



ASGARD

Advanced Fuels for Gen IV Reactors: Reprocessing and Dissolution

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Coordinator contact:	+46-31-7722801, info@asgardproject.eu
Administrative contact:	+420 245 008 599, amo@asgardproject.eu
Online contacts:	www.asgardproject.eu

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EXECUTIVE SUMMARY

The ASGARD dissemination, exploitation and networking plan has been designed to complement the main R&D programme. This deliverable stems from ASGARD WP1.3, the main objective of which is to guarantee dissemination of knowledge of the project. To achieve effective dissemination of the information on the project and its outcomes, the International Workshops planned have been attached to two different important international conferences in the field already during drafting the Initial Training Programme (D 1.2.1) at the start of the project.

The First International Workshops was thus organized during the Radchem 2014 conference (the 17th International conference on Nuclear- and Radiochemistry) in May 2014 in Marianske Lazne, Czech Republic. Christian Ekberg (Chalmers) and Vaclava Havlova (UJV Rez, CZ) were the session organisers, Ch. Ekberg with Vaclava Havlova and Mark Sarsfield (NNL) with Vasiliy Babain (Khlopin Radium Institute, St. Petersburg, Russia) were the conveners of the two verbal parts of the session. The workshop comprised two 1.5 hours verbal sessions and a poster session. The verbal part included two invited lectures, one of them delivered by the ASGARD coordinator, Ch. Ekberg, and the second one delivered by Rajamani Natarajan (IGCAR, India), a specialist in carbide fuels. The verbal sessions were complemented by poster presentations that presented broader topics from both the ASGARD field and the field of the Chemistry of Nuclear Fuel Cycle generally.

Both the verbal and poster parts of the First International Workshops were very well attended – the number of participants at the verbal session was well over 100. Thus, the global nuclear and radiochemical community received a very good picture of the status and achievements of the ASGARD project. Leading role of Europe in the research of reprocessing and dissolution of advanced fuels for Generation IV reactors was clearly confirmed.

1 INTRODUCTION

The ASGARD dissemination, exploitation and networking plan has been designed to complement the main R&D programme. This deliverable stems from ASGARD WP1.3, the main objective of which is to guarantee dissemination of knowledge of the project. To achieve effective dissemination of the information on the project and its outcomes, the International Workshops planned have been attached to two different important international conferences in the field already during drafting the Initial Training Programme (D 1.2.1) at the start of the project.

The First International Workshops was thus organized during the Radchem 2014 conference (<http://www.radchem.cz>). RadChem 2014 – The 17th international Radiochemical Conference – was held in Mariánské Lázně, Czech Republic, from Sunday 11 May 2014 to Friday 16 May 2014. The reason why the ASGARD International Workshop was attached to this conference is that the RadChem series is one of the major conference series in this field. Together with the NRC series (International conference on Nuclear and Radiochemistry), RadChem forms a series of biannual conferences guaranteed by the EuChemS – European Association of Chemical and Molecular Sciences. The conference gathered almost 300 hundred participants from all over the world; all continents were represented.

The ASGARD International Workshop formed a part of a broader session on the Chemistry of Nuclear Fuel Cycle, Christian Ekberg (Chalmers) and Vaclava Havlova (UJV Rez, CZ) were the organisers of the technical programme of this session. The ASGARD workshop comprised two 1.5 hours verbal sessions. Ch. Ekberg with Vaclava Havlova and Mark Sarsfield (NNL) with Vasilij Babain (Khlopin Radium Institute, St. Petersburg, Russia) were the conveners of the two verbal sessions. The verbal part included two invited lectures, one of them delivered by the ASGARD coordinator, Ch. Ekberg, and the second one delivered by Rajamani Natarajan (IGCAR, India), a specialist in carbide fuels. The verbal sessions were complemented by poster presentations that presented topics from both the ASGARD field and the broader field of the Chemistry of Nuclear Fuel Cycle generally.

Detailed programme of both verbal sessions is shown below, the following chapters of this deliverable present abstracts of the presentations delivered. The detailed programme of the poster session follows.

Chemistry of Nuclear Fuel Cycle 1 - Mirror Hall (13:30-15:00)

(1st ASGARD International Workshop)

- Conveners: Prof. Ekberg, Christian; Mrs. Havlová, Václava

time	[id] title	presenter
13:30	[21] Experiences of reprocessing plutonium rich mixed carbide fuels	RAJAMANI, Natarajan
14:00	[162] Dissolution of carbide fuel materials	MAHER, Chris
14:15	[200] Dissolution of Mo-based CERMET fuel: ESI-TOF MS Speciation in nitric acid medium	EBERT, Elena Laura
14:30	[241] Radionuclide distribution in corrosion layers of historic radioactive waste of NPP A1	ANDRIS, Boris
14:45	[174] Study on sorption and diffusion of Sr in crushed and intact basalt and granite investigated in column method	WU, Ming-Chee

Chemistry of Nuclear Fuel Cycle 4 - (13:30-15:00)

(1st ASGARD International Workshop)

- Conveners: Dr. Sarsfield, Mark; Dr. Babain, Vasiliy

time	[id] title	presenter
13:30	[451] ASGARD, a 15 month update	EKBERG, Christian
14:00	[253] New Fluorinated Diluents for Tributylphosphate	BABAIN, Vasiliy
14:15	[277] Dynamic Test of New Extraction System – TODGA in Meta-Nitrobenzotrifluoride	LOGUNOV, Mikhail
14:30	[380] Co-conversion of minor actinides in uranium based oxidic precursors by internal gelation	SCHREINEMACHERS, Christian
14:45	[390] Ceramic Waste Forms for the conditioning of Minor Actinides	NEUMEIER, Stefan

2 VERBAL PRESENTATIONS

2.1 EXPERIENCES OF REPROCESSING PLUTONIUM RICH MIXED CARBIDE FUELS

Natarajan Rajamani (Indira Gandhi Centre for Atomic Energy, India)

The mixed carbide (70 % Pu, 30 % U) spent fuel from the Fast Breeder Test Reactor (FBTR) at Kalpakkam, India is being reprocessed at the CORAL facility since 2003. Several campaigns with progressively increasing burnups and reducing cooling periods have been carried out in this facility. Presently spent fuels with a burn up of 155 GWd/Te with cooling periods as around two years are being reprocessed. The satisfactory operation of this facility has provided valuable inputs for the design of process, equipment and other systems. Sustained operation of critical process equipment such as chopper, dissolver and solvent extraction equipment enabled in the fine tuning of design for reliable operation and easier maintenance. Design optimization for the future plants DFRP and FRP which are under construction for closing the fuel cycle of FBTR and Prototype Fast Breeder Reactor (PFBR) respectively could be carried based on the operating experience with single pin chopper. The apprehension that mixed carbide fuel would be difficult to dissolve and not give a satisfactory solvent extraction performance, is alleviated by the experience of quantitative dissolution and recovery of plutonium. Typical hull losses have been experimentally found to be less than 0.08 % for plutonium. Though some carbide carbon was found to be there in the dissolver solution, it does not affect the solvent extraction performance. The highly oxidative dissolution conditions required for the dissolution of the spent fuel, call for material of construction other than the conventional stainless steel, as its corrosion rate of under such condition is unacceptably high. Alternate material of construction has been identified and deployed for the CORAL dissolver. Inspection of the dissolver after around three years of operation has revealed satisfactory performance. Though three solvent extraction cycles have been provided in the plant, it has been found that the required decontamination could be achieved with a single cycle. Typical decontamination factors of greater than 10^3 for Ru-106 and 10^4 for Cs-137 have been achieved. The recovery of plutonium and uranium are greater than 99.9 % and 99.8 % respectively. The centrifugal extractors have provided extremely satisfactory performance with progressive improvement in the performance in terms of reduced maintenance requirements with incorporation of design changes during the campaigns.

R&D work has been concurrently taken up based on the performance evaluation of the facility for improving the recovery, decontamination factors, economy and reducing the waste volumes. With the computer code PUSEP(Ver-II) developed by the reprocessing group, IGCAR, an innovative extraction flowsheet is formulated to meet the decontamination requirements of both ^{95}Zr and ^{106}Ru while reprocessing fuels with less than two years cooling period. With this code it has been possible to establish the flow

rate controls required for avoiding the third phase formation due to excessive plutonium loading in the solvent phase. Also, it has been found that closer to the stoichiometric requirement of uranous for separation of plutonium from uranium is possible. These findings will substantially reduce the number of solvent extraction cycles and hence the waste volumes. Reduction of solvent waste using vacuum distillation and the removal of dissolved organic by diluent wash using efficient contactors to address the red-oil formation during waste evaporation, are a few R&D activities in progress to improve the plant performance.

Another important offshoot of the operation of the CORAL facility is the development of a variety of hot cell equipment and systems for remote operation and maintenance with least plutonium contamination in the operating area. Based on the satisfactory experience, it is expected that the reprocessing of PFBR spent MOX fuel would not pose a challenging problem as the plutonium content in PFBR is much less (around 25 %).

2.2 DISSOLUTION OF CARBIDE FUEL MATERIALS

Mark Sarsfield, Tamara Griffiths, Katie Bell, Chris Maher (National Nuclear Laboratory, U.K.)

As part of the strategic research agenda for sustainable nuclear energy in Europe [1], carbide fuel is proposed as a potential candidate fuel for sodium cooled fast reactors and is the fuel of choice for gas cooled fast reactors. Carbide fuels have also been demonstrated to achieve high burn-up (> 155 GWd/t) in the sodium cooled Fast Reactor Fuel Reprocessing technology being pursued at the Indira Gandhi Center for Atomic Research (IGCAR), Kalpakkam. There are a number of issues that need to be addressed in the reprocessing of carbide fuel in order to demonstrate a sustainable closed nuclear fuel cycle.

Carbide fuel can be problematic when applying the traditional PUREX reprocessing technology of solvent extraction from a nitric acid solution. The dissolution of uranium carbide (UC) in hot nitric acid can lead to the formation of soluble organic molecules that can interfere with the extraction of uranium and plutonium reducing their extraction and recovery efficiencies. The organics can also lead to emulsions causing difficulties within industrial processes. Even when the U and Pu have been removed from the soluble organics the remaining liquor contains highly radioactive fission products in the presence of organic material that requires volume reducing before immobilising in a glass matrix. The presence of organics can present a safety issue and needs to be effectively managed.

In this paper we present the dissolution results from first titanium carbide (a potential barrier material in GCFRs) and then from unirradiated uranium carbide fast reactor blanket fuel pellets.

The kinetics of dissolution will be discussed together with comments on the organic materials produced and carbon mass balance.

[1] SNETP Strategic Research Agenda May 2009; Strategic Research and Innovation Agenda, Feb 2013.

2.3 DISSOLUTION OF MO-BASED CERMET FUEL: ESI-TOF MS SPECIATION IN NITRIC ACID MEDIUM

Elena Laura Ebert, Meijie Cheng, Michael Steppert, Clemens Walther, Giuseppe Modolo, Dirk Bosbach (Forschungszentrum Jülich GmbH; Leibniz Universität Hannover IRS; Karlsruher Institut für Technologie INE)

The main long term contributors to spent fuel radiotoxicity are plutonium followed by the minor actinides (MA = Np, Am, and Cm). A possibility to reduce the radiotoxic inventory and the footprint of the repository is to separate the most radiotoxic and long-lived elements from spent fuel and to transmute them into nonradioactive elements or elements with a much shorter lifetime. For the transmutation in accelerator-driven systems (ADS) fuels with a high content of Pu and MA are preferred. To increase the burn-up of transuranium elements (TRU) and to reduce the formation of new TRU inert matrix fuels (IMF) [1-3] are favored. These are ceramic substrates or metallic matrices with high thermal conductivity, which are free of uranium and also have small cross sections for reactions with neutrons. The reprocessability of (Pu,MA)-oxide within a metallic ^{92}Mo matrix (CERMET) is under investigation within the EU project ASGARD [4].

Dissolution in nitric acid is the first step in reprocessing. Therefore, detailed knowledge of the speciation of molybdenum in nitric acid medium is crucial on the one hand to understand this dissolution process and on the other hand as a basis for the design of a tailored extraction process. The speciation of molybdenum has been studied intensively in hydrochloric and perchloric acid medium [5,6], but little is known about the speciation in nitric acid medium, especially at high acidities, which are relevant for the dissolution of IMF. The solution species of molybdenum in strongly acidic nitric acid medium need to be extensively characterized and quantified. Therefore, electrospray ionization mass spectrometry, which can probe the stoichiometry and relative abundances of solution species, was applied.

Here, we present new experimental data on the speciation of molybdenum as a function of nitric acid concentration. Isotopically pure ^{98}Mo powder was dissolved in nitric acid and measured with the ALBATROS ESI-TOF [7]. Monomeric, dimeric, trimeric, tetrameric, and pentameric cationic molybdenum species have been detected. Besides

the presence of hexavalent Mo species the spectra show that pentavalent Mo species are present in solution in spite of the oxidizing condition in strong nitric acid.

- [1] Haas, D., et al., *Energ Convers Manage*, 2006. 47: p. 2724-2731.
- [2] Ouvrier, N. and H. Boussier, *Procedia Chemistry*, 2012. 7: p. 322-327.
- [3] Degueldre, C., *J Alloy Comp*, 2007. 444: p. 36-41.
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- [7] T. Bergmann et al., *Rev. Sci. Instrum.*, 1989. 60: p. 347.

2.4 RADIONUCLIDE DISTRIBUTION IN CORROSION LAYERS OF HISTORIC RADIOACTIVE WASTE OF NPP A1

Boris Andris, Milan Žatkulák (VUJE a.s., Trnava, Slovakia)

The radioactive waste management in Slovak Republic complies with the waste acceptance criteria for repository of Slovak Republic. The essential criterion is a declaration of radionuclides disposed in waste packages. The group of 19 limited radionuclides comprises various gamma, beta and alpha radionuclides. The activity of alpha radionuclides is monitored as a total alpha radioactivity, the limit for the total alpha activity per one waste package is 400 Bq.g⁻¹ in average, or a local activity and then the local limit is 4000 Bq.g⁻¹, which is usually applied for the smallest produced unit of a RAW (200 L drum, 60 L drum, or compacted product after high-pressure compacting).

Legacy radioactive wastes treated during D&D of NPP A1 represent greater amount of conditioned RAW disposed in the repository. Nuclear power plant A1 was shutdown after an INES 4 accident in 1977, when one of fuel assemblies had melted down in a reactor channel. Any kind of deactivation process had not been applied since shutdown of NPP and basically all deactivation and pre-decommissioning works have started in 90', and therefore there were lot of possibilities for corrosion of contaminated materials. This corrosion impacts also more than 300 pieces of casks used for spent fuel assemblies storing. Cladding deflections and also deformations caused by incorrect storage conditions caused other cladding defects, which led to massive contamination of spent fuel casks. Outer and inner surface of casks is contaminated mainly by ¹³⁷Cs, ⁹⁰Sr and alpha RN (²⁴¹Am and Pu isotopes). According to the pre-disposal measurements by alpha scanner fragmented casks cannot be disposed without treatment because of exceeding limit for total activity of alpha RN.

The paper describes analyses performed with samples taken from inner surfaces of fragments of spent fuel casks to prove that contamination is only in a corrosion layer and not in core material of casks (carbon steel). This proof would help to enhance waste

management of spent fuel casks. Determination of alpha isotopes by alpha PIPS spectrometry and determination of gamma emitting radionuclides by gamma spectrometry is described. Separation of ^{241}Am and Pu isotopes $^{238,239,240}\text{Pu}$ was carried out by means of extraction chromatography with TRU-resin sorbent. The depth distribution of contamination was performed on the assumption that during electrochemical sampling with identical conditions same amount of iron will be taken. After determination of iron concentrations by AAS it was possible to calculate thickness of corrosion and subsequently calculate depth distribution of radionuclides in several layers of corrosion. These data should help to enhance process of managing legacy metallic RAW from NPP A1.

2.5 STUDY ON SORPTION AND DIFFUSION OF SR IN CRUSHED AND INTACT BASALT AND GRANITE INVESTIGATED IN COLUMN METHOD

Ming-Chee Wu, Chuan-Pin Lee, Shih-Chin Tsai, Tsuey-Lin Tsai, Chun-Hua Pan, Lee-Chung Men (Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan; Nuclear Science and Technology Development Center, National Tsing Hua University, Hsinchu 30013, Taiwan; Chemistry Divisions, Institute of Nuclear Energy Research, Taoyuan 32546, Taiwan)

This study investigates sorption and diffusion of Strontium (Sr) in two potential host rocks (granite from Kinmen Island and basalt from Penghu Island) by using batch and through-diffusion methods in order to establish a reliable safety assessment methodology. These methods were applied to crushed and intact rock samples to investigate the actual geological environment. According to solid-phase analysis, including X-ray diffraction, elemental analysis, auto radiography, and polar microscopy, the sorption component primarily contained iron–magnesium (Fe–Mg) minerals in basalt and granite. Moreover, the distribution coefficient (K_d) of Sr in various concentrations ($\sim 10^{-2}$ – 10^{-7} M) obtained from batch tests indicated a higher sorption capacity in basalt than that in granite because of the 10 % Fe–Mg mineral content. The diffusion of Sr both in granite and basalt reach steady state after 100 days and apparent diffusion coefficient (D_a) were 3.29×10^{-11} m²/s (for Sr in crushed granite), 4.17×10^{-12} m²/s (for Sr in crushed basalt), respectively. However, diffusive result (D_a) of Sr in intact rocks was estimated a lower value than those obtained using crushed rocks. According to the diffusive results in crushed and intact rocks, it showed that major retardation of Sr depended on the microporous structure of tested media, such as decreases of constrictivity (δ) and increases of tortuosity (τ). In fact, the solid/liquid (S/L) ratio decreased as is the case when switching from batch to column experiments and the sorption effect on minerals became even more negligible in retardation of radionuclide migration.

2.6 ASGARD, A 15 MONTH UPDATE

Christian Ekberg, Teodora Retegan, Eva Devisser-Týnová, Janne Wallenius, Mark Sarsfield (Chalmers University of Technology, Gothenburg, Sweden; NRG Petten, The Netherlands; KTH Royal Institute of Technology, Stockholm, Sweden; National Nuclear Laboratory, UK)

The ASGARD project (Advanced for Generation IV reactors: Reprocessing and Dissolution) started in January 2012. Its main goal is to understand and bridge the gap between the fuel reprocessing/separation community currently represented by the ACSEPT project and the fuel manufacturing and irradiation community currently represented by the FAIRFUELS project. The main goal is to investigate the technical challenges posed by nuclear fuels for GEN IV fast reactors, namely: oxide and inert matrix fuels, nitride fuels, and carbide fuels. These three fuel groups also constitute the three scientific domains. In each domain similar issues are addressed concerning the fabrication and recyclability of these novel fuels. Thus different production routes are investigated and these routes are in parallel reviewed by our industrial partners to assess the feasibility of large scale manufacturing. The manufactured fuels are also investigated with respect to chemical and physical characterisation. When a suitable route for uniform production on lab scale has been settled, the possibilities for recycling is addressed by investigating possible dissolution routes. Different fuels have different issues, e.g. in the nitride case the isotopically enriched nitrogen (^{15}N) must be recycled and for the carbides the formation of different organic species produced upon dissolution needs to be addressed.

In parallel to this conversion issues for the possible recycling and separation processes are addressed in collaboration with the separation community. The final aim is to find a convenient route to convert the separated product solutions (U, Pu, MAs) from reprocessing and convert them into materials suitable for fuel production.

Since the ASGARD project deals with considerable amounts of nuclear material, training and education is a vital part of the project. During the course of the project several campaigns will be launched to educate younger scientists in the art of handling radioactive material in a safe and secure way. This will be carried out in collaboration with other relevant EU framework projects such as ACSEPT, SACSESS, FAIRFUELS and CINCH.

2.7 NEW FLUORINATED DILUENTS FOR TRIBUTYLPHOSPHATE

Vasiliy Babain, Andrey Konnikov, Mikhail Logunov, Ivan Tananaev, Mikhail Alyapyshev (Khlopin Radium Institute, St. Petersburg; PA "Mayak", Russia)

The extraction ability of ligands strongly depends on the type of the diluent. The fluorinated compounds provide an opportunity for variation of diluents structure and polarity. Different types of fluorinated compounds (alcohols, ethers and other fluorinated aromatic compounds) were tested as diluents for bidentate organophosphorus compounds, chlorinated cobalt dicarbollide and crown ethers. It was shown that in some cases using of polar diluents allowed to increase extraction ability of studied ligands. The main goal of the present work was to study the influence of new fluorinated diluents (fluorinated ethers and formals of fluorinated alcohols) on extraction ability of tributylphosphate (TBP) toward nitric acid and metals. It was found that fluorinated ethers and formals of fluorinated alcohols which contained in their structure $-CF_2H$ groups decrease the extraction ability of TBP like in the case of chloroform. Both classes of studied compounds are highly resistant to gamma-radiolysis in the presence of nitric acid.

From the technological point of view fluorinated diluents are very promising as they allow receiving of concentrated uranium solutions.

2.8 DYNAMIC TEST OF NEW EXTRACTION SYSTEM – TODGA IN META-NITROBENZOTRIFLUORIDE

Mikhail Logunov, Alexander Mashkin, Yuriy Voroshilov, V.S. Ermolin, R.N. Khasanov, Vasiliy Babain, M.Y. Alyapyshev, E.V. Kenf (PA "Mayak"; Khlopin Radium Institute, St. Petersburg, Russia)

Tetraoctyldiamide of diglycolic acid – (TODGA) is actively studied as promising extractant for actinide separation. Extraction properties of TODGA in various diluents were studied. It was shown, that maximal metal concentration in the organic phase can be achieved when meta-nitrobenzotrifluoride (F-3) was used as a diluents.

Actinide and lanthanide extraction from HLW by 0.2 M TODGA in F-3 was tested in dynamic test. Simulated HLW – PUREX process raffinate with high concentration of lanthanides was used as a feed solution. Extraction mock-up has worked more 110 hours, about 5.5 L of feed solution was used, solvent had more two cycles.

High efficiency of actinide (americium, thorium, uranium) and lanthanides extraction (more 99.9 %) was demonstrated. Zirconium and molybdenum partly remained in raffinate. The distribution of components between the stages of flow sheets was studied on the base of stage sampling. Lanthanide extraction is in the raw: $La < Ce < Nd < Gd <$

Sm < Eu < Y. Extraction of americium is very close to such lanthanides as Nd and Gd. These trends are in good accordance with literature data for TODGA – dodecane solvent.

The loss of TODGA with raffinate is about 10 mg/L. It is noted that Tc has not been fully stripped from solvent. TODGA – metanitrobenzotrifluoride is very promising solvent for HLW processing

2.9 CO-CONVERSION OF MINOR ACTINIDES IN URANIUM BASED OXIDIC PRECURSORS BY INTERNAL GELATION

Christian Schreinemachers, Andrey Bukaemskiy, Martina Klinkenberg, Stefan Neumeier, Giuseppe Modolo, Dirk Bosbach (Forschungszentrum Jülich GmbH, Germany)

In the context of advanced nuclear fuel cycles including partitioning and transmutation (P&T), actinide co-conversion processes, such as sol-gel routes, play an important role to close the fuel cycle. During the heterogeneous recycling of minor actinides, oxidic materials containing uranium as main matrix are used as innovative nuclear fuels.

Advanced fuel concepts replace the conventionally used pellets by particles (Sphere-pac or Vipac fuel) [1]. Particle fuels show good swelling behaviour and can easily be fabricated. A suitable dustless preparation method is the internal gelation. This wet chemical method is a conversion process which transforms an aqueous colloidal solution sol into a solid gel. The internal gelation method was used for the particle synthesis during this work. Acid deficient uranyl nitrate (ADUN) and neodymium nitrate solutions were used as precursor, while urea acts as complexing agent and hexamethylenetetramine (HMTA) as gelification agent [2]. Pure uranium oxide and uranium / neodymium oxide microspheres with a variable content of Nd (5 % - 40 %) were fabricated in the framework of the EU project ASGARD [3]. Neodymium is used as surrogate for trivalent actinides, such as americium.

Mass- and size- characteristics of the prepared particles were studied. TG/DSC analyses were performed to investigate the thermal behavior. Finally the particles were thermally treated under reducing conditions at 1300 °C and 1600 °C. The products were investigated by the use of SEM/EDX and X-ray powder diffraction (XRD). Lattice parameter calculations were performed using the XRD data.

The particles, treated at 1300 °C showed only one cubic phase, for the whole observed $\chi(\text{Nd})$ range. The expected linear behaviour according to Vegard's rule was observed for compositions $\chi(\text{Nd}) \leq 27.59\%$. The thermal treatment of the particles with compositions $\chi(\text{Nd}) \geq 33.49\%$ was repeated for 5 hours with a higher temperature (1600 °C). The expected linear trend could be confirmed and it could be demonstrated that equilibrium solid solutions of the $\text{UO}_2 / \text{Nd}_2\text{O}_3$ system can be fabricated with the internal gelation synthesizing route.

References

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2.10 CERAMIC WASTE FORMS FOR THE CONDITIONING OF MINOR ACTINIDES

Stefan Neumeier, Andrey Bukaemskiy, Felix Brandt, Sarah Finkeldei, Yulia Arinicheva, Julia Heuser, Giuseppe Modolo, Dirk Bosbach (Forschungszentrum Jülich GmbH, Germany)

The disposal of high level radioactive waste is one of the most pressing and demanding challenges. With respect to long-term safety aspects of geological disposal, the minor actinides (MA) such as Am, Cm and Np and long-lived fission products such as ^{35}Cl , ^{135}Cs , ^{79}Se , ^{90}Sr and ^{129}I may be of particular concern due to their long half-lives, their high radiotoxicity and mobility in a repository system, respectively. Ceramic waste forms for the immobilisation of these radionuclides have been investigated extensively in the last decades since they seem to exhibit certain advantages compared to other waste forms (incl. borosilicate glasses and spent fuel) such as high loadings and chemical durability. Currently, most on-going nuclear waste management strategies do not include ceramic waste forms. However, it is still important to study this option, e.g. with respect to specific waste streams and certain constraints regarding deep geological disposal.

In the present communication we report on the research program in Jülich regarding ceramic waste forms for the conditioning of MA. It is based on fundamental science and follows an integral approach that covers the separation of elements or elemental groups with similar chemical properties from a waste stream by liquid/liquid extraction as well as the immobilisation in ceramic materials as hosts. The research focuses on single phase ceramics such as Monazites and Zirconates with Pyrochlore structure and includes:

- 1) Development and optimisation of synthesis routes suitable for immobilisation of MA into ceramic waste forms and the handling of radionuclides such as sol-gel route, hydrothermal synthesis and co-precipitation,
- 2) structural and microstructural characterisation using state of the art spectroscopic (Raman, TRLFS, EXAFS), diffraction (powder and single crystal XRD) [3] and microscopic (SEM, FIB/TEM) techniques,
- 3) determination of thermodynamic data (calorimetry) and reactivity under conditions relevant to geological disposal, in particular with respect to leaching/corrosion in aqueous environments (static & dynamic dissolution experiments on powders and pellets) as well as

4) studies on radiation damages (irradiation with α -particles and/or heavy ions, and incorporation of short-lived actinides such as ^{238}Pu , ^{241}Am or ^{244}Cm).

Finally, a fundamental understanding of the long-term behaviour on the atomic scale will help to improve the scientific basis for the safety case of deep geological disposal concepts using ceramic materials.

3 POSTER SESSION

The detailed programme of the poster session is shown below. Abstracts of all the presentations are available from the Booklet of Abstracts available at the conference web at <http://www.radchem.cz>.

Poster Session - Chemistry of Nuclear Fuel Cycle / 1st ASGARD International Workshop -

(17:30-18:45)

[id] title	presenter	board
[60] A Study of Nitrogen Oxides Released into the Gas Phase During Uranium Nitride Dissolution in Nitric Acid	VOSKRESENSKAYA, Yulia	
[61] A Study of Nitrous Oxide Absorption in Aqueous Solutions	VOSKRESENSKAYA, Yulia	
[168] Ammonium Nitrate and Chelating Agents Decomposition in Autoclave During ILW Processing	MISHINA, Nadezhda	
[234] About choice of interface language for the solution of problems of mathematical modeling of chemical and technological processes	GROMOV, Oleg	
[306] Behavior Ca, Sr, Ba tungstates in alkali chloride melts LiCl-KCl	POTANINA, Ekaterina	
[7] Cementation of Liquid Radioactive Waste with High Content of Borate Salts	Горбунова, Ольга	
[8] Cementation of the Solid Radioactive Waste with Polymer-Cement Solutions Using the Method of Impregnation	GORBUNOVA, Olga	
[295] Corrosion and Dissolution of Intermetallic Compounds UPd ₃ and URu ₃ in 0.5-6.0 M HNO ₃	ZAVARZIN, Semen	
[290] Cesium containing β -tridymite and maricite type phosphate ceramics: synthesis, structure and thermophysical properties	KORCHEMKIN, Ivan	
[179] Change of hydro-geological and geochemical conditions of rocks of a near zone of storages	VESELOV, Evgeny	
[211] Characterization of Czech bentonites B75 and S65 and montmorillonite SAz-1: determination of acid/base titration curves and CEC	ADAM, Rostislav	
[2] Decontamination of Low Radioactive Liquid Waste from Oils and Petrochemicals Using UV Radiation at NPPs	KULEMIN, Vladimir	
[126] Diffusion of Selenium in Crystalline Rock	IKONEN, Jussi	
[346] Development and testing of electromigration technique to study radionuclide transport in compacted bentonite	HOFMANOVÁ, Eva	
[201] Dissolution behavior of MgO based inert matrix fuel for the transmutation of plutonium and minor actinides	EBERT, Elena Laura	
[199] Dissolution studies on molybdenum-based inert matrix fuel targets for the transmutation of minor actinides	EBERT, Elena Laura	
[296] Electrochemical dissolution of U – 5 mass. % Zr alloy, steel 316 and zircalloy in nitric acid	NIKITIN, Svyatoslav	
[344] Explosion hazards of mixtures of reductants and oxidants used in reprocessing SNF	RODIN, Alexey	
[225] Immobilization of long-lived iodine after incorporation into apatite and layered double hydroxide matrices	TORAPAVA, Natallia	
[381] Investigations of the uranyl and neodymium(III) adsorption behavior on ion exchange resins for the weak-acid resin process	SCHREINEMACHERS, Christian	

[381] Investigations of the uranyl and neodymium(III) adsorption behavior on ion exchange resins for the weak-acid resin process	SCHREINEMACHERS, Christian	
[387] Long term diffusion experiment (LTD): Analyses of ³ H, ²² Na and ¹³⁴ Cs diffusion in crystalline rock under real deep geological repository conditions	HAVLOVÁ, Václava	
[327] Migration parameter studies of Czech granitic rocks determined by electromigration methods	VEČERNÍK, Petr	
[274] Plutonium Salt-Free Stripping Agents - Advantages and Disadvantages	MURZIN, Andrey	
[323] Parametric safety study of a comprehensive model of deep geological repository in the Czech Republic	TRPKOŠOVÁ, Dagmar	
[144] Preliminary Research on Monitoring Uranium Fluoride Volatility Process by Fourier Transform Infrared Spectroscopy	SUN, Lixin	
[3] Purification of Isotopically Enriched ⁹² Mo from Reprocessing of CerMet Mo-based Transmutation Fuel	MAREŠ, Kamil Vavřinec	
[75] Reprocessing of Carbide Fuels in Molten Chlorides	BIKBAJEVA, Zana	
[263] Radiation-induced modifications on physico-chemical properties of diluted nitric acid solutions within advanced Spent Nuclear Fuel reprocessing	MOSSINI, Eros	
[142] Research on pyrohydrolysis of fluoride salts	LIU, Yuxia ZHANG, Lan	
[178] Statistical Analysis Methods Application for the Determination of the Radionuclide Migration in the Near-Surface Storage Facilities	VESELOVA, Elena	
[104] Selectivity for Actinides with N,N'-Diethyl-N,N'-Ditolyl-2,9-Diamide-1,10-Phenanthroline Ligand: A Hard-Soft Donor Combined Strategy	SHI, Weiqun	
[153] Sensitivity analysis of geological parameters influencing a solute transport from a deep repository of spent nuclear fuel	CHUDOBA, Josef	
[115] Sorption of americium(III) ions on the bentonite of the Volclay type or red clay	OSZCZAK, Agata	
[191] Sorption of radionuclides in the environment of uranium hexafluoride	GROMOV, Oleg	
[372] Stability of silica-supported monoamide resins with selectivity to U(IV) and U(VI) against γ -ray irradiation in HNO ₃	NOGAMI, Masanobu	
[259] Standard thermodynamic functions and conditional electrochemical potentials of hypothetical crystalline U(II) and Pu(II) chlorides in LiCl-KCl melt	POLYAKOV, Evgeny BARYSHEVA, Nina	
[216] Steady-state model of carbon dioxide absorption as a part of mathematical description of on-site nuclear fuel cycle	TKACHENKO, Vladimir	
[244] Study of ⁸⁵ Sr transport through crushed granite in the presence of colloids particles	VIDENSKÁ, Kateřina	
[98] Study of carbon dioxide solubility in nitric acid and metal nitrates solutions for estimation of carbon-14 distribution between gas phase and solution during dissolution of spent nuclear fuel	SHUDEGOVA, Olga	
[79] The Effect of pH and Ionic Strength on the Dissolution of TcO ₂ in Hyperalkaline Environments	EVANS, Nicholas	
[373] Technological Verification of Fluoride Volatility Method	ŠKAROHLÍD, Jan	
[233] The process of high-temperature saturation of sorbents lived radio nuclides from solutions of highly active waste and converted into mineral like matrices	KALENOVA, Maya ANANIEV, Alex GROMOV, Oleg	
[147] Thorium based Molten Salt Fuel Cycle	LI, Qingnuan	

[0] Using Basalt Containers for Storage of Glassed Radioactive Waste	KULEMIN, Vladimir	
[388] Use of 3H for characterisation of crystalline rock migration properties	HAVLOVÁ, Václava	
[158] neptunium extraction behavior in the plutonium purification process	YE, GuoAn	
[164] neptunium extraction behavior in the plutonium purification process	YE, GuoAn	

4 CONCLUSIONS

As foreseen already during drafting the Initial Training Programme (D 1.2.1) at the start of the project, the First International Workshops was organized during the Radchem 2014 conference (the 17th International conference on Nuclear- and Radiochemistry) in May 2014 in Marianske Lazne, Czech Republic. Christian Ekberg (Chalmers) and Vaclava Havlova (UJV Rez, CZ) were the session organisers, Ch. Ekberg with Vaclava Havlova and Mark Sarsfield (NNL) with Vasiliy Babain (Khlopin Radium Institute, St. Petersburg, Russia) were the conveners of the two verbal parts of the session. The workshop comprised two 1.5 hours verbal sessions and a poster session. The verbal part included two invited lectures, one of them delivered by the ASGARD coordinator, Ch. Ekberg, and the second one delivered by Rajamani Natarajan (BARC, India), a specialist in carbide fuels. The verbal sessions were complemented by poster presentations that presented broader topics from both the ASGARD field and the field of the Chemistry of Nuclear Fuel Cycle generally.

Both the verbal and poster parts of the First International Workshops were very well attended – the number of participants at the verbal session was well over 100. Thus, the global nuclear and radiochemical community received a very good picture of the status and achievements of the ASGARD project. Leading role of Europe in the research of reprocessing and dissolution of advanced fuels for Generation IV reactors was clearly confirmed.