

# SYMPOSIUM ET15

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Scientific Basis for Nuclear Waste Management  
November 26 - November 29, 2018

## Symposium Organizers

Lena Evins, Svensk Kärnbränslehantering AB  
Neil Hyatt, University of Sheffield  
John McCloy, Washington State University  
Wooyong Um, Pohang University of Science and Technology

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\* Invited Paper

SESSION ET15.01: Perspectives on Strategy, Risk and Uncertainty in Radioactive Waste Management  
Session Chairs: John McCloy and Wooyong Um  
Monday Morning, November 26, 2018  
Hynes, Level 3, Room 308

**8:30 AM \*ET15.01.01**

**An Integrated Strategy for Defense Waste Immobilization** [Kevin Fox](#); Savannah River Nat Lab, Aiken, South Carolina, United States.

The US Department of Energy is actively retrieving, treating, and immobilizing defense nuclear wastes at multiple sites. The Savannah River Site employs borosilicate glass and saltstone to immobilize high-level and low-activity wastes, respectively. The Hanford Site will use borosilicate glass for both of these waste streams. An integrated strategy is needed to guide the multiple unit operations necessary for the success of these operations. This strategy must bring together aspects of the feed streams, requirements of the final product, and manufacturing technologies in a manner that maximizes both waste throughput and operational flexibility. DOE's waste immobilization efforts will take decades to complete; therefore, advances in technology are needed to reduce mission schedule and cost. Recent advances include improved property/composition predictive models for glass waste forms, higher waste loading concentrations in cementitious waste forms, accelerated salt waste decontamination, reduced need for feed pretreatment, facility lifetime extension, and more economical disposal systems. Each of these advancements must consider impacts to the overall flow sheet, both up- and down-stream, to maintain an integrated processing strategy.

**9:00 AM ET15.01.02**

**What Has Been the Evolution and Structure of the Scientific Basis for Nuclear Waste Management?** [Francois Diaz-Maurin](#)<sup>1,2</sup>, Hilary C. Sun<sup>3</sup> and Rodney C. Ewing<sup>1,4</sup>; <sup>1</sup>Center for International Security and Cooperation (CISAC), Stanford University, Stanford, California, United States; <sup>2</sup>Amphos 21 Consulting S.L., Barcelona, Spain; <sup>3</sup>Computer Science Department, Stanford University, Stanford, California, United States; <sup>4</sup>Department of Geological Sciences, Stanford University, Stanford, California, United States.

Nuclear waste management is at the interface between the technologies of the nuclear fuel cycle and the natural hydrologic and geochemical cycles of geologic repositories. Yet, despite its clear interdisciplinary scope, nuclear waste management, as practiced, is not a unified scientific field. Subdisciplines continue to work in relative isolation from one another: materials science dealing with the immobilization of nuclear waste; engineering science dealing with the design of the waste package and engineered barriers; geoscience dealing with the long-term behavior of host rocks and the hydrology; health science dealing with the effects of radiation; social sciences dealing with the issues of trust, risk and ethics. Each one of these fields is just one way of looking at the same issues. Defining a unified scientific basis of nuclear waste management requires working at the interfaces of these subdisciplines. Based on a comprehensive review and analysis of the scholarly and scientific literature, we discuss the evolution and structure of research in nuclear waste management between 1940 and 2017. We performed a corpus analysis and a citation network analysis based on the Elsevier B.V.'s Scopus® database aiming to identify the main themes, methods and authors for each one of the relevant disciplines dealing with nuclear waste management issues. We also analyzed the level of interdisciplinarity for each of the subdisciplines by exploring their citation patterns and impact on the other subdisciplines. Using the proceedings published on the MRS Online Proceedings Library Archive, we also analyzed papers in the MRS symposia "Scientific Basis for Nuclear Waste Management" held since 1978 as a reference case and compare its structure and evolution with those of the main academic corpus. Based on this study, we suggest the framework of the scientific basis for nuclear waste management as a unified discipline.

**9:15 AM ET15.01.03**

**Uncertainty in Safety Assessments of Geological Repositories—Quantitative Performance Assessment vs the Safety Case Approach** [Francois Diaz-Maurin](#)<sup>1,2</sup> and Rodney C. Ewing<sup>1,3</sup>; <sup>1</sup>Center for International Security and Cooperation (CISAC), Stanford University, Stanford, California, United States; <sup>2</sup>Amphos 21 Consulting S.L., Barcelona, Spain; <sup>3</sup>Department of Geological Sciences, Stanford University, Stanford, California, United States.

Quantification of uncertainty is one of the key issues in analyzing the safety of geological repositories for the disposal of radioactive waste. In the U.S., quantitative performance assessments have been adopted as the standard method used in repository licensing. Quantitative performance assessment relies on the quantification of both stochastic (i.e., aleatory) and subjective (i.e., epistemic) uncertainties on parameters and models used as inputs to the models for the total system performance analysis. In this approach, both the random variations of aleatory uncertainties and the subjective variations of epistemic uncertainties are treated with the same mathematical methodology. Yet, although these "treatments" can be mathematically computed, the value of quantitative performance assessments has been challenged. In repository design, epistemic uncertainties arise when projecting coupled geophysical and geochemical processes involved over large scales. These uncertainties can be qualitatively characterized by expert judgment, but they limit the ability of the analysts to predict—thus quantify—the long-term behavior of the repository because of the unavoidable lack of knowledge about future geological conditions. Because of the large uncertainties in such assessments, one has to expect public skepticism of statements that a repository is "safe enough."

The “safety case” concept has been proposed as an appropriate method for analyzing the safety of a geologic repository. The safety case approach relies on the quantification of parameter variations and on scenarios that capture uncertainties in conceptual models and changing boundary conditions. Similar uncertainty quantification is still performed for stochastic parameter variations and uncertainties in projection models. But, the quantification of epistemic uncertainties will only be performed for guiding a qualitative argument (i.e., a “safety case”) about the possible long-term behavior of the repository. This hybrid approach to the safety analysis of geologic repositories thus seeks to address uncertainties for which the quantification poses epistemological constraints on the safety analysis of geologic repositories.

We discuss the use of uncertainty quantification in the safety case approach. Based on the methods of value of information and sensitivity auditing, we show simple examples of how to incorporate both quantitative and qualitative judgements in a performance assessment. In doing so, we seek to develop an analytical framework that better acknowledges the existence of unavoidable uncertainties in the assessment of the long-term performance of geologic repositories and better defines the safety case concept for its introduction in the US repository development program.

#### 9:30 AM \*ET15.01.04

**Reducing Risk and Uncertainty Associated with Nuclear Waste Processing and Disposal—A Hanford Tank Waste Case Study** Carolyn I. Pearce<sup>1</sup>, David K. Peeler<sup>1</sup>, Rolf Sjöblom<sup>2</sup>, Mark B. Triplett<sup>1</sup>, Kirk J. Cantrell<sup>1</sup>, Robert C. Moore<sup>1</sup>, Michael J. Schweiger<sup>1</sup>, Vicky L. Freedman<sup>1</sup>, Matthew S. Fountain<sup>1</sup>, Sue B. Clark<sup>1</sup> and Albert Kruger<sup>3</sup>; <sup>1</sup>Pacific Northwest National Laboratory, Richland, Washington, United States; <sup>2</sup>Luleå University of Technology, Luleå, Sweden; <sup>3</sup>U.S. Department of Energy—Office of River Protection, Richland, Washington, United States.

The Department of Energy’s Environmental Management cleanup effort is focused on developing and implementing innovative and high impact technologies and solutions that positively impact the overall mission lifecycle by: (1) reducing lifecycle costs; (2) accelerating lifecycle schedules; (3) mitigating mission uncertainties, vulnerabilities, and risks; and (4) minimizing the mortgage associated with long-term, post-closure and post-completion stewardship. Pacific Northwest National Laboratory and its partnering institutions, are focused on reducing risk and uncertainty across the integrated flowsheet which includes safe waste storage, retrieval, pretreatment, immobilization, disposal, and tank closure. In this presentation, an overview of the major Hanford flowsheet unit operations will be provided and examples of specific projects focused on reducing risks and uncertainties will be explored. For example, a key issue of Hanford tank waste processing and disposal is that, although radionuclides (e.g., technetium) drive the disposal risk for the low-activity flowsheet, the presence of “benign” elements (e.g., aluminum) dictate processing limits or rates in both retrieval and pretreatment unit operations and have other potential downstream negative impacts. Thus, safe, cost-effective, and efficient waste processing depends on a fundamental understanding of aluminum chemistry in high ionic strength, highly alkaline solutions where water activity is low. Once the waste has been retrieved, processed, and immobilized, controlling the behavior of risk driving elements (e.g., Tc and/or I for low-activity waste) in the waste form and the environment becomes essential for waste form disposal or tank closure.

With respect to low-activity waste form disposal, material solutions must demonstrate that the risk driving radioactive elements will be contained in a manner wholly consistent with statutory requirements. Modelling future performance remains a challenge for performance assessment (PA) formalism. An appealing option is to perform an inverse PA (IPA) and look far into the past. Archeological artifacts, analogous to wastefrom materials (i.e. glass and concrete) that have been left by our ancestors and exposed to the environment for thousands of years can be used to check for comprehensiveness as well as to validate and refine predicted wastefrom durability. An IPA describes the features, events and processes that have influenced the corrosion of a material over time and can help establish the most likely scenarios that should be included in PA for the future. An IPA for ancient glass from a hillfort at Broborg, Sweden (ca. 400-575 AD), used to fortify the fort walls will also be one of the key focal points of this presentation.

#### 10:00 AM BREAK

SESSION ET15.02: Ceramics for the Safe and Secure Immobilization of Actinide Wastes  
Session Chairs: Clémence Gausse and Daniel Gregg  
Monday Morning, November 26, 2018  
Hynes, Level 3, Room 308

#### 10:30 AM ET15.02.01

**Cerium Substitution in Zirconolite Ceramic Waste Form** S. K. Sundaram and Braeden M. Clark; Alfred University, Alfred, New York, United States.

Compounds with the formulae  $\text{CaZr}_{1-x}\text{Ce}_x\text{Ti}_2\text{O}_7$  with  $x = 0.1-0.5$  were synthesized by solid state reaction. Cerium was used as a surrogate for actinide elements. Sintering was carried out via spark plasma sintering (SPS), during which the perovskite phase ( $\text{Ca}_{0.4}\text{Ce}_{0.4}\text{TiO}_3$ ) was stabilized due to the reducing conditions of this technique. A transition from the 2M polymorph to the 4M polymorph (expanded unit cell due to cation ordering) in zirconolite was observed with increasing cerium content. In 2M-zirconolite, trivalent Ce co-substituted on both the Ca and Zr sites, while both trivalent (Ca and Zr sites) and tetravalent (Zr sites) Ce substituted into 4M-zirconolite. Conversion of 4M-zirconolite to perovskite and 2M-zirconolite occurred during the SPS process due to the reducing environment. This was due to the reduction of  $\text{Ce}^{4+}$  into  $\text{Ce}^{3+}$ , where the 2M-zirconolite was charge balanced by co-substitution of  $\text{Ce}^{3+}$  on the Ca and Zr sites and the perovskite formed due to the partial reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  leaving excess Ca and Ti to react with the trivalent Ce to form perovskite. The presence of both tri- and tetravalent Ce, contrary to formulation, was confirmed using X-ray absorption near edge spectroscopy (XANES), suggesting substitution on both Ca and Zr sites. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) revealed that the 2M polymorph was dilute in Ce content in comparison to the 4M-zirconolite. High temperature X-ray diffraction (HTXRD) was used to detail the kinetics of perovskite to zirconolite transition. It was found that  $\text{CaCeTi}_2\text{O}_7$  (cubic pyrochlore) forms as an intermediate phase during the transformation.  $\text{CaCeTi}_2\text{O}_7$  formed as an intermediate phase up until 1300°C, and 4M-zirconolite began at 1350°C. The re-oxidation of  $\text{Ce}^{3+}$  and  $\text{Ti}^{3+}$  to their tetravalent states allowed the original phase assemblage to be attained. The transformation to 4M-zirconolite was slow, but complete conversion to the original phase assemblage was achieved with a 24h heat treatment in air. Our results showed that a transition from 2M- to 4M-zirconolite occurred with increasing Ce content and the transition could be controlled by adjusting the  $P_{\text{O}_2}$  and the heat treatment temperature.

#### 10:45 AM ET15.02.02

**Immobilisation of Chlorine Contaminated Plutonium Residues in a Zirconolite-Glass Ceramic** Neil Hyatt<sup>2</sup>, Stephanie Thornber<sup>2, 1</sup>, Lucy Mottram<sup>2</sup>, Martin Stennett<sup>2</sup> and Amber Mason<sup>2</sup>; <sup>1</sup>National Nuclear Laboratory, Sellafield, United Kingdom; <sup>2</sup>The University of Sheffield, Sheffield, United Kingdom.

The immobilisation and disposal of fissile materials from civil and defence nuclear programmes requires compatible, passively safe and proliferation resistant wasteforms. In this study, we demonstrate the application of an albite glass – zirconolite ceramic material for immobilisation of chloride contaminated plutonium oxide residues in the United Kingdom. The chlorine solubility limit in the albite glass phase was determined to be  $1.0 \pm 0.1$  wt. %, above the maximum envisaged chlorine inventory of 0.7 wt. %. Cl K-edge of X-ray absorption Near Edge Spectroscopy (XANES) was exploited to confirm

partitioning of Cl to the glass phase, speciated as the chloride anion, with exsolution of crystalline NaCl above the chlorine solubility limit. Combinatorial fitting of Cl XANES data, utilising a library of chemically plausible reference spectra, demonstrated the association of Cl with Na and Ca modifier cations, with environments characteristic of the aluminosilicate chloride minerals. The partitioning of Ce, as a Pu analogue, within the glass-ceramic was not adversely impacted by incorporation of Cl. The significance of this research is in demonstrating the compatibility of the glass-ceramic wasteform toward Cl solubility at the expected incorporation rate, below the determined solubility limit.

#### 11:00 AM ET15.02.03

**Synthesis and Sintering of Th-Based Cheralites from Rhabdophane-Type Precursors** Danwen Qin, Adel Mesbah, Stéphanie Szenknect, Nicolas Dacheux and Nicolas Clavier; ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Bagnols/Cèze, France.

Monazite-type ceramic wasteforms have been investigated for long for the specific conditioning of actinides. Indeed, they are known to provide high weight loadings in actinides, good sintering capability and strong resistance to aqueous corrosion and radiation damages. The incorporation of tetravalent actinides generally processes through coupled substitutions, leading to monazite-cheralite solid solutions with the general formula  $M^{II}_xAn^{IV}_xLn_{1-2x}PO_4$ . Nevertheless, the preparation of such samples was mainly achieved using dry chemistry methods, which can lead to heterogeneities in the solid and to the degradation of the properties of interest.

The incorporation of thorium in  $Ca_xTh_xNd_{1-2x}PO_4$  solid solutions ( $0 \leq x \leq 0.15$ ) was then investigated through wet chemistry processes based on the initial precipitation of rhabdophane-type precursors. A multiparametric study was undertaken to specify the operating conditions (starting stoichiometry, temperature, heating time) leading to single-phase  $Ca_xTh_xLn_{1-2x}PO_4 \cdot nH_2O$  powdered samples. Particularly, the excess of calcium appeared to be a prevailing factor, with a suggested initial Ca:Th ratio of 10:1. Similarly, the recommended heating time should exceed 4 days while the optimal temperature of synthesis lies around 110 °C.

The transformation of rhabdophane-type precursors into highly durable  $Ca_xTh_xLn_{1-2x}PO_4$  cheralites was further studied. TG analyses showed that the conversion first proceeded with a dehydration step occurring around 210-220°C, this temperature increasing linearly with the thorium content in the sample. Additionally, the phase transition between anhydrous rhabdophane and cheralite was determined by dilatometric measurements and varied from 700°C to about 820°C depending on the chemical composition considered. After heating at high temperature (i.e. typically at 1100°C), XRD analysis revealed the formation of single phase cheralite-monazite solid solutions without any trace of side products such as  $\alpha-ThP_2O_7$  or  $Th_4(PO_4)_4P_2O_7$ .

Finally, first insights concerning the sintering of  $Ca_xTh_xLn_{1-2x}PO_4$  wasteforms directly from the shaping and heating of low-temperature precursors were obtained. Full densification (i.e. > 95%TD) was achieved after 4 hours of heating at 1400°C for all the samples investigated. Nevertheless, the chemical composition was found to strongly influence the sintering process and the final microstructure. Indeed, thorium incorporation was found to slightly enhance the densification temperature determined by dilatometry, while the presence of small amounts of calcium in excess can drastically increase the final grain size.

#### 11:15 AM ET15.02.04

**Microstructure Control of  $Gd_2Ti_2O_7$  Pyrochlore by Spark Plasma Sintering and Its Dissolution Behavior** Yachun Wang and Jie Lian; Rensselaer Polytechnic Institute, Troy, New York, United States.

Pyrochlore, with a chemical composition of  $A_2B_2O_7$  (A and B are metals), shows great potentials as advanced waste forms for effective nuclear waste immobilization due to its capability to incorporate wide range of radionuclides, exceptional radiation tolerance, and desirable chemical stability. Those properties can be profoundly affected by microstructure features. However, the effect of grain size, particularly of nanometer length scale, on the dissolution behavior of pyrochlore has not been studied yet. This study explored the connection between grain size of  $Gd_2Ti_2O_7$ , a type of Pyrochlore, and its chemical durability in acidic condition. Specifically, bulk  $Gd_2Ti_2O_7$  pellets with different grain sizes were fabricated by spark plasma sintering (SPS) and post sintering annealing. Subsequently, we focused on the dissolution behavior of different grain sized  $Gd_2Ti_2O_7$  pellet under aqueous condition (with isotope tracer ( $^{18}O$ ), at high temperature (90 °C) and acidic conditions (PH=1 and 2)). Dissolution rate of Gd and Ti were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Elements depth profile in dissolution alternated layer probed by secondary ion mass spectrometry (SIMS) showed the formation of a surface passivation layer enriched by  $O^{18}$ , providing new insights into the dissolution mechanism of  $Gd_2Ti_2O_7$ . The results highlighted the great potential for nano grain sized  $Gd_2Ti_2O_7$  with enhanced dissolution resistance for nuclear waste immobilizations.

SESSION ET15.03: Rational Design, Synthesis and Modelling of Framework Architectures for Radionuclide Sequestration

Session Chairs: Theo Cordara and Josef Matyas

Monday Afternoon, November 26, 2018

Hynes, Level 3, Room 308

#### 1:30 PM \*ET15.03.01

**New Engineered Forms of Zeolites for the Selective Removal of Cs and Sr from Effluent** Joe Hriljac, Ryan George, Mohamed Karmaoui and Tzu Yu Chen; University of Birmingham, Birmingham, United Kingdom.

Aluminosilicate zeolites, such as clinoptilolite and chabazite, are the traditional inorganic materials for removal of water-soluble radioactive cations such as  $^{137}Cs^+$  and  $^{90}Sr^{2+}$ . In addition to the need for excellent selective ion exchange properties, the materials need to be available in a physical form that is suitable for use in a gravity flow column. Use of very fine-grained powders will often cause problems due to a slow liquid flow causing blockage. Synthetic zeolites and other ion exchangers such as the titanosilicate CST used in IONSIV crystallise as submicron to a few micron sized powders. Therefore they are unsuitable for column use unless produced in an engineered form such as IONSIV R9120-B where the CST is blended with an inert binder material into a pellet form. We are investigating alternative means of producing new forms of ion exchange materials and in this talk I will discuss two of those. The first is the production of zeolite monoliths via 3D printing methods for use in traditional gravity flow columns. The second is producing magnetized systems which can be separated from effluent via magnetic trapping after use.

#### 2:00 PM ET15.03.02

**Sequestration of Radionuclides in Metal-Organic Frameworks from First Principles Calculations** Shubham Pandey<sup>1</sup>, Zhilin Jia<sup>1</sup>, Brian Demaske<sup>1</sup>, Ekaterina Dolgoplova<sup>2</sup>, Natalia Shustova<sup>2</sup>, Wahyu Setyawan<sup>3</sup>, Chuck J. Henager<sup>3</sup> and Simon R. Phillpot<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States; <sup>2</sup>Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States; <sup>3</sup>Nuclear Sciences Division, Pacific Northwest National Laboratory, Richland, Washington, United States.

Metal-organic frameworks (MOFs) could lead to development of novel class of hybrid materials emerging as potential wasteforms to sequester nuclear

waste. Density Functional Theory (DFT) calculations were used to determine the favorability of substitution of relevant radionuclides in various parent MOF clusters. The radionuclides of interest are U, Th, Am, Cm and Tc. Results from various levels of treatment of the exchange-correlation functional are compared to establish the robustness of the results. We find that Tc incorporation is energetically well-favored in all of the MOFs considered. The electronic structures of both the actinide-based MOFs and radionuclide substituted MOFs are analyzed and correlated with experimental data. We also study the effect of the electronic properties tunability as a function of transition metal incorporation.

This work was supported by the Center for Hierarchical Waste Form Materials (CHWM), an Energy Frontier Research Center (EFRC) funded by the United States Department of Energy Office of Basic Energy Sciences through Award DESC0016574.

### 2:15 PM ET15.03.03

**Synthesis and Ion Exchange Properties of Zirconogermanates** Ryan George and Joe Hriljac; School of Chemistry, University of Birmingham, Birmingham, United Kingdom.

The synthesis of novel ion exchange materials for uses in nuclear waste management and environmental remediation is a key area of research. The established methodology for the removal of caesium and strontium from effluent in the UK involves the use of a natural zeolite material clinoptilolite<sup>1</sup>, but future waste streams and POCO activities may be better tackled with other systems. Much effort is being placed in designing materials with better selectivity and ion exchange capacity than clinoptilolite.

One family of materials which have been widely investigated are mixed octahedral and tetrahedral framework metal silicates due to potentially interesting ion exchange properties as well as better chemical and radiation stability than aluminosilicate zeolites. One of these types of materials, a natural zirconosilicate mineral umbite ( $K_2ZrSi_3O_9 \cdot H_2O$ ), has been synthesised as have related materials with both Sn and Ti as the octahedral component replacing some or all of the Zr, for which the ion exchange properties have been explored in the literature<sup>2</sup>. The variation of the tetrahedral (Si) component has been explored in this work with the successful synthesis of a germanium derivative of the mineral umbite ( $K_2ZrGe_3O_9 \cdot H_2O$ ).

Subsequent ion exchange results shows both caesium and strontium uptake by Ge-Zr-umbite ( $K_2ZrGe_3O_9 \cdot H_2O$ ) but at low levels. This is substantially improved by chemical modification of the umbite structure with the incorporation of up to 25% Nb/Sb for Zr at the octahedral site. High resolution synchrotron X-ray powder diffraction data shows complex structural behaviour of these doped materials when they undergo caesium exchange. Further attempts at doping higher levels for Zr results in mixed phases with the formation of pharmacosiderite phases ( $HK_3Ge_7O_{16} \cdot 4H_2O$  and  $HK_3Ti_4Ge_3O_{16} \cdot 4H_2O$ ), with these also showing interesting ion exchange properties. The thermal decomposition products of the pharmacosiderite phases have also been analysed for potential wasteform candidates.

### References

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2. C.S.Fewox, A.Clearfield and A.J.Celestian, *Inorg. Chem*, 2011, **50**, 3596–3604.

### 2:30 PM BREAK

SESSION ET15.04: Corrosion in the Near Field Context of a Geological Repository  
Session Chairs: Claire Corkhill and Stefan Neumeier  
Monday Afternoon, November 26, 2018  
Hynes, Level 3, Room 308

### 3:00 PM \*ET15.04.01

**Nuclear Waste Form Corrosion** Gerald S. Frankel<sup>1</sup>, John Vienna<sup>2</sup>, Jie Lian<sup>3</sup>, John R. Scully<sup>4</sup>, Seong Ho Kim<sup>5</sup>, James Saal<sup>6</sup>, Joseph Ryan<sup>2</sup>, Stephane Gin<sup>7</sup>, Wolfgang Windl<sup>1</sup>, Jincheng Du<sup>8</sup>, Jianwei Wang<sup>9</sup>, Christopher Taylor<sup>1</sup>, Jenifer Locke<sup>1</sup>, Daniel Schreiber<sup>2</sup> and Daniel Perea<sup>2</sup>; <sup>1</sup>The Ohio State University, Columbus, Ohio, United States; <sup>2</sup>Pacific Northwest National Laboratory, Richland, Washington, United States; <sup>3</sup>Rensselaer Polytechnic Institute, Troy, New York, United States; <sup>4</sup>University of Virginia, Charlottesville, Virginia, United States; <sup>5</sup>The Pennsylvania State University, State College, Pennsylvania, United States; <sup>6</sup>QuesTek Innovations, Evanston, Illinois, United States; <sup>7</sup>French Alternative Energies and Atomic Energy Commission, Marcoule, France; <sup>8</sup>University of North Texas, Denton, Texas, United States; <sup>9</sup>Louisiana State University, Baton Rouge, Louisiana, United States.

This talk will summarize the activities of WastePD, an Energy Frontier Research Center focused on the performance and design of nuclear waste forms. The Center has 13 PIs from 9 institutions and comprises three thrusts based on materials classes: waste glass, crystalline ceramics, and metals. Commonalities in the degradation of these materials and synergies between the thrusts have led to new understanding of the environmental degradation processes. A framework for the design of materials with improved corrosion resistance was developed, called Science of Environmental Degradation of Materials, SEDMat. Existing approaches for design for corrosion resistance are largely empirical and based on qualitative models and experimental data. The ultimate goal is to develop a fully descriptive synthesis of detailed models of all of the elementary processes. While working toward that goal, calculable parameters are being combined to generate expressions with predictive capabilities. Examples of the scientific findings of each of the materials thrusts will be presented including state of the art characterization of the gel alteration layer on waste glass using flash freezing, cryo-processing of samples, and cryo atom probe tomography. New corrosion-resistant high entropy metallic alloys will be described, as well as studies of ceramic degradation in aqueous environments.

### 3:30 PM ET15.04.02

**Lead/Lead-Based Alloy Canister for High Level Nuclear Waste and Used Nuclear Fuel Revisited—Insight from Advances in Lead Solution Chemistry** Yongliang Xiong<sup>1</sup>, Yifeng Wang<sup>1</sup>, Sungtae Kim<sup>1</sup> and Greg Roselle<sup>2</sup>; <sup>1</sup>Sandia National Laboratories, Carlsbad, New Mexico, United States; <sup>2</sup>Brigham Young University-Idaho, Rexburg, Idaho, United States.

The canister for high level nuclear waste (HLW) and used nuclear fuel (UNF) is important for the safe disposal of such wastes, as a canister serves as the first line of defense in the multiple engineered barrier systems. The lead and lead based alloy canisters were proposed in several countries' repository designs. For instance, in the Argentina repository design, the containers for reprocessed and vitrified wastes have a thick intermediate layer made of lead with a 10 cm width, owing to its excellent radiological protection and corrosion resistance. In Russia, lead and lead-based alloys are also considered as

prospective matrices for containers for used nuclear fuel, and are being used for conditioning spent sealed radioactive sources at radioactive waste disposal facilities. Lead containers are also used in the Brazil repository design.

In this presentation, we revisit the lead and lead-based alloy canister for HLW and UNF, based on the insights from the recent advances in lead solution chemistry including lead corrosion experiments in corrosive, high ionic strength solutions, and recent archaeological studies on ancient lead artificial products.

In environments where dissolved sulfide and oxygen are absent or poor, the corrosion products of lead are likely to be lead oxide (litharge, PbO) or lead carbonate (cerussite, PbCO<sub>3</sub>). Archaeological studies have indicated that litharge was formed when lead was corroded under anoxic conditions. In our corrosion experiments with lead in high ionic strength solutions at  $P_{\text{CO}_2} > 10^{-2.82}$  atm, we observed cerussite and tamowitzite [(Ca, Pb)CO<sub>3</sub>] as corrosion products.

The solubility of lead corrosion products is a key to the performance of a lead canister, as the corrosion products usually behave as a protection layer. We have developed the thermodynamic model for lead solution chemistry valid to high ionic strengths, which can accurately describe solubilities of various lead solid species under various conditions. In this presentation, we evaluate lead solubilities in various repository designs by applying our thermodynamic model. The repository designs include those in granites, shales, crystalline rocks, salt formations, and sedimentary basins.

<sup>A</sup> This research is funded by the WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.

<sup>B</sup> Sandia National Laboratories is a multimission laboratory operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. SAND2018-5657A

### 3:45 PM \*ET15.04.03

**The Corrosion of Copper Nuclear Waste Containers in Sulphide-Containing Groundwaters** David Shoesmith, Jian Chen, Taylor Martino, Mengnan Guo and James Noel; University of Western Ontario, London, Ontario, Canada.

The Canadian/Scandinavian concept for the permanent disposal of high level nuclear waste is to seal it in a container with an outer copper coating/shell and bury it in a deep geologic repository. While the container could experience a number of corrosion processes, the most likely long term corrosion process will be the reaction of Cu with sulphide present in the groundwater. The nature of this corrosion process and the morphology of damage distribution will eventually determine the time to failure of the copper coating/shell.

We have been studying these processes using electrochemical, corrosion science and surface analytical techniques. with a particular emphasis on the nature of the corrosion product deposits (copper sulphides) and the morphology of the corroding copper/deposit interface. This latter feature will determine the local loss of wall thickness required to define the required copper coating/shell corrosion allowance.

Using electrochemical impedance spectroscopy (EIS), we have shown the corrosion product deposit to be porous at the low sulphide concentrations anticipated in a repository, and to vary in morphology depending on the sulphide concentration, groundwater anion type and concentration (in particular chloride), and the transport conditions prevailing at the copper surface. Using EIS and voltammetry techniques we have demonstrated that passivation of the copper surface, which could potentially lead to pitting, will not occur. Based on SEM images recorded on focussed ion beam cut cross sections, some localization of corrosion can be observed due to micro galvanic coupling of the copper substrate to the electrically conducting chalcocite (Cu<sub>2</sub>S) deposit. This localization is facilitated by the transport of copper, as either soluble complexes or neutral clusters (Cu<sub>3</sub>S<sub>3</sub>) from the corroding anodic locations to the cathodic locations where copper sulphide deposit occurs.

### 4:15 PM ET15.04.04

**DFT Investigation of the Interactions Between Cu Surfaces and H<sub>2</sub>S, HS and S—First Stages of Formation of Sulfide Layers** Claudio M. Lousada Patricio<sup>1</sup>, Johannes Johansson<sup>2</sup> and Pavel A. Korzhavyi<sup>1</sup>; <sup>1</sup>KTH Royal Inst of Technology, Stockholm, Sweden; <sup>2</sup>SKB Svensk Kärnbränslehantering AB, Stockholm, Sweden.

The presence of H<sub>2</sub>S in underground water is a factor that has to be considered in the safety assessments of deep geological repositories (DGR) for spent nuclear fuel because H<sub>2</sub>S drives the corrosion of many metal. The canister material that is planned to be used in the Swedish DGR, copper, is no exception to this and the formation of copper sulfide films has been observed in experiments where the metal was exposed to H<sub>2</sub>S(aq). In order to understand the phenomenon at the atomic-scale, we performed density functional theory (DFT) investigations of the molecular and dissociative adsorption of H<sub>2</sub>S and of its dissociation products, HS and S, at perfect and defective Cu(110) surfaces described using large supercells with c(6×6) periodicity. For single and pairs of adsorbates, we investigated the adsorption at a diversity of sites such as pits, terraces and holes. For the perfect surfaces we scanned through all possible binding sites for the adsorbates, studied the interactions between adsorbates as a function of their distance, and investigated electronic structure effects such as the formation of surface dipoles in order to develop a rationale for the construction of models for the growth of thick layers of surface products.

We found that the adsorption modes and energies of the products of dissociation of H<sub>2</sub>S are largely dependent on the presence of defects and that for high coverages, H<sub>2</sub>S forms stacked half-monolayers that interact with each other via a complex hydrogen bond network. The surface perturbation induced by S can be explained by the charge transfer model, H<sub>2</sub>S leads to a perturbation that arises mostly from Pauli exclusion effects, while HS shows mixed: charge transfer-Pauli exclusion effects. These effects have a large contribution to the long range adsorbate-adsorbate interactions observed. We considered then two models for the growth of a layer of S-atoms at the surface: the formation of islands vs the formation of more homogeneous surface distributions of S-atoms. For coverages lower than 0.5 ML, S-atoms cluster as islands that evolve to stripes with increasing coverage. At 0.5 ML a homogeneous distribution of S-atoms becomes more stable than the formation of stripes. For the coverage equivalent to 1 ML, the formation of two half-monolayers of S-atoms that disrupt the Cu-Cu bonds between the first and second layers is more favorable than the formation of 1 ML homogeneous coverage of S-atoms. Here the S-Cu bond distances and geometries are reminiscent of pyrite, covellite and to some extent chalcocite. The small energy difference of ≈0.1 eV that exists between this structure and the formation of 1ML suggests that in a real system at finite temperature both structures may coexist leading to a structure with even lower symmetry.

### 4:30 PM ET15.04.05

**Anoxic Corrosion of Low-Carbon Steel at Elevated Temperatures—Effects of Chloride and Sulfide** Charlotte Sisk-Scott<sup>1</sup>, Jonathan Icenhower<sup>1</sup>, Chase Kicker<sup>1</sup>, Cassie Marrs<sup>1</sup>, Leslie Kirkes<sup>1</sup> and Praveen Srirama<sup>2</sup>; <sup>1</sup>Repository Performance, Sandia National Laboratories, Carlsbad, New Mexico, United States; <sup>2</sup>Organic Laboratories, Center of Environmental Monitoring & Research Center, Carlsbad, New Mexico, United States.

Anoxic experiments were carried out on low-C steel coupons in dilute solutions and simulated brines with and without sulfide to determine gas generation rates, iron-release rates, and secondary corrosion phases. Corrosion rates were determined in a flow-through system (90°C) and a static apparatus (70°C) at

pH (25°C) = 9. The experiments comprised of two sets of solutions, consisting of either Simplified Generic Weep Brine or deionized water. Each of the sets had subsets containing sulfide in the form of NaHS. Polished coupons of steel were reacted in the flow-through experiments whereas unpolished cylinders were reacted in the static experiments. Dissolution rates were quantified by analysis of Fe released to solution ( $\text{Fe}^{2+}$  and total Fe) and by liberation of  $\text{H}_2$ . In the case of the flow-through experiments,  $\text{H}_2$  was collected in-stream and analyzed by GC-TCD. In the static experiments, the increase of pressure was monitored and  $\text{H}_2$  was collected and analyzed by GC-TCD at experiment termination. Steel coupons and cylinders, and the secondary corrosion products, were analyzed post-test and ex-situ by Raman, SEM and XRD. In sulfide-free SGWB at 90 °C the calculated surface retreat rate based on the Fe-release rate, measured in the flow-through system, was  $\sim 3.1 \pm 1 \mu\text{m}/\text{year}$ . In contrast, the retreat in sulfide-bearing SGWB was measured to be  $0.02 \mu\text{m}/\text{year}$ , a factor of  $\sim 160$  slower. In deionized water, the average surface retreat rate was measured to be  $0.06 \text{ mm}/\text{year}$ . In the static experiments, the highest gas generation rate based on  $\text{H}_2(\text{g})$  production was  $0.4 \text{ mol}/\text{m}^2\text{-yr}$ . Examination of the secondary phases by Raman spectroscopy indicated the presence of  $\text{Fe}(\text{OH})_2$  and magnetite in sulfide-free SGWB and DIW and mackinawite and pyrrhotite as reaction products in sulfide-bearing solutions. Green rust was also identified as a reaction product in sulfide-free SGWB experiments.

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SESSION ET15.05: Poster Session: Scientific Basis for Nuclear Waste Management  
Session Chairs: Neil Hyatt and John McCloy  
Monday Afternoon, November 26, 2018  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

#### ET15.05.01

**Development of Partially Automated Kr-85 Monitoring System for Nuclear Waste Management** Young Gun Ko, Hyuncheol Kim, Ji Young Park, Sang-Do Choi, Jong-Myoung Lim, Geun-Sik Choi and Wannoo Lee; KAERI, Daejeon, Korea (the Republic of)

The radioactive waste gas  $^{85}\text{Kr}$  (beta emitter,  $E_{\text{max}}$ : 687 keV, half-life: 10.76 years) is derived from anthropogenic sources such as nuclear weapons tests, nuclear-fuel reprocessing and nuclear reactors. To reduce the release of the radioactive gas waste to atmosphere, the  $^{85}\text{Kr}$  R&D encapsulation effort incorporated numerous materials, including sodalite, "thirsty" glass, and zeolite 5A, has been made for long-term storage. Therefore, monitoring of  $^{85}\text{Kr}$  radioactivity near  $^{85}\text{Kr}$  storage facilities is very significant to detect  $^{85}\text{Kr}$  leakage from the facilities.

To measure low-level  $^{85}\text{Kr}$  radioactivity in the atmosphere, a Bundesamt für Strahlenschutz - Institute of Atmospheric Radioactivity (BfS-IAR) system is the only commercialized system developed by the Bundesamt für Strahlenschutz (Germany). However, the system requires a lot of manpower because all stages to get data should be performed manually although reliable data with a high level of accuracy were obtained by using the system. For this reason, automation of the system is significant and should be rapidly carried out to get continuous data without manpower. The analysis system consists of steps of air sampling, first concentration, second concentration, separation/purification and determination of radioactivity.

At the sampling step, air including Kr flow into and adsorbed in an adsorption module cooled with liquid  $\text{N}_2$  after removal of moisture and  $\text{CO}_2$ . In this study, the sampling step was automated by using a membrane module, a heat exchanger, an automatic air-flow distribution system, a thermostat bath and newly designed modules. Our new automated sampling system for a  $^{85}\text{Kr}$  analysis was well operated. Used materials and equipments for automated sampling system were analyzed with FT-IR, SEM, GC, etc. In our presentation, we will talk about the analysis results and next plan for the automation of other steps for the  $^{85}\text{Kr}$  system. In addition, the distribution of air velocity and temperature in the adsorption module was analyzed with an ADINA software to design new adsorption modules. Numerical simulations of air flow into the module was presented. The finite element computational fluid dynamics module of the ADINA software (ADINA-CFD) was used to obtain various data based on the 2D structure of the adsorption module. We expect our study will be a stepping stone to develop the automated  $^{85}\text{Kr}$  analysis system for the nuclear waste management.

#### ET15.05.02

**Effect of Carbonate on the Migration Behavior of Strontium in Compacted Bentonite** Kazuya Idemitsu, Ryota Yamada, Masayuki Hirakawa, Yuki Kakoi, Hajime Arimitsu, Yaohiro Inagaki and Tatsumi Arima; Kyushu University, Fukuoka, Japan.

The apparent diffusion coefficients of strontium in compacted bentonites were investigated at various bicarbonate concentrations. Purified sodium-bentonite Kunipia-F was compacted with a jig into cylindrical pellets 10 mm in diameter and 10 mm high with dry densities of 1.0 to 1.6  $\text{Mg}/\text{m}^3$ . Each bentonite pellet was inserted into an acrylic resin column and saturated with carbonated water containing 0.01 to 1.0 M  $\text{NaHCO}_3$  for more than 1 month. Five mg of tracer solution as 1.0 M of  $\text{SrCl}_2$  spiked on a face of bentonite specimen. After a few weeks strontium diffusion profiles were measured with ICP-MS. The apparent diffusion coefficients of strontium tended to decrease slightly with increasing dry density. High carbonate conditions as high as 0.5 M made the apparent diffusion coefficients of strontium decrease half at a dry density of 1.0  $\text{Mg}/\text{m}^3$  and one sixth at 1.6  $\text{Mg}/\text{m}^3$ . At higher bicarbonate concentrations as high as 1.0 M diffusion profiles of strontium were not observed, on the other hand white precipitation was observed on the face of bentonite specimen where strontium was spiked. This white precipitate could be strontianite, strontium carbonate. Diffusion experiments using cesium were also carried out for comparison. The diffusion coefficient of cesium decreased slightly as the bicarbonate concentration was increased to 1.0 M. Cesium could not be affected chemically by carbonate, however carbonate precipitation could occur in pores of bentonite then disturb the diffusion of cesium.

#### ET15.05.03

**Structural Characterization of Ternary Salt Melts for LAW Applications** Emily T. Nienhuis, Muad Saleh and John S. McCloy; Washington State University, Pullman, Washington, United States.

This study seeks to understand the melt structure of molten salts in relation to the low temperature reactions and melts that occur during the vitrification of Hanford Low Activity Waste (LAW). Salts (such as nitrates, sulfates, carbonates, halides, borates, etc.) play a key role in these low temperature reactions as they form complex eutectic mixtures during early stage melting. In LAW melting, this alkali salt phase can preferentially incorporate radioactive Cs, halides, and pertechnetate. During melting of the feed, some of precursors sequentially break down during melting, such as nitrates, carbonates, and boric acid, to form gases, or partially volatilize, such as some halides. Sulfates, however, tend not to volatilize but have limited solubility in the final borosilicate glass waste form. Excess salts, usually related to high concentrations of sulfate, form a water soluble salt phase on the cooled glass surface compromising

the waste form long-term chemical durability. To better understand these low temperature processes, a scoping study was undertaken to synthesize melts of equimolar ratios of  $K_2SO_4$ - $ZnSO_4$  (a known glass-forming system) with added nitrates, halides, carbonates, or various halides. Some of the materials formed single phase glasses and some underwent more or less crystallization upon quenching. Characterization of these quenched materials, including thermal analysis, vibrational spectroscopy, and diffraction, will be discussed.

#### ET15.05.04

**Effect of  $TiO_2$  Doping on Crystallization of Alkali and Alkaline-Earth Molybdate Phases in an Improved High Level Waste Glass-Ceramic** Prashant Rajbhandari<sup>1</sup>, Kristian Barnsley<sup>3</sup>, John Hanna<sup>3</sup>, John S. McCloy<sup>2</sup>, Russell Hand<sup>1</sup> and Neil Hyatt<sup>1</sup>; <sup>1</sup>University of Sheffield, Sheffield, United Kingdom; <sup>2</sup>Washington State University, Pullman, Washington, United States; <sup>3</sup>University of Warwick, Coventry, United Kingdom.

The incorporation of high molybdenum and rare earth elements in the conventional borosilicate glass can induce liquid-liquid phase separation and that is followed by crystallization of alkaline-earth molybdates  $CaMoO_4$  (water-durable) and alkali molybdates  $Na_2MoO_4$  (water-soluble). The resistance against water attack can be significantly reduced due to the formation of water-soluble crystalline phase ( $Na_2MoO_4$ ) during the melt cooling. In this work, the impact of small amount of  $TiO_2$  (1-4 mol%) on the crystallization of Molybdate phases on simplified Mo-containing borosilicate glass is investigated. The differential thermal and XRD analysis were implemented to study the thermal behavior of the compositions and nature of the crystalline phases. The results indicated that the insertion of  $TiO_2$  significantly reduced the formation of water-soluble  $Na_2MoO_4$  phases. The morphology and structural modification of the material were investigated by implementing SEM and solid state NMR analyses respectively.

#### ET15.05.05

**Multinuclear NMR Methods for Characterising Precipitates During Simplified MW25 Glass Dissolution** Rui Guo and Ian Farnan; Univ of Cambridge, Cambridge, United Kingdom.

The presence of Mg in the UK high-level waste glass MW25 has shown to increase the aqueous reactivity when compared with Mg-free glasses like SON68 (the inactive analogue of French R7T7 high-level waste glass)<sup>[i], [ii]</sup>. The exact mechanism by which Mg reduces the aqueous durability of glasses is not clear, but it has been concluded that the effect is not a primary one in which changes induced in the glass structure (and composition) by the addition of Mg alter the initial dissolution rate<sup>[iii]</sup>.

The accepted mechanism of passivation in glass dissolution is that an altered layer forms on the surface of the underlying glass by in-situ mechanisms of hydrolysis and re-condensation of the glass network. This retards further dissolution by acting as a diffusion barrier or molecular sieve<sup>[iv]</sup>. A significant degree of re-incorporation of Mg, Al, Si had been observed during Mg-containing glasses dissolution in our experiments. Thus, it was proposed that the "passivating" altered layer formed on Mg-containing glasses have an inferior retarding efficacy because of the secondary co-precipitations that might alter the "conventional" passivating mechanisms.

Multinuclear (<sup>25</sup>Mg, <sup>17</sup>O, <sup>27</sup>Al, <sup>1</sup>H) NMR methods have been exploited to determine the atomic speciation of the precipitates (and altered layer) in question. In addition, first-principle electronic structure calculations combined with GIPAW to calculate NMR parameters on several Mg-silicate structures have been conducted to constrain the type of local atomic environments in support of interpreting experimental results.

[i] Curti, E. et al. (2006) Applied Geochemistry 21 pp. 1152-1168;

[ii] Brigden, C & Farnan, I (2016) RWM Reports. Retrieved from: <https://rwm.nda.gov.uk/publication/experimental-studies-of-the-durability-of-uk-hlw-and-ilw-glasses-the-effect-of-magnesium/>

[iii] Guo, R et al. (2018) Journal of Non-Crystalline Solids 497 pp. 82-92

[iv] Gin, S et al. (2015) Nature Communications 6 pp. 6360

#### ET15.05.06

**Rare-Earth Containing Crystalline Phases in Nuclear Waste Glass-Ceramics—Role of Rare Earth Ion Size** Hua Chen<sup>1,2</sup>, José Marcial<sup>2</sup>, Mostafa Ahmadzadeh<sup>2</sup>, Deepak Patil<sup>2</sup>, Muad Saleh<sup>2</sup> and John S. McCloy<sup>2,3</sup>; <sup>1</sup>Inner Mongolia University of Science and Technology, Baotou, China; <sup>2</sup>Washington State University, Pullman, Washington, United States; <sup>3</sup>Pacific Northwest National Laboratory, Richland, Washington, United States.

Three series of aluminoboro-silicate glass-ceramics containing alkali (Na), alkaline earth (Ca), rare earth (Sc, Y, La, Ce, Nd, Sm, Er, Yb, or Lu), and transition metal (Zr and Mo) were formulated to test the effects of peralkalinity and rare earth cation size on the crystallization of rare-earth containing phases in simulated nuclear waste glass-ceramics. Six-oxide glasses were formulated in three series: 1) peralkaline formulations (defined as  $Na_2O_{excess}=Na_2O-Al_2O_3-ZrO_2>0$ ) with ~5 mol% RE<sub>2</sub>O<sub>3</sub>; 2) metaluminous formulations ( $Na_2O_{excess}=0$ ) with 10 mol% RE<sub>2</sub>O<sub>3</sub> and 10 mol% B<sub>2</sub>O<sub>3</sub>; and 3) peraluminous formulations ( $Na_2O_{excess}<0$ ) with 10 mol% RE<sub>2</sub>O<sub>3</sub> and 15 mol% B<sub>2</sub>O<sub>3</sub>. Based on statistical analysis of and quantitative x-ray diffraction of previously formulated slow cooled glasses, the peralkaline and metaluminous glasses were expected to crystallize rare-earth doped powellite [(Ca,Na,RE)MoO<sub>4</sub>] and oxyapatite [(RE,Ca,Na)10Si<sub>6</sub>O<sub>26</sub>], while the peraluminous glasses were expected to crystallize powellite and RE-borosilicate [RE<sub>3</sub>BSi<sub>2</sub>O<sub>10</sub>]. On synthesis of these glass-ceramics, (Ce,Zr)O<sub>2</sub> (cerianite) and RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (keiviite) were identified as two other important crystals as well. For series 1, all quenched glasses were amorphous, except for the one containing Ce. All crystallized glass-ceramics contained ~3-5 wt% powellite. Y, La, Nd, Sm, and Er glass-ceramics contained 10-14 wt% oxyapatite. Ce glass-ceramic contained <4 wt% oxyapatite and ~3 wt% cerianite (Ce,Zr)O<sub>2</sub>. Glass-ceramics with small RE cations behaved differently. Sc glass-ceramic contained no other phases besides powellite. Yb and Lu glass-ceramics contained <2 wt% oxyapatite plus ~10 wt% keiviite. For series 2, only one of the quenched glasses (La) was amorphous. Glasses with Nd, Sm, and Y contained powellite and oxyapatite, while the one with Yb contained powellite and keiviite. On remelting and slow cooling, the same phases were formed. For series 3, containing more B<sub>2</sub>O<sub>3</sub> and less Na<sub>2</sub>O and CaO than series 2, all quenched glasses were amorphous except the Yb formulation which crystallized keiviite. On slow cooling, all systems formed powellite, but none formed oxyapatite. Y and Yb glass-ceramics formed a keiviite phase, while Sm and Nd formed a RE-borosilicate phase. The results of this study suggest that the glass formulation, peralkalinity, and rare earth size and concentration strongly influence the rare earth environment in the glass and hence the crystal phases formed on slow cooling. For formulations with high RE and B oxide concentration, large RE ions (La?,Nd,Sm) favor RE-borosilicate crystallization (RE CN=8,9 in this crystal structure), while small RE ions (Y,Yb) favor keiviite phases (RE CN=6 in this structure). When RE and B oxide concentration is lower, oxyapatite is the favored crystal structure (RE CN=7,9) for most RE ions (Y,La,Ce<sup>3+</sup>,Nd,Sm,Er) while the smallest RE ions (Yb,Lu) form keiviite and a Sc-containing phase does not form.

#### ET15.05.07

**Derivation of Apparent Diffusion Coefficients Based on Time Variation of the Relaxation Mass Depths of Cs-137 in Soil Contaminated by the Fukushima NPP Accident** Haruo Sato<sup>1</sup> and Masaharu Hirota<sup>2</sup>; <sup>1</sup>Graduate School of Natural Science and Technology, Okayama University, Okayama, Japan; <sup>2</sup>Faculty of Engineering, Okayama University, Okayama, Japan.

The accident at the Fukushima Daiichi Nuclear Power Plant (1F-NPP) occurred following the Great East Japan Earthquake on 11 March 2011, and led to

the release of volatile radionuclides, which were deposited on the environment in the Fukushima prefecture and the surrounding areas. After the short-lived I-131, radiocaesium such as Cs-134 and Cs-137 have controlled radiation dose rate. The authors derived the apparent diffusion coefficients ( $D_a$ ) of some radionuclides such as Cs-134 and Cs-137 based on time variation of the depth profiles of respective radionuclides in soil obtained in field investigations in earlier studies. Almost all  $D_a$ -values were of order  $10^{-14}$  ( $m^2/s$ ) and well consistent with distribution coefficients ( $K_d$ ) obtained from batch experiments. Whilst, field investigations for the relaxation mass depths of Cs-137 in soil by a scraper plate method were conducted at totally 85 locations over a period of nearly 6 years in Fukushima Prefecture, south part of Miyagi Prefecture and north part of Ibaraki Prefecture from December 2011 to October 2016, and time variation of the relaxation mass depths was recently reported. Consequently, the relaxation mass depths of Cs-137 showed a tendency to linearly increase with an increase of elapsed time. This indicates that radiocaesium gradually moves to the deeper part of soil with time. In this study,  $D_a$  based on Fick's diffusion equation was derived based on time variation of the relaxation mass depths of Cs-137 in soil. In order to calculate  $D_a$  based on Fick's law, correlation between relaxation depth and square root of elapsed time was derived from the correlation between relaxation mass depth and elapsed time (where, relaxation depth is defined as the depth of 1/e of radioactivity concentration at the ground surface and can calculate by relaxation mass depth/soil density). The calculated  $D_a$  of Cs-137 was of order  $10^{-12}$  ( $m^2/s$ ), which was about 2 orders of magnitude higher than  $D_a$ -values that we previously reported as described above. Considering that almost all relaxation depths of Cs-137 were shallow within 2cm in depth from the ground surface and near the surface layer of soil is unsaturated, it is considered that  $D_a$  derived in this analysis includes the effect of dispersion by advection (by flow in the vertical direction of rainwater).

#### SESSION ET15.06: Developments in Advanced Ceramic Wasteforms

Session Chairs: Nicolas Dacheux and Neil Hyatt

Tuesday Morning, November 27, 2018

Hynes, Level 3, Room 308

##### 8:30 AM \*ET15.06.01

**Hot Isostatic Pressing of Advanced Nuclear Waste Forms** Daniel Gregg, Eric Vance, Rohan Holmes and Gerry Triani; Australian Nuclear S&T Org, Sydney, New South Wales, Australia.

ANSTO Synroc Technologies has a significant focus on the use of hot isostatic pressing (HIPing) technology to fabricate tailored candidate glass-ceramic and ceramic waste forms for different types of actinide, high- and intermediate level wastes. Such advanced waste forms can offer performance and economic benefits for the immobilisation of different types of waste which are problematic for glass matrices or existing vitrification process technologies. The HIP technology itself offers several advantages such as increased density, minimum grain size and removes the need for costly and bulky off-gas systems. In addition, it has been demonstrated that glass, glass-ceramic, ceramic and metal encapsulated waste forms can all be produced using this one flexible process technology.

The industrial demonstration of Synroc technology will be achieved at ANSTO with the first of a kind Synroc Waste treatment Facility (SyMo) to treat waste arising from molybdenum-99 production. Construction of this facility commenced in 2018. Hot isostatic pressing is a key process for this facility, with significant technical challenges being addressed for industrial implementation. ANSTO Synroc's approach has been to employ a multidisciplinary team which uses systems integration and risk mitigation to nuclearize waste treatment processes. The plant delivery model has been to develop the process chemistry and the process engineering including mock up and full scale demonstration to mitigate integration risks. This paper will discuss the engineering principles behind the development of the SyMo facility for the treatment of Mo-99 wastes as well as the application of ANSTO Synroc Technology as an advanced waste form and technology platform for many other intractable nuclear wastes.

##### 9:00 AM ET15.06.02

**Vanadinite Ceramic Waste Forms by High Energy Ball Milling and Spark Plasma Sintering for Chlorine Confinement** Penghui Lei<sup>1,2</sup>, Tiankai Yao<sup>1</sup>, Guang Ran<sup>2</sup> and Jie Lian<sup>1</sup>; <sup>1</sup>Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States; <sup>2</sup>College of Energy, Xiamen University, Xiamen, China.

Apatite structure type, with a typical chemical composition of  $A_{10}(BO_4)_6C_2$  (e.g., A=Ca, Na, Pb, rare earth, fission product, actinides; B=P or V; C=F, Cl, I.) shows tremendous potentials as advanced waste forms for effective nuclear waste management. A wide range of radionuclides can be incorporated into its crystal structure by coupled substitutions at both cation and anion sublattices.  $Pb_5(VO_4)_3Cl$ , a potential waste form for long-lived Cl-36 immobilization, is used to confine highly volatile chlorine. In this work,  $Pb_5(VO_4)_3Cl$  powder samples are synthesized by solid state reaction at room temperature by using High energy ball milling (HEBM). Low-temperature consolidation of dense vanadinite pellets by spark plasma sintering (SPS) at various temperature (573K, 673K, 723K, 773K, 973K, 1073K) were performed. Microstructure analysis indicates a nanocrystalline ceramic with an average grain size less than 200nm at 723K. No significant chlorine loss was identified by HEBM and during densification SPS process. The effects of sintering on microstructure, density, thermal stability and mechanical properties were investigated. These results highlight the immense potential of SPS combining with HEBM as an advanced materials fabrication technology for immobilization of volatile radionuclides including radioactive chlorine.

##### 9:15 AM ET15.06.03

**Waste Form for Spent Fuel and U-Rich <sup>99</sup>Mo Production Waste** Eric Vance and Daniel Gregg; Australian Nuclear S&T Org, Sydney, New South Wales, Australia.

High level waste (HLW) waste form containers should take no aqueous durability credit when considering non-spent fuel HLW. Yet immobilisation of spent power plant fuel currently will rely strongly on metal encapsulation, particularly for the highly soluble fission products that do not inhabit  $UO_2$ . This is probably due to the absence of widely accepted waste form candidate phases other than a very low waste loaded glass at the time relevant research on spent fuel immobilisation began. More recent work however, has demonstrated relevant tailored waste form options with acceptable waste loadings. Here we propose a pyrochlore glass-ceramic made by hot isostatic pressing at  $\sim 1250^\circ C/100 MPa$  as a strong candidate wasteform for spent fuel. It is also as an ILW waste form for <sup>99</sup>Mo waste produced from irradiation of  $UO_2$  targets. The U oxide and rare earth fission products would be incorporated in the pyrochlore and the fission products in the glass. We have put forward the pyrochlore mineral phase before for the ILW but have more recently favoured a glass-ceramic containing around 70-80 wt% pyrochlore plus 20-30 wt% borosilicate glass. Depending on the redox conditions in calcination and the addition of Ti metal to the canister for HIP, the pyrochlore phase is sensitive to redox conditions with slightly oxidising conditions favouring brannerite as an extra ceramic phase and perovskite and  $UO_2$  as extra phases being favoured by highly reducing conditions. Optimisation of the phase assemblage is discussed.

##### 9:30 AM BREAK

SESSION ET15.07: Management and Long Term Behaviour of Spent Nuclear Fuel I  
Session Chairs: Olivia Roth and David Shoemith  
Tuesday Morning, November 27, 2018  
Hynes, Level 3, Room 308

**10:00 AM \*ET15.07.01**

**Dissolution of Uranium Dioxide and Associated Solid Solutions in Nitric Acid—Impact of Fission Products and Microstructure** Nicolas Dacheux, Theo Cordara, Thomas Dalger, Florent Tocino, Laurent Claparede, Stéphanie Szenknect, Nicolas Clavier, Adel Mesbah and Renaud Podor; ICSM, CNRS, CEA, ENSCM, Univ Montpellier, Bagnols sur Ceze, France.

The dissolution or leaching of the spent nuclear fuels (SNF) is a key step either in the field of their reprocessing or their long-term storage in underground repository. Their structure and microstructure become very complex due to the formation of actinides and Fission Products (FP). In order to discriminate the role of several parameters on the chemical durability, a large variety of sintered materials were prepared from hydroxide or oxalate precursors then submitted to multiparametric dissolution tests.

The impact of actinides incorporation was examined through the study of  $U_{1-x}Th_xO_2$  solid solutions dissolution in nitric acid. Uranium mole loading clearly impacted the chemical durability. Indeed, for the lower uranium incorporation rates ( $x_U < 0.5$ ), the dissolution was mainly controlled by surface-controlling reactions at the solid/solution interface involving the adsorption of protons on reactive sites. On the contrary, for uranium enriched materials ( $x_U > 0.5$ ), oxidation of uranium (IV) into uranyl at the solid/solution interface became clearly preponderant (leading to the decrease of the chemical durability, as shown for pure  $UO_2$ ). Partial order related to the proton concentration as well as apparent activation energy associated to the reaction of dissolution were affected by this change. The role of nitrous acid on the normalized dissolution rate of  $U_{1-x}Th_xO_2$  was particularly examined.

The impact on the chemical durability of several FP (lanthanides or PGM's) within the structure of  $UO_2$  was also studied. Thus, several samples incorporating 1 to 20 mol.% of a mixture of lanthanide elements (13% La; 7.4% Y; 25.6% Ce; 12% Pr; 42% Nd) or 0.6 to 3 mol.% of PGM's (55% Ru; 9.6% Rh; 35.4% Pd) were prepared through oxalate or hydroxide precipitation, respectively, then sintered.

The presence of lanthanide elements in  $UO_2$  did not affect significantly the normalized dissolution rates in concentrated nitric acid solutions ( $C > 1M$ ). On the contrary, the effect was more important in less concentrated solutions (e.g. a factor of 100 compared to pure  $UO_2$  observed in 0.5M  $HNO_3$ ) when the role of surface-controlling reactions on the overall dissolution became predominant. Moreover, the chemical durability of  $UO_2$  samples doped with PGM's was significantly lowered compared to pure  $UO_2$ . This effect was strengthened in less acid media; a factor of 4500 being observed after 175 days of leaching in 0.1M  $HNO_3$ .

Such a macroscopic description of the ceramics dissolution was connected to *operando* monitoring of the evolving solid/solution interface (including reactive surface area, composition) during dissolution tests. Preferential dissolution was observed within Ln-enriched  $UO_2$  grain boundaries or near the  $UO_2$ /PGM's interface, indicating different progresses of the dissolution at the solid/solution interface. Moreover, variations in the distribution of cations also affected the chemical durability of heterogeneous  $U_{1-x}Th_xO_2$  pellets through a clear incongruent dissolution.

**10:30 AM ET15.07.02**

**Effect of Nuclear Fuel Additives on the Spent Nuclear Fuel Reprocessing Dissolution Step** Theo Cordara, Hannah Smith, Claire L. Corkhill, Martin Stennett and Neil Hyatt; Department of Materials Science and Engineering, University of Sheffield, Sheffield, United Kingdom.

Nuclear power producers are seeking to lower the cost of generating electricity through the development and application of new fuels that are capable for being "burnt" for longer within the reactor. One of the main limitations for how long fuel can remain in the reactor is the ability of the fuel to accommodate fission products, especially fission gases like Kr, Xe, He, etc. The build-up of these gases can lead to a swelling of the fuel and to cladding failure, resulting in downtime of the reactor. The solution to this issue is to improve the  $UO_2$  fuel by promoting the growth of larger grains and increasing the rate of diffusion of fission products to the grain boundaries during fission. This is achieved by doping  $UO_2$  with additives; the most extensively applied are  $Cr_2O_3$ ,  $Al_2O_3$  and a mixture of  $Cr_2O_3$ - $Al_2O_3$ .

In this presentation, we describe the synthesis and characterisation of Cr, Al and Cr+Al doped- $UO_2$  materials, containing between 100 and 1,500 ppm of dopants. Samples were prepared by dry (oxides mixing) and wet (oxalic or nitrate precipitation) synthesis routes. Oxide powders thus obtained were pelletized and sintered at 1,700°C during 8h under a reducing atmosphere. SEM images and pycnometer measurements have respectively highlighted an increase of the grain size and of the densification rates in presence of additives. XRD patterns confirmed that the fluorite structure (space group Fm3m), the characteristic crystalline structure of  $UO_2$ , was retained when the samples were doped. Further characterisations (e.g. HR-XRD and EXAFS) were performed to further determine the solubility limit of Cr and Al within the  $UO_2$  lattice, the lattice parameter and the Cr-coordination in these materials. Finally, pellets produced through the above methods were compared to those obtained using hot-isostatic pressing (HIP), which is a sintering method where the pellet is heated at the same time as the application of gas pressure.

**10:45 AM ET15.07.03**

**Long Term Structural Stability During Storage of Self-Damaged Nuclear Spent Fuel Simulant** Oliver Dieste, Thierry Wiss, Emanuele de Bona, Jean-Yves Colle, Ondrej Benes, Dragos Staicu and Rudolph J. Konings; JRC, Karlsruhe, Germany.

The plutonium together with the minor actinides will be responsible for the long term radiotoxicity of spent nuclear fuel, and for the medium term heat loading of the fuel in open nuclear fuel cycles. As these transuranic elements present on the nuclear waste are mainly alpha-emitters, increasing amounts of alpha-damage and helium during spent fuel storage and in the repository will be generated. Most of the defects produced by alpha-decays are generated through elastic energy losses from the recoil of daughter nuclei. In addition, when the alpha-particle comes to rest it becomes a helium atom that can alter the microstructure of the material, e.g. by forming microscopic bubbles. The fluorite structure, shared by all actinide dioxides, is known as being a radiation damage resistant crystal configuration. However, high alpha-dose can have detrimental effects on the long term stability of materials envisaged as fuels. To be able to predict the behavior of the spent fuel on the very long term storage, surrogates are being used to simulate the high alpha damage that will be accumulated on the waste after millenniums of storage and beyond.

In the present work we report on experimental observations of alpha-damage effects on samples with high content of  $^{238}Pu$  that serve as surrogates for very old spent fuel by transmission electron microscopy (TEM), energy loss electron spectroscopy (EELS), x-ray diffraction (XRD) and thermal diffusivity, among others.

**11:00 AM ET15.07.04**

**Dissolution of Uranium Thorium Mixed Oxides—The Role of Nitrous Acid** Laurent Claparede<sup>1</sup>, Thomas Dalger<sup>2</sup>, Stéphanie Szenknect<sup>2</sup>, Philippe Moisy<sup>3</sup> and Nicolas Dacheux<sup>1</sup>; <sup>1</sup>ICSM, University of Montpellier, Bagnols sur Ceze, France; <sup>2</sup>ICSM, Commissariat à l'énergie atomique et aux énergies alternatives, Bagnols sur Ceze, France; <sup>3</sup>DMRC, Commissariat à l'énergie atomique et aux énergies alternatives, Bagnols sur Ceze, France.

Mixed actinide dioxides (MOX) are currently used as fuels in Gen III reactors. MOX-fuels with higher plutonium loading stand as potential candidates for several concepts of Gen IV fast reactors. In this field, the reprocessing of actinides coming from spent nuclear fuel is considered, but the hydrometallurgical processes need to be optimized. In particular, the dissolution step appears to be one of the main issues concerning the recycling of Gen IV MOX fuels. Although dissolution of MOX fuel in nitric acid is already used in industrial processes, the role of several nitrogen based species such as NO<sub>x</sub> and HNO<sub>2</sub> in the oxidative dissolution mechanism of uranium-based mixed oxides remains unclear. In this study, dissolution tests were performed on sintered pellets of U<sub>0.75</sub>Th<sub>0.25</sub>O<sub>2</sub> in various acid solutions (from 10<sup>-1</sup> M to 4 M) under dynamic conditions. Therefore, a multiparametric study of the kinetics of dissolution was achieved in order to quantify the influence of several species of interest. In aerated hydrochloric acid solutions, the kinetics of the overall dissolution reaction appeared to be controlled by adsorption and desorption of protons at activated surface sites. The dissolution rate determined in aerated sulfuric acid solution was enhanced compared to hydrochloric acid solution of the same acidity. This result was interpreted in terms of formation of sulfate ions surface complexes that favor the detachment of the actinides from the mixed oxide solid solution. In nitric acid solutions, the dissolution of the Th<sub>0.25</sub>U<sub>0.75</sub>O<sub>2</sub> pellets followed several successive steps. During this first steady state period, the kinetics of the overall dissolution reaction appeared to be controlled by the oxidation of U(IV) by HNO<sub>3</sub> at the solid/solution interface. A rate law was established by adding a redox contribution to the proton-promoted surface contribution defined for aerated hydrochloric acid solutions. Then, an increase of the normalized dissolution rate was observed, which was attributed to the simultaneous increase of the specific surface area of the pellet and of the HNO<sub>3</sub> concentration in solution. Therefore, the monitoring of the solid/liquid interface by ESEM during dissolution allowed to discriminate the impact of these phenomena on the normalized dissolution rate.

11:15 AM ET15.07.05

**The Relevance of Solid Solution—Aqueous Solution Systems to the Safety Case for Deep Geological Disposal of Nuclear Wastes** Dirk Bosbach, Felix Brandt, Martina Klinkenberg, Victor Vinograd, Juliane Weber and Guido Deissmann; IEK-6, Forschungszentrum Jülich, Juelich, Germany.

The waste containers emplaced in geological disposal facilities for nuclear wastes built in crystalline rocks or clay formations will inevitably come into contact with ground water post-closure, after re-saturation of the repository. Even in repositories in salt rocks, the presence of water cannot be completely ruled out for less probable scenarios, for example, an early failure of shaft seals and plugs. As a consequence, after container failure due to aqueous corrosion, radionuclides can be released from the degrading waste forms into the near-field water and subsequently migrate into the geo-/biosphere via the water pathway. The mobility of radionuclides released from the wastes into the repository near- and far-field is controlled by various processes such as sorption onto minerals and colloids (e.g. by surface complexation or ion exchange), precipitation/ dissolution of solid phases, as well as entrapment in, or solid solution formation with other minerals. However, the aspect of solid-solution thermodynamics and the effects of solid-solution formation on radionuclide solubility and mobility are considered only rarely in specific cases in long term safety assessments for nuclear waste repository systems at present.

Here, we present and discuss the development and application of thermodynamic models for solid solution – aqueous solution systems and their relevance to nuclear waste management and safety assessments for deep geological repositories, emphasizing the significance of complementary experimental and state of the art computational approaches (e.g. atomistic modelling). Using the uptake of radium by barite (BaSO<sub>4</sub>) as an example, it is demonstrated that an improved mechanistic understanding of solid solution thermodynamics and its consideration in performance assessments leads to a more realistic and scientifically corroborated picture on release, solubility, and subsequent migration of safety relevant radionuclides in the repository near- and far-field.

Thermodynamics of mixing for the binary (Ba,Ra)SO<sub>4</sub> and ternary (Ba, Sr, Ra)SO<sub>4</sub> solid solution system were determined on the basis of first principles calculations and experimentally validated by batch type Ra uptake experiments. The Ra uptake experiments yield homogeneous solid solutions via dissolution and re-precipitation within 1000 days at room temperature and also at elevated temperature up to 90 °C. These thermodynamic data allow for a full quantitative description of solid solution – aqueous solution equilibria. Application of state-of-the-art micro- and nano-analytical methods (FIB, TEM, ATP) provided a mechanistic understanding of the relatively fast Ra uptake and the fact that a homogeneous solid solution forms. This Ra uptake was established via internal micro- and nano-porosity opening the possibility to form a chemically homogenous mixed phase at room temperature via dissolution and re-precipitation (excluding solid state diffusion).

SESSION ET15.08: Performance of Near Field Barrier Materials in a Geological Disposal System

Session Chairs: Kazuya Idemitsu and Laura Leay

Tuesday Afternoon, November 27, 2018

Hynes, Level 3, Room 308

1:45 PM \*ET15.08.01

**Modeling the Long-Term Stability of Multi-Barrier Systems for Nuclear Waste Disposal in Geological Clay Formations** Francis Claret<sup>1</sup>, Nicolas Marty<sup>1</sup>, Mathieu Debure<sup>1</sup>, Yannick Linard<sup>2</sup> and Christophe Tournassat<sup>1</sup>; <sup>1</sup>BRGM, Orléans, France; <sup>2</sup>Centre de Meuse/Haute Marne, ANDRA, Bure, France.

Large amounts of nuclear waste await final disposal worldwide. Repository facilities that will host this waste must be capable of ensuring very long-term isolation to protect the environment and ensure the safety of the future generations. Because of this need, the concept of geological disposal of radioactive waste emerged in the late 1950s and is currently considered, in many countries, to be the best option to ensure safe, long-term containment of radioactive waste. A combination of waste overpacks (e.g. metal canisters, concrete), engineered barriers such as bentonite, and natural barriers such as clay rocks, constitutes the elements of the so-called “multiple-barrier system” between the waste matrix and the biosphere. These barrier properties will evolve with time in response to the physical and chemical interactions between the various constituents of the barriers and the surrounding environment. Consequently, predicting how these properties evolve is of prime importance for performance evaluations of the repository concepts. In recent decades, reactive transport modeling codes have become more and more efficient and are used as a bridge between current process knowledge and predictive capabilities for time-scales that are not accessible to experimentation. After describing the basic principles that have guided how these reactive transport models are constructed, their usefulness will be exemplified on the modelling of clay-concrete interaction. The modelling of a ten years in-situ experiment will illustrate the complexity of the multispace and temporal-scale issues that must be taken into account.

## 2:15 PM ET15.08.02

**Thermal and Thermophysical Behavior of Bentonite Investigated by Means of Thermal Analysis Techniques** Ekkehard Post; NETZSCH Geraetebau GmbH, Burlington, Massachusetts, United States.

Bentonite clay was investigated with regard to its potential application as a sealing material for nuclear material storage. Bentonite is a clay with high swelling ability under humid conditions. Due to this behavior and its chemical and physical properties, bentonite is widely used, e.g., in the oil drilling industry for sealing the bore hole. In nuclear waste management, in some countries it is considered or even used as a sealing material in repositories or waste containers.

Depending on the water content, the volume and density of bentonite (consisting mainly of montmorillonite) can vary considerably. Below a certain temperature, water loss and uptake are reversible, this means this material contracts during water loss, but also expands again in a humid atmosphere. In this contribution, bentonite clay was investigated by means of TGA-DSC, dilatometry/TMA, LFA and evolved gas analysis. The results for the thermal stability and thermal expansion in dry and under wet conditions and the thermal diffusivity will be discussed.

## 2:30 PM BREAK

### SESSION ET15.09: Processing and Performance of Vitrified Wasteforms I

Session Chairs: Kevin Fox and Daniel Neuville

Tuesday Afternoon, November 27, 2018

Hynes, Level 3, Room 308

## 3:00 PM \*ET15.09.01

**Raman and X-Ray Absorption Spectroscopic Studies of Hydrothermally Altered Borosilicate Nuclear Waste Glasses** David A. McKeown, Isabelle Muller, Andrew Buechele and Ian L. Pegg; Catholic Univ of America, Washington, District of Columbia, United States.

Raman spectroscopy and X-ray absorption spectroscopy (XAS) are used to characterize structural changes that take place in a variety of hydrothermally altered borosilicate glasses used in durability studies of these materials for nuclear waste storage. The glasses investigated range from simplified five component (Na,K)-alumino-borosilicates to complex composition borosilicates that include more than 20 components to more closely model actual nuclear waste glasses. The hydrothermal experiments, or vapor hydration tests (VHT), were performed on glass wafers up to 30 days from 200 to 238 °C to simulate and accelerate long-term alteration processes that may occur in a nuclear waste repository. Raman spectra indicate two major glass structure changes that take place during alteration: one, partial depolymerization of the alumino-borosilicate network, and two, introduction of water or OH in the altered layers that can approach 10 wt.%. Raman, as well as supporting X-ray diffraction and scanning electron microscopy (SEM) evidence indicate analcime and other tectosilicate crystals at or near the altered sample surface with some altered layers containing intergrowths of amorphous silicate gels with zeolites and fine-grained clays. More localized information from XAS show expanded Na environments in the VHT samples with longer Na-O distances and more nearest-neighbor oxygen atoms, compared with the original glasses, which may be due to hydrous species introduced into the Na-sites. Changes in Si K-edges also show some depolymerization of the network in the VHT altered samples, consistent with the Raman trends. SEM profiles indicate diffusion of many elements across the alteration layers, where one example, Tc, is enriched toward the altered sample surface. XAS measurements of the same samples show that much of the original oxidized Tc<sup>7+</sup> pertechnetate in the glass reduces to Tc<sup>4+</sup> species in six-fold coordination in the VHT altered sample. Latest Raman profiles and map images of VHT altered sample cross-sections will be presented to illustrate distributions of the different crystalline and amorphous phases within the altered layers, as well as how water is incorporated into the glass at different stages of the alteration process.

## 3:30 PM ET15.09.02

**On Alteration Rate Renewal Stage of Nuclear Waste Glass Corrosion** Michael I. Ojovan; IAEA, Vienna, Austria.

The four generically-accepted stages of glass corrosion are reviewed with focus on fourth stage termed alteration rate renewal (or resumption) stage when the glass may start corroding with the rate similar to that at the initial stage. It is emphasised that physical state and physical changes that occur in the near-surface layers can readily lead to effective increases of leaching rate similar to alteration rate renewals.

Corrosion of glass in a geological repository is typically considered to occur into four stages [1, 2]: **Stage I:** Upon initial contact by water alkali cations are extracted by interdiffusion. The process of interdiffusion is followed by two simultaneous reactions: hydration and dissolution of the glass network. **Stage II** is when glass corrosion rate becomes dependent on the solution saturation state. Unlike the rate of ion exchange, the dissolution rate of the glass network decreases. **Stage III:** The solution becomes saturated and secondary minerals begin to form; the alteration phase is often a simple clay mineral, such as a smectite or chlorite. **Stage IV: Alteration rate renewal** may occur depending on the type of alteration phase formed. Experimental data on long-term (during few decades) corrosion of radioactive borosilicate glass K26 designed to immobilise NPP radioactive waste evidence on resumptions of radionuclides (<sup>137,134</sup>Cs) leaching [3]. The cause of that was however related not to chemical changes in the leaching environment but rather to physical state of glass surface. Formation of small cracks on the surface results in new fresh-glass areas in contact with water. Both experimental and molecular dynamic simulations prove that the freshly formed glass surfaces are enriched in alkali elements including <sup>137,134</sup>Cs [3,4]. Because of that the leaching of radionuclides is not monotonic and has distinct step-like additives at the times of cracks formation which resembles resumption of initial stages of glass leaching. This paper emphasises that not only alteration phase formed can lead to an increased rate of corrosion and return to the forward rate, and that physical state and physical changes that occur in the near-surface layers can readily lead to an effective alteration rate renewal. Nuclear waste glass corrosion in the disposal environment is of primary importance for ensuring safety of nuclear waste disposal therefore the research programmes focused on long-term behaviour of glasses [5, 6] should account for both chemical and physical effects.

*References:* [1]. Bacon D., Pierce E. In: M. Ojovan. *Handbook of Advanced Radioactive Waste Conditioning Technologies*, Woodhead (2011). [2]. M.I. Ojovan, W.E. Lee. *An Introduction to Nuclear Waste Immobilisation*, Elsevier (2014). [3]. M.I. Ojovan. *J. Non-Cryst. Solids*, **434**, 71 (2016). [4]. M. Ren, L. Deng, J. Du. *J. Non-Cryst. Solids*, **476**, 87 (2017). [5]. G.S. Frankel et.al., *npj Materials Degradation*, **15**, 1-17 (2018). [6]. Gin S. et.al., *Mater. Today* **16**, 243–248 (2013).

## 3:45 PM ET15.09.03

**Method Development for High Temperature *In Situ* Neutron Diffraction Measurements of Glass Crystallization on Cooling from Melt** John S. McCloy<sup>1,2</sup>, Jarrod Crum<sup>2</sup>, José Marcial<sup>1</sup>, Joerg Neuefeind<sup>3</sup>, Deepak Patil<sup>1</sup> and Brian Riley<sup>2</sup>; <sup>1</sup>Washington State University, Pullman, Washington, United States; <sup>2</sup>Pacific Northwest National Laboratory, Richland, Washington, United States; <sup>3</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

A glass-ceramic waste form is being considered for immobilization of waste streams of alkali (A), alkaline-earth (AE), lanthanide (Ln), and transition metals generated by transuranic extraction for reprocessing used nuclear fuel. Benefits over an alkali borosilicate waste form are realized by the partitioning of the glass-insoluble fission product fraction into a suite of ceramic phases through controlled crystallization, including AEMoO<sub>3</sub> (powellite) and (Ln,A,AE)<sub>10</sub>Si<sub>6</sub>O<sub>26</sub> (oxyapatite). In this study, a simplified 8-oxide system was used, 33.5 SiO<sub>2</sub> - 21.9 Nd<sub>2</sub>O<sub>3</sub> - 9.6 CaO - 8.9 Na<sub>2</sub>O - 8.2 B<sub>2</sub>O<sub>3</sub> - 6.6 Al<sub>2</sub>O<sub>3</sub> - 6.4 MoO<sub>3</sub> - 4.9 ZrO<sub>2</sub> (in mol%).

*In-situ* neutron diffraction experiments were attempted to capture crystallization upon cooling from 1300°C. The combination of high temperatures and reactivity of borosilicate glass with typical containers such as vanadium and niobium prevented their use, so methods using sealed thick-walled silica ampoules were developed. Unexpectedly, high neutron absorption (despite isotope substitution with B-11), low crystal fraction, and high silica container background made quantification difficult for high temperature measurements. Proof of concept measurements were then performed on different potential high-temperature container materials, emphasizing crystalline materials so that residual glass in the sample could be more easily analyzed. Room temperature measurements were conducted with a crystallized sample in 'ideal' containers stable at low temperatures (vanadium and thin-wall silica capillaries) and compared to the same in containers stable at high temperatures (platinum, single crystal sapphire, and thick-walled silica ampoules). Results suggested that sapphire is probably the best choice if suitably sealed to prevent contamination from the sample after neutron activation. Companion experiments are suggested for high-temperature *in-situ* x-ray diffraction measurements. With high energy x-rays, levitation experiments may be possible despite sample volatility, since collection times are much shorter at synchrotrons than those required for neutron experiments. Additionally, wire heater methods using a very small amount of sample are also possible with x-ray interrogation. Other possibilities for obtaining *in-situ* crystallization data upon cooling from molten glass are suggested.

#### 4:00 PM ET15.09.04

**Structure/Dissolution Relationship of a ZnO/CaO-Modified Base Glass for High Level Waste—Compositional, Waste-Loading and Groundwater Effects** Adam J. Fisher, Prashant Rajbhandari, Neil Hyatt, Russell Hand and Claire L. Corkhill; Univ of Sheffield, Sheffield, United Kingdom.

The UK is currently in the process of adopting a modified seven-oxide base glass (ZnCa MW), containing ZnO and CaO for the vitrification of high level waste at a molar ratio of ZnO:CaO 40:60 in the nominal Mixed Windscale (MW) formulation. Previous studies have given an insight to how Zn and Ca may influence glass dissolution, however the dual role of Zn and Ca remains poorly constrained.

This investigation studied a series of six ZnCa MW compositions with different ZnO/CaO ratios, with the aim of understanding how the varying ratios influence the structure of the glass and how this relates to the aqueous durability in all stages of glass corrosion. Structural analysis using <sup>29</sup>Si and <sup>11</sup>B NMR has been utilised to determine the relative influence of Zn and Ca on the borosilicate glass network and on the altered glass post-dissolution. Dynamic flow-through (SPFT) and static (MCC-1 and PCT-B) batch dissolution experiments give insight to the behaviour of the various ZnO/CaO ratios, whereby dissolution rates and formed altered layers were sensitive to small compositional changes.

Waste-loaded ZnCa MW formulations with varying ZnO/CaO ratios and varying waste loads (20, 28 and 35 wt.%) were developed and subjected to static dissolution (MCC-1 and PCT-B) in clay, granite and saline groundwaters under conditions relevant to geological disposal. From these studies, optimised glass formulations have been suggested in terms of their long-term aqueous durability.

#### 4:15 PM ET15.09.05

**Probing the Temperature Dependence of Aqueous Glass Dissolution Mechanisms** Thomas L. Goulet<sup>1</sup>, Edward Tipper<sup>1</sup>, Sambuddha Misra<sup>2, 1</sup>, Madeleine Bohlin<sup>1</sup>, Rui Guo<sup>1</sup>, Aleksey Sadekov<sup>3, 1</sup> and Ian Farnan<sup>1</sup>; <sup>1</sup>University of Cambridge, Cambridge, United Kingdom; <sup>2</sup>Centre for Earth Sciences, Indian Institute of Science, Bengaluru, India; <sup>3</sup>School of Earth Sciences, The University of Western Australia, Crawley, Western Australia, Australia.

Countless simulant nuclear waste glass dissolution experiments have taken place at 90 °C to accelerate glass alteration. It is implicitly assumed that the dissolution mechanisms operating at 90°C would be the same as those in a deep geological disposal facility post-thermal pulse, which would be at around 40°C. Accurately predicting vitrified package lifespans within a repository therefore requires a comprehensive understanding of the dissolution mechanisms occurring at both temperatures; by extension an assessment of whether dissolution rates measured at 90 °C can be applied to repository conditions. Elemental releases and images of surface alteration alone from variable temperature experiments provide limited insight into the underlying dissolution mechanisms at each temperature, simply investigating whether glass dissolution rates follow an Arrhenius-type temperature dependence. Static batch experiments conducted on a simulant UK Magnox waste glass at temperatures of 40 °C, 60 °C, 70 °C, 80 °C and 90 °C investigated the temperature dependence of the concentrations leached into solution and the kinetics of alteration product formation, but could not discern the dominant dissolution mechanism at each stage of dissolution. Consequently, more evidence was required to provide a complete picture of glass alteration and complement the concentration and surface alteration results. Based on the significant differences in the morphology of the altered glass as predicted by conflicting models of glass alteration, it was expected that different magnitudes of isotopic fractionation for mobile glass species leached into solution would be observed depending upon the extent and structure of the altered layer and the dominant dissolution mechanism. Through preliminary proof of concept experiments on a simplified simulant Magnox waste glass analogue leached at 90 °C and a simulant Magnox waste glass leached at 40 °C and 90 °C, we observed systematic temperature-dependent isotopic fractionation which was consistent with the mechanisms and altered layer morphologies described in interdiffusion models of glass dissolution which arise from a highly passivating altered layer structure.

SESSION ET15.10: Radiation Damage Effects in Radioactive Wasteforms  
Session Chairs: Joe Hriljac and Carolyn Pearce  
Wednesday Morning, November 28, 2018  
Hynes, Level 3, Room 308

#### 8:30 AM \*ET15.10.01

**Production and Evolution of Radiation Damage in Nuclear Waste Ceramics** William J. Weber<sup>1, 2</sup>, Eva Zarkadoula<sup>2</sup> and Yanwen Zhang<sup>2</sup>; <sup>1</sup>University of Tennessee, Knoxville, Tennessee, United States; <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Self-radiation damage from the decay of radionuclides can affect microstructural evolution, phase stability, and thermodynamic properties in ceramic nuclear waste forms. The principal sources of radiation are beta-decay of the fission products and alpha-decay of the actinide elements. In general, beta-decay of the short-lived fission products is the primary source of radiation and heat generation in high-level waste forms during the first 600 years of storage; however, there is no evidence of significant long-term effects of fission product decay on the physical properties of nuclear waste forms. Because

of the long half-lives of the actinides and their daughter products, alpha-decay is dominant over very long timescales. Alpha decay produces energetic alpha particles (4.5 to 5.5 MeV) and recoil nuclei (70 to 100 keV), which result in both radiation damage and the accumulation of helium. The evolution of radiation damage due to alpha-decay has been studied using short-lived actinides, such as  $^{238}\text{Pu}$  and  $^{244}\text{Cm}$ , in several candidate ceramics for the immobilization of actinides. Ion beam irradiations of candidate ceramics are more frequently employed due to decreased costs, shorter irradiation timescales and the non-radioactive nature of the irradiated materials. Ion irradiations are performed over a wider range of irradiation conditions to implant helium, study radiation damage kinetics, understand the separate and combined effects of alpha particles and alpha recoils, and benchmark against alpha-decay damage due to short-lived actinides. At ion energies typically used to study alpha-decay damage in nuclear waste ceramics, the electronic and nuclear energy losses are both important, and local ionization along the ion path can affect damage production and evolution. For heavy ions used to mimic radiation damage from alpha recoil nuclei, the spatial coupling of electronic and nuclear energy loss can lead to reduced or enhanced damage production along the ion trajectory. The athermal annealing induced by electronic energy loss of heavy ions can significantly impact the evolution kinetics of radiation damage. While alpha particles are much less damaging than alpha recoils, the electronic energy loss from the alpha particles can also cause athermal annealing of heavy ion damage (i.e., alpha-recoil damage) that can impact the evolution of radiation damage. Helium implantation studies have shown that the accumulation of helium and heavy ion damage leads to the formation of helium bubbles above a threshold helium concentrations. These results have significant implications for interpreting and modeling the radiation response of nuclear waste ceramics in accelerated testing using MeV ion irradiation.

This work was supported by the U.S. DOE, BES, MSED.

#### 9:00 AM ET15.10.02

**Molecular Dynamics Simulation of Ballistic Effects in Simplified Nuclear Waste Glasses** Amreen Jan<sup>1,2</sup>, Jean-Marc Delaue<sup>1</sup>, Sebastien Kerisit<sup>2</sup> and Stephane Gin<sup>1</sup>; <sup>1</sup>CEA Marcoule, Bagnols-sur-ceze, France; <sup>2</sup>Geochemistry, Pacific Northwest National Laboratory, Richland, Washington, United States.

Immobilization of High Level Waste (HLW) in borosilicate matrix and further disposal into geological repository has been regarded as one of the best way for long term isolation of HLW from biosphere. Radionuclides are expected to stay confined until glass matrix has been breached by water and it begins to alter. Recently, an increase in glass alteration rate was observed in irradiated samples (with dominant ballistic dose) as compared to non-irradiated samples. Other studies using doped glasses, external irradiation techniques and molecular dynamics have now confirmed that ballistic effects caused by recoil nuclei, on alpha decay, will be the dominant source of irradiation damage on the long term. Ballistic effects have been observed to induce macroscopic and microscopic structural changes e.g. swelling, decrease in hardness, increase in fracture toughness and structural disorder and depolymerisation in the glasses. Thus, it becomes necessary to study such changes and their impact on the physical and chemical durability of this glass.

In the current study, molecular dynamics simulation of ballistic effects have been investigated in simple sodium borosilicate [ $\text{Na}_2\text{O}/\text{B}_2\text{O}_3=1$ ] and sodium aluminoborosilicate [ $(\text{Al}_2\text{O}_3-\text{Na}_2\text{O})/\text{B}_2\text{O}_3=1$ ] glass compositions, by exposing such glasses to series of displacement cascades, wherein heavy projectiles cause atomic displacements by elastic collisions and progressively damage the bulk glass. The accumulated pressure or stored energy inside the glass was found to saturate with deposited energy. Furthermore, structural analysis of the irradiated glasses revealed a decrease in density, depolymerisation, increase in intermediate, short range disorder and randomness. The magnitude of damage was found to depend on the glass composition and, in general, aluminosilicate glasses were found to be slightly less damaged, after irradiation, as compared to borosilicate glasses. An ongoing study on, impact of such structural evolutions under irradiation, on alteration of glass will also be discussed

#### 9:15 AM ET15.10.03

**Investigation of the Structural Behavior of YSZ Under Ion Impact—Effect of Grain Size, Temperature and Specific Energy Loss** Parswajit Kalita<sup>1</sup>, Santanu Ghosh<sup>1</sup> and Devesh K. Avasthi<sup>2</sup>; <sup>1</sup>Indian Institute of Technology Delhi, New Delhi, India; <sup>2</sup>Amity University, Noida, India.

A crucial issue regarding the use of nuclear energy is the safe management of radioactive plutonium and minor actinides since they are unavoidable byproducts of nuclear energy generation using the conventional uranium fuel technology. A possible solution to this problem might be the ‘inert matrix fuel’ (IMF) concept, which is based on “uranium free” plutonium or minor actinide compounds embedded in an inert material matrix. Since these fuels are being contemplated to burn plutonium or minor actinides instead of uranium, they have the dual advantage that they do not breed plutonium or higher actinides during burn-up and that the existing stockpiles of plutonium and minor actinides can also be reduced.

Amongst many different potential materials, the oxide ceramic yttria stabilized zirconia (YSZ) is considered to be very promising for application as the inert matrix material.

Now, the materials employed in nuclear reactors are prone to un-desirable damages (amorphization, point defect clustering, volume swelling, etc.) since they are subjected to an extremely harsh environment consisting of extensive radiation (fission fragments that create damage via electronic energy loss, alpha recoil particles that create damage via nuclear energy loss, neutrons etc.) and high temperatures (~ 1000 K). Accumulation of such radiation damage over a period of time may lead to material failure ultimately resulting in catastrophic nuclear accidents. It is therefore vital to understand the behavior of YSZ under such extreme conditions, before using it as the inert material matrix in IMFs, for the design of safe, durable and efficient nuclear energy systems.

A number of factors, such as: (i) Specific energy loss (electronic energy loss ( $S_e$ ) & nuclear energy loss ( $S_n$ )) of the energetic particles (ii) Grain size of the material (iii) Temperature of the environment (irradiation temperature) etc., needs to be taken into consideration for an in-depth understanding of the radiation induced damage.

Motivated by this, YSZ pellets having different grain sizes (ranging from tens of nano-meters to few microns) were irradiated with different ions (single beam irradiation with low energy ions or single beam irradiation with high energy ions or simultaneous dual beam irradiation with low and high energy ions) at different temperatures (room temperature and 1000 K) in an attempt to understand the dependence of radiation damage on the above mentioned factors. The low energy and high energy ions were chosen so as to simulate the damage produced by alpha recoil particles and fission fragments respectively, while the irradiations at 1000 K helped to better simulate a typical nuclear reactor environment. We will show that the irradiation damage depends critically, and in a complex manner, on the crucial interplay between the specific energy loss/type of irradiation (single beam or simultaneous dual beam), grain size (grain boundaries) and environmental temperature.

#### 9:30 AM BREAK

**10:00 AM \*ET15.11.01**

**Role of Volatile Elements, Halogen and Noble Gases in Glass and Melt** Daniel R. Neuville, Maria Rita Cicconi and Eric Pili; IPGP-CNRS-USPC, Paris, France.

Volatile elements in glass and melt can induce very strong changes both in properties and structure. They can play a fundamental role during glass making, glass processes, and also in Earth Sciences since they can change drastically the dynamism of some eruptions, in particular during degassing processes. In detail, volatile elements, such as water or CO<sub>2</sub>, play a fundamental role in the generation, dynamics and evolution of magmas as they influence the solidus of minerals as well as the melts viscosity and thermodynamic properties. This results, for example, in a strong control of the main volatile element that is water on the extraction rate of magmas from the upper mantle and crust. At surface, the amount of water and CO<sub>2</sub> dissolved in magmas influence the dynamic of volcanic eruptions. Furthermore, other elements such as SO<sub>2</sub> and iodine also affect the melt properties as well as on their geochemical signature. Fluorine and chlorine can also produce produce very big disasters especially during andesitic volcanic eruptions. Therefore, volatile elements influence in various ways the geologic dynamic of the Earth and play important role in materials science. Therefore, we need to quantify the proportion and understand the speciation of dissolved volatiles in silicate melts. In order to tackle such challenging subject, we propose to investigate glasses, including natural magmatic compositions and industrial glasses, which contain dissolved CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, I<sub>2</sub>, F, and Cl by using Raman spectroscopy, a powerful and non-destructive technique.

**10:30 AM ET15.11.02**

**Glass Structure and Crystallization in Boro-Alumino-Silicate Glasses Containing Rare Earths and Transition Metals** John S. McCloy<sup>1, 2, 5</sup>, José Marcial<sup>1</sup>, Deepak Patil<sup>1</sup>, Muad Saleh<sup>1</sup>, Jarrod Crum<sup>2</sup>, Brian Riley<sup>2, 1</sup>, Hrishikesh Kamat<sup>3</sup>, Antoine Brehault<sup>3</sup>, Ashutosh Goel<sup>3</sup>, Kristian Barnsley<sup>4</sup>, John Hanna<sup>4</sup>, Prashant Rajbhandari<sup>5</sup>, Claire L. Corkhill<sup>5</sup>, Russell Hand<sup>1</sup> and Neil Hyatt<sup>5, 1</sup>; <sup>1</sup>Washington State University, Pullman, Washington, United States; <sup>2</sup>Pacific Northwest National Laboratory, Richland, Washington, United States; <sup>3</sup>Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; <sup>4</sup>University of Warwick, Coventry, United Kingdom; <sup>5</sup>The University of Sheffield, Sheffield, United Kingdom.

Nuclear wastes generated from reprocessing of used nuclear fuel tend to contain a large fraction of rare earth metals (RE e.g., Nd), transition metals (TM e.g., Mo, Zr), alkali metals (A e.g., Cs), and alkaline earth metals (AE e.g., Ba, Sr). Various strategies have been considered for immobilizing such waste streams, varying from nominally crystal-free glass to glass-ceramic to multi-phase ceramic waste forms. For glass and glass-ceramic waste forms, the added glass-forming system is generally alkali-alkaline earth-alumino-boro-silicate (i.e., Na-Ca-Al-B-Si oxide).

In this US-UK collaborative project, we investigate the glass structure and crystallization dependence on compositional changes in simulated nuclear waste glasses and glass-ceramics. Compositions ranged in complexity from 5 oxides to 8 oxides. Specifically, the roles of Mo and lanthanides are investigated, since a proposed glass-ceramic waste form contains crystalline phases such as powellite [(AE,A,RE)MoO<sub>4</sub>] and oxyapatite [(RE,AE,A)<sub>10</sub>Si<sub>6</sub>O<sub>26</sub>], and the precipitation of molybdenum phases is known to be affected by rare earth concentration in the glass.

Additionally, the effects other chemical additions have been systematically investigated, including Zr, Ru, P, and Ti. A series of studies was also undertaken to ascertain the effect of the RE size on glass structure and on partitioning to crystal phases, investigating similarities and differences in glasses containing single RE oxides of Sc, Y, La, Ce, Nd, Sm, Er, Yb, or Lu. Finally, the effect of charge compensation was investigated by considering not only the commonly assessed peralkaline glass, but also metaluminous and peraluminous compositions.

Glass structure and crystallization studies were conducted by spectroscopic methods (Raman, x-ray absorption, nuclear magnetic resonance, optical absorption, x-ray photoelectron spectroscopy), microscopy (scanning electron microscopy, transmission electron microscopy, electron probe microanalysis), scattering (x-ray and neutron diffraction, small angle measurements) and physical characterization (scanning calorimetry, viscosity, density). This talk will give an overview of the research program and some characteristic results.

**10:45 AM \*ET15.11.03**

**Alkali-Silica Gel Reaction in Glasses Dissolved at High pH—Implications for Co-Disposal of Vitrified and Cementitious Nuclear Wastes** Colleen Mann<sup>1</sup>, Jeremy Eskelsen<sup>2</sup>, Karine Ferrand<sup>3</sup>, Karel Lemmens<sup>3</sup>, Eric Pierce<sup>2</sup> and Claire L. Corkhill<sup>1</sup>; <sup>1</sup>University of Sheffield, Sheffield, United Kingdom; <sup>2</sup>Oak Ridge National Laboratory, Knoxville, Tennessee, United States; <sup>3</sup>SCK.CEN, Mol, Belgium.

International consensus is that vitrified nuclear waste should be disposed of underground where it can safely undergo radioactive decay, isolated from the environment and future populations. Cement will be ubiquitous in all disposal facility concepts. For example, cement will be used to line vaults, in seals and plugs, as buffer material and in general construction. It is expected to play a key role in the Belgian and UK deep geological disposal concepts for high- and intermediate-level vitrified waste, respectively, and possibly also for the shallow disposal facility at Hanford site in the USA. The interaction of cement with vitrified waste is a key issue, since the generation of a hyperalkaline plume could accelerate glass dissolution mechanisms, thereby enhancing radionuclide release from the vitrified waste.

Here, we discuss the results of investigations developed to elucidate the mechanisms and kinetics of sodium aluminoborosilicate glass dissolution in the presence of simplified, buffered high-pH alkali solutions (K<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, CaSiO<sub>3</sub>, MgSiO<sub>3</sub> and H<sub>2</sub>SiO<sub>4</sub>), synthetic cement leachates, including a young cement water (K, Na-rich; pH 13.7), an evolved cement water (Ca, Na rich; pH 12.5) and an old cement water (Ca, Na-rich, pH 11.8), and also real cement leachates (containing mixed alkalis; pH ~13). The surfaces of glass powders and monoliths were characterised using SEM, TEM, EDX, XRD and NMR. The rate of degradation of the glass in these solutions was found to be the result of two key mechanisms: i) the formation of a porous alkali- or alkaline-earth silica gel, where mean pore diameter was governed by pH, and the type of alkali or alkaline-earth element retained depended on the relative abundance of K, Na, Ca or Mg, the hydrated ionic radius and the ΔG of hydration of the alkali or alkaline-earth species; and ii) the precipitation of crystalline phases—including zeolite (e.g. phillipsite-K), phyllosilicate (e.g. rhodesite) and clay (e.g. smectite)—that, depending on the combination of glass composition, solution chemistry and the phase, either formed a dense layer, impervious to solution species, that protected the surface from further dissolution or, conversely, promoted the ongoing dissolution of the glass through continual consumption of dissolved silica and re-precipitation of Si-bearing phases. These results highlight the complex, but significant effects of high pH, cementitious solutions on the dissolution of nuclear waste glasses, which should be included in future models of vitrified waste disposal in a cement-containing geological disposal facility.

**11:15 AM ET15.11.04**

**The Influence of Glass Composition on Iodine Solubility and Speciation** Maria Rita Cicconi, Eric Pili and Daniel R. Neuville; Institut de Physique du Globe de Paris, Paris, France.

Researchers in many fields are interested in the understanding of iodine behavior in solid and molten materials, however, only a few data on iodine

solubility and speciation are available in the literature.

Iodine is the heaviest stable halogen element, and in spite of its low natural abundance, it is interesting in Geosciences, mainly because of its link to xenon since most of the iodine isotopes become xenon isotopes by  $\beta$ -radioactive decay. In the framework of the Comprehensive Nuclear-Test-Ban Treaty, the atmospheric radioxenon analyses provide the only distinctive signature of a nuclear explosion.

$^{129}\text{I}$  is of particular concern because it will be a major contributor to the radioactivity released by a geological repository site for nuclear wastes, but previous studies show that iodine mobility is strongly dependent on the redox.

For all these reasons, it is important to understand the mechanisms related to the solubility of iodine depending on the composition of the glass and to analyze its solubility, redox state, and distribution in a glass network.

We investigated the iodine solubility, speciation, and the influence on properties and glass structure, depending on bulk chemistry, temperature and pressure. Iodine redox state studies were carried out both by Raman and X-ray Absorption Spectroscopy. Our studies on silicate glasses show that iodine could be stabilized with different valences (as  $\text{I}^{-1}$ ,  $\text{I}^0$  and  $\text{I}^{+5}$ ) and with concentrations up to 3.3 wt.% when B is introduced.

#### 11:30 AM \*ET15.11.05

**Tellurite Glasses to Immobilize Highly Volatile Radioactive Technetium and Iodine** Jong Heo, Jaeyoung Pyo and Cheongwon Lee; Pohang University of Science and Technology (POSTECH), Kyungbuk, Korea (the Republic of).

Spent fuel contains several fission products of uranium including highly volatile nuclides of Tc and I.  $^{99}\text{Tc}$  has a long half-life of 211,000 years and freely migrates in groundwater because of its high water solubility.  $^{129}\text{I}$  also shows high solubility and mobility in water with a long half-life time of approximately 15.7 million years. Both elements are also generated during the pyrochemical reprocessing of the spent fuel. They evaporate from the spent fuel during the voloxidation step of the pyrochemical processing and are captured through the off-gas treatment system by forming  $\text{Ca}(\text{TcO}_4)_2$  and  $\text{AgI}$ , respectively. Vitrification using borosilicate glasses has been investigated to immobilize Tc and I with limited success due to the volatilization during melting at  $T > 1100^\circ\text{C}$ . In addition, Tc and I have low solubility in these glasses with values less than 0.3 and 1 wt.%, respectively. Therefore, it is necessary to develop new tellurite glass hosts with low melting temperatures and high Tc and I solubility.

Alumino-borotellurite glass of  $64\text{TcO}_2\text{-}11\text{Al}_2\text{O}_3\text{-}10\text{B}_2\text{O}_3\text{-}8\text{Na}_2\text{O-}7\text{CaO}$  (mol%) composition was developed to vitrify Tc wastes. Re was used as a surrogate for Tc and up to 90% of Re added into the starting batches remained in the glass after melting. Normalized elemental releases after the standard product consistent test (PCT) satisfied the US regulatory standard of  $<2\text{ g/m}^2$  for glasses containing up to 9 wt.% of  $\text{Ca}(\text{ReO}_4)_2$ . Raman and X-ray absorption spectroscopy (XAS) analyses suggest that Re ions have +7 oxidation state forming  $[\text{ReO}_4]^-$ . Surfaces of the bulk glasses after leaching in liquid water showed the formation of an alteration layer depleted with Na, B, and Ca. Rates of elemental leaching decreased as the thickness of the alteration layer increased with time. It suggests that the alteration layer serves as a passivation layer and leads to a decrease in leach rates.

Silver tellurite glass of  $53\text{TcO}_2\text{-}23\text{Ag}_2\text{O-}5\text{Bi}_2\text{O}_3\text{-}19\text{AgI}$  (mol%) was used to vitrify  $\text{AgI}$  waste. The glass contains 11.21 wt.% of I and the retention of iodine during melting is as high as 95.7%. Silver tellurite glass has glass transition temperature of  $165\pm 3^\circ\text{C}$  and it is high enough to avoid any unexpected crystallization and flow property changes in the deep geological site. The chemical durability of the glass also satisfies the US regulatory standards. Iodine has an oxidation state of -1 and is surrounded by four  $\text{Ag}^+$  ions at a distance of 0.275 nm and forms  $[\text{Ag}_4\text{I}]^{3+}$  tetrahedral units.  $\text{Ag}_4\text{I}$  tetrahedral units are connected to the glass network through Coulomb interaction between  $[\text{Ag}_4\text{I}]^{3+}$  and non-bridging oxygens (NBOs).

SESSION ET15.12: Managing Corium and Degraded Nuclear Fuels from Severe Accidents  
Session Chairs: Nicolas Clavier and Claire Corkhill  
Wednesday Afternoon, November 28, 2018  
Hynes, Level 3, Room 308

#### 2:00 PM ET15.12.01

**Synthesis, and Characterisation and Preliminary Corrosion Behaviour Assessment of Simulant Fukushima Nuclear Accident Fuel**

**Debris** Clémence Gausse<sup>1</sup>, Martin Stennett<sup>1</sup>, Neil Hyatt<sup>1</sup>, Charilaos Paraskevoulakos<sup>3</sup>, Mahmoud Mostafavi<sup>3</sup>, Tomooki Shiba<sup>2</sup> and Claire Corkhill<sup>1</sup>; <sup>1</sup>University of Sheffield, Sheffield, United Kingdom; <sup>2</sup>Japan Atomic Energy Agency, Tokai-mura, Japan; <sup>3</sup>University of Bristol, Bristol, United Kingdom.

The earthquake and the tsunami that occurred on the 11<sup>th</sup> March 2011 at the Fukushima Daiichi Nuclear Power Plant (NPP) induced a loss of coolant accident and the partial meltdown of boiling water reactor Units 1 to 3. The temperature within the reactor rose in excess of  $2000^\circ\text{C}$  causing melting and reaction of  $\text{UO}_2$  pellets with the steam-oxidised zircaloy fuel cladding, forming nuclear accident fuel debris (NFD) and, where melting of other reactor components occurred (e.g. concrete, steel from the pressure vessel), corium. We present results of an investigation aimed at simulating NFD and corium, including an assessment, by  $\mu$ -focus XAS methods, of the distribution of simulant fission products (Ce as a surrogate for Pu and Nd to represent trivalent rare earth fission products), which is an important prerequisite to fuel debris retrieval from the Fukushima reactors, due to commence in 2021. Synthesis of materials in the  $\text{U}_{1-x}\text{Zr}_x\text{O}_2$  solid solution was performed by wet and dry chemistry routes, and materials in the  $\text{U}_{1-x}\text{Ln}_x\text{O}_2$  ( $\text{Ln} = \text{Ce}$  and/or  $\text{Nd}$ ) solid solutions were mixed with Zr metal and heated  $>2000^\circ\text{C}$  by oxyfuel processing. Selected phases were further melted with concrete and steel to synthesise simulant corium materials. Analysis of each phase was performed by techniques including XRD, SEM/EDX, XPS and Raman spectroscopy.

After the accident, continuous filtered water injection (firstly seawater, followed by Fukushima NPP ground water and filtered water) has been used to cool the NFD and corium, and reduced the temperature below  $100^\circ\text{C}$ . [1]. In this so-called stable cold shutdown situation, analysis of coolant water effluent evidenced the presence of Pu, indicating the fuel debris is dissolving. Since the aqueous alteration of fuel debris is expected to alter its chemical and mechanical properties, and may also result in the formation of secondary alteration products, we here present preliminary results of leaching experiments of the above materials in relevant solution compositions.

[1] Technical Strategic Plan 2016, 2016, Nuclear Damage Compensation and Decommissioning Facilitation

#### 2:15 PM ET15.12.02

**Stability of Melted Irradiated Nuclear Fuel (Corium) Debris Under Fukushima Post-Accidental Conditions** Daniel Serrano Purroy, Vincenzo V. Rondinella, Laura Aldave de las Heras and Albert Martínez-Torrents; JRC Karlsruhe, Eggenstein-Leopoldsh, Germany.

During the tsunami-caused 2011 meltdown at Fukushima Daiichi nuclear power plant, melted nuclear fuel (corium) was exposed to emergency cooling

aqueous media, especially borated and sea water, which may have an effect on the stability of the fuel. The corium consists of solidified melt of nuclear fuel, fission products, cladding, control rods and other structural materials. Up to 600 tons of corium debris lies in Fukushima damaged units. It is important to provide data on stability of corium in these aqueous media in order to provide indications about potential radionuclide release mechanisms and their environmental impact and science-based advice for the decommissioning and remediation of the damaged sites.

In order to assess the stability of corium in aqueous cooling media used in Fukushima, experiments were carried out at JRC-Karlsruhe in collaboration with CRIEPI (Japan) using genuine irradiated corium samples taken from the TMI-2 accident.

Static leaching experiments were performed in air and at hot-cell temperature in deionized water and in water containing 2g/L of boric acid. In all cases the solution was continuously stirred and renewed several times during the experiments. The results are compared with similar experiments carried out on LWR spent nuclear fuels (with average burnups of 54 and 60 GWd/t<sub>HM</sub>), carried out in deionized water and boric acid water, but also in sea water and simplified groundwater (1 mM NaHCO<sub>3</sub> and 19 mM NaCl).

After approximately one year of experimental campaign, the releases of matrix elements such as uranium, neptunium, cerium, the instant release fraction of elements like caesium as well as the release of less soluble elements like zirconium in water containing boric acid do not differ significantly from the releases observed in deionized water. The results reveal no significant effect due to the origin of the sample, core or crust, and to the presence of boric acid on the mobility of the radionuclides in the studied samples. As partial exception, the amount of silver found in solution was higher in experiments carried out with core samples. The presence of heterogeneously distributed silver metallic spheres in TMI-2 corium samples (originating from control rod material) has been previously reported and is most probably responsible for this specific effect. Chemical analysis to determine the inventory of the samples will be used for normalisation and comparison.

A detailed comparison between corium samples and undamaged irradiated fuel samples is complicated because of the different morphology of the fragments. The results of surface area determination by SEM image analysis will be reported.

The present experimental results are part of a programme dedicated to the analysis and the management of LWR after severe accidents. In particular, they will be useful in support to defining the decommissioning and remediation strategies of the Fukushima Daiichi nuclear power plant.

## 2:30 PM BREAK

### SESSION ET15.13: Advances in Cement, Geopolymers and Related Wasteforms for Radioactive Waste Management

Session Chairs: Felix Brandt and Michael Ojovan

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 308

## 3:30 PM \*ET15.13.01

**Tc-99 and I-129 Immobilization by Ettringite Formation in Cementitious Waste Forms** Sarah Saslow<sup>1</sup>, Sebastian Kerisit<sup>1</sup>, Tamas Varga<sup>1</sup>, Matthew Asmussen<sup>1</sup>, Wooyong Um<sup>2</sup>, Gary L. Smith<sup>1</sup> and Reid Peterson<sup>1</sup>; <sup>1</sup>Pacific Northwest National Laboratory, Richland, Washington, United States; <sup>2</sup>Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Immobilization of technetium-99 (Tc) and iodine-129 (I) at the Hanford site in Washington State, USA, is a persistent challenge that can be assisted by using cementitious waste form (CWF) technologies. In response to the dynamic compositional range of Tc- and I-containing low activity waste (LAW) and secondary waste streams generated by LAW vitrification, the development of alternative CWF formulations is required to address composition-specific challenges related to contaminant immobilization. For example, sulfuric acid neutralization of highly alkaline waste streams generates a high-sulfate liquid waste that cannot be immobilized by the baseline Cast Stone CWF formulation (8% ordinary portland cement (OPC)/47% blast furnace slag (BFS)/45% fly ash (FA)). At the anticipated sulfate concentrations in these waste streams the Cast Stone CWFs are less likely to cure and prolonged formation of ettringite [Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>•26(H<sub>2</sub>O)] will lead to expansion and subsequent cracking that increase risk of contaminant release.<sup>1-2</sup> Recently, some of these challenges were overcome by increasing the calcium content in the waste form through substitution of hydrated lime (HL, Ca(OH)<sub>2</sub>) for FA, providing a sink for excess sulfate during the early curing period.<sup>2</sup> However, the most striking observation came from contaminant leach tests, where Tc effective diffusivity decreased by two orders of magnitude as ettringite-growth continued relative to previous testing campaigns.<sup>3</sup> This suggests that ettringite may aid contaminant retention throughout the CWF life cycle. Here, the mechanism for Tc and I incorporation into ettringite is explored using X-ray diffraction and X-ray absorption spectroscopy techniques combined with *ab initio* molecular dynamics simulations. Evidence for TcO<sub>4</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup> substitution for sulfate and competitive incorporation and redox processes as a function of the chemical environment of the CWF will be discussed relative to the development of improved CWFs.

1. Sarkar, S.; et. al. *Cement and Concrete Composites*. **2010**, 32 (3), 241-252.

2. Saslow, S. A.; et. al. 2017. *Updated Liquid Secondary Waste Grout Formulation and Preliminary Waste Form Qualification*; PNNL-26443. Pacific Northwest National Laboratory, Richland, WA.

3. Um, W.; et. al. 2016. *Liquid Secondary Waste Grout Formulation and Waste Form Qualification*; PNNL-25129. Pacific Northwest National Laboratory, Richland, WA.

## 4:00 PM ET15.13.02

**Establishing Radiation Effects in Silica Based Waste Forms** Laura Leay, Aaron Daubney and Alex J. Potts; University of Manchester, Moor Row, United Kingdom.

In order to fully understand the performance of a nuclear waste form, the effects of radiation must be understood. Silica based materials can be used to treat waste; glass is the material of choice for HLW immobilisation and geopolymers are now being considered as an alternative to cementitious grouts for ILW. These materials are both comprised of an amorphous network of silica modified by elements such as Al or B as well as cationic species such as Na or K. This represents a complex system where the effects of network reorganisation and ion migration must be understood. In addition, mechanisms of energy transfer to an aqueous phase in contact with this material, and the radiolysis effects, must also be considered. Ongoing experimental studies into radiation effects using external radiation sources such as gamma and heavy ion acceleration are underway. Here we present some preliminary finding and invite further discussion into irradiation effects in amorphous silica based waste forms.

## 4:15 PM ET15.13.03

**Solidification of HyBRID Waste Using Metakaolin Based Geopolymer Waste Form** Jinmo Ahn<sup>1</sup>, Seongye Kwon<sup>1</sup>, Won-Seok Kim<sup>1</sup>, Seonbyeong Kim<sup>2</sup>, Wangkyu Choi<sup>2</sup> and Wooyong Um<sup>1</sup>; <sup>1</sup>Division of Advanced Nuclear Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of); <sup>2</sup>Decontamination and Decommissioning Research Division, Korea Atomic Energy Research Institute, Daejeon, Korea (the Republic of).

The hydrazine based reductive metal ion decontamination (HyBRID) process is recently developed for decontamination of primary coolant system of nuclear power plant and considered as an attractive process because of no organic chelates used. The HyBRID sludge waste is the final product of HyBRID process formed through BaSO<sub>4</sub> precipitation, containing high content of sulfate. The presence of sulfate in HyBRID sludge waste may cause defective cement waste forms due to the potential formation of sulfate bearing mineral such as ettringite [Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26(H<sub>2</sub>O)]. Therefore, instead of cement waste form, geopolymer waste form was developed in this study for solidification of HyBRID sludge waste. Metakaolin was used as geopolymer precursor and the two types of alkaline activators were prepared to test: sodium hydroxide solution with fumed silica and potassium hydroxide solution with fumed silica. Geopolymer waste forms were formulated with desired molar ratio of Si/Al (1.6-2), (Na<sup>+</sup> or K<sup>+</sup>)/Al (0.8-1), and H<sub>2</sub>O/Al (5-7.8). All geopolymer pastes were poured into cylindrical mold (23 mm in diameter x 46 mm in height) and cured for 7 days at room temperature. Geopolymer waste forms with waste loading (>30%) were successfully synthesized to meet the acceptance criteria (>3.45 MPa). Potassium-based geopolymer has better waste loading than sodium-based geopolymer. Moreover, geopolymer waste forms with 1 (Na<sup>+</sup> or K<sup>+</sup>)/Al molar ratio showed higher compressive strength than geopolymers formed with 0.8 (Na<sup>+</sup> or K<sup>+</sup>)/Al molar ratio, where the absorbance band of amorphous silica was detected. This suggests that amorphous silica was not fully dissolved when geopolymers were formed with 0.8 (Na<sup>+</sup> or K<sup>+</sup>)/Al ratio. Besides, the result of FT-IR spectra showed that the absorbance band at 964-976 cm<sup>-1</sup> indicated the vibrations of Si-O-Si and Si-O-Al groups of the geopolymer gel network. The each geopolymer waste forms were characterized by X-Ray diffraction (XRD) and scanning electron microscopy with X-ray energy dispersive spectrometry (SEM-EDS): (1) XRD results revealed that there was no change in the crystalline structure of HyBRID sludge after geopolymerization process. (2) Elemental mapping results indicated the HyBRID sludge constituents distributed homogeneously in geopolymer. Geopolymer can be used as stable waste form to solidify radioactive waste with high-sulfate content like HyBRID sludge.

#### 4:30 PM ET15.13.04

**Uptake of Ra and Eu in Cementitious Systems by Joint Solution Chemistry and Atomistic Modeling Studies** Piotr Kowalski<sup>1</sup>, Steve Lange<sup>1</sup>, Katja Burek<sup>2</sup>, Sean McGee<sup>2</sup>, Milan Psenicka<sup>3</sup>, Victor Vinograd<sup>1</sup>, Martina Klinkenberg<sup>1</sup>, Stephan Rohmen<sup>1</sup>, Michael Kumke<sup>2</sup>, Dirk Bosbach<sup>1</sup> and Guido Deissmann<sup>1</sup>; <sup>1</sup>Forschungszentrum Juelich, Juelich, Germany; <sup>2</sup>Potsdam University, Potsdam, Germany; <sup>3</sup>Charles University, Prague, Czechia.

Cementitious materials are widely applied in nuclear waste management in particular due to their capability for radionuclide retention and immobilization. However, the mechanisms governing the immobilization of various safety relevant radionuclides in these materials on the molecular scale are still not completely understood. Here we present combined experimental and computational approaches to enhance the mechanistic understanding of radionuclide uptake and retention in cementitious materials. To obtain a more detailed understanding of the radionuclide uptake by the different constituents of hardened cement pastes and concretes, a bottom-up approach is applied by investigating radionuclide interactions with various synthesized cement model phases like calcium silicate hydrates (C-S-H), monosulfoaluminate (AFm) and ettringite (AFt) phases, as well as hardened cement pastes made from ordinary Portland and low pH cement. Batch-type sorption experiments under anoxic conditions were performed to analyze the sorption kinetics and the effects of solution composition and solid to liquid ratio on radionuclide uptake. We observed a strong retention of Ra by C-S-H phases with a distinct dependency of the distribution coefficients on the Ca/Si ratio of the C-S-H and the alkali content in solution. TRLFS studies on the uptake of Eu by C-S-H phases indicated two different Eu(III) species in the C-S-H structure, in addition to the formation of a surface precipitate (probably Eu(III)-hydroxide). In order to interpret the experimental data and to obtain closer insights into the incorporation mechanisms, we constructed a set of structural models for the Ra and Eu uptake in C-S-H phases with different Ca/Si ratios based on modified tobermorite structures suitable for *ab initio* calculations. Using density functional theory (DFT) simulations we computed the energetics of the uptake of Ra and Eu species into the C-S-H phases, comparing in particular the incorporation of the Ra and Eu cations on different crystallographic sites. We found that, in addition to Ra sorption on surface sites, Ra can be exchanged also for Ca in the C-S-H interlayer, in particular at low Ca/Si-ratios, which is in line with the experimental findings on Ra uptake. The calculations of Eu uptake give a slightly different picture, confirming the possible Eu uptake on both interlayer and Ca intralayer positions, consistent with the experimental observations. We will discuss the importance of atomistic modeling studies for the interpretation of radionuclide uptake mechanisms and further possible developments for such joint experimental and computational studies on cementitious materials.

#### 4:45 PM ET15.13.05

**Influence of Mineral Salts Solubility on Bituminized Wastes Products Leaching Behavior in Free Swelling Conditions** Jean-Baptiste Champenois<sup>1</sup>, Rémi Blinder<sup>2</sup>, Arnaud Leclerc<sup>1</sup>, Armel Guillermo<sup>3</sup>, Michel Bardet<sup>2</sup> and Arnaud Poulesquen<sup>1</sup>; <sup>1</sup>CEA Marcoule, Bagnols-sur-Cèze, France; <sup>2</sup>Univ. Grenoble Alpes, CEA, INAC, Grenoble, France; <sup>3</sup>Univ. Grenoble Alpes, CEA, CNRS, INAC, SYMMES-UMR 5819, Grenoble, France.

During the last decades, some nuclear wastes of low/intermediate activity level were incorporated into a bituminous matrix. The behavior under water-induced leaching of the resulting bituminous waste products, which were elaborated by extrusion process and composed of approximately 60 wt % of bitumen and 40 wt % of various salts, has to be evaluated in the prospect of their acceptability into a deep geological disposal. This work aims at assessing the influence of the solubility of the incorporated salts on the water uptake, by studying the leaching behavior of simplified bituminized waste products (containing only one type of salt).

In order to model bituminized waste products, a series of simplified bituminized waste products was elaborated by incorporating 40 wt % of mineral salts of increasing solubility ranging from 2.5 10<sup>-3</sup> to 912 g / L, by using barium, strontium, calcium, magnesium, sodium sulfates and sodium nitrate. The amount of water uptake was monitored for each sample as a function of time by using gravimetric measurements. In addition, the ingress of water was simultaneously monitored by using <sup>1</sup>H-nuclear magnetic resonance and the corresponding samples morphology was evaluated with environmental scanning electron microscopy.

Gravimetric measurements show that the higher the solubility of the incorporated salt, the higher the amount of uptake water. Simultaneously, it was observed that the lower the solubility, the lower the mean diameter of pores, and the deeper the water ingress. These results were of particular interest to discuss the leaching behavior of industrial bituminized waste products that incorporated many salts with a similarly wide range of solubilities.

SESSION ET15.14: Strategies for the Immobilisation of Iodine-129 and Technetium-99

Session Chairs: John McCloy and Sarah Saslow

Thursday Morning, November 29, 2018

Hynes, Level 3, Room 308

#### 8:30 AM ET15.14.01

**Preliminary Investigation of the Structural Effects of Technetium in Iron Phosphate Glasses—A Rhenium Analogue Study** Daniel Bailey, Martin Stennett, Erik V. Johnstone and Neil Hyatt; University of Sheffield, Sheffield, United Kingdom.

Technetium is a high yield fission product with 22 isotopes all of which are radioactive. Due to its long half-life ( $t_{1/2} = 211,000$  years), Tc-99 requires immobilisation in a suitably robust host matrix prior to final disposal in a GDF. Iron phosphate glasses are an attractive solution as they can accept a wide range of ions in the glass network and have sufficient aqueous durability. The inherent difficulty of working with technetium and its compounds necessitates prior investigation using analogues before beginning investigations proper. A series of 40:60 iron phosphate glasses doped with rhenium were produced and characterised by Raman spectroscopy, powder X-ray diffraction, scanning electron microscopy and Mössbauer spectroscopy to determine the effect of rhenium addition on the glass network and iron redox. The results of this investigation provide useful insight as to the possible influence of technetium on iron phosphate glasses.

#### 8:45 AM \*ET15.14.02

**Strategies for the Capture and Immobilization of Radioiodine** Josef Matyas; Pacific Northwest National Laboratory, Richland, Washington, United States.

To support the revival of nuclear energy, advanced materials and processes are needed to capture and safely store radioiodine released during reprocessing of spent nuclear fuel. During this process, about 94–99% of the total iodine is volatilized to the dissolver off-gas, with the rest partitioned among off-gas streams from the vessel ventilation, cell, and melter. The iodine is primarily present in the form of  $I_2(g)$  with small concentrations of organic iodides (e.g.,  $CH_3I$ ), HI, and HOI. The two most common types of iodine capture technologies have been wet scrubbing and solid sorbents. The waste form development efforts have focused mainly on waste forms with iodide or iodate salts (e.g., AgI,  $PbI_2$ , NaI,  $NaIO_3$ ) stabilized by encapsulation in a glass, ceramic, or cementitious material. The presentation will discuss prior and novel technologies for radioiodine capture and candidate processes to produce different waste forms. Recommendations for future research in this area will also be included.

#### 9:15 AM ET15.14.03

**Durability Testing of Iodine Waste Forms** Matthew Asmussen, Joseph Ryan, Jarrod Crum and Nancy Avalos; Pacific Northwest National Laboratory, Richland, Washington, United States.

The release of radioiodine would need to be controlled in the off-gas management system during the dissolution of used nuclear fuel. Several material classes have been investigated for the capture of radioiodine including solid sorbents. Two examples are silver mordenite (AgZ), which is considered the benchmark material and silver functionalized aerogels (SFA), which have higher iodine capacity than AgZ. Both materials capture iodine through the formation of silver iodide (AgI). Due to the long half-life of I-129 (15.7 million years), this captured inventory of iodine must be safely managed for disposal in a repository. While AgI has low water solubility ( $K_{sp} = 8 \times 10^{-17}$ ) it can have deleterious interactions with the environment; examples being pH changes in the near field, redox processes that destabilize the AgI, and interference from species such as sulfide. Thus, a durable waste form will be required to ensure containment of the radioiodine upon the disposal of these AgI-laden materials. However, limited work to date has been performed to assess the durability of iodine waste forms. This presentation will provide an overview of recent corrosion testing efforts carried out on iodine waste form materials. Two examples systems were investigated: iodine-loaded AgZ material processed with hot isostatic pressing (HIP) and iodine-loaded SFA processed with spark plasma sintering. These materials were assessed using aqueous corrosion methods including single-pass flow-through testing (SPFT), the product consistency test (PCT), dilute reactor analysis (DRCA), and electrochemical analyses. The results from these tests were supplemented with characterization of the microstructure to track the progression of corrosion on the surface using scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction, and optical profilometry. It was generally observed that corrosion attack was most prominent in areas of low Si for SFA and at low Si and Al for the AgZ samples. As well the boundaries between Si- and Al-rich particles and the remaining matrix experienced general inward attack.

#### 9:30 AM \*ET15.14.04

**Compositional Dependence of Nepheline Crystallization in High Level Waste Glasses** Ashutosh Goel<sup>1</sup>, Ambar Deshkar<sup>1</sup>, Ping Lu<sup>1</sup>, Yaqoot Shaharyar<sup>1</sup>, José Marcial<sup>2</sup>, Mostafa Ahmadzadeh<sup>2</sup>, Paul Bingham<sup>3</sup> and John S. McCloy<sup>2</sup>; <sup>1</sup>Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; <sup>2</sup>Washington State University, Pullman, Washington, United States; <sup>3</sup>Sheffield Hallam University, Sheffield, United Kingdom.

Owing to high concentrations of  $Al_2O_3$  from dissolved fuel cladding and  $Na_2O$  from basification of the waste, about half of the high-level waste by volume at Hanford, Washington, USA is rich in both Na and Al. Formulations of high waste-loading glasses result in lower amounts of  $SiO_2$ , which often leads to undesirable precipitation of nepheline ( $NaAlSi_3O_8$ ). Nepheline crystallization can be affected by both framework and non-framework cations which are either part of the waste or are added to the batch feed to facilitate vitrification. Given the existence of various natural minerals of the stoichiometries  $(Na, Li, Ca_{0.5})(Al, Fe, B, P)Si_3O_8$ , we sought to study the effects of substitution in the nepheline based glasses on the resulting crystallization. We summarize here several years of work, including characterization by nuclear magnetic resonance, vibrating sample magnetometry, Mossbauer spectroscopy, thermal analysis, x-ray diffraction, electron microscopy, and electron microprobe.

#### 10:00 AM BREAK

SESSION ET15.15: Materials for Nuclear Safeguards

Session Chair: Daniel Bailey

Thursday Morning, November 29, 2018

Hynes, Level 3, Room 308

#### 10:30 AM \*ET15.15.01

**Microparticle Production as Reference Materials for Particle Analysis Methods in Safeguards** Stefan Neumeier, Philip Kegler, Martina Klinkenberg, Irmgard Niemeyer and Dirk Bosbach; Forschungszentrum Juelich GmbH, Juelich, Germany.

The International Atomic Energy Agency (IAEA) implements technical measures, or safeguards, in order to verify the compliance of member states their international legal obligations to use nuclear material and technology only for peaceful purposes. Predisposal and geological disposal of high-level radioactive waste and spent nuclear fuel, if declared as waste, is also subject to safeguards. One of the technical measures used are analytical measurements of samples taken during inspections of nuclear facilities. The application of this measure goes hand in hand with the development and advancement of analytical measurements and of reference materials for quality control purposes.

To this end, a two-step process has been developed and established at Forschungszentrum Juelich which is capable to produce microparticles intended as source material for certified reference materials for particle analysis methods applied in safeguards. The first step is an aerosol-based particle production process. A monodisperse particle size distribution as well as the single phase  $U_3O_8$  structure was confirmed by SEM, mass spectrometry and  $\mu$ -X-ray methods. Mass spectrometry analysis performed on single uranium microparticles confirmed consistency of the uranium isotopic ratios in comparison to the initial precursor solutions. In the second step the particles are transferred into suspensions for which the stability of the particles in suspension was investigated with respect to dissolution. It turns out that ethanol is a suitable medium for the storage of particles over a period of several months. Our results from systematic particle analyses by SEM/EDX demonstrate that the two-step process developed at Forschungszentrum Juelich enables the reproducible production and homogeneous distribution of monodisperse microparticles and particle mixtures on several types of substrates, such as quartz discs and cotton swipes. Hence, it allows for a very flexible and time-saving preparation of various types of test samples suitable as reference materials for particle analysis methods applied in safeguards.

#### 11:00 AM ET15.15.02

**Wet Chemistry Route to Uranium Oxide Microspheres as Reference Materials for Nuclear Safeguards** Nicolas Clavier<sup>1</sup>, Jérôme Maynadié<sup>1</sup>, Victor Trillaud<sup>1</sup>, Jérémie Manaud<sup>1</sup>, Laure Sangély<sup>2</sup>, Thippatai Tranpaphan<sup>2</sup> and Nicolas Dacheux<sup>1</sup>; <sup>1</sup>ICSM, Bagnols, France; <sup>2</sup>IAEA, Vienna, Austria.

The preparation of morphology-controlled uranium oxide particles is currently attracting a growing interest, notably due to its importance in the field of nuclear safeguards. Particularly, provided certain homogeneity and stability requirements, such particles could act as reference materials for micro-analytical methods. In this framework, several protocols have been already tested, but frequently required specific equipment and cannot be easily implemented in standard chemistry labs. On this basis, we developed from several years original wet chemistry routes aiming to precipitate directly morphology-controlled actinide oxides from mixtures of solutions. Such methods are mostly based on the hydrolysis of tetravalent actinides which leads to the formation of amorphous  $An(OH)_4$  samples, finally aging to  $AnO_2 \cdot nH_2O$ .

In this aim, hydrochloric solution containing tetravalent uranium (natural isotopic composition) was first mixed with aspartic acid, used both as complexing and shaping agent, to yield an amorphous uranium(IV) aspartate precipitate. Solid phase and supernatant were then transferred in a Teflon-lined autoclave and placed under mild hydrothermal conditions ( $T = 160^\circ C$ ). A multiparametric study was then undertaken, in order to evidence the impact of pH, aspartic acid concentration, or mechanical stirring. On the one hand, acid concentration was found to be the most critical parameter, as microspheres were only obtained for pH values close to 2. On the other hand, the size dispersion of the particles produced could be improved by using a large excess of aspartic acid during the initial precipitation step. Finally, the addition of a mechanical stirring during the hydrothermal treatment step allowed us to control more accurately the size of the particles produced in the range 100 nm – 1  $\mu m$ . For all the compounds prepared, further XRD analysis attested the formation of  $UO_2 \cdot nH_2O$  samples, while TG experiments revealed the presence of residual organics. Nevertheless, additional heat treatments performed up to  $600^\circ C$  led to produce anhydrous and carbon-free dense particles without altering their initial morphology.

Finally, preliminary tests of these samples as reference materials for nuclear safeguards were performed. In this aim,  $UO_2$  microspheres were first deposited on carbon planchets after dispersion and dilution with ethanol. The number of particles deposited, the spacing between them, the cleanliness of the areas not intended for particle deposition and the absence of uranium background between the particles was found to be satisfying. Also, first LG-SIMS experiments aiming to determine the isotopic composition of uranium led to very good results, the behaviour of the particles under the SIMS beam being comparable to typical field sample particles.

#### SESSION ET15.16: Management and Long Term Behavior of Spent Nuclear Fuel II

Session Chairs: Dirk Bosbach and Laurent Claparede

Thursday Afternoon, November 29, 2018

Hynes, Level 3, Room 308

#### 1:30 PM \*ET15.16.01

**Leaching of Spent Nuclear Fuels—Influences of Sample Preparation and Matrix Composition on Radionuclide Release Patterns** Olivia Roth<sup>1</sup>, Anders Puranen<sup>1</sup>, Daqing Cui<sup>1</sup>, Alexandre Barreiro Fidalgo<sup>1</sup>, Lena Evins<sup>2</sup> and Kastriot Spahiu<sup>2</sup>; <sup>1</sup>Studsvik Nuclear AB, Nyköping, Sweden; <sup>2</sup>SKB, Stockholm, Sweden.

The rate of release of the radionuclide content from spent nuclear fuel during water contact is a central issue to the safety assessment of spent nuclear fuel repositories. Although the area has been subject to studies for several decades there are still issues to be resolved. The general trend among reactor operators is to increase the burn-up of the fuel. There are also new fuel types on the market where additive or dopants have been added to the fuel matrix in order to enhance the in-reactor fuel performance. Both these factors alter the spent fuel matrix and can be expected to influence the leaching behavior. Many spent nuclear fuel deep repository designs involve large amounts of iron in the disposal canister. Due to the expected anaerobic conditions at disposal depth, hydrogen formation by anoxic iron corrosion is expected upon groundwater intrusion into the disposal canister. The presence of hydrogen is expected to inhibit or reduce the matrix dissolution rate for  $UO_2$  fuel. It is however not known if and how additives in the fuel matrix affect this behavior. In the present we have studied how high burn-up and matrix dopants affect the matrix dissolution as well as the leaching behavior of fission products segregated to the fuel-cladding gap and grain boundaries. In order to compare the leaching from grain boundaries relative to leaching from the fuel-cladding gap, the samples have been prepared in different manners. Furthermore, the effect of fuel matrix dopants on the hydrogen effect has been studied by performing leaching of Al/Cr doped fuel both in aerated conditions and under hydrogen atmosphere and comparing the results with results from leaching of standard  $UO_2$  fuel.

#### 2:00 PM ET15.16.02

**Electrochemical Simulation of the Influence of Radiolytically-Produced Hydrogen on the Corrosion of Uranium Dioxide** Nazhen Liu<sup>1</sup>, Fraser King<sup>2</sup>, David Shoosmith<sup>1</sup> and James Noel<sup>1</sup>; <sup>1</sup>University of Western Ontario, London, Ontario, Canada; <sup>2</sup>Integrity Corrosion Consulting Ltd, Nanaimo, British Columbia, Canada.

The ability of hydrogen to inhibit the corrosion of uranium dioxide has received considerable attention since this process has the potential to suppress radionuclide release from spent fuel exposed to groundwater inside a failed nuclear waste container emplaced in a deep geologic repository. A number of mechanisms have been proposed to explain this inhibition. Hydrogen oxidation on the noble metal particles present in spent fuel leading to the prevention of oxidation of the galvanically-coupled uranium dioxide matrix has been clearly demonstrated. However, the direct reaction of hydrogen on the uranium dioxide surface also appears capable of preventing fuel corrosion and radionuclide release by consuming the OH radicals produced by

hydrogen peroxide dissociation on the oxide surface. In addition, the combination of radiation (gamma) and hydrogen can be shown to suppress the corrosion potential of uranium dioxide to values below which the oxide should be thermodynamically immune to oxidation. This suppression appears to be partially irreversible suggesting a chemical reduction of the oxide matrix by H radicals.

In this study, we have attempted to simulate this influence of radiation by generating H atoms via water/proton reduction on the oxide surface. A similar suppression of the corrosion potential is achieved and, on removing the radiation field, only a partial recovery of the corrosion potential, towards the value which prevailed before irradiation, is observed. By conducting a series of electrochemical experiments on oxides with various degrees of non-stoichiometry, it is shown that the oxide matrix is reduced with the extent of reduction depending on the degree of non-stoichiometry of the oxide. Also, by performing similar experiments in solutions with a range of pH values, it was shown that the extent of oxide reduction increases at low pH when the generation rate of H atoms is increased.

These studies indicate that a combination of radiation and hydrogen can lead to the direct reduction of the oxide matrix via a reaction with absorbed H atoms.

## 2:15 PM ET15.16.03

**Powder Leaching Study for Grain Boundary Inventory of Two High Burnup Fuels** Alexandre Barreiro Fidalgo<sup>1</sup>, Olivia Roth<sup>1</sup>, Anders Puranen<sup>1</sup>, Lena Evins<sup>2</sup> and Kastriot Spahiu<sup>2</sup>; <sup>1</sup>Studsvik Nuclear AB, Nyköping, Sweden; <sup>2</sup>SKB, Stockholm, Sweden.

In the context of a deep geological repository safety assessment, the Instant Release Fraction (IRF) is defined as the fraction of radionuclides in spent fuel which rapidly dissolves in contact with water. The IRF is sourced both from the pellet-cladding gap and the grain boundary. It is however uncertain how much the grain boundary inventory contributes to the IRF. Commonly, the IRF is determined by using short-term dissolution experiments, which does not distinguish between these two fractions. However, a few experiments have been performed to specifically investigate the grain boundary fraction through simultaneous grinding and leaching experiments [1-2].

For this study, the main goal is to establish the closed grain boundary inventories of two Swedish fuels with high burnup (local burnup 58 and 65 MWd/kg). In addition, the results will be compared to those already obtained for another high burnup fuel (local burnup 75 MWd/kg) [3].

The experiments are performed on fuel fragments without cladding. The selected fragments are samples that have already been leached in previous campaigns and therefore the IRF of exposed grains and matrix dissolution behavior under aerated conditions have already been established [4-5].

The fuel fragments were exposed to an initial leaching period under aerated conditions in 10:10 mM NaCl:NaHCO<sub>3</sub> solutions for 3 months. The main objective of this initial step is to wash away any pre-oxidized phases formed during humid-air storage in cell.

After the washing step, the fuel fragments are placed in a mill together with simplified groundwater (10:2 mM NaCl:NaHCO<sub>3</sub> solution) under oxidizing conditions (air) at room temperature. The grinding and simultaneous leaching is performed in similar conditions as tested in a previous campaign [3]. The solutions are analyzed with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and gamma spectroscopy. Additionally, the grinded fuel is taken for Scanning Electron Microscope (SEM) analysis.

The preparations, experimental setup as well as the experimental results will be presented and discussed in the conference presentation.

## References

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- [2] Gray, W.J. "Inventories of Iodine-129 and cesium-137 in the gaps and grain boundaries of LWR spent fuels" Mat. Res. Soc. Symp. Proc. Vol. 556 p. 487- 493 (1999)
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- [4] Ekerot H. E. et al. "Instant Release Fractions from Corrosion Studies with High Burnup LWR Fuel" Mater. Res. Soc. Symp. Proc. Vol. 1475, imrc11-1475-nw35-o36, 2012
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## 2:30 PM BREAK

## 3:00 PM ET15.16.04

**Radionuclides Present at Inner Cladding Surfaces of Irradiated PWR Fuel Rod Segments in the Context of Safety of Extended Dry Storage of Spent Nuclear Fuel** Michel Herm, Ernesto González-Robles, Nikolaus Müller, Tobias König, Kathy Dardenne, Jörg Rothe, Dieter Schild, Ron Dagan and Volker Metz; Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

In the German waste management concept, spent nuclear fuel (SNF) is designated for direct disposal in a deep geological repository available by 2050 at the best. However, considering the delay in the site selection process so far as well as the time needed for exploration, construction, and commissioning of a repository for high-level waste, start of waste emplacement is expected by the end of this century. Thus, a prolonged dry interim storage of SNF assemblies is inevitable.

Integrity of the irradiated Zircaloy cladding after 50 to 100 years of dry interim storage is of importance e.g. to ensure a safe reloading of fuel assemblies from storage casks to final disposal casks. However, cladding integrity is affected by various processes during reactor operation and beyond, e.g. fuel cladding chemical interactions. Moreover, inner cladding surfaces exposed to precipitates of fission/activation products released from fuel pellets are possibly prone to corrosion processes. In particular, the presence of cesium, iodine, tellurium, and chloride at the fuel-cladding interface and their impact on the integrity of the cladding are analyzed.

Irradiated Zircaloy-4 specimens, currently under investigation, are sampled from the plenum section as well as cladding tube in contact with SNF of an UO<sub>2</sub> fuel rod segment (50.4 GWd/t<sub>HM</sub>). Experiments with irradiated cladding in contact with MOX fuel (38.0 GWd/t<sub>HM</sub>) have been started recently. Composition of agglomerates found on the inner surface of the plenum cladding and fuel-cladding interaction layers were analyzed by means of SEM-EDS, XPS, and synchrotron based techniques. In addition, the radionuclide inventory present in irradiated Zircaloy was experimentally determined and compared to calculated values using a MCNP/CINDER approach. Radionuclides difficult to measure such as C-14, Cl-36, and I-129 were separated from

other radionuclides first, and then measured by IC, ICP-MS,  $\gamma$ -spectroscopy as well as LSC.

Measured inventories of activation products in the plenum Zr-alloy are in good agreement with calculated values. However, amounts of actinides and fission products exceed the calculated inventory by factor of about 50 (Pu isotopes) and of about 120 (Cs-137). Excess Pu and part of excess Cs inventory originate from fuel residues on the inner cladding surface, whereas vast amount of Cs had been volatilized from subjacent fuel pellets and transported to the plenum during reactor operation.

Precipitates found in the plenum contain Rb besides Zr, Ba, Cs, and U. The analysis of fuel-cladding interaction layers show the presence of Te and Cl besides Zr, Ba, Cs, and U.

### 3:15 PM ET15.16.05

#### **Uranium IV, V and VI Oxidation States on UO<sub>2</sub>(s) Surface Consecutive to UO<sub>2</sub>(s) Corrosion Under Gamma Radiation and H<sub>2</sub> Overpressure** Volker Metz; Institute for Waste Disposal, Karlsruhe Institute of Technology, Karlsruhe, Germany.

In a deep geological repository, the fate of spent UO<sub>2</sub> fuel and the associated release of radionuclides depend on UO<sub>2</sub>(s) corrosion kinetics, precipitation kinetics of secondary phases as well as on thermodynamic constraints. These processes are influenced by a variety of factors such as the radiation field, the resulting dose rate, the availability of oxidizing radiolytic products, the groundwater composition and the redox potential. As a result of numerous studies it turns out that corrosion of spent UO<sub>2</sub> fuel is strongly inhibited under hydrogen overpressure. In contrast to earlier results, radiolysis driven fuel corrosion appears to be less relevant for most repository concepts. Even though the protective hydrogen effect on corrosion of spent UO<sub>2</sub> fuel has been evidenced in many experiments open questions remain related to the exact mechanism.

Using batch-type corrosion experiments with depleted UO<sub>2</sub>(s) under gamma-irradiation, we studied alteration of the UO<sub>2</sub>(s) surface under H<sub>2</sub> overpressure. Prior to the corrosion experiments, a series of UO<sub>2</sub>(s) samples were annealed at 1150° C in Ar/H<sub>2</sub> gas stream. Immediately after cooling of the samples to ambient temperature, surfaces of one sample were characterized by XPS. The other UO<sub>2</sub>(s) samples, annealed in the same batch, were placed in autoclaves with aqueous near neutral pH solution. The autoclave experiments were irradiated for several months in the GB77 Co-60 source at Institut für Oberflächenmodifizierung, Leipzig. The mean gamma-dose rate at the position of the autoclaves were measured with a Fricke dosimeter and was below 600 Gy/h. Surfaces of UO<sub>2</sub>(s) samples recovered from the autoclave experiments were analyzed by means of SEM-EDS, Raman spectroscopy, and XPS techniques. A UO<sub>2</sub>(s) reference sample (CBNM#106, EC Reference Material no. 106) was fractured in ultra high vacuum of our XPS device, to provide baseline measurements for uranium oxidation states.

Solely 4f elemental lines and respective satellite signals were detected in the reference sample with a UO<sub>2</sub>.0 stoichiometry. Similarly, the depleted UO<sub>2</sub>(s) sample measured immediately after annealing in Ar/H<sub>2</sub> gas stream contained solely U(IV). After storing the annealed UO<sub>2</sub>(s) under dry conditions in a glovebox with Ar atmosphere (containing < 1 ppm O<sub>2</sub>) for one year, both U(IV) and U(V) were detected on the sample surface. We detected metaschoepite and Na-diuranate type precipitates on the UO<sub>2</sub>(s) samples recovered from the gamma-radiolysis experiments. Besides layers of U(VI) secondary phases, U(IV) was detected at these samples when precipitates were removed. Experimental results and conclusions with respect to the spent UO<sub>2</sub>(s) matrix alteration model will be presented.

### 3:30 PM ET15.16.06

#### **Chromium Doped UO<sub>2</sub>-Based Model Systems—Synthesis and Characterization of Model Materials for the Study of the Matrix Corrosion of Spent Modern Nuclear Fuels** Felix Brandt<sup>1</sup>, Philip Kegler<sup>1</sup>, Steve Lange<sup>1</sup>, Martina Klinkenberg<sup>1</sup>, Andrey Bukaemskiy<sup>1</sup>, Guido Deissmann<sup>1</sup>, Sarah Finkeldei<sup>2</sup> and Dirk Bosbach<sup>1</sup>; <sup>1</sup>Forschungszentrum Juelich, Juelich, Germany; <sup>2</sup>Nuclear Fuel Materials Group, Oak Ridge National Laboratory, Oakridge, Tennessee, United States.

The current efforts to improve fuel performance in nuclear power generation resulted in an increased utilization of a variety of new types of light-water reactor (LWR) fuels such as Cr-, Al-, and Si-doped UO<sub>2</sub> fuels. For these modern types of LWR fuel it is still not known, whether their performance in a deep geological waste repository will be similar to conventional spent LWR-fuels. Corrosion experiments with spent nuclear fuel (SNF) cannot unravel all of the various concurring dissolution mechanisms entirely due to the chemical and structural complexity of SNF and its high beta- and gamma radiation field. Technical restrictions allow only for a very limited number of experiments. Therefore, within the EU-DISCO project ([www.disco-h2020.eu](http://www.disco-h2020.eu)) experiments on irradiated modern fuels are complemented with systematic dissolution studies carried out with synthesized and well characterized, simplified UO<sub>2</sub>-based model materials. A bottom up approach is followed to understand how the addition of Cr-oxide into the fuel matrix affects SNF dissolution behavior under repository relevant conditions.

Here, we show recent results on the development and optimization of the process steps for a wet-chemical route to produce nominally pure UO<sub>2</sub> reference pellets, Cr-doped UO<sub>2</sub> as well as Cr- and alpha doped (<sup>238</sup>Pu) pellets. A wet chemical route was favored due to the very low doping levels of <sup>238</sup>Pu required to mimic fuel ages between 1,000 and 10,000 years, later in DISCO. Syntheses were performed by co-precipitation and wet-coating methods and had to be free of any grinding steps to be applicable in a dedicated glove box line. Process optimization was achieved by a systematic investigation of various process parameters such as calcination temperature and pressing forces. In order to provide insights into the effects of the material's micro structure on the dissolution behaviour e.g. regarding the larger grain size in doped fuels and contributions of grain boundaries, the model material pellets were synthesized. The micro structure, in particular grain size, grain orientation and dopant distribution (i.e. either in solid solution within the UO<sub>2</sub> matrix or segregated on grain boundaries) in the model materials were characterized using various complementary methods e.g. SEM, EBSD, and XRD. First results of accelerated dissolution studies with UO<sub>2</sub>-based Cr-containing model systems were performed using H<sub>2</sub>O<sub>2</sub> to mimic the oxidative radiolysis species to study the effect of micro structure and Cr-doping upon the dissolution rate.