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Book of Abstracts

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Glass Wasteforms / 53

(Scholarship application) Thermal Treatment of Magnox Sludge Intermediate Level Nuclear Waste through Vitrification

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Vitrification of sludge waste arising from legacy nuclear activities such as Magnox reprocessing is a promising alternative to the current baseline plan of cementation with superior long-term durability, improved waste loadings and significant volume reduction. Glass products were produced from oxidized and metallic uranium and magnesium, representative of the extremes found with the First Generation Magnox Storage Ponds, in simple 3 or 4 component systems.

Magnesium aluminosilicate (MAS) and magnesium borosilicate (MBS) glasses were analytically characterised by X-ray diffraction, scanning electron microscopy, differential thermal analysis, X-ray absorption spectroscopy and inductively coupled plasma optical emission spectrometry. Accelerated dissolution testing was performed at 90 °C for 28 days with periodic sampling of the leachate solution.

Surrogate materials neodymium and the rare-earth alloy mischmetal were used alongside uranium and subject to the same testing regime to determine the effectiveness and validity of using such substitute materials in scientific studies of uranium bearing glass.

Summary:

Thermal treatment of problematic radioactive sludge waste in durable glass wasteforms.

Ceramic and Glass-Ceramic Wasteforms / 13

A New Method for Production of Glass-Y₂Ti₂O₇ Pyrochlore

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The actinide immobilisation research group at ANSTO has been investigating pyrochlore glass-ceramics for plutonium immobilisation. A novel method of glass ceramic preparation via a soft chemistry route has been designed recently. Significant advantages over a more traditional mixed oxide route include removal of the need for an organic solvent in synthesis and milling steps, and product devoid of potentially deficient minor phases. Glass-Y₂Ti₂O₇ pyrochlore was fabricated by sintering the mixture of glass precursor powder and (YTi)-composite prepared by a soft chemistry route. XRD and Raman confirmed phase pure pyrochlore crystallized in-situ in amorphous glass matrix at 1200°C. Pyrochlore formation in glass was independent of cooling rates and addition of metal fluorides. Glass matrix was able to accommodate/dissolve small amounts of impurities and the mean pyrochlore particle size was between 1 and 2 µm in glass.

Glass Wasteforms / 85

A study to develop a new glass formulation for the immobilisation of HLW containing molybdenum and large amounts of sodium.

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A study to develop a new high level waste (HLW) glass formulation for waste from the highly active liquor storage (HAL) tanks at Sellafield is described. A likely washout scenario for the tanks at the end of operations involves the use of sodium carbonate as a tank washout reagent [1] leading to a high soda wastestream. Titanium is not currently used in existing HLW formulations in European nuclear waste glasses, however, literature suggests that titanosilicate glasses can accommodate large amounts of sodium [2-4], even up to 50 mol% [5]. Following a combinatorial type approach exploring the effects of variation of alumina (Al₂O₃), boron oxide (B₂O₃), calcium and mixed alkali content in sodium titanosilicate formulations with and without waste simulant (including molybdenum and zirconium oxides) and durability assessment, two promising formulations are currently being trialled and full product waste simulant containing glass being prepared via base glass frit plus waste simulant combination. Further durability trials and structural characterisation are also being investigated and results will be reported.

1 M. J. Edmondson et al., "A Methodology for Post Operational Clean Out of a Highly Active Facility Including Solids Behaviour", 12386, 2012 (Submitted for the WM2012 Conference, Phoenix, Arizona, USA).

2 Hamilton, E. H. and G. W. Cleek (1958). "Properties of sodium titanium silicate glasses" J. Res. Nat. Bur. Standards. 61 (2) 89-94.

3 Turnbull, R. C. and W. G. Lawrence (1952). "The role of titania in silica glasses" J. Amer. Ceram. Soc. 35 (2) 48-53.

4 Strimple, J. H. and E. A. Giess (1958). "Glass formation and properties of glasses in the system Na₂O-B₂O₃-SiO₂-TiO₂" J. Amer. Ceram. Soc. 41 (7) 231-237.

5 Washburn, E. W. and E. N. Bunting (1934). "Note on phase equilibria in the system Na₂O-TiO₂." J. Res. Nat. Bur. Standards 12 (2) 239-239.

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Spent Fuel & Zircaloy Cladding / 33

Activation energy for parabolic corrosion kinetics of Zircaloy-4 by consecutive hydrogen measurement at 30 – 80°C

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On the issue related on a safe disposal of spent fuel claddings is the corrosion and the subsequent gas and radionuclides release. The Zircaloy corrosion under a prospected disposal condition has recently been investigated by sensitive hydrogen measurements at 30°C, and reported that the kinetics in the rate around nm/y follows the parabolic rate law.

In the present work, an improved equipment to be usable even at higher temperatures up to 80°C has been applied for measuring hydrogen gas generated from Zircaloy-4 corrosion for 90 days. The Arrhenius relation of the parabolic rate constants for the corrosion kinetics has showed the activation energy of 84.4 ± 8.4 kJ/mol, the value of which is lower than that for the general pre-transition corrosion under the in-pile temperature above 260°C (i.e. 113-135 kJ/mol), suggesting that simple mass transfer through a thin and firm oxide film is limiting the low temperature corrosion of Zircaloy.

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Adsorptive Removal of the Radionuclides by Granulated Mesoporous Materials

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Radioactive compounds leached from radioactive wastes have been considered as widespread contaminants to threaten human health and environment due to their radioactivity in aqueous phase. They are exposed from radioactive waste disposal facility and ubiquitously presented in water. To protect human health and environment, adsorptive removal is one of the most effective technology for separation and purification due to its simplicity and convenience. In this study, granulated mesoporous materials (GMM) are successfully synthesized by using powdered mesoporous materials and organic binders through a one-step and economical granulation approach. Characterization results were obtained by scanning electron microscope, X-ray diffraction, as well as surface and porosity analysis. Also, batch adsorption experiments for removal of radionuclides were carried out to evaluate the adsorption affinity. Adsorption characteristics revealed that GMM showed higher adsorption capacities due to ordered mesoporous structure and excellent physical properties such as BET surface area and pore volume.

Partitioning & Transmutation / 6

Advanced Materials and Processes for Application to the Back-end of the Nuclear Fuel Cycle

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The nuclear industry generates a wide variety of radioactive waste streams during reactor operations and maintenance and in virtually all parts of the fuel cycle. In order to improve the sustainability of the industry it is necessary to develop improved methods and processes for treating, conditioning

and disposing of this waste. The talk will provide an overview of research being conducted at the Comisión Nacional de Energía Atómica emphasizing the development of novel solid-extractants with the ability to selectively extract radionuclides from complex solutions and with compositions that facilitate end-of-life management by being able to be converted to extremely stable ceramics. Topics to be covered will include 1) a proposed process for the conversion of spent polymeric ion exchange resins to stable pyropolymer and carbon materials and their subsequent immobilization, 2) synthesis of coordination polymers suitable for the selective extraction of radiolanthanides and their subsequent immobilization, 3) potential new targets for a cleaner production of Mo-99 and 4) the use of phenolic resins as matrices for spent organic and inorganic ion exchange media.

National & International Waste Management Programs: Session Chairs Greg Lumpkin & Simone Richter / 1

Advances in conditioning of low and intermediate nuclear waste

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Radioactive waste with widely varying characteristics is generated from the operation and maintenance of nuclear reactors, nuclear fuel cycle facilities, research facilities and medical facilities and the through the use of radioisotopes in industrial applications. The waste needs to be treated and conditioned as necessary to provide wasteforms acceptable for safe storage and disposal. Conditioning of radioactive waste is an important step to prepare waste for long-term storage or disposal and includes the following processes:

- Immobilization which may or may not also provide volume reduction, including (a) Low temperature processes and (b) Thermal processes;
- Containerization for (a) Transport, (b) Storage, and (c) Disposal;
- Overpacking of primary containers (a) Prior to disposal and (b) In a disposal facility as part of disposal process.

Conditioning consists of operations that produce a waste package suitable for handling, transportation, storage and/or disposal and may be performed for a variety of reasons including standardization of practices and/or wasteforms, technical requirements for waste stability in relation to a repository design or safety case, technical requirements related to waste transportation, societal preferences, regulatory preferences, etc. This report aims to give an overview of recent advances in conditioning of low and intermediate nuclear waste.

Summary:

The report is based on IAEA Handbook "Conditioning of Low- and Intermediate-Level Liquid, Solidified and Solid Waste" which is one of eight IAEA handbooks intended to provide guidance for evaluating and implementing various characterisation and radioactive waste processing and storage technologies before final disposal – see e.g. the recently published Handbook on Treatment of Gaseous Waste [1].
1. Treatment of Radioactive Gaseous Waste. IAEA-TECDOC-1744, IAEA, Vienna (2014).

Special topic on Tc and Re / 111

Alkali technetium oxides and their relation to Tc loading in nuclear waste glasses

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Because of their radioactive nature, solid technetium-99 oxides have been rarely studied, and there is a dearth of modern spectra and diffraction patterns in the literature. This publication aims to address this by detailing a low-temperature synthesis method for pure, crystalline alkali pertechnetates, along with complete analysis by static and magic-angle-spinning nuclear magnetic resonance, Raman, neutron diffraction (ND), and X-ray absorption spectroscopy (XAS). Insight gained from these studies brings a deeper understanding of the periodic chemistry of alkali (Na,K,Rb,Cs) pertechnetates. Additionally, we report attempts to make 5- and 6-coordinate pertechnetate compounds of K, Na, and Li, i.e. TcO_5^- and TcO_6^- . It was found that higher coordinated species are very sensitive to water, and easily decompose into their respective pertechnetates. It was difficult to obtain pure compounds, but mixtures of the pertechnetate and other phases were frequently found, as evidenced by XAS, ND, and Raman spectroscopy. Additionally, we summarize other work on Tc loading in glasses, effect on glass structure, and salt formation in overloaded samples. For glasses, XAS chemometrics based on principal component analysis and linear combination fitting suggests that Tc is speciated first as isolated Tc^{4+} , as Tc content is increased, there is more Tc^{7+} which partitions first to K neighbors then to isolated sites. Preliminary work is reported assessing $HTcO_4$ and related compounds and their relationships to mechanisms of Tc volatility

Glass Wasteforms / 63

Alkali tin silicate glass as a wasteform for the immobilisation of plutonium

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UK stocks of separated civil plutonium are projected to exceed 140 tons at the end of reprocessing. This material may require immobilisation in a proliferation resistant wasteform, should it prove uneconomic to recycle in MOX fuel. We have investigated and optimised alkali tin silicate glass compositions for the immobilisation of this stockpile using CeO_2 as a PuO_2 surrogate. A remarkable two-fold increase in Ce solubility was achieved by in-situ reduction of CeO_2 to Ce_2O_3 , as demonstrated by Ce L3 XANES, through addition of zero valent iron, which also assisted in reducing the processing temperature. Preliminary investigation showed this approach to be compatible with Hot Isostatic Pressing, enabling batchwise processing of alkali tin silicate glasses, which is advantageous from fissile material accountancy and criticality considerations. This work demonstrates the feasibility of an alternative and simple approach to conditioning the plutonium stockpile, through hot isostatic pressing of a full glass wasteform, potentially compatible with the full envelope of plutonium feedstock.

Radiation Damage / 97

Ambient-Cured Geopolymers for Low Level Nuclear Waste Storage

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Radioactive materials are used for several key applications in Australia, and resultantly, ~4248 m³ of low level and 656 m³ of intermediate level waste are currently stored on site. The present work investigates the development of an ambient-cured geopolymer composition for storage of low level radioactive wastes. These geopolymers were fabricated by ambient curing of mixtures of fly ash and blast furnace slag with an alkaline activator. Samples were fabricated both with sand (mortar) and without sand (paste). The cured compositions (25x25x25 mm³ cubes showed high compressive strengths of ~100 MPa. Microstructural and mineralogical characterisation was conducted using scanning electron microscopy and X-ray diffraction analysis. The samples will be subjected to gamma irradiation to simulate exposure from incorporated Cs-137 for a few hundred years at ANSTO. Samples will be removed at different time points (1-12 months) and microstructural and mechanical testing will be done to assess its stability.

Radionuclide solubility, speciation, sorption & migration / 75

Apparent Diffusion Coefficients Consistent with Sorption Derived Based on Changes in Depth Profiles of Radiocaesium in Soil Contaminated by the Fukushima Nuclear Accident and Future Prediction of Depth Profile

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The accident at the Fukushima Daiichi Nuclear Power Plant occurred following the Great East Japan Earthquake in March 2011, and led to the release of volatile radionuclides (RNs) which were deposited on the surrounding environment in the Fukushima prefecture. The authors conducted twice investigations on the depth profiles of RNs in soil at 11 locations in the city of Nihonmatsu and the towns of Kawamata and Namie.

The apparent diffusion coefficients (Da) of Cs-134 and Cs-137 were derived from changes in the depth profiles, and the distribution coefficients (Kd) also calculated from the relation with Da. The calculated Kd-values ranged 1E4-1E5 ml/g, which were consistent with Kd-values (2,080-61,000 ml/g) obtained by a batch method. The Da-values of both nuclides were approximately of order 1E-14 m²/s and movement by diffusion was very slow. Furthermore, the authors simulated change in the depth profiles of both nuclides for 30 years following the accident.

Safeguards, Decontamination & Decommissioning / 31

Application of Nuclear Waste Management and Remediation Experience and Lessons Learned

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Applying Successful Global Programs to the International Nuclear Decommissioning Market

CH2M has successfully managed waste management, remediation and nuclear decommissioning programs incorporating both innovations and lessons learned that have broad applicability to upcoming major decommissioning programs throughout Australia and globally.

This abstract presents an international perspective, from CH2M, on the importance of establishing an integrated waste management strategy with the decommissioning program to better support the waste generating projects in minimizing the amount of waste generated and more effectively comply with regulatory waste acceptance criteria. The overall success of a nuclear decommissioning program can be dependent on accurate waste volume projection; waste disposal pathway identification and integration; waste treatment options identification; waste characterization, treatment, packaging and transportation; and waste disposal (including low-level disposal cell operations). An integrated Waste Management Strategy is integrated with the decommissioning and demolition activities; nuclear material management and disposition; waste retrieval, treatment and disposal; and environmental remediation activities.

Spent Fuel & Zircaloy Cladding / 52

Aqueous leaching of high burnup UO₂ fuel under hydrogen conditions

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Leaching results on fragments of high burnup (65 MWd/kgU) UO₂ fuel from a commercial pressurized water reactor are presented. The experiments were performed in simplified granitic groundwater under a hydrogen pressure of up to 5 MPa, representing conditions in a water intrusion scenario for a Swedish KBS-3 design spent nuclear fuel repository. The freshly crushed fragments were pre-washed under aerated conditions for 6 days to remove part of the instant release fraction of the radionuclide inventory and transferred to an autoclave for leaching under hydrogen conditions. Following an initial release of U attributed to dissolution of oxidized phases from the aerated handling, the U concentration decreased to levels of 2-5x10⁻⁹ M, in-line with the solubility of amorphous UO₂. The release of radionuclides such as Cs and Sr gradually declined indicating a transition towards inhibition of the fuel matrix dissolution.

Ceramic and Glass-Ceramic Wasteforms / 72

Atomistic simulation of interfaces in glass/crystal composites for nuclear waste forms

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High-Level Waste (HLW) resulting from fuel reprocessing is immobilised in a borosilicate glass matrix, particularly in France and the UK.

Some HLW components have higher melting points than the glass, and thus never dissolve into the melt.

Other crystalline phases may also form during fabrication due to limited solubility.

Separation could also occur later through a process of devitrification.

The resultant waste form may therefore demonstrate significant heterogeneity with secondary crystal phases embedded in a glass matrix.

The purpose of this study is to improve understanding of the issues associated with such microstructures in vitrified wasteforms.

We will present results from atomistic simulations showing properties of glass/crystal interfaces in a surrogate composite formed of $(\text{Na}_2)_x(\text{SiO}_2)_{1-x}$ glass and rutile TiO_2 crystals.

The potentials employed have been widely used for glass materials. We will discuss their applicability to glass/crystal composite structures.

We will show structural and energetic features predicted for these interfaces and consider the effect of radiation damage.

Repositories & Geological Disposal / 96

Behaviour of sand-bentonite buffer material of deep geological repository under high confining pressure

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Deep geological repositories have been proposed as a safe waste management system for high-level radioactive wastes. Sand-bentonite buffer materials are used in engineered barrier system of deep geological facilities thank to their excellent swelling properties. In this research, volumetric and strength behaviour of sand-bentonite buffer material under high confining pressures of 1-3MPa were studied using a newly developed double-cell triaxial testing apparatus. The specimens were prepared with 30% of sand as proposed for geological repositories in Japan. The suction behaviour of sand-bentonite specimens were also studied.

The results indicate that the degree of saturation influences the strength and volumetric behaviour significantly, which suggests that local groundwater flow affects the performance of buffer material upon decommissioning of a deep geological repository. It also indicates that suction behavior is significantly affected by the degree of saturation, although it was less affected by confining pressure.

Repositories & Geological Disposal / 61

Best Practice in the Management of Site Investigations for Geological Disposal Facilities

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The disposal of intermediate- and high-level radioactive waste requires emplacement in suitably engineered underground facilities in order to ensure an adequate level of isolation and containment for safety and security. We now have several examples of radioactive waste management organisations who have designed and undertaken extensive multi-disciplinary site investigation projects to characterise environments for waste disposal in geological formations. However, many countries requiring such facilities are still to initiate their own investigations. It is therefore timely to compile lessons learnt on the management of site investigations for geological disposal facilities in order to support the sharing of knowledge and provide a platform for well-planned investigations to be undertaken in the future. Consequently, this presentation identifies important considerations associated with the planning and implementation of requirements-driven site investigation projects for geological radioactive waste disposal facilities.

Repositories & Geological Disposal / 30

Characterisation of the UK cement backfill material pre- and post-groundwater leaching experiments

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In the UK, the volume of intermediate level waste (ILW) requiring final disposal in a geological disposal facility, is almost 450,000 m³. In one of the UK conceptual scenarios for the geological disposal facility in a high-strength crystalline rock, the vaults will be backfilled with a cement-based material, known as Nirex Reference Vault Backfill (NRVB). This material will provide a physical and chemical barrier to radionuclide release to the environment. Over the expected long lifetime performance of a cementitious backfill material, NRVB will age and alter, specifically due to interactions with groundwater. Understanding how these interactions will affect the properties of this material is of crucial importance for the development of a robust safety case for the geological disposal facility. We here present the results of a detailed characterisation of NRVB pre- and post- groundwater leaching experiments, using three different types of groundwater (granitic, clay and saline groundwater), as analysed using conventional and advanced (e.g. tomography, synchrotron XRD) techniques.

Glass Wasteforms / 41

Chemical Durability of Borosilicate Glass-Ceramic High-Level Waste Form in Dilute and Static Conditions

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A borosilicate glass-ceramic waste form is being developed to significantly increase waste loading of high-level waste relative to single phase glass. The glass-ceramic waste form is comprised of approximately 70% borosilicate glass, 20% oxyapatite ($X_2Ln_8Si_6O_{26}$), and 10% powellite (XM_oO_4), by mass, where X = alkaline earth and Ln = lanthanides. Understanding the overall corrosion behavior of the glass-ceramic is complicated because each phase corrodes at a different rate and there are matrix effects. Durability of the multiphase waste form was investigated with single-pass flow-through and static leach testing, but the results were convoluted because elements were present in multiple phases. In an effort to deconvolute the corrosion process of the full waste form, additional corrosion testing was performed on the full waste form and individually-synthesized phases (remainder glass, oxyapatite, and powellite). Results of these tests are presented and comparisons between the glass-ceramic waste form and individual phases are discussed.

Safeguards, Decontamination & Decommissioning / 103

Chornobyl NPP Cooling Pond: Decommissioning

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The Cooling Pond of Chornobyl NPP (hereinafter referred to as CP) was formed by constructing an embankment on the flood plain of the Prypiat River, its area made about 22.9 km²; its water volume making 151 million m³ was calculated for cooling Chornobyl NPP four units in mode of electric power generation.

When CP was operated the water level was maintained up to the design level which made 111m of BHS (meters as per the Baltic height system).

The average annual water level in CP within its operation was 7 meters higher than the water level in the Prypiat River.

The special feature of the Cooling Pond is its location within the area of Exclusion Zone and Absolute (Obligatory) Resettlement Zone - the area which was radioactively contaminated resulting from Chornobyl NPP Unit 4 accident in 1986.

Due to the reduction of cooling water demand after termination of the electric power generation such a facility is not required any more and now its decommissioning programme is implemented.

The Cooling Pond decommissioning activities cover radiation and ecological monitoring, namely:

- radiation condition in the surface layer of the atmosphere;
- exposure dose rate within the dry sections of the Cooling Pond;
- radionuclide content in groundwater;
- water level, radiological and chemical changes of the Cooling Pond water;
- the changes of the hydrobiological condition and geobotanical changes.

The presentation demonstrates the results of radiation and ecological monitoring.

Spent Fuel & Zircaloy Cladding / 54

Comparison of calculated and measured radionuclide inventory of a Zircaloy-4 cladding tube plenum section

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Cladding tubes of water-cooled nuclear reactors are usually made of Zircaloy and are an important retaining element for radionuclides present in the fuel. However, cladding integrity is affected by various processes during reactor operation and beyond, e.g. oxidation, hydrogen uptake, PCI, fission product precipitation, alpha-decay, and radiation damage. Using experimental and modelling methods, the radionuclide inventory of an irradiated Zircaloy-4 plenum section is analyzed.

Quantities of U-235/238, Np-237, Pu-238/239/240/241/242, Am-241/243, Cm-243/244 besides C-14, Fe-55, Sb-125, Cs-134/137 were (radio-)chemically determined in digested Zircaloy-4 subsamples. Measured inventories of activation products in the Zr-alloy are in good agreement with calculated values. However, amounts of actinides and fission products exceed the calculated inventory by factor ~50 (Pu isotopes) and ~120 (Cs-137). Excess Pu and part of excess Cs inventory originate from fuel residues on the inner cladding surface, whereas vast amount of cesium is volatilized from subjacent fuel pellets and transported to the plenum.

Special topic on Tc and Re / 88

Comparison of thermal expansion of Tc and Re salts.

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⁹⁹Tc is the most significant long-lived product of uranium fission, producing the largest fraction of the total long-lived radiation emissions of nuclear waste. Tc 7+ compounds are highly mobile in the environment. Relatively little is known regarding the solid state chemistry of Tc. Recently we studied the structural properties of (NH₄)TcO₄ (Tc⁷⁺) and confirmed that this is isostructural with (NH₄)ReO₄ adopting a tetragonal scheelite type structure in space group I4₁/a. The unit cell parameters of (NH₄)TcO₄ are strongly temperature dependent with the structure showing negative thermal expansion along both the a- and c-axis, albeit at different temperatures. This behavior is significantly different to that previously reported for the isostructural oxide (NH₄)ReO₄, although we note that the data for (NH₄)ReO₄ was collected at much lower resolution. Nevertheless it is clear in the literature that the thermal expansion behavior of (NH₄)ReO₄ is highly anisotropic. Despite the difference in the thermal expansion between what we have observed for (NH₄)TcO₄ and that described by others for (NH₄)ReO₄ it is likely that the origin of the anomalous thermal expansion in is the same in both cases, namely it is a consequence of re-orientation of the ammonium ions in the surrounding cage of eight oxygen atoms. To verify this for (NH₄)TcO₄ requires we replace the ammonium cation with another small cation. Therefore we have compared the thermal behavior of AReO₄ with ATcO₄ to determine if Re oxides are suitable surrogates to predict the behavior of Tc oxides and how they may behave in the environment.

Ceramic and Glass-Ceramic Wasteforms / 82

Current advances on titanate-based glass-ceramics for actinide immobilization

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Glass-ceramics have attracted recent attention as they have the advantage of combining the chemical flexibility of glasses with the excellent durability of ceramics, making them potential waste forms for the immobilization of actinide wastes with processing chemicals. Glass-ceramics based on titanate ceramic phases, e.g. zirconolite, pyrochlore and brannerite have been developed at ANSTO. The formations of these titanate dominated glass-ceramics have been demonstrated with uranium as proof of concept and plutonium with gadolinium and/or hafnium as neutron absorbers. This talk will focus on the current advances in the field including the formation and crystallization of titanate phases in glass, structure and microstructure characterization, actinide incorporation and actinide valences.

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Development of Pyro-waste Treatment Process Technology

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This paper is to review the status for developing the systemic waste treatment and storage/transportation process by reduction of the final waste volume, fabrication of durable wasteforms applicable to disposal environment and the safe packaging and storage system.

Systemic framework of technologies for treating waste filter, metal waste and waste salt from KAERI pyroprocessing was established by a series of experiments from bench scale to engineering scale. As some activities for development of key technologies, the off-gas treatment process in hot cell was performed to demonstrate some materials/process and the de-cladding hull was analyzed for finding proper process for the metal waste.

Next, engineering-scale salt purification process was performed to obtain the information on performance of eng-scale process. Also, a series of wasteforms related with pyro-waste from KEARI pyroprocessing was fabricated by using some synthetic materials and specific Lab-scale equipment.

Summary:

This paper is to review the status for developing the systemic waste treatment and storage/transportation process by reduction of the final waste volume, fabrication of durable wasteforms applicable to disposal environment and the safe packaging and storage system.

Spent Fuel & Zircaloy Cladding / 67

Development of solid state MAS NMR techniques for the characterization of alteration products formed during the dissolution of spent nuclear fuel.

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The migration of radionuclides from underground nuclear waste repositories will involve the formation of uranium secondary minerals when ground water reacts with the spent nuclear fuel.

During oxic or anoxic spent fuel dissolution, amorphous phases can precede the development of well-defined crystalline mineral phases. Nuclear magnetic resonance (NMR) can probe the structure of these amorphous alteration products and trace the evolution of secondary phases.

To develop the technique, potential secondary phases of ¹⁷O-enriched uranium minerals have been fabricated to establish the oxygen environments of becquerelite, Ca(UO₂)₆O₄(OH).8(H₂O), andersonite, Na₂Ca(UO₂)(CO₃)₃.6H₂O and grimselite, K₃Na(UO₂)(CO₃)₃.(H₂O). These contain calcium (Ca²⁺), carbonate (CO₃²⁺), and other ubiquitous ions.

Solid state ¹⁷O MAS-NMR spectra of uranium minerals have been obtained in a 9.39T magnetic field.

Detailed differences in oxygen local environments such as uranyl bond lengths and interlayer OH and H₂O can be distinguished by analyzing the spectra, which can elucidate the alteration of UO₂ by ¹⁷O water.

Radionuclide solubility, speciation, sorption & migration / 59

Digital autoradiography on C-14 labelled PMMA impregnated rock samples using the BeaverTM

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In Finland and Sweden KBS-3 concept has been chosen for disposal of spent nuclear fuel in crystalline rock. Recent transport experiments have shown that heterogeneity of rock may play a major role in transport of radionuclides. Autoradiographic methods has been proven to be able to assist the characterization of heterogeneous structures. In this study we tested a novel digital autoradiographic device called BeaverTM which applies a Micro Patterned Gaseous Detector in order to quantitatively map beta emissions by C-14 atoms. The studied samples were impregnated with C-14 labelled MMA (Methyl MethAcrylate) and polymerized to PMMA using heat. The BeaverTM was then used to determine concentration of C-14 atoms which can then be converted to porosity based on the amount of C-14 intruded into the rock sample. The resulting images show a heterogeneous distribution of porosity which arises from the different porosities of minerals. The samples were chosen from three sites that has been used recently in *in situ* diffusion experiments: Olkiluoto (Finland), Äspö (Sweden) and Grimsel (Switzerland).

Glass Wasteforms / 78

Dissolution Behavior of Lead Borate Glass under Simulated Geological Disposal Conditions

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Lead borate glass vitrified at a low temperature is regarded as one of the promising immobilization materials of Iodine-129 which will be removed from a spent AgI filter generated from reprocessing plants and may cause significant effect onto long term safety of geological disposal.

Immersion tests in various solutions have been conducted to understand glass dissolution behaviors in possible geological disposal conditions. Boron dissolved with the highest rate in all types of the solutions and was regarded as an index element to represent the glass dissolution rate. On the other hand, lead dissolved with a far slower rate. Chemical species and the possible precipitating minerals of lead were examined by a geochemical calculation code for typical underground water. Altered glass surfaces were investigated by SEM, TEM and XRD. XRD analysis showed that the main constituent phase of the altered layer was hydrocerussite, $Pb_3(CO_3)_2(OH)_2$ that was predicted by the geochemical simulation as well

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Effect of Carbonate on Lanthanides Migration Behavior in Compacted Bentonite

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The apparent diffusion coefficients of La, Nd, Eu, Dy, Er and Lu in compacted bentonites were investigated in various bicarbonate concentration. The apparent diffusion coefficients of lanthanides tended to decrease with increase of dry density. In the lower bicarbonate conditions than 0.25 M lanthanum had the largest diffusion coefficient of ca. 10-13 m²/s at 1.0 Mg/m³ and diffusion coefficient was small as atomic number becomes big. On the other hand in the higher bicarbonate conditions than 0.25 M Lutetium had the largest diffusion coefficient and diffusion coefficient was small as atomic number becomes small. Especially Lanthanum and Neodymium had smaller diffusion coefficient than 10-14 m²/s even at 1.0 Mg/m³. Diffusion coefficient of Europium was around 10-13 m²/s at 1.0 Mg/m³ and less influence of bicarbonate concentration. Diffusion coefficient of Lutetium increased from 2 x 10⁻¹⁴ to 10⁻¹² m²/s with bicarbonate concentration up to 1.0 M.

Spent Fuel & Zircaloy Cladding / 64

Effect of platinoid elements on the dissolution of uranium dioxide

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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. Moreover, SNF contain a wide variety of fission products including platinoid elements (PGM's) either incorporated in the UO₂ matrix, or present in various separated phases for which the specific impact on the overall dissolution kinetics has not been yet fully discriminated. In order to answer this question, several samples doped with 0.6 to 3 mol.% of PGM's (55 % Ru ; 9.6 % Rh ; 35.4 % Pd) were prepared from hydroxide based synthesis [1,2]. After conversion then sintering, the prepared pellets were submitted to multiparametric dissolution tests in various media (0.1 to 4 M HNO₃) and temperatures (25°C to 60°C). The macroscopic description of the dissolution showed that the normalized dissolution rates were significantly increased for UO₂ doped with PGM's compared to pure UO₂ used as reference compound. This effect was strengthened in less acid media. As instance, a factor of 4500 was observed after 175 days of leaching in 0.1M HNO₃. Simultaneously, the dissolution of the pellets was followed in operando by ESEM. The combination of macroscopic and microscopic approaches confirmed the modification of the preponderant mechanism occurring at the solid/liquid interface from redox-controlled dissolution in strong nitric acid media to surface-controlled dissolution for less acidic media.

1. Martinez, J. et al., J. Nucl. Mater., 462, 173-181, 2015
2. Martinez, J. et al., J. Europ. Ceram. Soc., 35, 4535-4546, 2015

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Effect of thiosulfate on the SCC behavior of carbon steel welds exposed to concrete pore water under anoxic conditions

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The Supercontainer (SC) is the reference concept for the post-conditioning of vitrified high-level nuclear waste and spent fuel in Belgium. It comprises a prefabricated concrete buffer that completely surrounds a carbon steel overpack. Welding is being considered as a final closure technique of the carbon steel overpack in order to ensure its water tightness. Welding is known to induce residual stresses near the weld zone, which may lead to an increased susceptibility to stress corrosion cracking (SCC). In this study, slow strain rate tests were conducted to study the SCC behavior of plain and welded P355 QL2 grade carbon steel exposed to an artificial concrete pore water solution that is representative for the SC concrete buffer environment. The tests were performed at 140°C, a constant strain rate of 5×10^{-7} s⁻¹ and at open circuit potential under anoxic conditions. The effect of thiosulfate on the SCC behavior was investigated up to levels of 5.35 mM S₂O₃²⁻ (600 mg L⁻¹).

Glass Wasteforms / 42

Effects of Li, Ca, Fe, and B on NaAlSiO₄ nepheline crystallization in high level waste glasses

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Owing to high concentrations of Al₂O₃ from dissolved fuel cladding and Na₂O 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 SiO₂, which often leads to undesirable precipitation of nepheline (NaAlSiO₄). Nepheline crystallization can be affected by modifiers (Li, Ca) added to lower viscosity and improve electrical conductivity of the melt. Also, B is frequently added to reduce viscosity, and Fe is present in varying amounts from steel tank corrosion. Given the existence of various natural minerals of the stoichiometries (Na,Li,Ca_{0.5})(Al,Fe,B)SiO₄, we sought to study the effects of substitution in the stoichiometric nepheline glass on the resulting crystallization. We summarize here several years of work, including characterization by nuclear magnetic resonance, vibrating sample magnetometry, Raman spectroscopy, thermal analysis, x-ray diffraction, electron microscopy, and electron microprobe.

Ceramic and Glass-Ceramic Wasteforms / 8

Efficient remediation of radiodine with silver-functionalized silica aerogel

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Various volatile radionuclides are being released into gas streams and aqueous solutions during reprocessing of used nuclear fuel and vitrification of radioactive waste. Radioactive iodine-129 is of a particular concern because of its long half-life of 15.7 million years and the potential for biological processes to concentrate iodine. A number of materials are being developed worldwide to capture and immobilize iodine in a waste form of a high chemical durability; however, none of them can be used as both a sorbent and a viable waste form. They can either encapsulate iodine-loaded sorbent or sequester iodine that was removed from it. In the U.S., the current benchmark for radioiodine capture is reduced silver mordenite (AgZ) and that for the waste form is AgZ immobilized in a low-temperature glass composite material. However, the primary alternative option is a silver-functionalized silica aerogel (Ag-aerogel). Ag-aerogel exhibits high capture efficiency (~ 500 mg/g) and selectivity for iodine (DF > 10000), and good resistance against aging in nuclear fuel reprocessing off-gas streams. Its sorption performance is retained in deionized water and in a dilute salt solution with neutral pH containing iodide or iodate. A key advantage of an Ag-aerogel is that, after loading with iodine, it can be consolidated into a dense and high-iodine-loaded silica-based waste form by simultaneous application of the heat and pressure. Presentation will discuss the sorption performance of Ag-aerogel in different environments and provide an overview on the development of waste form.

Partitioning & Transmutation / 49

Emulsions as a powerful tool to design silica monoliths able to selectively uptake radioactive caesium

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This work deals with the development of new templating routes to design porous nanostructured materials with innovative properties and/or easier to prepare. For example, we have shown that copper hexacyanoferrate nanoparticles could stabilize High-Internal Phase Emulsions or HIPE (**Mayer et al., J. Coll. Int. Sci., 2017, doi.org/10.1016/j.jcis.2017.05.113**) that can be used in a second step as a template for functionalized monoliths. It is of great interest considering that these coordination polymers come from Prussian blue analogues family, the most effective sorbent for caesium, and therefore relevant in nuclear decontamination purposes of ¹³⁷Cs or ¹³⁴Cs. To be active at oil/water interface and stabilize emulsions, CuHCF particles have to be modified with a polyelectrolyte, PDDA. The presence of CuHCF all around the oil droplets of the emulsions makes these particles located all around the macropores inside the final silica monolith due to the fact that the oil droplets are used as a template and should be therefore emptied after sol/gel gelification of the emulsions in order to create macropores. However, CuHCF can also be used without any PDDA surface modification. In this case, CuHCF nanoparticles are hydrophilic and remain in the water phase of the HIPE. The water outer part of the HIPE is the place where sol/gel reactions occur. Therefore, CuHCF nanoparticles are finally located in the monoliths walls if no PDDA is used. However CuHCF nanoparticles are still accessible to caesium in this case due to the mesoporosity of the walls because of the use of surfactant in this case to stabilize the HIPE (**Causse et al., J. Mater. Chem. A, 2014, 2, 9461**). And finally, we have also developed a third synthesis route of functionalized silica monoliths with CuHCF, CoHCF and ZnHCF. In this latter example, the HIPE is prepared only with the metal species, either Cu or Co or Zn. After the sol/gel reaction a meso/macroporous silica monoliths containing metal species is obtained. And finally after an impregnation step with K₄[Fe(CN)₆], the corresponding metal hexacyanoferrate particles precipitate inside the porosity of the silica monolith (**Sommer-Marquez et al., RSC Adv., 2016, 6, 73475**).

This global study showed that we can play with particles of interest in order to change their location in the templating soft matter (HIPE) and therefore inside the final monolith. Results of inorganic materials characterization (N₂ adsorption/desorption, SAXS, SEM, FTIR) as well as Cs sorption isotherms will be shown.

Partitioning & Transmutation / 92

Functionalised Titania and Zirconia Materials for Selective Actinide and Lanthanide Separations

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Actinides and lanthanides are targets for partitioning from solutions of spent nuclear fuel. Traditionally, actinide separation processes are based on liquid-liquid extraction. However, use of solid phase

sorbent materials has several advantages such as the lack of organic solvent wastes. Framework materials based on titania and zirconia have been developed and functionalised with organic ligands in order to impart selectivity. Titania and zirconia based framework materials were chosen due to their radiolytic and hydrolytic stability, as well as the fact they can be easily converted to transmutation matrices or wasteforms once they are loaded with actinides. The framework materials used vary in complexity from simple nanoparticles to millimetre sized, spherical, hierarchically porous beads. In terms of organic ligands, functionalisation with phosphonates, amines and bistriazinylpyridine (BTP) has been performed to impart selectivity for lanthanides, uranium or minor actinides.

Partitioning & Transmutation / 60

Highly porous and stable metal–organic frameworks for uranium extraction

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Transformative technologies are needed in order to achieve economic uranium extraction from waste to generate a new fuel or for a safe storage. Metal–organic frameworks (MOFs) are a class of hybrid materials composed of organic bridging ligands coordinated to metal ions or metal ion clusters. The result is the formation of a porous crystalline solid that possess adequate stability in aqueous solution for potential application in U extraction. These materials can selectively precipitate with a specific metal to extract it or they have large pore apertures to facilitate the transport of hydrated actinide

ions through the interior of the frameworks for the extraction. In this way pollutants such as actinides can be targeted for selective precipitation as a MOF or bind inside the framework by the ligand. This material can be easily recovered by simple filtration or centrifugation and actinide can be stored after a thermal treatment of the material to finally generate an original strategy to combine extraction and storage.

Summary:

We propose here an original way with the use of coordination polymers (MOFs) for the uranium extraction to generate new fuel or for the storage.

Ceramic and Glass-Ceramic Wasteforms / 24

Hot isostatic pressing of ion exchange materials, from the Fukushima and Sellafield sites, to produce ceramic wasteforms.

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Decommissioning and clean up of nuclear facilities requires the development of new technologies to condition radioactive wastes, producing passively safe waste packages of minimal volume, to reduce storage and disposal costs. We have applied hot isostatic pressing to demonstrate conceptual

wasteforms for ion exchange materials and sludges present on the Sellafield site, UK, and Fukushima site, Japan. These radioactive wastes pose several challenges which demand early conditioning to produce a passively safe wasteform, including: i) the materials are of a wet and granular nature, and hence dispersible as a result of loss of containment; ii) the materials are characterised by very high dose rates as a result of their selectivity for short lived radionuclides (e.g. Sr-90, Cs-137, Co-60); iii) the materials exhibit radiogenic self heating, as a result of the concentration of such lived radio nuclides; iv) the materials exhibit hydrogen production as a result of radiolysis of entrained water. In this presentation we demonstrate the conversion of several commercial and natural inorganic ion exchange materials into multiphase ceramic wasteforms, achieving a waste loading of 100 wt% and density in excess of 97% theoretical. High resolution thermogravimetric analysis coupled with mass spectroscopy was utilised to characterise the evolution of water and volatiles during the in-can bake out step, prior to the HIP cycle. This allowed optimisation of the bake out parameters (temperature, time and vacuum) to enable complete removal of water and volatiles, affording ceramic bodies with minimal residual porosity by hot isostatic pressing at 1250oC for 4h in stainless steel cans. Characterisation of the ceramic wasteforms by SEM /EDX and X-ray diffraction revealed the nuclides of concern to be incorporated within well known natural mineral and synthetic phases, with Sr partitioning into the SrTiO₃ perovskite phase and Co, Fe, Mn and Cr partitioning into a spinel phase. Dynamic alteration experiments revealed matrix dissolution rates of less than 10-4 g m⁻² d⁻¹ under forward rate conditions at 90 oC.

Overall, hot isostatic pressing of inorganic ion exchange materials yields durable glass, glass-ceramic, and ceramic wasteforms, with minimal voidage and porosity, in which the radionuclide partitioning between glass and ceramic phases can be controlled by wasteform composition and processing parameters. The resulting ceramic wasteforms are considered to meet the disposability requirements of a UK Geological Disposal Facility for radioactive wastes.

Repositories & Geological Disposal / 56

Identification of chemical form of stable carbon released from type 304 and 316 stainless-steel powders in alkaline solution and in acidic solution under low-oxygen condition

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The chemical form of carbon-14 released from irradiated stainless steel is a key parameter in the safety assessment of the sub-surface disposal system in Japan. In this study, unirradiated 304 and 316 stainless-steel powders were immersed in HCl solution and in NaOH solution under a low-oxygen condition to identify the chemical form of the released carbon. The main chemical forms of the carbon were formic and acetic acids in the HCl solution and colloidal carbon in the NaOH solution. Point analysis of the colloidal particles by transmission electron microscopy equipped with energy dispersive spectroscopy showed that C was accompanied with Fe and Cr. Fe and Cr tended to precipitate thermodynamically as hydroxides in an alkaline environment, suggesting that carbon sorbed onto the hydroxide. Meanwhile, in the HCl solution, the hydroxides did not precipitate thermodynamically, so carbon appeared to be released as an ionic form without the formation of metallic hydroxides.

Spent Fuel & Zircaloy Cladding / 66

Impact of lanthanide elements on the dissolution of uranium dioxide

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Due to the concomitant formation of oxygen vacancies in the fluorite structure, it was found that the incorporation of trivalent lanthanide elements in ThO₂ or CeO₂ strongly affect their chemical durability during dissolution or leaching tests [1-4]. On the contrary, the impact of such elements on the dissolution of UO₂ remains largely unknown. For this purpose, several lanthanide – uranium mixed based samples incorporating 1 to 20 mol.% of a mixture of lanthanide elements (with the mole ratio : 13 % La ; 7.4 % Y ; 25.6 % Ce ; 12 % Pr ; 42 % Nd) were prepared through quantitative oxalate precipitation. After conversion to the final oxides then sintering, they were characterized from chemical and microstructural points of view and finally submitted to multiparametric dissolution tests in several nitric acid solutions and at various temperatures. Contrarily to Th- and Ce-based mixed oxides, the presence of lanthanide elements in UO₂ 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 or 100 compared to pure UO₂ observed in 0.5M HNO₃) when the role of surface-controlling reactions on the overall dissolution become predominant. Such observations related to the macroscopic description of the dissolution were connected to in operando following of the evolving solid/liquid interface that underlined the preferential dissolution of lanthanide enriched grain boundaries and triple junctions.

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Partitioning & Transmutation / 14

Inert matrix fuel deployment for reducing the plutonium stock-pile in reactors

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Abstract – The 450 reactors operating (Nov. 2016) around the world (30 countries) produce about 100 tonnes of plutonium annually, in spent fuel. Some amounts are separated through reprocessing. While the recycling of plutonium as MOX fuel derives additional energy from this resource, it does little to address the issue of growing plutonium inventories. If a political objective is to reduce the amount of plutonium, then inert matrix fuel (IMF) provides an option for plutonium destruction. More generally, the utilization of plutonium in IMF provides flexibility in balancing the quantity of plutonium, by enabling the net burning of plutonium. This approach is viable in existing cores (Gen II&III) that already utilize MOX fuel. IMF can be used both to manage plutonium inventories and to contribute to reduce the long-term radiotoxicity of the spent fuel by minor actinide destruction. Some of these IMF materials are also being considered for Gen IV reactors, because of their advanced performance, economics, safety features, sustainability, and application to waste minimization in a closed fuel cycle.

Several promising candidate materials have been identified for both fast and thermal reactors: MgO

(magnesia), ZrO₂ (zirconia), SiC (silicon carbide), Zr (alloys), ZrN (zirconium nitride); some of these have undergone test irradiations and post irradiation examination. These materials may be used as cylindrical pellets, prismatic designed blocs, or as micro-spheres utilized as sphere-pac or kernels. They can be utilized at the fuel assembly level as prismatic (vertical or horizontal) set up such as in Light Water Reactors, Pressured Heavy Water Reactors or Liquid Metal Fast Reactor, or, as spherical such as in a High Temperature Gas-cooled Reactor. The fuel itself may be homogeneously composed of IMF or heterogeneously loaded with the IMF and uranium material. The assemblies may be homogeneously or heterogeneously loaded with the IMF, and the reactor core may be homogeneously or heterogeneously loaded with IMF assemblies. These three levels, i.e. fuel, assembly and core, of IMF utilization in LWR are considered within a homogeneous-heterogeneous concept scheme as recently reported in the IMF workshop. Modelling and testing IMF fuel performance and safety analysis have progressed. Fabrication methods have also been developed or adapted from existing technologies. System studies have identified strategies for both implementation of IMF fuel in existing reactors in the shorter term, as well as in new reactors in the longer term. Finally for the backend the burned IMF should be an attractive waste form to dispose or in specific conditions easy to reprocess. The work to date has established the feasibility of these IMF materials, and core loadings and reactor strategies for utilizing these fuels. Further developments are required before commercial deployment of IMF, which will require additional resources. Additional in-pile irradiations have been suggested, both for normal operating and accident conditions. Further safety analysis and tests are required. Some development is needed for analysis tools and computer programs. Irradiations in commercial reactors should be undertaken in a staged approach as soon as possible: segmented rods, full-length rods, then lead assemblies. IMF can play an important role in the future of nuclear power.

Safeguards, Decontamination & Decommissioning / 23

Interaction of nuclear safeguards and safety requirements when planning for waste disposal

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Waste conditioning is an important step in minimising and controlling the migration of radionuclides from disposed wastes into the environment. However, when nuclear materials are present, consideration of nuclear safeguards is also needed. Safeguards is the set of tools and techniques used to ensure nuclear materials are only used for peaceful purposes. As part of a safeguards system, nuclear materials need to be available for verification or rendered inaccessible in accordance with International Atomic Energy Agency requirements. Inaccessibility requirements are not driven by environmental degradation factors, but on preventing recovery by motivated state actors. This presentation looks at the overlap between safety and safeguards requirements in Australia as well as safeguards-specific requirements when conditioning or disposing of nuclear materials.

Radiation Damage / 84

Investigating Local Defect Structures in Nuclear Waste Form Materials

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For the past 30 years, the development of durable materials for radionuclide immobilization has been central to efforts to dispose of wastes generated by the nuclear fuel cycle. There still exist, however, large gaps in the understanding of fundamental modes of waste form degradation under repository conditions. Comprehensive evaluation of waste form performance, including resistance to corrosion, requires detailed knowledge of the atomic-scale effects of long-term self-irradiation. We have recently shown that pair distribution function (PDF) analysis of neutron total scattering measurements can be applied to uniquely characterize radiation effects in a wide range of waste form materials, including fluorite-derivative pyrochlores, actinide oxides, and glasses. These measurements allow a detailed analysis of both cation and anion defect behavior, and short range order and disorder, which is particularly important for the investigation of aperiodic glasses. Recent results have shown complex disordering in pyrochlores, and oxygen defect clustering in actinide oxides.

Radionuclide solubility, speciation, sorption & migration / 35

Investigation of C-14 in the CRUD collected on the coolant filter for safety disposal of radioactive waste containing C-14 (I)- C-14 release behavior and thermal decomposition characteristics of crud particles collected from the coolant filter of commercial PWR -

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In the safety assessment of radioactive waste repository, it is important to evaluate the migration behavior of long half-life radionuclides in the disposal environment. It was reported that insoluble C-14 was generated in PWR. However, the knowledge about the chemical form of C-14 is little.

In this study, particles including C-14 collected from the coolant filters in PWR were analyzed by TG/MS to identify the chemical forms of these particles. In addition, C-14 in released gases and the residue in TG measurements were also investigated.

Resultantly, it was revealed that fragments which were considered to be organic compounds derived from the ion-exchange resin were detected from the released gas, and that majority(>90%) of C-14 inventory were detected in the residue after the inert gas heating.

While the chemical forms of C-14 in the residue are not clarified, it is suggested that insoluble C-14 may exist in the thermo-stable compounds.

Radionuclide solubility, speciation, sorption & migration / 39

Investigation of C-14 in the CRUD collected on the coolant filter for safety disposal of radioactive waste containing C-14 (II) – Chemical alternation of ion exchange resin under simulated condition in primary coolant of PWR –

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Radiocarbon (C-14) is recognized as a radionuclide that includes significant impact on public exposure in safety assessment of radioactive waste disposal. Its origin, generation mechanism and chemical forms in the wastes are required to be understood for the reasonable and proper safety assessment of the radioactive waste disposal. Some previous studies have reported occurrence of insoluble C-14 in PWR, and suggested that ion-exchange resin could be its origin. However, this hypothesis has not been well evidenced yet, because information about the generation mechanism and chemical form of the insoluble C-14 is still limited.

In this study, alternation of the resin under heating and/or irradiation was investigated to understand the alternation of the resin in PWR. In addition, characteristics of CRUD on a coolant filter for the actual PWR were compared to those of the heated/irradiated resin. The results suggested that the insoluble C-14 arises from alternation of the ion-exchange resin.

National & International Waste Management Programs: Session Chairs Greg Lumpkin & Simone Richter / 4

Invited Lecture: Plutonium Waste Management in the UK

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Plutonium has arisen from large scale reprocessing over many decades. When the programmes ends around 2020 there will be approx. 140te of separated plutonium in UK. Current policy is safe and secure long term storage in modern purpose built stores. This requires ongoing active management and institutional controls including significant security costs and is not a lifecycle solution. Disposition options are being considered in order to put the material "beyond reach":

- Reuse as LWR MOX
- Reuse in Candu EC6 Reactors (CANMOX)
- Reuse in GEH Prism Fast Reactor
- Immobilisation – Hot Isostatic Pressing (HIP) along with other technologies including low spec MOX and downblending.

The current status of these options will be outlined along with work planned over the next few years further develop them in support of future UK Government policy decisions.

Radiation Damage / 87

Ion Beam Irradiation of Ceramic-glass Waste Form at ANSTO

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Radioactive wastes are generated from the entire nuclear fuel cycle from mining to the burning of uranium fuel in the nuclear reactors. Pyrochlore (ABTi₂O₇) and zirconolite (CaZrTiO₇) based glass-ceramics have become an emerging candidate waste form matrix and attracted attention as it combines the process and chemical flexibility of glasses with the chemical durability of ceramics. It also has a potential ability to immobilize some compositionally diverse actinide-rich radioactive wastes, e.g. plutonium residue wastes and separated minor actinides. The efforts to evaluate the radiation resistance of the glass-ceramic waste form by ion beam irradiation have been undertaken using accelerators at ANSTO. This paper reported ANSTO's capability and development in this area and gave the results of the irradiation-induced structure modification in the glass-ceramics irradiated by helium and gold ions.

Radiation Damage / 51

Ion irradiation used as surrogate for neutron irradiation to understand nuclear graphite evolution during reactor operation: consequences for the long lived radionuclide's behavior

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Graphite has been widely used in different types of reactors such as gas or water cooled reactors. Disposal of the irradiated graphite waste is a current management strategy for the resulting graphite waste for which two main radionuclides, ¹⁴C and ³⁶Cl, might be dose determining at the outlet. In order to simulate both ballistic and electronic effects induced by irradiation, model and nuclear graphite samples implanted with ³⁷Cl or ¹⁴C (to simulate the radionuclides) have been irradiated using ions by varying the Sn(nuclear)/Se(electronic) stopping power ratio. Extrapolating to reactor irradiation, we show that depending on the initial graphite ordering level and texture (binder/grain) and according to the subsequent neutron flux and temperature, graphite irradiation results into a structural "zoning" impacting the radionuclide behavior: except when located close to open pores, ¹⁴C is stabilized into graphite whereas ³⁶Cl's release is strongly correlated to the counteracting effects of irradiation and temperature.

Safeguards, Decontamination & Decommissioning / 100

Management of the Radioactive Waste arising from the Decommissioning of the WWR-S Research Reactor from IFIN-HH, Magurele, Romania

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The WWR-S research reactor from National Institute for R&D in Physics and Nuclear Engineering Horia Hulubei (IFIN-HH), Magurele site, Romania, is currently in the year 2 of the phase 3 of the decommissioning project. Big components are cut in small parts to reduce the size for a proper packing and temporary disposal. Segregation is used to separate different type of materials depending on their physical and chemical properties. After that, the radioactive waste is accommodated in a standard barrel (220L) and send to radiological characterization laboratory before its arrival to the Waste Treatment Plant. High activated/contaminated materials are stored in shielded containers. In Romania, all the radioactive waste coming from decommissioning of the research reactor is treated and packed at the Radioactive Waste Management Department (RWMD) and sent for final disposal at the National Radioactive Waste Repository (NRWR) in Baita, Bihor County.

Safeguards, Decontamination & Decommissioning / 57

Microparticle Production as Reference Materials for Particle Analysis Methods in Safeguards

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The application of safeguards measures by the International Atomic Energy Agency (IAEA) involves analytical measurements of samples taken during inspections and requires the development and advancement of analytical techniques. For quality control purposes, the IAEA has expressed the need to acquire reference materials for particle analysis methods applied in safeguards.

To this purpose, a particle production facility was implemented at Forschungszentrum Jülich, which is capable of producing microparticles intended as source material for certified reference materials for particle analysis methods applied in safeguards. A monodisperse particle size distribution as well as the single phase triuranium octoxide structure was confirmed using SEM and μ -XRD/XANES, respectively. Analysis performed on single uranium microparticles confirmed consistency of the uranium isotopic ratios in comparison to the initial precursor solutions. To improve the homogeneity and particle handling, the particles are transferred into suspensions, for which the stability was investigated with respect to dissolution and isotopic exchange.

Spent Fuel & Zircaloy Cladding / 16

Modelling the Corrosion of Spent Nuclear Fuel Inside a failed Waste Container

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The internationally accepted approach for the disposal of spent nuclear fuel is to seal it in corrosion-resistant metal containers and bury it in a stable deep geologic repository. If containers were to fail, and the fuel become exposed to groundwater, radiolytic corrosion of the fuel could release radionuclides to the groundwater, the critical first step in their transport into the environment. Two corrosion fronts will exist within a failed container, one on the fuel surface driven by radiolytic oxidants and a second on the carbon steel vessel sustained by water reduction. Based on an extensive series of electrochemical, corrosion and chemical dissolution studies, a finite-element based model has been developed to determine this evolution in redox conditions and its influence on fuel corrosion. Particular attention will be paid to the influence of hydrogen, produced radiolytically and by corrosion of the steel container vessel, on the corrosion rate.

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Multinational Waste Repositories: A South Australian Initiative

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On the 19th of March 2015, the Nuclear Fuel Cycle Royal Commission (NFCRC) was established by the South Australian Government, and tasked to undertake an independent examination into the opportunities and risks for South Australia's further involvement in the Nuclear Fuel Cycle. This presentation will review the process, findings and recommendations delivered by the NFCRC, with particular emphasis on the proposed opportunity for the storage and disposal of international high-level and intermediate-level waste in South Australia and the potential value-add that this could provide on a global scale.

Outcomes of the State-wide 'KnowNuclear' community consultation program will also be discussed, as well as the possible next steps needed in advancing the South Australian multinational repository concept forward.

Spent Fuel & Zircaloy Cladding / 17

NEW ASPECTS OF THE MECHANISM OF HYDROGEN EFFECT ON SPENT FUEL DISSOLUTION

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Our experimental data indicate that the hydrogen effect is a complex phenomenon and has several aspects. The decomposition of hydrogen peroxide on the surface of SIMFUEL is followed by the reaction of the produced hydroxyl radicals with hydrogen to give water, or their reaction with H₂O₂

to give O₂. Only a very small part of the initial hydrogen peroxide (<0.02%) causes oxidative dissolution of the SIMFUEL producing U(VI) in solution.

In another study, the leaching of a high Pu content (~24%) un-irradiated MOX fuel was investigated under anoxic conditions (Ar) and in the presence of 1 MPa D₂(g). The results obtained under 1 MPa deuterium indicate a complete absence of oxidative dissolution during the first 29 days. Isotopic D/H analysis of the water sampled in the autoclave and analysis of the gas atmosphere of the autoclave makes possible to draw conclusions about the fate of radiolytic oxidants.

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NMR Methods for Study of Waste Glasses

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11B MAS NMR methods for analysis of borosilicate glasses for storage of high-level waste.

Summary:

As part of a wider project looking at the use of borosilicate glasses as a high-level nuclear waste form undertaken by a group of four universities in the UK and USA, MAS NMR has been used at The University of Warwick as a tool for investigating structure and speciation in these glasses. This study was motivated by recent findings that waste loading rate could be greatly increased from 18 to 45 %mass by targeting certain phases.

Multiple fields were used to assist in producing accurate simulations of the quadrupolar parameters of the nuclear sites, as well a software package that allows for the inclusion of disorder in these parameters. Low field 11B MAS NMR (2.3 T) was also found to be a very promising tool for the analysis of these glasses, with the broadened lineshapes making the separate features more distinct.

Ceramic and Glass-Ceramic Wasteforms / 11

New aspects of U(V) chemistry in oxo-materials: from ambient to extreme conditions

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Using extreme pressure (10GPa/1200°C) we obtained a new modification of U₂O₅ with an extraordinary dense structure. The crystal structure of resulting HP (high pressure)-U₂O₅ is dramatically differs from ambient pressure polymorph so called delta-U₂O₅. The structure of HP-U₂O₅ is more related to the cubic UO₂ than to the layered delta-U₂O₅. Using state of the art ab initio methods we reveal the stability ranges of both ambient and high pressure forms of U₂O₅ and demonstrated a potential pathway of phase transition under pressure.

In second case we demonstrated that the pentavalent uranium (U(V)) can be stabilized in [Ln(UVO₂)W₄O₁₄] (Ln = Nd-Tm and Y) series via aliovalent substitution of Ca²⁺ cations. We confirmed U(V) stabilization using state of the art methods such as U M₄ edge high energy resolution X-ray absorption near edge structure (HR-XANES). Magnetic study reveals low temperature ordering of 5f₁ and 4f_n systems. All the phases tend to demonstrate the antiferromagnetic properties with significant difference between pure 5f₁ system (Y-beating phase) and 5f₁-4f_n compounds (Nd-Tm).

Ceramic and Glass-Ceramic Wasteforms / 15

New route for synthesis of Synroc-like ceramic using non-selective sorbent LHT-9

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Immobilization of bulk liquid high level waste (HLW) in Synroc ceramic is well-known reliable way for final isolation of waste from biosphere. It is proposed the alternative method of synthesis of titanate Synroc-like ceramic. Radionuclide incorporation into crystalline titanate host-phases can be provided as a result of direct radionuclide sorption from liquid HLW using non-selective sorbent – layered hydrazinium titanate (LHT-9). Such an approach allows excluding expensive multi-stage procedure of precursor preparation. The precipitate obtained after sorption can be easily transformed into Synroc-like ceramic by cold pressing and sintering in air at 1000-1100°. The highly radioactive samples of titanate ceramic loaded with 10 wt.% of real HLW were synthesized and studied at KRI hot-cell facility. Chemical durability of these samples was tested using MCC-1 static leach test (in distilled water at 90°C) and the leach rate was found to be comparable with Synroc ceramic.

National & International Waste Management Programs: Session Chairs Greg Lumpkin & Simone Richter / 22

Nuclear Waste Management update in Australia

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Australia is currently in the process of establishing a National Radioactive Waste Management Facility and seeking to identify a site to host the facility.

The lecture will focus on the history of waste production in Australia, the current management of the diverse waste arisings, particularly focussed on operational and legacy wastes held at the Australian Nuclear Science and Technology Organisation and the strategy applied to the management of those wastes.

The process adopted to establish the facility will be discussed as well as potential future options for the disposal of Intermediate Level Wastes. Australia's focus on investing in optimum wasteforms, such as the vitrified residues from reprocessing spent fuel elements from current and previous research reactors and the synroc waste form for treating Intermediate Level Liquid Wastes, will be discussed as case studies.

Radiation Damage / 102

P-31 Nuclear Magnetic Resonance as a Probe of Plutonium Incorporation and Radiation Damage in Phosphates

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Plutonium doped YPO₄ was prepared to test the extent of solid solution and the effect of radiation damage over several years. Y_{0.92}238Pu_{0.08}PO₄ showed the presence of a Pu substituted xenotime phase and a 238PuP₂O₇ phase by X-ray diffraction (XRD). The ³¹P magic-angle spinning nuclear magnetic resonance (MASNMR) spectrum showed peaks for PuP₂O₇ and peaks assigned to phosphorus coupled to Pu³⁺ substituted randomly into Y³⁺ sites. A time series of ³¹P MASNMR and XRD measurements observed the loss of the reflections due to the 238PuP₂O₇ phase in the XRD pattern of the Y_{0.92}238Pu_{0.08}PO₄ sample within 4 weeks. The MASNMR spectra obtained at longer times in both the Y_{0.92}238Pu_{0.08}PO₄ and Y_{0.96}238Pu_{0.04}PO₄ samples showed an additional broadened and shifted ³¹P resonance assigned to amorphised xenotime with a chemical shift consistent with Q₀ orthophosphate. Thus, the amorphised local structure is assigned to a predominantly Q₀ phosphate arrangement subject to local densification.

Summary:

This paper is about understanding the solid solubility of Pu in crystalline phosphates and the effect of its alpha decay on the local structure of the crystal. We use novel actinide enabled magic angle spinning nuclear magnetic resonance to elucidate the nature of bonding in the amorphised phase.

Ceramic and Glass-Ceramic Wasteforms / 83

Partitioning of Ce, as a Simulant for Pu, in a Multiphase Ceramic Nuclear Waste Form

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A multi-phase titanate waste form was synthesized using high temperature sintering in air or Ar with the composition of Ca_{0.71}Y_{0.088}Ce_{0.52}Hf_{0.22}Ti₂O_x. The phase assemblage was investigated as a function of the sintering atmosphere. X-ray diffraction measurements indicated that oxidizing sintering atmosphere (air) favors the formation of pyrochlore, whereas neutral environment (Ar) promotes the formation of perovskite, although both sintering atmospheres produced samples containing three phases (pyrochlore, perovskite and rutile under air or zirconolite, perovskite and rutile under Ar). Scanning electron microscope (SEM) analysis revealed that Ce is present in perovskite and pyrochlore (or zirconolite), but not in rutile. Micro-X-ray-Absorption-Near-Edge-Structure (micro-XANES) measurements conducted at the Ce L-edge, in combination with electron energy loss spectroscopy (EELS), showed that Ce⁴⁺ prefers to inhabit the pyrochlore (or zirconolite) phase and Ce³⁺ the perovskite phase. This knowledge is valuable for the further development of titanate waste forms to immobilize Pu.

Repositories & Geological Disposal / 40

Porosity distribution in a heterogeneous clay-rich fault core

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Fault zones influence the mechanical properties and seismological behaviour of the Earth's crust and also the migration and trapping of sub-surface fluids. In addition to natural processes, their behaviour has broad implications to issues such as oil and gas production, the sequestration of carbon dioxide and the geological disposal of radioactive wastes.

Recent investigations carried out at the Tournemire Underground Laboratory (URL), run by the French Institute for Radiological Protection and Nuclear Safety (IRSN) have highlighted heterogeneous fault gouge strengthening processes within a small-scale vertical strike slip fault affecting a low-permeability shale.

The aim of this project is to determine precisely, in an apparently heterogeneous and poorly consolidated brecciated rock, the porosity variations in and around the different fault gouges and define their relationship to chemical and/or mechano-chemical processes.

Ceramic and Glass-Ceramic Wasteforms / 46

Preparation of Ln_{1-2x}CaxThxPO₄.nH₂O rhabdophane-type as low precursors to monazite-Cheralite ceramics

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Monazite, i.e. LnPO₄ (Ln = La-Gd), has been widely studied as specific ceramic for the conditioning of trivalent and tetravalent actinides.¹ Owing to its chemical and structural flexibility, the monazite allows a variety of possible substitutions following different mechanisms.² Among them, the so-called cheralite-family, i.e. Ln_{1-2x}CaxAnIVxPO₄. In this frame, the major part of protocols reported in the literature was based on solid-state chemistry routes. However, this method requires the use of repetitive grinding steps and re-heating of actinide bearing powders and usually forms heterogeneous compounds in term of cationic distribution.

In this work, we present an alternative method based on wet chemistry route to prepare thorium-based cheralites. It is based on the initial precipitation of Ln_{1-2x}CaxThxPO₄.nH₂O³ low temperature precursors crystallizing in the rhabdophane type structure (monoclinic, C2 space group).⁴ A multi-parametric study allowed the determination of the appropriate conditions to form homogeneous and single phase powders. Then these hydrated precursors were converted to monazite-cheralite ceramics through thermal treatment. A coupled in situ PXRD/TGA allowed the identification of the different dehydration steps before the irreversible stabilization of the cheralite anhydrous compounds.⁵ Moreover, since such hydrated phases could also control the release of radionuclides from the ceramics in the field of underground repository, dissolution and solubility experiments have been finally carried out.

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Partitioning & Transmutation / 73

Pyrolysis and Plasma applied to Nuclear ion Exchange Resins Treatment

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Spent ion exchange resins (IER) represent an important waste stream that is generated during the operation of both light and heavy-water reactors. Over the past 60 years of nuclear activity Argentina has accumulated over 300 m³ of spent IERs that to this day remain interim storage. With a view toward achieving a significant volume reduction and improved product stability we are investigating a two-step process involving initial low-temperature (< 350 oC) pyrolysis followed by immobilization in a polymeric matrix such as Epoxy or Phenol formaldehyde and nanocomposites thereof without any significant volume increase. Also contemplated as part of the overall process is the destruction of radioactive off-gas using an induction plasma system with subsequent trapping of radioactive gases using high performance adsorbents. This talk will provide an overview of the overall process that is being investigated paying particular attention to the waste form structure and efficient off-gas treatment system.

Radiation Damage / 86

Quantification of irradiation induced structural disorder in nuclear waste-form ceramics with μ -luminescence spectroscopy of lanthanides

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The investigation of radiation damaged or metamict minerals and their synthetic analogues has increased appreciably over the past two decades, stimulated by the potential use of mineral-like ceramics as waste forms for the immobilisation of reprocessed spent nuclear fuel and other radioactive

waste. In this research field, however, a fast and inexpensive technique operating in the micrometre range may open up new opportunities in the characterisation of radiation damage.

We present first results of a heavy-ion (Au) irradiation-study of the important nuclear waste-form matrices zircon ($ZrSiO_4$), xenotime-(Y) (YPO_4) and zirconolite ($CaZrTi_2O_7$). Bulk, poly-crystalline ceramics were irradiated with accelerated heavy ions (Au) with energies up to 35 MeV. Comparably high heavy-ion energies are chosen to ensure irradiation penetration-depths of 4 - 5 μm accessible to the spatial resolution of optical confocal spectrometers.

Summary:

We use surface-sensitive, grazing-incident X-ray diffraction of irradiated bulk ceramic pellets for the estimation of the amorphous fraction produced and demonstrate how photoluminescence spectroscopy may be used as a tool for the characterisation and quantification of irradiation-induced structural damage in nuclear waste-form materials on a μm -scale. Ln³⁺ ions are common substitutes on regular lattice sites in respective ceramic hosts. Their luminescence emissions may be used as structural probe and are very sensitive to their local crystal field

Radiation Damage / 21

Radiation stability study of melt processed and hot isostatically pressed multi-phase ceramic waste forms

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Multi-phase ceramic waste forms were fabricated by melt-processing and hot isostatic pressing (HIP) to immobilize alkaline/alkaline earth (Cs/Sr-CS) + lanthanide (LN) + transition metal (TM) fission product waste streams from nuclear fuel reprocessing. Al₂O₃ and TiO₂ were combined with these waste components to produce multi-phase crystalline ceramics containing hollandite-type phases, perovskites, zirconolite/pyrochlores and other minor phases. In this study, ion irradiations are performed to test and compare radiation tolerance of multi-phase ceramics produced via melting processing and HIP techniques.

For the radiation stability test, selected crystalline ceramic samples are exposed to charge particles generated by an ion accelerator, which is used to simulate self-radiation in a waste form. Ion irradiation-induced microstructural modifications, volume swelling and microcracking are examined using X-ray diffraction, transmission electron microscopy, scanning electron microscopy and other characterization methods. Our preliminary results reveal similar radiation tolerance in these multi-phase ceramics with different fabrication techniques.

Ceramic and Glass-Ceramic Wasteforms / 93

Radioactive Iodine-129 Capture in Mixed Cation Sodalites: ab initio modelling

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Sodalites have been investigated experimentally for the capture and long-term containment of iodine-129, a significant and hazardous waste product of the nuclear fuel cycle. Sodalites are zeolite-type structures commonly occurring in nature in alkaline igneous rocks and having the prototype formula $\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$. The crystal structure is based around β -cages consisting of corner-sharing SiO_4 and AlO_4 tetrahedra. In the centre of the β -cage is an anion X. Iodine captured by sodalites sits in the centre of the β -cages as iodide anions. Silver iodide (AgI) plays an important role in the capture and subsequent processing of iodine-129 in the nuclear fuel cycle. Using *ab initio* density functional theory (DFT) modelling, we investigate the energetics and feasibility of iodine capture and containment in mixed cation sodalites $\text{Na}_{8-x}\text{Ag}_x(\text{AlSiO}_4)_6\text{I}_2$, and compare the results with experimental observations.

Radiation Damage / 101

Radionuclide Sorption Behaviour on Fresh and Aged Cementitious Materials: A Comprehensive Database with 25 Elements

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Cementitious materials are being widely used as solidification/stabilisation and barrier materials for a variety of radioactive wastes. The retention properties result from mineral phases in hydrated cement that (i) possess a high density and diversity of reactive sites for the fixation of radionuclides through a variety of sorption reactions (surface adsorption, incorporation and solid-solution formation), and (ii) buffer pH in the range 10–13. A quantitative database on the solid/liquid distribution behaviour (“sorption database”) of 25 elements (Ag, Am, Be, C, Ca, Cl, Cs, H, I, Mo, Nb, Ni, Np, Pa, Pb, Pd, Pu, Ra, Se, Sn, Sr, Tc, Th, U, Zr) in hydrated cement systems is established on the basis of a consistent review and re-evaluation of literature data. Effects of geochemical evolution or ageing cements on sorption/incorporation processes are explicitly evaluated and quantified. In addition to recommended values, all underlying original experimental data and key experimental information are provided.

Summary:

The database and the scientific underpinning of its derived sorption values will be of use to support the safe disposal of radioactive waste and other cemented industrial wastes. They are specifically useful for incorporation in safety assessment modelling using advective-dispersive transport models with incorporation of radionuclide retardation processes relevant for fresh and aged cement. Time-dependent sorption properties are required because the long-term degradation of engineered barriers and their containment capacity over time has to be explicitly assessed through scenario-modelling in any safety case.

Spent Fuel & Zircaloy Cladding / 70

Radionuclide containing solid phases on the inner surface of a Zircaloy-4 cladding tube

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Zircaloy claddings of fuel rods for nuclear reactors are considered as first technical barrier for retention of radionuclides produced in the nuclear fuel. The integrity of the cladding is influenced by various processes during reactor operation and beyond, e.g. oxidation, hydrogen uptake, PCI, fission product precipitation, α -decay, and radiation damage. Composition of agglomerates found on the inner surface of the plenum section of an irradiated Zircaloy-4 cladding tube are investigated by SEM-EDX, XPS, and synchrotron based techniques.

μ -XRF investigations show uranium hot spots and fission products. Grooves from cladding tube production contain uranium residues from fuel pellets insertion. Plutonium, cesium and rubidium are present ibidem. Another type of agglomerates contains cesium, rubidium, and minor amounts of actinides. Cesium and rubidium may originate from three sources: uranium traces within the cladding, uranium residues in surface grooves, and Cs/Rb released from subjacent fuel pellets.

Glass Wasteforms / 69

Simplified UK Magnox waste glass alteration layer characterisation using ²⁹Si, ¹⁷O and ²⁵Mg NMR techniques

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The magnesium content of UK Magnox waste glass makes its aqueous durability much poorer than glasses such as SON68, which does not contain Mg. The glass dissolution kinetics is ultimately dependent on the composition/structures of the altered layers(1), here we try to elucidate formation mechanisms.

Alteration layers formed by in-situ precipitation have been discussed widely(2,3), but any direct identification of precipitated phases is not yet known. The altered layers of simplified Magnox waste glasses were examined using a variety of ¹⁷O, ²⁵Mg and ²⁹Si solid-state NMR techniques. In terms of quantification and species identification, the Mg containing glass incorporates 3-4 times the amount of ¹⁷O derived from the ¹⁷O enriched leachate compared with a Ca glass, identified as bridging oxygen and hydroxyl oxygen species. At least two types of amorphous surface phases were characterised by proton cross-polarisation (CP) that show local environments similar to clay mineral phases(4). ²⁵Mg and ²⁹Si NMR spectra corroborate the active chemical role of Mg in precipitation and the multiphase nature of the alteration layer.

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Ceramic and Glass-Ceramic Wasteforms / 43

Sodalite waste forms for iodine

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Iodine-129, released in the off-gas stream during nuclear fuel reprocessing, is problematic due to its long half-life, high mobility in the earth's environment, incorporation into the human thyroid, and difficulty in immobilizing it using traditional vitrification methods. Iodosodalite (Na₈Al₆Si₆O₂₄I₂) has been considered as to immobilize iodine-129 due to feasibility of synthesis at low temperature (<200°C) and compatibility with glass matrices for encapsulation of sodalite crystallites. Our study focused on synthesis and characterization of glass-bonded sodalite waste forms, in which we sought to study the effects of process variables on the resulting crystallization and iodine retained. X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, electron microscopy, neutron activation analysis, and thermal analysis were performed to characterize the physical and chemical properties of the specimens. Chemical durability tests were also performed on synthesized pellets.

Ceramic and Glass-Ceramic Wasteforms / 50

Solubility of the rhabdophane, LnPO₄·0.667 H₂O (Ln = La to Dy): implications for the long-term stability of monazite matrices.

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Minerals belonging to the monazite family, REEPO₄ (REE: Y, Sc, La to Dy) could incorporate in their structure substantial amounts of Th and U [1]. Moreover, monazites maintain their crystallinity even after geological times of exposure to self-irradiation. Therefore, this phase appears as a promising candidate for the specific conditioning of transuranic elements (AnIV, AnIII). Already, many thermodynamic properties of monazite are reported in the literature [2]. However, its hydrated form namely, rhabdophane, REEPO₄·0.667 H₂O could be stabilized at low temperatures, and thus control the concentrations of actinides in solution after the leaching of the monazite matrices [3, 4].

For the first time, a systematic study of the solubility of the rhabdophane, LnPO₄·0.667 H₂O (Ln = La to Dy) was performed using over-saturated and under-saturated experiments at different temperatures (298 to 363 K) to demonstrate the reversibility of the solubility equilibrium [5]. The structure of the neoformed phases was carefully controlled in the entire range of temperatures in order to attribute unambiguously the solubility products and the derived thermodynamic data associated to the rhabdophane phases. The obtained results indicate that the stability domain of the rhabdophane phase is limited in temperature and depends on the ionic radius of the lanthanide. The values of the solubility constant depend also slightly on the lanthanide with log K_{S,0°} (298 K) ranging from -25.6 ± 0.8 (Pr) to -24.9 ± 1.7 (Eu) with minimum values for Pr to Sm. The values of the standard free energy of formation at 298 K varied between -1984 ± 2 and -2004 ± 2 kJ.mol⁻¹ whatever the lanthanide element considered, except for Eu-rhabdophane that presented the highest value for the Gibbs energy of formation (-1896 ± 2 kJ.mol⁻¹).

From the solubility data obtained at various temperatures, the values of enthalpy of formation of the rhabdophanes were found between -2151 ± 13 and -2130 ± 12 kJ. mol⁻¹ excepted for Eu for which

it reached -2057 ± 9 kJ.mol⁻¹. It is worth noting that the data reported by Ushakov et al. [6] for monazites LnPO₄ (Ln = La to Gd) determined by oxide melt calorimetry and recalculated by taking into account the contribution of the water molecules are in very good agreement with the data obtained for rhabdophane in this work. This result indicates that the enthalpy of formation of the rhabdophane can be simply deduced from the enthalpy of formation of the monazite by adding the contribution of 0.667 molecule of structural water.

These results could be used to estimate the thermodynamic properties of AnIIIPO₄ .0.667 H₂O (with AnIII =Am, Pu or Cm) by analogy with the lanthanides of close ionic radii. The rhabdophane structure can also incorporate AnIV by coupled substitution of LnIII by MII and AnIV. In this field, Nd_{0.8}Ca_{0.1}Th_{0.1}PO₄ .n H₂O were prepared by wet chemistry route and preliminary solubility data were determined, which showed that this phase is metastable in solution at 298 K, Th and Nd being released leading to the formation of Th₂(PO₄)₂(HPO₄). H₂O (TPHPH) [7] and NdPO₄.0.667 H₂O, respectively.

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National & International Waste Management Programs: Session Chairs Greg Lumpkin & Simone Richter / 2

Status of Used Nuclear Fuel and Radioactive Waste Long-term Management Programs in Canada

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In Canada, used CANDU (CANada Deuterium Uranium) nuclear fuel from the operation of 22 current and former nuclear power reactors, as well as several prototype and demonstration reactors, is stored in water-filled pools for about seven to ten years before it is transferred to licensed dry storage containers at the nuclear reactor sites. Although safe, this storage practice requires continuous institutional controls such as security, safeguards, monitoring and maintenance.

In November 2002, the Canadian Parliament passed the Nuclear Fuel Waste Act (NFWA). It required the major owners of used nuclear fuel in Canada to establish the Nuclear Waste Management Organization (NWMO). The initial phase of the mandate was to perform a three year study of suitable approaches for the safe, long-term management of used nuclear fuel, and to recommend a preferred approach to the Government of Canada. The study, which included extensive dialog across Canada with elected officials, specialists and the general public, was completed and the report with a recommendation was submitted to the Government in November 2005.

In June 2007, the Government of Canada approved the recommended Adaptive Phased Management (APM) approach. It is consistent with long-term management best practices adopted by other countries with nuclear power programs. The NWMO was given the mandate to implement APM.

APM is both a technical method and a management system. The end point of the technical method is the centralized containment and isolation of Canada's used fuel in a Deep Geological Repository

(DGR) in an area with suitable geology and an informed and willing host community. APM also involves the development of a transportation system to move the used fuel from the facilities where it is currently stored to the new site.

The management system involves realistic, manageable phases, each marked by explicit decision points. It allows for flexibility in the pace and manner of implementation, and fosters the sustained engagement of people and communities throughout its implementation.

APM is also designed to meet rigorous safety standards throughout all aspects of its design and implementation. As per this approach, the used fuel will be isolated and contained in a DGR located in a stable crystalline or sedimentary rock formation at a nominal depth of 500 m below ground surface in a willing and informed host community.

The DGR concept contains multiple engineered barriers to safely contain and isolate the used fuel over the long-term. The geosphere enclosing the repository provides a natural barrier to protect the waste form and EBS, and to mitigate repository releases at time frames relevant to repository safety.

This presentation focusses on the current status of the APM program but will also briefly discuss the status of other long-term radioactive waste management activities in Canada.

Ceramic and Glass-Ceramic Wasteforms / 34

Structural incorporation of Cm³⁺ and Pu³⁺ in phosphate ceramics with monazite structure.

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Phosphate ceramics with monazite structure are considered as potential waste forms for the conditioning of specific nuclear waste streams (e.g. minor actinides and plutonium) due to their outstanding properties. In this study, the incorporation of actinides (Cm³⁺ and Pu³⁺) into the monazite structure has been investigated combining X-ray diffraction (XRD) as well as X-ray absorption (XAS) and time-resolved laser fluorescence spectroscopy (TRLFS).

The results demonstrate the incorporation of the actinides on defined lanthanide lattice sites in the monazite ceramics. From TRLFS measurements of Cm-doped (50 ppm) (La,Gd)PO₄ solid solutions, a decrease of short-range order for the solid solution compositions was observed in comparison to the end-members. Additionally, XAS investigations on pure-phase La_{1-x}Pu_xPO₄ (x = 0.01 – 0.15) solid solutions verify the incorporation of plutonium in the +III oxidation state in the monazites. The results provide a refined structural insight into mechanisms of actinide incorporation into monazite ceramics and solid solution formation.

National & International Waste Management Programs: Session Chairs Greg Lumpkin & Simone Richter / 74

Synroc Waste Treatment Plant for fission-based Molybdenum-99 Production

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A new nuclear medicine facility is being built which will enable ANSTO to meet both domestic and global demand for Molybdenum-99. Co-located on the site will be an innovative waste treatment facility that deploys ANSTO's Synroc technologies; a waste form tailored for immobilizing all the waste elements and fission products and an integrated process line for converting intermediate level liquid waste into a solid compact via hot isostatic pressing (HIP), producing a durable waste form suitable for final disposal. This presentation will provide a high-level overview of the program, including various stages of development that are important in building this first of a kind nuclear waste treatment plant.

Ceramic and Glass-Ceramic Wastefoms / 94

Synthesis and Structure of Novel Oxide Compounds Containing RE = Y, Yb, Gd, Sm, and La and M = Zr, Ti, and Sn

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With the aim of creating novel ceramics with high radiation tolerance and ionic mobility, multiple samples with A-B-O stoichiometries ranging from 215 to 227 were synthesized and characterized by a combination of SEM, XRD, and TEM methods. Single-phase defect-fluorite-type compounds with A = Sm or Yb and B = Ti, Zr, and/or Sn are reported; whereas, pyrochlore compounds were also found as a second major RE-phase in numerous samples. We describe some interesting TEM data showing selected area diffraction patterns with complex modulations. The details of the modulation wave vectors observed in these samples are reported in some detail. The use of ionic radii to predict the structure of these ceramics appears to be substantially limited by Sn-O bonding characteristics and somewhat limited for zirconate compounds. Some single phase ceramics were irradiated with a low dose of helium and no significant radiation damage was observed by comparative GIXRD and nano-indentation.

Ceramic and Glass-Ceramic Wastefoms / 55

Synthesis and characterisation of rare Ce₃NbO₇ compounds for use as nuclear space batteries by neutron powder diffraction and X-ray absorption spectroscopy

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Ce₃NbO₇ weberite-type materials, an inactive analogue for Am₃NbO₇, have potential use in americium radioisotope thermoelectric generators to be developed by the European Space Agency for scientific missions beyond the orbit of Jupiter. Ceramics with greater than 97% purity were synthesised by thermal solid-state reaction and analytically characterised by X-ray diffraction, neutron diffraction, helium pycnometry, Raman spectroscopy and X-ray absorption spectroscopy. The Magnetochemistry of the system was calculated with the Weiss temperature and magnetic moment per unit volume derived, in good agreement against the theoretical values. Reitveld refinement of neutron data was employed to identify the crystal structure of the novel cerium niobate and determine the correct orthorhombic space grouping from either Cmcm (No.63) or Pnma (No.62) space groups. Ce₃NbO₇ refined well under both systems indicating possible pseudosymmetry. Cerium in the +III oxidation state was observed by X-ray absorption spectroscopy confirming the chemical speciation within the structure.

Summary:

Designing space batteries from UK reprocessed plutonium stockpiles.

Ceramic and Glass-Ceramic Wasteforms / 47

Synthesis and characterization of brannerite UTi₂O₆

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The share of nuclear energy in order to supply electricity continues to increase, which makes a growing need for more uranium resources. Currently uraninite (UO₂) and coffinite (USiO₄) are the two most abundant and exploited minerals. With the exhausting of these resources, other minerals are currently considered and are subject to multiple studies. Among them brannerite (UTi₂O₆) represents the third source of tetravalent uranium on Earth and could be considered for uranium recovery.¹ However, brannerite is known to be very difficult to dissolve quantitatively even in very aggressive conditions.² Consequently, the multiparametric study of dissolution of this phase has to be studied in details.

In this work, we first focused on the synthesis of pure brannerite by developing new methods of synthesis free from heavy grinding steps in contrary of the alkoxide/nitrate based routes.³ The impact of several parameters were studied such as heating temperature of synthesis, holding time and atmosphere. Therefore a new method was developed based on the preparation of hydroxides mixture then it direct heating under Ar or N₂ atmosphere for 72 hours at 1300°C.

Finally, dissolution experiments were carried out under different conditions in order to provide multiparametric expression of the normalized dissolution rate.

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Special topic on Tc and Re / 113

Tc reduction by bacteria from soda lake

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One of the problematic types of LRW are alkaline wastes generated in some types of spent nuclear fuel reprocessing. Environmental friendly biological techniques of LRW treatment are not widespread because of its extremely high salt contents and alkalinity usually not suitable for organisms. The aim of this work was to explore the use of microorganisms from extremely alkaline habitat to process liquid alkaline radioactive waste. This involved a search of promising microbial cultures from extremely alkaline lakes of the Kulunda steppe, which composition is close to alkaline wastes. The lake sediments with medium (44-85 g/L) and extremely high (300-400 g/L) salt content were selected for investigations; the microbial associations, which capable to reduce radionuclides were received. Experiments on reduction of technetium and uranyl acetate + pertechnetate were performed. The bacteria present in the sediments and sludge of soda lakes reduced pertechnetate ions in both experiments with high salinity (2.3 M - 84% technetium reduced) and in experiment with a lower salinity (0.8 M - 86% technetium reduced) wherein uranium had no competitive effect on the recovery of technetium - in experiments with 1) technetium and 2) with technetium + uranyl acetate reduced approx. 84% of pertechnetate. When using the mixed sludge from lower salt content lake the amount of reduced technetium was lower compared to the high salinity - 55-60%. This work was supported by RFBR grant 15-05-08919

Spent Fuel & Zircaloy Cladding / 26

The Corrosion of Copper Nuclear Waste Containers under Deep Geologic Disposal ConditionsF

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The corrosion of high level copper nuclear waste containers under permanent disposal conditions can occur via a number of processes which change in importance as the environment within a deep geologic repository evolves from warm and oxic to cool and anoxic. Under warm and oxic conditions the container could be exposed to gamma irradiated conditions which evolve from aerated vapour to fully saturated aqueous conditions. During this period the possibility of localized corrosion (e.g., pitting) must be considered. Over extended exposure periods when anoxic conditions prevail corrosion will be sustained by reaction with sulphide produced either by remote microbial activity or the dissolution of sulphides present in the clays compacted around the container. Studies to understand and quantify both these corrosion processes are underway. In this presentation these studies will be discussed and their use in the development of corrosion models described.

Ceramic and Glass-Ceramic Wasteforms / 95

The Fabrication and Characterisation of Novel Complex Ceramic Oxides (Ln₂TiO₅) For Polyphase Ceramic Waste-Forms.

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The structure types within the Ln₂TiO₅ (Ln = lanthanides) system have similarities with many of the proposed phases within the titanate ceramic waste-form Synroc. Certain compounds might also be suitable for inert matrix fuel applications. Previous studies have shown a relationship between lanthanide radii and polymorph type for the Ln₂TiO₅ system. By using multiple lanthanides the average lanthanide radius can be controlled and so the structure. In this study four different combinations of lanthanide titanates were fabricated with the aim of producing single phase, novel design materials with cubic symmetry. Whilst it is possible to fabricate homogeneous materials with the general Ln₂TiO₅ stoichiometry using multiple lanthanides there appears to be limited solubility. The ratio of the lanthanides influences the final structure type and also the solubility. The structure type influences the heavy ion irradiation response of these compounds and we report on TEM in-situ experimental results related to this.

National & International Waste Management Programs: Session Chairs Greg Lumpkin & Simone Richter / 32

The Need for Integrating the Back End of the Nuclear Fuel Cycle

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The recognition that the endpoint of spent fuel management practices will be deep geologic disposal of radioactive wastes leads to questions about how alternative options for spent nuclear fuel (SNF) management might affect performance of a geologic repository. Do some options for SNF management simplify the siting and design of a geologic repository? Do some geologic disposal concepts

favor specific SNF management practices? Do some SNF management options favor specific geologic disposal concepts? Are some waste forms inherently preferable than others for geologic disposal? Given the historical difficulty in many nations associated with siting and licensing geologic repositories for permanent disposal of SNF and high-level radioactive waste (HLW), are there activities that the spent fuel management community could or should undertake today to facilitate future disposal operations?

Long-term repository safety is, in general, independent of specific treatments of SNF or HLW other than its packaging. However, multiple aspects of the form in which the waste will be disposed are relevant to repository design and performance, including waste volume, radionuclide content, thermal power, waste package size, and waste form and package lifetime in a range of geologic environments. Consideration of how these factors impact repository performance suggests that choices made now regarding SNF management may affect future flexibility in repository siting and design.

In the U.S., due to the absence of a final disposal site (since the suspension of the Yucca Mountain Project in 2009), nuclear utilities have been storing SNF at their nuclear reactor sites using dual-purpose casks. These casks are large and, depending on the burn-up of the SNF contained therein, can also be very hot. This current practice can have significant implications for transportation and, ultimately, disposal. This paper shall discuss these implications based on the current U.S. practice and will suggest ways in which these implications can be addressed.

The principal message that we intend to convey is the need for careful planning while implementing upfront and temporary SNF management practices because of their potential costly implications to transportation and disposal. An integrated view of the entire back end of the nuclear fuel cycle (interim storage, transportation, and disposal) upfront during the planning phases is paramount to develop and implement an effective SNF management program.

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Ceramic and Glass-Ceramic Wasteforms / 29

The development of zirconolite glass-ceramics for the immobilisation of Pu-residues in the UK.

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The UK has over 100 tonnes of separated PuO₂ stored at the Sellafield site. The UK policy for managing this plutonium stockpile is to reuse this material as MOx fuel. However, not all of the material is suitable for reuse and a proportion has been classified as higher activity waste. These plutonium wastes, and any material which is not ultimately reused, will require immobilization, in a passively safe wasteform, for long-term storage and eventual geological disposal. One proposed treatment plan is hot isostatic pressing of the plutonium waste / stockpile material, with suitable precursors, to form a glass-ceramic or full ceramic wasteform, inside stainless steel canisters. Glass-ceramic materials are proposed for the low purity and highly variable wastes, in which the glass phase provides wasteform flexibility to accommodate impurities and variations in the waste feed composition. The plutonium partitions into the more durable ceramic phase, zirconolite (CaZrTi₂O₇). Zirconolite has excellent wasteform properties including durability and radiation tolerance, and readily accepts actinides and rare earths into its crystal structure.

In this work, the formation of zirconolite is shown to depend sensitively on glass fraction and composition, such that an Al rich glass promotes a higher yield of zirconolite. The thermodynamic activity

of Si in the system drives the crystalline phase assemblage, by determining whether it is consumed in the amorphous glass phase or undesired accessory crystalline phases, such as sphene (CaTiSiO₅) and zircon (ZrSiO₄). The design of an optimized glass-ceramic formulation is demonstrated, to maximize the yield of zirconolite and minimise the yield of accessory phases. The partitioning of CeO₂, within the glass-ceramic wasteform, as a PuO₂ surrogate, was studied using various charge compensation mechanisms, under an imposed Fe/FeO and Ni/NiO buffer. Analysis by SEM/EDX, XRD, and Ce L3 edge XANES, demonstrated reduction of Ce(IV) to Ce(III) to favour incorporation of Ce within a perovskite accessory phase and the glass matrix. Ce partitioning in the zirconolite phase was maximized when retained as Ce(IV). These results demonstrate a feasible wasteform formulation for disposition of UK plutonium wastes and stockpile material.

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Thermodynamic behavior of monazite-type La_{1-x}Ln_xPO₄ (Ln = Pr, Nd, Eu Gd) solid solutions

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Monazite-type orthophosphates (monoclinic LnPO₄; Ln = La – Gd) are promising candidates as potential waste forms for the immobilization of specific nuclear waste streams, such as separated Pu from civilian or military sources unsuitable for further use, or separated minor actinides due to their specific physicochemical properties.

The thermochemical behavior of single phase La_{1-x}Ln_xPO₄ (Ln = Pr, Nd, Eu, Gd) solid solutions has been investigated by high temperature oxide melt solution calorimetry. The experimental enthalpy of mixing, as well as complementary atomistic modelling methods, demonstrate the thermodynamic stability of the solid solutions. Margules interaction parameters were calculated applying both approaches. The obtained values are in good agreement, emphasizing the progress of modern numerical methods. These results are an essential basis for thermodynamic models for the assessment of the long term stability of monazite solid solution ceramics as matrices for the safe immobilization of radionuclides in a geological repository.

Ceramic and Glass-Ceramic Wasteforms / 48

Thorium incorporation in phosphates matrices: the case of xenotime

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The management and the conditioning of radwaste represents a major challenge in the nuclear industry. Therefore a variety of host matrices have been studied, including several phosphate based ceramics.¹ They represent promising candidates for the specific conditioning of actinides (III, IV) owing to their easy way of preparation and high chemical durability.²

The incorporation of actinides in such phases has been extensively studied through solid-state routes. Thus, it often requires repetitive grinding steps and re-heating to avoid the formation of heterogeneous compounds.³ For such reasons, the synthesis of target compounds in aqueous solution were developed to prepare pure and homogenous phases.

In this study, a particular attention was paid to the incorporation of tetravalent actinides (Th⁴⁺, U⁴⁺) in the zircon structure type through the coupled mixed (An(IV) + SiO₄ / Ln(III) + PO₄) substitution. In this frame, solid solutions of Er-xThx(PO₄)_{1-x}(SiO₄)_x were obtained in application of the method developed to prepare pure coffinite (USiO₄), i.e. hydrothermal conditions at 250°C for 7 days.⁴ The analysis of the PXRD data showed the formation of single phases. The structure crystallizes in the zircon-type structure (I41/amd group, tetragonal system) as observed for the end-members ThSiO₄ and ErPO₄. From Rietveld refinements, the formation of a complete solid solution was confirmed in agreement with the Vegard's law. A thorough analysis was also carried out by Raman spectroscopy and EXAFS at the Er and Th edges and showed an exciting structural evolution.⁵

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Safeguards, Decontamination & Decommissioning / 9

Towards a '3S toolbox' for providing safety, security and safeguards at geological disposal of high-level radioactive waste and spent fuel

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Safety, security and safeguards aspects regarding the geological disposal of high-level radioactive waste and spent fuel are usually addressed separately. Thus, apparently different methods and techniques exist for each of the three "S's". However, by identifying both synergies in overlapping methods or techniques and differences in the requirements with respect to safety, security and safeguards, advantage of inherent synergies and conflicting requirements can be taken at the same time.

[1]

The paper identifies methods and technologies (a '3S toolbox') that would be best suited for the holistic consideration of safety, security and safeguards provisions. Such a toolbox could include, first, measurement techniques for spent fuel verification already at the encapsulation plant. Second, a set of measures based on remote monitoring, nuclear measurements, containment and surveillance for application at the encapsulation plant, the geological repository and transfers between both. Third, measures for detecting unauthorized activities, e.g. the analysis of open source information including satellite imagery, geophysical monitoring and environmental sampling.

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Glass Wasteforms / 25

Towards understanding the dissolution of vitrified nuclear waste in a cementitious geological disposal facility

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Under the generic scenario envisaged for the geological disposal of vitrified UK high- and intermediate-level waste glass (HLW and ILW, respectively), high pH environments, formed through degradation of the cementitious engineered barrier, are expected to dominate the ground water chemistry thousands of years into the future. We highlight the main findings of a number of recent and ongoing studies that aim to evaluate and understand how cementitious groundwater compositions influence the dissolution rate of vitrified wasteforms, including: simulant UK HLW; the International Simple Glass; natural basaltic glass and glasses designed for ILW. Briefly, we discuss results detailing the mechanisms of alteration layer formation in Ca-rich systems; we describe the influence of idealised cement leachate solutions on ion-exchange processes during the initial stages of dissolution; and we review the application of single-pass flow-through methods to derive the fundamental parameters necessary to model the dissolution kinetics of vitrified waste.

Ceramic and Glass-Ceramic Wasteforms / 110

U-rich ceramics for Spent Fuel or Acidic 99Mo Production ILW

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Spent fuel has long been unofficially classified as HLW which is cooled for a few years to allow the dissipation of short-lived fission products and then is to be contained in thick-walled Cu or carbon steel containers for deep repository disposal where it is argued that the containers will perform immobilisation for ~105 yr. However immobilisation assumes highly reducing conditions in which UO₂ is essentially unreactive and even water-soluble fission products will be contained. The only published engineered waste form for spent UO₂ fuel is synroc-F in which the U concentration is nearly 50 wt.% and the fission products are incorporated in resistate titanate mineral phases. We have tried to extend this concept by hot isostatic pressing glass-ceramics in which synroc-F constitutes the ceramic phase and the glass furnishes a second phase for fission product immobilisation and increases the general reactivity. We have also used the same approach for acidic 99Mo production ILW.

Ceramic and Glass-Ceramic Wasteforms / 76**Unique capabilities and methods for analysing nuclear waste form materials using ANSTO's landmark infrastructure****Author(s):** Gabriel Murphy¹**Co-author(s):** Brendan Kennedy²; Helen Brand³; Helen Maynard-Casely⁴; Maxim Avdeev⁴; Zhaoming Zhang⁵¹ *University of Sydney*² *The University of Sydney*³ *Australian Synchrotron.*⁴ *Australian Nuclear Science and Technology Organisation*⁵ *ANSTO***Corresponding Author(s):** gmur5714@uni.sydney.edu.au

In situ investigations of nuclear waste form related materials under extreme conditions are highly desirable for understanding and optimising applications of these materials, however they are often exceedingly challenging from a safety and radiological perspective. As a part of our investigations into actinide materials, we have developed a number of novel experimental methodologies which utilize ANSTO's landmark research infrastructure, the Opal nuclear reactor and Australian Synchrotron, towards examining the behaviour of actinide materials related to nuclear waste forms under extreme conditions. This presentation will highlight some of our successes in advancing the study of actinide and nuclear materials including

- High temperature in situ redox chemistry of uranium using X-ray absorption spectroscopy.
- The behaviour of uranium oxides under high pressure (>6 GPa) using neutron diffraction.
- High temperature studies of thorium oxides using synchrotron X-ray and neutron diffraction.
- Chemistry of uranium oxides under high purity hydrogen gas reduction and high temperature conditions (1000 °C) using synchrotron X-ray diffraction.

Special topic on Tc and Re / 114**Unusual redox neighborhood in technetium compounds****Author(s):** Konstantin German¹**Co-author(s):** Alexander FEDOSSEEV²; Andrey AFANASIEV¹; Mikhail GRIGORIEV³¹ *A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences*² *(A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of*³ *(A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences***Corresponding Author(s):** guerman_k@mail.ru

Technetium has a great number of oxidation states (usually we say 9 but in fact much more) and is evidently one of the elements with the most complicated chemistry. This is due its position in the center of 4d elements row with 7 electrons available for chemical bonding. One of the very special options complicating technetium chemistry is its ability to cluster formation and especially the possibility for Tc cluster to be reduced by consecutive addition of electrons one by one. So the oxidation states of Tc in hydrochloric acid could be 4+ (in K₂TcCl₆), 3+ (in [Bu₄N]₂Tc₂Cl₈), 2.5+ (in K₃Tc₂Cl₈), 2+ (in K₂Tc₂Cl₆), 11/6+ (in [Me₄N]₃Tc₆Cl₁₄ and 10/6+ (in [Me₄N]₂Tc₆Cl₁₂). We could imagine the number of

hydroxides that could be formed starting from these compounds. Another option is the presence of Tc atoms in different oxidation states within the same compound (p.e. Tc_2Ac_4 where Tc^{3+} and Tc^{7+} coexist in the one compound. New example is the red pertechnic acid. According to new synthesis and X ray structure study it contains 4 TcO_6 octahedra with Tc^{6+} , that is usually considered extremely unstable and 16 $\text{Tc}(\text{VII})$ tetrahedra arranged in a joint compound $[\text{TcVI}_4\text{TcVII}_{16}]\cdot 16\text{H}_2\text{O}$: $a = 11.1743(6)$, $b = 12.8839(6)$, $c = 14.0661(6)$ Å, $\alpha = 71.128(2)$, $\beta = 69.015(2)$, $\gamma = 74.340(2)^\circ$, $P-1$, $Z = 1$. Of next extreme interest is new $\text{Pu}(\text{III})(\text{DMSO})_6[\text{TcO}_4]_3$ compound where reducing and oxidizing parts coexist.

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Volume reduction of uranium catalyst waste used for production of acrylonitrile

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A large volume of problematic radioactive waste of spent uranium catalyst, which was used to produce acrylonitrile for fabrication of synthetic fibers, was generated by a private company in Korea until 2004. This has been stored onsite awaiting a management strategy that is to minimize the volume/cost requirements for the final disposal. This work will introduce a process to greatly reduce the waste volume to be disposed. The process consists of several steps including the selective dissolution of the SiO_2 support, precipitation of dissolved silicon ions including purification, treatment of uranium-containing effluent formed during the process before released, and solidification of final solid uranium waste to be disposed, etc. Also various chemical characteristics of uranium, and other elements relevant to the process will be evaluated and discussed.