comparison between the results obtained by TR_EVOL and ARCAS project (by means the NRG Model) shows that the economic model works correctly for the three components of the LCOE analysed: investment costs, fuel cost and O&M cost.

On the other hand, the estimation of the key parameters and unit costs for the implementation of the ID and FD economic models was carried out making use of the current information available about those disposal costs.

For the ID model, the Swedish and Spanish concepts were evaluated considering that they may provide useful information to the model for a generic ID when the user does not have enough data.

For the verification of the FD model the information about a number of FD concepts (Spanish, Finnish, Swedish, Canadian, French and Swiss) was used to predict the FD cost for once-through and reprocessing strategies. Results revealed that the parameters and unit costs calculated and used in the model led to satisfactory approximations for the cost of the FD required in these scenarios.

It can be concluded that the TR_EVOL economic module is prepared for the economic assessment of a generic fuel cycle scenario, making use of the unit costs provided by bibliography or developed here.

Acknowledgements

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References


Assessment of Proliferation Risk Related to Various Fuel Cycle Scenarios in Finland

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Abstract

Some advanced fuel cycle scenarios have been previously calculated with the COSI6 code in order to determine the potential impact of partitioning and transmutation (P&T) technologies on spent nuclear fuel management in Finland. The focus has been on the transuranic inventories and decay heat production in the final repository, the latter of which was assumed to be the restricting factor for the repository capacity. As an extension to these calculations the proliferation resistance considerations were added to the fuel cycle scenarios in the present study. The simulations were again performed with COSI6 and one of the objectives was to investigate its applicability to proliferation resistance analysis.

The calculated scenarios comprised a reference scenario and fuel cycle scenarios aiming at plutonium and minor actinide incineration through P&T. The reference scenario comprised the currently operating four light-water reactors (LWR) with the combined capacity of ~2 800 MWe and the ones under construction or in preparation, with additional ~4 400 MWe. The last of these units will be closed around 2090 and no new LWRs will be built thereafter. In the basic P&T scenario, some of the retired capacity is replaced with sodium-cooled fast reactors (SFR) and a gradual nuclear phase-out is assumed in 120 years.

Proliferation resistance is a broad subject comprising several factors such as government policy, facility security and nuclear material properties. The present study concentrates on the technical features of the nuclear material streams and inventories at each time step. The main factors of interest with this focus are fissile materials, heat producers and even plutonium isotopes due to their role as major spontaneous neutron source. These figures do not directly provide comparable information about the related proliferation risk, so several methods have been developed to convert them into single comparable risk values. One of them is the Charlton’s method that is based on the multi-attribute utility analysis. It was utilised in the present study as far as applicable with COSI6.

Introduction

The once-through fuel cycle has been adopted as the currently valid policy for the spent nuclear fuel management in Finland. The preparations to open the geologic repository at Olkiluoto have progressed both technically and administratively and the first nuclear waste capsules could be deposited into the repository soon after 2020. As there are no plans to initiate recycling of the spent fuel in the foreseeable future, a significant amount of waste will be disposed before any kind of reprocessing could be started, as far as no drastic delays to the final disposal schedule is assumed.

However, the current yet uncertain plans suggest that nuclear power is going to play an important role in the Finnish electricity generation far into the future, leading to the continuous issue of spent fuel management. Furthermore, it will be possible to retrieve the disposed spent fuel before the repository caves are sealed. We may therefore assume in purely academic fuel cycle studies – like the present one – that all the spent fuel resulting from the operation of the Finnish power plants can be recycled.
When partitioning and transmutation technologies are introduced, the question of proliferation resistance of the system becomes more relevant than in the currently valid once-through strategy including no reprocessing. The present study concentrates purely on the technical barriers of the material at various steps of the cycle. At this moment with no information about any technical or administrative details related to the hypothetical nuclear energy system it is impossible to evaluate the risks that depend on the quality of the safeguard measures and the political environment.

Overview of the simulated scenarios

The current nuclear power production fleet in Finland consists of two VVERs with 488 MWe output (Loviisa-1 and -2) and two Nordic BWRs (Olkiluoto-1 and -2) producing 880 MWe each. They started their commercial operation within a rather short time period around 1980. A 1 600-MWe EPR is under construction to become Olkiluoto-3, in addition to which two major units are under consideration: Olkiluoto-4 and Hanhikivi-1 (FH-1). These units were granted the decision-in-principle, or the political go-ahead, in 2010 by the parliament, but since then both of these projects have been subjected to a new political consideration after the power utilities behind the projects have been bound to diverge essentially from their original plans. Decisions are expected during the autumn of 2014, but the fate of the projects is open at the moment of writing the present study.

Regardless of these uncertainties, it is assumed in the reference scenario of this study that both of the planned units will be built in the near future. The current and expected fleet of nuclear power plants in Finland is expressed in Table 1 as modelled in the simulations. The uncertainties related to the construction and operating schedules are assumed to cause negligible deterioration to the results. Larger inaccuracies are due to the assumptions of for example constant power and removal burnup throughout the whole operating history.

Table 1: The current and anticipated nuclear reactor fleet in Finland in the simulations without any better information, the Ol-4 unit is presumed to be EPR

<table>
<thead>
<tr>
<th>Unit</th>
<th>Operator</th>
<th>Power (MWe)</th>
<th>Reactor Type</th>
<th>Estimated Lifetime</th>
<th>Average burnup (GWD/tHM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loviisa-1 (Lo-1)</td>
<td>Fortum</td>
<td>488</td>
<td>VVER V-213</td>
<td>1977-2027</td>
<td>40.6</td>
</tr>
<tr>
<td>Olkiluoto-1 (Ol-1)</td>
<td>TVO</td>
<td>880</td>
<td>BWR-2500</td>
<td>1979-2039</td>
<td>39.5</td>
</tr>
<tr>
<td>Loviisa-2 (Lo-2)</td>
<td>Fortum</td>
<td>488</td>
<td>VVER V-213</td>
<td>1981-2029</td>
<td>40.6</td>
</tr>
<tr>
<td>Olkiluoto-2 (Ol-2)</td>
<td>TVO</td>
<td>880</td>
<td>BWR-2500</td>
<td>1982-2042</td>
<td>39.5</td>
</tr>
<tr>
<td>Olkiluoto-3 (Ol-3)</td>
<td>TVO</td>
<td>1 600</td>
<td>EPR</td>
<td>2015-2075</td>
<td>45.1</td>
</tr>
<tr>
<td>Olkiluoto-4 (Ol-4)</td>
<td>TVO</td>
<td>~1 600</td>
<td>?</td>
<td>2030-2090</td>
<td>45.1</td>
</tr>
<tr>
<td>Hanhikivi-1 (FH-1)</td>
<td>Fennovoima</td>
<td>1 200</td>
<td>VVER AES-2006</td>
<td>2024-2084</td>
<td>46.0</td>
</tr>
</tbody>
</table>

Source for the average burnup information of Loviisa-1 and -2 and Olkiluoto-1, -2 and -3: the construction licence application of the Olkiluoto repository. The burnup figures for OL-4 and FH-1 are based on the estimate that they are similar to that of OL-3, but the estimate is rather conjectural.

The basic partitioning and transmutation (P&T) scenario of the study follows the previous fuel cycle scenario simulations that were performed to assess the transuranic waste inventory [1] and the capacity of the final disposal repository [2] in Finland. It is assumed that when the LWRs of the reference scenario are closed near the end of the century, only fast reactors will be built thereafter. At first two large sodium-cooled reactors (SFR) would be built to operate for 60 years, after which a similar reactor would operate for another 60 years. The two fast reactors would generate similar amount of power as all the four units online at the moment put together. It may be worthwhile to mention that there is no official Finnish energy strategy stretching to that far, and the scenarios presented in this study could be as good or bad guess as any other scenarios.
The fuel cycle simulations were performed with the COSI6 code [3], developed by CEA, France. The simulated fast reactor model is based on the French SFR-V2B [4] concept with oxide fuel and electric power 1450 MW. The core model of the concept represents a break-even core in the sense that the fissile inventory remains approximately constant over the irradiation period. Even if the concept does not represent the most up-to-date design for a large base-load fast reactor in the French plans – the state-of-the-art concept is called CFV – the conclusions from fuel cycles’ point of view should be reasonable enough. A practical restriction for possible reactor concepts to be simulated was defined by the availability of the cross-section libraries that CESAR [5] - the fuel depletion code that COSI employs – requires.

The following scenarios were simulated within the present study:

- **Reference (later in tables LWR ref):** only the LWR fleet presented in Table 1 and a complete nuclear phase-out thereafter.
- **Basic P&T with plutonium recycling (Pu recycling):** LWR fleet of the reference scenario followed by two fast reactors (1450 MWe) operating for 60 years and one similar fast reactor after them; only plutonium was recycled with 100% reprocessing efficiency.
- **LWR-MOX and P&T with Pu recycling (MOX + Pu recycling):** as the basic P&T with Pu recycling, but Olkiluoto-4 was partly fuelled with U-Pu mixed-oxide (MOX) fuel, or more precisely, the fuel consisted of 75% UOX and 25% MOX.
- **P&T with homogeneous minor actinide (MA) recycling (MA recycling):** like the P&T with Pu recycling, but all minor actinides (Am, Np, Cm) were recycled along with plutonium; 99.9% reprocessing efficiency was assumed.

### Proliferation resistance

The earlier simulations concerning advanced fuel cycles in the future in Finland have provided some quantity to the anticipated transuranic inventories and repository capacity requirements following the transition to P&T policy. The transition would involve many issues to be considered, proliferation resistance being one of them. The once-through cycle with final disposal into a deep geological repository is generally accepted to be strongly proliferation resistant because of for example unfavourable plutonium isotope composition for weapon production and low fissile material concentration bound in highly radioactive mixture. If the spent fuel is deposited into a deep repository quickly enough with respect to the attenuation of the radioactivity, the hundreds of meters of rock impede the potential proliferator while the attractiveness of the material is slightly improved.

When partitioning and transmutation are introduced, some proliferation resistance features are compromised because of the need to separate the transuranic elements from the whole spent fuel matrix. On the other hand, multiple recycling affects the plutonium quality and it can be made less suitable for weapon manufacturing with proper partitioning and transmutation strategies. Several methods have been created to assess the proliferation risk or resistance related to various fuel cycles, but ultimately all of them contain some subjectivity. The Charlton method [6], based on the multi-attribute utility analysis (MAUA), was utilised in the present study where applicable.

The method ultimately yields a single nuclear security value. One of its key elements is the proliferation resistance value (PR) for each process in the system. It is a weighted sum of utility functions of various attributes with each process:

\[
P R_i = \sum_{j=1}^{J} w_j u_j(x_{ij})
\]

where \( w_j \) represents the weight for attribute \( j \), \( u_j \) the utility function for attribute \( j \) and \( x_{ij} \) the input value for the utility function for attribute \( j \) in process \( i \).
The full method consists of 14 attributes, some of which – such as the heating rate of plutonium and radiation dose rate caused by the material - are measurable quantities and some very subjective or good guesses at best, like the frequency of measurement or probability of unidentified movement. Furthermore, some of the attributes would be clearly measurable, but would require detailed information of the system. Thus, we concentrate on the material features that result from the simulations of the chosen fuel cycle strategies. For each utility function zero denotes no proliferation resistance at all and unity the maximum resistance.

The measurable nuclear material properties of the Charlton’s method provided by the COSI6 code are:

- Heating rate of plutonium (in watts per kilogram of Pu), weight of utility function \( w = 0.05 \)
- Weight fraction of even plutonium isotopes, \( w = 0.06 \)
- Fissile material concentration in significant quantities (SQ/t), defined by the IAEA to express the minimum amount of material above which the production of an explosive nuclear device cannot be excluded, \( w = 0.10 \)
- Inventory of fissile material (in SQs), \( w = 0.05 \).

The fifth technical measure that could be extracted from the simulation results is the radiation dose originating from the material, but the dose calculation function of COSI had not been completed at the time of these calculations.

According to the Charlton’s method, the fuel element should be tracked from the uranium mine through the whole cycle into the final repository and the proliferation resistance value calculated at each process step. In the present study, the method is applied in a rather simplified way. The evaluation of the PR values is performed at process steps where the nuclear material is somehow handled or transferred. In our rough analysis these steps are removal from the reactor into intermediate store and later final disposal in the once-through scenario. When P&T scenarios are considered, the output from intermediate LWR spent fuel store, fabrication of FR fresh fuel and fuel removal from FR to the intermediate SF store are the additional steps. Also the MOX in- and output values are studied in the scenario where MOX is burned in one of the LWRs.

For simplicity, it was assumed in the simulations that the average removal burnup for all reactors remains constant over the whole operating history. The assumption results in constant spent fuel composition when the LWRs are considered, whereas the composition of the fresh and consequently also the spent FR-fuel change over time. Therefore it is essential to evaluate the proliferation resistance at multiple time points, but it was observed that, in general, the variations over time at the process steps are rather small.

**Heating rate of plutonium**

The utility function \( u \) for heat production rate \( x \) from plutonium is calculated according to:

\[
\begin{align*}
u &= 1 - \exp \left[ -3 \left( \frac{x}{x_{\text{max}}} \right)^{0.8} \right] \\
\end{align*}
\]

where \( x_{\text{max}} \) is 570 W/kg representing the heating rate of pure Pu-238. For the spent LWR fuel the heat production varies between 44.5 and 54.7 W/kg with the average of 50.5 W/kg over the whole time of the LWRs in operation. In terms of the respective utility function, this would result in the range 0.323-0.369 and the average \( u = 0.351 \). A 40-year on-ground cooling period was assumed between unloading from the reactor and final disposal. During the ~110 years of disposal, the heating rate varies between 12.5 and 14.5 W/kg, resulting in \( u = 0.132-0.147 \).
Most of the advanced fuel cycle u-values are lower at the process steps, or approximately equally high. The most notable exception is the MA recycling scheme, where the utility function scores much higher at disposal, i.e. 0.200-0.240 with decreasing trend towards the end of the simulated time.

The average values of the heating rate utility function at the process steps (described above) of each scenario are listed in Table 2. However, the average value should be regarded as more like indicative particularly for the fresh FR fuel. The cooling time of the spent fuel, i.e. the raw material for the FR fuel varies a lot, causing also large variation to the heating rate of plutonium.

Table 2: The utility function values of the heating rate of plutonium

<table>
<thead>
<tr>
<th>Scenario</th>
<th>LWR ref</th>
<th>Pu recycling</th>
<th>MOX + Pu recycling</th>
<th>MA recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOX SF out of LWR</td>
<td>0.345</td>
<td>0.345</td>
<td>0.345</td>
<td>0.345</td>
</tr>
<tr>
<td>LWR-SF out of interim store</td>
<td></td>
<td></td>
<td>0.138</td>
<td>0.144</td>
</tr>
<tr>
<td>MOX loaded into LWR</td>
<td></td>
<td></td>
<td>0.143</td>
<td></td>
</tr>
<tr>
<td>MOX out of LWR</td>
<td></td>
<td></td>
<td>0.726</td>
<td></td>
</tr>
<tr>
<td>Fuel loaded into FR</td>
<td>0.102</td>
<td></td>
<td>0.109</td>
<td>0.233</td>
</tr>
<tr>
<td>Fuel out of FR</td>
<td>0.116</td>
<td></td>
<td>0.125</td>
<td>0.279</td>
</tr>
<tr>
<td>SF into repository</td>
<td>0.139</td>
<td>0.079</td>
<td>0.080</td>
<td>0.201</td>
</tr>
</tbody>
</table>

Weight fraction of even plutonium isotopes

The PR impact caused by the fraction \( x \) of the even Pu isotopes of the total amount of plutonium is quantified according to the Charlton’s method as:

\[
u = 1 - \exp\left(-3.5 \cdot x^{1.8}\right)
\]

The fraction is a little above one third for the spent LWR fuel and a little less at the time of disposal. The fraction varies over time because the LWR units that are operating later have larger removal burnup, which tends to increase the amount of the even Pu isotopes. These fractions yield utility function values from 0.33 to 0.35 for the just irradiated fuel, whereas the value varies between 0.39 and 0.41 at the disposal.

In all fast reactor scenarios the weight fraction of even plutonium isotopes is at most of the process steps at least equally large or notably larger than at the calculated steps in the once-through scenario. The mere Pu recycling does not increase the fraction much, but introducing some MOX usage in LWR or MA recycling would cause more significant change. All the figures are listed in Table 3.

Table 3: The values of the utility function that describes the proliferation resistance resulting from the weight fraction of even plutonium isotopes.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>LWR ref</th>
<th>Pu recycling</th>
<th>MOX + Pu recycling</th>
<th>MA recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOX SF out of LWR</td>
<td>0.339</td>
<td>0.339</td>
<td>0.339</td>
<td>0.339</td>
</tr>
<tr>
<td>LWR-SF out of interim store</td>
<td></td>
<td></td>
<td>0.405</td>
<td>0.395</td>
</tr>
<tr>
<td>MOX loaded into LWR</td>
<td></td>
<td></td>
<td>0.396</td>
<td></td>
</tr>
<tr>
<td>MOX out of LWR</td>
<td></td>
<td></td>
<td>0.484</td>
<td></td>
</tr>
<tr>
<td>Fuel loaded into FR</td>
<td>0.433</td>
<td></td>
<td>0.489</td>
<td>0.496</td>
</tr>
<tr>
<td>Fuel out of FR</td>
<td>0.432</td>
<td></td>
<td>0.468</td>
<td>0.505</td>
</tr>
<tr>
<td>SF into repository</td>
<td>0.401</td>
<td>0.460</td>
<td>0.483</td>
<td>0.498</td>
</tr>
</tbody>
</table>
Fissile material concentration

The fissile material concentration $x$ is measured in significant quantities (SQs) of fissile material per metric ton of total material. An SQ is achieved with for example 8 kg plutonium, 75 kg low-enriched uranium or 25 kg americium. This metric is converted into PR utility function with:

$$u = \begin{cases} 
1, & \text{if } x < 0.01, \\
\exp \left( -2.5 \cdot \frac{x}{x_{\text{max}}} \right), & \text{if } x \geq 0.01,
\end{cases}$$

where $x_{\text{max}}$ denotes the maximum concentration 125 SQs/t that refers to pure plutonium. The Equation (4) gives values of 0.75 for both fuel removal from the reactors and final disposal, when the LWR reference scenario is studied. The variations over the period are of magnitude $10^{-3}$.

In the advanced fuel cycle scenarios the utility function yields values around 0.55 at all steps, especially when the Pu recycling scenario is studied. The scenario involving also minor actinide recycling shows slightly smaller values and some more fluctuation between the steps, but at most points the value is around 0.53. The moment of disposal shows a bit larger values, but not more than 0.57. When a MOX-fuelled LWR is considered, figures at about 0.59 are obtained at fuel input and 0.73 for output. All the average values are presented in Table 4.

Table 4: The utility function values resulting from the fissile material concentration

<table>
<thead>
<tr>
<th>Source of waste</th>
<th>LWR ref</th>
<th>Pu recycling</th>
<th>MOX + Pu recycling</th>
<th>MA recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOX SF out of LWR</td>
<td>0.756</td>
<td>0.756</td>
<td>0.756</td>
<td>0.756</td>
</tr>
<tr>
<td>LWR-SF out of interim store</td>
<td>0.758</td>
<td>0.758</td>
<td>0.758</td>
<td>0.758</td>
</tr>
<tr>
<td>MOX loaded into LWR</td>
<td></td>
<td>0.596</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOX out of LWR</td>
<td></td>
<td>0.726</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel loaded into FR</td>
<td>0.551</td>
<td>0.544</td>
<td>0.528</td>
<td></td>
</tr>
<tr>
<td>Fuel out of FR</td>
<td>0.555</td>
<td>0.550</td>
<td>0.536</td>
<td></td>
</tr>
<tr>
<td>SF into repository</td>
<td>0.758</td>
<td>0.572</td>
<td>0.555</td>
<td>0.569</td>
</tr>
</tbody>
</table>

According to these figures, it seems apparent that at all process steps higher fissile material concentration is on the move compared to the LWR scenario and the impact on proliferation resistance features of the material is significant. The only exception in the models appears with the waste flow from reprocessing to disposal. The flow contains only reprocessing losses – and in the Pu recycling scheme also fissile MAs – so the amount of fissile material is understandably relatively low. In terms of the utility function for fissile material concentration in the processing waste flow, values of 0.96 for Pu recycling and as much as 0.99 for MA recycling are achieved. The waste flow contents were not included into values of Table 4 for simplicity and because of their relatively small total mass.

Proliferation resistance values

The fourth metrics calculated by COSI, that is, the total fissile inventory at each site, does not affect this analysis, since it is essentially targeted to distinguish small and large stores. However, what is modelled in COSI simulations with respect to stores probably differs much from what could be anticipated for the real world. The storage sites in the COSI model were supposed to share all the waste of the same kind in the system, which makes some of the sites larger and the others smaller than what would be realistic. In practice, all of them would probably be large enough such that their proliferation resistance utility function would be zero.
Therefore the inventory was ignored and the proliferation resistance values were calculated on the basis of the three utility functions described above using the Equation (1). The PR values at each process steps are presented in Table 5. The figures suggest that in all P&T scenarios the proliferation resistance value calculated from the nuclear material properties is smaller than in the once-through cycle. The only exceptions are the final disposal in the minor actinide recycling scenario and the spent MOX fuel immediately after irradiation. Taking into account the radiation dose could alter the evaluation results. It is worthwhile to remember that these figures are comparable only between various scenarios. The PR values would be much higher, if all attributes of the Charlton’s method were taken into consideration.

**Table 5: The proliferation resistance values at various process steps (first column) in the simulated fuel cycle strategies**

<table>
<thead>
<tr>
<th></th>
<th>LWR ref</th>
<th>Pu recycling</th>
<th>MOX + Pu recycling</th>
<th>MA recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF out of LWR</td>
<td>0.113</td>
<td>0.113</td>
<td>0.113</td>
<td>0.113</td>
</tr>
<tr>
<td>LWR-SF out of interim store</td>
<td>0.107</td>
<td>0.107</td>
<td>0.107</td>
<td>0.107</td>
</tr>
<tr>
<td>MOX loaded into LWR</td>
<td></td>
<td>0.091</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOX out of LWR</td>
<td></td>
<td>0.118</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel loaded into FR</td>
<td>0.086</td>
<td>0.089</td>
<td>0.094</td>
<td></td>
</tr>
<tr>
<td>Fuel out of FR</td>
<td>0.087</td>
<td>0.089</td>
<td>0.098</td>
<td></td>
</tr>
<tr>
<td>SF into repository</td>
<td>0.107</td>
<td>0.088</td>
<td>0.088</td>
<td>0.124</td>
</tr>
</tbody>
</table>

**Long-term proliferation properties of the spent fuel**

It is known that over a very long time period the nuclear waste becomes less proliferation resistant in the repository due to the faster decay of Pu-238 and Pu-240 compared to Pu-239. Therefore we performed also very long-term repository inventory calculations with COSI for the scenarios of the study. The repository was assumed to accommodate no more waste after the 23rd century. According to the COSI calculations, thousands of significant quantities of fissile material will remain in the repository even several millennia after the disposal. The calculations also suggest that the plutonium isotope distribution approaches weapons-grade up to the surroundings of the year 30 000, as far as the mass fraction of even plutonium isotopes is considered as the limiting factor. This is depicted in Figure 1. Decreased heat production and radioactivity will have further reduced the proliferation resistance.

**Figure 1: The mass percentage of even plutonium isotopes of the total plutonium mass in the final disposal repository**

![Weight fraction of even Pu isotopes (%)](image-url)
Thus, the engineering analysis seems quite clearly indicating that a nuclear waste repository would transform towards weapons-grade plutonium mine. However, it is a completely different issue, whether this would actually provide any help to a potential proliferating regime of those days. They would probably have several easier ways to produce weapons of mass destruction than excavating plutonium from hundreds of meters of depth underground. Further speculation on the topic is left outside this study.

Conclusions

A simplified evaluation was performed to investigate the proliferation resistance associated with the advanced fuel cycle scenarios in the future in Finland. The fuel cycles were simulated using the COSI6 code. The obtained material data was converted into proliferation resistance measures using the Charlton’s method as far as applicable with COSI6. As a result of the calculations, somewhat weaker proliferation resistance for the process steps was encountered in the advanced fuel cycle scenarios compared to the reference scenario using only LWRs.

However, since our evaluation was based only on the nuclear material composition related features, not more than 4 out of 14 attributes comprising the Charlton’s method were considered in the study. Therefore the results must be taken at most indicative. The fifth – and extremely important – material feature would be radiation dose rate, which was not available from the COSI calculations. However, the dose rate could be, in principle, calculated with some other software using the COSI outputs, but that would require a major effort. Even in that case the evaluation based on the material properties would comprise only the first step in determining the absolute proliferation resistance values for various fuel cycle scenarios.

Modifying the simulation model of COSI would probably be the most productive next step towards more comprehensive analysis, since our model excluded a few Charlton’s attributes to be taken into account. Improvements could be achieved by adding more realistic elements into the spent fuel handling steps. These could be a finite time for reprocessing, fuel fabrication and transportation – instead of the zero time in our simulations - and modelling the interim storage sites so that the model corresponds to the physical locations of each site. The latter would enable credible evaluations for the inventory utility function.

Acknowledgements

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References


Performance Evaluation of a Transmutation Sodium-Cooled Fast Reactor in Recycling Scenarios

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Kyung Hee University, Republic of Korea
*Corresponding author

Abstract
Four recycling scenarios of spent fuel (SF) with pyroprocessing have been investigated for the 600 MWe transmutation sodium-cooled fast reactor, KALIMER. Performance evaluation was done with the code system REBUS connected with TRANSX and TWODANT. Scenario#1 involves pyroprocessing of CANDU SF. Since the recycling of CANDU SF does not present any safety issues, CANDU-Pyro-SFR system will be possible if the capacity of pyroprocessing is large enough. Scenario#2 consists of recycling PWR SF, with a different cooling time. As the cooling time increases, shutdown margin can be better due to decreasing excess reactivity. Scenario#3 is a case study for various levels of recovery factors of transuranics (TRU). The waste that is not recovered in the pyroprocess is classified as LILW (low and intermediate liquid waste) when the waste cooling time exceeds 300 years with TRU recovery factor of 99.9%. Scenario#4 considers the recovery factor of rare earth isotopes (RE). The RE recovery factor should be lowered to 20% or less in order to make the sodium void reactivity less than $7$.

Introduction
One of the current most important issues in the nuclear industry is the safe and reliable management of high-level radioactive wastes (HLW), such as spent fuel (SF). In Korea, SFs are temporarily stored at the power plants, but the storage capacity is expected to be full within the next 10 years. As in other parts of the world, option study on SF incineration has been actively pursued for the last few decades. One option is the recycling of SF for reuse as a fuel in sodium-cooled fast reactors (SFR).

Korea Atomic Energy Research Institute (KAERI) has redesigned a Gen-IV SFR, KALIMER reactor as a dedicated transmutation reactor for the recycling option with pyroprocessing [1]. This could be regarded as the best way to reduce the amount of SFs. These two technologies have been developed separately. However, the performance of pyroprocessing is not determined yet and no studies have so far been performed on the influence of options that can be changeable during the recycling system process using KALIMER reactor cores for TRU transmutation. Thus, SFR performance needs to be evaluated according to options that can be changeable during pyroprocessing.

In this study, the researchers aimed to design an SFR for TRU transmutation using the design parameters of KALIMER developed by KAERI and examine the design feasibility in advance by identifying the nuclear characteristics of reactor cores caused by various parameters in the material flow scheme of SF recycling. To achieve this goal, various achievable scenarios feasible in Korea have been tested to compare and evaluate impact on nuclear safety of SFR core and TRU transmutation efficiency.
Reference core design

The reactor core to be evaluated in this study was designed with reference to the design parameters in the KALIMER-600 TRU Burner Report, which was a SFR designed for transmutation developed at KAERI. The code used for the design and evaluation was a TRANSX/TWODANT/REBUS-3 code system [2-4], which is used for nuclear design in KAERI; nuclear data used were the ENDF/B-VII-based KAFAX library, recently modified by KAERI.

Figure 1: Radial configuration and R-Z two-dimensional model

<table>
<thead>
<tr>
<th>Table 1: KALIMER-600 TRU burner core design parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
</tr>
<tr>
<td>Core electric power (MWe)</td>
</tr>
<tr>
<td>Core thermal power (MWt)</td>
</tr>
<tr>
<td>Active core height (cm)</td>
</tr>
<tr>
<td>Number of rods per fuel assembly</td>
</tr>
<tr>
<td>Number of fuel assemblies (inner/outer)</td>
</tr>
<tr>
<td>Reactor core I/O temp. (°C)</td>
</tr>
<tr>
<td>Number of batches I/O cores</td>
</tr>
<tr>
<td>Cycle length (EFPD, days)</td>
</tr>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td>Fuel type</td>
</tr>
<tr>
<td>Smear density (inner/outer, %)</td>
</tr>
<tr>
<td>Assembly pitch (mm)</td>
</tr>
<tr>
<td>P/D ratio</td>
</tr>
<tr>
<td>Duct thickness (mm)</td>
</tr>
<tr>
<td>Fuel element length (cm)</td>
</tr>
<tr>
<td>Upper fission gas plenum length (/Na filled) (cm)</td>
</tr>
<tr>
<td>Gap distance between ducts (mm)</td>
</tr>
<tr>
<td>Lower end plug and shielding (cm)</td>
</tr>
<tr>
<td>Wire wrap diameter (mm)</td>
</tr>
<tr>
<td>Fuel rod outer diameter (mm)</td>
</tr>
<tr>
<td>Fuel cladding thickness (mm)</td>
</tr>
<tr>
<td>Cladding material</td>
</tr>
</tbody>
</table>
Evaluated recycling scenarios

Change in external feed composition

Korea has two types of reactors: PWR and CANDU. The nuclear power plants in Korea temporarily store SFs discharged from less than one year to more than 30 years. Researchers need to determine which characteristics can be obtained if SFs are processed using pyroprocessing and used in the SFR. There is less than 0.4% of TRU contained in SFs in CANDU. Therefore, the efficiency and economic feasibility is low in pyroprocessing to recover TRU. However, pyroprocessing of CANDU SF may still be meaningful to reduce the volume of HLW.

Thus, the aim of Scenario#1 is to compare the performance of SFR core consisting of the fuels made from CANDU SF with the reference scenario. In addition, the capacity of a pyroprocessing facility to be commercialised needs to be determined to introduce CANDU-Pyro-SFR connection system.

The aim of Scenario#2 is to evaluate the SFR performance while changing nuclide composition ratios by differentiating the cooling time of PWR SF, which is considered in the reference recycling scenario.

The performance of pyroprocessing in these two cases assumes that the recovery factors of uranium, TRU, and Rare Earth element (RE) are 100%, 99.9%, and 5% respectively.

TRU recovery factor in pyroprocessing

Although pyroprocessing has been advanced considerably, the recovery factor has not yet been finalised, and recycling has not been achieved to date by implementing a recycling system. As such, the recovery factor can vary unexpectedly and differently from the estimation in a real site. In particular, research on increases in the TRU recovery factor in pyroprocessing has continued. As the TRU recovery factor increases, transmutation and incineration of more amounts of TRU can be done, and TRU content within the remaining uncollected waste is reduced, thereby making it easier to process waste due to the reduced radioactive level. Thus, the goal of Scenario#3 is to determine the radioactivity and decay heat generation of waste and SFR performance according to changes in the TRU recovery factor.

RE recovery factor in pyroprocessing

Pyroprocessing is an electrochemical treatment technology using molten salt medium and electricity. RE is thus collected when TRU is collected because of their similar electrochemical properties. The RE recovery factor of 5% in the existing recycling scenario is difficult to achieve with the current technology level and requires a number of pyroprocessings to reduce the collection of RE as much as possible. The recovery factor of RE can differ greatly according to the number of pyroprocessings. If the RE recovery factor decreases, the RE content in the fuels loaded in the SFR decreases as well, which makes the SFR performance significantly different as well as enhancing safety. Thus, Scenario#4 evaluates the SFR performance and safety according to increases in the RE recovery factor.
Table 2: Purpose of each recycling scenario

<table>
<thead>
<tr>
<th>Recycling Options</th>
<th>Reason &amp; Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario #1 Pyroprocessing</td>
<td>Need to reduce the volume of a radioactive waste.</td>
</tr>
<tr>
<td>of CANDU SF</td>
<td>To evaluate SFR performance using CANDU SF and to check the capacity of pyroprocess facility.</td>
</tr>
<tr>
<td>Scenario #2 Change in cooling time of PWR SF</td>
<td>SFR design is easier and safer when the SFR fuels are made of the same composition; same cooling time of PWR SF.</td>
</tr>
<tr>
<td></td>
<td>To check the transmutation efficiency or excess reactivity of SFR using PWR SF having different cooling times and to choose the time that has a good result.</td>
</tr>
<tr>
<td>Scenario #3 TRU recovery factor in Pyro</td>
<td>Radioactivity and heat generation rate of the waste from pyroprocessing depend on TRU recovery factor. Actually, the effects of FP are dominant in initial period. But TRU is more effective than FP when the waste storage time is longer and longer.</td>
</tr>
<tr>
<td>Scenario #4 RE recovery factor in Pyro</td>
<td>The target value of RE recovery factor is 5% but this value needs many times the process of electro-winning. So that is not economical and not efficient.</td>
</tr>
<tr>
<td></td>
<td>No need to reduce RE recovery factor to 5% if it has no problem about safety.</td>
</tr>
</tbody>
</table>

Sensitivity test results

The criteria of several performance parameters were set to identify the validity and safety limit in each scenario, and each scenario was evaluated based on the criteria:

1. To have sufficient shutdown margin, smaller excess reactivity is better.
2. The purpose of the limit value of sodium void reactivity is to make the total reactivity that is inserted into the core under $1 when an emergency accident occurs. For metal fuels, it should be $7$ to $8$ at a maximum.
3. The TRU support ratio should be above 1.2 and as large as possible in order to consume the TRU in PWR effectively.
(4) The TRU transmutation ratio should be above 20% and as large as possible to increase efficiency of the TRU transmutation.

(5) The TRU content ratio of the ternary alloy fuel of U-TRU-Zr should not exceed 30wt.% recommended by the currently useable metal fuel database.

The definition of the TRU transmutation ratio in Criteria (4) is the ratio of TRU transmutation out of the loaded TRU amount. This definition can be expressed as follows:

\[
\text{TRU transmutation ratio} = \frac{\text{Amount of charged TRU} - \text{Amount of discharged TRU}}{\text{Amount of charged TRU}}
\]

(1)

**Scenario#1: Pyroprocessing of CANDU SF**

In Korea, the amount of SF generated in four CANDU units is almost same as in twenty PWR units; about 97 tons of SF is generated in one CANDU unit for 1 year. If pyroprocessing of CANDU SF is realised, the volume of HLW could be significantly reduced and there would be no need to import natural uranium. Therefore, this scenario of pyroprocessing of CANDU SF is reasonable unless SFR has bad performance or safety problems.

The composition of heavy metal nuclides is listed in Table 3. CANDU SF contains a small amount of TRU because of a low discharged burnup, but the fissile Pu composition ratio is high. If fissile material is denser or the amount is larger, fission reaction is more likely to happen and the reactivity is increased. Thus, using CANDU SF composition has larger excess reactivity at BOEC (beginning of equilibrium cycle) than using PWR SFs. But it does not have safety problem about reactivity control or shutdown margin.

**Table 3: Composition of external feed after pyroprocessing**

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>PWR SF→SFR fuel</th>
<th>CANDU SF→SFR fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-234</td>
<td>0.0002</td>
<td>0.0000</td>
</tr>
<tr>
<td>U-235</td>
<td>0.0077</td>
<td>0.0022</td>
</tr>
<tr>
<td>U-236</td>
<td>0.0069</td>
<td>0.0008</td>
</tr>
<tr>
<td>U-238</td>
<td>0.9853</td>
<td>0.9970</td>
</tr>
<tr>
<td>Total U</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>Pu-238</td>
<td>0.0278</td>
<td>0.0010</td>
</tr>
<tr>
<td>Pu-239</td>
<td>0.4264</td>
<td>0.6545</td>
</tr>
<tr>
<td>Pu-240</td>
<td>0.2019</td>
<td>0.2483</td>
</tr>
<tr>
<td>Pu-241</td>
<td>0.0790</td>
<td>0.0305</td>
</tr>
<tr>
<td>Pu-242</td>
<td>0.0685</td>
<td>0.0117</td>
</tr>
<tr>
<td>Total Pu</td>
<td>0.8036</td>
<td>0.9460</td>
</tr>
<tr>
<td>Np-237</td>
<td>0.0583</td>
<td>0.0067</td>
</tr>
<tr>
<td>Am-241</td>
<td>0.0532</td>
<td>0.0191</td>
</tr>
<tr>
<td>Am-242m</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Am-243</td>
<td>0.0204</td>
<td>0.0004</td>
</tr>
<tr>
<td>Cm-243</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Cm-244</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td>Cm-245</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>Cm-246</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>RE</td>
<td>0.0575</td>
<td>0.0278</td>
</tr>
<tr>
<td>Total TRU,RE</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

* PWR discharged burnup, 4.5 wt.%, 55,000MWD/tU, cooling time 10 yr
* CANDU discharged burnup, 0.71 wt.%7500MWD/tU, cooling time 10 yr
To reach the equilibrium cycle of SFR using CANDU SF, TRU external feed (EF) supplied about 200 kg and TRU composition ratio is 0.41% in CANDU SF. So, about 49 tons of CANDU SF is needed to make TRU EF for SFR equilibrium cycle. Thus, the recycling facility to be commercialised must have a pyroprocessing capacity of 49 tHM/cycle.

### Table 4: Performance parameters using CANDU SF and PWR SF

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PWR SF</th>
<th>CANDU SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excess reactivity at BOEC (pcm)</td>
<td>3 892</td>
<td>4 312</td>
</tr>
<tr>
<td>Total fissile / Total HM charged in SFR each cycle (kg)</td>
<td>495.89 / 3 486.09</td>
<td>538.18 / 3 494.15</td>
</tr>
<tr>
<td>TRU transmutation ratio (%)</td>
<td>20.32</td>
<td>20.43</td>
</tr>
<tr>
<td>Amount of TRU EF for SFR equilibrium cycle (kg/391days)</td>
<td>218.24</td>
<td>199.91</td>
</tr>
<tr>
<td>TRU composition ratio in the SF (%)</td>
<td>1.4</td>
<td>0.41</td>
</tr>
<tr>
<td>Amount of SF needed to pyroprocess for TRU EF supplying (ton/391days)</td>
<td>15.59</td>
<td>48.76</td>
</tr>
</tbody>
</table>

### Scenario#2: Change in cooling time of PWR SF

As the cooling time of PWR SF changes, heavy metal nuclides start to decay with different half-lives from each other, resulting in a change in the composition ratio. This scenario determines the SFR performance when PWR SFs cooled from a minimum of one year to a maximum of 50 years are supplied to SFR using pyroprocessing. As shown in Table 5, a nuclide amount of Pu-241, which produced a relatively large amount and had shorter half-life among TRUs, decreased greatly so that the amount of Am-241, its daughter nuclide, increased greatly.

### Table 5: Amounts of nuclides in 1ton of SF according to the cooling time

<table>
<thead>
<tr>
<th>Cooling time</th>
<th>1.0 yr</th>
<th>10.0 yr</th>
<th>20.0 yr</th>
<th>30.0 yr</th>
<th>40.0 yr</th>
<th>50.0 yr</th>
<th>Diff.(50-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-234</td>
<td>183.4</td>
<td>213.4</td>
<td>244.3</td>
<td>272.9</td>
<td>299.3</td>
<td>323.7</td>
<td>140.3</td>
</tr>
<tr>
<td>U-235</td>
<td>7117.9</td>
<td>7119.5</td>
<td>7121.3</td>
<td>7123.1</td>
<td>7124.9</td>
<td>7126.7</td>
<td>8.8</td>
</tr>
<tr>
<td>U-236</td>
<td>6365.9</td>
<td>6368.7</td>
<td>6371.8</td>
<td>6375</td>
<td>6378.1</td>
<td>6381.3</td>
<td>15.4</td>
</tr>
<tr>
<td>U-238</td>
<td>915405</td>
<td>915405</td>
<td>915405</td>
<td>915405</td>
<td>915405</td>
<td>915405</td>
<td>0.0</td>
</tr>
<tr>
<td>Np237</td>
<td>859.8</td>
<td>866.9</td>
<td>883.1</td>
<td>904.6</td>
<td>929.2</td>
<td>955.6</td>
<td>95.8</td>
</tr>
<tr>
<td>Pu238</td>
<td>438.4</td>
<td>413.8</td>
<td>382.5</td>
<td>353.4</td>
<td>326.6</td>
<td>301.9</td>
<td>-136.5</td>
</tr>
<tr>
<td>Pu239</td>
<td>6346.2</td>
<td>6345.1</td>
<td>6343.7</td>
<td>6342.3</td>
<td>6340.8</td>
<td>6339.4</td>
<td>-6.8</td>
</tr>
<tr>
<td>Pu240</td>
<td>2969.6</td>
<td>3004.8</td>
<td>3030.9</td>
<td>3047.7</td>
<td>3058.1</td>
<td>3064.2</td>
<td>94.6</td>
</tr>
<tr>
<td>Pu241</td>
<td>1815.1</td>
<td>1175.1</td>
<td>724.8</td>
<td>447.1</td>
<td>275.8</td>
<td>170.1</td>
<td>-1645.0</td>
</tr>
<tr>
<td>Pu242</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
<td>1020</td>
<td>0.0</td>
</tr>
<tr>
<td>Am241</td>
<td>159.1</td>
<td>791.9</td>
<td>1225.7</td>
<td>1481.5</td>
<td>1627.8</td>
<td>1767.5</td>
<td>1547.6</td>
</tr>
<tr>
<td>Am242m</td>
<td>1.6</td>
<td>1.5</td>
<td>1.4</td>
<td>1.4</td>
<td>1.3</td>
<td>1.2</td>
<td>-0.4</td>
</tr>
<tr>
<td>Am243</td>
<td>303.4</td>
<td>303.1</td>
<td>302.8</td>
<td>302.6</td>
<td>302.3</td>
<td>302</td>
<td>-1.4</td>
</tr>
<tr>
<td>Cm242</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-6.0</td>
</tr>
<tr>
<td>Cm243</td>
<td>1</td>
<td>0.8</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>-0.7</td>
</tr>
<tr>
<td>Cm244</td>
<td>132.4</td>
<td>93.8</td>
<td>63.9</td>
<td>43.6</td>
<td>29.7</td>
<td>20.3</td>
<td>-112.1</td>
</tr>
<tr>
<td>Cm245</td>
<td>6.3</td>
<td>6.3</td>
<td>6.3</td>
<td>6.3</td>
<td>6.3</td>
<td>6.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Cm246</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 6 shows the performance parameters according to the cooling time. As the cooling time becomes longer, the composition ratio of Pu-241 within TRU coming from PWR SF is reduced. Since a composition ratio of Pu-241 whose fission XS is large is reduced, the burnup reactivity swing will be reduced as well, which causes the shutdown margin to increase, thereby enhancing safety. Then, in order to achieve a threshold at the ending of equilibrium cycle (EOEC), a supplied amount of TRU is increased by an amount that corresponds to the reduced amount of Pu-241. The increased amount of TRU supplied externally in every cycle means that TRU transmutation increases every cycle. Although the transmutation ratio of Pu is reduced due to the reduced composition ratio, the transmutation efficiency of MA increases greatly so that the total TRU transmutation ratio shows a minimal difference around 0.03% between reference and 50 years of cooling. The TRU supply amount increases, but the TRU transmutation ratio is slightly reduced so that the amount of TRU left in waste increases, but only minimally. The TRU content ratio loaded in the fuel also increases, but within the range of design standard 30wt.%. Thus, in the scenario where the cooling time of PWR SF changes, the reactivity control becomes easier as the cooling time becomes longer, resulting in better safety and MA transmutation performance.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cooling time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excess reactivity (pcm)</td>
<td>4174 4031 3891 3688 3557 3485 3438</td>
</tr>
<tr>
<td>Amount of TRU transmutation (kg)</td>
<td>216.16 216.45 216.80 217.30 217.64 218.01 218.28</td>
</tr>
<tr>
<td>TRU support ratio</td>
<td>1.264 1.266 1.268 1.271 1.273 1.275 1.276</td>
</tr>
<tr>
<td>TRU transmutation ratio (%)</td>
<td>20.34 20.33 20.32 20.31 20.30 20.30 20.29</td>
</tr>
<tr>
<td>Pu transmutation ratio (%)</td>
<td>20.48 20.19 19.90 19.46 19.18 19.01 18.90</td>
</tr>
<tr>
<td>MA transmutation ratio (%)</td>
<td>19.37 21.21 22.88 24.94 26.09 26.77 27.18</td>
</tr>
<tr>
<td>TRU conversion ratio</td>
<td>0.7006 0.7011 0.7015 0.7020 0.7023 0.7024 0.7023</td>
</tr>
<tr>
<td>Amount of U external feed (kg)</td>
<td>312.74 312.45 312.08 311.56 311.21 310.83 310.55</td>
</tr>
<tr>
<td>Amount of TRU external feed (kg)</td>
<td>217.59 217.88 218.24 218.73 219.08 219.45 219.72</td>
</tr>
<tr>
<td>TRU/Waste (%)</td>
<td>0.1553 0.1556 0.1559 0.1564 0.1567 0.1570 0.1572</td>
</tr>
<tr>
<td>TRU content in charged fuel (%)</td>
<td>25.78 25.82 25.87 25.95 26.00 26.05 26.09</td>
</tr>
</tbody>
</table>

Scenario #3: TRU recovery factor in pyroprocessing

In pyroprocessing, 99.9% of the TRU recovery factor is applied as the current technology level, while a number of studies are underway to increase the recovery factor. However, this experimental value is obtained from simulated SF. In practice, PWR and SFR SF are processed, and the recovery factor can be different. Thus, in this scenario, performance changes when the TRU recovery factor is reduced to 99% or increased to 99.9999%, and the specific activity and heat generation rate of waste that is not recovered in pyroprocessing are determined. These two terms are the reference to distinguish between high-level waste (HLW) and low-and intermediate-level waste (LILW). If specific activity of alpha-particle is lower than 4 000 Bq/g or heat generation rate is lower than 2 kW/m³, the waste is LILW according to Korean nuclear laws and it is easy to deposit the waste.

Since the recovery factor changes 1% or less, SFR performance is not greatly affected. However, the TRU concentration in waste is reduced exponentially, thereby greatly decreasing specific activity and heat generation rate.
The results were compared with the specific activity and heat generation rate of 1t natural uranium ore (Density, 19.05 g/cm$^3$). Although the radiotoxicity of natural uranium is extremely low, the radiotoxicity of uranium ore contains Rn and Po generated by uranium decay, and thus it is 4 to 5 times larger than that of natural uranium.

**Figure 3: Activity and heat generation of uranium ore**

![Activity and heat generation of uranium ore](image)

**Figure 4: Specific waste activity (unit: $\times 10^4$ Bq/g)**

![Specific waste activity](image)

Figure 4 shows the computed values of waste’s specific activity. The specific activity was computed using the radioactivity of actinide that performs alpha decay. When the TRU recovery factor is 99.9999%, waste’s specific activity was lower than that of the uranium ore level, regardless of the waste’s cooling period. On the other hand, when the recovery factor is 99.999%, the waste’s specific activity is reduced to the uranium ore level if cooled for about 1,500 years.

Figure 5 illustrates the heat generation rate of the original waste. In the figure, even if the TRU recovery factor was increased to 99.9999%, the heat generation rate was not reduced to the same as that of the uranium ore level. The reason for this is that long-lived fission product (LLFP) exists in the waste.
Sr-90 and Sn-126 among the LLFPs account for large content ratios in the waste, and their daughter nuclides decay with the discharge of energy as large as 2 to 4 MeV. In addition, nuclides that decay to LLFP with a large energy discharge of more than 1.3 MeV and large content ratios are Mo-99(→Tc-99) and Te-129m(→I-129). Other than those, long-lived FPs with large content ratio are Se-79, Zr-93, Pd-107, Tc-99, and Sm-151.

Assuming that the aforementioned LLFPs are separable in pyroprocessing, the heat generation rates were computed. As shown in Table 7, under the cooling time of 500 years at the TRU recovery factor of 99.999%, it is reduced to that of uranium ore level.

It is not only important to increase the TRU recovery factor in pyroprocessing, but also highly critical to separate LLFPs in terms of the safe disposal of radioactive waste and the management period. In order to minimise the volume of HLW disposal as well as to make management more convenient, in pyroprocessing, LLFPs have to be separable. In this state, if the TRU recovery factor is 99% and waste cooling time is 500 years, the waste will be LILW. In the reference case, 300 years of waste cooling time is sufficient to reach the LILW.

### Table 7: Performance parameters according to the cooling time

<table>
<thead>
<tr>
<th>Cooling time (yr)</th>
<th>99%</th>
<th>99.9%</th>
<th>99.99%</th>
<th>99.999%</th>
<th>99.9999%</th>
<th>Natural uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6545.0</td>
<td>6466.1</td>
<td>6470.8</td>
<td>6471.5</td>
<td>6471.6</td>
<td>0.0019</td>
</tr>
<tr>
<td>300</td>
<td>2.6412</td>
<td>0.2670</td>
<td>0.0267</td>
<td>0.0027</td>
<td>0.0003</td>
<td>0.0019</td>
</tr>
<tr>
<td>500</td>
<td>1.8175</td>
<td>0.1841</td>
<td>0.0184</td>
<td>0.0018</td>
<td>0.0002</td>
<td>0.0019</td>
</tr>
<tr>
<td>700</td>
<td>1.3889</td>
<td>0.1408</td>
<td>0.0141</td>
<td>0.0014</td>
<td>0.0001</td>
<td>0.0019</td>
</tr>
<tr>
<td>1000</td>
<td>1.0507</td>
<td>0.1066</td>
<td>0.0107</td>
<td>0.0011</td>
<td>0.0001</td>
<td>0.0019</td>
</tr>
<tr>
<td>1300</td>
<td>0.8697</td>
<td>0.0883</td>
<td>0.0088</td>
<td>0.0009</td>
<td>0.0001</td>
<td>0.0019</td>
</tr>
<tr>
<td>1500</td>
<td>0.7914</td>
<td>0.0804</td>
<td>0.0080</td>
<td>0.0008</td>
<td>0.0001</td>
<td>0.0019</td>
</tr>
</tbody>
</table>

**Scenario#4: RE recovery factor in pyroprocessing**

The RE recovery factor of 5% in the reference scenario is an achievable value after a number of electro-winning in pyroprocessing are done. As the number of electro-winning increases, the RE recovery factor decreases greatly from a maximum of 55% to the reference of 5%. As the RE recovery factor is reduced, the TRU content ratio of U-TRU-Zr fuel becomes smaller to make a critical state at EOEC so that
excess reactivity at BOEC decreases. Then, sodium void reactivity is affected directly by the TRU amount and FPs (impurities). Since the amounts of RE and TRU decrease, it is important to check whether sodium void reactivity has valid values.

Table 8 shows the performance parameters according to the RE recovery factor. If the amount of TRU decreases, the excess reactivity at BOEC becomes smaller. If the recovery factor of RE becomes lower than 45%, the excess reactivity becomes smaller than 4,900 pcm, permitting sufficient reactivity control. Since supply of TRU is reduced, the amount of TRU transmutation and the burnup contribution due to TRU becomes smaller, thereby worsening the transmutation ratio. The transmutation ratio of Pu, which has a high contribution to fission, worsens greatly while the transmutation ratio of MA also slightly worsens. Since the amount of RE coming from PWR decreases greatly, even if the RE recovery factor is reduced in the pyroprocessing of SFR SF, the discarded amount of RE decreases. Thus, the TRU content ratio within the waste increases, thereby increasing specific activity. The TRU content ratio in the loaded fuel becomes less than 30wt.% if the RE recovery factor reaches 45%, meeting the design criteria. As the RE recovery factor becomes smaller, the TRU and RE content in the driver fuel decreases, thereby reducing the sodium void reactivity, becoming 7$ level at the EOEC if the recovery factor is reduced to about 23%. In order to prevent prompt criticality while having a sufficient shutdown margin, the maximum recovery factor of RE is 23%. Currently, a study with respect to pyroprocessing has been focused on the reduction of the RE recovery factor as much as possible. It is right to decrease the recovery factor as much as possible to maximise safety. On the other hand, as the recovery factor increases, other benefits can be found, such as increased transmutation performance or reduced processing cost. Thus, in pyroprocessing, 23% at a maximum of the RE recovery factor is deemed to be feasible in our conclusion.

**Table 8: Performance parameters of different recovery factors for REs**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RE recovery factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td>TRU:RE mass ratio in charged fuel</td>
<td>2.18:1</td>
</tr>
<tr>
<td>Excess reactivity (pcm)</td>
<td>5348</td>
</tr>
<tr>
<td>Amount of TRU trasmutation (kg)</td>
<td>342.49</td>
</tr>
<tr>
<td>TRU support ratio</td>
<td>2.003</td>
</tr>
<tr>
<td>TRU transmutation ratio (%)</td>
<td>25.96</td>
</tr>
<tr>
<td>Pu transmutation ratio (%)</td>
<td>26.50</td>
</tr>
<tr>
<td>MA transmutation ratio (%)</td>
<td>23.41</td>
</tr>
<tr>
<td>Amount of U external feed (kg)</td>
<td>187.20</td>
</tr>
<tr>
<td>Amount of TRU external feed (kg)</td>
<td>344.30</td>
</tr>
<tr>
<td>Amount of RE external feed (kg)</td>
<td>226.70</td>
</tr>
<tr>
<td>TRU/Waste (%)</td>
<td>0.1285</td>
</tr>
<tr>
<td>TRU content in charged fuel (%)</td>
<td>32.00</td>
</tr>
<tr>
<td>Sodium void reactivity BOC/EOC ($)</td>
<td>7.9/8.9</td>
</tr>
</tbody>
</table>
Conclusion

In this study, a range of achievable scenarios was investigated based on four potential recycling parameters: recycling CANDU SF, cooling time of PWR SF, TRU recovery factor and RE recovery factor in pyroprocessing. Results are applicable only for 600 MWe SFR in equilibrium cycle with pyroprocessing. Scenarios were evaluated on the basis of only the core calculation that does not consider design of thermal-hydraulic, chemical reaction of materials, etc.

As the recycling of CANDU SF does not have any safety problems, CANDU-Pyro-SFR system will be possible if the Pyroprocessing capacity is large enough. Core performance and safety in transient cycle from PWR-Pyro-SFR to CANDU-Pyro-SFR equilibrium cycle need to be evaluated later.

The longer cooling time of PWR SF is able to increase the safety of SFR and transmutation of MA. So the longest cooled SF should be pyroprocessed and recycled to SFR.

The waste that is not recovered in through pyroprocess is classified as LILW and it is sufficient to be disposed of in an underground site due to a very low heat generation rate when the waste cooling time becomes more than 300 years at TRU recovery factor of 99.9%, but the pyroprocess has to be able to separate LLFPs from the waste.

Finally, RE recovery factor has to be reduced to only 20% in order to satisfy safety, efficiency, and economic feasibility.

References

Coolant Chemistry Control: Oxygen Mass Transport in Lead Bismuth Eutectic

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Abstract

In lead-bismuth cooled transmutation systems, oxygen, dissolved in the coolant at defined quantities, is required for stable long-term operation by assuring the formation of protective oxide scales on structural steel surfaces. Extracted oxygen must be permanently delivered to the system and distributed in the entire core. Therefore, coolant chemistry control involves detailed knowledge on oxygen mass transport. Beside the different flow regimes a core might have stagnant areas at which oxygen delivery can only be realised by diffusion. The difference between oxygen transport in flow paths and in stagnant zones is one of the targets of such experiments.

To investigate oxygen mass transport in flowing and stagnant conditions, a dedicated facility was designed based on computational fluid dynamics (CFD). CFD also was applied to define the position of oxygen sensors and ultrasonic Doppler velocimetry transducers for flow measurements.

This contribution will present the test facility, design relevant CFD calculations and results of first tests performed.

Introduction

In order to reduce the volume and the decay time of nuclear waste, the strategy of partitioning and transmutation in critical and/or sub-critical fast spectrum transmuters (ADS) has been recognised as promising. One of the designs foresees the use of heavy liquid metals like PbBi as coolant and spallation target of such ADS system. The MYRRHA reactor planned to be built at SCK-CEN in Mol, Belgium, is one of the most prominent projects for this technology at time [1]. PbBi as a coolant has several safety related benefits, but compatibility problems with potential structural materials like 316l type steels require adequate and continuous liquid metal chemistry control. The solubility of steel alloying elements is the major driving force for steel corrosion and finally disintegration. Such corrosion process can be controlled and mitigated by adding and controlling appropriate amounts of oxygen into the liquid metal and by surface engineering the steels to be employed [2-4]. In a real reactor the liquid metal flow is due to the inserts highly complex and even stagnant areas might exist. Therefore, oxygen addition and transport and interaction with impurities are of interest for operating such type of reactors. The total demand of oxygen and the required supply rate have been discussed already [5,6]. The control, mass transport and the interaction of oxygen, metallic and non-metallic impurities with the coolant Lead-Bismuth Eutectic (LBE) was not addressed explicitly.

A vessel-type experimental device containing about 200 kg molten LBE is designed and used at the Karlsruhe Institute of Technology to investigate mainly absorption of oxygen from the cover gas of the liquid metal and its transport within the flowing LBE. Quantitative experimental investigations include local oxygen concentration measurements as well as Doppler ultrasonic velocimetry of the fluid flow.

This presentation introduces simulations based on computational fluid dynamics (CFD) as a support for the design of the experimental device from a fluid mechanical point of view. CFD helps to elaborate
and evaluate design variants based on fluid mechanical aspects by identifying main flow regimes and patterns and by optimising the position of oxygen sensors and ultrasonic Doppler velocimetry transducers for flow velocity measurements. Based on the simulations the design and construction of the experimental facility is presented and 1st experiments and obtained results will be discussed.

**Design supporting computational fluid dynamics**

One major strategy adopted during the design process and the accompanying CFD is to force an asymmetry of the flow field by the choice of the vessel design (geometry and boundary conditions). This strategy avoids to rely on the existence of large scale symmetric flow patterns which can be destroyed either by an intrinsic instability of the symmetric flow field itself or by inaccuracies and deviations in fabrication and assembly of the vessel parts.

**Computational setup**

A sketch of the computational domain is shown in Figure 1 (left). The cylindrical vessel includes a quasi-stagnant flow region used to separate convective and diffusive transport of dissolved oxygen. Oxygen concentration sensors inserted from the top of the vessel are considered in the numerical model. The treatment of the free liquid surface is simplified by imposing a slip wall condition at the top of the computational domain. The flow driving unit consists in a vertical tube with three radial orifices at the top. The spatial region containing the axial impeller and flow guiding and conditioning parts (perforated plates and guiding sheets) can be modelled and simulated separately (Figure 1, right).

![Sketch of the computational domain](image1.png)

**Figure 1**

The fluid Lead-Bismuth Eutectic (LBE) is treated as an incompressible fluid with constant properties (density, viscosity) at T=400°C. The simulations are performed with the commercial CFD software STAR-CCM+® [7] which uses Finite-Volume spatial discretisation. Automatic polyhedral meshing is employed. A segregated flow model that solves the conservation equations in a sequential way is used, with pressure-velocity coupling achieved by the SIMPLE algorithm. A second order upwind scheme is used as convection scheme.
The Reynolds-Averaged Navier-Stokes equations with a Boussinesq approximation for Reynolds-stresses are solved. The eddy viscosity is determined by a realisable k-ε-model. A two-layer (all y+) wall treatment is employed. The rotation of the impeller blades is modelled by assigning a constant rigid rotating motion to the spatial region containing the impeller blades and solving for a steady state solution. The momentum conservation equations are formulated in absolute velocity components. The rotating motion of the impeller region thus introduces an additional grid flux in all convective terms and one additional body force in the momentum equations.

The results presented here have been obtained with a simplified representation of the flow driving unit. The spatial region containing the flow driving unit (green cylinder in Figure 1, left) is not part of the main computational domain of the vessel. Instead, the lower boundary of the flow driving unit is treated as a constant pressure outlet condition whereas a velocity inlet condition is assigned to the upper boundary.

Results

The main structure of the resulting flow field is shown in Figure 2, where the left part visualises the existence of a low-speed core region in the vessel. The right part of Figure 2 shows the main circumferential flow structure resulting from the asymmetric distribution of three jets exiting the radial orifices in the vertical flow driving unit.

Figure 2

Visualisation of ‘low-speed core region’ (computational cells with velocity magnitude lower than 4 mm/s are shown) in the main vessel

Fast jets from vertical flow driving unit and large scale circumferential flow pattern visualised by stream lines

The left part of Figure 3 shows the location of three measurement paths (UDV1-UDV3) for ultrasonic Doppler velocimetry in the main vessel. The measurement line of UDV3 points in radial direction and enters one of the three radial jets. The measurement line of UDV1 covers three main flow regions in the vessel, which can also be identified in the normal velocity profiles in the right diagram in Figure 3. The origin of the normal coordinate is situated at the height of the liquid surface (upper boundary of computational domain). The measurement line first enters the region of the fast radial jet below the liquid surface (Part a in diagram), then crosses the low speed core region of the vessel (part b) and finally reaches the outer region (part c) with the large circumferential flow pattern near the wall of the vessel. The location of the measurement line of UDV2 follows a similar strategy as UDV1. Both lines cross in one point in the low core speed region.
In order to study the absorption of oxygen from the cover gas as well as the transport of dissolved oxygen in the flowing LBE, oxygen sensors are placed at different locations of the flow field (Figure 1, left). Figure 4 shows the simulated temporal evolution of a passive scalar representing the dissolved oxygen concentration at the measurement locations of the oxygen sensors. At \( t=0 \) s, the passive scalar value is set instantaneously to the value 1 at the upper boundary of the computational domain representing the free surface of the flowing LBE. The curves in Figure 4 show clearly distinguishable and characteristic time signals at the different locations.

**Figure 4:** Temporal evolution of signals at selected probing locations of a passive scalar representing the concentration of dissolved oxygen.
Experimental setup

The MiNIPOT (Modular mINI reactor Pool for Oxygen Transport measurements) has three different vessels (Figure 5). The total inventory of liquid PbBi is about 200 kg. The conditioning vessel is used for storage and conditioning the PbBi, the smallest vessel depicted on figure 5 is employed for Ni dissolution and transport experiments and the main vessel for the oxygen transport and interaction tests. All vessels are equipped with type K thermocouples and at least one oxygen sensor. All three vessels are heated by a bottom heating plate and by heating rods placed circumferential around the vessel. The maximum temperature in the conditioning and main vessel is limited to 550°C and to 650°C in the small vessel with the sacrificial Ni electrode. To ensure and speed up the mixing and by that conditioning of the PbBi a simple impeller is installed in the conditioning vessel. Due to the stringent requirements regarding oxygen partial pressure in the gas phase, the feed through is realise using a magnetic coupling. The main vessel (Figure 5 right) is equipped with five different oxygen sensors that are placed at positions derived from the design supporting CFD calculations (Figure 1 left). One of the sensors is placed in the pocket that should avoid any interaction with the main flow and represents a quasi stagnant zone. All oxygen sensors are accompanied by a thermocouple to have the actual temperature at each of the sensors positions. The pump was constructed from stainless steel (1.4571) after the design recommendations from the CFD simulations. Like for the conditioning container a magnetic coupled feed through is selected to transfer the rotation movement to the pump impeller. To measure the velocity distribution two UDV sensors are placed at two of the three ports at the main vessel. One is attached to the left port at the main vessel and the other at one of the two ports (UDV1, UDV2) that are located on the lateral area of the cover of the vessel. The gas conditioning is done via the gas phase using a defined H₂/H₂O ratio provided by an oxygen control system described in previous publications [Mueller 2003]. The gas phase oxygen partial pressure is measured after leaving the main vessel employing an oxygen sensor by ZIROX company.

Data acquisition is realised employing the TMX module from Astro-med having dedicated thermocouple measurement ports. The oxygen sensor signals are measured using zero amplification modules that simulate a high impedance to assure the correct measurement of the signals.

First experiments and results

The experiments were all performed in a similar way. The PbBi was conditioned in the conditioning chamber. The H₂/H₂O ratio was about 0.0166, which corresponds to an oxygen content in the melt at
400°C of about 2.6x10⁻⁸ wt% and an oxygen partial pressure at 750°C according to a Zirox reading of ~ 800 mV. The gas from the oxygen control system is continuously purged over the liquid metal interface. When the oxygen sensor located in the conditioning vessel shows the expected value the PbBi is pumped at a temperature of 300°C via gas overpressure into the main vessel, which was purged beforehand with Ar+5%H₂.

Typical experiments are done the following way: at constant oxygen partial pressure in the gas phase the temperature of the liquid PbBi was increased or decreased or the pump was stopped or at constant temperature the oxygen partial pressure in the gas phase was increased or decreased. To understand the time scale of the response of the oxygen sensors on changes in the gas phase one has to consider the volume of the gas phase (about 7l) and the flow rate of the gas (100 cm³/min). One full exchange of the cover gas volume requires about 70 min (4200s).

Typical measured data of the 5 oxygen sensors and of two of the thermocouples are depicted in Figure 6. On the left abscissa the voltage reading of the oxygen sensors and on the right abscissa the temperature reading of the thermocouple in °C and the oxygen partial pressure at 750°C (Zirox reading) in mV are given. The temperature signals of both sensors are overlapping indicating that the temperature distribution in the main container is very homogenous. The signals of the oxygen sensors are beside the one of sensor number 2 also pretty close to each other after about 20 000 s at a temperature of 390°C.

Figure 6: Typical measured data of a test done using the MiniPot facility

A further increase of temperature to 420°C results in some not yet understandable behaviour. Some sensors show an increase some no changes or a decreasing voltage. A sudden reduction of the oxygen partial pressure (Zirox reading is dropped to -977mV) is followed by a slowly increase of oxygen sensor voltage. After ~85000s the gas phase composition was changed back and the sensor response is at least qualitatively as expected.

A more detailed investigation of the oxygen sensor response on the increasing oxygen content in the gas phase is depicted in Figure 7.

The oxygen sensors 1 to 4 show an almost immediate response to the increase of the oxygen partial pressure. All 4 sensors react with decreasing voltage. Instead, the sensor No. 5 that is located in the quasi stagnant zone of the PbBi flow does show a decreasing voltage. Such behaviour clearly indicates the differences in convective and diffusion transport of oxygen and the necessity to understand and quantify both transport processes.
A gas phase modification in the opposite direction, decreasing the oxygen content, was also performed in another experiment. It also shows qualitatively the expected response of the oxygen sensors on a changing oxygen partial pressure in the gas phase. The time scales are of course quite different compared to the one derived from the CFD simulation (Figure 4). This can be easily explained regarding the real exchange time of the cover gas (4-200 s) and the comparing that with the instantaneous step that was used for the simulation.

As reported a pump is used to assure a stable PbBi flow in the main container of the MiNIPot. Unluckily the UDV sensors foreseen to measure the flow profile did not give a reliable signal so far. This problem is actually discussed with the supplier and might be explained by the required use of the waveguide design. However, the functioning of the pump itself could be tested by switching the pump off at constant temperature conditions (the PbBi is at this stage still to be reduced). The temperature of the PbBi was set to 400°C and the oxygen partial pressure in the gas phase was kept constant at reducing values of -1300 mV (Figure 8). The pump was running for the first 7000 s and was than switched off and switched on again after 11000 s.

As expected all the sensors show an increasing voltage in the first period. After 7000 s, when the pump was switched off, the sensors 1 to 4 basically do not show any further increase. A plateau was more or less reached. Switching the pump on again resulted in an increasing of the voltage signal. A slight different behaviour can be seen at sensor 5 that is located in the dead zone area. Here the difference in inclination of the voltage signal between pump on and off is less significant than for the other sensors.
One very specific course of the oxygen sensor signal is depicted in Figure 9. Here at constant temperature in air ingress was simulated.

**Figure 9: oxygen sensor response on an air ingress in the cover gas**

All the sensors react almost immediately on the increased oxygen content and show a sharp drop in voltage. At 76000s a sudden increase of voltage is observed that is reversed after some time and the expected drop of voltage continues. No temperature effect and flow differences can be considered for this behaviour. One possible explanation is the oxidation of dissolved impurities. One can assume that dissolved metallic impurities like Fe, Cr, Ni getter the increasing amount of oxygen and than after all impurities are oxidised the dissolving of oxygen in the PbBi continuous. At this oxygen activity most likely Ni is oxidised.

**Conclusions and outlook**

Computational fluid dynamics have been employed to support the design process of an experimental vessel for liquid LBE from a fluid mechanical point of view. A design leading to large scale asymmetric flow structure has been chosen. The positions of sensors for oxygen concentration and for ultrasonic Doppler velocimetry have been selected in order to obtain unambiguous and strong measurement signals. The fabrication and assembly of the experimental device is finished and the first experiments performed are presented. One problem still to be solved is the UDV measurement of the velocity profile.

The temperature distribution during the experiments was very homogenous. No stratifications are observed. The response of the sensors on changing oxygen activity was at least qualitatively as expected. The sensor in the quasi stagnant zone, which is almost totally separated from the PbBi flow, shows a distinct different behaviour compared to the other oxygen sensors. Diffusion transport is much slower than the convective oxygen transport. This was clearly supported when the pump was switched off and all oxygen transport does relay on diffusion. One difficulty for measuring the oxygen activity is associated with metallic impurities dissolved in the PbBi. Such impurities might significantly alter the free oxygen that can be considered for steel surface oxidation. This phenomena and especially the quantification of all observed results is one of the objectives for future work.

**Acknowledgements**

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References


The MYRRHA ADS Project in Belgium Enters the Front End Engineering Phase

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Abstract

The MYRRHA project started in 1998 by SCK•CEN. MYRRHA is a MTR, based on the ADS concept, for material and fuel research, for studying the feasibility of transmutation of minor actinides and long-lived fission products arising from radioactive waste reprocessing and finally for demonstrating at a reasonable power scale the principle of the ADS. The MYRRHA design has progressed through various framework programmes of the European Commission in the context of Partitioning and Transmutation. The design has now entered into the Front End Engineering Phase (FEED) covering the period 2012-2015. The engineering company, which will handle this phase, has been selected and the works have begun in the late 2013. In the meantime we have made some refinements in both primary systems and plant layout, including reactor building design. In this paper, we present the most recent developments of the MYRRHA design in terms of reactor building and plant layout as existing today.

Introduction

MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) is the flexible experimental accelerator driven system (ADS) in development at SCK•CEN. MYRRHA is able to work both in subcritical (ADS) as in critical mode. In this way, MYRRHA should target the following applications catalogue [1]:

- To demonstrate the ADS full concept by coupling the three components (accelerator, spallation target and sub-critical reactor) at reasonable power level to allow operation feedback, scalable to an industrial demonstrator;
- To allow the study of the efficient technological transmutation of high-level nuclear waste, in particular minor actinides that would request high fast flux intensity (\(\Phi_{>0.75\text{MeV}} = 10^{15}\ \text{n/cm}^2\cdot\text{s}\));
- To be operated as a flexible fast spectrum irradiation facility allowing for:
  - fuel developments for innovative reactor systems;
  - material developments for GEN IV systems;
  - material developments for fusion reactors;
  - radioisotope production for medical and industrial applications by:
    - holding a backup role for classical medical radioisotopes;
    - focusing on R&D and production of radioisotopes requesting very high thermal flux levels;
  - industrial applications, such as Si-doping.

MYRRHA has started from the ADONIS project (1995-1997), which was the first project at SCK•CEN where the coupling between an accelerator, a spallation target and a subcritical core was studied. ADONIS was a small irradiation facility, having the production of radioisotopes for medical purposes as its single objective. In 1998, the ad-hoc scientific advisory committee advised extending the
purpose of the ADONIS machine to become a material testing reactor for material and fuel research, to study the feasibility of transmutation of minor actinides and to demonstrate the principle of the ADS at a reasonable power scale. Since 1998, the project is called MYRRHA.

MYRRHA consists of a proton accelerator delivering its beam to a spallation target coupled to a subcritical core. In 2005 MYRRHA consisted of an accelerator delivering 350 MeV * 5 mA to a windowless spallation target coupled to a subcritical fast core of 50 MW\textsubscript{th}. This 2005 design was used as a starting base within the FP6 EUROTRANS integrated project (2005-2010), which resulted in the XT-ADS [2] (Experimental Demonstration of the Technical Feasibility of Transmutation in an Accelerator Driven System) design, where a linear accelerator delivers a 600 MeV * 3.2 mA beam into the spallation target. The reactor power of XT-ADS was 57 MW\textsubscript{th}.

The XT-ADS design was taken as a starting point for the work performed in the FP7 CDT project [3], [4]. Since the end of the CDT project in 2012, the MYRRHA team has performed some further engineering work in its core knowledge, the primary system and core design, leaving the more classical engineering (called “balance of plant”) to a specialised contractor in the field. This Front End Engineering Design (FEED) has started in the late 2013. In this paper, we recall some basic characteristics of the accelerator (section 2) and of the core and primary system design (Section 3). Then we present the current design of reactor building and plant layout (Section 4).

The MYRRHA accelerator

The accelerator is the driver of MYRRHA since it provides the high energy protons that are used in the spallation target to create neutrons which in turn feed the core. In the current design of MYRRHA, the machine must be able to provide a proton beam with energy of 600 MeV and an average beam current of 3.2 mA. A basic layout of the MYRRHA accelerator, aiming at maximising its efficiency, its reliability and its modularity, is provided in Figure 1.

Figure 1: A schematic layout of the MYRRHA accelerator reference design.

The beam is delivered to the core in continuous wave (CW) mode. Once a second, the beam is shut off for 200 µs so that accurate on-line measurements and monitoring of the sub-criticality of the reactor can take place. The beam is delivered to the core from above through a beam window.

Accelerator availability is a crucial issue for the operation of the ADS. A high availability is expressed by a long mean time between failure (MTBF), which is commonly obtained by a combination of over-design
and redundancy. On top of these two strategies, fault tolerance must be implemented to obtain the required MTBF. Fault tolerance will allow the accelerator to recover the beam within a beam trip duration tolerance after failure of a single component. In the MYRRHA case, the beam trip duration tolerance is 3 seconds. Within an operational period of MYRRHA the number of allowed beam trips exceeding 3 seconds must remain under 10, shorter beam trips are allowed without limitations. The combination of redundancy and fault tolerance should allow obtaining a MTBF value in excess of 250 hours.

At present proton accelerators with megawatt level beam power in CW mode only exist in two basic concepts: sector-focused cyclotrons and linear accelerators (linacs). Cyclotrons are an attractive option with respect to construction costs, but they do not have any modularity, which means that a fault tolerance scheme cannot be implemented. Also, an upgrade of its beam energy is not a realistic option. A linear accelerator, especially if made superconducting, has the potential for implementing a fault tolerance scheme and offers a high modularity, resulting in the possibility to recover the beam within a short time and increasing the beam energy.

Design of the core and primary system

The main components/systems of the current design are of the same XT-ADS type, as defined within the EUROTRANS project, with only increased size. The primary and secondary systems have been designed to evacuate a maximum core power of 100 MWth. All the components are optimised for the extensive use of the remote handling system during components replacement, inspection and handling. Figure 2 shows a section of the MYRRHA reactor with its main internal components.

Figure 2: Section of the MYRRHA reactor

![Section of the MYRRHA reactor](image)
Since MYRRHA is a pool-type ADS, the reactor vessel houses all the primary systems. In the current design, the reactor pit serves as secondary containment, improving the capabilities of the reactor vault auxiliary cooling system. The vessel is closed by the reactor cover which supports all the in-vessel components. A diaphragm inside the vessel functions to separate the hot and cold lead-bismuth eutectic (LBE), to support the In-Vessel Fuel Storage (IVFS) and to provide a pressure separation. The core is held in place by the core support structure consisting of a core barrel and a core support plate.

At the present state of the design, the reactor core (Figure 3) consists of mixed oxide (MOX) fuel pins, typical for fast reactors. To better accommodate the central target, the fuel assembly’s size is a little bit increased as compared to the XT-ADS design. Consequently the In-Pile test Sections (IPS), which will be located in dedicated fuel assembly (FA) positions, are larger in diameter giving more flexibility for experiments. Thirty seven positions can be occupied by IPSs or by the spallation target (the central one of the core in sub-critical configuration) or by control and shutdown rods (in the core critical configuration). This gives a large flexibility in the choice of the more suitable position (neutron flux) for each experiment.

**Figure 3: Cut in the core, showing the central target, the different types of fuel assemblies and dummy components**

The requested high fast flux intensity has been obtained optimising the core configuration geometry (fuel rod diameter and pitch) and maximising the power density. We will be using, for the first core loadings, 15-15Ti as cladding material instead of T91 that will be qualified progressively further on during MYRRHA operation. The use of LBE as coolant permits to lower the core inlet operating temperature (down to 270°C) decreasing the risk of corrosion and allowing to increase the core ΔT. This together with the adoption of reliable and passive shutdown systems will permit to meet the high fast flux intensity target.

As depicted in Figure 3, showing a critical core layout (with seven central IPS) at the equilibrium of the fuel cycle, 37 positions are available for Multi-Functional Channels (MFC) that can host indifferently:

- fuel assembly and dummy, loaded from the bottom (in all the 151 positions);
- IPS, control and scram rods, loaded from the top.

In subcritical mode the accelerator (as described in the previous section) is the driver of the system. It provides the high energy protons that are used in the spallation target to create neutrons which in their turn feed the subcritical core. The accelerator is able to provide a proton beam with energy of 600 MeV and a maximum current of 4 mA. In subcritical mode the spallation target assembly, located in the central position of the core, brings the proton beam via the beam tube into the central core region. The assembly evacuates the spallation heat deposit, guarantees the barrier between the LBE and the reactor hall and assures optimal conditions for the spallation reaction. The assembly is conceived as an IPS and is easily removable or replaceable.
Differently from the critical layout depicted in Figure 3, in ADS mode the six control rods (buoyancy driven in LBE) and the three scram rods (gravity driven in LBE) will be replaced by absorbing devices to be adopted only during refuelling. Thanks to the (aimed and reached) flexibility, such absorbing devices will be implemented by adopting the Control Rods, but they will be controlled manually only by the operator. The primary, secondary and tertiary cooling systems have been designed to evacuate a maximum thermal core power of 110 MW. The 10 MW more than the nominal core power account for the power deposited by the protons, for the decay power of fuel in the IVFS and for the power deposited in LBE by $\gamma$-heating and decay of radio-active products. The average coolant temperature increase in the core in nominal conditions is 140°C with a coolant velocity of 2 m/s. The primary cooling system consists of two pumps and four primary heat exchangers (PHX).

The primary pumps shall deliver the LBE to the core with a mass flow rate of 4750 kg/s (453 l/s per pump). The working pressure of the pump is 300 kPa. The pump will be fixed at the top of the reactor cover, which is supposed to be the only supporting and guiding element of the pump assembly. The secondary cooling system is a water cooling system while the tertiary system is an air cooling system. These systems function in active mode during normal operation and in passive mode in emergency conditions for decay heat removal.

The main thermal connection between the primary and secondary cooling systems is provided by the primary heat exchangers. These heat exchangers are shell and tube, single-pass and counter-current heat exchangers. Saturated pressurised water at 200°C is used as secondary coolant, flowing through the feed-water pipe in the centre of the PHX to the lower dome. All the walls separating the LBE and water plena (feed-water tube, lower dome and upper annular space) are double walled to avoid pre-heating of the secondary coolant and to prevent water leaking in the LBE in case of tube failure.

In case of loss of the primary flow (primary pumps failure), the primary heat exchangers aren’t able to extract the full heat power. In such cases, the beam must be shut off in the subcritical case and the shutdown rods inserted in the critical case. The decay heat removal (DHR) is achieved by natural convection. Ultimate DHR is done through the reactor vessel coolant system (RVACS, reactor vessel auxiliary cooling system) by natural convection.

The interference of the core with the proton beam, the fact that the room situated directly above the core will be occupied by lots of instrumentation and IPS penetrations, and core compactness result in insufficient space for fuel handling to (un)load the core from above. Since the very first design of MYRRHA, fuel handling is performed from underneath the core. Fuel assemblies are kept by buoyancy under the core support plate.

Two fuel handling machines are used, located at opposite sides of the core. Each machine covers one side of the core. The use of two machines provides sufficient range to cover the necessary fuel storage positions without the need of an increase for the reactor vessel when only one fuel handling machine is used. Each machine is based on the well-known fast reactor technology of the ‘rotating plug’ concept using SCARA (Selective Compliant Assembly Robot Arm) robots. To extract or insert the fuel assemblies, the robot arm can move up or down for about 2 meters. A gripper and guide arm is used to handle the FAs: the gripper locks the FA and the guide has two functions, namely to hold the FA in the vertical orientation and to ensure neighbouring FAs are not disturbed when a FA is extracted from the core. An ultrasonic (US) sensor is used to uniquely identify the FAs.

The in-vessel fuel handling machine (IVFHM) will also perform in-vessel inspection and recovery of an unconstrained FA. Incremental single-point scanning of the diaphragm can be performed by an US sensor mounted at the gripper of the IVFHM. The baffle under the diaphragm is crucial of the strategy as it limits the work area where inspection and recovery are needed. It eliminates also the need of additional
recovery and inspection manipulators, prevents items from migrating into the space between the diaphragm and the reactor cover, and permits side scanning. Table I below summarises the main physical characteristics of the MYRRHA core and primary system.

**Table 1: Main MYRRHA characteristics of core and primary system**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reactor power</td>
<td>110 MW&lt;sub&gt;th&lt;/sub&gt;</td>
</tr>
<tr>
<td>Total primary mass flow rate</td>
<td>9,500 kg/s</td>
</tr>
<tr>
<td>LBE mass inventory</td>
<td>4,500 Ton</td>
</tr>
<tr>
<td>Core inlet temperature at full power</td>
<td>270°C</td>
</tr>
<tr>
<td>Hot plenum temperature at full power</td>
<td>350°C</td>
</tr>
<tr>
<td>Average core temperature difference at full power</td>
<td>140°C</td>
</tr>
<tr>
<td>Cold shut down temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Temperature of secondary cooling loop</td>
<td>200°C saturated water/steam</td>
</tr>
<tr>
<td>Number of fuel assemblies in a critical reference case</td>
<td>69</td>
</tr>
<tr>
<td>Number of penetrations for experiments and other applications</td>
<td>37</td>
</tr>
<tr>
<td>Total neutron flux in first 6 experimental positions</td>
<td>(<del>2-3 \times 10^{15} \text{n/(cm}^2\text{s)</del>} )</td>
</tr>
<tr>
<td>Fast neutron flux in first 6 experimental positions</td>
<td>(<del>4 \times 10^{14} \text{n/(cm}^2\text{s)</del>} ) for E &gt; 0.75 MeV</td>
</tr>
</tbody>
</table>

**Reactor building and plant layout**

The plant (Figure 4) comprises a reactor building, a LINAC tunnel, an accelerator front-end building, control buildings, a spent fuel storage building and other auxiliary buildings needed for plant services. All buildings of the plant are constructed above ground, except for the reactor building where the reactor vessel and reactor cover lie completely under ground level. An important point in this general layout is that the buildings are aligned with the overall grid present on the SCK•CEN site to obtain an easy and effective relation to the existing buildings and infrastructure. The minimum distance between buildings depends on the fire prevention regulations and also takes into account the accessibility of the buildings. The fixed junction of the front-end building, the LINAC tunnel and the reactor building, which add up to a total length of approximately 400 m determine a large part of the general layout. The location of the reactor building has also taken into account a sufficient distance (now larger than 200 m) to the limits of the SCK•CEN technical facilities.

**Figure 4: The present MYRRHA facility within the existing installations**
The design of the reactor building started off with the reactor hall in the centre of the building. The reactor vessel is located in the reactor hall, where the safety systems, the beam line and some auxiliary systems come together. After determining the shape and size of the reactor hall, other rooms housing the safety and non-safety systems have been added to the building design. Their locations and dimensions are determined by the concept of the different systems and estimated component sizes. Some of these rooms are also part of the primary containment as the source term that is present in these systems is relatively high. The other rooms define the secondary confinement.

An important element in the reactor hall is the beam line connecting the accelerator with the reactor. This metallic structure with a length of approximately 23 m has to be removed during maintenance periods in order to be able to load and unload experiments in and from the reactor core. The dismantling of the beam line and the re-alignment afterwards is done by a remote handling system as the primary containment is not accessible by workers during normal operations. The width of the reactor hall is determined by the maximum length of the boom of a proven technology remote handling system. The height of the hall is determined by the longest component that has to be replaced, the height of the overhead crane with a capacity of 400 tons and the upper part of the beam line vacuum tube.

The location of the radio-isotope and Si-doping facilities within the reactor building has been iterated several times. The solution presently favoured consists of a dedicated room above the reactor building (Figure 5) allowing a production of radio-isotopes and Si-ingots on a weekly or even daily basis without disturbing the other tasks (mostly on three-month basis) of the reactor. With the current building configuration the first seismic response spectra in the main equipment locations have been calculated. Our safety approach comprises three levels of seismic loading: the operating-, the design- and the beyond design-basis earthquakes. Special attention to the seismic calculations is the consequence of the Fukushima accident. Attention is also paid to the potential implementation of seismic isolation devices, taking into account the preliminary results of the FP7 SILER project [5].

Figure 5: Vertical cross-section in the reactor building, showing the beam line entry in the reactor vessel

Conclusions

SCK•CEN is proposing to replace its ageing flagship facility, the Material Testing Reactor BR2, by a new flexible irradiation facility, MYRRHA. Considering the international and European needs, MYRRHA is conceived as a flexible fast spectrum irradiation facility able to work in both sub-critical and critical mode. Despite several non-obvious design challenges like among others the use of LBE, the increased
level of seismic loading (consequence of Fukushima) or the choice of passive mode for decay heat removal in emergency conditions, we found no significant showstopper in the design. The R&D programme that is running in parallel has taken into account international recommendations from experts concerning the remaining technological challenges as mentioned in section VI above.

MYRRHA is now foreseen to be in full operation by 2025 and it will be able to be operated in both operation modes: subcritical and critical. In subcritical mode, it will demonstrate the ADS technology and the efficient demonstration of MA in sub-critical mode. As a fast spectrum irradiation facility, it will address fuel research for innovative reactor systems, material research for GEN IV systems and for fusion reactors, radioisotope production for medical and industrial applications, such as Si-doping.

The MYRRHA design has now entered into the Front End Engineering Phase covering the period 2012-2015. The engineering company that handles this phase has currently started the works. At the end of this phase, the purpose is to have progressed in such a way in the design of the facility that the specifications for the different procurement packages of the facility can be written.

Acknowledgements

The bases for the current MYRRHA design have been performed under two projects co-funded by the European Union, respectively the Integrated Project EUROTRANS (Ref. FI6W-CT-2004-516520, 6th Framework Programme) and the Collaborative Project CDT (Ref. FP7-232527, 7th Framework Programme). Acknowledgment is also due to all the colleagues of the participant institutes for their contributions in many different topics associated with the XT-ADS and FASTEF design and operation.

References


Neutronic Analysis of Minor Actinide Transmutation in MYRRHA

SCK•CEN, Belgium

Abstract

MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) is a multipurpose research facility currently being developed at SCK•CEN. It will be able to work in both critical and subcritical modes and, cooled by lead-bismuth eutectic, it will play a key role in the development of the Pb-alloy technology needed for the LFR (Lead Fast Reactor) GEN IV concept. MYRRHA will demonstrate the ADS (Accelerator Driven System) full concept by coupling a proton accelerator, a spallation target and a subcritical reactor at a reasonable power level to allow operation feedback. MYRRHA will also contribute to the study of partitioning and transmutation of high-level waste. In this paper, the Minor Actinide (MA) transmutation capabilities and performance are investigated in the MYRRHA critical core as well as the impact of the MA loading on the safety-related neutronic parameters, $\beta_{\text{eff}}$ and $\Lambda_{\text{eff}}$.

Introduction

Over the last years the European Commission (EC) promoted research studies on advanced nuclear systems by funding collaborative projects focused on fast systems aiming at closing the fuel cycle. In the framework of the Generation IV initiative, advanced fuel cycles (e.g. multi-reprocessing) along with Partitioning and Transmutation (P&T) strategies have been investigated to enhance the sustainability of nuclear energy while relaxing the burden on geological disposals. An advantage of Minor Actinide (MA) transmutation is indeed the reduction of the required repository volume due to reduced decay heat at the initial loading.

As is well-known, an efficient transmutation of MAs (Am, Np, Cm) can only be envisaged in fast spectrum systems, such as nuclear reactors and Accelerator Driven Systems (ADSs). While the MAs’ homogeneous loading in critical reactors has to be limited to avoid the deterioration of some safety related parameters (e.g. delayed neutron fraction, Doppler and coolant void coefficients), the subcriticality of the ADS allows operating with rather high MAs’ loadings. In the last decade, within the 5-7th Framework Programmes (FPs) of the European Atomic Energy Community (EURATOM), Accelerator Driven Systems were investigated as the “reference” solution for MAs transmutation.

In 1997, the MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) project has been launched at SCK•CEN aiming at the design of a research facility planned to replace the BR2 reactor, one of the flagships of its nuclear infrastructure [1,2]. In the FP5 PDS-XADS project [3] the basic design of the installation – a pool type ADS - was elaborated. The studies continued in the FP6 EUROTRANS project [4], in which the main design achievements were: a small scale eXperimenTal-ADS (XT-ADS; ~ 50 MW, LBE cooled), also conceived as a test bed for the main components and irradiation scheme of a full scale ADS named EFIT (~ 400 MW, lead cooled). The MYRRHA design has been adopted as the starting point for the design of the XT-ADS leading to the so-called “MYRRHA XT-ADS”. Within the 7th FP, a new collaborative project called Central Design Team (CDT) for a FAST Spectrum
Transmutation Experimental Facility (FASTEF) was launched. The CDT gathered experts from 17 European organisations, universities, research centres and industry, and a design team was established at the Belgian Nuclear Research Centre SCK•CEN in Mol [5].

Extending the scope of the MYRRHA XT-ADS, the MYRRHA FASTEF was conceived to operate in both critical and sub-critical modes with a nominal power raised to 100 MWth. The design of the spallation target component was revised to enable easy shifting from critical to subcritical operation mode. The typical Beginning-Of-Cycle (BOC) critical core contained 69 fuel assemblies (FA) consisting of 5 fuel batches (15-15-15-12-12 FA) at different burnups ranging from zero (fresh) to ~37 MWd/kgHM. The fresh fuel pellet contained 34.5 wt% (Pu+Am) MOX.

Recently, the core layout of the MYRRHA has been optimised on the core fuel management: 6 fuel assembly batches, hence only 6 fresh fuel assemblies per cycle and higher discharge burnup, were adopted while meeting the design requirements on the DPA damage in the structural components such as the core barrel and the core support plate. The Pu+Am content in the MOX fuel was reduced to 30 at%, the loss in reactivity being compensated by increasing the number of fuel assemblies (108 versus 69) and increasing slightly the active core height (65 cm versus 60 cm).

Previously many papers have been devoted to the MA transmutation in the MYRRHA ADS mode [6,7]. In this paper, the MA transmutation capabilities and performance in the updated MYRRHA critical core are investigated as well as the impact of the MA loading on the safety-related neutronic parameters, $\beta_{eff}$ and $\Lambda_{eff}$.

**Description and modelling of the MYRRHA critical layout**

The typical MYRRHA critical core at beginning of Life (BoL) configuration is depicted in Figure 1. It consists of 78 driving MOX fresh fuel assemblies (FA), 6 control rods (CR) and 3 scram rods (SR) bundles, various in-pile section (IPS) rigs and four ex-core rigs for neutron transmutation doping of silicon ingots. Two (outer) rings of reflector sub-assemblies are used to reduce the DPA damage on the core barrel. Figure 2 (left) shows a patch of driving FA (inner batches) along with an IPS containing a bundle of various fuel sample pins loaded in the central channel. A zoom view of the bundle is displayed in Figure 2 (right).

**Figure 1: Cut-view of the BOC critical core configuration**
Methodology

To investigate the MA transmutation capabilities and performance in the MYRRHA critical core, twelve sample sets (6 pins per set) were loaded in the testing fuel assembly shown above. Amongst them were 5 sample sets consisting of inert matrix fuel (IMF) uranium-free targets with a high content of plutonium, americium and curium: a blend of (Np-Am-Cm, Pu)O\(_{1.88}\) in MgO matrix with 50 vol% each one [6].

The five sample sets differ from each other by their MA-to-(Pu+MA) ratio: 60, 50, 40, 30, 20 and 10 wt%, respectively. Four other sets of sample consist of MYRRHA-like driving (Am+Pu-U)MOX fuel but with Am/Pu ratios of 8, 2.59, 1.65 and 0.71 wt%, respectively. The MYRRHA driver MOX fuel consists of a blender of natural uranium with a typical reactor-grade plutonium with a content of 241\(^{241}\)Am isotope varying from 0.71 to 2.59 wt.% of Pu which corresponds to plutonium “ageing” time (1.2 to 6.3 years between the spent fuel reprocessing and the new MOX loading in the reactor). For the reference fuel composition of MYRRHA, the ratio mean value of 1.65 wt% has been adopted. The additional sample with 8 wt% ratio represent the case the Am/Pu ratio is beyond its (assumed) equilibrium value in the discharged fuel.

It is indeed instructive to look at the impact of the Am/Pu-ratio on the transmutation rate. The samples with (Ma-Pu)O+MgO pellet are, indeed, typical cases of heterogeneous MA burning mode while the sample with MYRRHA MOX give insight on the homogeneous burning mode. The composition of both (original) IMF target and MYRRHA driving MOX pellets is given in terms of mass fraction in [7]. The testing fuel assembly and the sample pins were assumed to have the same geometry as the driving MYRRHA FA and pins, except for the pin active height. They were shorter (40 cm versus 65 cm). The sample pins of every set were loaded in equivalent position inside the testing assembly. The last two additional sets of samples consist of U-free IMF (MA-Pu) in ThO matrix (instead of MgO) and of simple ThOx targets. The results regarding these latst sets are not reported in the present paper. A dummy pin containing YZrO\(_2\) matrix was loaded in central pin position within the MA testing bundle.

For the transmutation calculations described in this paper, the irradiation history spreads over 6 MYRRHA cycles consisting of 90 effective full power days (EFPD) operation at 100 MW\(_{th}\) with 30-days shutdown periods in between for maintenance and core reloading (540 EFPD in total). The sample pin sets are burned along with the driving fuel batches during throughout the assumed operational period.
### Table 1: Composition of MYRRHA MOX fuel and MA samples

<table>
<thead>
<tr>
<th></th>
<th>MOX fuel</th>
<th>IMF (MA-Pu)O$_2$ + MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density</strong> g/cm$^3$</td>
<td>6.780</td>
<td></td>
</tr>
<tr>
<td>Pu/(U+Pu+Am)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>MA/(Pu+MA)</td>
<td>10-20</td>
<td>30-40</td>
</tr>
<tr>
<td>Pu/Am/Np/Cm</td>
<td></td>
<td>30.86/33.89/1.41/1.61</td>
</tr>
<tr>
<td>Mg/O wt%</td>
<td>14.33/17.90</td>
<td></td>
</tr>
<tr>
<td>Am/Pu</td>
<td>0.71-1.65, 2.59-8.00</td>
<td></td>
</tr>
<tr>
<td>U 234/235/238 wt%</td>
<td>0.005/0.711/99.284</td>
<td></td>
</tr>
<tr>
<td>Pu 238/239/240/241/242/244</td>
<td>2.33/56.87/27.00/6.10/7.96/0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.71/46.30/34.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.87/11.96/0.001</td>
</tr>
<tr>
<td>Am 241/242m/243</td>
<td>100.0</td>
<td>82.12/0.28/17.60</td>
</tr>
<tr>
<td>Cm 243/244/245</td>
<td></td>
<td>1.53/69.76/26.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.07/0.04/0.002</td>
</tr>
</tbody>
</table>

### Computer tools

Steady state critical core calculations have been carried out taking benefits of the new capability of the general purpose Monte-Carlo radiation transport code MCNP5 version 1.60 [12] to calculate the point-kinetics parameters ($\beta_{\text{eff}}$ and $\Lambda_{\text{eff}}$) using continuous-energy and adjoint weighting approach for criticality problems.

Multi-zone core burnup calculations have been performed to define the BOC core partition and to carry out the MA transmutation calculation. These have been done using the continuous energy Monte-Carlo burnup code ALEPH that is being developed at SCK•CEN since 2004 [8]. It models the burnup history in a sequence of irradiation and decay steps. Each time step consists of Monte Carlo calculation of particle fluxes and spectra which then are used by a deterministic depletion solver to obtain the nuclide concentrations at the end of time step. Any version of MCNP code can be used for the Monte Carlo part. In the present case, the MCNPX 2.7.0 code version has been used [10,11].

The recent release, ALEPH2 [9], possesses two major features which make the tool so flexible and powerful, namely an extensive nuclear data treatment and a numerical solver for the Bateman equations. The nuclear data library covers neutron and proton induced reactions, neutron and proton fission product yields, spontaneous fission product yields, radioactive decay data and total recoverable energies per fission. The numerical solver is an implicit Runge-Kutta method of the RADAU-IIA family which shows excellent accuracy. The versatility of the ALEPH2 code allows using it for time behaviour simulation of various systems ranging from single pin to full-scale reactor models, including such specific facilities as accelerator driven systems. An appealing feature of the ALEPH code is its ability to work either for critical systems or for external fixed source-driven sub-critical systems, such as ADS. Another key feature is the use of the same nuclear data at all calculation steps. For the present study, the JEFF 3.1.2 nuclear data library [13] has been used.

### Results and discussion

To save computation time, the neutron spectrum has been updated at the beginning, middle and end of the irradiation cycle only during the first year. The latest update of neutron spectra were used thereon One additional calculation has been carried out to obtain the core reactivity and point-kinetics parameters at beginning of live, with and without the test fuel bundle in the central IPS (loaded with SS steel sample).
Table 2 gathers the leading core reactivity parameters calculated for the start-up MYRRHA core layouts at BOL, for the fuel samples with and without the testing fuel sample in the central channel. In the usual critical core layout (without MA bundle) the central channel hosts an IPS dedicated to steel tensile irradiation and additional thermal spectrum IPSs are loaded in the outskirt of the fuellied zone for radioisotope production (namely Mo-99 and Ac-227).

<table>
<thead>
<tr>
<th>Core configuration and parameters</th>
<th>Standard layout</th>
<th>Start-up core</th>
<th>Start-up core</th>
</tr>
</thead>
<tbody>
<tr>
<td>#FA</td>
<td>78</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Irradiation rigs loaded</td>
<td></td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>IPS for DPA damage in SS steel samples</td>
<td>4</td>
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<td></td>
</tr>
<tr>
<td>IPS with test fuel bundle</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPS for Mo-99 production</td>
<td>4</td>
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<td></td>
</tr>
<tr>
<td>IPS for Ac-227 production</td>
<td>2</td>
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<td></td>
</tr>
<tr>
<td>Ex-core rigs for Silicon Doping</td>
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<td>Core reactivity effects and coefficients</td>
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<td>Initial reactivity excess</td>
<td>pcm</td>
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<td>3 608</td>
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<td>Core expansion reactivity effect</td>
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<td>Reactivity swing over 90 EFPDs</td>
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<td>-1 344</td>
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<tr>
<td>Doppler constant ( C_D = \frac{T_d}{dT} )</td>
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<td>-485</td>
<td></td>
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<tr>
<td>LBE-coolant density effect</td>
<td>pcm/K</td>
<td>-1</td>
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<tr>
<td>Point reactor kinetics parameters</td>
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<td></td>
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<tr>
<td>Effective delayed neutron fraction ( \beta_{eff} )</td>
<td>pcm</td>
<td>335 ± 2</td>
<td>335 ± 5</td>
</tr>
<tr>
<td>Prompt neutron generation time ( \Lambda_{eff} )</td>
<td>( \mu )sec</td>
<td>2.018 ± 0.005</td>
<td>1.187 ± 0.005</td>
</tr>
</tbody>
</table>

The burnup evolution in the various samples is depicted in Figure 3. In the driving (Pu+Am,U) MOX fuel samples, average burnup levels from 48-50 MWd/kg iHM are achieved. The burnup levels achieved in the U-free (MA, Pu) IMF samples go from 82-120 MWd/kg iHM. For every type of sample, the higher the Pu content, the higher the burnup, as would be expected. Since the fissile Pu (Pu-239/241) mass fraction is even a bit higher in the MOX samples (16.5 wt% versus 15.5 wt%) the lower level of burnup in the driving MOX fuel samples may be explained by captures of neutrons in U-238.

Figure 3: Time-evolution of Burnup of various samples
Figure 4 displays the mass evolution, as a function of the fuel sample burnup, of actinide elements in the two MYRRHA-like MOX fuel samples (with Am-to-Pu ratio of 0.71, 1.65, 2.59 and 8 wt%, respectively). The following features are worth to be outlined:

- The plutonium content decrease rate is the same in both samples.
- The behaviour of the MA looks quite different. In the fuel sample with 8 wt% Am-to-Pu ratio, the Am and total MA(Np-237+Am+Cm) contents keep on decreasing (by 10% for Am and about 4% for total MA) as function of sample burnup. The trend is opposite for the MOX sample with 2.59, 1.65 and 0.71 wt% ratios. Here the Am, Np and Cm amounts steadily build-up during the irradiation history and the lower the ratio, the higher the build-up. The above indicate that a net incineration is only achieved when the initial content is beyond a given value.

Figure 5 shows the evolution of the plutonium content in the various IMF samples. The “original” IMF samples with a MA content higher than the Pu’s, the burned Pu amount and hence the burnup level is so low. The evolution of MA elements, namely Am and Np) are depicted in Figures 6 and 7 respectively. For Am, the higher the initial content, the higher incinerated mass fraction which remains so close for the samples containing 60, 50, 40 and 30 wt% MA/HM, respectively. This indicates that transmutation of americium in the sample with the highest Am content is favoured by capture and decay, rather than fission. Figure 7 shows that the transmutation rate of neptunium is the same in the various IMF samples, independently of the sample burnup. Figure 8 displays the evolution of the Cm in the IMF samples. It may be observed that the higher the initial MA/HM ratio, the slower the increase of Cm.

**Figure 4: Evolution of various elements in the MOX fuel sample**
Figure 5: Evolution of Plutonium content in the various IMF samples

Figure 6: Evolution of the Americium content in various IMF samples

Figure 7: Evolution of the Neptunium content in the various IMF samples
VI. CONCLUSIONS

(Pu+Am, U) MOX fuel and (Np+Am+Cm,Pu) Inert Matrix Fuel test samples have been loaded in the central channel of the MYRRHA critical core and have been irradiated during five cycles, each one consisting of 90 days of operation at 100 MWth and 30 days of shutdown. The impact of loading such a test fuel assembly on the point-kinetics parameters is quite low, i.e., does not jeopardise the reactor safety.

A wide range of burnup level has been achieved, extending from 48 to 120 MWd/kg iHM, the samples with lower MA-to-Pu ratios reaching the higher burnup. This study has highlighted the importance of the initial MA content, expressed in terms of MA/Pu ratio, on the transmutation rate of MA elements.

For (Pu+Am, U) MOX fuel samples, a net build-up of MA is observed when the initial content of MA is very low while a net decrease in MA is observed in the sample with an initial content of 8 wt%.

This suggests the existence of some ‘equilibrium’ initial MA content value beyond which a net transmutation is achievable.

The above observations underline how MYRRHA can be a key irradiation facility for the development of fuels dedicated to GEN-IV fast reactors and for the design of targets dedicated to MA transmutation.

Acknowledgements

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References


Elemental Technologies for Lead-Bismuth Spallation Target System in J-PARC

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Abstract

Japan Atomic Energy Agency (JAEA) has been researching and developing an Accelerator-Driven System (ADS) as a dedicated system for the transmutation of long-lived radioactive nuclides. The ADS proposed by JAEA uses the lead-bismuth eutectic (LBE) alloy as a spallation target material and a coolant. In the various R&D for ADS, construction of the Transmutation Experimental Facility (TEF) is planned under the framework of the J-PARC project as a preceding step before the construction of demonstrative ADS. In this R&D, TEF is considered for the experimental investigation of the feasibility of the beam window, the structural materials, and to investigate the operation properties of the target system by using 400MeV-250kW proton beam. This target system is consisted of various elements and must be able to operate without troubles during an operation period of TEF facility. Furthermore, in the maintenance period after the operation, because the inside of a hot cell storing a target is exposed to strong radiations, all elements must be designed as remote control devices. In this study, the present conditions of the design and the result of performance test of each important elements were confirmed in the realisation of the LBE target system, such as the monitoring system of flow rate by using the ultrasonic method, the heater system with the metallic heat insulator joined to a flow channel of LBE, and the operability of remote handing.

Introduction

Japan Atomic Energy Agency (JAEA) has been researching and developing an Accelerator-Driven System (ADS) as a dedicated system for the transmutation of long-lived radioactive nuclides. The ADS proposed by JAEA uses the lead-bismuth eutectic (LBE) alloy as a spallation target material and a coolant. To promote JAEA’s research and development (R&D) for ADS, construction of the Transmutation Experimental Facility (TEF) is planned under the framework of the J-PARC project as a preceding step before the construction of a demonstrative ADS. TEF is composed of two experimental facilities, Transmutation Physics Experimental Facility (TEF-P) and ADS Target Test Facility (TEF-T). This paper will focus on TEF-T, and will report some of the required elemental technologies.

The main purposes of TEF-T are the experimental investigation of feasibility of beam window and structural materials, and operation properties of the spallation target system by using 400 MeV-250 kW proton beam. This target system must be operated without significant troubles during its operation period. Hence, R&D of the elemental technologies to perform the measurement control of the important parameters in operation management of the target system is necessary. Furthermore, the target system is highly radioactive due to the proton beam irradiation; all components should be maintained by remote handling devices. In this study, elemental technologies to realise the target system, such as the monitoring system of flow rate by using the ultrasonic method, the heater system with the metallic heat insulator joined to a flow channel of LBE, and the operability of remote handing were tested.
Elemental technologies

Figure 1 shows the photograph and schematic illustration of a prototype design of target head of TEF-T. This design has the coaxially arranged annular and tube type channels. The irradiation sample holder, shown in Figure 2 was installed in the front side of inner tube. There were eight irradiation specimens, arranged every 4 mm in the horizontal direction. In this situation, the specimen of both ends acts as the side wall for the sample holder. The inlet temperature of LBE was set to 350°C, and its flow rate was 1 liter/sec. As a result of thermal-fluid analysis, it was confirmed that the local temperature of LBE and a beam window increased to around 500°C by the incidence of proton beam.

![Figure 1: Photo and schematic illustration of target head](image1)

![Figure 2: Photo of remote operation flange and PMIP](image2)

It is known that general liquid metals such as LBE are opaque, and have a higher melting point than usual fluid. Liquid metal is used as a coolant for nuclear systems due to its superior heat transfer properties; however working temperature condition is very high except for mercury. Therefore, applicable measurement technique is limited because the heat resistance is required to the measurement system. In addition, radiation-resistant is required. Furthermore, LBE can lead to corrosion/erosion of the component materials. Practically, in JAEA’s LBE loop, the blockage was confirmed in a narrow region of flow channel. To deal with the significant trouble caused by the various issues, each component of the target system installed to a hot cell needs periodical exchange/maintenance. Considering all these, this section introduces some elemental technology for the target system.

Packaged metallic heat insulator and preheating device

In the target system, the preheating device and the heat insulator are indispensable component in order to use LBE as a coolant/target material. As noted previously, in the regions where exchange/maintenance is required frequently, the disassembly mechanism is needed to support various significant trouble caused by the characteristic of flowing LBE such as erosion/corrosion. Then, the preheating device and the heat insulator must be removable by remote control easily. Therefore, R&D of the “Packaged Metallic heat
Insulator and Preheating device (PMIP)” is encouraged at JAEA. PMIP consists of the metallic insulator and the heater, and it is applied to cover the remote operation flange which has been applied to Material and Life Science Experimental Facility (MLF) in J-PARC. Figure 2 shows a photograph of PMIP. The main body of PMIP consists of a cylinder-shaped metallic heat insulator of 520 mm diameter with half breaking structure, and a heater is attached to its inner wall. PMIP and the remote operation flange were installed to a test stand in JAEA, and a preliminary disassembly test by remote control using a crane and a master slave manipulator (MSM) were performed. As a result of this preliminary test, the disassembly of PMPI was successful. In near future, the shape/performance optimisation in consideration of remote operability will be performed immediately.

![Figure 3: Photo of continuous level gauge and pressure gauge](image)

**Pressure gauge and Continuous level gauge**

In the operation management of the primary circuit, the pressure of each parts and the liquid level of surge tank is the important information. A liquid pressure gauge was installed for monitoring the local pressure and the pressure loss, to detect any blockage at the filter or flow channel. Also, it has the function as the sub-flowmeter (differential pressure-type flowmeter) in TEF target system. Practically, this method was adopted in MLF. The pressure gauge is a diaphragm type, and its transmission medium is mercury. The material of the diaphragm is 316L stainless steel, and the measurement range is 0-1 MPa. The maximum temperature is 330 °C. The accuracy was found to be ±1.5 % at F.S. The continuous level gauge was installed for the monitoring of LBE’s level behaviour inside of surge tank, to detect a slow leak. This phenomenon has been often caused by the jamming of slag on a seat of drain valve in JAEA’s LBE loop. The continuous level gauge is an induction type, and enables to obtain the level information of 0-300 mm continuously. The maximum temperature is 500 °C. In consideration of the corrosiveness of LBE and the exchangeability, a sheath tube covered the measurement probe. The material of a sheath tube is 316 stainless steel. The accuracy was ±5 % at F.S. This type of level gauge is adopted for fast reactor systems.

To check the operation of each gauge, a simple experiment was performed by using test stand. In this experiment, pressure measured by pressure gauge was compared with the LBE head pressure derived
by the measurement value of level gauge. The temperature condition was 300°C constant. And cover gas pressure was 0 Pa. Figure 4 shows the experimental results. In this figure, the horizontal axis represents the liquid level in a surge tank, and the vertical axis represents the pressure. Each error bar represents the error range of each gauge. The gradient of measured pressure was consistent with LBE head pressure, and each measurement value was within their accuracy.

**Figure 4: result of operation test in static condition**

![Figure 4: result of operation test in static condition](image)

**Flowmeter**

The flowmeter was installed to measure the flow rate of LBE circulating through a primary circuit. This is because LBE flow rate has a great influence in the cooling performance for each component of the target system, especially the beam window. Therefore, in safety operation of the target system, flow rate must be monitored by some methods and it must be managed.

Usually, Electro Magnetic Flowmeter (EMF) is applied to monitoring of LBE flow. However, the instability of its output is a serious problem at long-term operation. Because wettability and corrosiveness or operating conditions of LBE act complicatedly, effective measures to solve this problem are difficult. And the periodic calibration is necessary. However its procedure is complicated and is unsuitable for use in the remote environment. Therefore, In TEF-T, the installation of the flow measurement technique by using ultrasonic is considered.

The ultrasonic flowmeter is a general flow measurement technique and it has been applied to various fields such as engineering, industry and the production. Usually, propagation time difference type is used for the measurement system. Because this system does not need tracer particles, it is a suitable measurement technique for the actual system such as fast reactor and TEF. Typically, this measurement technique has little influence on change of sound speed and it is usually a contactless technique and has high versatility. Figure 5 shows the schematic illustration of the measurement configuration.

**Figure 5: Measurement principle of propagation time difference method**

![Figure 5: Measurement principle of propagation time difference method](image)
The propagation time of ultrasonic signal changes depending on the velocity of the flowing medium. This measurement system emits/receives ultrasonic signals between an upstream ultrasonic transducer “TDX-a” installed on one side and a downstream transducer “TDX-b” installed on the other side. By using the propagation time differences between the forward direction “$t_{ab}$” and the reverse direction “$t_{ba}$”, the mean velocity of the measurement section is derived in the following expressions.

Forward direction \[ \frac{1}{t_{ab}} = \frac{c - V \cos \theta}{d / \sin \theta}. \] (1)

Reverse direction \[ \frac{1}{t_{ab}} = \frac{c + V \cos \theta}{d / \sin \theta}. \] (2)

\[ V = \frac{d}{2 \sin \theta \cos \theta} \left( \frac{1}{t_{ba}} - \frac{1}{t_{ab}} \right). \] (3)

\[ Q = KVA. \] (4)

where  
- $d$: Diameter of flow channel  
- $c$: Sound speed  
- $V$: Mean velocity  
- $A$: Cross section of flow channel  
- $K$: Profile factor

Furthermore, the heat resistance of the measurement system is important. When the ultrasonic flowmeter is used in the target system, excellent heat resistance of the ultrasonic transducer in contact with heated wall of the flow channel is required. Usually, Ultrasonic Velocity Profiler (UVP) uses PZT as a piezoelectric element for its transducer. Because the efficiency of PZT is very high, it is suitable for a technique which uses the extremely feeble echo from the flowing medium for a measurement like UVP. However, its curie point is approximately around 350 °C and is not suitable for use in the operation temperature of the target system of TEF-T. And PZT is easy to be damaged by a radiation environment. Therefore, developed system in JAEA uses niobic acid lithium (LiNbO3) as the element of transducer. The curie point of LiNbO3 is 1140 °C, and even a temperature condition of LBE in the target system does not have any problem at all. The efficiency of LiNbO3 is extremely worse than PZT. However, there is only slight influence because ultrasonic flowmeter uses the time difference of emitted signal simply. Furthermore, it has the superior resistance to radiation environment. Practically, the dominant change of emitting signal was not confirmed after having $\gamma$-irradiation of about 22 MGy either.

**Figure 6: Photo and schematic illustration of JAEA’s high temperature ultrasonic transducer**
Figure 6 shows a photograph and schematic illustration of JAEA’s high temperature ultrasonic transducer. This transducer mainly consists of the main part of transducer and a couplant and a sensor plug. The material of a couplant is copper. Because the semi-contactless measurement is adopted at a present state, a sensor plug made by high chrome steel is installed to reduce the thermal influence to the main part of transducer.

Table 1: Experimental conditions of verification test of ultrasonic flowmeter

<table>
<thead>
<tr>
<th>Setting of Ultrasonic flowmeter</th>
<th>Basic frequency of emitted burst signal</th>
<th>4 MHz</th>
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<tr>
<td>Wave number</td>
<td>1 cycle</td>
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<tr>
<td>Flight path of burst signal</td>
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<td>Time resolution</td>
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<tr>
<td>Number of transducer couple</td>
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<tr>
<td>Material of couplant</td>
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</tr>
<tr>
<td>Material of sensor plug</td>
<td>9Cr-1Mo steel</td>
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</table>

<table>
<thead>
<tr>
<th>Setting of LBE flow</th>
<th>Temperature of LBE</th>
<th>400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate of LBE</td>
<td>0 - 30 liter/min (0-0.4 m/sec)</td>
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</table>

Figure 7 shows the experimental configuration for the verification test of ultrasonic flowmeter. This test was performed in JAEA Lead Bismuth Loop-4 (JLBL-4). In this loop, LBE was driven by Electro Magnetic Pump (EMP) and reference flow rate was measured by EMF. A π-shaped test pipe was connected to the test section of JLBL-4, and two transducers of ultrasonic flowmeter were installed in the up/down stream side in the straight line region. Table 1 shows the experimental conditions. The basic frequency of emitted burst signal was 4 MHz, and the wave number was 1 cycle. The flight path between the two sensor plug was 115 mm. To derive the averaged velocity by using measured values that was measured every dozens of milliseconds, the time resolution of ultrasonic flowmeter was set for 1 second. A temperature of LBE was 400 °C, and the flow rate was 0 – 30 liter/min. In this experiment, flow velocity/rate measured by ultrasonic flowmeter was compared with flow rate/velocity measured by EMF.
Figure 8 shows an example of experimental result. The horizontal axis represents the reference flow rate measured by EMF, and the vertical axis represents the mean velocity in the test section. The solid line represents the theoretical mean velocity derived by flow rate (EMF), and the data points represents the velocity measured by ultrasonic flowmeter. The error bar represents the deviation of 241 data in each flow rate. The correlation coefficient of the measured value of EMF and ultrasonic flowmeter was 0.9992. As a result of this experiment, reasonable linearity (correlativity) was confirmed, and the usefulness of the ultrasonic flowmeter in the monitoring of LBE flow was verified.

**Figure 8: Experimental result of verification test in LBE loop**

Summary

In JAEA, some elemental technologies such as the packaged insulator & preheating device, the monitoring system of liquid level/pressure and the monitoring system of flow rate were tested. As a result of this preliminary test, the disassembly of PMPI and the operation test of the level/pressure gauge in static condition were succeeded. And the ultrasonic flowmeter was successfully applied to flow velocity/rate measurement of LBE. At present, R&D of the completely contactless measurement system is ongoing. In near future, the construction of remote operation procedure and the radiation proof test for each component will be performed.

References


Design Study of Accelerator-Driven System for Minor Actinide Transmutation in JAEA

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Abstract

The Japan Atomic Energy Agency (JAEA) has been conducting research and development (R&D) on Accelerator-Driven System (ADS) as a dedicated transmutation system for long-lived radioactive nuclides. The ADS proposed by JAEA is a lead-bismuth eutectic (LBE) cooled fast subcritical reactor with a thermal output of 800 MW. Several critical issues have to be resolved before ADS can play important roles in the nuclear fuel cycle. The critical issue in the design of the ADS is the engineering feasibility of the beam window for the high power spallation target. Although a feasible concept of the beam window for the ADS was proposed in our previous work. To mitigate the thermal load of the beam window not only in the normal operation but also in the transient situations, the R&D for the mechanism of reactivity adjustment and the accelerator design have been performed at JAEA.

Introduction

To continue the utilisation of the nuclear fission energy, the management of the high-level radioactive waste (HLW) is one of the most important issues to be solved. The difficulty of the HLW management exists in its long-lasting radioactive toxicity which has to be isolated for more than millions years and its heat generation which may affect the structural integrity of deep geological repositories. Partitioning and Transmutation (P&T) technology of HLW is expected to be effective to mitigate the burden of the HLW disposal by reducing the radiological toxicity and heat generation. The Japan Atomic Energy Agency (JAEA) has been continuously implementing research and development (R&D) on P&T technology to reduce the burden of the back-end of the nuclear fuel cycle. R&D on P&T in JAEA is based on two kinds of concepts: one is the homogeneous recycling of minor actinide (MA) in commercial fast breeder reactors and the other is the dedicated MA transmutation, so-called “double-strata” strategy, using an accelerator-driven system (ADS).

The ADS proposed by JAEA is a lead-bismuth eutectic (LBE) target/coolant system with fast subcritical core. To realise the ADS, some technical issues should be studied and developed. JAEA has started a (R&D) programme since 2013. The programme w continued for four years, and the objective of this research programme is to enhance the technology from a basic research phase to a semi-engineering research phase for the main component of the double-strata P&T concept, MA partitioning process and the ADS technologies. In the working package for the ADS, the conceptual design study for the ADS and the experimental study in the critical assembly connecting with the proton accelerator have been carried out to solve R&D issues of the ADS. The results of this R&D programme will be reflected on the assessment of the technically feasibility for each technology. Items of R&D for the conceptual study of the ADS are concentrated on three technical areas peculiar to the ADS: (1) superconducting linear accelerator, (2) reactivity adjustment to compensate the burnup swing, and (3) passive decay heat removal system. In this paper, the outline and the results in the first year of the programme are reported.
General description of JAEA proposed ADS

JAEA’s reference design of ADS [1] is a tank-type subcritical reactor, where lead-bismuth eutectic (LBE) is used as both the primary coolant and the spallation target, as shown in Figure 1. The central part of the core is the spallation target region. The target region is provided by substituting central seven assemblies to a target module. In the target region, LBE is flowing from the core bottom. The proton linac with the proton energy of 1.5 GeV is used for the accelerator to operate the ADS.

Figure 1: JAEA proposed LBE-cooled 800 MWth ADS for transmutation of MA

A tank-type system is adopted to take advantage of a simple design and to eliminate the necessity of heavy primary piping. All primary components, including primary pumps, steam generators, and auxiliary heat exchangers, are accommodated within the reactor vessel. The primary cooling system includes two mechanical pumps and four steam generators. The heat generated in the target and the core is removed by forced convection of the primary LBE, and transferred through the steam generators to a secondary water/steam system for power conversion. The auxiliary cooling system is provided as a backup system for decay heat removal. The inlet and outlet temperature of the LBE coolant were set to 300 and 407°C, respectively. For the core fuel, (MA,Pu)-nitride is used. As inert matrix, zirconium-nitride (ZrN) is used with the fuel. To minimise the burnup swing and the power peaking, the fuel region is divided into two zones with the different initial Pu loading. The MA inventory is about 2500 kg. Since the transmutation rate of MA is 250 kg/yr as described before, the relative transmutation efficiency of MA is about 10%/yr. The maximum keff during whole burnup cycles was set to 0.97. The burnup swing in whole cycles is about 3%Δk/k. The maximum beam current is 20 mA (30 MW).

The beam window, which forms a boundary between the vacuum proton beam tube and the subcritical core, is one of the most important technical issues in the engineering feasibility of ADS. The beam window will be used in the severe conditions; (a) external pressure by LBE, (b) heat generation by the proton beam, (c) creep deformation by high temperature, (d) corrosion by LBE, and (e) irradiation damage by neutrons and protons. The design study for the beam window [2] was performed considering the results of thermal-hydraulic and structural analysis. The external pressure and the heat generation were considered and feasible concepts have been determined. Hence, the shape and the thickness of the beam window were optimised to prevent the buckling failure by the parametric survey. For the shape of the beam window, an ellipse model is adopted, as shown in Figure 2. The ellipse model consists of a top part, a transient part and
a cylinder part. The results of the parametric survey show that the ellipse shape concepts with the thickness of 2.0-2.4[mm] at the top and the thickness of 2.0-4.0[mm] at the transient part were acceptable under the current ADS design parameters. The concept with t1/t2/t3=2.0/3.0/3.0mm is employed as the reference design of the beam window. In addition, T91 steel is assumed as a material of the beam window.

**Figure 2: Beam window design with the ellipse concept of MA**

Research and development in the working package of the ADS design

**Design study of super conducting linear accelerator for ADS**

The proton accelerator for the ADS should have high intensity of power with good reliability. To realise such an accelerator, energy efficiency should be enhanced to assure the self-sustainability for electricity of the whole system. Taking account of these requirements, the superconducting linac (SC-Linac) is regarded as the most promising choice. Considering the production efficiency of the spallation neutrons in LBE, the accelerated energy of the SC-Linac was set at 1.5 GeV. The maximum beam current of the SC-Linac was set at 20 mA (30 MW). Basic parameters of the SC-linac, such as the number of cryomodules, the output power of the klystron and the total length of the SC-linac, were optimised for accelerated energies from 100 MeV to 1.5 GeV [3]. The SC-Linac consists of a series of 89 cryomodules, each of which is connected with a klystron supplying 972 MHz radio frequency (RF) wave. These klystrons were classified into three categories, according to rated output power: 197, 425, and 750 kW.

**Acceptable beam trip frequencies of accelerators for ADS**

Although the high reliability is necessary for the accelerator of ADS, frequent beam trips are experienced in existing high power proton accelerators. The beam trip may cause thermal fatigue problems in ADS components which may lead to degradation of their structural integrity and reduction of their lifetime. To achieve the high reliability for the accelerator, the requirements for the beam trip frequencies were estimated [4]. For this object, thermal transient analyses were performed to investigate the effects of beam trips on the reactor components. These analyses were made on the thermal responses of four parts of the reactor components; the beam window, the fuel clad, the inner barrel, and the reactor vessel. The results indicated that the acceptable frequency of beam trips ranged from 42 to 2×10⁴ times per year depending on the beam trip duration. The former corresponded to the beam trip duration exceeding five minutes. On the other hand, the latter corresponded to the beam trip duration of 10 seconds or less. And the plant availability was estimated to be 70% or greater in cases where the beam trip frequency decreased to the acceptable frequency of beam trips.
In order to consider measures to reduce the frequency of beam trips on the high power accelerator for ADS, the acceptable frequency of beam trips were compared with the operation data of existing accelerators. In this analysis, operation data of a proton linac of LANSCE [5,6] and an electron/positron injector linac at High Energy Accelerator Research Organisation (KEK) [7]. By using the distribution of beam trip durations obtained from the data of the LANSCE and the KEK, the down time distribution of the SC-linac for ADS was estimated and compared with the acceptable beam trip frequencies. The results are shown in Figure 3. The comparison showed that even at the present technological level of accelerators, the beam trip frequency for durations of 10 seconds or less is within the acceptable level. On the other hand, the beam trip frequency for durations of exceeding five minutes should be reduced to about 1/35 to satisfy the plant availability conditions.

![Figure 3: Comparison of the acceptable frequency of beam trips and the estimated frequency of the SC-Linac for ADS](image)

One of the methods to improve the reliability is redundancy which the duplication of critical components or functions of a system. In this study, technical feasibility and possibility for parallelization of the beam line were investigated for the enhanced redundancy of the ADS accelerator. The SC-Linac is mainly composed of low and high energy portions. The low energy portion consists of negative ion source, RFQ, DTL/SDTL and RF source. The high energy portion above 100 MeV, consists of a series of cryomodules which contain two units of superconducting cavities made of high-purity niobium in the reference design. It is very difficult to converge the multiple proton beam in the high energy portion in terms of beam transport and controllability. Therefore, two methods of the parallelisation were considered. One is the parallelisation of the low energy portion in which the duplicated proton beams will be converged at the injection of the high energy portion. The other is multiplication of the entire beam line in which the multiple proton beams will be injected to the beam window. In both concepts, multiplicity was assumed as 2. The necessary components and the technical feasibilities were compared for both concepts.

In this study, we assumed the duplicated parts in operation, that is, half of the proton beams necessary for the operation of the ADS continue to be transported in both parts. In case of the duplication of the low energy part, each proton beam about 100 MeV must be deflected by electromagnet and injected to the high energy portion by kicker magnet. Since the cryomodule for the SC-Linac assumed to be designed to accept 972 MHz RF wave, the frequency for each low energy portion should be adjusted to 486 MHz. In this case, if one of the low energy proton beam supply were stopped, it will be difficult to readjust the RF wave for
the cryomodule to fit into the single beam injection. Moreover, the development of the kicker magnet for the proton beam with 100 MeV is a significant technical challenge. From these difficulties for the duplication of the low energy portion, we assume to adopt the duplication of the entire proton beam line. Figure 4 shows a conceptual view of the ADS with two proton beam lines. In this concept, although the construction cost will become expensive, the reliability of the SC-Linac will be significantly improved. Preliminary estimation of the beam trip frequencies shows the possibility to satisfy the acceptable beam trip for the ADS. The conceptual design study including the components design, equipment layout and beam dynamics have been carried out.

**R&D for the reactivity adjustment method of the ADS**

In the neutronics design of the ADS, the most significant problems are large burnup reactivity swing and considerable radial peaking [8]. These problems are closely related to each other. Since the peaking factor depends on the effective multiplication factor ($k_{\text{eff}}$), increase of the minimum $k_{\text{eff}}$ value during burnup cycle, namely the minimisation of the burnup reactivity swing, is important to reduce the peaking factor. Moreover, the minimised burnup reactivity swing also means reduced proton beam current, since the proton beam current required to keep predefined power level is directly related to $k_{\text{eff}}$. Hence, reducing burnup reactivity swing is one of the most important design requirements for the ADS. In order to keep the thermal power at 800 MW, the beam current was adjusted from 8 to 18 mA (i.e. 12 to 27 MW) depending on the burnup swing. Although we considered the feasible concept of the beam window to accept the maximum beam power of 30 MW, it is desired the minimised burnup swing to enhance the engineering feasibility of the ADS.

![Figure 4: Conceptual view of the ADS with duplicated SC-Linac](image)

In the conceptual design study of the ADS with absorber, the core configuration with heterogeneously arranged absorber should be considered. For such complicated core configuration, the Monte Carlo calculation code is suitable. However, for the optimisation of the burnup swing, the burnup calculations for multiple burnup cycle are needed. The Monte Carlo calculations for these multiple burnup calculations will take much calculation time and are not suitable for the parametric survey calculations. Therefore, for the three-dimensional heterogeneous calculations, we developed the calculation code system, ADS3D, based on the deterministic method.

The ADS3D was developed base on comprehensive and versatile reactor analysis code system, MARBLE [9]. MARBLE is designed as a software development framework for reactor analysis, which
offers reusable and extendible functions and data models based on physical concepts, rather than a reactor
analysis code system. From a viewpoint of the code system, it provides a set of functionalities utilised in a
detailed reactor analysis scheme for fast criticality assemblies and power reactors, and nuclear data related
uncertainty quantification such as cross-section adjustment. Since the MARBLE was originally developed
for the reactor analysis code system for fast reactor, some calculation schemes were additionally integrated
in the ADS3D:

- A high energy particle transport code, PHITS [10], was involved to estimate the spallation
  neutron by the proton induced reaction in the spallation target.
- Fuel exchange function was expanded to treat multiple fuel exchange whether the MARBLE
treats one time of fuel exchange.
- Fuel composition adjustment function to fit the adequate $k_{\text{eff}}$ values was newly added.

**Figure 5: Calculation flow of the ADS3D**

The SLAROM-UF [11] and the PARTISN [12] codes are used for the cell calculation and the
transport calculation, respectively. The calculation flow of the ADS3D is shown in Figure 5. The
calculation results of the developed ADS3D were compared with those by the Monte Carlo burnup
calculation code, MVP-BURN [13]. The results showed that the discrepancies between the calculated $k_{\text{eff}}$
values by both codes were less than 0.2%. At present, the conceptual neutronics study for the core with
absorber has been performed.

**R&D for the passive decay heat removal system for the ADS**

After recent Fukushima Daiichi Nuclear Power Plant accidents, removal of the decay heat from the
reactor core has turned out to be more demanding than provision of reliable reactivity control from safety
point of view. The ADS has been considered more as a safety system than conventional critical reactor
because shutdown of the ADS can easily be achieved by stopping supply of the proton beam. However, our
previous work [14] showed the possibility of core damage in case of heat sink loss accident for the ADS.
In this programme, firstly, the plant dynamic analysis code is improved for the LBE cooled ADS. Next,
based on the calculation results for the ADS plant dynamics during typical accidents, for instance, PLOHS
(Protected Loss of Heat Sink), by the improved calculation code, the passive decay heat removal system is
investigated.
As the plant dynamic calculation code, the RELAP/mod3.2 [15] was selected. RELAP was developed for transient simulation of LWR and widely used for the safety analysis of the power plant. The code was modified for LBE thermal-hydraulic simulation introducing LBE thermophysical property data and heat transfer correlations for heavy liquid metal. The RELAP5 nodalisation scheme was employed for the transient analysis of the ADS as shown in Figure 6. The sub-critical core was divided to three zones, one is for the spallation target and two are for the fuel regions. The primary pump and the steam generator inside the core were modelled. At present, the transient analyses have been carried out by using this calculation model.

Figure 6: Calculation model of the ADS for the RELAP calculation

Conclusion

To improve the technology level from basic research phase to semi-engineering research phase for the main component of the double-strata P&T concept, JAEA has started a R&D programme. In the working package of the programme for the ADS design study, items of R&D were concentrated on three technical areas peculiar to the ADS:

1. Superconducting linear accelerator.
2. Reactivity adjustment to compensate the burnup swing.

In the design study of SC-Linac, duplicate accelerator concept was proposed to improve the reliability of the SC-Linac. In the R&D of the reactivity adjustment method, ADS3D calculation code was developed for the three-dimensional heterogeneous burnup calculation of the ADS. In the R&D of the passive decay heat removal system, the calculation model simulating the ADS was prepared. Based on the results of the first year, the conceptual design study for the ADS with enhanced technical feasibility and reliability has been carried out.
Acknowledgements

This study is the result of “Research and development to solve the engineering Issues for transmutation system using accelerator-driven system” carried out under the Innovative Nuclear Research and Development Programme by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References


Homogeneous Minor Actinide Transmutation in SFR: Neutronic Uncertainties Propagation with Depletion

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Abstract

In the frame of next generation fast reactor design, the minimisation of nuclear waste production is one of the key objectives for current R&D. Among the possibilities studied at CEA, minor actinides multirecycling is the most promising industrial way achievable in the near-term. Two main management options are considered:

- Multirecycling in a homogeneous way (minor actinides diluted in the driver fuel). If this solution can help achieving high transmutation rates, the negative impact of minor actinides on safety coefficients allows only a small fraction of the total heavy mass to be loaded in the core (~ few %).
- Multirecycling in heterogeneous way by means of Minor Actinide Bearing Blanket (MABB) located at the core periphery. This solution offers more flexibility than the previous one, allowing a total minor actinides decoupled management from the core fuel. As the impact on feedback coefficient is small larger initial minor actinide mass can be loaded in this configuration.

Starting from a breakeven Sodium Fast Reactor designed jointly by CEA, Areva and EdF teams, the so called SFR V2B, transmutation performances have been studied in frame on the French fleet for both options and various specific isotopic management (all minor actinides, americium only, etc.). Using these results, a sensitivity study has been performed to assess neutronic uncertainties (i.e. coming from cross section) on mass balance on the most attractive configurations. This work in based on a new implementation of sensitivity on concentration with depletion in the ERANOS code package. Uncertainties on isotopes masses at the end of irradiation using various variance-covariance is discussed.

Introduction

The next nuclear reactors generation have to demonstrate their capacity to reduce the volume of their own radwaste but also those coming from the existing reactors (PWR). The minor actinides (MA) having the advantage of being fissile in fast neutron spectrum, most of GEN-IV reactors are thus the privileged tools to implement the transmutation of minor actinides. Among the many possible strategies, two main minor actinides management are being studied at CEA:

- The homogeneous mode, in which the actinides are diluted in fuel,
- The heterogeneous mode, in which the actinides are placed in dedicated assemblies in core or periphery (radial blankets) allowing, to decouple their management from the standard fuel.

Within this framework, it is necessary to evaluate the transmutation capacity of these two principal modes for current Sodium Fast Reactors (SFR) studied at CEA in the frame of the french fleet. The corresponding Minor Actinides transmutation rate level and corresponding consumption (or mass balance) are of major importance regarding industrial issues such as heavy nuclei inventories, fabrication and reprocessing material flows or evaluation of the size of the nuclear waste ultimate repository.
One of the main points of these evaluations is the mass balance with irradiation which gives basic parameters for front end and back end of the whole fleet in the frame of closed fuel (multirecycling) cycle.

Beside the estimation of the level of “absolute” values, associated uncertainties have also to be evaluated for the whole set of relevant data. These estimations have to be performed for different core state such as end of cycle core for feedback coefficient or end of life for mass balance. This means that uncertainties have to be obtained not only at a fixed time but also have to be propagated all through irradiation. To do so, coupling both Boltzman and Bateman equations at sensitivities level is needed. This coupling is in progress in ERANOS code system and a first estimation of sensitivities on Bateman equation can be performed for mass balance purpose.

After a brief theoretical description of Boltzman/Bateman coupling in progress, the study presented in this paper focuses on transmutation performances and associated sensitivities with depletion for the SFR V2B core design [1] for which several fuel cycle scenarios involving minor actinides transmutation are available. Some uncertainties are presented using various covariance matrices available at CEA.

Bateman/Boltzman coupling strategy

Neutronic uncertainties are usually computed using the Perturbation Theory [2,3] approach allowing estimation of sensitivity factors for any linear and bilinear fonctional of the flux such as multiplication factor or reaction rates (derived from Boltzman equation only). These estimations usually used “static” hypothesis: the state of core (irradiated or not) is always considered at a specific time.

As macroscopic cross sections are a function of the irradiation time, the coupling of Boltzman and Bateman equations is required to have global uncertainties propagation with irradiation.

The inherent change on $N_i$, the concentration of isotope $i$, under irradiation by flux level $\phi$ is driven by the Bateman equation:

$$\frac{dN_i}{dt} = -\phi \sigma_a^i N_i + \sum_{j \neq i} \phi \sigma_c^i N_j - \lambda_i N_i + \sum_{j \neq i} \lambda_{i,j} N_j$$

with $\sigma_a$ and $\sigma_c$ the absorption and capture cross sections respectively, and $\lambda_i$ the decay constant of isotope $i$. Equation (1) can also be written as follows:

$$\frac{d\tilde{N}}{dt} = (R\phi + D)\tilde{N} = M\tilde{N}$$

where $\tilde{N}$ stands for isotopic vector and $M$ the Bateman operator is splitted into cross sections operator ($R$) and decay constant operator ($D$). The effective coupling is performed by building a functional [4] linking Boltzman equation, Bateman equation, direct and adjoint flux renormalisation by mean of Lagrange multipliers ($N^\Gamma, T^\Gamma, P^\Gamma$). The minimisation of this functional with respect to Lagrange multipliers leads to the most general form of the sensitivity $S$ of an integral value $T$ relative to parameter $p$:

$$S(T, p) = \frac{1}{T} \left( \langle p \frac{\partial T}{\partial p} \rangle + \int \left( \langle \tilde{N} \phi \frac{\partial R}{\partial p} \tilde{N} \rangle dt \right) + \left( \langle \Gamma^\Gamma \frac{\partial H}{\partial p} p^\phi \rangle + \langle \Gamma^\Gamma p \frac{\partial H^\Gamma}{\partial p} \phi \rangle \right) + \left( \langle p^\Gamma \frac{\partial H^\Gamma}{\partial p} \tilde{N} \phi \rangle \right) \right)$$

(3)
where the brackets stand for integration on space, and energy and $H$ is the Boltzmann operator ($H = A - F/k$).

The first term in equation (3) is the traditional Boltzmann sensitivity and second one is the Bateman sensitivity. The third and fourth ones are relatives to direct and adjoint flux normalisation, while the last one corresponds to power renormalisation.

In the second term appears $N^+$ which is solution to the adjoint form of the equation (1):

$$\frac{dN^+}{dt} = -M^+ \dot{N}^+$$  \hspace{1cm} (4)

For the “direct” concentration, the adjoint concentration $N^+$ plays a similar role as the adjoint flux toward the direct flux. For a final isotope $i$ at some specific irradiation time, it represents the “weight” of the $n$ previous isotopes (“fathers”) which lead to $i$ by nuclear reactions present in the operator $M$. This adjoint depletion occurs backward in time from a final state ($t = t_F$) to the origin of the direct irradiation ($t = 0$). The final adjoint concentration associated to the integral value $T$ is given by the following formula:

$$\dot{N}^+(t_F) = \frac{\partial T}{\partial N}$$  \hspace{1cm} (5)

If $T$ is a concentration or a linear combination of isotopic concentration $T = \langle u, N \rangle$ with $u$ the vector of individual isotopic weight, the adjoint concentration is $u$ itself.

New developments in the ERANOS code system have been performed [5] in order to solve Bateman adjoint equation and to compute second term of the general sensitivity expressed in equation (3). In addition, initialisation of adjoint concentration is available for $T$ corresponding to a linear isotopic concentration combination and also for multiplication factors such as single $k_{eff}$ or $\Delta\rho = \Delta k/k^2$ (using Equivalent General Perturbation Theory assumptions). The last three terms of equation (3) imply estimation of parameters $\Gamma, \Gamma^+$ and $P^+$ that are solutions of source calculations (analogue to importance calculation) involving complex combination of direct and adjoint concentrations. Although implementation of such source is still in progress, functionalities were not available for this study. The uncertainty level $\varepsilon$ of value $T$ is evaluated using the well-known “sandwich” formula:

$$\varepsilon(T) = \sqrt{S(T)^T V S(T)}$$  \hspace{1cm} (6)

where $V$ is the cross sections variance-covariance matrix.

**SFR core description**

The design of the reference SFR 3 600 MWth MOX core (named SFR V2B hereafter) has been widely described in the past [1]. The design of the fuel assembly is based on a concept with large pins (10.73 mm diameter) and a spacer wire of small diameter (1 mm). The nominal performances of the core reach a burnup of 100 GWd/t with a residence time of fuel of approximately 2000 EFPD and a null internal breeding gain (IBG), this last point being a design goal. As the tightening of the pin bundle in the fuel assembly requires a cladding material which does not swell significantly to reach the expected burnup, an advanced ferritic steel (ODS) is consider.

The reference core design is presented briefly in Table 1. The core configuration ensures self-breeding without the help of fertile blankets.
Table 1: Nominal performances of the reference core SFR V2B

<table>
<thead>
<tr>
<th>SFR V2 B – main characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (MWth/MWe)</td>
<td>3600/1450</td>
</tr>
<tr>
<td>Power density (W/cm³)</td>
<td>207</td>
</tr>
<tr>
<td>Number of fuel elements</td>
<td>453 (267/186)</td>
</tr>
<tr>
<td>Life time</td>
<td>5 × 410 = 2050 EFPD</td>
</tr>
<tr>
<td>Pu</td>
<td>239PuEq content (%)</td>
</tr>
<tr>
<td>E1</td>
<td>E2 (%)</td>
</tr>
<tr>
<td>HN Pu+AM inventory (t)</td>
<td>12.5 (incl. 0.095 Am241)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SFR V2 B – main Performances</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LHR MAX (W/cm)</td>
<td>420</td>
</tr>
<tr>
<td>( \Delta \rho ) cycle (pcm) / (pcm/EFPD)</td>
<td>-450/-1.1</td>
</tr>
<tr>
<td>GBGnst (BOC/ EOC)</td>
<td>-0.001/-0.004</td>
</tr>
<tr>
<td>GBGeff</td>
<td>0.000</td>
</tr>
<tr>
<td>( B_{inv} / B_{max} ) (GWd/t)</td>
<td>99/139</td>
</tr>
<tr>
<td>Damage Max (dpa NRT Fer)</td>
<td>148</td>
</tr>
</tbody>
</table>

Calculation hypothesis

Minor actinides configurations

Two specific scenarios relative to the French fleet are retained as bases for the transmutation evaluations [6]:

- Scenario \( F2A \): homogeneous multirecycling of all actinides in homogeneous mode on the basis of SFR V2B core. Here the minor actinides content is adjusted with respect to a mixt PWR/SFR fleet inventory
- Scenario \( F1G \): heterogeneous multirecycling of all actinides in heterogeneous mode on the basis of SFR V2B core with minor actinide bearing blankets. Here the minor actinides (MA)O₂ content in the UO₂+(MA)O₂ mixture loaded in the blankets is always set to 20%.

These scenarios take into account the transition between a fleet constituted of 100% PWR (beginning of the SFR deployment) and a 100% SFR fleet (equilibrium). Here, we focus on homogeneous mode.

Figure 1: Time evolution of the MA content in initial loading, “scenario F2A”
Figure 1 shows the time evolution of the minor actinide content necessary to ensure the transition between a PWR fleet and a SFR fleet in the frame of the F2A scenario. This content presents a maximum around 3.88% corresponding to the beginning of the transient of SFR deployment and does stabilise around 1.20%. The evolution of the composition shows that the contribution of curium increases regularly to be stabilised after a few decades. One can see that the MA content peak occurs at the very beginning of the SFR deployment. The content quickly increases from residual content (~0.4%) to nearly 4.0%. In this case it is interesting to investigate sensitivity and uncertainty levels relative mass balance.

To do so, a parametric study on the level of the MA content is one carried out from reference case (MOX) up to the maximum value of the scenario (4%). Minor actinides isotopic composition used here are presented in Table 3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Mass content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>U235</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>U238</td>
<td>99.75</td>
</tr>
<tr>
<td>Plutonium</td>
<td>Pu238</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>Pu239</td>
<td>47.39</td>
</tr>
<tr>
<td></td>
<td>Pu240</td>
<td>29.66</td>
</tr>
<tr>
<td></td>
<td>Pu241</td>
<td>8.23</td>
</tr>
<tr>
<td></td>
<td>Pu242</td>
<td>10.37</td>
</tr>
<tr>
<td></td>
<td>Am241</td>
<td>0.78</td>
</tr>
</tbody>
</table>

**Depletion scheme**

Calculations were performed using the ECCO/ERANOS code package using the JEFF3.1 library [7]. The transport option (Bistro S8) has been used for all calculations with a 33-group working library which has been generated from a 1968-group master library. For comparison, fine-group (1968 groups) ECCO cell calculations were also performed, and provide an accurate description of the reaction thresholds and resonances. The fine-group calculation has been performed for the 2-dimensional description of a sub-assembly. Because the broad 33-group library has been generated from this master fine group library, it has been found that differences on the core parameters are small.

For the core geometry model of the core, a cylindrical (RZ) model is adopted. Validity of the RZ model was assessed against the results of heterogeneous (hexagonal-Z) calculation using the TGV/VARIANT 3-dimensional nodal transport code.

Heavy nuclei depletion calculations are performed with an extended chain form Th230 up to Cf252 isotope for a total of 33 heavy nuclei. A simplified model is used for fission product description: a set of 15 lumped fission product for major isotopes (U isotopes, Pu isotopes, Am isotopes, Np237, Cm243, Cm244, Cm245) for which an effective capture cross section has been settled to be representative of real isotopic fission yield distribution.

Core depletion is performed using a simplified averaged irradiation scheme, so mass balance will be estimated between beginning of life (full core loading) and end of life (full core unloading). Using this hypothesis leads to quite good accuracy on core average mass balance at the end of irradiation since it preserves total core fluence.
Covariance data

Uncertainties calculation needs a set of variance-covariance covering the widest range of isotopes and associated cross-sections. As we only focus isotopic mass balance we have to deal with actinides isotopes and the main cross sections that appear in the Bateman equation: capture, fission and \((n,xn)\).

At international level, several teams devoted to nuclear data work on cross section evaluation and associated variance-covariance data. In the frame of GENIV reactor design, CEA is involved in that process and does produce new measurements and/or evaluations on some energy range of interest for both LWR and Fast Reactors.

In the present work, two set of variance-covariance data were used:

- **BOLNA** [8] from the OECD NEA/WPEC Sungroup 26
- **COMAC V0.1** [9] from the CEA work analysis.

The frame of COMAC data set is to provide accurate and up to date variance-covariance data for JEFF3.1 cross section library (and the new JEFF3.2 to come) for main isotopes (heavy nuclei, coolant and structures’ material used in both LWR and FR). As this work is an iterative process, accuracy on data coming from measurements (analytic, differential and integral experiments) and models continuously improve.

Here, the goal is not to discriminate between the two sets but to illustrate their impact on relevant parameters such as mass balance, neutronic feedback coefficients, etc.

Mass balance and uncertainties for homogeneous mode

Mass balance

Table 5 displays the mass balance between begin and end of irradiation for minor actinides. Transmutation rate \( r \) and associated consumption \( c \) are estimated via the following simple formulas:

\[
\begin{align*}
    r &= \frac{\text{mass}_{\text{Unloaded}} - \text{mass}_{\text{Loaded}}}{\text{mass}_{\text{Loaded}}} \\
    c &= \frac{\text{mass}_{\text{Loaded}}}{P_{\text{core}} \Delta t} \times r
\end{align*}
\]

Positive values stand for isotopic creation while negative ones stand for isotopic disappearance.

For MOX case, the minor actinides content resumes to lonely Am241 coming from Pu241 decay between manufacturing and loading. In this case, the core exhibits net production of minor actinides for neptunium (Np), americium (Am) and curium (Cm).

For 1% MA content initially loaded the minor actinides mass balance at end of irradiation is quite close to zero. Although there is a MA equilibrium, the core shows a net production of curium while the Am and Np initial mass are reduced by 10% and 30% respectively.

From 1% to 4%, although the Np and Am transmutation rates show no linear increase, the corresponding mass consumption is linear.

The main isotopes that contribute to minor actinides final mass are:

- Np237 produced by \((n,2n)\) reaction from U238
- Am241 produced by Pu241 decay


- Am243 coming from captures on Pu242 and Am241
- Cm244 coming mainly from capture on Am243

Table 5: Minor actinides mass balance and transmutation performance, homogeneous mode

<table>
<thead>
<tr>
<th>MOX</th>
<th>1%</th>
<th>2%</th>
<th>3%</th>
<th>4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Load (kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np237</td>
<td>0</td>
<td>154</td>
<td>309</td>
<td>463</td>
</tr>
<tr>
<td>Np239</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Np</td>
<td>0</td>
<td>154</td>
<td>309</td>
<td>463</td>
</tr>
<tr>
<td>Am241</td>
<td>95</td>
<td>472</td>
<td>945</td>
<td>1417</td>
</tr>
<tr>
<td>Am242m</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Am243</td>
<td>0</td>
<td>91</td>
<td>182</td>
<td>273</td>
</tr>
<tr>
<td>Am</td>
<td>95</td>
<td>564</td>
<td>1129</td>
<td>1693</td>
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<tr>
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<td>0</td>
<td>0</td>
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<td>1</td>
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<tr>
<td>Cm244</td>
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<td>12</td>
<td>24</td>
<td>37</td>
</tr>
<tr>
<td>Cm245</td>
<td>0</td>
<td>4</td>
<td>8</td>
<td>12</td>
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<td>Cm246</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
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<td>Cm</td>
<td>0</td>
<td>17</td>
<td>34</td>
<td>51</td>
</tr>
<tr>
<td>M.A</td>
<td>95</td>
<td>736</td>
<td>1472</td>
<td>2207</td>
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<tr>
<td>Final unload (kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np237</td>
<td>30</td>
<td>98</td>
<td>171</td>
<td>247</td>
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<tr>
<td>Np239</td>
<td>10</td>
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<td>257</td>
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<td>696</td>
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<td>26</td>
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<tr>
<td>Cm</td>
<td>89</td>
<td>119</td>
<td>174</td>
<td>228</td>
</tr>
<tr>
<td>M.A</td>
<td>495</td>
<td>731</td>
<td>1121</td>
<td>1520</td>
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<tr>
<td>Transmutation rate (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>-29.8</td>
<td>-41.2</td>
<td>-44.5</td>
<td>-45.8</td>
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<tr>
<td>Am</td>
<td>285</td>
<td>-10.9</td>
<td>-32.2</td>
<td>-38.9</td>
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<tr>
<td>Cm</td>
<td>+609</td>
<td>+416</td>
<td>+350</td>
<td>+316</td>
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<td>M.A</td>
<td>420</td>
<td>-0.68</td>
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<td>-31.1</td>
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<tr>
<td>Mass balance (kg/TWeh)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>M.A</td>
<td>+5.6</td>
<td>-0.1</td>
<td>-4.9</td>
<td>-9.6</td>
</tr>
</tbody>
</table>

Final concentration sensitivity

In order to estimate uncertainties, one first needs to get sensitivity coefficients. For mass balance, as stated in Equation (3), Bateman sensitivity combines direct and adjoint concentrations and derivative of Bateman equation relative to cross section. Table 6 shows cross section dependence of sensitivity (integrated over energy and space) for the main final minor actinides isotopic mass for MOX and 4% MA content cases. Only absolute values greater than 0.05 are shown.
Table 6: Minor actinides final concentration sensitivity

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Nxn</th>
<th>MOX 4%</th>
<th>Capture</th>
<th>Fission</th>
</tr>
</thead>
<tbody>
<tr>
<td>U238</td>
<td>+0.895</td>
<td>+0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U235</td>
<td>+0.059</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>U236</td>
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<td></td>
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<tr>
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<tr>
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<td>-0.570</td>
<td>-0.061</td>
<td>-0.120</td>
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<table>
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<th>Isotope</th>
<th>Nxn</th>
<th>MOX 4%</th>
<th>Capture</th>
<th>Fission</th>
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<tr>
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<td>-0.302</td>
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<td></td>
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<tr>
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<tr>
<td>Pu242</td>
<td>+0.916</td>
<td>+0.233</td>
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<tr>
<td>Am243</td>
<td>+0.764</td>
<td>+0.602</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cm244</td>
<td>-0.126</td>
<td>-0.186</td>
<td>-0.059</td>
<td>-0.091</td>
</tr>
</tbody>
</table>

For Np237, initial concentration in MOX case is null and final concentration comes from \((n,2n)\) reaction on U238 and thus the corresponding sensitivity is close to 1. For 4% MA content case, the initial mass is greater than was is produced in the MOX case at end of irradiation so the final mass balance is almost no sensitive to \((n,xn)\) cross section. For both cases, the final Np237 concentration/mass is also sensitive to its own capture cross section with negative values.

For Am241, the production process involves decay from Pu241. In the MOX case, as the initial Am241 is quite small, the final concentration show high sensitivity level to cross sections that “impact” Pu241 concentration during irradiation: neutron capture on Pu240 and fission of Pu241.

For 4% MA content, as for Np237 case, the initial Am241 content is by far greater that what is produced by MOX case, the sensitivity on Pu240 capture cross section decrease from 0.24 to less than 0.05.

The same effect can be observed for Am243 and Cm244 isotopes: if the initial concentration is small, sensitivity of the final concentration to “ancestor isotopes” exhibits high level.

**Final concentration/mass uncertainties**

Tables 7 shows uncertainty levels for BOLNA and COMAC variance-covariance data set respectively. On general level, COMAC results show improvements of uncertainties values for main minor actinides value the whole range of MA content tested here. Relative uncertainties tend to reduce with MA content since “coupling” of sensitivity between isotopes far from each other in the depletion chain becomes small.
Table 7: Final concentration/mass uncertainties for BOLNA and COMAC data (%), homogeneous mode

<table>
<thead>
<tr>
<th>Content</th>
<th>MOX</th>
<th>2%</th>
<th>4%</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>BOLNA</td>
<td>COMAC</td>
<td>BOLNA</td>
</tr>
<tr>
<td>Np237</td>
<td>5.07</td>
<td>5.57</td>
<td>2.17</td>
</tr>
<tr>
<td>Am241</td>
<td>3.50</td>
<td>1.13</td>
<td>1.32</td>
</tr>
<tr>
<td>Am242m</td>
<td>6.96</td>
<td>5.01</td>
<td>7.51</td>
</tr>
<tr>
<td>Am243</td>
<td>19.83</td>
<td>4.30</td>
<td>12.64</td>
</tr>
<tr>
<td>Cm242</td>
<td>3.39</td>
<td>1.26</td>
<td>1.53</td>
</tr>
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<td>Cm243</td>
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<td>18.96</td>
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<td>Cm244</td>
<td>20.98</td>
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<tr>
<td>Cm245</td>
<td>24.52</td>
<td>35.25</td>
<td>15.16</td>
</tr>
</tbody>
</table>

COMAC values lead to lower uncertainties than BOLNA for the main americium isotopes whose mass is still important at the end of irradiation: Am241 and Am243.

For Np237, the MOX cases are driven by U238(n,xn) uncertainty level which is similar for BOLNA and COMAC. Beyond MOX, Np237 uncertainty is driven by Np237 capture data for which COMAC contribution is twice BOLNA a first order.

Results for Cm243 and Cm245 show a net increase for COMAC values. For main (quadratic) contributions to the Cm243, the uncertainty levels are:

- Cm242 capture: 28% for COMAC compared to 12% for BOLNA.
- Cm243 fission: 3% for COMAC compared to 14% for BOLNA.

The same analysis on Cm245 shows different contribution level from its “fathers” namely Pu242, Cm244 for COMAC and BOLNA data.

This first set of results have to be analysed more in depth to provide feedback on nuclear data evaluators on specific isotope, cross section and energy range to decrease uncertainty level. These results have been provided to fuel cycle scenario in order to evaluate impact on global parameter such as mass inventory, radiotoxicity reduction, etc.

Conclusions

Minor actinides transmutation issue is one of the main concerns of the fourth generation reactors design. Uncertainties on mass balance are needed in order to see the impact on core conception (viability) as well as on fuel cycle back end and front end. In this scope nuclear uncertainty data propagation with depletion has been made available in the frame of the ERANOS deterministic code system by means of Bolzttman/Bateman coupling.

Minor actinides mass uncertainties were estimated using COMAC variance-covariance data. Considering homogeneous management using SFR V2B core these uncertainties are ranging 1% to 5% for Americium and Neptunium isotopes. Larger values are obtained for Curium isotopes. Some work still have to be done at the evaluation level to reduce these values to comply with acceptable uncertainty level required by scenarios.
References


Area and Prompt Decay Constant Techniques for Reactivity Assessment in Deep Subcritical Configuration: A Case Study within the Framework of the FREYA Project

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Abstract

Accelerator Driven Systems (ADS) are under study as a possible mean to transmute minor actinides, thus reducing the issues linked to nuclear waste management. The Fast Reactor Experiments for hYbrid Applications (FREYA) FP7 project was launched in 2011 to support the design of the envisaged production of ADS MYRRHA. One of the aims of the FREYA project is to study robust and efficient methods for reactivity monitoring during different phases of a working ADS. For this purpose, the continuous/pulsed deuteron accelerator GENEPI-3C was coupled to the subcritical VENUS-F fast lead zero power reactor at SCK–CEN in Mol, Belgium. An important stage of ADS operations is the on-line monitoring and control of reactivity changes during start-up and fuel replacement. The aim of this study is to compare the results obtained with the use of two reactivity extraction methods in Pulsed Neutron Source experiments foreseen in the FREYA programme: the area and prompt decay constant techniques. In this paper, these two methods are discussed in relation to their applicability in a deep-subcritical configuration (\(k_{\text{eff}} \approx 0.90\)). Finally, in order to take into account the spatial effects in the different detector positions during the Pulsed Neutron experiments, Monte Carlo correction factors were calculated and applied to the experimental reactivity values.

Introduction

The investigation of accurate and reliable reactivity monitoring methods at different subcriticality levels during the operation of an ADS, is one of the main objectives of the FREYA project [1]. Previous experiments, such as the ones carried within the MUSE project [2], showed that, for on-line subcriticality monitoring, the current-to-flux method is a solid technique able to detect changes in reactivity. On the other hand, strategies enabling the measurement of the absolute reactivity will be essential in order to guarantee the reference for procedures to be performed on a regular basis during ADS operation, as for example fresh/spent fuel replacement in shuffle strategies, or during start-up. In this study, a deep subcritical configuration (\(k_{\text{eff}} \approx 0.90\)) was taken into account in order to test some reactivity monitoring methods. The FREYA project foresees the investigation of different methods, such as the AREA method (also called Sjiotrand method [3]) and prompts decay constant method [2]. Both methods are based on Pulsed Neutron Sources (PNS) experiments, which consist in the injection of neutron pulses at a fixed frequency in the reactor core [4]. The AREA method is a robust and simple technique for reactivity assessment, as reported by previous experiments and studies [2,5]. Nevertheless, these studies have
demonstrated also that spatial effects could affect this strategy. Spatial correction factors could be necessary in order to obtain the reactivity of the system consistently from all detectors. On the other hand, the prompt decay constant method could present some problem, especially when the time window after neutron pulse injection must be chosen in order to perform the linear fit (point kinetic approximation) [2]. In this work, the analysis of deep subcritical experiments with the area and the prompt decay constant methods is presented.

**Materials and methods**

*The facility*

The FREYA experimental facility is hosted at the SCK-CEN site in Mol (Belgium). It features the coupling of the VENUS-F subcritical fast core, composed of enriched uranium and solid lead, with the GENEPI-3C accelerator delivering a deuteron beam impinging on a tritium target installed in the reactor core. Fast neutrons, produced by the T(d,n) fusion reactions, provide the external neutron source. The accelerator can operate in pulsed or continuous mode with periodic short beam interruptions (beam trips). The VENUS-F core consists of a 12x12 grid filled by fuel and lead assemblies (FA and LA), control rods (CR) and safety rods (SR). The experimental setup benefits from the experience gained during the implementation of the MUSE and GUINEVERE programmes [6,7]. The fuel rodlets (height 20.32 cm and diameter 1.27 cm) are arranged in a 5x5 square lattice. Figure 1 shows the “subcritical” configuration of the core with the 4 central FAs replaced by the beam line of the GENEPI-3C accelerator. The reactor is composed by 87 FAs, 44 LAs, 2 boron-carbide CRs, 1 PELlet Absorber Rod (PEAR) used for rod drop experiments and 6 SRs made of uranium in the lower half and of boron carbide in the top half [8]. All the 6 SRs account for about 10000 pcm of reactivity. In order to study a low reactivity state with a \( k_{\text{eff}} \) around 0.9, a dedicated core configuration, called “deep subcritical”, has been used. It features 64 FAs (58 FAs plus 6 SR completely withdrawn), 73 LAs inserted, 1 PEAR inserted and 2 CRs partially inserted (Figure 1). Fission chambers locations, at the core middle plane, are indicated in Figure 1: only one fission chamber (CFUF34) has been placed in the fuel zone while the other chambers are located in the inner (RS-10071, RS-10072, RS-10074, CFUL659, CFUM-667, and CFUM-668) and outer reflector (RS-10075, CFUL653 and CFUL673).

**Figure 1: The VENUS-F subcritical core configuration (64 FAs)\nMeasurement channels are showed together with detector identification codes.**

*Area method*

The area method or Sjotrand method [3] relies on the analysis of the time response of the neutron population after a source pulse. The distribution of the time of arrival of neutrons at a fixed location in the reactor, e.g. a detector, features a rapid fall, when the contribution from prompt neutrons dominate, followed by a flatter trend, where delayed neutrons dominate. The integral of the prompt component (\( A_p \))
and the delayed component (\(A_d\)) over time leads directly to the expression of the reactivity in dollars described by Equation (1):

\[
\frac{\rho}{\beta_{\text{eff}}} = -\frac{A_p}{A_d} \tag{1}
\]

The robustness of this method was extensively investigated in past experiments [5,6]. However, an open issue related to the reliability of the method lies on the computation of proper spatial correction factors needed to compensate among each single detector response with respect to its position inside the reactor core [8]. An example of the neutron counts of three detectors placed in three different zones is shown in Figure 2.

Figure 1: Counts time distribution for three detectors placed in three different reactor zones: core, inner and outer reflector. The beam neutron pulse frequency used is 500 Hz, while the beam intensity is 20 mA.

**Prompt decay constant (PDC) method**

Neglecting the delayed neutrons, the point kinetic equations for a reactor without source take the following form [5]:

\[
\frac{dn(t)}{dt} = \alpha n(t) \tag{2}
\]

This equation has an exponential solution given by:

\[
n(t) = n_0 e^{\alpha t} \tag{3}
\]

Where \(\alpha\) is the prompt decay constant:

\[
\alpha = \frac{\rho - \beta_{\text{eff}}}{\Lambda} \tag{4}
\]

Where \(\rho\) is the reactivity, \(\beta_{\text{eff}}\) the effective delayed neutron fraction, and \(\Lambda\) the neutron mean generation time. In the short time scale after the neutron pulse injection, neglecting the delayed neutron is legitimate and thus the decay is mainly described by the PDC method. By measuring \(\alpha\) experimentally, the reactivity can be calculated provided \(\beta_{\text{eff}}\) and \(\Lambda\) are known. For this study \(\beta_{\text{eff}}\) was calculated by MCNPX simulations (\(\beta_{\text{eff}} = 770 \pm 18\) pcm), while for the mean neutron generation time the value reported in [9] was used (\(\Lambda_{\text{eff}} = 0.44 \pm 0.03\) μs).
Results

Area method

By using the methodology described in the previous section, the experimental reactivity values were assessed and the results for each detector are shown in the Figure 3. As showed, the detector in the core and the ones in the inner reflector are quite in agreement. The reactivity values in the outer reflector (RS-10075, CFUL673 and CFUL653) are clearly underestimated and this is probably due to the fact that the delayed neutron level was not completely reached considering the neutron pulse frequency of 500 Hz. In order to decrease the statistical errors, five PNS data runs with the same acquisition parameters were summed. In this way an average statistical error of less than 1% was obtained for all detectors except for the CFUF34 detector (about 2%), where the small deposit material limits the statistic in this channel. The systematic errors were calculated according to the methodology reported in [10] and the average value is of about 3%.

In order to study spatial effects due to the different locations of the detectors, also MCNPX [11] Monte Carlo (MC) correction factors (CF) were calculated according to the methodology described in [12]. As showed in Figure 4, considering the correction factors there is no too much improvement in the alignment of the reactivity values in the different detectors positions, especially for the ones placed in the outer reflector. It is worth to say that the Monte Carlo calculations of the CF are very time consuming. For example, performing the MC calculation of the fission count rate in each detector position, it takes about 9 days with a 2.93 GHz processor and 4 GB of RAM. In this case the error associated with our MC results was in average of about 0.50%. Since the error precision of the calculated reactivity in each detector position should be one order less than 0.50%, it is possible to understand the oscillation values reported in Figure 4. On the other hand lowering the MC error of one order of magnitude means prohibitive computational time, even through the use of clusters.

Figure 3: Reactivity values obtained with the AREA method.
Red bars represent the systematic errors calculated by the methodology in [12]. Blue bars represent statistical errors.

Figure 4: Reactivity values obtained with the AREA method with and without correction factors
MCNPX correction factor were calculated according to the methodology in [10]. The CF for the CFUM21-667 was not taken into account in these calculations and for this reason only the raw value is present in the plot.
Prompt decay constant method

The reactivity was calculated by using the equation (4). In order to extract the $\alpha$ value form the PNS experimental data, a time window of 10 $\mu$s was considered (Figure 4). In particular this time window was chosen because here the linear fit of logarithm of the counts (equation 2-3) has a correlation coefficient (R-coefficient) greater than 0.99 (Table 2). Namely for all the detectors in this time interval, the neutron distribution presents a behaviour quite close to the exponential one (Point-Kinetic approximation). The reactivity values are shown in Table 3. In this case the major sources of uncertainties are represented by the error on the $\Lambda_{eff}$ value (of the order of 6%) and on the $\alpha$ value (average error on the fit of about 2%). Using this method in deep subcritical configurations, the influence of higher spatial modes especially in reflector positions, make the use of the $\Lambda_{eff}$ value not so appropriate (second column of Table 3) if a static reactivity value is required. In fact, under these conditions this issue could introduce some bias for the final reactivity assessment. In this case a spatial dependent $\Lambda_s$ value could be more appropriate in order to obtain more aligned reactivity values. For this reason a semi-empirical $\Lambda_s$ value was also used according to the following expression [14]:

$$\Lambda_s = \frac{1}{\alpha} \left( 1 - \frac{1}{K_{eff}} - \beta_{eff} \right)$$  

(5)

Where the $\alpha$-values are the experimental ones (Table 2), and $K_{eff}$ and $\beta_{eff}$ are calculated by MCNPX simulations (Table 3). The $\Lambda_s$ values calculated by the above expression are showed in Table 2.

Figure 5: Neutron distribution in the time interval 15-25 $\mu$s, after the neutron pulse.

<table>
<thead>
<tr>
<th>Detector</th>
<th>$\alpha$(s$^{-1}$)</th>
<th>R-coefficient</th>
<th>$\Lambda_s$ (s)</th>
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<tr>
<td>CFUL659</td>
<td>118050</td>
<td>0.998</td>
<td>1.01095E-6</td>
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<td>CFUL673</td>
<td>114170</td>
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<td>1.04530E-6</td>
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<td>CFUL653</td>
<td>195460</td>
<td>0.995</td>
<td>6.10571E-7</td>
</tr>
<tr>
<td>RS-10071</td>
<td>112980</td>
<td>0.998</td>
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<td>1.08267E-6</td>
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<tr>
<td>CFUF34</td>
<td>221110</td>
<td>0.995</td>
<td>5.39741E-7</td>
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Table 3: Reactivity comparison with the two methods used in this work and with the value obtained by MCNPX Monte Carlo simulations

<table>
<thead>
<tr>
<th>Detector</th>
<th>ρ($)-prompt decay method*</th>
<th>ρ($)-prompt decay method**</th>
<th>ρ($)-area method</th>
<th>ρ($)-MCNPX***</th>
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<td>7.40</td>
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<td>8.74</td>
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<td>10.74</td>
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<tr>
<td>CFUF34</td>
<td>13.63</td>
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<td>CFUM21-667</td>
<td>9.75</td>
<td>16.49</td>
<td>15.31</td>
<td></td>
</tr>
</tbody>
</table>

* Reactivity obtained by using the $\lambda_{eff}$ value (0.44 μs).
** Reactivity obtained using the different $\lambda_{s}$ values reported in Table 2.
*** This value was obtained through two MCNPX simulations: one to calculate $K_{prompt} (=0.89264 ± 0.00013)$, the other to calculate $K_{eff} (=0.89957 ± 0.00013)$.

Discussions and conclusions

The AREA and the PDC methods were used for PNS experiments in the VENUS-F core at a deep subcritical level characterised by a multiplication factor of about 0.9. Considering the AREA method, the results showed that the reactivity values in the core and in the inner reflector are quite consistent between them and with the MCNPX calculations (the maximum difference between simulations and experimental results is of about 11% for the value extracted in the detector placed in the core), whereas the values extracted by the three detectors placed in the outer reflector are clearly underestimated (Figure 3). MC correction factors could solve the problems of spatial effects, but for the three detectors placed in the outer reflector (where a complete delayed neutron level is not reached), also the CF are not able to align the reactivity values. The reactivity trend obtained with this method and in this deep subcritical configuration, is quite in agreement with other results obtained always in the frame of the FREYA project, where a core configuration with a $K_{eff}$ of about 0.95 was considered [8]. This case study give the indication that the Area method in fast reactors works reasonably well for core and inner reflector detector positions. For the external detectors, probably this time interval (0-2 ms) is not enough to reach the condition where the delayed neutron level is in equilibrium with the flux of the fundamental mode. Considering the PDC method (and taking into account the $\lambda_{eff}$ value), only the reactivity value extracted in the central detector presents small differences (of about 6%) with the MCNPX one (Table 3). The reason could be in the fact that in the central part of the reactor core, the fundamental mode play a major role for the neutron time distribution after 10 μs [13]. On the other hand, taking into account semi-empirical $\lambda_{s}$ values calculated by the equation (5), it is possible to obtain more uniform reactivity values (third column of Table 3) in each detector position, but with a higher difference with respect to the MCNPX reactivity simulated value (about 12%). It is clear how in this method is important to get a very precise position-dependent $\lambda_{s}$ estimation to have uniform reactivity values in the different detector positions. Finally it is possible to note how in the Area method (and for the core and inner reflector positions where the reactivity values are quite in agreement between them) the presence of higher spatial modes in these channels have a small influence on the final reactivity estimation, probably because in this method it is more important to reach the equilibrium state, whatever is the magnitude of the higher spatial modes. Instead in the PDC method the presence of higher spatial modes could influence the determination of the α-constant and consequently the reactivity strongly depend on the time interval chosen to perform the...
analysis. Moreover another drawback of this method is that the reactivity deeply depend on the precision of calculated parameters, such as $\beta_{\text{eff}}$, $K_{\text{eff}}$ and $\Lambda_{\text{eff}}$.

Acknowledgements

This work has been supported by the 7th Framework Programmes of the European Commission (EURATOM) through the FREYA Contract No. 269665. We want to thank the VENUS reactor and GENEPI-3C accelerator technical teams and all the FREYA collaboration for their fundamental support in data analysis and acquisition.

References

Preparation of Minor Actinides Irradiation in Accelerator-Driven System with 100 MeV Protons at Kyoto University Critical Assembly

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Abstract

The Accelerator-Driven System (ADS) with high-energy protons has been under the development of transmutation of minor actinides (MAs) and long-lived fission products in high-level radioactive waste. The neutron capture and fission reactions of MAs are important to accomplish their transmutation in ADS. In the present study, the measurement of capture reaction rates of $^{237}$Np in ADS has been conducted at the core of the Kyoto University Critical Assembly. The core is composed of uranium, polyethylene, and lead-bismuth plates, and the effective multiplication factor is approximately 0.96. The lead-bismuth target is set to generate pulsed spallation neutrons. The γ-ray spectra of the $^{237}$Np foil before and after irradiation are measured with the high-purity Ge detector. From the experimental results, radioactive nuclides caused by neutron capture reactions of $^{237}$Np are difficult to observe clearly under the current experimental setting, including the shielding and activation of $^{237}$Np foil.

Introduction

In the 1990s, the Accelerator-Driven System (ADS) has been proposed as an energy amplifier for generating electricity [1] or a transmutation system for long-lived nuclear system [2]. The ADS using lead-bismuth (Pb-Bi) for MA transmutation has been investigated in the Japan Atomic Energy Agency (JAEA) [3-5]. In the ADS, the role of Pb-Bi is spallation target and coolant of subcritical core.

In the Kyoto University Critical Assembly (KUCA) [6], a series of ADS experiments had been conducted with the combined use of core and the FFAG accelerator [7]. Spallation neutrons were generated by an injection of 100 MeV protons onto the tungsten target. Static and kinetic parameters in reactor physics have been investigated through experiments and numerical calculations [8,9]. Fission and capture reaction rates of $^{237}$Np and $^{241}$Am had been previously measured at the KUCA core in critical state [10-12]. Experimental analyses of fission and capture reaction rates of the minor actinides (MAs) in ADS are important to verify the uncertainty of MA cross sections, because neutron spectrum of the core in ADS is dominant over the high-energy neutrons, compared with that of the core in critical state.

The purpose of this study is to prepare experimental setup of ADS for the MA transmutation. In this study, $^{237}$Np foil was irradiated in the subcritical core ($k_{eff} \geq 0.96$) by the injection of 100 MeV protons onto the Pb-Bi target, and the spectrum of γ-ray from irradiated foil was measured with the use of HPGe detector.

Experiments

Experiments were conducted in the KUCA core with combination of the FFAG accelerator, and the energy of proton beam was 100 MeV. Spallation neutrons were generated by the injection of 100 MeV protons onto the Pb-Bi target in the core. The core configuration is shown in Figure 1, and this core
-contained fuel and polyethylene reflector rods. The fuels are composed of highly enriched uranium, Pb-Bi, and polyethylene. The structures of fuels are shown in Figure 1, and six control rods were installed in the core. In the present study, the condition of six rods was fully withdrawn from the core. The effective multiplication factor $k_{eff}$ of the core was approximately 0.96. The $^{237}$Np foil was used as the same as one described by reference [13], and the number of $^{237}$Np was $(1.99\pm0.01)\times10^{17}$. The $^{237}$Np sample was covered with aluminium (Al) box case, and set in the centre of the fuel at the position (15, K), shown in Figure 1. Two Au foils with and without cadmium (Cd) plates were used for measuring $^{197}$Au(n, $\gamma$)$^{198}$Au reaction rate and Cd ratio. After the irradiation, spectrum of $\gamma$-ray from activated foils was measured with a high purity germanium detector, and energy of $\gamma$-ray and emission rates of $^{238}$Np and $^{198}$Au are listed in Table 1. These foils were irradiated by the spallation neutrons generated from the injection of 100 MeV protons. The irradiation time was 6 hours, and the FFAG accelerator conditions were as follows: beam current 1 nA; pulse repetition period 50 ms; and pulse width 100 ns.

**Figure 1:** Top view of experimental set up at the KUCA A-core

![Diagram of experimental setup](image)

**Table 1:** $\gamma$-ray energy and emission rate of $^{238}$Np and $^{198}$Au

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half life [day]</th>
<th>$\gamma$ ray energy [keV]</th>
<th>Emission rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$Np</td>
<td>2.12</td>
<td>984</td>
<td>27.8</td>
</tr>
<tr>
<td>$^{198}$Au</td>
<td>2.70</td>
<td>412</td>
<td>95.6</td>
</tr>
</tbody>
</table>
Results and analysis

γ-ray of the $^{237}$Np foil before and after irradiation were measured with the Ge detector. The measured spectrum before irradiation is shown in Figure 2(a). The peaks of γ-ray of $^{233}$Pa were observed in this spectrum from 300 to 416 keV, and other of natural radioactive nuclides at 609 keV of $^{209}$Bi, 1460 keV of $^{40}$K, and 1764 keV of $^{214}$Bi. Figure 2(b) shows the spectrum of the $^{237}$Np foil after irradiation. The result after 2 days shows that high count rate was found in 1364 and 1732 keV of $^{24}$Na, and this nuclide is mainly considered produced by $^{27}$Al(n,α)$^{24}$Na reaction of the Al case. The results after 4 and 17 days show that the count rates of $^{24}$Na with a half-life 15 hour were decreased. The spectrum shows other peaks coming from Mn, Co, and V. It was found that the Al case contains some impurities, including Cr, Mn, and Fe. The peaks of γ-ray were generated from activated impurities of the Al case. For instance, $^{48}$V was considered generated from $^{50}$Cr(n,t) reaction of the Al case. From the results, the peak of γ-ray from $^{238}$Np was difficult to be found in the measurements.

![Figure 2: γ-ray spectra of the $^{237}$Np foil: a) before and b) after irradiation from 2 to 17 days](image)

To investigate the reaction rate of $^{237}$Np(n,γ)$^{238}$Np reaction, we executed numerical calculation using the MCNP6 code [14] with ENDF/B-VII.0[15] and JENDL Dosimetry File 99 [16]. Figure 3 shows calculation results of neutron spectrum inside the Al case at the position (15, K) in the core. Pb-Bi means another core which is hard spectrum core at the KCUA, and this fuel assembly is composed of uranium and polyethylene. Neutron spectrum of Pb-Bi is harder than that of EE1 core, which shows thermal neutron ratio in Pb-Bi core is lower than that of EE1 core. Additionally, measured result of Cd ratio was 1.14, as listed in Table 3, which also means the neutron spectrum in core using Pb-Bi is hard. Calculated results of Au and Np are listed in Table 4. This results show that the reaction rate of $^{237}$Np(n,γ)$^{238}$Np reaction is $10^4$ times lower than that of $^{197}$Au(n,γ)$^{199}$Au reaction. From calculated and measured results, measured reaction rate of $^{238}$Np was 5.7 [s⁻¹]. Considering irradiation time 6 hour and detection efficiency 1%, the measured count rate was less than $4.5 \times 10^{-3}$ [s⁻¹]. Hence γ-ray from $^{238}$Np were difficult to be found in the experiments.
Figure 3: Calculated neutron spectra in the core using Pb-Bi and EE1 assemblies

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half life</th>
<th>$\gamma$ ray energy [keV]</th>
<th>emission rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{24}$Na</td>
<td>15.0 hour</td>
<td>1 369</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 754</td>
<td>99.9</td>
</tr>
<tr>
<td>$^{48}$V</td>
<td>16.0 day</td>
<td>944</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>984</td>
<td>100.0</td>
</tr>
<tr>
<td>$^{52}$Mn</td>
<td>5.59 day</td>
<td>1 312</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>744</td>
<td>90.6</td>
</tr>
<tr>
<td>$^{22}$Na</td>
<td>2.60 year</td>
<td>1 274</td>
<td>99.9</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>312.3 day</td>
<td>835</td>
<td>100.0</td>
</tr>
<tr>
<td>$^{56}$Co</td>
<td>77.3 day</td>
<td>847</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 238</td>
<td>67.6</td>
</tr>
</tbody>
</table>

Table 3: Measured reaction rates of Au foils

<table>
<thead>
<tr>
<th>Foils</th>
<th>Size</th>
<th>Weight [mg]</th>
<th>Reaction rate [/s]</th>
<th>Cd ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>diameter 10 mm</td>
<td>82.7</td>
<td>(4.73±0.04)$\times 10^4$</td>
<td>1.14</td>
</tr>
<tr>
<td>Au with Cd</td>
<td>length 50 µm</td>
<td>84.9</td>
<td>(4.27±0.05)$\times 10^4$</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Calculated reaction rates of Au and Np foils

<table>
<thead>
<tr>
<th>Foils</th>
<th>Reaction</th>
<th>Reaction rate [/source]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$^{197}$Au(n,$\gamma$)$^{198}$Au</td>
<td>(4.70±0.35)$\times 10^{-6}$</td>
</tr>
<tr>
<td>Au with Cd</td>
<td></td>
<td>(2.92±0.29)$\times 10^{-6}$</td>
</tr>
</tbody>
</table>

Conclusion

To prepare experimental set up for MA irradiation, $^{237}$Np foil was irradiated in the subcritical core with the spallation neutrons. The results showed that the $\gamma$-ray peaks of $^{237}$Np foil after the irradiation were not observed clearly. This was due to low capture reaction rates of $^{237}$Np and high background $\gamma$-ray caused by the activation of aluminium shielding case covering $^{237}$Np foil. Considering the experimental results, an
improvement of a further activity of $^{237}\text{Np}$ foil and the $^{237}\text{Np}$ foil shielding could be inevitable to accomplish measuring neutron capture and fission reaction rates of $^{237}\text{Np}$ and $^{241}\text{Am}$ in ADS.

Acknowledgements

The authors are grateful to Mr. M. Yamanaka and all KUCA staff members for their assistance in conducting these experiments. A part of this study is the result of “Research and Development for Engineering Resolution of Nuclear Transmutation Cycle by Accelerator-Driven System” carried out under the Innovative Nuclear Research and Development Programme by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References


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Uptake of Caesium from Aqueous Solutions by Microcapsules Enclosing Natural Minerals

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Abstract

Caesium-137 having a relatively long half-life of about 30 years exhibited high radioactivity, heat generation, and large amounts of Cs group are contained in HLLWs or spent fuel. Therefore, selective separation of Cs-137 from HLLWs is a very important environmental issue for nuclear waste management. In addition, the purified Cs is also expected for the reuse as radiation and heat sources in the field of medicine and industry.

It has been proved that geological minerals presented a favourable environment for sorption of Cs, such as zeolite, illite, montrollite, and kaolinite. Zeolite, a natural mineral (Na₈ (AlO₂)₈(SiO₂)₄₀ ·20H₂O), exchanger having high selectivity toward Cs⁺ were encapsulated in the biopolymer matrices (calcium alginate, CaALG). The characterisation of microcapsules (MCs) was examined by SEM-EDS, and the uptake of Cs⁺ were investigated by batch methods. Spherical and elastic granules were obtained, and the particle size of microcapsules was about 700 μm. A relatively high uptake (%) of Cs above 90% for MCs enclosing zeolite was obtained in the presence of 0.1-6 M HNO₃ and 0.001-1 M NaCl solution, and the uptake equilibrium was attained within 5 h. The uptake isotherm of Cs followed a Langmuir-type adsorption equation. The relatively larger K₅ value (120 and 50 cm³/g) for Cs showed a selective uptake property in the presence of various metal ions under 2.5 N HNO₃ and 1 M NaNO₃.

Introduction

The way to properly and safely reprocess or dispose of the radioactive waste is a very urgent and critical topic in Chinese Tapei and it has also become a highly controversy and dispute between public and government during 10 years. In fact, a large amount of the high-level radioactive wastes was produced after 40 years of operation of nuclear power plants including about 5 000 tU of spent fuel that exist in various states of origin, chemistry and physics, similar to other toxic or hazardous wastes [1]. The unstable characteristic of decay and long half-life for radioactive waste is extremely different to that of other wastes.

Microencapsulation is a unique technique for enclosing active component in a porous polymeric matrix [2-5]. It is well known that alginites (ALG), a kind of biopolymer, has high immobilisation ability and this method has been extended to industrial, medical and agricultural fields. Alginate is a salt of alginic acid having carboxyl groups capable to form gels by crosslinking with multivalent metal ions. This immobilising property of alginate has led to its extensive applications to the microencapsulation of enzymes, subcellular organelles, and living cells [6,7]. Thus, the granulation with alginate gel has several advantages such as simplicity for preparation, mechanical strength and strong acid resistance [2-5].

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For long-term geological investigation in international disposal project of high-level radioactive waste (HLW), it was commonly found that cesium strongly sorbs on clay minerals, especially illite, kaolinite, and montmorillonite [8-13]. In general, cesium adsorption on minerals mainly involves an ion exchange process. Moreover, it was found that cesium adsors on clay minerals to balance the negative charge on the alumino-silicate structure. This charge arises as a result of partial replacement of $\text{Si}^{4+}$ or $\text{Al}^{3+}$ ions by cations of lower charge.

In this study, an innovative microcapsule enclosing with specific natural minerals, environmentally friendly as well as low-cost will be developed. Besides, we have attempted to encapsulate the fine clay minerals including zeolite, illite, montmorillonite, and kaolinite as ion exchangers into the biopolymer matrices (calcium alginate, CaALG) by using its high immobilising ability for the selective removal of Cs$^+$ from the waste solution containing highly concentrated HNO$_3$ and NaNO$_3$. The present paper deals with the preparation of microcapsules (MCs), characterisation and uptake properties.

**Experimental**

**Materials**

The natural clay minerals including zeolite ($\text{Na}_8(\text{AlO}_2)_{8}(\text{SiO}_2)_{40} \cdot 20\text{H}_2\text{O}$), illite ($\text{K}_{0.65}\text{Al}_2$) ($\text{Si}_{3.35} \text{Al}_{0.65}\text{O}_{10}(\text{OH})_2$), montmorillonite ($\text{Ca}_{0.33}\text{Na}_{0.33}[(\text{AlMg})_2][\text{Si}_4\text{O}_{10}(\text{OH})_2]$, and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) consisting of alumino-silicate structure and exchangeable Na$^+$ ions (or K$^+$ ions) were used as active components. Sodium alginate (NaALG, 500-600 cP) was purchased from Wako Pure Chemical Ind. Cs$^+$ solutions were obtained by diluting the standard solutions (1000 ppm, Merck Pure Chemical Ind.)

**Preparation of MCs**

The alginate gel enclosing natural clay minerals was prepared as follows. The different clay minerals (0.5 g) were kneaded with the NaALG solution (50 cm$^3$, 2 wt%) and fully dispersed by using kneader equipped the function of rotation and revolution. The well-kneaded sol was injected dropwise into a 0.5 M CaCl$_2$ solution using a medical needle under constant stirring at room temperature to form MCs. The MCs were stirred gently for 24 h to enhance the aging. The MCs were then separated from the solution, washed with distilled water and finally air-dried at 25°C overnight.

**Characterisation**

The surface morphology MCs was observed by optical microscope and scanning electron microscope (SEM, Hitachi TM-1000). In order to estimate the acid resistance, the different microcapsules specimens (50 mg) were analysed by SEM after drying.

**Determination of distribution coefficient ($K_d$)**

The distribution of Cs ions for MCs was estimated by batch method. An aqueous solution (10 cm$^3$) containing 10 ppm Cs ion was contacted with 1 g of MCs at 25±1°C up to 1 day, which was found to be sufficient for attaining equilibrium. The concentrations of Cs ions were measured by atomic absorption spectrometer (AAS, Thermo Solaar system). The uptake percentage ($R$, %) of Cs$^+$ ions removed from the solution and the distribution coefficient ($K_d$, cm$^3$/g) are defined as:

$$R = \frac{C_0 - C_t}{C_0} \times 100$$

$$K_d = \frac{(C_0 - C_t)}{C_t} \times \frac{V}{m}$$

where $C_0$, $C_t$, and $C_e$ (ppm) are the concentration of metal ions at initial, at time $t$, and at equilibrium, respectively; $m$ (g) the weight of microcapsules; $V$ (cm$^3$) the volume of aqueous phase.
Results and discussions

Surface morphology and acid resistance

Figure 1 shows the SEM images of the surface of microcapsule enclosing natural clay minerals. The structure of gel matrices is composed of crosslinked polymer networks with ionic bonding of $\text{Ca}^{2+}$ and carboxyl groups. Obvious spherical and elastic granules were obtained in different microcapsules. On the surface of microcapsule, a numbers of fine clay minerals (~1 µm in diameter) were easily seen to be encapsulated. Some creases were observed on the surface of microcapsule. The practical sizes of MCs were estimated to be 700 µm (0.7 mm) in diameter by optical microscope and SEM image. The clay minerals content in MCs was estimated to be 15 wt%.

Figure 1: SEM images and EDS analysis of the surface of microcapsules:
(a)-(c): kaolinite; (d)-(f): zeolite; (g)-(i): illite; (j)-(l): montmorillonite
Uptake of Cs by MCs enclosing natural minerals

In order to check the equilibration time of Cs for MCs, the effect of uptake (%) was examined in the presence of shaking time (1-24h), 0.1-6 M HNO₃ or 0.001-1 M NaCl solutions by batch method (Figure 2). The uptake rates of Cs for MCs attained equilibrium rather fast in the initial stages within 5 h, and relatively large R value above 70% was obtained in 3M-MCs enclosing zeolite. The uptake of Cs in the initial stage was probably due to the adsorption on the surface, followed by a step controlled by mass transfer through gel matrices [14]. On the other hand, in the presence of 3M HNO₃ or 1 M NaCl, the uptake of Cs was tended to decrease. The reason may be due to the swelling of MCs in the presence of highly concentrated Na ion resulted in the lowering of the uptake rate of Cs.

![Figure 2: Effects of Cs uptake(%)](image)

Uptake isotherm of Cs

The Langmuir isotherm model is expressed as:

\[ Q = \frac{M K C}{1 + K C} \]  \hspace{1cm} (3)

where \( Q \) is the amount sorbed per unit sorbent and \( C \) is the equilibrium solution concentration of sorbent. Two parameters, maximum sorption (\( M \)) and bonding energy coefficient (\( K \)), were used to describe the sorption capacity and affinity of the material. However, the theoretical assumption of the Langmuir model is that the bonding energy on each sorption site is completely equal. Thus, the heterogeneity of sorption energy has been taken into account.

The uptake isotherm of Cs for MCs was obtained in a wide range of initial Cs⁺ concentration from 10 ppm to 500 ppm. The equilibrium amount of Cs adsorbed on MCs approached a constant value with increasing concentration, suggesting that the uptake of Cs follows a Langmuir-type adsorption equation [15]. The Langmuir equation (3) can be rewritten as follows:

\[ C_{eq}/Q_{eq} = \frac{1}{K Q_{max} + (1/Q_{max})C_{eq}} \]  \hspace{1cm} (4)

where \( C_{eq} \) (mol/mL) and \( Q_{eq} \) (m mol/g) are the equilibrium concentrations of Cs in the aqueous and solid phases, respectively; \( Q_{max} \) (m mol/g) is the maximum amount of Cs taken up; \( K \) (cm³/mol) is the Langmuir constant.

As seen in Figure 3(b), a fairly linear relation between \( C_{eq}/Q_{eq} \) and \( C_{eq} \) was obtained from Langmuir-plots for MCs. The result shows that the \( Q_{max} \) value of Cs for MCs was zeolite (8.06 mmol/g) > montmorillonite (2.20 mmol/g) > illite (2.03 mmol/g) > kaolinite (0.59 mmol/g).
Selective uptake of Cs in the presence of different metal cations

The $K_d$ value of various metal ions is shown in Figure 4. Relatively large $K_d$ value for Cs above 121 cm$^3$/g was obtained in the presence of 2.5N HNO$_3$, indicating that MCs enclosing zeolite has strong adsorption ability to Cs in strong acid solution. The uptake of Cs tended to slightly decrease and the $K_d$ value was around 50 cm$^3$/g even in the presence of 2.5 N HNO$_3$ and 1 M NaNO$_3$ at V/m value of 10 cm$^3$/g.

Conclusion

The uptake properties of Cs, characterisation and dynamic adsorption properties were investigated by using MCs enclosing natural minerals. The uptake of Cs for MCs was fairly fast in the initial stage and the uptake equilibrium attained within 5 h. The uptake isotherm of Cs followed a Langmuir-type adsorption equation. The $K_d$ for Cs showed a relatively larger value (120 and 50 cm$^3$/g) in the presence of 2.5 N HNO$_3$ and 1 M NaNO$_3$. 
Acknowledgements

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References

Different Methods for Conditioning Chloride Salt Wastes

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Abstract

Three different methods have been used to condition chloride salt wastes coming from pyroprocesses. Two of them allow to synthesise sodalite, a naturally occurring mineral containing chlorine: the former, starting from Zeolite 4A, which transforms the zeolite into sodalite; the latter, which starts from kaolinite, giving sodalite as well. In addition, a new matrix, termed SAP (SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5}), has been synthesised. It is able to form different mineral phases which occlude fission metals. The products from the different processes have been fully characterised. In particular the chemical durability of the final waste forms has been determined using the standard product consistency test. According to the results obtained, SAP seems to be a promising matrix for the incorporation of chloride salt wastes from pyroprocesses. Financial support from the Nuclear Fission Safety Programme of the European Union (projects ACSEPT, contract FP7-CP-2007-211 267, and SACSESS, Collaborative Project 323282), as well as from Italian Ministry for Economic Development (Accordo di Programma: Piano Annuale di Realizzazione 2008-2009) is gratefully acknowledged.

Introduction

The pyrometallurgical processing of spent nuclear fuel, carried out at 500°C in a molten salt medium (LiCl-KCl, 59-41 mol\%), generates a chloride salt waste containing alkali-metal, alkaline-earth, and some rare-earth fission products \cite{1}. Sodalite (Na\textsubscript{8}Al\textsubscript{6}Si\textsubscript{6}O\textsubscript{24}Cl\textsubscript{2}), a naturally occurring mineral containing chlorine, has been investigated as an immobilisation matrix for this salt waste. To this end, various synthesis methods have been studied \cite{2,3}: on one hand, a synthesis from Zeolite 4A used for preliminary decontamination of the salt by ion-exchange; on the other hand, direct synthesis from kaolinite, metakaolinite, and nepheline. The addition of a glass powder is necessary to obtain a durable waste form. Very recently, a novel method proposed by Korea Atomic Energy Research Institute (KAERI) has also been applied, with some modifications, to the treatment of chloride salt wastes. It is based on a matrix, termed SAP (SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5}), synthesised by a conventional sol-gel process, able to stabilise the volatile salt wastes owing to the formation of metalaluminosilicates, metalaluminophosphates, and metalphosphates. The addition of a borosilicate glass and a treatment at around 1100°C gives the final waste form.

The present paper examines the three different methods and compares the characteristics of the final products, with a particular attention to the leaching behaviour.

Incorporation of molten salts into zeolite 4A

Zeolite 4A is an aluminosilicate open framework structure with \(\alpha\) and \(\beta\) cavities. Sodium ions in the framework provide charges compensation. The cavities near the sodium ions possess an internal electrostatic field, stabilised when polar molecules are occluded within the cavities. When the zeolite is
exposed to molten salts, salt molecules can enter the voids thereby minimising the free energy of the system. Only ions small enough to pass through the entrances of the cavities can be occluded, in the case of sodium zeolite (zeolite 4A) these are 0.4 nm for the α cavity and 0.22 nm for the β cavity.

Simulated chloride salt wastes have been ground to a powder and mixed with zeolite 4A of particle size < 10 μm at 500°C for 15 hours in order to have the salt melted and absorbed into the zeolite. As the chloride ions are not chemically bonded in the zeolites and are expected to be relatively easily ion-exchanged, the zeolite structure has to be transformed by heating to form the stable mineral phase sodalite (Figure 1), which exhibits higher chloride retention. In practice, after cooling, the salt-occluded zeolite is mixed with a borosilicate glass at ambient temperature and then heated in order to get a salt-occluded sodalite, which is the final ceramic waste form. The addition of glass is required in order to bind the sodalite product together to form a monolithic wasteform [4].

**Figure 1: Crystal structure of Zeolite 4A (left) and sodalite (right)**

XRD and FTIR spectra of salt-occluded sodalite obtained starting from Zeolite 4A are shown in Figures 2 and 3 respectively. The XRD spectrum corresponds completely with the sodalite phase 37-0476 present in the XRD library. Similarly, the FTIR spectrum shows the typical peaks of sodalite at 465 [O-Al(Si)-O bending vibrations], 668, 712 and 735 cm⁻¹ [Al(Si)-O-Al(Si) symmetric stretching]. The expected peak at 978 cm⁻¹ [Al(Si)-O-Al(Si) asymmetric stretching] is shifted slightly to 983 cm⁻¹.

**Figure 2: XRD spectrum of salt-occluded sodalite synthesised from Zeolite 4A (Z.SOD.BG)**
Synthesis of sodalite from kaolinite

Sodalite has also been synthesised starting from kaolinite through nepheline, according to the following reactions:

\[
\begin{align*}
\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} & \rightarrow 2\text{NaAlSiO}_4 + 3\text{H}_2\text{O} \\
\text{Kaolinite} & \rightarrow \text{Nepheline} \\
6\text{NaAlSiO}_4 + 2\text{(Li, K)}\text{Cl} & \rightarrow \text{Na}_6(\text{Li, K})_2\text{(AlO}_2\text{)}_6(\text{SiO}_2\text{)}_6\text{Cl}_2 \\
\text{Nepheline} & \rightarrow \text{Sodalite}
\end{align*}
\]

The intermediate nepheline was prepared from kaolinite and sodium hydroxide: the powders were mixed, milled, and heated at 700°C for two hours (procedure repeated twice); the resulting product, brought into an argon atmosphere glove box, was mixed with the eutectic salt and borosilicate glass at ambient temperature, put into an alumina crucible and slightly pressed with another alumina crucible of a smaller diameter, inside which a stainless steel bar was inserted (see insert in Figure 5). The entire assembly was introduced in a little furnace and the temperature was raised to 500°C where it was held for about one hour, in order to allow any residual moisture to evaporate. The temperature was then raised to 925°C for 7 hours.

XRD and FTIR spectra of salt-occluded sodalite synthesised from nepheline are shown in Figures 4 and 5 respectively. The XRD analysis shows typical peaks of sodalite, in particular phase 79-0091, together with various peaks, mainly at 27.3 and 31.8 degrees, which can be attributed to halite (NaCl). FTIR shows the same peaks recorded for Z.SOD.BG, even after 3 hours of reaction.
A new matrix for conditioning chloride salt wastes: SAP

The composite SAP (SiO$_2$-Al$_2$O$_3$-P$_2$O$_5$) has been prepared by a sol-gel process (Figure 6), starting from tetraethyl ortho-silicate, aluminum trichloride hexahydrate (AlCl$_3$$\cdot$6H$_2$O) and phosphoric acid (H$_3$PO$_4$) as sources of Si, Al, and P, respectively [5]. The molar ratio of Si/Al/P has been adjusted to 1/1/1.25 (SAP 125), following the optimum ratio investigated by KAERI [6]. All reagents have been dissolved in a hydroalcoholic solution and the mixture placed in an electric oven at 70°C after being tightly sealed. After a gelling/aging for 3 days, the transparent hydrogels have been dried at 110°C for 3 days and then thermally treated at 600°C for 2 hours. After grinding to about 100 microns, SAP powder has been used as a stabilizer for the salt waste. The prepared SAP has been reacted with metal chlorides at 950°C for 30 hours, after mixing it at a chloride/SAP ratio of 1:2. Prior to heating, the mix has been homogenized with a laboratory mill.
During the first stage of SAP synthesis, TEOS acts as a gelling agent, aluminum trichloride is a property promoter, and phosphoric acid is the acidic catalyst and stabiliser. The just mixed solution is left in covered glass containers for gelation. During this period the reagents give rise to a series of hydrolysis and polycondensation reactions, like the ones shown below:

\[
\text{AlCl}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{POCl}_3 + \text{Al(OH)}_3 \quad (3)
\]

\[
\text{POCl}_3 + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{POCl}_3\text{x(OCH}_2\text{CH}_2\text{)}_x + \text{HCl} \quad (4)
\]

\[
\text{POCl}_3 + \text{H}_2\text{O} \rightarrow \text{POCl}_3\text{x(OH)}_x + \text{HCl} \quad (5)
\]

Reaction (3) generates phosphoryl chloride, POCl₃ which, in turn, reacts with both ethyl alcohol and water. The product of reactions (4) and (5), among others, is HCl, which causes an increase in the HCl/H₂O ratio in the solution, and consequently, the increase of acidity. Since HCl plays the role of a catalyst of the hydrolysis reaction, this accelerates both hydrolysis and polycondensation in the solutions containing AlCl₃, thus shortening the time of gelation.

On its own, TEOS reacts with water (6), forming triethoxysilane, which gives rise to the polycondensation reaction (7).

\[
\text{Si(OCH}_2\text{CH}_2\text{)}_x\text{H}_2\text{O} \rightarrow \text{Si(OCH}_2\text{CH}_2\text{)}_x\text{(OH)} + \text{CH}_2\text{CH}_2\text{OH} \quad (6)
\]

\[
\text{H}_3\text{C}-\text{H}_2\text{CO} \quad \text{OCH}_2\text{-CH}_3 \quad \text{H}_3\text{C}-\text{H}_2\text{CO} \quad \text{OCH}_2\text{-CH}_3
\]

\[
\text{H}_3\text{C}-\text{H}_2\text{CO} \quad \text{Si-OH} + \text{HO-Si-OCH}_2\text{CH}_3 \rightarrow \text{H}_3\text{C}-\text{H}_2\text{CO-Si-O-Si-OCH}_2\text{CH}_3 + \text{H}_2\text{O} \quad (7)
\]

\[
\text{H}_3\text{C}-\text{H}_2\text{CO} \quad \text{OCH}_2\text{-CH}_3 \quad \text{H}_3\text{C}-\text{H}_2\text{CO} \quad \text{OCH}_2\text{-CH}_3
\]
The transparent gels are then heated at 110°C for 3 days, during which both water and ethyl alcohol evaporate. Reactions (3), (4) and (5) are exothermic, while (6) and (7), characterised by water and alcohol release, are endothermic. The dried gels are finally heated at 600°C for two hours.

The thermal treatment brings about crystallisation, and the following phases have been established: SiO₂-Al₂O₃-P₂O₅ and aluminum phosphate, AlPO₄.

The so-obtained SAP matrix, grinded to a very fine powder, has then been mixed with LiCl-KCl (59-41 mol%), containing or not other chloride metals at a mixing ratio of 2 and then reacted at 950°C for 30 hours. The reaction products have been milled for subsequent tests and analyses.

Figures 7 and 8 show XRD and FTIR spectra of LiCl-KCl/SAP products, respectively. The XRD spectrum is quite complex, due to the presence of several peaks attributable to different phases not yet well identified. In the 19°<2θ<25° region, a phase similar to the aluminium phosphate phase 48-0652 is present, even if with a slight shift and a different intensity ratio. The region around 2θ=30° is still to be thoroughly evaluated. FTIR spectrum shows the absence of unreacted chloride salts, while the main peaks can be attributed as follows [7]: the band at 9.1 micron (1100 cm⁻¹) is assigned to a combination of P=O stretching of the P-O-P and P-O-Si bridging units; the band at 12.8 micron (781 cm⁻¹) is attributed to the bending motion of P-O-P, Si-O-P, and O-P-O units; at 21.3 (470 cm⁻¹) there is the band due to O-P-O bending vibrations, while the weak shoulder at about 24.0 micron (417 cm⁻¹) can be assigned to the skeletal deformation of phosphate units.

**Figure 7: XRD spectrum of the reaction product of LiCl-KCl with SAP matrix (SAP.BG)**

![XRD spectrum](image)

**Figure 8: FTIR spectrum of the reaction product of LiCl-KCl with SAP matrix**
Product consistency test on conditioned salts

Chemical durability of the final waste forms has been determined by the product consistency test (PCT). The test involves grinding, sizing, and cleaning sample material, then placing the material in deionised water at 90°C for 7 days. The water leachate solution is then filtered to remove any solid material and analysed by ICP-MS for leached constituents of the waste form. The results from the test are expressed as normalised mass loss in g·m⁻². The obtained values for the waste forms taken into account are shown in Table 1, where Si, Al, and K represent the matrix elements, while Li and Na are the salt components.

Table 1: Normalised release (g·m⁻²) after 7 days leaching at 90°C

<table>
<thead>
<tr>
<th>Element</th>
<th>Z.SOD.BG</th>
<th>N.SOD.BG</th>
<th>SAP.BG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.42</td>
<td>2.23</td>
<td>1.31</td>
</tr>
<tr>
<td>Al</td>
<td>0.12</td>
<td>0.056</td>
<td>0.041</td>
</tr>
<tr>
<td>Si</td>
<td>0.06</td>
<td>0.17</td>
<td>0.049</td>
</tr>
<tr>
<td>Na</td>
<td>0.32</td>
<td>1.94</td>
<td>3.41</td>
</tr>
<tr>
<td>K</td>
<td>0.34</td>
<td>0.40</td>
<td>2.00</td>
</tr>
<tr>
<td>Cs</td>
<td>0.39</td>
<td>0.28</td>
<td>0.81</td>
</tr>
<tr>
<td>Sr</td>
<td>0.052</td>
<td>0.014</td>
<td>0.004</td>
</tr>
</tbody>
</table>

As shown in Table 1, the products coming from different processes for conditioning chloride salt wastes from pyroprocesses give, in general, comparable results about the release of matrix elements and salt components.

Conclusions

The process of occluding salt into a suitable matrix and encapsulating it in glass seems to be a robust method for isolating the salt by-product from electrochemical treatment of spent nuclear fuel.

Different matrices can be used to this purpose. Among these, synthetic sodalite, a mineral phase which contains chlorine, has been considered as one of the most promising incorporation matrices. It can be synthesised according to various processes. Quite recently, however, studies on a new matrix termed SAP have been undertaken, as it proved able to better stabilise the volatile salt wastes due to the formation of metalaluminosilicates, metalaluminophosphates and metalphosphates. The first obtained results on
conditioned wastes proved quite promising, while further research efforts are presently addressed to improve its retention capacity towards fission elements.

References


Preparation and Characterisation of tri-n-octylamine Microcapsule (TOA-MC) as Selective Separation of Re (VII)

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c: National Cheng Kung University, Chinese Tapei
d: National Tsing Hua University, Chinese Tapei

Abstract

Much attention has been paid on the selective separation and effective utilisation of $^{99}$Tc from high level radioactive liquid waste (HLLW). TOA-MC was developed as an absorbent for Re (VII), a substitute for Tc (VII) due to their similarities of chemical behaviour in this study. The uptake (%) of Re (VII) for TOA-MC in the presence of dilute HNO$_3$ (0.01~0.1M) was strongly retained and decreased with higher HNO$_3$ concentration by batch method. The surface morphology and thermal stability of microcapsules were characterised by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA), respectively. The diameters in the range of 700-800 μm and size distribution of the microcapsules were examined using digital microscope (DM). The chemical structures of the synthesised microcapsules and two starting materials of TOA and sodium alginate (NaALG) were performed using Fourier transform infrared spectroscopy (FTIR).

Introduction

Recently, significant attention has been focus on the selective separation, recovery and effective utilisation of rare metals resulting from conversion to valuable resources from high-level radioactive liquid wastes (HLLW) [1-3]. $^{99}$Tc, is only a major radioactive nuclide with a long half-life ($t_{1/2}=2.14\times10^5$ years) in isotopic abundance of fission products (FPs) in the nuclear reactor. The most stable oxide state of technetium (Tc) is pertechnetate anion, TeO$_4$$^-$ and dissolved TeO$_4$ is easily migrated into geochemical environment due to its high mobility, and solubility under oxidising conditions. Therefore, Tc is considered to be one of the important hazardous elements in HLLW [4]. The stable element, $^{100}$Ru, can be generated and utilised as one of valuable and rare metals to the leading industries as for the second resource [5] from $^{99}$Tc by transmutation after reprocessing of spent nuclear fuels.

In this paper, tri-n-octylamine (TOA)-xerogel microcapsules have been successfully synthesised. Core-Shell encapsulation or microencapsulation is a process of enclosing micrometer-sized particles of solids or droplets of liquids or gases in an inert shell, which in turn isolates and protects them from the external environment. The commercial applications of micro-encapsulation are numerous, e.g., adhesives, powder perfume, pesticides, herbicides, essential oils, flavors, self-healing material, time release technology for pharmaceuticals and so forth [6]. Most microcapsules have pores with diameters between a few micrometers and a few millimeters. The coating materials generally used for coating include ethyl cellulose, poly vinyl alcohol, gelatine and sodium alginate. The sodium alginate has been employed in the preparation of gels for the delivery of biomolecules such as drugs, peptides and proteins [7]. Generally a hydrophobic core is usually protected by a hydrophilic shell [8].
Recently the applications of microcapsules (MCs) enclosing extractants for the separation and recovery of metal ions attracted considerable interests [9-11]. In this study, an organic extractant having a strong affinity for Re (VII), tri-n-octylamine (TOA), was encapsulated by NaALG, as shown in Figure 1. Alginate is the salt of alginic acid with carboxyl groups capable of forming gels by ion-exchange reaction with multivalent metal ions. This immobilising property of alginate has led to its extensive applications [12]. However, the characterisation of tri-n-octylamine microcapsule (TOA-MC) has not been thoroughly studied. Therefore, in this paper, it aims at the preparation of TOA-xerogel microcapsules, surface morphology, thermal stability, characterisation of chemical structures of the TOA-MCs, and uptake properties of Re(VII).

![Figure 1: Chemical structures of (1) NaALG and (2) the extractant, TOA](image)

\[(C_6H_{14}O_6Na)_n\]

\[CH_3(CH_2)_{17}N\]

**Experimental**

**Materials**

The sodium alginate (NaALG) with viscosity of 500-600 cP and the organic extractant, tri-n-octylamine (TOA, tertiary amine) were purchased from Wako Pure Chemicals Ind. Ltd and Tokyo Chemical Ind. Co., respectively. Dropping needles (27 G×3/4", 0.4×19 mm) were supplied by Terumo Medical Corporation. Rh (III), Ru (III), Re (VII), Mo (VI) and Pd (II) were supplied by Wako Pure Chemicals Ind. Ltd. Here, Re(VII) ions (ReO$_4^-$) were used as a substitute for Tc(VII) ions (TcO$_4^-$) as ReO$_4^-$ ions are chemical analogues of TcO$_4^-$ ions.

**Preparation of TOA microcapsules (MCs)**

0.75g of sodium alginate (NaALG) and 50 mL deionised water (DIW) were mixed as solution type (1.5 wt%), which was kneaded with 1 g of TOA for 15 min mixing and 5 min deforming twice. The well-kneaded sol-gel was injected dropwise into 0.5 M Ca(NO$_3$)$_2$ solution (200 mL) using a syringe needle tip by peristaltic pump (EYELA MP-1000) with constant stirring at room temperature to obtain creamy white suspension of hydrogel beads. These hydrogel beads were stirred gently in the solution for 3 hours and allowed to stand for about 12 hours to enhance the aging. After filtration and separation from the Ca(NO$_3$)$_2$ solution, the TOA-CaALG xerogel microcapsules (MCs) were washed with DIW for several times and spread gently on a laboratory tray, and then were dried at ambient temperature for 3 hours and finally dried at 30°C for 2 days. The TOA-CaALG xerogel MCs were further shaken with 0.1 M HNO$_3$ for 24 hours, washed with DIW, subsequently spread on a laboratory tray, dried at room temperature for 3 hours and finally air-dried at 30°C for 2 days to form hydrogen type TOA-HALG xerogel MCs, abbreviated as TOA-MC in this study.
Instrumentation for characterisation of microcapsules

Scanning electron microscopy (SEM)

The surface morphology of the microcapsules was observed using scanning electron microscopy (TM3030 Miniscope, Hitachi).

Fourier transform infrared spectroscopy (FT-IR)

The chemical composition and functional groups of microcapsules were confirmed by FT-IR spectrometer (Horiba FT-730 spectrometer, Kyoto, Japan) in the frequency range between 4000 and 400 cm\(^{-1}\), and 4 cm\(^{-1}\) resolution. The samples were prepared by grinding the samples with dried potassium bromide (KBr) powder in the concentration range of 0.2% to 1% and compressed into a disc to obtain a clear pellet.

Thermogravimetry analysis (TGA)

The thermal stability of microcapsules was determined with thermogravimetry analyser (TG 8120, Thermo PlusEvo, Rigaku Corporation). The samples were heated from 25 to 1200°C at heating rate of 10°C/min under air flow. Pt crucible was used as the sample pan holder and about 10 mg of dry TOA-MC was used as sample mass.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The concentrations of five elements of Rh, Ru, Re, Mo and Pd were determined using ICP-AES analysis (SPS7800, SII Nano Technology Inc.).

Determination of uptake (%) and distribution coefficient (K\(_d\))

The uptake and distribution of Rh (III), Ru (III), Re (VII), Mo (VI) and Pd (II) ions for TOA-MCs from different concentrations of HNO\(_3\) solution were performed by the batch method. 50 mg of TOA-MCs was placed in an aqueous solution (5 cm\(^3\)), 10 ppm of each metal ion solution at 25±1°C and vibrated for 24 hours, which was sufficient to achieve equilibrium. The concentrations of these metal ions in the solution were measured by ICP-AES. The uptake percentage (R, %) and the distribution coefficient (K\(_d\), cm\(^3\)/g) are defined as:

\[
R = \frac{(C_0 - C_t)}{C_0} \times 100, \text{ (\%)} \\
K_d = \frac{[(C_0 - C_f)/C_f]}{m \times V/m, \text{ (cm}^3/\text{g)}}
\]

where \(C_0\), \(C_t\), and \(C_f\) are the concentration of metal ions initially, at time \(t\) and at equilibrium, respectively; \(m\) (g) is the weight of MCs; \(V\) (cm\(^3\)) is the volume of the aqueous phase.

Results and discussions

Surface morphology

SEM images of synthesised microcapsules are shown in Figure 2. The MCs are spherical and porous and the diameter is in the range of 700-800 µm. On the surface of the MCs, oil droplets of TOA extractant (~10 µm) are found to be encapsulated, as shown in Figure 2 (b).
Figure 2: SEM images of synthesised microcapsules (a) X 150 (b) X 2000

Chemical structure characterisation of microcapsule

Figure 3 shows the IR spectra of TOA-MC and its starting materials (NaALG and TOA). The presence of relatively broad absorption peak appeared at 3 200-3 500 cm\(^{-1}\) is assigned as strong hydrogen bond, O-H group and absorption peak observed at around 1 700 cm\(^{-1}\) is related to C=O of stretching vibration of carboxyl group. The strong absorption peak at 1 050-1 150 cm\(^{-1}\) is associated with C-O stretching vibration, whereas the C-N stretching vibration of aliphatic amines appears as medium band in the approximate region of 1 020-1 250 cm\(^{-1}\) shown in Figure 3 (b) TOA and it seems overlapped with the former C-O single bond absorption. All the above characteristic peaks are able to find in the spectra of TOA-MC and NaALG, affirming that the shell of NaALG is formed. The multi-banded absorption peaks located at 2 800-3 000 cm\(^{-1}\) belong to the saturated aliphatic C-H group (sp\(^3\) carbon) and the absorption peaks at around 1 375 and 1 465 cm\(^{-1}\) are identified as CH\(_3\) and CH\(_2\) bending group vibrations, indicating the core content is TOA.

Thermal stability of the microcapsules

Figure 4 shows the thermogravimetry (TG) and derived thermogravimetry (DTG) curves of TOA-MC. The former curve measures the mass change of the sample with a thermo-balance, whereas the latter one measures the slope or derivative of the mass change with temperature. With increase in temperature, the weight loss increases until all the TOA-MC gets burnt. The TG curve indicates that the mass loss (~10%) between 50 and 200°C, is mainly due to the dehydration, i.e., the removal of entrapped residual
water from TOA-MC, and the sharper mass loss (~60%) at temperatures between 200 and 290°C is mainly attributed to the thermal decomposition of alginate polymer [7]. Obviously, the microcapsules are chemically stable below 200°C, indicating that the prepared microcapsules have a good thermal stability to endure the decay heat of HLLW. In addition, the residual weight fraction has been decreased to less than 3% for the final stage of TG profile, implying that the TOA-MC has environmentally friendly character.

**Figure 4: TG (solid)/DTG(dashed) curves of TOA-MC**

**Uptake (%) of Re and HNO₃ concentration**

As shown in Figure 5, when much higher concentration of HNO₃ (aq) was used, an elution efficiency of greater than 80% was achieved using the TOA-MC. This suggests that at lower concentrations of HNO₃, the uptake of Re (VII) using TOA-MC (represented as R₃N, an aliphatic quaternary amine, where TOA-MC denoting C₈H₇ or C₁₀H₂₁) is governed by the solvent extraction ability of pertechnetic acid with resin (Equation 1). In contrast, the uptake (%) of Re (VII) tends to gradually decrease above concentrations of 0.1 M HNO₃. This may be due to the effects of related reactions including solvent extraction (Equation 2) and ion exchange (Equation 3), indicating that nitric acid extraction using TOA-MC is the dominant process and that the forward reaction of Equation 3 is restricted at higher concentrations of HNO₃.

\[
\begin{align*}
R_3N(o) + H^+ + ReO_4^{-(aq)} & \rightleftharpoons R_3NH^+ReO_4^{-(o)} \quad (1) \\
R_3N(o) + H^+ + NO_3^{-(aq)} & \rightleftharpoons R_3NH^+NO_3^{-(o)} \quad (2) \\
R_3NH^+NO_3^{-(o)} + 2ReO_4^{-(o)} & \rightleftharpoons R_3NH^+ReO_4^{-(o)} + NO_3^{-(aq)} \quad (3)
\end{align*}
\]

**Figure 5: Uptake of Rh(III), Ru(III), Re(VII), Mo(VI) and Pd (II) by TOA-MCs at different concentrations of HNO₃**
Conclusion

TOA-MCs were successfully synthesised by sol-gel method. The FT-IR results show that the core material, TOA had been completely encapsulated inside NaALG shell. The regular spherical and granules MCs are observed by SEM with average size of 750 μm. The TGA results reveal that MCs has the thermal stability. The uptake (%), normally above 95% of Re (VII) for TOA-MC in the presence of dilute HNO₃ (0.01~0.1M) was strongly retained and decreased with higher HNO₃ concentration by batch method. Therefore, TOA xerogel MCs are effective for the separation of Re (VII) and Tc(VII) ions from radioactive waste solutions.

Acknowledgements

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References


Preparation and Electrochemical Properties of PuPd3 in 3LiCl + 2KCl

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Abstract

The electrochemical behaviour of the intermetallic compound (IMC) PuPd₃, one of the possible components of the anodic slurry of (U,Pu)N spent FBR fuel electrorefining in 3 M LiCl – 2M KCl eutectic mixture, was studied at a temperature range from 450 to 650°C. The PuPd₃ electrode for electrochemical measurements was prepared using the melting of the stoichiometric mixture of Pu and Pd metals in vacuum induction furnace. X-ray diffraction data indicated the presence of only PuPd₃ in the material. Scanning electron microscopy and analysis of EDX spectra of the PuPd₃ surface indicated the presence of three metastable phases p₀, p₁ and p₂ with increasing content of Pd. The data of cyclic voltammetry measurements indicated that three anodic irreversible reactions, corresponding to the oxidation of three metastable IMC forms, present at the electrode surface, occurred at the potentials Eₚ₀ about -1.77 V, Eₚ₁ about -1.2 V and Eₚ₂ about -0.027 V / Ag/AgCl. Their values were increasing slightly with the increase of the potential scan rate and the electrolyte temperature. The increase of the electrolyte temperature also caused the increase of all the observed anodic current peaks. The increase, corresponding to the oxidation of Pu rich phases p₀ and p₁ was more pronounced in comparison with the Iₚ₂ matching with Pd rich phase. The rate of oxidation of Pd rich phase was diffusion controlled, while the dependence Iₚ₁ and Iₚ₂ on dE/dt¹/² declined from linearity at a potential scan rate exceeding 100 mV/s indicating apparently that the reactions, resulting in Pu rich phase formation occur rather slowly in the studied temperature interval. The latter observations were confirmed with the data of current controlled electrolysis, carried out at 450°C anodic current densities of 15, 7 and 35.3 mA/cm² corresponding to the peak values of the anodic current at Eₚ₁ and Eₚ₂. The continuous 2 – 3 hour electrolysis revealed that the electrode potential was maintained constant at -0.15 V and at +0.60 V / Ag/AgCl correspondingly. Dissolution of Pu in the electrolyte prevailed in both experiments though the Pd current efficiency during electrolysis at 35.3 mA/cm² increased from 41 to 77%. The data of X-ray diffraction and SEM analysis of electrode surface after accomplishing of electrolysis demonstrated that only plutonium metal solid solution in palladium metal phase rather than PuPd₃ was present at the electrode surface. The results of the study indicate, that the electrochemical oxidation of PuPd₃ in 3 M LiCl – 2M KCl eutectic mixture at the potential -1.5 - -1.2 V / Ag/AgCl may result in the recovery of major part of Pu to the salt electrolyte.

Introduction

Modern Russian nuclear science and industry is currently working actively on closing of nuclear fuel cycle. The solution of the issue of Pu recycling lies in the use of fast breeder reactors; for instance (U,Pu)N fuel, development of its reprocessing, providing more than 99.9% Pu recovery and corresponding fuel refabrication. In order to provide the feeding of the reprocessing under study with a fuel of high activity and thus reduce the spent fuel cooling time the pyroelectrochemical technique head end of the reprocessing
under study is previewed for the separation of U and Pu from minor actinides (MA) fission products (FP) in fused chloride eutectics. If the pyroelectrochemical step of the process does not result in the satisfactory purification of U and Pu, further refinement using hydrometallurgy techniques are envisaged [1]. Thereby the electrorefining of the (U,Pu)N spent fuel is considered as a key process of the combined spent nuclear fuel reprocessing under development.

Russian R&D programmes dealing with pyroelectrochemical reprocessing of irradiated nitride fuel focus on the study of the behaviour of FP noble metals Ru – Pd, which should be accumulated in the anodic slurry of the electrorefining. High thermodynamic stability of the intermetallic compounds (IMC) of U [2,3] and Pu are known to be close to the stability of (U,Pu)N [4]. This similarity means that the IMC of actinides with noble metals could be one of the most probable chemical states of actinides in the irradiated (U,Pu)N. The assumption was recently reported as a 10-12% retention of Pu in anodic slurry of (U,Pu)N electrorefining [5]. In order to find out the conditions of the process allowing to achieve the quantitative dissolution of U and Pu, the knowledge of the fundamental electrochemical properties of IMC with Ru and Pd seems to be essential. This work deals with the synthesis of PuPd3, and presents the first results of the study of the prepared IMC ingot electrochemical properties in fused 3LiCl – 2 KCl eutectic melt.

**Experimental**

**PuPd3 preparation: Fabrication of PuPd3 electrode for electrochemical studies**

Plutonium metal and palladium oxide (analytical grade) were used as starting materials for the PuPd3 preparation. Pd metal was prepared by thermal decomposition of PdO at 1173 K in atmosphere of high purity Ar followed by the melting of the formed sponge in vacuum at a residual pressure of less than 5 \times 10^{-4} Pa. The weights of Pu and Pd ingots corresponding to mole ratio 1/3 were taken, pressed slightly and melted in MgO crucible placed to the induction heater furnace. The inner volume of a furnace was evacuated to the residual pressure less than 5 \times 10^{-4} Pa and the metal charge was melted 1-2 seconds. It should be mentioned that the reaction of IMC formation occurred with a significant heat evolution. The reaction temperature was estimated to 2100-2300 K. Therefore, the initial weights of starting metals were optimised to avoid the IMC loss due to charge spraying. The electrode for the electrochemical studies was prepared by the immersion of Ta needle to the IMC melt followed by the immediate cooling of the sample.

**Electrochemical facility**

Electrochemical facility for the studies of PuPd3 electrochemical properties in chloride melts was installed in conventional glove box, providing secure handling of gram amounts of plutonium metal. It consisted of three principal parts, including resistance furnace providing the rapid and precise (±1 K) regulation of the salt electrolyte temperature in the interval from 500 to 1100 K, quartz three electrode electrochemical cell and the Ar purification system from moisture and O2 traces to less than 5 ppm and 0.5 ppm correspondingly. The measurements of cyclic voltammetry (CV) and current controlled electrolysis (CCE) were carried out in quartz cell in continuous stream of high purity Ar. The working PuPd3 electrode with form close to sphere, Ag/AgCl reference electrode and 6 mm diameter glassy carbon rod counter electrode comprised the three electrode systems for electrochemical measurements. Reference electrode inner volume was filled with the 3LiCl-2KCl electrolyte, containing 0.75 mol kg\(^{-1}\) (4.4 mol\%) AgCl and separated from the electrolyte volume by Pyrex membrane. The potentiostate PGSTAT 302 (Autolab) piloted with Nova 1.2 software was used as a source of the electric signals and for preliminary treatment of the obtained data in all the electrochemical experiments presented in the actual summary. Each recording of CV curves was repeated 7 times and the current values for each potential value were averaged for further analysis.
Results and discussion

PuPd₃ characterisation and properties

Phase composition of the PuPd₃ ingot surface used as a working electrode for the electrochemical measurements was determined using X-ray diffraction analysis with the help of Empyrean (Panalytical). Diffractograms were registered in CuKα irradiation with nickel filter and X'Celerator. The diffractogram of PuPd₃ surface is presented in Figure 1. The presented data indicate that PuPd₃ appeared to be principal phase in the obtained samples. The lines, observed at \( \theta = 10^\circ \) and \( \theta = 54^\circ \) were not identified, but the comparison of these values with the known patterns of Pu metal, Pd metal and PuO₂ shown that the observed line did not belong to the mentioned phases. In is necessary to mark that the crystallite size of the studied surface did not exceed to 10 mkm, causing the diffusion character of the observed peaks. The latter observation may be accounted for the extremely high rate of the sample cooling.

The study of the PuPd₃ ingot microstructure was carried out using Philips XL 30 ESEM-TMP, instrument coupled with X-ray spectrometer of wave dispersion Inca Wave 700 and energy dispersion spectrometer x-Max. The typical microphotograph taken from the centre of the sample is presented in Figure 2. In a whole the PuPd₃ sample could be characterised technologic porosity of 2-3% and a presence of three principal phases. The results of the EDX analysis in the points marked in Figure 3 are shown in Table 1. The presented data indicate that the Pd/Pu ratio in the principal phase observed in the prepared PuPd₃ ingot was found to be 2.28±0.05. The content of Pu in small regular crystals with dimension of about 40-60 mkm reduced to give the Pd/Pu ratio 4.4.

To our opinion, the crystallisation of two separate types of crystallites, corresponding to general formula PuPd₃ is due to the different crystallisation temperatures of two forms, corresponding to PuPd₃ formation boundaries, observed at the Pu – Pd phase diagram [6]. The concentration of the found impurities of light elements including Si and Cd was found to increase from the centre to the outer surface of microsection. The presence of Cd in the sample may be accounted for the use of the Wood alloy in a process of a sample preparation. The presence of Mg, W, Ta and Mo traces was also found at the surface of the sample.

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**Figure 1:** X-ray diffraction pattern of PuPd₃ ingot surface. CuKα₁ - irradiation without monochromator

**Figure 2:** Microphotograph of the microsection centre of PuPd₃ sample and the characteristic points of element determination using EDX technique
PuPd₃ electrochemical properties in 3LiCl-2KCl melt

The curves CV recorded at PuPd₃ electrode in 3LiCl-KCl at different temperatures and potential scan rates are presented in Figure 3. The presented data indicate that the processes occurring at the processes occurring at the electrode change their character significantly with the increase of electrolyte temperature. At 450°C and the scan rates below 100 mV/s three ill-defined peaks of anodic current (p₀, p₁ and p₂) are observed at the potentials Eᵣ₀ about -1.77 V, Eᵣ₁ about -1.2 V and Eᵣ₂ about -0.027 V / Ag/AgCl increasing slightly with the increase of the potential scan rate. It is necessary to mention that at T = 450°C the peak p₀ was observed only at scan rates less than 40 mV/s. The increase of the scan rates from 10 to 1000 mV/s resulted in the increase of Eᵣ₁ potential and corresponding intensity Iᵣ₁. However the increase of potential scan rate worsened the peak resolution. In all the studied range of potential scan rates and electrolyte temperatures no definite cathodic current changes corresponding to the anodic processes was observed. This observation indicates the irreversibility of the anodic processes corresponding to the peaks of the anodic currents observed at the CV curves under study.

The peak of anodic current at PuPd₃ surface p₂ at the potential scan rates below 100 mV/s at 450°C occurred at the potentials Eᵣ₂ about -0.2 V / Ag/AgCl. Eᵣ₂ also shifted to positive direction with the increase of potential scan rate with corresponding increase of the peak intensity. The oxidation process corresponding to the anodic peak current p₂ also seems to be irreversible since no corresponding current changes are observed at the cathodic branches of CV curves traced at 450°C.

The comparison of the values of Eᵣ₀, Eᵣ₁ and Eᵣ₂ with the known values of the conditional standard potentials [7] of Pu(III)/Pu and Pd(II)/Pd couples (Table 2) showed that all the observed values were found inside the interval of oxidation potentials of IMC components. The appearance of several peaks of anodic
current at the recorded CV curves (Figure 3) to our opinion is due to the simultaneous existence of three forms of PuPd$_3$ at the electrode surface (Figure 2 and Table 1). The comparison of the decomposition temperatures of the UPd$_3$ non-stoichiometric IMC, observed at the Pu-Pd phase diagram [6], at 1060°C and 1240°C correspondingly is leading to the conclusion that the IMC form with greater content of Pd is more thermodynamically stable than the palladium depleted phase. The latter conclusion is found to be in good compliance with SEM data (Figure 2) indicating the presence of three IMC forms at the electrode surface and the data of CV (Figure 3) demonstrating the difference in their stability towards anodic oxidation.

Table 2: Comparison of $E_{p1}$ and $E_{p2}$ with conditional standard potentials of Pu(III)/Pu, Pd(II)/Pd and Cd(II)/Cd couples

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Pu(III)/Pu</th>
<th>Pd(II)/Pd</th>
<th>Cd(II)/Cd</th>
<th>$E_{p0}$</th>
<th>$E_{p1}$</th>
<th>$E_{p2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, V Ag/AgCl</td>
<td>-1.79</td>
<td>0.636</td>
<td>-0.464</td>
<td>-1.73</td>
<td>-1.24</td>
<td>-0.087</td>
</tr>
</tbody>
</table>

The increase of the electrolyte temperature from 450 to 650°C resulted in the increase of the anodic currents $I_{p0}$, $I_{p1}$ and $I_{p2}$ and by insignificant shift of corresponding peak potentials towards positive direction (Figure 4). At the potential scan rates less than 100 mV/s, the increase of the latter parameter leads to the decrease of the $I_{1}/I_{0}$ ratio. Simultaneously, the current corresponding to the anodic process occurring at the potentials, close to $E_{p0}$ also increased. The increase of the peak currents $I_{p0}$ and $I_{p1}$ with simultaneous decrease of $I_{p2}$, especially noticeable at 650°C was observed. However, the increase of potential scan rate to the values higher than 100 mV/s results in the complete disappearance of $p0$ indicating the complex kinetics of occurring electrode processes. To our opinion the observed shift could be accounted for the changes in the structure of the PuPd$_3$ electrode surface occurring with the temperature increase. Apparently the increase of the temperature resulted in the increase of the Pu rich phases concentrations at the electrode surface followed to their rapid anodic dissolution. The rate of the latter process appeared to be so high that the steady state concentration of Pu rich phase, corresponding to $p0$ oxidation process, at the electrode surface became too small to maintain the significant $I_{p0}$ value. The comparison of the dependencies of the $I_{p1}$ and $I_{p2}$ on potential scan rates (Figure 4) and the least square technique analysis of the curves $I_{p1} \cdot (dE/dt)^{1/2}$ (Table 3) revealed that the kinetics of the electrochemical reaction, corresponding to $I_{p2}$ was controlled by diffusion, while the rate of the reaction associated with $I_{p1}$ increased with the increase of the scan rate from 20 to 200 mV/s. The further increase of the potential scan rate did not cause the increase of $I_{p1}$ value, proving that the rate of the Pu – Pd phase, responsible for the anodic oxidation at this range of potentials, could be determined as the rate determining step of its oxidation. Thus the CV study of PuPd$_3$ at different temperatures demonstrated that the increase of the temperature caused the preferential acceleration of the oxidation of the species with greater plutonium content at the electrode surface.

Figure 4: Dependencies of $I_{p1}$ and $I_{p2}$ anodic oxidation of PuPd$_3$.
Experimental conditions: $S_{эл} = 2.55$ cm$^2$, $dE/dt=20 – 1000$ mB/c, $T = 450 - 650°C$. 
Table 3: Results of linear regression analysis of the curves $I_p - \sqrt{dE/dt}$ of PuPd$_3$ anodic oxidation in fused 3LiCl – 2KCl (p<0.05)

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>Anode peak</th>
<th>Slope, A$s^{1/2}$V$^{-1/2}$10$^{-3}$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>$I_{p1}$</td>
<td>1.70±0.09</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>$I_{p2}$</td>
<td>3.58±0.08</td>
<td>0.995</td>
</tr>
<tr>
<td>550</td>
<td>$I_{p1}$</td>
<td>2.6±0.1</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>$I_{p2}$</td>
<td>5.6±0.1</td>
<td>0.99</td>
</tr>
<tr>
<td>650</td>
<td>$I_{p1}$</td>
<td>2.7±0.4</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>$I_{p2}$</td>
<td>7.3±0.2</td>
<td>0.991</td>
</tr>
</tbody>
</table>

The latter observations were confirmed with the data of current controlled electrolysis (CCE), carried out at a 450°C anodic current densities 15.7 and 35.3 mA/cm$^2$ corresponding to the peak values of the anodic current at $E_{p1}$ and $E_{p2}$. The curves demonstrating the change of the PuPd$_3$ electrode potential in time are presented in Figure 5. The insignificant shift of the electrode potential towards more negative values was observed at the curve registered at $i = 15.7$ mA/cm$^2$ during first 10 – 15 min of CEE. After this period of time the potential value became practically constant $E = -0.160±0.005$ V / Ag/AgCl. Comparing this value with the date presented in Figure 3 it may be concluded that the observed CCE potential was close to the potential of the electrochemical oxidation $p3$, corresponding to the oxidation of the Pu – Pd phase richest in Pd. The increase of the CCE current density to 35.3 mA/cm$^2$ caused the shift of the steady state CCE potential to $E = +0.607±0.005$ V / Ag/AgCl. At this potential value the PuPd$_3$ electrode was in a transpassive state (Figure 3), corresponding to the stoichiometric electrochemical dissolution of both IMC components. The shift of the electrode potential to 0.69 V / Ag/AgCl followed by the return of its value to the steady state may be accounted for the impoverishment of the electrode surface in plutonium due to the rapid oxidation of Pu rich phases, followed by the restitution of Pu steady state concentration at the electrode surface due to the diffusion from the bulk of the electrode.

Figure 5: Chronopotentiometric curves of PuPd$_3$ electrode during CCE at current densities, corresponding to $E_{p1}$ and $E_{p2}$.

Experimental conditions: $S_{эл} = 2.55$ cm$^2$, $T = 450$°C. 1 – $i = 15.7$ mA/cm$^2$; 2 – $i = 35.3$ mA/cm$^2$

After accomplishing CCE at a given current density, the electrode was extracted from the electrolytic cell rinsed with distilled water and ethanol, and weighted. Simultaneously, samples of the electrolyte were taken to determine the yield of Pu and Pd electrochemical dissolution. The results of the electrolyte analysis are presented in Table 4. The presented data demonstrate that the CCE carried out the current density, corresponding to $E_{p0}$ (15.7 mA/cm$^2$) resulted in the preferential accumulation of plutonium in the electrolyte. Apparently the intermetallic compound PuPd$_3$ was oxidised at the applied potential, forming
Pu$^{3+}$ and Pd$^{2+}$ ions. However the potential value corresponding to the applied current density being sufficient for the electrochemical IMC oxidation was too small to maintain the Pd$^{2+}$ in the oxidised state (Table 2). Therefore the latter ions were reduced at the IMC electrode forming the Pd metal cover at its surface. The data of the Table 5 show that only about 5% of the oxidised Pd remained in the electrolyte after accomplishing the CCE process. The increase of the applied anodic current density to 35.5 mA/cm$^2$ causing the shift of the electrode potential to the transpassivation region caused the increase of the Pd$^{2+}$ yield and correspondingly increased the current efficiency of the anodic oxidation of both IMC electrode components. The current efficiency of Pu oxidation in this process according to the calculated material balance exceeded 90% (Table 5).

Table 4: Material balance of CCE at PuPd$_3$ electrode in 3LiCl – 2KCl eutectic mixture at different current densities. Experimental conditions: $S_{\text{el}} = 2.55$ cm$^2$, $T = 450^\circ$C.

<table>
<thead>
<tr>
<th>Current density, mA/cm$^2$</th>
<th>Time, H</th>
<th>Pu found in the electrolyte, mg</th>
<th>Pd found in the electrolyte, mg</th>
<th>Electrode mass loss, mg</th>
<th>Pu oxidation current efficiency, %</th>
<th>Pd oxidation current efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.7</td>
<td>3</td>
<td>104±6</td>
<td>62±7</td>
<td>110±2</td>
<td>88±4</td>
<td>41±5</td>
</tr>
<tr>
<td>35.3</td>
<td>2</td>
<td>162±8</td>
<td>175±9</td>
<td>337±2</td>
<td>91±6</td>
<td>77±6</td>
</tr>
</tbody>
</table>

Table 5: The results of the analysis of PuPd$_3$ electrode surface after CCE in 3LiCl – 2KCl eutectic mixture at different current densities. Experimental conditions: $S_{\text{el}} = 2.55$ cm$^2$, $T = 450^\circ$C.

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Ga, at. %</th>
<th>Pd, at. %</th>
<th>Cd, at. %</th>
<th>Pu, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectre 1</td>
<td>1.14</td>
<td>0.893</td>
<td>1.65</td>
<td>8.65</td>
</tr>
<tr>
<td>Spectre 2</td>
<td>1.03</td>
<td>0.883</td>
<td>0.76</td>
<td>10.63</td>
</tr>
<tr>
<td>Spectre 3</td>
<td>0.35</td>
<td>0.278</td>
<td>72.06</td>
<td>-</td>
</tr>
<tr>
<td>Spectre 4</td>
<td>0.94</td>
<td>0.862</td>
<td>0.12</td>
<td>13.42</td>
</tr>
<tr>
<td>Averaged at the surface*</td>
<td>1.0±0.1</td>
<td>88±1</td>
<td>5.3±20.8</td>
<td>7±2</td>
</tr>
</tbody>
</table>

* excluding data from spectre 3

The conclusions about the mechanism of PuPd$_3$ electrochemical oxidation made taking into account the data of the material balance of CCE in 3LiCl – 2KCl eutectic mixture were confirmed using X-ray diffraction, SEM and EDX spectra analysis of the PuPd$_3$ electrode surface after to CCE runs, mentioned in the Table 4. The X-ray diffraction pattern of a powder collected from the PuPd$_3$ electrode surface with a help of a diamond needle file is presented in Figure 6. The full collections of reflections, characteristic for the Pd metal face centred cubic cell with cell parameter $a = 3.890$ Å, being in good compliance with the data of literature [8] (phase 1) is observed at a presented pattern. At the same time another collections of the similar reflections slightly shifted towards smaller angle values in respect of collection of Pd metal reflections (phase 2) also was present at the diffractogram. The calculated cell parameter $a = 3.942$ Å for the phase 2 was a little bit greater in comparison with the value observed for the phase 1. Taking into account the initial phase composition of the electrode corresponding to PuPd$_3$ ordered primitive cubic structure with the parameter $a = 4.098$ Å (Figure 1) its transformation during CCE seemed to be due to the loss of Pu atoms with the appearance of the ordered Pd metal phase and disordered face centred cubic phase of the solid solution in Pd metal with composition Pu$_{1-x}$Pd$_{3+x}$, in which Pu atoms are statistically distributed in the cell position. According to Vegard’s law [9] in application to the composition of solid solutions between PuPd$_3$ and Pd the Pd mole fraction in the phase 2 should be close to 0.92, i.e. phase 2 has a composition Pu$_{0.08}$Pd$_{3.92}$. 

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The PuPd$_3$ electrode was fixed in the Wood alloy to form the sample for the SEM measurements. After treatment with a diamond needle file the electrode surface with a diameter about 3 mm was open and exposed to the electron beam. Since the special metallographic treatment of the sample was not carried out the recorded spectra EDX provided only semi-qualitative information about the sample composition. The obtained microphotograph of the electrode surface microsection centre is presented in Figure 7. The comparison of the presented microphotograph with the photo of the PuPd$_3$ surface before the electrochemical treatment shows that the light regular particles with high plutonium content up to 30 at. % (Table 1) disappeared completely from the electrode surface during electrolysis. The irregularities observed at the surface indicated that the electrochemical reaction occurred mainly at the intercrystallite surfaces and proved the conclusion about metastable character of a prepared PuPd$_3$ sample. The relative concentrations of plutonium and palladium according to the data of EDX spectra analysis of the PuPd$_3$ electrode surface are presented in Table 5.

The presented data indicate that the Pu distribution over the electrode surface within the uncertainty experimental was uniform and correlated with the Pd/Pu ratio value in the Pu solid solution in palladium metal calculated using the results of X-ray diffraction analysis. The traces of Cd at the electrode surface were found due to the application of Wood alloy for the fixation of the sample before the SEM measurements.

Conclusion

The study of the PuPd$_3$ electrochemical properties in 3LiCl – 2KCl revealed a number of regularities which seem to be carefully considered in process of elaboration of the industrial process of spent nitride fuel electrorefining in chloride melts, in particular, in 3LiCl-2KCl eutectic mixture. The results of the cyclic voltammetry measurements indicated that PuPd$_3$ passed to transpassive state at the potentials, exceeding +600 mV / Ag/AgCl, i.e. exceeding the $E^{o}_{\text{Pd(II)/Pd}}$ value (Table 1). At E<0.6 V /Ag/AgCl according to the data of CCE material balance its anodic oxidation results in the oxidation of plutonium to form Pu(III) occurred. Pd originating from PuPd$_3$ is apparently also oxidised in such conditions. However, the electrode potential provides the value which is sufficient for the Pd(II) reduction at the electrode surface. Therefore the low current efficiencies of Pd oxidation along with the formation of Pu – Pd solutions at the electrode surface during CCE at 15.7 mA/cm$^2$ could be accounted for the electrochemical reduction of Pd(II) ions formed in the electrolyte due to the electrochemical oxidation of PuPd$_3$. 

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According to available literature data, UN undergoes the electrochemical dissolution in 3LiCl - 2KCl at the potentials, exceeding -0.2 V Ag/Ag⁺, i.e. about 800 mV more negative in comparison with the PuPd₃ electrochemical oxidation potential. That means that in a steady state of nitride SNF electrorefining cell operation, the effective UN – PuN dissolution could be achieved at the anode potential about -100-200 mV / Ag/AgCl. Thus, the obtained data on the electrochemical properties of PuPd₃ in 3LiCl – 2KCl indicate that during the significant part of the process, Pu could be retained in the anodic slurry of the electrorefining process. However, if liquid Cd or another metal or alloy is used in the electrorefining facility to improve the electric contacts between the fuel and anodic basket, the retention of Pu at the anode could be significantly reduced due to the interaction of PuPd₃ with the liquid metal, resulting in the formation of soluble forms in metal phase at the working temperature of SNF electrorefining. The study of this interaction and of electrochemical properties of ternary systems, containing actinides, noble metals and cadmium is expected to be a future part of our research work.

References

[8] PCP-DF database, ref. 05-0681 Pd metal
Investigations of Hydrophilic Schiff Base Ligands for the Separation of Actinyl and Lanthanide Cations

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a: University of California, United States
b: Los Alamos National Laboratory, United States

Abstract

The water soluble tetradentate Schiff base, N,N’-bis(5-sulfonatosalicylidene)-ethylenediamine (H2salen-SO3) and water soluble pentadentate Schiff base, N,N’-bis(5-sulfonatosalicylidene)-diethylenetriamine (saldien-SO3), have been evaluated for their ability to form aqueous complexes with uranyl(VI) cation and trivalent lanthanide cations. Using spectrophotometric and 1H NMR titrations, both ligands were demonstrated to readily coordinate with the uranyl(VI) cation, but not to the same extent with trivalent lanthanide cations. Solvent extraction systems employing HDEHP in toluene and these Schiff bases in nitrate media have resulted in holdback factors for uranyl(VI) of up to 3-orders of magnitude. Extraction of europium(III) under similar conditions resulted in holdback factors of no more than 3 and DEu of less than 1 by H2salen-SO3. However, the system with saldien-SO3 resulted in Eu/U separation factors of approximately 1000 (DEu ~800, DU < 1) between 0.5 hours and 5 hours. Although Schiff base hydrolysis is prevalent under the studied conditions, these results indicate that the mixed-donor chemistry of these ligands may be a useful scaffold for actinyl holdback reagents to accomplish Ln(III)/An(V,VI) solvent extraction selectivity.

Introduction

Developing new actinide separation strategies is essential if many of the challenges related to used nuclear fuel processing and nuclear waste management are to be addressed [1]. As the first step of a typical used fuel separation flowsheet, the conventional PUREX (Plutonium and Uranium Reduction Extraction)-based solvent extraction processes relies on the extraction of uranyl(VI) nitrate by tri-n-butyl phosphate into an organic phase [2]. However, keeping the bulk of the uranium out of the solvent phase could significantly reduce the volume of solvent required for used nuclear fuel processing operations. Therefore, extraction of the minor components (e.g., Ln(III) and transuranic elements) from the majority uranium would be preferred. Moreover, the proposed separation of minor actinide and lanthanide cations frequently employs organophosphorus reagents. Yet, these extractants do not often display large selectivity between trivalent actinides and lanthanides, due to the similarities in the chemical properties of these elements. Consequently, these extractants are frequently applied in combination or in sequence with soft donor ligands to achieve An(III)/Ln(III) separations. The concept of selectively retaining ions in an aqueous phase during a solvent extraction process has been shown to hold great promise in processes for An(III)/Ln(III) separation such as TALSPEAK (Trivalent Actinide – Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Complexes) and Reverse TALSPEAK, as well as more recent innovative SANEX (Selective ActiNide Extraction) process concepts [3,4].

On the other hand, several of the actinides have higher oxidations states (i.e., V and VI) available under conditions in which they exist as linear dioxo cations. Under this configuration the actinides behave significantly different from trivalent lanthanides. The stability of these oxidation states can be a challenge
for some transuranic actinides under acidic conditions. Studies suggest, however, that these oxidation states may be stabilised by coordination of ligands to the equatorial plane of the actinyl ion. For example, recent studies indicate that Schiff bases may stabilise U(V)[5-8]. The ability of 4 or 5 dentate Schiff base ligands to accommodate the steric demands of the linear dioxo uranyl moiety has led to interest in their application as extractants for uranyl(VI) ion [9,10]. Considering these reports, we are investigating ligands for the selective complexation of An(V/VI)-cations and their separation by solvent extraction. A recent study employing an aqueous soluble salen-based compound demonstrated that U(VI) could be selectively complexed and retained in the aqueous phase, while the representative trivalent lanthanide Eu(III) was extracted by bis(2-ethylhexyl)phosphoric acid (HDEHP) [11]. These results and continued progress are discussed in this paper.

Experimental results

General methods

Acid and base solutions were standardised by potassium hydrogen phthalate (analytical standard), and solution pH and pC\text{H} (-log [H\text{+}]) measured by potentiometry using a semi-micro refillable electrode (Beckman-Coulter, Indianapolis, IN), which was calibrated by standard pH solutions (Fisher Scientific,) and by strong acid-strong base titrations.

Materials

All chemicals used in these procedures were certified reagent grade or higher and used without further purification, unless noted otherwise. Deionised water was obtained from a deionised feed such that the resistivity was at least 18 M\text{Ω}*cm\text{+1}. For the solution spectroscopy and solvent extraction experiments a 0.010 M UO\text{2(NO\text{3})_2} working stock solution was prepared from a commercial ICP standard solution of depleted (0.2% 235U) uranyl nitrate (1 000 ppm, Inorganic Ventures, Christiansburg, VA, USA) by diluting with deionised water and adjusting the pH to 4.0 dropwise with a KOH solution. Lanthanide nitrate stock solutions were prepared from their oxides (Michigan Metals & Manufacturing, Inc., West Bloomfield, MI, 99.99%) by dissolving in concentrated nitric acid. Excess nitric acid was removed by evaporating to near dryness and adding dilute nitric acid in several cycles. The final solutions were reconstituted to 0.1 M lanthanide ion with 1×10\text{-3} M HNO\text{3} and the concentrations were verified by ion-exchange titration or ICP-MS. HDEHP (Di(2-ethylhexyl)phosphate, 95%, ACROS Organics, Geel, Belgium) was purified using the Cu(II) complexation method [12].

Synthesis and characterisation

Synthesis of N,N’-bis(5-sulfonato-salicylidene)-ethylenediamine disodium salt (H\text{2}salen-SO\text{3})

The synthesis of H\text{2}salen-SO\text{3} was carried out in accord with previously published procedures [13-15] by the steps described in Scheme 1.

The pale yellow product (4) was collected after drying \textit{in vacuo} (85% yield in the final step, 24% overall yield). Electrospray ionisation (ESI) mass spectrometry was carried out using a ESI LC-TOF (Micromass LCT 3) in negative ion mode with methanol solvent and operated with Waters MassLynx software (v.4.0). ESI-MS-TOF (-ve) m/z = 213.2 (M-2Na). \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded using a Bruker GN-500 (500 MHz, \textsuperscript{1}H) spectrometer, equipped with a BBO probe. Proton chemical shifts are reported in units of ppm (\(\delta\)) by the proteo solvent signal relative to external tetramethylsilane (TMS, \(\delta = 0.00\) ppm). \textsuperscript{1}H NMR (500 MHz, DMSO) \(\delta\): 3.94 (s, (C\text{H}_2)\text{2}), 4H); 6.80, 6.82 (d, C(6)H, 2H, J = 8.54); 7.54 – 7.56 (dd, C(6)H, 2H, \(J = 2.16, 8.53\)); 7.70, 7.71 (d, C(6)H, 2H, \(J = 2.14\)); 8.69 (s, C(6)H, 2H), 13.61 (br s, C(6)OH, 2H). \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (500 MHz, DMSO) \(\delta\): 58.9 (C(6)H); 116.3, 117.6, 129.4, 130.5 (C(6)-CH\text{2}-N and C(6)-H), 139.7(Ph-SO\text{3}), 161.5 (CH=N), 167.5 (Ph-O). The NMR spectra are provided as Figures S1 and S2.
Scheme 1: Synthesis of 5-sulfonato-salicylaldehyde sodium salt and N,N’-bis(salicylidene-5-sulfonato)-diaminoethane disodium salt

The synthesis of saldien-SO$_3$ was similar to Scheme 1 performing the last step with diethylenetriamine. The pale yellow product (4) was collected after drying in vacuo (83% yield in the final step, 22% overall yield). ESI-MS-TOF (-ve) $m/z = 234$ (M/2 –Na) and 468 (M-2Na). $^1$H NMR (500 MHz, DMSO) $\delta$: 2.87 (br m, (C$_H$_2)$_2$), 4H); 3.67 (br m, (C$_H$_2)$_2$), 4H); 6.77 (d, C(6)H, 2H, $J = 7.49$); 7.52 (d, C(6)H, 2H, $J = 7.49$); 7.67 (s, C(6)H, 2H); 8.52 (s C$_H$N, 2H), 13.56 (br s, C(6)O$_H$, 2H). Scheme 2 displays the structure of this pentadentate ligand.

Scheme 2: Structure of saldien-SO$_3$

Estimation of uranyl-Schiff base stability constants

Acid dissociation constants of the phenolic groups were determined by potentiometric titration with 0.1 M NaOH. Titration of 7.5×10$^{-4}$ M UO$_2$(NO$_3$)$_2$ by H$\text{salen}$-SO$_3$ or saldien-SO$_3$ (1.0×10$^{-4}$ M to 4.0×10$^{-3}$ M) in 0.1 M ammonium acetate buffer pH 5.5 was monitored by UV–vis spectrophotometry (Cary 14 spectrophotometer with Olis upgrade, 3 points per datum, 25 ± 0.5 ºC) utilising a ligand-to-metal charge transfer (LMCT) band at 460 nm. Spectra from 443 nm to 549 nm were input to HypSpec software (v. 1.1.33) with a speciation model including the measured pH, water autoprotolysis constant at 0.1 M ionic strength, acetate pKa, uranyl hydrolysis and acetate stability constants [16], and the estimated phenolic pKa values for the Schiff bases (4.6 and 8.9, by potentiometry). The use of acetate buffer was required to maintain solution pH after addition of the ligand-containing titrant. The concentrations of the ligands were compensated by the extent of hydrolysis estimated by $^1$H NMR of the 10 mF stock solution used to prepare the solutions.

Similarity between the values in Table 1, and yet the significantly lower log $\beta_{1,-2,1}$ of UO$_2$(saldien-SO$_3$)$^{\circ}$, suggests that the additional nitrogen donor in the pentadentate ligand does not contribute significantly to
complex stability in the aqueous solution. Moreover, if there were a difference in the strength of these complexes, then the red-shift of the LMCT bands should reflect such a difference, they do not.

**Table 1: Estimated stability constants for aqueous UO$_2$(salen-SO$_3$)$_2^-$ and UO$_2$(saldien-SO$_3$)$_2^-$ complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>log$<em>{10}$ $\beta</em>{1-2,1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$(salen-SO$_3$)$_2^-$</td>
<td>6.70 ± 0.04</td>
</tr>
<tr>
<td>UO$_2$(saldien-SO$_3$)$_2^-$</td>
<td>6.40 ± 0.03</td>
</tr>
</tbody>
</table>

$^1$H NMR studies of H$_2$salen-SO$_3$ complexation with uranyl and europium(III)

Investigations of the H$_2$salenSO$_3$ chemistry in aqueous solution and verification of the UO$_2$(salen-SO$_3$)$_2$ stoichiometry were facilitated by acquiring proton spectra (Figure 1) in nitrate media under conditions similar to those that were being used in extraction studies. Samples were prepared by dissolving 4.7 mg of the ligand salt in UO$_2$(NO$_3$)$_2$ solutions (pH 4) diluted with sufficient volume of 0.1 M KNO$_3$ pH 4 (adjusted using acetic acid). To 0.900 mL of these solutions was added 0.100 mL of D$_2$O (99.98%, Cambridge Isotope Labs, Tewksbury, MA, USA). Spectra were recorded using a Bruker GN-500 (500 MHz, $^1$H) spectrometer, equipped with a BBO probe, employing gradient pulses for water solvent suppression [17]. Proton chemical shifts are referenced by the proteo solvent signal relative to external tetramethylsilane. Due to the prevalence of water in these samples, the phenolic protons are not observable. Thus, the spectral width was maintained at 16 ppm centred at 4.9 ppm.

**Figure 1: $^1$H NMR downfield spectra from the titration of H$_2$salenSO$_3$ by uranyl nitrate in aqueous solution**

Several features of the spectra in Figure 1 demonstrate strong coordination of the imines with the uranyl ion and corroborate the LMCT, indicated by the large downfield shift of the azomethine (B to B*) and phenyl proton resonances. Prior to equivalence, resonances of species involved in the equilibria exhibit line broadening due to chemical exchange. In some cases, the signals are not well-enough resolved to identify them. Significant, but not complete hydrolysis is revealed by the 5-sulfonato-salicylaldehyde...
resonance (A'), two distinct azomethine environments (B and B_p), and the third set of phenyl protons associated with the partially hydrolysed ligand. The sum of complete and partial hydrolysis of the ligand without uranium present is estimated to be roughly 57% based on the A'/B_p integral ratio and the A'/A' + B*/2 ratio. However, after equivalence there remain three phenyl proton resonances (C', D', E') characteristic of the aldehyde, three phenyl proton resonances (C*, D*, E*) as well as a single azomethine signal, indicating one complex with the intact ligand. Estimating the extent of hydrolysis at 5 mM uranyl by the ratios of these analogous integrals, and taking into account stoichiometry (e.g., E*/2 / (E*/2 + E')), results in only 50% conversion, which suggests that a slight protective effect may be present with excess uranyl. This effect may be the result of faster kinetics of complexation than those of hydrolysis. Weaker complexation of the uranyl ion with the aldehyde than with the intact ligand is illustrated by the sudden shift in the E' doublet after equivalence. Thus, in cases where the \(\{\text{UO}_2\}^{2+}\) concentration is lower than that of \(\text{H}_2\text{salen-SO}_3\) (e.g., tracer extraction studies), the \(\text{UO}_2(\text{salenSO}_3)^2\) complex will predominate.

Evaluation of the interaction between Eu(III) and \(\text{H}_2\text{salenSO}_3\) were performed in a similar manner, except that the risk of metal ion hydrolysis required that the pH of the stock solutions be lower, and thus a 10 mF \(\text{H}_2\text{salen-SO}_3\) solution was prepared at pH 5.3 in 0.1 M KNO_3, rather than dissolving the ligand salt in the metal ion solution.

**Figure 2: \(^1\text{H} \text{NMR downfield spectra from the addition of Eu(NO}_3)_3 \) to aqueous \(\text{H}_2\text{salenSO}_3\)**

**Extraction studies**

Extraction experiments were conducted using 0.01 M HDEHP in toluene as the organic phase and 0.01 M \(\text{H}_2\text{salen-SO}_3\) in 0.1 M KNO_3 with 0.01 M acetic acid (equilibrium pH = 5.3) as the aqueous phase. The aim was to investigate the partitioning behaviour of U(VI), Eu(III), and Np. Acetic acid was used to adjust the acidity of the initial aqueous solutions and proved to be useful in avoiding drastic changes in acidity post-extraction. The aqueous phase was prepared by dissolving an appropriate weight of the Schiff base sodium salt in 0.1 M KNO_3 (pH = 4.4) containing \(1\times10^{-4}\) M \(\text{UO}_2\text{(NO}_3)_2\) and adjusting the pH to 5.3 using 0.2 M acetic acid to produce a 10 mF solution of the ligand. Relatively mild acidity was chosen for these systems based on the range of pK_a values between 5 and 9 for the phenolic protons of this and analogous Schiff bases, and that f-element metal ions tend to hydrolyse to insoluble products above pH 6 [16]. The experiments employed continuous contact between 5 mL of the organic phase (pre-equilibrated with the aqueous phase without metal ion present) and 5 mL the aqueous phase containing the nitrate salts.
of the metal ions. The time-dependent partitioning of \( \{UO_2\}^{2+} \) \((1 \times 10^{-4} \text{ M})\) and \( \text{Eu}^{3+} \) \((1 \times 10^{-5} \text{ M radiotracer +}

carrier)\), in the presence of \( \{UO_2\}^{2+} \) \((1 \times 10^{-4} \text{ mol L}^{-1})\) in the case of the \( \text{H}_2\text{salen-SO}_3 \) system, and \( ^{237}\text{Np} \) \((8 \times 10^{-6} \text{ M radiotracer})\) were examined in separate experiments by vortex mixing or rapid stirring with a magnetic stir bar to generate an emulsion. At each timepoint, the phases were disengaged by centrifugation and equal volume aliquots of the phases were removed and sampled in triplicate for analysis. Comparison to extraction without the holdback reagent was made possible by preparing a similar system without a Schiff base present and mixing for 30 minutes. The extent of extraction was calculated as a distribution ratio (ratio of summed count rates in equilibrated organic phase to that in the aqueous phase). For ICP-MS analysis of uranium the saldien-SO\(_3\) system, only the diluted aqueous phase was analysed and the organic phase content was inferred by the difference from the aqueous phase before contact.

Uranium samples (0.100 mL) from \( \text{H}_2\text{salen-SO}_3 \) experiments were analysed by neutron activation analysis at the UC Irvine Mark I TRIGA nuclear reactor. \(^{238}\text{U}\) was allowed to decay and the \(^{239}\text{Np}\) daughter was counted using a Canberra high purity germanium (HPGe) detector operated with Genie\textsuperscript{TM} 2000 (v. 3.2.1) gamma acquisition and analysis software. Aqueous uranium samples from the saldien-SO\(_3\) experiments were analysed by ICP-MS (Agilent 7500 series equipped with an ASX-500 series autosampler, using ICP-MS ChemStation v. B.03.07). Europium-252/254 samples were analysed in polyethylene tubes by a Packard Cobra 5003 automatic gamma counter. Neptunium-237 samples were prepared by combining 0.100 mL of each phase in liquid scintillation cocktail (Beckman-Coulter, Fullerton, CA) and measured using a Beckman LS6500 liquid scintillation counter. The oxidation states of Np in the aqueous phase were determined to be +V and +VI by optical spectroscopy. Overall uncertainties in the measurements were reported as the sum of the relative counting errors and relative standard deviations from triplicate samples at the 95% confidence interval.

Figure 3: Extraction of U(VI), Eu(III), and Np by HDEHP in toluene in absence and presence of \( \text{H}_2\text{salen-SO}_3 \)

Effect of phase contact time on the distribution of U(VI), Eu(III), and Np(V/VI) between 0.01 M HDEHP in toluene and 0.1 M K\(_2\text{NO}_3\) pH 5.3 with and without 0.01 F \( \text{H}_2\text{salen-SO}_3\). Data for U(VI) and Eu(III) were first published in reference [11].

The distribution ratios of U(VI), Eu(III), and Np(V/VI) in the absence of \( \text{H}_2\text{salen-SO}_3\) at 30 minute contact time are shown in Figure 3. In accord with previous studies [18], the extraction of uranyl by HDEHP is considerably greater than that of Eu(III). Addition of \( \text{H}_2\text{salen-SO}_3\) into the aqueous phase results in much diminished extraction for the actinyl ions, at least 100-fold in the first few hours. In contrast, Eu(III) may be retained by no more than 3-fold in the same time frame. Holdback of the actinyl
ions is clearly related to the selective complexation of those ions by the intact Schiff base. However, the distribution ratios for Eu(III) are between 1 and 2, clearly not a sufficient extraction for a process. At this pH, however, the low DL may be the result of a combination of somewhat variable HDEHP concentration after pre-conditioning by transfer of DEHP into the aqueous phase and the unknown activity of HDEHP(DEHP) dimer, which is the effective extracting agent in systems employing this extractant. Extracted neptunium is expected to be primarily in the +IV or +VI state, as Np(V) is not well extracted by HDEHP [19].

**Figure 4: Extraction of U(VI) and Eu(III) by HDEHP in toluene in absence and presence of soldien-SO$_3$**

Effect of phase contact time on the distribution of U(VI) and Eu(III) between 0.01 M HDEHP in toluene and 0.1 M KNO$_3$, pH 5.3 with and without 0.01 M soldien-SO$_3$.

Figure 4 displays extraction data for U(VI) and Eu(III) in the presence and absence of soldien-SO$_3$, under conditions that mimic those from experiments with H$_2$salen-SO$_3$. While similar results are found for uranyl extraction/holdback, those for europium are very different from the previous system. Notably, the very high extraction efficiencies in the presence of soldien-SO$_3$ yield Eu/U separation factors that vary from 20 000 at 30 minutes of phase contact to 200 at 32 hours of mixing, exceeding the highest SF in the presence of H$_2$salen-SO$_3$ by 50 to 5000 times. DL in the absence of aqueous ligand is 10-fold higher than that in Figure 3. However, this result may be a consequence of only 72% recovery, where the solubility of Eu(III) complexes in the aqueous phase could increase the effective DL. Such low recovery in the absence of soldien-SO$_3$, while recovery in the presence of the ligand are between 99% and 107%, suggest that soldien-SO$_3$ may help solubilise the lanthanide ion and facilitate its phase transfer.

**Conclusions**

We have structurally and spectroscopically characterised {UO$_2$}$_{2+}$ complexes with aqueous soluble N$_2$O$_2$-donor (H$_2$salen-SO$_3$) and N$_3$O$_2$-donor (saldien-SO$_3$) Schiff bases. Under most conditions U(VI) is readily extracted from aqueous solution by HDEHP into toluene. However, when either Schiff base is added, U(VI) is held back in the aqueous phase, with a ca. 3 order magnitude decrease in distribution coefficient. Similar holdback factors are observed for neptunium, which may be in part due to the extractability of the oxidation states present. Under similar conditions, Eu(III) is held back to a much lesser extent by H$_2$salen-SO$_3$. Yet, Eu(III) extraction is enhanced by at least an order of magnitude in the presence of soldien-SO$_3$. Although the proclivity of these imines toward acid hydrolysis renders them unsuitable to a separations process for used nuclear fuel, the behaviour of the intact ligands suggests that
similar structures with a stable backbone may be useful under certain conditions. These results hold promise for the application of aqueous Schiff base ligands in the development of novel lanthanide/actinide separation schemes.

References


Dissolution Behaviour of MgO- and Mo-Based Inert Matrix Fuel for the Transmutation of Plutonium and Minor Actinides

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Abstract
Experimental work on the reprocessability of inert matrix fuel (IMF) is being performed within the EU project ASGARD. (Pu,MA)-oxide fuel within a metallic $^{92}$Mo matrix (CERMET) and within a ceramic MgO matrix (CERCER) are under investigation. Here, we present new experimental data on the dissolution behaviour of the matrix materials (Mo, MgO) in nitric acid as a first head-end step prior to plutonium and minor actinides separation by solvent extraction. The influence of temperature and nitric acid concentration was investigated in laboratory dissolution experiments. The dissolution rate of MgO is strongly dependent on the temperature, but is rather similar for different nitric acid concentrations. The dissolution of molybdenum is complex due to its multiple redox chemistry. Mo is soluble in HNO$_3$, but is oxidised to MoO$_3$, which then precipitates. The addition of ferric nitrate to the acid can improve the dissolution characteristics and prevent precipitations at low acid concentrations.

Introduction

Used fuel from commercial light water reactors (LWR) contains about 95.5% uranium, 3.5% fission products and approximately 1% plutonium and minor actinides (MA = Np, Am, Cm). Pu and MA are of particular concern with respect to long-term radiotoxicity, heat load issues and proliferation risks. It is estimated that in the year 2006 about 110 tons of MA were contained in spent fuel storages worldwide and 40 tons were contained in high-level waste products from reprocessing. This amount is foreseen to double by year 2020 [1].

The transmutation of Pu and MA in subcritical accelerator-driven reactors (ADS) is one option for solving this problem. Fuels with a high content of Pu and MA, which are free of U-238 and thus avoid the build-up of new transuranium (TRU) isotopes, are favoured. To increase the burnup of TRU elements and to reduce the formation of new TRU, inert matrix fuels (IMF) are preferred [2-4]. A non-fissile, inert matrix is added to the fuel to improve the thermal properties. These inert matrices are ceramic substrates or metallic matrices which have to meet different criteria such as high melting point and thermal conductivity, low thermal expansion, high radiation resistance and low cross section for the absorption of neutrons.

Within this work, magnesia and molybdenum are considered as matrix materials. The irradiation performance of IMF with matrix content >60 vol.% has been investigated in various experiments such as FUTURIX-FTA, HELIOS, BODEX, and ECRIX-H [5-8]. MgO-based inert matrix fuels are superior with regard to transmutation performance; Mo-based fuels show advantages in safety [9].

The presence of large amounts of matrix material poses additional challenges with respect to the various reprocessing steps of the transmutation target (Figure 1). A major difficulty will be to optimise the dissolution process of the used target after ADS operation. The well-known hydrometallurgical PUREX process is used today for the industrial reprocessing of used fuel and serves as a reference [10]. The PUREX process utilises
HNO₃ for the dissolution step. A complete dissolution of the inert matrix and the actinide oxide, or a selective dissolution, where the inert matrix remains undissolved, can be considered. The dissolution of MgO should not cause any problems. MgO is soluble in HNO₃ with fast dissolution kinetics and without precipitation occurring [11,4, 12]. Mo as an inert matrix poses additional challenges with respect to its REDOX chemistry. Mo is soluble in nitric acid but is oxidised to MoO₃ which might form precipitates. The target contains significant amounts of inert matrix (MgO, Mo) which will interfere and disturb the extraction process using e.g. DIAMEX/SANEX concepts [4].

Since enriched ⁹²Mo is used to limit the build-up of ⁹⁹Tc and because of its favourable neutronic parameters [9], it is necessary to recover the Mo, which is a challenging task. Furthermore, the separation of Mg should be considered, since large amounts cannot be incorporated in the glass.

**Figure 1: Schematic flow sheet for the hydrometallurgical reprocessing of used IMF targets**

The selected inert matrix should not give rise to new radioactive waste that must be safely disposed of as low or medium level waste.

The current paper focuses on experimental dissolution studies. The aim of this work is to optimise dissolution parameters and finally implement semi-hot tests (fresh PuO₂ + Mo matrix pellets).

**Material and methods**

**Pellet fabrication**

For the production of Mo pellets, 1 g Mo powder (Strem Chemicals, 99.9%) was pressed at a compaction pressure of 640 MPa using a cold uniaxial press. The pellets were then sintered at 1600°C for 5 h in an argon atmosphere. The density of all pellets was measured by the geometrical method and was 91.5%TD.

MgO powder (Merck, pro analysis) was calcined at 600°C for 2 h and then milled by hand. The powder (500 mg) was compacted into cylindrical pellets with 10 mm diameter by cold uniaxial pressing. The range of pressures used for the investigation of optimal pressing and sintering conditions varied from 130 MPa to 765 MPa. All MgO pellets were sintered for 5 h in air atmosphere at 1600°C. The density of the MgO pellets used for dissolution experiments was 95.5%TD. Moreover, MgO pellets with a CeO₂ content of 40 wt.% were synthesised. Ce(OH)₄ (Sigma Aldrich) powder was calcined at 600°C to obtain
CeO$_2$. The CeO$_2$ was then carefully hand mixed with magnesia. The powder (500 mg) was then pressed with a cold uniaxial press at a compaction pressure of 320 MPa. The resulting pellets were sintered at 1600°C for 5 h in air.

**Dissolution experiments**

The set-up for dissolution experiments consisted of a rotating heater with temperature control, an oil bath, a two-necked flask, a magnet, a Liebig condenser and two washing flasks. Dissolution experiments were performed at different acid concentrations as well as at different temperatures. HNO$_3$ (Merck, pro analysis) was used for all dissolution experiments. In the case of molybdenum, ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) (Sigma Aldrich, ≥ 98%) was used as an additive in some cases. 20 mL acid were used per 1 g pellet. During the dissolution process, 50 µL samples were taken until the pellet was either dissolved completely or remained in a stable condition. The samples were diluted 1:10$^6$ in suprapure 1% HNO$_3$ for ICP-MS analysis.

The dissolution experiments were compared by plotting the average dissolution rate (mg·min$^{-1}$) (equation 1) against the percentage pellet dissolved (equation 2).

\[
a_{\text{Mg}} = \frac{[\text{Mg}]V_t}{t} \tag{1}
\]

\[
P = \frac{100[\text{Mg}]V_t}{m} \tag{2}
\]

where $a_{\text{Mg}}$ is the average dissolution rate of magnesium (mg·min$^{-1}$), [Mg] is the magnesium concentration (g·L$^{-1}$), $V_t$ is the volume at the time of sampling (mL), $t$ is the time (min), $P$ is the percentage of pellet dissolved (%) and $m$ is the mass of magnesium in the pellet (mg).

**Results and discussion**

**Dissolution of Mo pellets**

Typical examples of the dissolution kinetics of pure metallic Mo pellets at different conditions are presented in Figure 2. The dissolution behaviour was strongly dependent on the acid concentration; the dissolution velocity in 2 mol/L HNO$_3$ was significantly higher than in 1 mol/L HNO$_3$. In the latter case, only the incubation period was observed during 80 h of dissolution. Higher acid concentrations (> 2 mol/L HNO$_3$) resulted in higher dissolution velocities, but also in more precipitate formation. Precipitates (MoO$_3$, < 80 at.%%) occurred at all HNO$_3$ concentrations. An increase in temperature resulted in faster dissolution velocities but also greater extent of precipitation. During the dissolution of an Mo pellet in 7 mol/L HNO$_3$ at 90°C a large amount of precipitation occurred within the first 30 min of the dissolution time, whereas at RT only a very low amount of precipitation occurred instantly.

**Figure 2: Dissolution of Mo pellets (1 g) in 20 mL HNO$_3$ of different concentrations at RT**
The dissolution of molybdenum metal in HNO₃ was studied quite intensively in the late 1950s and early 1960s in the context of the reprocessing of uranium-molybdenum alloy nuclear fuels [13-16]. Mo as an inert matrix poses additional challenges with respect to its REDOX chemistry. Molybdenum is already attacked by cold HNO₃; however, dilute acid has a stronger effect than concentrated acid. In the heat, molybdenum is dissolved quickly independent of the concentration; the reaction is very vigorous [17]. The attack of molybdenum by concentrated HNO₃ solutions results from the oxidising power of HNO₃. The corrosion rate of molybdenum decreases with the contact time. Mo is usually attacked even by a dilute HNO₃ solution. The reaction in dilute acid is presumed to be:

\[
\text{Mo} + 2\text{HNO}_3 \rightleftharpoons \text{H}_2\text{MoO}_4 + 2\text{NO} \quad \text{(3)}
\]

\[
\text{Mo} + 6\text{HNO}_3 \rightleftharpoons \text{H}_2\text{MoO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O} \quad \text{(4)}
\]

MoO₃(NO₃)₂ or [MoO₂·MoO₃](NO₃)₂ are formed in more concentrated HNO₃ solutions. In concentrated HNO₃ molybdenum dissolves according to:

\[
\text{Mo} + 2\text{HNO}_3 \rightarrow \text{MoO}_3 + 2\text{NO} + \text{H}_2\text{O}. \quad \text{(5)}
\]

However, the produced MoO₃ does not dissolve readily in HNO₃ but rather precipitates [18]. There is a need to avoid co-precipitation with Pu, thus leading to Pu losses. Iron(III) nitrate is known to significantly increase the solubility of uranyl molybdate in HNO₃. Anion exchange resin studies indicate that a negatively charged iron-molybdenum complex ion is present in such solutions [15]. Heteropolymolybdate ions are formed by reactions similar to the following [13]:

\[
2\text{Fe}^{3+} + 12\text{MoO}_3 + 6\text{H}_2\text{O} \rightleftharpoons (\text{Fe}_2\text{Mo}_{12}\text{O}_{42})^{6-} + 12\text{H}^+ \quad \text{(6)}
\]

Our results show that complete dissolution can be achieved by adding at least 1 mol/L Fe(III). The addition of Fe(III) also increases the dissolution velocity, as shown in Figure 2. Without the addition of iron to the 1 mol/L HNO₃ only about 40% of the pellet was dissolved after three days, whereas with the addition of 1 mol/L Fe(NO₃)₃ the pellet completely dissolved within about one day.

Electrospray ionisation mass spectrometry, which can probe the stoichiometry and relative abundances of solution species, was applied to characterise the solution species of molybdenum in strongly acidic nitric acid medium. In addition to the presence of hexavalent Mo species, the spectra show that pentavalent Mo species are present in solution despite the oxidising condition in strong nitric acid. Moreover, mixed iron-molybdenum-species were detected in iron(III)-containing solutions [19].

**Fabrication of MgO pellets**

For the determination of optimal pressing and sintering conditions, the magnesium oxide powder calcined at 600 °C was compacted by applying pressures of between 130 MPa and 765 MPa. The relative green densities are plotted in Figure 3 as a function of the logarithm of the compaction pressure as recommended in references [20,21]. In these coordinates, the dependency should be linear for ceramic powders. For our investigated samples, the relative green density (open diamonds) of the pellets linearly increased with the logarithm of the pressure. At 765 MPa (log P = 2.88), it reached 60.1% of the theoretical density (3.58 g·cm⁻³). After compaction, the pellets were sintered for 5 h in air at 1600°C.

The dependence of the sintered densities reached a pronounced maximum at P = 480 MPa, as shown in Figure 3 for the representative case of sintering at 1600 °C. The value of the sintering density in dependence on the compaction pressure varied from 95%TD to 99%TD. At P > P_max cracks formed in the pellets. The value of P_max and the region of \(\rho_S\) strongly depended on the calcination temperature. On the basis of our study, pellets with densities ranging between 85%TD and 99.5%TD were fabricated and used in the following dissolution investigation.
Dissolution of MgO pellets

The dissolution kinetic of MgO pellets is similar to that of the Mo pellets. Figure 4 shows the dissolution rates $a_{Mg}$ (cf. eq. 1) at 90°C as a function of $P$ (cf. eq 2). The dissolution rates in 4 mol/L HNO₃ and 7 mol/L HNO₃ were similar. The dissolution rate increased during the incubation period and then remained constant until it decreased during the final period of complete dissolution. However, the dissolution rate of magnesium in 2 mol/L HNO₃ was higher at the beginning of the dissolution experiment before it strongly decreased after about 60% of the pellet had been dissolved because the entire acid was consumed.

A literature survey showed that MgO powders were used in the majority of dissolution studies. Important factors for determining the dissolution kinetics are atomic surface details, surface morphology, and bond strength for the solid and diffusion, pH, and electrolyte concentration for the solution [22].

At a low pH (2-5), MgO (periclase) dissolves in HNO₃ by first forming a brucite-like (Mg(OH)₂) layer on the surface [23,24]. Therefore, the dissolution rates of periclase and brucite are equal in this pH range. A two-step protonation of periclase has been proposed [24,25]. In the first fast step, surface oxygen is protonated whereby a brucite-like layer is formed (equation 7) followed by a second protonation, which is rate determining.

$$\text{Mg} = \text{O} + \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{OH}^- \quad (7)$$
$$\text{Mg} - \text{OH}^+ + \text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O} \quad (8)$$
The average dissolution rate $a_{\text{Mg}}$ of MgO pellets in HNO$_3$ was strongly dependent on the temperature, as shown in Figure 5 for 4 mol/L HNO$_3$. The average dissolution rate at 90°C was six times as high as the dissolution rate at room temperature and 1.5 times as high as at 60°C.

**Figure 2: Average dissolution rates $a_{\text{Mg}}$ of MgO pellets (0.5 g) in 100 mL 4 mol/L HNO$_3$ at different temperatures**

The influence of the pellet density (84.6%TD, 90.1%TD, 95.8%TD and 99.4%TD) on the dissolution velocity was also studied in 4 mol/L HNO$_3$ at a temperature of 90°C. The dissolution rates of the pellets with densities below 96%TD were very similar whereas the dissolution velocity with a density of 99.4%TD was six times smaller.

**Dissolution of MgO/CeO$_2$ pellets**

The dissolution of MgO/CeO$_2$ (60/40) pellets showed the same typical kinetic as for pure MgO pellets. Figure 6 compares the dissolution of Mg and Ce from mixed MgO/CeO$_2$ (60/40). The MgO was completely dissolved, whereas only about 0.6 at.% of the CeO$_2$ dissolved. The rest of the CeO$_2$ remained undissolved as a powder.

**Figure 6: Dissolution of MgO/CeO$_2$ (60/40) pellets (0.5 g) in 100 mL 7 mol/L HNO$_3$ at 90°C**

The same trend was found even at very mild conditions (2 mol/L HNO$_3$, RT) as depicted in Figure 7, although dissolution was significantly slower at these conditions. PuO$_2$ was not expected to dissolve at either of these conditions, which allowed a selective dissolution of the matrix material.
Conclusions and outlook

The dissolution velocity of molybdenum was strongly dependent on the acid concentration as well as the temperature. The dissolution of Mo pellets in HNO₃ was complex. It was accompanied by precipitation, especially at high acid concentrations and temperatures. The addition of 1 mol/L ferric nitrate to the acid can prevent precipitation at low nitric acid concentrations and accelerate the dissolution. However, it is unclear whether adding such an amount of Fe³⁺ to the dissolver solution could influence the subsequent extraction process. Further dissolution optimisation studies are planned in the near future in glove boxes (fresh PuO₂ + Mo matrix pellets).

The dissolution of MgO is possible even under mild conditions (2.5 mol/L HNO₃, RT). The average dissolution rates of MgO in HNO₃ of different concentrations are rather similar, and the dissolution rate is strongly dependent on the dissolution temperature.

The dissolution of the MgO/CeO₂ pellets shows that during dissolution of MgO, the bulk CeO₂ remains undissolved allowing a rough separation of MgO and CeO₂. A dissolution behaviour similar to that of CeO₂ is expected for PuO₂ so that MgO could be separated in a first dissolution step at mild conditions, while the PuO₂ would be dissolved in an additional step utilising e.g. boiling concentrated HNO₃ and Ag(II) as catalysts.

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References

Electrochemical Studies on Important Elements for Zirconium Recovery Form Irradiated Zircaloy-4 Cladding

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Abstract

Since Zircaloy cladding accounts for about 16 wt. % of used nuclear fuel assembly, decontamination process is required to reduce the final waste volume from spent nuclear fuel. To develop Zircaloy-4 electrorefining process as an irradiated Zircaloy cladding decontamination process, electrochemical studies on Sn, Cr, Fe and Co which are major or important elements in the irradiated cladding were conducted based on cyclic voltammetry in LiCl-KCl at 500°C. Cyclic voltammetry for Sn, Fe, Cr and Co elements that should be eliminated was conducted and revealed that redox reactions of these ions are much simpler than Zr and more reductive than Zr. The reliability of cyclic voltammetry was verified by comparing diffusion coefficients and formal reduction potentials of these ions obtained in this study to previous studies.

Introduction

Zirconium alloys have low thermal neutron absorption cross section, high corrosion resistance and superior mechanical characteristics. These alloys have been used for structure materials in nuclear reactor systems that must maintain integrity over long period of time in harsh conditions such as high temperature, high pressure and strong radiation [1]. Nuclear power plants in the Republic of Korea utilise zirconium alloys for fuel cladding, pressure tube and calandria tube in both Pressurised Water Reactors (PWR) and CANada Deuterium Uranium reactors (CANDU). Therefore, a large amount of radioactive zirconium alloy waste is inevitably generated as results of nuclear power plant operation. Claddings of spent nuclear fuels constitute the largest portion of radioactive zirconium alloy wastes as about 16 wt. % of spent nuclear fuel assembly. In addition, the cladding separated from spent nuclear fuels is classified as an intermediate level waste in the latest radioactive waste classification of the International Atomic Energy Agency (IAEA) since non-negligible amount of long-living actinide elements and fission products could penetrate into fuel claddings during irradiation in nuclear reactor and activation products such as Co-90 is produced by neutron activation [2]. If zirconium can be chemically separated from irradiated claddings, the final volume of radioactive waste in geological repositories can be greatly reduced and recovered zirconium could be recycled for reutilisation in nuclear industry.

For this reason, limited but active investigations have been conducted in recent years to decontaminate spent nuclear fuel zirconium alloy cladding. Rudisill attempted to remove actinide elements and fission products by surface removal using hydrogen fluoride acid [3]. However, since penetration depths of these elements at the concentration limit of the U.S. Class C level waste was as deep as 180 μm, the surface removal was ineffective. It is concluded that volumetric decontamination processes such as gaseous reaction methods or molten salt electrorefining techniques were required. Iodination and chlorination methods have been developed as a gaseous reaction method [4,5]. While gaseous methods can separate zirconium with high purity there are some drawbacks. In iodination methods, concentration of moisture in the reaction chamber should be maintained very low since ZrI4 is very hygroscopic. In
addition, reduction of ZrI₄ into Zr metal would be very slow. In chlorination or Kroll process, large amount of Mg waste could be generated from reduction of ZrCl₄ into Zr metal.

Electrorefining could be an effective decontamination process with simple reaction steps and relatively compact size of the reactor. In this study, in order to develop electrorefining process for decontaminating the irradiated Zircaloy-4 cladding in LiCl-KCl salts, electrochemical studies on Sn, Cr, Fe and Co (major or important elements in the irradiated cladding) were conducted based on cyclic voltammetry (CV) in LiCl-KCl at 500°C. Diffusion coefficients and standard reduction potentials for these elements were calculated and compared to other literatures.

**Experimental setup**

All of experiments were carried out in a sealed glovebox filled with Ar gas of 99.999%. The concentrations of moisture and oxygen were maintained below 0.1 ppm by a purifier during the experiments. A furnace was installed inside the glovebox to keep the temperature of electrochemical cell to 500°C within ±1°C. Two identical quartz cells containing equivalent molten salts were prepared inside the furnace for electrochemical experiments and temperature measurements as shown in Figure 1. An anhydrous LiCl-KCl eutectic mixture with a purity of 99.99% was obtained from Sigma Aldrich, and anhydrous SnCl₂, CrCl₂, FeCl₂ and CoCl₂ with purity of 99.99% were also received from the same supplier. The working and counter electrodes made of 99.99% tungsten were arranged inside the quartz cell. The diameter of these electrodes was 1 mm. The reference electrode was a 1 wt. % Ag/AgCl electrode prepared with Pyrex glass tube.

**Figure 1: Experimental setup for electrochemical experiments** [6]

Since concentration of SnCl₂, CrCl₂, FeCl₂ and CoCl₂ would be much smaller than that of ZrCl₄ during electrorefining of Zircaloy-4 cladding, redox behaviours of these elements should be investigated in low concentration as 0.1 wt. %. To prepare low concentration reagents, the salts with 10 wt. % were produced and they were diluted down to 0.1 wt. %. For CV measurement, 2.54g of molten salts were used.
Results and discussion

The CVs for 0.1 wt. % SnCl₂, CrCl₂, FeCl₂ and CoCl₂ salts are represented in Figures 2 (a), (b), (c) and (d) respectively. For SnCl₂, FeCl₂ and CoCl₂, single oxidation peak and reduction peak were identified. For CrCl₂, two oxidation peaks and two reduction peaks were observed (Figure 1b).

Since there was only a pair of redox peak for SnCl₂ at low concentration (0.1 and 0.2 wt. %), redox reaction for Sn in LiCl-KCl could be determined as reactions between Sn and Sn(II):

\[ \text{R₁: } \text{Sn(II)} + 2e^- \rightarrow \text{Sn} \]  
\[ \text{O₁: } \text{Sn} \rightarrow \text{Sn(II)} + 2e^- \]  

At high concentration of SnCl₂ (0.5 and 1.0 wt. %), the oxidation peak looks like a superposed shape of two peaks (O₂ and O₃). Therefore, it would be expected that the oxidation of Sn occurs in two steps:

\[ \text{O₂: } \text{Sn} \rightarrow \text{Sn(I)} + e^- \]  
\[ \text{O₃: } \text{Sn(I)} \rightarrow \text{Sn(II)} + e^- \]  

However, since the melting point of Sn is about 232°C which is much lower than molten salt temperature of 500°C, reduced Sn metal from Sn(II) could move away from electrode surface as a liquid metal state and this could result in changes of effective area of working electrode and distortion of oxidation peak shape. This phenomenon could become serious at high concentration of SnCl₂ salts with
low scan rate. While the potential sweeps from the positive to the negative side in high concentration salts, more amount of liquid Sn metal could be produced at the working electrode and this could make the electrode surface complicated. If the scan rate is fast enough, most of the reduced Sn would stay near the working electrode and the effective area of the working electrode would not severely be changed.

For all concentrations of CrCl₂ salts, two clear redox peak pairs were observed. Since peak O₁ of CVs for CrCl₂ shows almost symmetric shape with peak potential as the centre without a diffusion tail which would be produced by ion mass transfer, peak O₁ might be related to an oxidation reaction of Cr metal and peak R₁ might be related to a reduction reaction producing Cr metal. Peaks O₂ and R₂ have more fluent curves with diffusion tail and it would mean that they are related to redox reactions between soluble-soluble states. Since it was revealed that Cr(II) and Cr(III) are stable ion state in LiCl-KCl, redox reactions for redox peaks of CrCl₂ CV would be defined as follow [7]:

\[ R₁: \text{Cr(II)} + 2e^- \rightarrow \text{Cr}, \]
\[ O₁: \text{Cr} \rightarrow \text{Cr(II)} + 2e^- , \]
\[ R₂: \text{Cr(III)} + e^- \rightarrow \text{Cr(II)} \quad \text{and} \]
\[ O₂: \text{Cr(II)} \rightarrow \text{Cr(III)} + e^- . \]

CVs for FeCl₂ and CoCl₂ have a single redox peak pair. Therefore, redox reactions for these elements in LiCl-KCl could be determined relatively easily. Redox reaction of FeCl₂ for each peak would be determined as:

\[ R₁: \text{Fe(II)} + 2e^- \rightarrow \text{Fe} \quad \text{and} \]
\[ O₁: \text{Fe} \rightarrow \text{Fe(II)} + 2e^- . \]

The redox reaction of CoCl₂ for each peak could be determined as follows:

\[ R₁: \text{Co(II)} + 2e^- \rightarrow \text{Co} \quad \text{and} \]
\[ O₁: \text{Co} \rightarrow \text{Co(II)} + 2e^- . \]

Diffusion coefficients and formal reduction potentials were calculated for Sn, Cr, Fe and Co. Since the redox peak behaviours are close to reversible with small peak potential changes, a peak current equation for reversible reaction introduced by D. J. Schiffrin was used to estimate diffusion coefficient [8]:

\[ i_p = 1.082nFAC \sqrt{\frac{nFDv}{RT\pi}} \]

Since reversible behaviour is intensified at high concentration and low scan rate, the equation is applied at the highest concentration where peak could be defined clearly with the lowest scan rate. Diffusion coefficient of Sn(II) is estimated as 3.732E-9 m²/s in molten salt of 0.1 wt. % with a scan rate of 0.1 V/s. The measured diffusion coefficient of Sn(II) is consistent with previous studies. H. El Ghallali measured diffusion coefficients of Sn(II) as from 2.86 to 3.94E-9 m²/s using chronopotentiometry and as from 3.60 to 4.40E-9 m²/s using cyclic voltammetry [9]. The diffusion coefficient of Cr(II) is calculated as 1.14E-9 m²/s in 0.1 wt. % CrCl₂ salts with 0.1 V/s scan rate. The measured value is quiet similar to diffusion coefficients reported in previous study. D. Inman measured diffusion coefficient of Cr(II) as from 1.21E-9 to 1.86E-9 m²/s in different concentration of LiCl-KCl-CrCl₂ salts at 500°C by chronopotentiometry [10]. The diffusion coefficient of Fe(II) is obtained as 2.61E-9 m²/s in 0.1 wt. % FeCl₂ salts with 0.1 V/s scan rate. The measured value is also 5 similar to diffusion coefficients reported in previous study. D. Inman reported the diffusion coefficient of Fe(II) as from 2.08E-9 to 2.26E-9 by conducting chronopotentiometry in different concentration at 500°C [11]. Diffusion coefficient of Co(II) is measured as 3.24E-9 m²/s in 0.1 wt. % CoCl₂ with 0.1 V/s scan rate. The measured value is almost equivalent to the diffusion coefficients reported in previous study. H. Groult reported the diffusion
coefficient of Co(II) as 3.74E-9 m²/s by conducting chronopotentiometry in 0.02 mol/l CoCl₂ salts at 500°C [12].

Formal potentials for Sn, Cr, Fe and Co are calculated by Eq. (14) [8]:

\[ E_p = E^{\circ'} + \frac{RT}{nF} \ln C_{M^{n+}} + 0.8540 \frac{RT}{nF} \]  \hspace{1cm} (14)

where \( E^{\circ'} \) is the standard reduction potential and \( C_{M^{n+}} \) is the concentration of \( M^{n+} \) ion. The formal potentials are listed in Table 1 and compared to values from a previous study conducted by M. Iizuka [13]. Since the standard potentials found by M. Iizuka are reported based on a reference electrode of Cl⁻/Cl₂, if differences to values from previous study are equivalent regardless of elements, it could be clarified that measured values are reliable. As shown in Table 1, the differences are almost similar with a value of 1.1 V. Therefore, it could be concluded that CVs were conducted in a reliable manner. Since the formal potentials of these elements are more positive than that the one of Zr of -0.994 V (vs. Ag/AgCl) [14], only Zr would be selectively oxidised from the anode basket and other elements would be remained in the basket in a metallic form.

| Table 1: Formal potential of Sn(II), Cr(II), Fe(II) and Co(II) in LiCl-KCl at 500°C |
|---------------------------------|----------------|----------------|
| Reaction          | This study [V vs. Ag/AgCl] | M. Iizuka [13] [V vs. Cl⁻/Cl₂] | Difference between this study and previous study [V] |
| Sn²⁺/Sn          | -0.156          | -1.298         | 1.142          |
| Cr³⁺/Cr          | -0.601          | -1.641         | 1.040          |
| Fe²⁺/Fe          | -0.288          | -1.388         | 1.100          |
| Co³⁺/Co          | -0.089          | -1.207         | 1.118          |

**Conclusion**

To identify the feasibility of electrorefining of irradiated Zircaloy-4 cladding, redox behaviours of significant elements in irradiated Zircaloy-4 cladding (Sn, Cr, Fe and Co) were investigated based on CV experiments and it confirmed that these elements are much more reductive than Zr and redox mechanisms are much simpler than Zr. Therefore, by managing the potential at the anode, it might be possible to selectively dissolve Zr. The elements investigated in this study would remain in the anode basket after electrorefining.

**Acknowledgements**

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**References**


Abstract

Extraction chromatography is one of the promising technologies for minor actinides (MA: Am and Cm) recovery from high-level liquid waste. The degradation behaviour of the organic species in the adsorbents under radiation exposure is important to discuss the safety and durability of the adsorbent in the extraction chromatography process. In this study, gamma-ray irradiation experiments on TODGA/SiO₂-P adsorbent were carried out to investigate the degradation products from radiolysis of the adsorbent. The degraded organic species eluted from the adsorbent and those remaining inside the adsorbent were thoroughly identified by GC/MS, FT-IR and NMR analyses. The species suspected as hydrolysis products of TODGA were mainly detected from the analyses. Since some radicals such as •H or •OH are generated by the gamma-ray irradiation on water molecules, it was discussed that the radicals products from radiolysis of HNO₃ solution are related to the degradation reaction of the extractants.

Introduction

Extraction chromatography has been developed at Japan Atomic Energy Agency (JAEA) as one of the desirable technologies for minor actinides (MA: Am and Cm) recovery from high level liquid waste [1]. JAEA has been developing an advanced aqueous reprocessing method (Figure 1) for fast breeder reactor (FBR) fuel reprocessing, and the MA recovery using the extraction chromatography is one of remarkable issues in the advanced method. Especially, the MA partitioning and transmutation are contributed to the reduction of amount and toxicity of the final vitrified waste.

In this technology, solid adsorbents with extractants based fine porous silica particle are used for the separation process and the extractant for MA is impregnated in the silica particle. Compared to solvent extraction system, the extraction chromatography has some advantages which are no organic diluents for the extractant use, compact equipments, and reuse of the adsorbent for vitrification. The adsorbents include some organic species consequently to get good separation performances such as higher yield and decontamination factor of MA products. Therefore, the degradation behaviour of the organic species in the adsorbents under radiation exposure is greatly important to discuss the safety and durability of the adsorbent in the extraction chromatography process.

As mentioned above, the adsorbent for extraction chromatography is prepared by impregnating an extractant into the support of porous silica particle coated with styrene-divinylbenzene polymer (referred as SiO₂-P). It is packed inside a column, and then MA is efficiently recovered through adsorption/elution reactions in solid-liquid system. Radioactive elements, not only MA but also other radioactive fission products such as ¹⁵⁵Eu or ⁹⁰Sr form complexes with the extractant during the operation, thus degradations by irradiations of materials contained in the adsorbent are unavoidable in the separation process.

Previous studies reported that the radiolysis of the adsorbent brings distinct changes on adsorption/elution behaviour [2,3]. The gamma-ray irradiation effect on adsorption/elution performances of the adsorbents has been investigated; however the detailed information about the degradation products has not been reported. In order to secure the process safety based on the extraction chromatography
technology, chemical forms and behaviour of the degradation products have to be figured out. In this study, the degradation products of representative adsorbents for the extraction chromatography process (TODGA/SiO₂-P) were investigated after gamma-ray irradiation.

**Figure 1 Advanced aqueous reprocessing process**

![Advanced aqueous reprocessing process diagram](image)

**Experimental**

**γ-ray irradiation**

In this study, N,N,N’,N’-tetra-n-octyl-diglycolamide (TODGA, Figure 2) was impregnated into SiO₂-P particles, as described in [4]. The irradiation experiments were performed in the irradiation room No. 1 of the Co-60 Gamma-ray Irradiation Facility No. 1 in Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency (JAEA, Japan). Figure 3 shows the experimental setup for gamma-ray irradiation. The dose rate was calculated from the measured value obtained by the alanine–ESR method [5,6]. 50 g of the adsorbents were immersed in 100 mL of 1 M HNO₃ solution, and were then irradiated by gamma-ray with a dose rate of 3 kGy/h up to 1.98 MGy. Adsorbent samples without irradiation were also prepared to investigate degradation products produced by exposure to acid. After irradiation or exposure to acid, the adsorbent was separated from the supernatant solution. The appearance of irradiated adsorbents and the supernatant solutions are shown in Figure 4. The colour of the adsorbent changed from white to yellow after irradiation, while that of unirradiated adsorbent did not change. The degradation of the extractant and/or the polymer by the irradiation is considered to influence on the appearance. The floating of oil ingredient were found on the supernatant solution for both irradiated and unirradiated samples. The TODGA impregnated into the adsorbent must be leached during the irradiation or the exposure to the acid.

**Figure 2: N,N,N’,N’-tetra-n-octyl-diglycolamide (TODGA)**

![N,N,N’,N’-tetra-n-octyl-diglycolamide (TODGA)](image)
Identification of the degradation products

The adsorbents separated from the nitric acid were washed with 1,2-dichloroethane, then the degradation products remaining on the adsorbent were transferred to the organic phase. The organic species in the supernatant solution were also extracted by liquid-liquid extraction with 1,2-dichloroethane. The chemical species extracted in the 1,2-dichloroethane from the adsorbent and the supernatant solution were analysed by GC/MS, NMR and FT-IR measurements.

The ingredients in the 1,2-dichloroethane were derivatised by N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA: CF₃C(OSi(CH₃)₃)=NSi(CH₃)₃), and then they were also analysed by GC/MS to detect the products which are hardly eluted from the column. The derivation by BSTFA is proceeded by the following equation:

\[ HY + SiR₃X \rightarrow SiR₃Y + HX. \]  

where HY, R and X are the degradation products, alkyl-chain and CF₃C(OSi(CH₃)₃)=N, respectively. Therefore, the structure of the degradation products can be obtained by replacing SiR₃ of the predicted product to H. In order to perform the NMR and FT-IR measurements, the 1,2-dichloroethane was evaporated in advance, and then the residual product was obtained as samples for the measurements. The
FT-IR and NMR analyses were carried out on the product and the product dissolved in deuterated chloroform, respectively.

Results and discussion

**GC/MS analysis**

In the GC/MS chromatograms, 2 and 13 peaks were found in the supernatant solutions for the unirradiated and irradiated samples, respectively. Some degradation products were produced by the irradiation and were eluted into the nitric acid. The chemical forms were predicted on the mass spectra of those chromatograms. Heptane acid and propionaldehyde were predominant species in the supernatant solution for unirradiated and irradiated samples, respectively. Benzaldehyde was also detected in the unirradiated sample, and this product is considered to be produced by degradation of the polymer in the adsorbent.

Those degradation products predicted for the irradiated sample can be attributed to the products produced by cleavage reaction around the octyl in the TODGA molecule. After the derivatisation on the supernatant solutions, 5 and 10 peaks were found for unirradiated and irradiated samples, respectively. Those peaks are also attributed to the degradation products of the polymer and to the decomposed product of TODGA.

Consequently, the benzaldehyde and heptane acid were mainly observed in the unirradiated samples, while propionaldehyde and acetic acid were the species produced mainly by irradiation. Those products are suspected to mix in the product solution. Among those identified products, the benzaldehyde has relatively low flash point (i.e. 336 K), therefore the amount of the product produced in the process is necessary to be evaluated quantitatively in the future.

27 and 53 peaks were found in the chromatograms obtained for the adsorbent of unirradiated and irradiated samples, respectively. The number of products remaining on the adsorbent is distinctly larger than those dissolved into the nitric acid. The predominant product in the unirradiated adsorbent was N,N-dioctylacetamide, and this product is supposedly produced by hydration of the TODGA molecule. After γ-ray irradiation, N,N-dioctylformamide and a product shown in Figure 5 were found in the samples. Those products are considered to be produced by decomposition of the TODGA molecule. Since the irradiation degradation of TODGA in the solvent extraction system is originated by radicals of solvent induced by the irradiation [7], some radicals such as 'H and 'OH owing to radiolysis of water must be one of the significant factors for the degradation.

**NMR analysis**

The 1H-NMR spectrum of the supernatant solutions for the irradiated and unirradiated samples showed signals which could be attributed to alkanes and methylene (-CH2-). Those results reasonably agreed with those obtained by GC/MS analysis.

The degradation products could not be identified in the 1H-NMR spectrum obtained for the adsorbents. In order to perform a more detail analysis, 2 dimensional NMR charts of 1H and 1H or 13C were analysed for the adsorbents. The correlations between those nuclides suggested that the species shown in Figure 6 were produced by gamma irradiation, where the position indicated as X marks could not be identified. Those two products could also be attributed to the decomposed products of the TODGA molecule.
Figure 6: Degradation products of the adsorbents proposed by 2-D NMR analysis

FT-IR analysis

FT-IR spectrum on the supernatant solutions showed that the absorption peaks correspond to C-H, C=O and nitric ester bonds. Products with those bonds must be eluted from the adsorbents. Since the nitric ester did not detect in the supernatant solutions by GC/MS analysis, it must overlap with the peaks in the chromatogram. Nitric esters generally have low flash points, therefore the quantity of the ester contaminated in the products or waste solution is necessary to be comprehended.

In the FT-IR spectrum for the unirradiated adsorbents, N-H bonds could not be attributed to any absorption peaks while C-H and amidic C=O bonds were confirmed. Therefore the existences of TODGA molecule eluted from the adsorbent or tertiary amides (R-(C=O)-NR1R2) are anticipated in the samples. After irradiation, absorption of C=O bonds originated from carbonyl group was observed. The carbonyl group is considered to be produced by oxidation of the octyl in the TODGA molecule.

As a conclusion of the FT-IR analysis, the dominant degradation products remaining on the adsorbents must be produced by cleavage of the ether oxygen in TODGA molecule and by oxidation of the octyl. Those results are consistent with those evaluated by GC/MS and NMR analyses.

Summary of the identification on the degradation products

The dominant degradation products produced by exposure to acid and by γ-ray irradiation are summarised in Tables 1 and 2, respectively. The exposure to the acid tends to cleave the octyl in the TODGA molecule, while oxidation reactions also proceed simultaneously with the cleavage reaction during the irradiation. The radicals generated from radiolysis of water are considered to progress the oxidation reactions.

In our previous study, it was reported that the adsorption performance of the adsorbent decreased by 90% under 1 MGy γ-ray irradiation [2]. Therefore, the degradation products remaining on the adsorbents should loss extraction ability. Since two doubly bonded O atoms in the TODGA molecule contribute to the extraction reaction for cations [9], the decrease in the adsorption performance could be explained by missing one or both O atoms. The loss in the extraction ability might lead to the elution of charged MA, and the elution will result in a decrease of the MA yield. Controls in amount and behaviour of the eluted MA are important for safety of this process as well as for the quality management. Therefore, production rates not only of the products with low flash points but also of those missing the extraction ability should be evaluated precisely for safety management.
## Table 1: Dominant degradation products of TODGA/SiO$_2$-P by exposure to the acid

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<th>Name</th>
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## Table 2: Dominant degradation products of TODGA/SiO$_2$-P by $\gamma$-ray irradiation

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Conclusion

$\gamma$-ray irradiation degradation products of TODGA/SiO$_2$-P adsorbent were investigated by GC/MS, NMR and FT-IR analyses to secure the safety of the extraction chromatography technology. Several chemical species were found in the irradiated adsorbents and the supernatant solutions. Heptane acid and acetic acid were confirmed as representative dissolvable degradation products, and N,N-dioctyloctaneamide, N,N-dioctyleacetamide and etc. remained on the adsorbent. Some of those species were suspected to be hydrolysis products of the TODGA molecule. Since radicals such as $^\cdot$H or $^\cdot$OH are known as significant products from $\gamma$-ray irradiation on water molecules, they are considered to oxidise the extractant components.

In addition to those degradation products, some products with relatively low flash points were also confirmed in this study. In the respect of safety for this technology, their accumulation behaviour inside packed columns should be studied in the future.

References


Selection of the Sorbent for Separation of Curium and Americium by Sorption Technique

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Abstract

In this study 17 samples of sulphocationites with varying sizes grain granulation have been tested. It is shown that on monodisperse sorbents graining 0.5-0.75 mm effective separation of REE does not occur. In this case tailings are formed due to the significant internal diffusion effect. At the same time efficient separation is observed on monodisperse sorbents grain size less than 0.3 mm. Based on the results of the studies, the Purolite PCR 833\(^a\), Purolite PCR642H, Amberlite CR1320K, Amberlite CR1310Na, KU-2×4 and KU-2×8 could be recommended for separation Cm, Am and REE. For all samples the radiation stability is comparable with sulphocationite KU-2×8.

Introduction

Nowadays long-term and sustainable development of nuclear power engineering is impossible without fast neutron reactors (FNR) especially as FNR allows closing of the nuclear fuel cycle (NFC) cycle and burning up of minor actinides (MA). It will allow solving the problem of handling Am radionuclides – one of the most toxic elements generated during irradiation of nuclear fuel. Besides FNR will enable a sharp increase of the raw materials base of atomic power engineering by means of\(^{238}\)U involved into NFC.

Available methods of the irradiated nitride fuel treatment for production of pure americium intended for transmutation were considered and the method of displacement chelation chromatography involving the use of strong-acid cation-exchange resin with active sulphonic-acid groups as a sorbent was chosen. American as well as Russian specialists have been using this technology since the early 70s (20th century) to produce ten kilograms of americium and curium [1-6]. Several kilograms of americium and several tens of grams of curium were produced on the FGUP PO “Mayak” nuclear installation now in force. KU-2×8 cation resin was used as a sorbent. Currently only a single enterprise in the Kemerovo city produces this sorbent. Resin size is 0.2-1.5 mm according to GOST. It should be noted that such a range of the grain sizes does not allow a chromatographic separation process with a high efficiency. Preliminary disintegration and (or) coarse screening (sizing) are conducted to get finer fraction. This procedure considerably increases the cost of the sorbent, and using the crushed sorbent increases pressure in the system. At the moment all top companies produce monodisperse resins. Monodisperse resins are resins with a coefficient of uniformity less than 1.2.

Experimental

Types of the examined sulphocationite resins and some of their specifications are presented in Table 1.
Volume capacity of the sorbents was determined by the dynamic method, exchange constants of the test samples were determined under static conditions at room temperature according to standard methods. Since the capacities of all sorbents are different, it is reasonable to use the following ionic exchange constant for compassion of selectivity of the sorbents:

\[ K^*_{Eu-H,Na} = K^*_{Eu-Na} = Q^*_v \]  

(1)

where \( Q_v \) – volume capacity of the sorbent.

Test results of the examined sorbents are presented in Table 1.

During separation of REE and TPE by the chromatographic method under laboratory conditions it is difficult to work with amounts of Am and Cm by weight. Simulators of these elements shall be selected to study the conditions of their extraction (production). Holmium was selected as the simulator according to the separation coefficients [7].

Chromatographic system for separation of REE consisted of two temperature-stabilised glass columns: \( H_1=30 \text{ cm}, H_2=90 \text{ cm}, S_1=0.3 \text{ cm}^2, S_2=0.32 \text{ cm}^2 \). General volume of the columns was 45 ml. An equimolar mixture of REE was used for separation. The quantities of the mixture corresponded the capacity of the test sorbent, so that the sorption volume was 11 ml, and number of the separation bands \( v = V_p/V_c \geq 3 \), where \( V_p \) – volume of the separation part of the columns, \( V_c \) – volume of the sorption part of the columns.

### Table 1: Specification of the examined sulfocationite resins

<table>
<thead>
<tr>
<th>№</th>
<th>Resin</th>
<th>Resin size (mm)</th>
<th>Capacity (mg-eq/ml)</th>
<th>Swelling (ml/g)</th>
<th>( K^*_{Eu-H} )</th>
<th>( K^*_{Na-H} )</th>
<th>( K^*_{Eu-Na} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KU-2×8 (sizing)</td>
<td>0.125-0.25</td>
<td>1.57</td>
<td>2.49</td>
<td>150</td>
<td>1.66</td>
<td>32.8</td>
</tr>
<tr>
<td>2</td>
<td>Purolite PCR 833</td>
<td>0.18-0.3</td>
<td>1.66</td>
<td>2.37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>KU-2x4</td>
<td>0.27</td>
<td>1.18</td>
<td>3.54</td>
<td>60.2</td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>Amberlite CR1310Na</td>
<td>0.28-0.32</td>
<td>1.56</td>
<td>2.66</td>
<td>33.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Purolite PCR642H</td>
<td>0.295-0.335</td>
<td>1.5</td>
<td>2.72</td>
<td>91.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Amberlite CR1320K</td>
<td>0.31-0.35</td>
<td>1.61</td>
<td>2.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Amberlite IRN99</td>
<td>0.3-0.85</td>
<td>2.19</td>
<td>1.72</td>
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<tr>
<td>8</td>
<td>Purolite SST60</td>
<td>0.3-1.2</td>
<td>1.59</td>
<td>2.36</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Purolite SST80AL</td>
<td>0.3-1.2</td>
<td>2.03</td>
<td>2.1</td>
<td></td>
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<tr>
<td>10</td>
<td>KU-2×8</td>
<td>0.4-0.55</td>
<td>1.64</td>
<td>2.34</td>
<td>328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Dowex 50×8</td>
<td>0.4-0.8</td>
<td>1.88</td>
<td>2.26</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Purolite C160</td>
<td>0.43-1</td>
<td>1.84</td>
<td>2.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Amberlite IRN97</td>
<td>0.525</td>
<td>2.19</td>
<td>1.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Dowex C600H</td>
<td>0.6</td>
<td>1.8</td>
<td>2.37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Dowex 650CH</td>
<td>0.65</td>
<td>1.86</td>
<td>2.12</td>
<td>305</td>
<td>0.64</td>
<td>1138</td>
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<tr>
<td>16</td>
<td>Amberlite IRN77</td>
<td>0.65</td>
<td>1.78</td>
<td>2.25</td>
<td>197</td>
<td>1.07</td>
<td>162</td>
</tr>
<tr>
<td>17</td>
<td>Dowex 750C</td>
<td>0.75</td>
<td>2.03</td>
<td>1.98</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experiments on the separation of REE were conducted at 70°C. H⁺ or Ni²⁺-ions were used as retainers. Eluent was pumped through the column by the Grundfos (France) pump at a rate of 4 ml/(min·cm²). Concentrations of holmium and neodymium were determined spectrophotometrically. Compositions of the applied eluents are presented in Table 2.
Table 2: Eluents compositions

<table>
<thead>
<tr>
<th>№</th>
<th>Chelation</th>
<th>Chelation concentration $\tilde{A}_p$</th>
<th>pH eluent</th>
<th>Displacer concentration $\tilde{D}_p$, mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DTPA</td>
<td>20 g/l (0.0509)</td>
<td>7.41</td>
<td>0.157</td>
</tr>
<tr>
<td>2</td>
<td>DTPA</td>
<td>10 g/l (0.0254)</td>
<td>7.35</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>Cit</td>
<td>5 g/l (0.0238)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>DTPA</td>
<td>9.9 g/l (0.0252)</td>
<td>7.47</td>
<td>0.182</td>
</tr>
<tr>
<td></td>
<td>NTA</td>
<td>9.9 g/l (0.0518)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rate of the REE front movement was calculated by Wilson equation:

$$
\nu = 60 \cdot u \cdot \frac{\tilde{D}_p}{\varepsilon \cdot \tilde{D}_p + Q}
$$

(2)

where, $\nu$ – rate of the REE front movement along the column, cm/hour; $u$ – feeding speed of the eluent, ml/min·cm²; $\varepsilon$ – quantity corresponding to volume of the solution between the particles of the resin in the column (0.3 usually).

Displacement chelation chromatography systems are generally described by nonlinear equations of the material balance, electroneutrality, equations of the functional binding of the complex formation and ionic exchange, as well as by the recurrent relations characterising a steady state of the zones being formed [8-11] for the zone of every element being separated. While solving such systems of equations the concentrations of all ionic types in both phases (Table 3) were calculated. The $K_{Ho-H}$ and $K_{Nd+H}$ (Table 1) exchange constants for KU-2×8 (sizing), Amberlite IRN77, Dowex 650 CH sorbents obtained from experiments have been used in the calculations.

Table 3: Comparison of calculated and experimental parameters of the chromatographic process for some sorbents resin

<table>
<thead>
<tr>
<th>Resin Parameters</th>
<th>Ho calculated</th>
<th>Ho experimental</th>
<th>Nd calculated</th>
<th>Nd experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>KY-2×8 (sizing)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$pH$</td>
<td>1.91</td>
<td>1.96</td>
<td>2.26</td>
<td>2.22</td>
</tr>
<tr>
<td>$M_p$</td>
<td>0.0332</td>
<td>0.0304</td>
<td>0.0313</td>
<td>0.0295</td>
</tr>
<tr>
<td>$A_p/\tilde{A}_p$</td>
<td>1.13</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_R M$</td>
<td>63.8</td>
<td>58.2</td>
<td>60.1</td>
<td>56.6</td>
</tr>
<tr>
<td>$x_R D$</td>
<td>23.5</td>
<td></td>
<td>36.4</td>
<td></td>
</tr>
<tr>
<td>$x_R H$</td>
<td>5.61</td>
<td>2.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_R A$</td>
<td>7.0</td>
<td>0.96</td>
<td></td>
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</table>
Table 3: Comparison of calculated and experimental parameters of the chromatographic process for some sorbents resin (Cont’d)

<table>
<thead>
<tr>
<th>Resin</th>
<th>Parameters</th>
<th>Ho calculated</th>
<th>Ho experimental</th>
<th>Nd calculated</th>
<th>Nd experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IRN77</td>
<td>pH</td>
<td>1.89</td>
<td>1.94</td>
<td>2.30</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>[M_p]</td>
<td>0.0260</td>
<td>0.0226</td>
<td>0.0301</td>
<td>0.0248</td>
</tr>
<tr>
<td></td>
<td>A_p/\tilde{A}_p</td>
<td>1.44</td>
<td></td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x_pM</td>
<td>49.9</td>
<td>43.4</td>
<td>57.9</td>
<td>47.7</td>
</tr>
<tr>
<td></td>
<td>x_pD</td>
<td>16.9</td>
<td></td>
<td>37.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x_pH</td>
<td>7.70</td>
<td></td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x_pA</td>
<td>25.5</td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Dowex 650CH</td>
<td>pH</td>
<td>2.11</td>
<td>1.94</td>
<td>2.51</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>[M_p]</td>
<td>0.0230</td>
<td>0.0224</td>
<td>0.0266</td>
<td>0.0258</td>
</tr>
<tr>
<td></td>
<td>A_p/\tilde{A}_p</td>
<td>1.36</td>
<td></td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x_pM</td>
<td>44.1</td>
<td>43.1</td>
<td>51.2</td>
<td>49.5</td>
</tr>
<tr>
<td></td>
<td>x_pD</td>
<td>27.3</td>
<td></td>
<td>44.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x_pH</td>
<td>7.76</td>
<td></td>
<td>3.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>x_pA</td>
<td>20.9</td>
<td></td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>

The indicated value of the height equivalent to a theoretical plate which was calculated from the elution curve by the equation (3) developed by Tremion [12] from the general plate theory was a quantitative characteristic of the separation effectiveness:

$$
h^* = \frac{\text{HEPT}}{\lg \alpha} = \frac{\tilde{D}_p \cdot \Delta V}{s \cdot (Q + \varepsilon \cdot \tilde{D}_p) \lg \frac{C_A}{C_B}}
$$

where, $C_A$, $C_B$ – concentration of the elements being separated on the elution curve, $\alpha$ – separation coefficient, $s$ – cross-section area of the column, cm$^2$; $\Delta V$ - solution volume corresponding to the volume of the eluates measured from the middle of the front (where $C_A = C_B$).

The results of the separation of REE on the examined sorbents are presented in Figures and 2 and in Table 4.
Figure 1: Separation Ho - Nd on resin KU-2 (sizing) in the H\(^+\) form eluent 20 g/l DTPA, pH 7.46

Figure 2: Separation Ho-Nd on resin Dowex 650CH in the H\(^+\) form eluent 20 g/l DTPA, pH 7.41

\[
[M_p] \text{ - concentration REE in liquid phase, mol/l; } A_p / \bar{A}_p \text{ - the ratio of the concentration of the metal chelator in the area to the initial concentration; } x_{R M}, x_{R D}, x_{R H}, x_{R A} \text{ - content in the solid phase of rare earth ions, the displacer, hydrogen, chelator, respectively, in% of capacity}
\]

Experimental values \(h^*\) were defined as a slope ratio of the linear trend line of the \(\lg(C_A/C_B)\) dependence on \(\Delta V\). The results are presented in Table 4.

Table 4: Parameters of the separation of REE on the examined sorbents resin

<table>
<thead>
<tr>
<th>Resin</th>
<th>Ion</th>
<th>Eluent</th>
<th>(\nu), cm/h</th>
<th>(Mp, \text{ mol/l})</th>
<th>(h^*, \text{ cm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>KV-2×8(sizing)</td>
<td>Ni(^{2+})</td>
<td>1</td>
<td>23.2</td>
<td>Ho 0.0333, Nd 0.0303</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>H(^+)</td>
<td>2</td>
<td>22.1</td>
<td>Ho 0.0278, Nd 0.0267</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>H(^+)</td>
<td>1</td>
<td>23.2</td>
<td>Ho 0.0304, Nd 0.0295</td>
<td>2.6</td>
</tr>
<tr>
<td>Purolite PCR 833</td>
<td>Ni(^{2+})</td>
<td>1</td>
<td>22.0</td>
<td>Ho 0.0344, Nd 0.0315</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>H(^+)</td>
<td>2</td>
<td>20.9</td>
<td>Ho 0.0293, Nd 0.0274</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>H(^+)</td>
<td>1</td>
<td>22.0</td>
<td>Ho 0.0297, Nd 0.0304</td>
<td>2.09</td>
</tr>
<tr>
<td>KU-2×4</td>
<td>H(^+)</td>
<td>1</td>
<td>30.6</td>
<td>Ho 0.0264, Nd 0.0307</td>
<td>1.31</td>
</tr>
<tr>
<td>Amberlite CR1310Na</td>
<td>H(^+)</td>
<td>1</td>
<td>23.3</td>
<td>Ho 0.0305, Nd 0.0296</td>
<td>2.59</td>
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<tr>
<td>Purolite PCR 642H</td>
<td>H(^+)</td>
<td>1</td>
<td>24.2</td>
<td>Ho 0.0267, Nd 0.0310</td>
<td>2.31</td>
</tr>
<tr>
<td>Amberlite CR1320K</td>
<td>H(^+)</td>
<td>1</td>
<td>22.6</td>
<td>Ho 0.0301, Nd 0.0302</td>
<td>3.03</td>
</tr>
<tr>
<td>KV-2×8</td>
<td>H(^+)</td>
<td>1</td>
<td>22.2</td>
<td>Ho 0.0230, Nd 0.0275</td>
<td>7.8</td>
</tr>
</tbody>
</table>
Table 4: Parameters of the separation of REE on the examined sorbents resin (Cont’d)

<table>
<thead>
<tr>
<th>Resin</th>
<th>Ion</th>
<th>Eluent</th>
<th>$v$, cm/h</th>
<th>$M_p$, mol/l</th>
<th>$h^*$, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$H_0$</td>
<td>$Nd$</td>
</tr>
<tr>
<td>AmberliteIRN97</td>
<td>H+</td>
<td>1</td>
<td>16,8</td>
<td>0,0210</td>
<td>0,0235</td>
</tr>
<tr>
<td>Dowex C600H</td>
<td>Ni$^{3+}$</td>
<td>1</td>
<td>20,3</td>
<td>0,0302</td>
<td>0,0293</td>
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<tr>
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<td>H+</td>
<td>2</td>
<td>19,3</td>
<td>0,0273</td>
<td>0,0284</td>
</tr>
<tr>
<td></td>
<td>H+</td>
<td>1</td>
<td>20,3</td>
<td>0,0223</td>
<td>0,0245</td>
</tr>
<tr>
<td>Dowex 650CH</td>
<td>Ni$^{3+}$</td>
<td>1</td>
<td>19,7</td>
<td>0,0328</td>
<td>0,0288</td>
</tr>
<tr>
<td></td>
<td>H+</td>
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<td>19,7</td>
<td>0,0224</td>
<td>0,0258</td>
</tr>
<tr>
<td></td>
<td>H+</td>
<td>2</td>
<td>18,7</td>
<td>0,0274</td>
<td>0,0272</td>
</tr>
<tr>
<td></td>
<td>Ni$^{3+}$</td>
<td>3</td>
<td>22,8</td>
<td>0,0276</td>
<td>0,0231</td>
</tr>
<tr>
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<td>H+</td>
<td>1</td>
<td>20,5</td>
<td>0,0330</td>
<td>0,0279</td>
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<tr>
<td>Dowex 750C</td>
<td>H+</td>
<td>1</td>
<td>18,1</td>
<td>0,0193</td>
<td>0,0166</td>
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</tbody>
</table>

Experiments on irradiation of the samples in water and with air access were conducted on the “UELV-10-20-S-70-1” waveguide electron linear accelerator with 10 MeV energy and 20 kW beam. The SO PD(F)R-5/50 film-type chemical detectors of the absorbed dose were used as a dosimeter.

Experimental data on changes in the characteristics of the sorbents during irradiation depending on the absorbed dose are presented in Table 5.

Table 5: The dependence of capacity, mass, and swelling of the various sorbents absorbed radiation dose

<table>
<thead>
<tr>
<th>№№</th>
<th>Capacity, mg-eq/ml $D_c$, MGy</th>
<th>Mass resin, g $D_c$, MGy</th>
<th>Swelling, ml/g $D_c$, MGy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>1,57</td>
<td>1,32</td>
<td>1,13</td>
</tr>
<tr>
<td>2</td>
<td>1,66</td>
<td>1,36</td>
<td>1,31</td>
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<tr>
<td>3</td>
<td>1,18</td>
<td>0,87</td>
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</tr>
<tr>
<td>4</td>
<td>1,56</td>
<td>1,14</td>
<td>1,09</td>
</tr>
<tr>
<td>5</td>
<td>1,50</td>
<td>1,15</td>
<td>0,97</td>
</tr>
<tr>
<td>6</td>
<td>1,61</td>
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<td>0,97</td>
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<td>2,19</td>
<td>1,92</td>
<td>1,92</td>
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<tr>
<td>8</td>
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Results and discussion

Capacity of all examined resin samples varied from 1.18 to 2.19 mg-eq/ml, and swelling varied from 1.72 to 3.54 mg/l according to submitted experimental data. All examined sorbents were of different colour: their colour varied from light-yellow to dark-brown or even black.

According to the experimental data (Table 4), the characteristics of the monodisperse sorbents with 0.3 mm grain are close to characteristics of the KU-2×8 (sizing) sorbent. Effective separation of REE, minimum volume of the mixing zone (\(h^*\) within the range from 1 to 3) and presence of the strongly marked “plateau” on the elution curve (Figure 1) were observed for these sorbents. The concentration of the eluted REE was about 5 g/l (Ho ~ 5 g/l, Nd ~ 4.5 g/l). The concentration of Ho is always higher than the concentration of Nd (for different eluents, as well as for different retaining ions).

Monodisperse sorbents with 0.5-0.75 mm grain size have higher capacity values and less swelling values as compared to KU-2×8 (Table 1). Besides, increasing of exchange constant of differently charged cations is observed for them. The \(K^+_{Eu-Na}^*\) exchange constant increases by more than ten times, and the \(K^+_{Na-H}^*\) exchange constant for equally charged ions decreases considerably, and even a selective conversion is observed for the Dowex 650CH sorbent. The “plateau” is not always formed on the elution curve (Figure 2) during separation of REE on these cation resins due to strong diffusion of the fronts. Concentrations of REE in ululates are greatly lower than on smaller sorbents (2.5-3 g/l for Ho). At that the concentration of Ho is lower than the concentration of Nd. As we already said [17], the concentration of REE in the eluates decreases and pH of eluates increases while the REE-Na exchange constant increases. It can be observed in this case for Nd (Table 3). Decrease of the Ho concentration is mainly caused by great increase of the chelator sorption in the REE zone from 7 to 25 % due to decrease of the \(H_{Na-K}^*\) exchange constant. When the Ni\(^{2+}\)-form of the cation resin is used, the REE concentration increases to 5 g/l, as well as for fine sorbents, though no noticeable increase of the separation effectiveness can be seen. The \(h^*\) value is greatly higher (from 7 to 22) for these cation resins and separation effectiveness of REE on these sorbents is inadequate. A great diffusion of the back fronts of the elements being separated is typical for the internal diffusion mechanism of ion exchange, whose contribution increases with increase of the squared value of the grain radius [12,14]. But it is not the only reason of deterioration of the separation on the large sorbents. Sorbents seem to be more rigid structures which make an additional contribution into the internal diffusion mechanism. It was typical for highly cross-linked (12-16%) cation resins in 60\(^{th}\)-80\(^{th}\). E.g. the KU-2×8 monodisperse sorbent (0.4-0.55 mm grain size) possesses the same capacity and swelling as fine sorbents. But value of the \(K^+_{Eu-H}^*\) exchange constant equal to 328 (Table 1) indicates its harder structure, which explains inefficient separation of REE on this cation resin. Hence, the results testify that monodisperse sorbents with grain size 0.5 mm and more are unsuitable for effective separation of REE and TPE. Nevertheless, they can be successfully used at the sorption stage of the parent mixtures since the values of their capacity and exchange constants are high. Hence they will allow sorption from the stronger salt solutions.

Effect of the strong radiation fields represents one of the features occurring during processing of highly radioactive solutions in the radiochemical industry. The evaluation absorbed dose during extraction of radionuclides of promethium-147, americium-241, curium-244 on the sulfocationites can reach 6 MGy. Such a radiation load on the organic compound (cation exchanger) is very high. Therefore it is necessary to undertake special studies on the radiation stability of the cation exchangers.

According to the submitted experimental data, the destruction processes generally happen during irradiation of the test cation resins, as well as during irradiation of all cation resins of polymerisation type in water [15]: capacity and weight of the cation resin samples decrease. Mass reduction of the examined sorbents is somewhat greater as compared to KU-2×8 (sizing), and capacity reduction at 8 MGy absorbed
dose is conversely less as compared to KU-2×8 (sizing) (Table 5). Perhaps it is caused by emergence of the new ionic groups (such as carboxyl or phenolic ones). When the absorbed dose increases to 8 MGy, the weight of the sorbents decreases by 25-45%, and volume capacity – by 20-50%. (Table 5).

The color of all observed samples noticeably darkened up to black along the increase of the absorbed dose. At first swelling of the sorbents was increasing, and then it was decreasing. This may be due to the fact that at first the polymeric chains were breaking, and then new polymeric chains were formed [20]. However reduced swelling can be due not only to the increase of the cation resin cross-linking degree under irradiation, but also to decrease of quantity of strongly hydrated sulpho groups caused by radiolysis. Radiation effects to the KU-2×4 sorbent are somewhat greater as compared with other samples. It is due to its smaller cross-linking degree and, correspondingly, a greater amount of water present in the resin phase. Radiation-chemical resistance of other sorbents is at least equal or even a little greater as compared to the resistance of the analysed KU-2×8 (sizing) sorbent.

Conclusions

Characteristics of 17 home-produced and foreign made sulfocationite samples were specified. The characteristics of the foreign made sulfocationite samples with 0.3mm grain size are close to the KU-2×8 (sizing) sorbent (effective separation of REE). Capacity values of the monodisperse sorbents with 0.5-0.75 mm grain size obtained by the seed polymerisation method are greater. Their swell value is less and the structure is more rigid. Besides, the values of exchange constants of differently charged cations for them are greater as compared with KU-2×8 (sizing).

Separation of REE was conducted on the submitted cation resins by the displacement chelation chromatography method using different eluents. Effective separation of REE, minimal volume of the mixing zone and presence of the “plateau” on the elution curve were observed for monodisperse sorbents, as well as fine sorbents. Sorbents with grain size 0.4 mm and larger are not effective for separation of REE by the displacement chelaton chromatography method. The parameters of the chromatographic process were calculated. A good agreement of the experimental and calculated values was obtained.

The influence of radiation on the characteristics of the submitted cation resins samples was analysed: variation of capacity, weight, and swell values. The behaviour of all tested samples in the ionising radiation fields is similar to the KU-2×8 cation resin with minor fluctuations.

The following brands of the tested cation resins: Amberlite IRN99, Amberlite IRN97, Dowex 50×8, Dowex C600H, Dowex 750C. Purolite SST80ΔL are not suitable for separation of REE and TPE, but can be used in the sorption stage.

The following brands of the examined sorbents can be recommended for separation of REE and TPE by the displacement chelation chromatography method: KU-2×8 (sizing), Purolite PCR833, KU-2×4, Amberlite CR1310Na, Purolite PCR642H, Amberlite CR1320K.

References


A Study on Pyrochemical Process for Treating Fuel Debris from the Fukushima-Daiichi Reactors

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Abstract

After the severe accident at Fukushima-daiichi nuclear power plants, CRIEPI and JAEA started a feasibility study on the pyrochemical treatment of the corium that mainly consists of UO$_2$-ZrO$_2$ solid solution. In this study, reduction behaviours of zirconium oxide compounds were investigated in LiCl-Li$_2$O salt bath at 923 K. It was experimentally verified that uranium in the simulated corium could be reduced to the metallic form and a part of zirconium was converted to Li$_2$ZrO$_3$. At higher Li$_2$O concentrations in LiCl, Li$_2$ZrO$_3$ was converted to Li$_6$Zr$_2$O$_7$ and Li$_8$ZrO$_6$. In the subsequent electrorefining, Li$_2$ZrO$_3$ reacts with UCl$_3$ dissolved in the electrolyte salt to give UO$_2$ precipitate. Therefore, how to remove the Li$_2$ZrO$_3$ from the reduction product is a key point for the pyrochemical treatment of the corium.

Introduction

A pyrochemical process to separate actinides from spent oxide fuels, shown in Figure 1, has been studied as part of a development of the metal fuel fast breeder reactor cycle [1-3]. In the electrolytic reduction step, spent oxide fuels are loaded at the cathode in a LiCl-Li$_2$O salt bath. The oxygen is electrochemically ionised to dissolve in the salt, and metals remain at the cathode (reaction (1)). If lithium metal forms at the cathode, the chemical reduction of oxides may proceed (reactions (2) and (3)). The O$_2^-$ ions are transported through the salt and are discharged at the anode to form O$_2$ gas (reaction (4)).

\[ \text{Cathode: } \text{MO}_2 + 4 \text{e}^- \rightarrow \text{M} + 2 \text{O}^2^- \quad (1) \]
\[ \text{Li}^+ + \text{e}^- \rightarrow \text{Li} \quad (2) \]
\[ 4 \text{Li} + \text{MO}_2 \rightarrow \text{M} + 4 \text{Li}^+ + 2 \text{O}^2^- \quad (3) \]
\[ \text{Anode: } 2 \text{O}^2^- \rightarrow \text{O}_2 + 4 \text{e}^- \quad (4) \]

where M denotes actinides such as uranium and plutonium. The electrorefining is subsequently conducted in a LiCl-KCl eutectic salt bath to remove the residual fission products. The actinide metals in the reduction product are anodically dissolved in the salt. At the same time, uranium metal is deposited on the solid cathode made of iron. A mixture of plutonium, uranium and other actinide metals is collected by employing a liquid cadmium cathode.

After the severe accident at Fukushima-daiichi nuclear power plants in March 2011, the treatment of the damaged fuel debris is a big issue in Japan. Then, CRIEPI and JAEA started a study on the applicability of the pyrochemical process to the corium mainly consisting of UO$_2$-ZrO$_2$ solid solution. It has been reported that UO$_2$ and UO$_2$-PuO$_2$ mixed oxide can be easily reduced to the metallic form [1-4]. On the other hand, a little effort has been devoted to ZrO$_2$ whose behaviour is expected to be complicated due to the formation of stable complex oxide compounds [1,2]. Table 1 shows the standard Gibbs free energies of formation (\(\Delta G_f^0\)) of actinide, zirconium, lithium and rare earth oxides at 923 K [5]. \(\Delta G_f^0\) of
ZrO$_2$ is almost equal to that of UO$_2$. However, $\Delta G_f^0$ of the complex oxide, Li$_2$ZrO$_3$, is more negative than that of Li$_2$O, indicating that the reduction of Li$_2$ZrO$_3$ to zirconium metal may proceed if the activity of Li$_2$O in the LiCl salt bath is sufficiently low. In fact, La$_2$O$_3$ is hardly reduced to the metallic form even in a LiCl salt bath without dissolved Li$_2$O [6]. Moreover, the Li$_2$O-ZrO$_2$ phase diagram [7] suggests that Li$_2$Zr$_2$O$_7$ and Li$_2$ZrO$_4$ likely form at high Li$_2$O concentrations. Thus, the formation and reduction behaviours of zirconium oxide compounds have to be clarified to assess the feasibility of the pyrochemical treatment of the corium.

**Figure 1: Schematic diagram of pyrochemical reprocessing for spent oxide fuel, consisting of (a) electrolytic reduction of oxides and (b) electrorefining of reduction product**

In this study, zirconium oxide compounds forming in the LiCl-Li$_2$O system at 923 K were identified as a function of Li$_2$O concentration. Then, electrolytic reduction tests were conducted on ZrO$_2$, Li$_2$ZrO$_3$ and UO$_2$-ZrO$_2$ solid solution containing PuO$_2$.

**Table 1: $\Delta G_f^0$ of metal oxides at 923 K**

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<thead>
<tr>
<th>Oxide</th>
<th>$\Delta G_f^0$ (kJ/mol-O)</th>
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<tr>
<td>ZrO$_2$</td>
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<tr>
<td>UO$_2$</td>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
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<tr>
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<td>-509.6</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>-515.1</td>
</tr>
</tbody>
</table>

**Experimental**

**Materials**

ZrO$_2$ (99.8% purity, <200 mesh) and Li$_2$ZrO$_3$ (<80 mesh) were supplied by Newmet and Sigma-Aldrich, respectively. Simulated corium specimens of UO$_2$-ZrO$_2$ solid solution containing a small amount of PuO$_2$ were prepared in JAEA [8] for measuring their physical and thermal properties, and some of them were subjected to this study. The ZrO$_2$ compositions of the three simulated corium specimens used for the electrolytic reduction test were 25, 50 and 75 atom%, respectively and the ratio of plutonium to uranium was in the range of 4-9 atom%.
Electrolytic reduction of zirconium oxide compounds

The cells used for electrolytic reduction tests were similar to that reported before [6]. LiCl was melted in a MgO crucible (50 mm inner diameter) at 923 K using an electric furnace. Then, a given amount of Li2O was added. A Li-Bi reference electrode, a platinum sheet anode and a type-K thermocouple sheathed in a MgO tube were immersed in the melt. The Li-Bi electrode consisted of a tantalum wire immersed in liquid Li-Bi alloy contained in a closed-end MgO tube with two pinholes on the side. The potential of the Li-Bi electrode was calibrated against lithium metal electrodedeposited on a tungsten wire.

A cathode was prepared as follows. A zirconium oxide compound in powder form was loaded in a closed-end MgO tube (5 mm inner diameter) that had a window on its side, and a tungsten conductor wire was inserted in the oxide powder. The cathode was immersed in the melt and then current-controlled electrolysis was performed to reduce the oxide powder. After the electrolysis, the reduction product removed from the MgO tube was analysed by X-ray diffraction (XRD) method. Salt samples were taken and were dissolved in water. The Li2O concentration was then analysed by neutralisation titration. All of the experiments using molten salt were conducted in a high-purity argon atmosphere glove box.

Formation of zirconium oxide compounds

A Li2O titration test was conducted to identify the solid phases containing zirconium in LiCl-Li2O melts with various Li2O concentrations. A stainless-steel crucible (20 mm inner diameter), in which LiCl (14.004 g) and ZrO2 (1.401 g) were loaded, was placed in the electric furnace at 923 K. Then, Li2O was incrementally added and the change in the Li2O concentration was examined. Finally, the crucible was removed from the electric furnace and the melt was poured into a stainless-steel pan. The residue at the bottom of the crucible was analysed by XRD method.

Results and discussion

Electrolytic reduction of zirconium oxide compounds

0.208 g of ZrO2 powder was loaded in a MgO tube for the cathode and current-controlled electrolysis with a current of 50 mA was performed in a LiCl-1.0 wt% Li2O salt bath. During the electrolysis, the cathode potential was mostly negative (vs Li/Li+), indicating that some Li+ ions might have been reduced to metallic lithium. To prevent excess amount of lithium metal from depositing at the cathode, the electrolysis was often interrupted. After the lithium metal was consumed by the chemical reduction of ZrO2, the electrolysis was resumed. The total electric charge passed was 494 coulombs, which corresponds to 76% of the theoretical electric charge required to reduce all the ZrO2 to metallic zirconium. The potential of the platinum anode was in the range of 2.4-2.7 V (vs Li/Li+) throughout the electrolysis, indicating that O2 gas was evolved at the anode. Figure 2 shows a XRD pattern of the reduction product. It is clearly shown that the reduction product consisted of zirconium metal, Li2ZrO3 and adhering LiCl salt. The Li2ZrO3 was formed by the following reaction, when the O2- ions were supplied by the reduction of ZrO2.

\[
\text{ZrO}_2 + \text{O}^{2-} + 2 \text{Li}^+ \rightarrow \text{Li}_2\text{ZrO}_3
\]  

(5)

Then, an additional electrolytic reduction test on Li2ZrO3 was conducted in a LiCl salt bath without the addition of Li2O. As a result, the Li2ZrO3 remained at the cathode and zirconium metal was not obtained.

The electrolytic reduction tests on simulated corium were conducted using (U,Pu,Zr)O2 solid solutions with various U/Pu/Zr compositions. Figure 3 shows a typical XRD pattern of the reduction product. 0.211 g of (U0.48Pu0.02Zr0.50)O2 powder (<106 μm, impurities of Sn, Cr, Fe, etc. coming from Zircaloy-2 alloy were contained) was loaded in a MgO tube for the cathode and current-controlled electrolysis with a current of 50 mA was performed in a LiCl-0.74 wt% Li2O salt bath. The total electric charge passed was 150 coulombs, which corresponds to 67% of the theoretical electric charge required to reduce all the (U,Pu,Zr)O2 to metallic zirconium.
charge passed was 641 coulombs, which corresponds to 155% of the theoretical electric charge required to reduce all the oxide to metallic form. As shown in Figure 3, there are distinct peaks for uranium metal and small peaks for Li$_2$ZrO$_3$. The peaks for the (U$_{0.48}$Pu$_{0.02}$Zr$_{0.50}$)O$_2$ solid solution completely disappeared. Although the zirconium and plutonium in the metallic form could not be detected by XRD analysis, they probably formed alloys with uranium. The results of electrolytic reduction tests on (U$_{0.68}$Pu$_{0.07}$Zr$_{0.25}$)O$_2$ and (U$_{0.23}$Pu$_{0.02}$Zr$_{0.75}$)O$_2$ solid solutions were similar. The formation of uranium metal was verified in both the reduction products. The intensity of the peaks for Li$_2$ZrO$_3$ increased with increasing the ZrO$_2$ composition of the solid solution.

![Figure 2: XRD pattern of ZrO$_2$ after electrolytic reduction in LiCl-Li$_2$O](image)

![Figure 3: XRD pattern of (U$_{0.48}$Pu$_{0.02}$Zr$_{0.50}$)O$_2$ after electrolytic reduction in LiCl-Li$_2$O. The reduction product was rinsed with ethanol to remove the adhering LiCl salt](image)

**Formation of zirconium oxide compounds**

To investigate the formation behaviours of Li$_2$O-ZrO$_2$ compounds, 0.113 g of Li$_2$O was added to a LiCl melt (14.004 g) in the presence of 1.401 g of ZrO$_2$ powder. The Li$_2$O concentration gradually decreased and then reached an equilibrium value of 0.018 wt% at 20 h after the addition of the Li$_2$O. Next 0.313 g of Li$_2$O was added, and the Li$_2$O concentration increased to 0.56 wt%. The mass balance of Li$_2$O indicates the formation of Li$_2$ZrO$_3$ by reaction (6). The precipitates collected at high Li$_2$O concentrations were subjected to XRD analysis and the formation of Li$_6$Zr$_2$O$_7$ and Li$_8$ZrO$_6$ by reactions (6) and (7) was verified.

\[
\begin{align*}
\text{ZrO}_2 + \text{Li}_2\text{O} & \rightarrow \text{Li}_2\text{ZrO}_3, \quad (6) \\
\text{Li}_2\text{ZrO}_3 + 1/2 \text{Li}_2\text{O} & \rightarrow 1/2 \text{Li}_6\text{Zr}_2\text{O}_7, \quad (7) \\
1/2 \text{Li}_6\text{Zr}_2\text{O}_7 + 5/2 \text{Li}_2\text{O} & \rightarrow \text{Li}_8\text{ZrO}_6. \quad (8)
\end{align*}
\]
Conclusions

A feasibility study on the pyrochemical treatment of the corium generated by Fukushima-Daiichi reactor accident was conducted. It was experimentally demonstrated that uranium in the simulated corium of (U,Pu,Zr)O₂ solid solution could be reduced to the metallic form by electrolytic reduction in LiCl-Li₂O salt bath at 923 K. The plutonium and zirconium might form alloys with uranium. However, a part of the zirconium was converted to Li₂ZrO₃ that is too stable to be reduced. Because the equilibrium Li₂O concentration in LiCl in which ZrO₂ and Li₂ZrO₃ coexist is no more than 0.018 wt%, the formation of Li₂ZrO₃ might be inevitable during the electrolytic reduction in the LiCl system. In the subsequent electrorefining step, shown in Figure 1b, Li₂ZrO₃ reacts with UCl₃ dissolved in LiCl-KCl electrolyte to give UO₂ precipitate. Therefore, how to remove the Li₂ZrO₃ from the reduction product is a key point for the pyrochemical treatment.

Acknowledgements

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References

Design of the MYRRHA Spallation Target Assembly

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Abstract

MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) is a multi-purpose research facility currently being developed at SCK•CEN. MYRRHA is based on the ADS (Accelerator Driven System) concept where a proton accelerator, a spallation target and a subcritical reactor are coupled. MYRRHA will demonstrate the ADS full concept by coupling these three components at a reasonable power level. As a flexible irradiation facility, the MYRRHA research reactor will be able to work in both critical and subcritical modes. In this way, MYRRHA will allow fuel developments for innovative reactor systems, material research for GEN IV and fusion reactors, and radioisotope production for medical and industrial applications. MYRRHA will be cooled by Lead Bismuth Eutectic (LBE) and will play an important role in the development of the Pb-alloys technology needed for the LFR (Lead Fast Reactor) GEN IV concept.

This paper describes the evolution of the MYRRHA spallation target design. In the early phase of the MYRRHA project (XT-ADS), the target design was based on a dedicated spallation loop inside the primary reactor vessel. Within the core, the 3 central fuel assembly positions were occupied by the spallation target, which enabled a windowless design created by a free surface of LBE facing the proton beam. The windowless option was preferred because of high heat loads in combination with severe irradiation damage in the target region would result in unacceptably short lifetimes of a target window. The LBE in the loop served as spallation target and as target coolant, but was separated from the LBE cooling the reactor core. The loop was equipped with its own pump, heat exchanger and conditioning system.

The change from cyclotron to linear accelerator allowed the increase in proton energy from 350 MeV to 600 MeV. This modification led to an important reduction of the specific heat load at the target level and an improvement of the neutronic performance. In addition to this evolution of the MYRRHA accelerator, the realisation and the successful execution of the MEGAPIE project at PSI, with SCK•CEN as one of the funding partners, resulted in the re-evaluation of the spallation target leading to the current window design without a dedicated cooling loop.

Different aspects of the new design of the MYRRHA window spallation target assembly are addressed: the material choice, the hydraulic design, the proton beam optimisation and the mechanical evaluation.

Introduction

MYRRHA (Multi-purpose hYbrid Research Reactor for High-tech Applications) is a multi-purpose research facility currently being developed at SCK•CEN in Mol, Belgium. From the early conceptual design of the MYRRHA Accelerator Driven System (ADS), where a cyclotron was coupled to a subcritical reactor by means of a windowless spallation target, to the current detailed design of a multipurpose research facility with a high-energy linear accelerator, many steps have been taken. MYRRHA will be operable with a subcritical core driven by spallation neutrons and with a critical core. Both modes of operation have their
specific energy and flux distributions which permit a wide range of applications, from transmutation to isotope production for medical and industrial applications. With the flexible core design, many positions for experimental rigs are available to test materials for e.g. fusion reactors and new types of fuel.

The working fluid of the MYRRHA reactor is Lead Bismuth Eutectic (LBE), which has been selected because of its low melting point compared to lead. Moreover, the heavy liquid metal can also be used as spallation target for the ADS. The experience with LBE will be of interest in the further development of the lead-cooled fast reactors of GEN IV.

The MYRRHA XT-ADS windowless loop spallation target [1]

In the early conceptual design of MYRRHA (before 2005), a commercial cyclotron producing a 350 MeV proton beam with a current of 5 mA, was coupled to the subcritical core. The spallation target material was liquid LBE, circulating in an inventively designed and dedicated spallation loop, separated from the LBE coolant of the subcritical core (Figure 1a). The beam line entered the spallation loop from the top and the proton beam passed from the vacuum in the beam line to the spallation zone with the LBE free surface, without passing any structural material (Figure 1c). In this way direct interaction of the proton beam with a window could be avoided. Irradiation damage in combination with high heat loads was considered as too limiting for the lifetime of the window.

The free surface was created in a funnel occupying the 3 central positions of the core (Figure 1b). The proton beam entered from the top into the wide stem of the funnel parallel to the LBE which flowed downwards into the funnel via an annular nozzle.

Figure 1:  a. Spallation target loop; b. Use of 3 core channels and c. Free surface target

The spallation loop was closed around the core, i.e. off-centre, with the implication of a split core plate. The loop was a complex system with magnetohydrodynamic circulation pump, LBE-LBE heat exchanger, buffer tank, conditioning system and level control system. The ability to extract the module with all active components, simplified maintenance, but the high neutron flux on the closing elements of the loop made frequent replacement unavoidable, with subsequent remote handling operations like cutting and welding.
Other issues which had to be solved were the stability of the free surface, splashing, evaporation of the spallation products, the creation of a recirculation zone at the interface and the cooling of the target zone. An extensive R&D programme addressed these issues with positive results [2].

From 350 MeV to 600 MeV protons

In the further search for an optimal design of the spallation loop, the choice between an off-centre or centred spallation target loop design was discussed again in 2004 [3]. For the centred window target design, a reverse flow concept would be an advantage to avoid the spallation loop around the core and without the need to split the core plate. But the number of core positions needed to accommodate the reversed-flow spallation loop, increased to 7. As a consequence, the core performance (flux) decreased. This was the motivation to reassess also the MYRRHA accelerator parameters. Using higher-energy protons with a reduced current level leads to the same total neutron production. Table 1 shows a comparison between the 350 MeV and 600 MeV proton beam with similar total neutron yield. As the neutron yield per incident proton increases with the proton energy, the beam current can be reduced with the same factor. Another important advantage of the increased energy is the larger penetration depth in the LBE. This reduces the linear power in the target (Figure 2). Above this the Bragg peak for the 600 MeV beam has disappeared almost completely and the fraction of energy deposited in the target zone is reduced from 81.7% to 62%.

The reverse flow concept with window was not developed further, but the results of the study with respect to the increased beam energy were retained. Together with the operating experience of the MEGAPIE (MEGAWatt PIlot Experiment) spallation target window [4] from 2009, a new design with window and without loop was investigated.

<table>
<thead>
<tr>
<th>Table 1: Comparison proton beam characteristics at 350 and 600 MeV [5]</th>
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<tr>
<td>Proton energy [MeV]</td>
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<tr>
<td>Beam current [mA]</td>
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<td>Beam power [MW]</td>
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<tr>
<td>Position of Bragg peak in LBE [cm]</td>
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<tr>
<td>Peak/plateau</td>
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<tr>
<td>Fraction of heat deposit in target zone [%]</td>
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<td>Convective cooling needs [MW]</td>
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Figure 2: Linear power comparison with similar total neutron yield [5]
The MYRRHA FASTEF loopless window spallation target

The new design started from the most simplified ADS configuration where the primary coolant simultaneously serves as a spallation target. The beam tube and the beam window separate the vacuum from the target material. The window is positioned at the centre of the sub-critical core almost at half height and is cooled by the upward flowing primary coolant under forced convection by the primary pumps. The MYRRHA FASTEF (FAst Spectrum Transmutation Experimental Facility) [6] complies with this concept.

Figure 3: MYRRHA FASTEF loopless window target

The beam tube and the window make part of the spallation target assembly. The assembly is designed as an In Pile Section (IPS) which can easily be introduced into the reactor via a dedicated hole in the reactor cover. The assembly consists of a long protective structure surrounding the window and vacuum tube and the velocity profile and pressure drop devices. The lower part of this structure has the same dimensions as the fuel assembly hexcans. The spallation target assembly is fixed to the reactor lid with a standardised plug. The beam tube is connected to the beam line above the reactor cover.

To optimise the occupied space of the beam tube into the core, the size of the fuel assemblies was enlarged from 91 to 127 pins keeping the same pitch. By this modification it was possible to fit the spallation target assembly into one core position only instead of the 3 positions before.

The life-limiting phenomena of the beam window are the degradation of the material due to irradiation by protons and fast neutrons, the interaction with the LBE, the thermal loads and fatigue.

Beam profile shaping

The main challenge for the cooling of the hemispherical window is the stagnation point that forms where the LBE flow hits the window in the centre. It was clear from the beginning, that with a normal Gaussian beam along the beam tube axis, the stagnation point would coincide with the highest heat load on the window. To shift the maximum heat load on the window away from the stagnation point, the proton beam is swept along the tube axis with a small radius resulting in an annular-shape beam footprint on the window. This beam profile shaping has the additional advantage that the window area is more effectively used, which lowers the maximum local current density and thus irradiation damage.

A parametric study was performed to find the optimal shape of the beam profile. The sweeping radius and the beam width were varied. A limiting condition was set to the power fraction reaching the beam tube and keeping the load at the window axis low. The maximum value of the time averaged current density for the optimised swept beam is 35 µA/cm²/mA (Figure 4).
Maximum irradiation damage in a T91 steel window of a swept beam varying over one cycle (90 days) from 1.68 to 2.45 mA is evaluated by MCNPX calculation at 22 dpa and 1192 appmHe [7].

Figure 4: Current density of the optimised sweeping beam (600 MeV, 1 mA)

Calculation of spallation energy deposition

The optimised beam shape was introduced into an MCNPX model [8-9] to calculate the real spallation heat load in the target zone (Figure 5a) and to determine the spallation neutron distribution. The optimum vertical position of the window in the core is defined by this neutron distribution (Figure 5b). The detailed 3D results are transferred to the Computational Fluid Dynamics (CFD) code.

Figure 5: a. Power density and b. Neutron source linear density

Thermal hydraulic evaluation

Detailed thermal hydraulic evaluations are performed with the general purpose CFD code Ansys CFX [10]. For the velocity profile device, the multi-tube design [11] with three concentric regions has been applied. An optimisation of the tube radii and the mass flow rate for each region results in enhanced local cooling at the most loaded part of the window. The reduction of the residence time in the most heavily loaded LBE zone results in lower hotspot temperatures. A typical CFD result of velocity and temperature distribution is shown in Figure 6.

The spallation target assembly forms a parallel channel to the fuel assemblies in the core. This means the pressure drop at the design mass flow rate in the target assembly must be the same as the pressure drop over the fuel assemblies in the core. To equalise the pressure difference, extra flow resistance is added into
the target assembly by the pressure drop device in the form of a series of plates with staggered holes. The principle of plates with holes is also used to obtain the correct mass flow distribution between the 3 concentric regions. To avoid erosion, high velocities in LBE are not acceptable (above 2m/s).

Figure 6: Velocity and temperature distribution (beam current 3.5mA)

Above the core region the hexagonal tube enlarges and openings allow the target cooling LBE to mix with the outlet flow of the core.

Window material considerations

Although the increase of proton energy to 600 MeV significantly reduced thermal load and therefore mitigates some of the restrictions, the evaluation of a window design cannot be made without looking at the material limitations caused by the harsh radiation environment and the interactions with the LBE.

A target window service life of at least three full-power months (FPM) combined with a simplified design that allows easy replacement has been set as the minimum requirement in order to make this option acceptable.

The main candidate material for the window is ferritic-martensitic steel T91. The main factors determining the degradation of material properties in a liquid metal spallation environment are:

- Irradiation damage by protons and neutrons.
- Liquid metal corrosion.
- Liquid metal embrittlement.

All of these effects are strongly temperature dependent. A suitable and realistic choice of the operating temperature for a window made from T91 has to cope with these degradation modes.

Irradiation damage

The radiation damage of the window can be split into 2 parts. On one hand there is the effect of the high-energy protons inducing Helium in the material, on the other hand there is the damage caused by the spallation neutrons.

SINQ Target Irradiation Programme (STIP) data demonstrate that specimens irradiated at different temperatures under representative conditions show significant hardening compared to the unirradiated specimens. But specimens irradiated to higher doses (>10.9 dpa at >300°C) recover due to work hardening and display uniform elongation. Ductility is retained in T91 specimens even at dose levels up to 20 dpa. At
lower doses and lower temperatures (<200°C) tensile specimens show prompt necking behaviour (Figure 7a). Tensile tests performed at high temperature show similar behaviour although the overall strength decreases (Figure 7b). The data indicates that T91 has sufficient strength to be used as a structural material.

Figure 7: STIP-III T91 steel at different irradiation temperatures [12]

High-temperature fast-neutron irradiation data for EM10, which is very similar to T91, are documented in [13]. Even after irradiation damage up to 90 dpa at 439°C, some ductility remains. Helium production due to neutron irradiation is much smaller compared to proton irradiation.

In summary, there is evidence that T91, if irradiated at temperatures above 300°C, does not suffer from the He-embrittlement effects observed at lower irradiation temperatures and that 20 dpa or more should be acceptable.

Liquid metal embrittlement

The effect that the ductility of solid metals can be significantly reduced when in prolonged contact with a liquid metal is commonly referred to as Liquid Metal Embrittlement (LME). For the system T91 – LBE it has been investigated in the context of MEGAPIE at PSI [14].

Figure 8: Curves of total elongation versus testing temperature for specimens tested in Ar and LBE under irradiation [14]

A significant reduction of the total elongation in tensile tests in LBE is observed at temperatures below 450°C, but ductility can be seen to recover above 500°C. Test data from samples under irradiation in LBE however tend to exhibit even lower total elongations compared to unirradiated samples. Ductility is recovered only partly above 500°C.
These data suggest that an operating temperature of 450°C or more for a T91 window is desirable also from the point of view of liquid metal embrittlement, but the combination of irradiation and LBE embrittlement imposes major objections on the use of T91 in the range 200-400°C.

**Liquid metal corrosion**

When the oxide layer that protects structural material against corrosion has been removed, material transport from hot to cold regions is a problem common to all liquid metal systems. Its prevention has been the subject of a fair amount of R&D in recent years. The key is maintaining a suitable oxygen concentration in the liquid metal, high enough to prevent destruction of the oxide layer on the walls and low enough to avoid formation of Pb-oxide crud on the liquid metal surface. A system to achieve this control is foreseen in MYRRHA. Unfortunately its effectiveness is strongly temperature dependent and may be limited above 500°C. However, even if some liquid metal corrosion were to occur at the target window, this is a slow and continuous process and it should be possible to design the window such that enough wall thickness remains at the end of its postulated service life.

**MEGAPIE experience**

The MEGAwatt PIlot Experiment at PSI (MEGAPIE) was operated between August and December 2006. The safe operation of a LBE spallation target hit by a 1 MW 590 MeV proton beam was demonstrated. The proton beam had a current of 1.74 mA. The beam entrance window was made from T91 steel and was cooled by the main LBE flow combined with a cold LBE jet extracted at the heat exchanger outlet.

The LBE temperature range near the window varied from 220°C to 350°C. Maximum window temperature was estimated at 470°C. Due to beam trips, accelerator shut down and maintenance the number of thermal cycles of the window was in the order of magnitude of 10 000 per year [15].

**Conclusion on the use of T91**

Given the fact that the MEGAPIE experiment proved the feasibility of a target window in the same power range as the one needed in the loopless window concept for MYRRHA, that irradiation effects as well as liquid metal embrittlement are less serious above 450°C, that the strength of steels in general decreases rather rapidly and corrosion protection becomes ineffective above 500°C, it is recommended to design and control the liquid metal flow system around the window in such a way, that a temperature between 450 and 500°C can be maintained at the side of the window facing the liquid metal.

**Mechanical design**

The evaluation of the mechanical design for the beam tube/window is based on the design rules given by the RCC-MRx code [16]. The loads accounted for are the pressure, thermal and cyclic loads. The thickness of the beam tube and window are adapted to the pressure loads. For the long structure of beam tube a buckling analyses determined the number of support points necessary. A fatigue analyses for thermal cycles was included as well.

In this evaluation, the creep effects are considered negligible which is a valid hypothesis below 550°C.

**Irradiation capabilities for fusion**

The spallation target does not only provide neutrons to the subcritical core, it also allows irradiation experiments in its own. The central peak flux in the spallation zone is boosted to values which can (almost) simulate the conditions at the first wall of the fusion reactor, in terms of dpa/y, appmHe/dpa and temperatures.
A double walled module containing test samples which can be inserted in the spallation zone allows material experiments under representative fusion wall conditions. The sample specifications that are planned during irradiation are:

- sample surface temperature: 100°C – 650°C
- dpa-levels: up to 30 dpa/y
- appmHe/dpa: up to 20 appmHe/dpa
- Volume: 18×120mm×dia. 8mm

Central sample temperatures depend on the shape of the samples. The preferred coolant is He gas at very high pressure. Control of the sample temperature is done by local temperatures measurement and adapting the mass flow of the coolant or the pressure in the vacuum layer. Other instrumentation, like a gamma-thermometers to measure the local flux on-line and dosimeters that can be checked afterwards are optional.

**R&D and test programme**

The design of the MYRRHA spallation target assembly is supported by an extensive R&D programme. Next to the lessons learned from development of the MEGAPIE experiment, and the operational experience and post-test investigation results, the research extends over different fields within SCK•CEN and in international collaboration. Only the thermal hydraulic and mechanical test programme is detailed further herein, but important efforts are also made on e.g. material research, spallation chemistry and beam control.

**Thermal hydraulic and mechanical research**

Verification of the target zone cooling by means of an integral test experiment is difficult because of the high specific volumetric heating. Consequently, the design study uses advanced numerical tools, both for the thermal hydraulic simulations and the associated structural analyses.

To validate the target thermal-hydraulics computations with respect to velocity distribution around the beam window and the pressure drop distribution in the wrapper, one-to-one scale model experiments of the beam tube in the wrapper with pressure drop and velocity profile devices will be investigated in the COMPLOT facility at SCK•CEN.

COMPLOT is a highly instrumented isothermal LBE loop with 2 test sections representative of a MYRRHA core position.

Analogous validation comparisons are made on data from experiments with a highpower resistance heated target window configuration performed by JAEA in the JLBL-3 loop [17] and the design tools used at SCK•CEN.

A similar approach is used for the mechanical verification of e.g. buckling, positional accuracy, stability and fluid-structure interaction of the beam tube. Dedicated vibration instrumentation on the beam tube and wrapper will be investigated in the COMPLOT facility and compared to 3D numerical simulations using a partitioned fluid-structure interaction technique, developed in collaboration with Ghent University [18].

**Conclusions**

The transformation from windowless spallation loop to a window design without dedicated loop for MYRRHA in ADS mode was only possible through the increase of the accelerator proton beam energy from 350 to 600 MeV. The complexity of the design could be reduced significantly by careful analyses of recently obtained representative material data, the experience gained by the MEGAPIE experiment and design optimisation.
Advanced numerical tools are used to optimise the design parameters. The detailed design of the spallation target assembly is ready to be tested in the new COMPlot facility, with respect to thermal hydraulics and mechanical evaluation. International collaboration and SCK•CEN driven research programmes are ongoing to get additional insight in material behaviour in LBE under high irradiation doses and experiments are set up to validate numerical tools.

Interesting possibilities for material testing experiments placed below the window in the spallation are evaluated. The irradiation conditions are representative for fusion first wall irradiation conditions.

Acknowledgements

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Recent Progress and Future R&D Plan of Nitride Fuel Cycle Technology for Transmutation of Minor Actinides

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Abstract

Uranium-free nitride fuel was chosen as the first candidate for transmutation of long-lived minor actinides (MA) using accelerator-driven system (ADS) under the double strata fuel cycle concept by Japan Atomic Energy Agency (JAEA). The advantages of nitride fuel are good thermal properties and large mutual solubility among actinide elements. A pyrochemical process has been proposed as the first candidate for reprocessing spent nitride fuel, because this technique has some advantages over aqueous process, such as the resistance to radiation damage, which is an important issue for fuels containing large amounts of highly radioactive MA. This paper overviews the recent progress and future R&D plan of the study on the nitride fuel cycle technology at JAEA.

Introduction

Uranium-free nitride fuel was chosen as the first candidate for transmutation of long-lived minor actinides (MA: Np, Am, Cm) using accelerator-driven system (ADS) under the double strata fuel cycle concept by Japan Atomic Energy Agency (JAEA). The advantages of nitride fuel are good thermal properties and large mutual solubility among actinide elements. Though $^{15}$N enrichment is necessary to prevent the formation of long-lived $^{14}$C, the cost is considered reasonable because of the small throughput [1].

A pyrochemical process has been proposed as the first candidate for the reprocessing of spent nitride fuel, because this technique has some advantages over aqueous process, such as the resistance to radiation damage, which is an important issue for the fuels containing large amounts of highly radioactive MA. In addition, compactness of the facility, margin of criticality, and recycling feasibility of $^{15}$N are also advantages of the pyrochemical process [1,2].

This paper overviews the recent progress and future R&D plan of the nitride fuel cycle technology in JAEA. Outline of the fuel cycle, our recent study on fuel fabrication, fuel property, and reprocessing of spent fuel, and our R&D plan based on the roadmap of the development are introduced.

Outline of the MA nitride fuel and MA transmutation fuel cycle

Typical composition of the fuel is considered as 30 wt.% of MA nitride, 20 wt.% of Pu nitride, and 50 wt.% of ZrN; Pu is added to mitigate the burnup reactivity swing, and ZrN is the first candidate of the dilution material to adjust the power density. Flexibility of the ratio of MA, Pu, and Zr in the solid solution type fuel compound (MA, Pu, Zr)N is appropriate for the detailed design of the fuel [1].

The total inventory of heavy metal (Pu+MA) in an ADS core is planned to be about 4400 kg (containing about 2640 kg of MA). 500 kg of MA is transmuted during each burnup cycle of 600 effective full power days (EFPD) with 800 MWth power. The transmutation ratio of MA per cycle is supposed to be about 20%. All the fuel used in each cycle are removed from the core and heavy metal (Pu+MA) remained
in the spent fuel is recycled for the next burnup cycle [1]. MA recovered from HLW, the amount of which is equivalent to that of transmuted MA in the previous burnup (~500 kg), should be added to the recycled fuel. Figure 1 shows the outline of the proposed MA transmutation fuel cycle.

**Achievable MA transmutation ratio**

Our target is to transmute 99% of MA contained in high level waste (HLW) to reduce its radiotoxicity. The period until the radiotoxicity drops below that of natural uranium can be dropped from about 5000 years which is supposed for HLW without partitioning and transmutation, to about 300 years [1,3].

Cumulative loss of MA elements by multi-recycling of the fuel should be considered to evaluate the achievable MA transmutation ratio. Calculations of the cumulative ratio of transmuted MA were made using parameters indicated in Figure 1: the loss ratio of MA on partitioning process (l₁), fuel fabrication process (l₂), pyrochemical reprocess (l₃), and transmutation ratio per cycle (trc). The transmuted ratio of MA which is contained in HLW and to be used as fuel of the first cycle, on the n-th transmutation cycle (tr(n)) and cumulative ratio of transmuted MA (ctr) were calculated by:

\[
\begin{align*}
tr(1) &= (1 - (1 - l_1) l_2) \times trc, \\
tr(n) &= (1 - tr(n-1)) \times (1 - (1 - l_3) (1 - l_2)) \times trc \quad (n \geq 2), \\
ctr &= \sum_{n=1}^{\infty} tr(n). 
\end{align*}
\]

On the other hand, the loss ratio of MA contained in HLW and to be used as fuel of the first cycle, on the n-th transmutation cycle (lr(n)) and cumulative loss ratio of MA (clr) were calculated by:

\[
\begin{align*}
lr(1) &= l_1 + (1 - l_1) l_2, \\
lr(n) &= (1 - tr(n-1)) \times (l_3 + (1 - l_3) l_2) \quad (n \geq 2), \\
clr &= \sum_{n=1}^{\infty} lr(n). 
\end{align*}
\]

**Figure 1: Outline of the proposed MA transmutation fuel cycle and parameters used in the calculations of achievable transmutation ratio by multi-recycling**
Figure 2 shows the calculated cumulative transmutation ratio and the cumulative loss of MA elements vs number of the cycle; (a) the effects of the transmutation ratio per cycle calculated with 10, 15, and 20%, whereas the ratio of the loss in each process is fixed to 0.1%, and (b) the effects of the ratio of the loss on the processes calculated with the loss of MA in each reprocessing and fuel fabrication process as 0.1, 0.2, and 0.3%, whereas the transmutation ratio per cycle was fixed to 20%. From these calculations, transmutation of 99% MA can be achieved if transmutation ratio per cycle is over 20% and the loss of MA in each reprocessing and fuel fabrication process is below 0.1%. Development of the method suitable to minimise the loss of MA in fuel fabrication and fuel reprocessing is needed besides realising high burnup of the MA fuel.

Figure 2: Calculated cumulative transmutation ratio (left) and cumulative loss of MA elements (right) versus number of transmutation cycle

(a) Transmutation ratio per cycle used as a parameter

(b) The ratio of the loss on each process per cycle used as a parameter

Outline of the MA nitride fuel cycle technology

Process flow of the MA nitride fuel fabrication and that of pyrochemical treatment of the spent nitride fuel are shown in Figures 3 and 4, respectively. Basic design of fuel rods and fuel pellets are similar to those of the commercial light water reactor (LWR). Fuel fabrication process is also similar to that of LWR, though the materials are different and nitride fuels have to be handled in an inert gas atmosphere because they easily react with oxygen or moisture in air. Our developments have been focused on the processes which are different from that of LWR fuel. Preparation of nitrides and their solid solutions has been a main topic of development. On the other hand, for pyrochemical process, which had been originally developed for metal fuel treatment, electrolysis of nitride fuels and refabrication of nitrides from the recovered actinides have been our main concerns; other main processes have been developed mainly in metal fuel treatment technology. For nitride fuels, chemical dissolution of an anode residue has also been developed to maximise the recovery ratio of TRU in this process [4,5].
Recent study on MA nitride fuel cycle technology

Property database of MA nitride fuel

Our efforts on nitride fuel development have focused on the preparation and property measurements of transuranium (TRU) nitrides. Recently, we compiled property data including the data we had obtained, in a data book [6]. The relation of the property data and fuel design, or irradiation behaviour is illustrated in Figure 5. It also has thermal conductivity data of $\text{(Zr,Pu}_{1-x})_{2}\text{Am}_{x}\text{N}$ [7], which is a prototype compound of the MA transmutation fuel, as an example of the compiled data. At this moment, we need to utilise some of the data of UN and (U,Pu)N which were measured in development of the fuels for fast reactor or space reactor, instead of TRU nitrides, to examine the fuel behaviour, because a number of
Property data sets of TRU nitride fuel is limited, especially on mechanical property and behaviour under irradiation.

**Figure 5: Relationship between property database and fuel design or irradiation behaviour with an example of the property data [6, 7]**

Property data of CmN is necessary to develop MA nitride fuel, though they had not been reported enough. We successfully prepared 10 mg-scale Cm sample from an aged 244Cm oxide sample (Pu0.8Cm0.2)O2, in which 240Pu had been accumulated by α-decay of 244Cm (t1/2=18.1 year) over long-term storage. Pu was removed from the nitric acid solution, in which (Pu0.8Cm0.2)O2 had been dissolved, using an ion-exchange resin, and Cm oxalate was precipitated from the solution [8]. CmN sample with a small amount of impurity (0.35%Pu and 3.59%Am) prepared by the carbothermic reaction of the oxide obtained by calcination of the oxalate, was used for property measurements. Linear thermal expansion and change in lattice parameter of CmN caused by self-irradiation were reported (Figure 6) [9] and complied in the data book mentioned above [6].

**Figure 6: Linear thermal expansion of nitrides (left) and change in lattice parameter of 244CmN caused by self-irradiation (right) [9]**
Physicochemical property of CmCl₃ and electrochemical property of Cm in molten chlorides

4 mg of CmCl₃ sample was successfully prepared by the solid state reaction of CmN with CdCl₂ [10] in a manner similar to that of other TRU trichlorides. To obtain highly pure Cm sample, Am removal (Am/Cm separation) from the Cm-Am solution by a chromatographic method using the tertiary pyridine resin with the nitric acid/methanol mixed solvent (Figure 7), was followed by Pu removal from the nitric acid solution of (Pu₀.₈Cm₀.₂)O₂ [8]. Using the highly pure CmCl₃ sample, not only basic physicochemical property such as melting temperature of CmCl₃ (970±3 K) [10], but also electrochemical property of Cm (redox potential of Cm³⁺/Cm) in LiCl-KCl eutectic melt was measured as basic data of the pyrochemical process [11].

Figure 7: Am/Cm separation by chromatographic method using the tertiary pyridine resin with the nitric acid/methanol mixed solvent [8]

Future plan

According to an interim report issued in November 2013 about partitioning and transmutation technology by Japan’s Ministry of Education, Culture, Sports and Technology (MEXT), R&D of technology related to partitioning and transmutation using ADS was classified at the basic level (“concept development category,” in the technology readiness levels (TRL) evaluation [12,13]). The interim report also noted that some work, including experiments using an appropriate amount of MA, would need to be completed before R&D of the fuel cycle technology could be advanced to the next stage (“proof of principle” category in the TRL evaluation) [14,15].

As shown in the road map of the development indicated in the interim report, our first tasks at this moment are to advance the technology by conducting bench scale tests using MA samples including those
recovered from irradiated fuels, as well as engineering scale tests with surrogate materials [14,15]. In addition, an analysis code for fuel behaviour simulation using the compiled nitride fuel property database, and irradiation tests of MA nitride fuels are also planned to develop the MA nitride fuel. After completing these tasks, we will conduct bench scale tests of pyrochemical process using irradiated nitride fuels in order to demonstrate the engineering feasibility [14,15]. The tests will require the construction of new hot facilities in which an appropriate amount of irradiated nitride fuels can be handled in an inert gas atmosphere.

Conclusion

We have summarised our recent study on nitride fuel cycle technology for transmutation of minor actinides by ADS. Our study was classified at the “concept development category,” in the technology readiness levels (TRL) evaluation. Our next tasks are to advance the technology by conducting bench scale tests using MA samples, including those recovered from irradiated fuels, as well as engineering scale tests with surrogate materials.

References


Casting Development of Metallic Fuel for SFR

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Abstract

U-Zr metal fuel for SFR is now being developed by KAERI as a national R&D programme of Korea. In order to recycle transuranic elements (TRU) retained in spent nuclear fuel, the generation of long-lived radioactive wastes and a loss of volatile species should be minimised during the recycled fuel fabrication step.

In this study, fuel slug fabrication method has been introduced to develop an innovative fabrication process of metal fuel of SFR for preventing the evaporation of volatile elements such as Am. Metal fuel slugs were fabricated with an improved injection casting method in KAERI. Volatile species can be retained through the use of a cover gas with over pressure and covered crucibles.

Experimental results show that the Mn was not volatilised and conserved in inert gas conditions compared to the vacuum condition. The volatility of Mn can be controlled by changing the casting process, and minimal Mn (and Am) loss is possible. An improved casting method under an inert atmosphere is more effective in the prevention of vaporisation than casting under a vacuum and reduced atmosphere. In addition, improved casting under a reduced atmosphere shows a considerable effect in the prevention of vaporisation.

Introduction

The Korea Atomic Energy Research Institute (KAERI) seeks to develop and demonstrate the technologies needed to transmute the long-lived transuranic actinide isotopes in spent nuclear fuel into shorter-lived fission products, thereby dramatically decreasing the volume material requiring disposal and the long-term radiotoxicity and heat load of high level waste sent to a geological repository. Metal fuel for an SFR has advantages such as simple fabrication procedures, good neutron economy, high thermal conductivity, excellent compatibility with Na coolant and inherent passive safety [1]. U-Zr metal fuel for SFR is now being developed by KAERI as a national R&D programme of Korea. In order to recycle transuranic elements (TRU) retained in spent nuclear fuel, remote fabrication capability in a shielded hot cell should be prepared. Moreover, the generation of long-lived radioactive wastes and a loss of volatile species should be minimised during the recycled fuel fabrication step. The fabrication technology of metal fuel for SFR has been under development in Korea as a national nuclear R&D programme since 2007 [2-5]. The reference fuel for the Korean SFR is a metal alloy. Metal fuel has been studied and is also considered a leading candidate for advanced driver and transmutation fuels under the Fuel Cycle Research and Development (FCRD) programme, formerly the Advanced Fuel Cycle Initiative (AFCI) programme. The fabrication process for SFR fuel is composed of (1) fuel slug casting, (2) loading and fabrication of the fuel rods, and (3) fabrication of the final fuel assemblies. Fuel slug casting is the dominant source of fuel losses and recycled streams in this fabrication process.

The development of the vacuum injection casting method for fuel slugs was initiated in 1956 with centrifugal casting considered as the backup process. Because the injection casting process is simple and compact, it is cost efficient and has the advantage of mass production while reducing the amount of radioactive waste. U-Zr and U-Pu-Zr fuel slugs for test sub-assemblies irradiated in EBR-II and FFTF were
fabricated by this injection casting method. More than 100,000 metal fuel slugs including both U-5wt.%Fs and U-10wt.%Zr fuels were fabricated by injection casting in the United States. U-Zr-Pu alloy fuels have been used related to the closed fuel cycle for managing MA actinides and reducing high radioactivity levels since the 1980s.

However, casting alloys containing volatile radioactive constituents, such as Am, is problematic in the conventional injection casting method, because the furnace containing the fuel melt is evacuated. Not only is the retention of Am important for the successful transmutation of MA in a fast reactor, but any material lost must be efficiently recovered in a waste stream and subsequently dealt with, increasing the overall facility cost and safety requirement. This is especially challenging in a remote fabrication environment, where all operations must either be automated or conducted with manipulators. Although injection casting has been a well-established fabrication method for metal fuel for decades [6], Am addition to the metal fuel hampers conventional fuel fabrication processes because of the high vapour pressure of Am at the melting temperature of the uranium alloys [7]. An advanced fuel casting system to control the transport of volatile elements during melting of a fuel alloy with MA has been developed. It is necessary to minimise the vaporisation of Am and the volume of radioactive wastes [8].

In this study, alternative fuel slug fabrication methods have been introduced to develop an innovative fabrication process of metal fuel of SFR for preventing the evaporation of volatile elements such as Am. Metal fuel slugs were fabricated by gravity casting and improved injection casting method in KAERI. Volatile species can be retained through the use of a cover gas with over pressure, covered crucibles, and short cycle times under these fuel fabrication methods, and melted under an inert atmosphere [9-11].

**Experiment details**

The feasibility of improved injection casting method including melting under an inert atmosphere was evaluated in a small-size induction-melting furnace. As experimental equipment, its primary purpose was to explore and define various casting variables, e.g. casting temperature and pressure, pressurising rate, and mold coating method. For a preliminary test, pure copper was selected as a surrogate material, which has a melting temperature similar to uranium. The crucible is inductively heated up to 1400°C, which is sufficiently higher than the liquidus temperature of the surrogate material. All operations were done under an argon atmosphere. At a predetermined superheat, the mold was lowered, immersing the open tip into the metal melt. When the metal has solidified, the mold is raised. After cooling, the surrogate fuel slug is taken out of the mold. Elemental lumps of depleted uranium, zirconium, manganese, and rare-earth elements were used to fabricate U-10wt.%Zr, U-10wt.%Zr-5wt.%RE (RE: Nd 53wt.%, Ce 25wt.%, Pr 16wt.%, La 16wt.%), U-10wt.%Zr-5wt.%Mn and U-10wt.%Zr-5wt.%RE-5wt.%Mn fuel slug by gravity casting method. Graphite crucibles coated with a high-temperature ceramic plasma-spray coating method and quartz molds coated with a high-temperature ceramic by a slurry-coating method were used.

After fabricating the fuel slugs in a casting furnace, the fuel losses in the crucible assembly and the mold assembly were quantitatively evaluated. The soundness and chemical composition of the as-cast fuel slugs were identified and analysed. As-cast fuel slugs were inspected by gamma-ray radiography. The densities of the fuel slugs were also measured using an Archimedean immersion method. A scanning electron microscope (SEM) was used to study the microstructure of as-cast fuel slugs. Chemical compositions of as-cast fuel slugs were measured by energy-dispersive spectroscopy (EDS). After a surrogate fuel slug was generally soundly cast by the improved injection casting method under an inert atmosphere, fuel slugs by improved casting method have been successfully fabricated in KAERI for the prevention in evaporation of volatile elements such as Am. Metal fuel slugs were then examined with casting soundness and density to evaluate the feasibility of the fabrication method.
Results and discussion

An alternative fabrication method was used to fabricate the fuel slugs using a low pressure gravity casting system in which the melt in a crucible is cast into the mold under the crucible through a distributor by a gravity force under low pressure [3]. The melting and casting parameters of the fuel slug casting process such as the melting batch size, coating method, pouring method, melting and casting temperature, mold pre-heating temperature, and melt distributor pre-heating temperature were investigated to obtain the sound fuel slugs. Metal fuel slugs with a diameter of 5 mm and a length of 300 mm were fabricated using the advanced fuel casting system, as shown in Figures 1-3.

Gamma-ray radiography was performed to detect internal defects such as cracks and pores inside the metal fuel slugs. The feeding yielding of fuel alloy melt to casting molds was about 90%. The alloy compositions and the densities of U-10wt.%Zr, U-10 wt.%Zr-5 wt.%RE, and U-10 wt.%Zr-5 wt.%RE-5 wt.%Mn fuel slugs are shown in Tables 1 and 2. It can be seen that the losses of these volatile elements such as Am can be effectively controlled to below detectable levels using modest argon overpressures. Based on these results there is a high level of confidence that Am losses will also be effectively controlled by application of a modest amount of overpressure. The scanning electron micrographs of the metal fuel slugs fabricated by gravity casting under low pressure are shown in Figure 4. The microstructure of U-10wt.%Zr fuel slugs showed UZr$_2$ or Zr particulate dispersions of about 5 μm in size and a laminar
structure below 0.5 μm in thickness in the matrix. The disperse precipitates of U-10 wt.%Zr-5wt.%RE fuel slugs, over-etched with an etchant, were finely distributed below 5μm in size. The microstructure of U-10 wt.%Zr-5wt.%RE-5wt.%Mn fuel slugs, over-etched with an etchant, showed some eutectic Mn-rich precipitate dispersions below 3 μm in thickness. There was an increased amount of dendritic dispersion phases compared with U-10 wt.%Zr fuel slugs, irrespective of the atmospheric pressure.

Table 1: Densities of U-10Zr, U-10Zr-5RE, and U-10Zr-5RE-5Mn fuel slugs

<table>
<thead>
<tr>
<th>Nominal composition location</th>
<th>U-10Zr</th>
<th>U-10Zr-5RE</th>
<th>U-10Zr-5RE-5Mn</th>
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</thead>
<tbody>
<tr>
<td>Top (g/cm³)</td>
<td>15.9</td>
<td>14.7</td>
<td>12.5</td>
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<tr>
<td>Middle (g/cm³)</td>
<td>16.1</td>
<td>14.7</td>
<td>14.0</td>
</tr>
<tr>
<td>Bottom (g/cm³)</td>
<td>16.1</td>
<td>14.7</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Table 2: Alloy compositions of U-10Zr, U-10Zr-5RE, and U-10Zr-5RE-5Mn fuel slugs

<table>
<thead>
<tr>
<th>Nominal composition element</th>
<th>U-10Zr</th>
<th>U-10Zr-5RE</th>
<th>U-10Zr-5RE-5Mn</th>
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<tr>
<td>U (wt%)</td>
<td>90.4</td>
<td>84.1</td>
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<td>Zr (wt%)</td>
<td>8.7</td>
<td>10.2</td>
<td>10.0</td>
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<td>RE (wt.%)</td>
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<td>Mn (wt.%)</td>
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<td>N (ppm)</td>
<td>17</td>
<td>40</td>
<td>50</td>
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Figure 4: Typical scanning electron micrographs of
(a) U-10Zr, (b) U-10Zr-5RE, and (c) U-10Zr-5RE-5Mn fuel slugs; × 5 000

A considerable amount of Mn was contained in the periphery of the dendritic dispersions, and in the eutectic dispersions, approximately 1-2 μm in size. There was a greater amount of eutectic matrix in the alloy melted under Ar atmosphere compared to the alloy melted under a vacuum. This increased amount of eutectic phase in the U-10wt.%Zr-5wt.%Mn alloy melted under Ar atmosphere, resulted from a higher Mn content than the U-10wt.%Zr-5wt.%Mn alloy melted under a vacuum.

The typical material balance in the crucible assembly and mold assembly after fabrication of volatile surrogate U-10wt.%Zr-5wt.%Mn, and U-10wt.%Zr-5wt.%RE fuel slugs are shown in Tables 3 and 4. A considerable amount of dross and melt residue remained in the crucible after melting and casting; however, most charge materials were recovered after fabrication of the fuel slugs.

The mass fraction of fuel loss relative to the charge amount after fabrication of U-10wt.%Zr-5wt.%Mn, and U-10wt.%Zr-5wt.%RE fuel slugs was low, at about 1.5%, and 0.1% respectively. It is thought that a lower fuel loss in the case of casting of U-10wt.%Zr-5wt.%Mn and U-10wt.%Zr-5wt.%RE fuel slugs was related to the melting of the U-Zr-Mn and U-Zr-RE alloy in a densely plasma-sprayed graphite crucible with high-temperature ceramic materials, compared with the casting of U-10wt.%Zr fuel alloy in a sparsely slurry-sprayed graphite crucible with high-temperature ceramic materials.
Table 3: Material balance after casting of U-10wt.% Zr-5wt.%Mn fuel slugs

<table>
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<th>Melting/casting part</th>
<th>Mass (g)</th>
<th>Fraction (%)</th>
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<tr>
<td>Before casting</td>
<td>Crucible</td>
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<tr>
<td>After casting</td>
<td>Crucible assembly</td>
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<tr>
<td>After casting</td>
<td>Mold assembly</td>
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<td>Fuel loss</td>
<td></td>
<td>18</td>
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</tbody>
</table>

Table 4: Material balance after casting of U-10wt.%Zr-5wt.%RE fuel slugs

<table>
<thead>
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<th>Melting/casting part</th>
<th>Mass (g)</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before casting</td>
<td>Crucible</td>
<td>1464</td>
</tr>
<tr>
<td>After casting</td>
<td>Crucible assembly</td>
<td>167</td>
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<tr>
<td>After casting</td>
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<tr>
<td>Fuel loss</td>
<td></td>
<td>2</td>
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</table>

As shown in Figure 5a, the surrogate fuel slug was soundly cast using the improved injection casting method and a melted surrogate material under an inert atmosphere. The general appearance of the slug was smooth and the length was about 250 mm. Some hot tears were observed in the upper part, resulting from quick cooling. It is thought that this area of casting was not allowed to shrink quickly, placing the area under tension from metal contraction near the solidus temperature of the alloy. Contraction of the metal between the fronts above the solidus temperature tore away from the solidified casting. Gamma-ray radiography of an as-cast surrogate slug was performed to detect internal defects such as cracks and pores, as shown in Figure 5b. Propagation of the solidification front occurred toward the thermal centre of the casting and grain growth simultaneously occurred in the partially liquid portion of the casting, which creates an increasing resistive path for molten metal to flow.

Figure 5: Typical scanning electron micrographs of
(a) U-10Zr, (b) U-10Zr-5RE, and (c) U-10Zr-5RE-5Mn fuel slugs; × 5 000.

The pores detected in the upper part region were expected to occur in areas of the casting where the grain growth starved the shrinkage areas of the molten metal. This kind of defect becomes much more evident and challenging to overcome the increasing alloying element contents in the fuel alloy, as the freezing range continues to widen. In order to control the void created by microshrinkage, it was judged to increase the pressure during casting and cooling, which effectively increases the feeding distance resulting in reducing the number and size of the gas pores that are trapped at the grain boundaries, and therefore allowing an extended nucleation and growth process 11. However, the internal integrity of the as-cast metal fuel slugs in the lower part was generally satisfactory.

Optical micrographs of the surrogate fuel slug cast according to the solidifying position are shown in Figure 6. The grain size was seen to increase from the lower position to the upper position. This is because the solidification rate at the upper position, where molten melt solidifies first, is very high compared to the lower position.
Through the experience of the surrogate fuel slug, U-10wt.%Zr-5wt.%Mn fuel slugs containing a volatile surrogate element, Mn, shown in Figure 7, were soundly cast by improved injection casting for prevention of evaporation of volatile elements such as Am under various atmospheres such as a vacuum state, reduced atmosphere, and an inert atmosphere. The gamma-ray radiography of the as-cast surrogate slug was performed to detect internal defects such as cracks and pores. The general appearance of the slug was smooth, and the diameter and length were 5.4 mm and about 200-250 mm, respectively. The density variations according to the location of the fuel slugs are shown in Table 5. The density of the fuel pins prepared using an injection casting method shows a different way in accordance with the casting process conditions. The U-10Zr(#S13-03) fuel pins when the surrogate Mn for volatile radioactive constituents was not added, showed the lowest density because of the lighter density of Mn elements, but the others such as U-10Zr-Mn(#S13-04, #S13-05, #S13-06) by adding an equal amount of Mn elements such as 5wt.% showed a difference owing to the conditions of the casting process. The density of the fuel pins in an inert atmosphere showed the lowest value, which means the highest evaporation because of the consumption for light elements. However, the U-10Zr-Mn fuel pins(#S13-05) for a reduced atmosphere in which a vacuum was applied for a short time showed a higher density even when the volatile amount of Mn was small compared to the other casting method. The U-10Zr-Mn fuel pins (#S13-04) in a vacuum state showed the highest density as expected.

This limited experiment results show that the Mn was not volatilised and conserved in the inert gas conditions compared to the vacuum condition. The volatility of Mn can be controlled by changing the casting process, and minimal Mn (and Am) loss is possible. An improved casting method under an inert atmosphere is more effective in the prevention of vaporisation than casting under a vacuum and reduced

Figure 6: Optical micrographs of the surrogate fuel slug cast according to solidifying position: (a) lower position, (b) middle position, (c) upper position

Figure 7: U-10wt.%Zr-5wt.%Mn fuel slugs fabricated by improved casting method: (a) vacuum, (b) reduced atmosphere, and (c) inert atmosphere.
atmosphere. In addition, improved casting under a reduced atmosphere shows a considerable effect in the prevention of vaporisation.

Table 5: Alloy density of U-10Zr fuel pins prepared by injection casting method

<table>
<thead>
<tr>
<th></th>
<th>U-10Zr (S13-03)</th>
<th>U-10Zr-Mn (S13-04)</th>
<th>U-10Zr-Mn (S13-05)</th>
<th>U-10Zr-Mn (S13-06)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Upper</strong> (g/cm³)</td>
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<td></td>
<td></td>
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<tr>
<td>1</td>
<td>15.7</td>
<td>8.8</td>
<td>15.3</td>
<td>14.9</td>
</tr>
<tr>
<td>2</td>
<td>15.7</td>
<td>14.9</td>
<td>15.3</td>
<td>14.9</td>
</tr>
<tr>
<td>3</td>
<td>15.7</td>
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<td>15.3</td>
<td>14.9</td>
</tr>
<tr>
<td><strong>Middle</strong> (g/cm³)</td>
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<td>1</td>
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<td>14.9</td>
<td>15.3</td>
<td>14.8</td>
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<td><strong>Bottom</strong> (g/cm³)</td>
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<td>1</td>
<td>15.8</td>
<td>14.9</td>
<td>15.4</td>
<td>14.8</td>
</tr>
<tr>
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<td>15.8</td>
<td>14.8</td>
<td>15.3</td>
<td>14.8</td>
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<tr>
<td>3</td>
<td>15.73</td>
<td>14.8</td>
<td>15.3</td>
<td>14.8</td>
</tr>
</tbody>
</table>

Conclusion

In order to prevent the evaporation of volatile elements such as Am, alternative fabrication methods of metal fuel slugs have been applied and examined with gravity casting and an improved injection casting method at KAERI. U-10wt.%Zr, U-10wt.%Zr-5wt.%RE (RE: Nd 53wt.%, Ce 25wt.%, Pr 16wt.%, La 16 wt.%), U-10wt.%Zr-5wt.%Mn, and U-10wt.%Zr-5wt.%RE-5wt.%Mn fuel slugs were soundly fabricated with gravity casting for the retention of the volatile surrogate element. Based on these results there is a high level of confidence that Am losses will also be effectively controlled by application of a modest amount of overpressure. After a surrogate fuel slug was generally cast by improved injection casting method under an inert atmosphere, fuel slugs have been successfully fabricated at KAERI for the prevention of evaporation of volatile elements such as Am. Fuel slugs for SFR were characterised to evaluate the feasibility of the alternative fabrication method. The general appearance of the slug was smooth, and the diameter and length were 5.4 mm and about 250 mm, respectively. The mass fraction of the fuel loss relative to the charge amount after fabrication of U-10Zr-5Mn was quite low, up to 0.2%. The Mn element was almost recovered with the prevention in evaporation of the volatile surrogate, Mn. It was seen that the losses of these volatile elements such as Am can be effectively controlled below detectable levels using modest argon pressure.

Acknowledgements

This study was supported by the WCU programme of the Korean Science & Engineering Foundation, which is being funded by the Korean government (MOEHRD, Grant No. R32-2008-000-10124-0).

References


Abstract

Minor actinide (MA)-bearing MOX fuels have been developed as candidate fuels which are used in fast neutron spectrum cores such as sodium-cooled fast reactor (SFR) cores and experimental accelerator driven system (ADS) cores. Americium (Am) which is one of the MA elements significantly affects basic properties. It is known that Am content causes oxygen potential to increase and that influences irradiation behaviour such as fuel-cladding chemical interaction (FCCI) and chemical state of fission products. However, the effects of Am content on changes of basic properties are not clear. In this work, the oxygen chemical diffusion coefficients were calculated from measured data and the relationship between oxygen diffusion and oxygen potential of (Pu,Am)O$_{2-x}$ was discussed.

Introduction

Minor actinide (MA)–bearing oxide fuels have been developed for fast reactors and accelerator-driven systems (ADS) with the aim of reducing the amounts of radioactive wastes. In the development of MA–bearing fuels, the physical properties must be known to carry out irradiation behaviour analyses and fuel design. Various physical property measurements and irradiation tests of MA-bearing uranium and plutonium mixed oxide (MOX) fuels have been carried out for fast reactor fuel developments [1]. Additionally, some (Pu,Am)O$_2$-MgO inert matrix fuels have been developed for ADS fuel developments [2]. These studies showed that Am content significantly affected fuel properties.

Matsumoto et al. [3] and Nakamichi et al. [4] have reported the effects of Am content on oxygen potentials. The content of Am caused oxygen potential to increase and oxygen-to-metal (O/M) ratio to decrease in sintering process. Hence, it is important to investigate behaviour of oxygen in Am-bearing oxide fuels. In this work, oxygen chemical diffusion in (Pu,Am)O$_{2-x}$ was investigated and compared with that of PuO$_{2-x}$.

Experimental

(Pu$_{0.928}$Am$_{0.072}$)O$_2$ powder was used in this research. The Am in this powder was formed by beta decay of $^{241}$Pu during storage of about 30 years. The powder was pressed into a pellet and sintered at 1 873 K in 5% H$_2$/Ar gas mixture with added moisture. The pellet was annealed at 1123 K for 4 h in air to adjust to the stoichiometric composition and then the pellet was sliced into a thin disc of 1.7 mm thickness.

Measurements of the O/M ratio change rate were carried out by the thermo-gravimetric technique at temperatures of 1873, 1773, 1673 and 1473 K. The oxygen partial pressure in the atmosphere was changed rapidly by changing the ratio of hydrogen partial pressure to moisture partial pressure and the changes of the disc specimen weight were measured as function of time. Table 1 shows the experimental conditions, which were the temperature, oxygen partial pressure and O/M ratio.
Results and discussion

Oxygen chemical diffusion coefficients were estimated from thermo-gravimetric data measured from the reduction process that occurred in the hypo-stoichiometric composition range. For diffusion from and into the plate, the following equation is given [5].

\[ F = \frac{\bar{C} - C_i}{C_f - C_i} = \frac{1}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\left( \frac{(2n+1)\pi}{h} \right)^2 \right] \]

(1)

Here, \( F \) is the change fraction of the O/M ratio, \( C \) is the average O/M ratio in the specimen, \( C_i \) is the initial O/M ratio, \( C_f \) is the final O/M ratio, \( h \) is the diffusion distance, \( D \) is the oxygen chemical diffusion coefficient, and \( t \) is the reaction time. The measured data were fitted by Equation (1) as a parameter of \( D \). Figure 1 shows an example of fitting results, and the measured data could be fitted well by the plate diffusion model. Oxygen chemical diffusion coefficients obtained by this method are summarised in Table 1.

\( \bar{D} \) of \((\text{Pu}_{0.928}\text{Am}_{0.072})\text{O}_{2-x}\) and \(\text{PuO}_{2-x}\) are plotted in Figure 2 as a function of \(1/T\). \( \bar{D} \) values of \((\text{Pu}_{0.928}\text{Am}_{0.072})\text{O}_{2-x}\) were greater than those of \(\text{PuO}_{2-x}\) at all temperatures. However temperature dependence of \( D \) was not clearly observed in this figure.

Figure 1: Change fraction of O/M ratio
Table 1 Experimental conditions and oxygen chemical diffusion coefficient $D$ values

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature (K)</th>
<th>O/M Initial</th>
<th>O/M Final</th>
<th>$P_{O_2}$ (atm)</th>
<th>$D$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
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</table>

Figure 3 shows the O/M ratio dependence of $D$. $D$ of PuO$_{2-x}$ had O/M ratio dependency, and its values became a minimum in the vicinity of O/M = 1.98. $D$ of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ slightly decreased with decreasing O/M ratio; however, its values did not have the same trend as PuO$_{2-x}$.

**Figure 2**: Oxygen chemical diffusion coefficients versus $1/T$  
**Figure 3**: Oxygen chemical diffusion coefficients versus O/M ratio
Matsumoto et al. [3] reported that Am$^{4+}$ in (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ was reduced earlier than Pu$^{4+}$ in the reduction process. It is possible to determine the reduction zone of Am$^{4+}$ and Pu$^{4+}$ by the following equation.

$$x = \left[ \frac{107814}{4} \exp\left(-379 \times 10^3/RT\right)\exp\left(-281 \times 10^3/RT\right)\exp\left(-447 \times 10^3/RT\right) \right]^{-3} + (0.036)^{-3}$$

$$+ \frac{420082}{10281} \exp\left(-281 \times 10^3/RT\right)\exp\left(-447 \times 10^3/RT\right)$$

$$+ \frac{83931}{10781} \exp\left(-281 \times 10^3/RT\right)\exp\left(-447 \times 10^3/RT\right)$$

(2)

Here, $x$ is the deviation from stoichiometry, $R$ is the gas constant, $T$ is temperature, and $P_{O_2}$ is oxygen partial pressure. Figure 4 shows the relationship between oxygen potential and O/M ratio of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ calculated from equation (2). Oxygen potential changed in two stages with the transition point at O/M = 1.964. The region from O/M = 2.00 to 1.964 represented the Am$^{4+}$ reduction. The region less than O/M = 1.964 represented Pu$^{4+}$ reduction.

From the results of Figure 4, it was found that $D$ values of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ were plotted in the region where Am$^{4+}$ was completely reduced. Thus, it was possible that $D$ values of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ increased due to presence of Am$^{3+}$.

**Figure 4: Calculation results of oxygen potential of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$**

Conclusions

The oxygen chemical diffusion of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ was studied at high temperatures under a controlled oxygen partial pressure. The oxygen chemical diffusion coefficients of (Pu$_{0.928}$Am$_{0.072}$)O$_{2-x}$ were greater than those of PuO$_{2-x}$. Moreover, the former slightly decreased with decreasing O/M ratio. It seems that the increase of the oxygen chemical diffusion coefficient was caused by presence of Am$^{3+}$. 

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References


