1. Introduction

TRANSCEND

Ion-exchange is a facile, cost-effective and consistent method to successfully remove radioactive Cs⁺ and Sr²⁺ cations from liquid nuclear waste. What must be considered is the performance of ion exchange materials in the presence of many competing ions and the pH of the waste solution. We are focused on researching new methods and materials that can be used to improve the effectiveness of the decontamination process.

Here, we present our work on how tin umbites $(K_2SnSi_3O_9 \cdot H_2O)$ can be doped to enhance ion exchange properties.

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- Influence of high pH
- Simulant solutions

New materials and methods for decontamination of effluent

A. Nearchou, T-Y. Chen and J. A. Hriljac Correspondence: A.Nearchou@bham.ac.uk School of Chemistry, University of Birmingham, Edgbaston, B15 2TT

2) Improved Material Properties

Structural defects – doping

2. Methods

Our research into ion-exchange materials follows the five primary streams shown in the diagram on the right. This includes study into both the synthesis of these materials in addition to assessments of their selectivity to exchange with Cs⁺ and Sr²⁺ ions.

3. Results and Discussion

Figure 1 shows the umbite structure viewed down the *c* and *a* axes. The framework consists of oxygen bridged $[SnO_6]^{8-}$ octahedra and $[SiO_4]^{4-}$ tetrahedra, producing 6-ring and 8-ring channels parallel to the *c* axis that are connected by 7-ring windows. As the Sn is six-coordinate the network retains a negative charge which is counter balanced by K⁺ cations which are present in the channels. It is these K⁺ cations that can potentially be exchanged for Cs⁺ and Sr²⁺.



- Mesoporosity
- Morphology
- 3) Alternative Remediation Processes
 - Magnetisation

5) Column Experiments

- Exchange under solution flow
- Ion breakthrough
- Bulk and simulant solutions

Table 1. A summary of the elemental substitutions researched to dope the tin umbite. Substitutions made to the tetrahedral T-sites and octahedral O-sites. The resulting materials can be described by one of the two molecular formulas below.

$$K_2Sn(Si,Ge)_3O_9 \cdot H_2O$$
 or $K_{2-x}Sn_{1-x}M^V_xSi_3O_9 \cdot H_2O$

		Substitution
25Ge	T-site:	25% Ge ⁴⁺ for Si ⁴⁺
25Nb	O-site:	25% Nb ⁵⁺ for Sn ⁴⁺
25Sb	O-site:	25% Sb ⁵⁺ for Sn ⁴⁺
25(Y, Nb)	O-site:	12.5% Y ³⁺ and 12.5% Nb ⁵⁺ for Sn ⁴⁺
		$12 E_0 / C_0^{3+}$ and $12 E_0 / N = 5 + f_{0,0} C_0^{4+}$

Figure 1. The umbite structure viewed down the *c* axis (left) and down the *a* axis (right). Tetrahedra are shown in blue and octahedra in grey. Included are the K⁺ cation sites which are shown in green.



Figure 2. Powder X-ray diffraction pattern of the Sb-doped Sn Umbite. Taken on a Bruker D8 Diffractometer.

Table 1 summarises the doped tin umbites prepared, and figure 3 the degree of Cs⁺ and Sr²⁺ uptake from static batch ion exchange assessments. Doping the O-sites is shown to improve the ion uptake. Introducing dopants with a higher oxidation state produces a deficiency of K⁺ cations. We suspect that this deficiency in the umbite's channels enhances ion mobility throughout the structure and hence the ion exchange capability. This is supported by the observation that the 25Nb and 25Sb samples, which have the highest average O-site oxidation state, express the greatest uptake of both Cs⁺ and Sr²⁺.



Figure 3. Static batch ion exchange tests. Normalised molar ratio of Cs/Sr uptake to octahedral elements M = Sn⁴⁺, Nb⁵⁺, Sb⁵⁺, Y³⁺, Sc³⁺. Conducted by T-Y. Chen

4. Conclusions and Future Work

Doped tin umbites are promising materials that show enhanced uptake of Cs⁺ and Sr²⁺ cations. In order to fully assess the utility of these materials in industry we need to study their selective ion exchange capabilities in the presence of competing ions present in liquid nuclear waste. We can then go on to test these materials using simulant solutions and within packed columns. Finally, we intend to investigate whether magnetic umbites can be prepared so simpler remediation processes can be implemented.

5. Acknowledgements

We thank the EPSRC for funding under the TRANSCEND project. We also thank Dan Parsons, Ryan George and James Reed for their contribution to this research.



Transformative Science and Engineering for Nuclear Decommissioning





Background

TRANSC

At the Sellafield site, the decommissioning of accumulated waste is estimated to last 100 years, costing 10's of billions of pounds in the process.¹ It is therefore critical that the processing of this waste is efficient, ensuring both environmental risk and cost are minimized. One of the main aims in remediation of this waste is removal of ¹³⁷Cs from effluent, which poses massive risk to human health due to its high solubility and half life of 30 years. Due to cost effectiveness, simplicity and selectivity, ion exchange materials, such as zeolites, are often employed, such as clinoptilolite in SIXEP plant at the Sellafield site. The anionic framework of interconnected SiO₄ and AlO₄ tetrahedra forms uniform channels and cavities, which provides an ideal site to trap radioactive caesium cations. These structures also have a very high porosity that enhances exchange rates and high resistance to radiation, further aiding their appeal.^{1,2}

Natural Zeolites for Caesium Ion-Exchange

Treatments to Improve Natural Materials

As different zeolites are renowned for reacting differently to the same solution, being highly sensitive to

Scoping Studies of New Ion-Exchange Materials

James Reed,^{a*} Joseph Hriljac^b

^{a,b}School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom JLR552@student.bham.ac.uk, J.A.Hriljac@bham.ac.uk

Whilst synthetic zeolites have been shown to display higher selectivities for caesium, the relatively high cost, synthesis time and availability lessens their appeal in radionuclide removal, as often vast quantities of material are needed in a short space of time. Therefore, many treatment plants favour the use of naturally occurring zeolites. For example clinoptilolite at used at the Sellafield site and chabazite was used at Three Mile Island and at.^{1,3} On the other hand, natural materials are rarely found pure, which reduces their ion exchange efficiency and have slightly different compositions due to formation under different geological conditions. This means that no two natural zeolites are ever identical, meaning even isostructural zeolites must be assessed if sourced from a different location.¹

Clinoptilolite

Clinoptilolite is one of the worlds most abundant natural zeolites and readily exchanges its sodium cations for caesium.¹ Clinoptilolite has ideal formula of Na₆Al₆Si₃₀O₇₂ • 24H₂O, with channels of similar radius to a hydrated caesium cation, partially explaining its high selectivity.¹ However, its application is limited as samples from other sources exhibit lessened exchange capabilities. Clinoptilolite sourced from the Mud Hills region of California has been shown to be excellent and is used extensively at Sellafield.¹ Finding out what makes this mud hills clinoptilolite so effective in radionuclide removal is one aim of this project, as this will help target other potential materials.

Other natural zeolites

Two natural zeolite structures that have received attention within the remit of caesium removal are chabazite (figure 1) and mordenite.^{4,5} Both are abundant and have demonstrated good levels of caesium uptake. Mordenite has larger pores than chabazite, which has a similar pore size to clinoptilolite but with a higher Al/Si ratio.^{4,5}



the conditions, which can result in contrasting ion exchange capabilities. In light of this, it is difficult to predict the outcome of treatments and each source of zeolite much be examined separately.

The following properties are trying to be introduced, at varied temperatures and pressures, to different natural zeolite sources worldwide. The ability of the modified zeolites to remove caesium from effluent will then be assessed.

Conversion to homoionic form

Lots of zeolites contain different species of exchangeable cations. If these can be exchanged for a cation more easily released then this could aid both the exchange capacity and rate. This could be achieved by simple ion exchange experiments, under forcing conditions if necessary.⁶

Desilication

Removing some silicon from the framework results in a higher Al/Si ratio which naturally increases the cation capacity, in order to maintain charge neutrality. This can be achieved with treatment of base, although too much could result in breakdown of framework.⁷

Introduction of mesoporosity

Bigger pores in the zeolites can lead to better transport within the zeolites, allowing faster diffusion times and better access to innermost cations and micropores. This can be achieved by desilication/dealumination by base/ acid treatment respectively. Introduction of mesoporosity does however decrease micropore volume and crystallinity. The faster diffusion will increase the decontamination factor of the plant.⁷





Current Solution at Sellafield

The site ion exchange effluent plant (SIXEP) removes radioactive ¹³⁷Cs and ⁹⁰Sr from effluent at the Sellafield site. A simplified diagram (figure 2) displays each stage of the SIXEP plant:



Figue 2: Schematic outlining the SIXEP plant at the Sellafield site. Diagram taken directly from: A. Dyer, J. Hriljac, N. Evans, I. Stokes, P. Rand, S. Kellet, R. Harjula, T. Moller, Z. Maher, R. Heatlie-Branson, J. Austin, S. Williamson-Owens, M. Higgins-Bos, K. Smith, L. O'Brien, N. Smith, N. Bryan, J. Radioanal. Nucl. Chem., **2018**, *318*, 2473-2491.

Settling tanks remove large particles from the feeds, before the sand bed remove suspended solids by filtration. The carbonation tower adjusts the pH to between 7 and 11 in order to protect the upcoming clinoptilolite beds, which can degrade in acidic conditions. Finally, two ion exchange columns packed with Mud Hills clinoptilolite operate in series, reducing the caesium and strontium content to allow for environmental release.¹



These treatments will provide the initial scope of my project, with likely other areas of scope focusing on similar treatments under more cost effective microwave conditions. Successful treatments will be explored further so we can gain understanding of what is happening exactly and whether this will be effective at treating Mud Hills clinoptilolite or other zeollite sources worldwide.

This research is supported by the National Nuclear Laboratory and Sellafield Ltd.

This plant treats 100's of m³ effluent per day, selectively removing 1 M Sr²⁺ and 20 M Cs⁺ over 7.5×10^5 M Na⁺, 6.5×10^3 M Mg²⁺ and 5×10^3 Ca²⁺. Despite these numbers being impressive, there is only so much Mud Hills clinoptilolite and other sources have not shown the same level of selectivity. Alternative materials with better properties would allow for effluent to be processed more efficiently and until all material has been treated. A higher capacity of material would also allow for the columns to be replaced less frequently and hence allowing for more material to be processed.¹



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In-situ synchrotron X-ray diffraction studies of ion exchange in zeolites

Clinoptilolite

H. A. Parish¹, G. Cutts, C. C. Tang and J. A. Hriljac

¹University of Birmingham - hap431@student.bham.ac.uk

Introduction

Zeolites and related inorganic materials with open framework structures are often used in the clean up of radionuclides from nuclear waste streams. These materials have high stability towards heat and radiation and can also be highly selective towards radioactive cations, even in the presence of other competing ions. ¹³⁷Cs is a common and particularly problematic radionuclide; it is water soluble and harmful to humans. This work will focus on the analysis of zeolite structures in order to determine their ability to act as efficient ion exchangers for radioactive Cs.

Structure and Properties of Zeolites

Zeolites are a class of porous aluminosilicates with the general formula Candidate for Waste Clean-Up

 $M_{x/n}[Al_xSi_yO_{2(x+y)}]$.pH₂O, where M is a cation such as Na, K or Ca and n is the charge on the cation. Their structures are made up of SiO_4 and AlO_4 tetrahedra that are linked by corner sharing of oxygen atoms to form a 3D network of rings and cages. The tetrahedra give the structure an excess negative charge, which is accounted for by cations occupying the pores. Pores in the framework also contain water molecules.



In-Situ Diffraction Cell The flow cell designed by Dr Geoff Cutts for in-situ ion exchange.



Clinoptilolite is a naturally occurring zeolite with ideal formula the $(Na,K,Ca)_6Al_6Si_{30}O_{72}\cdot 24(H_2O)$. The selectivity of clinoptilolite towards Cs is well documented in the literature and it was used during the clean-up after the Chernobyl incident. Furthermore, clinoptilolite from Mud Hills, California, has been used in the SIXEP effluent treatment plant at Sellafield for the past 30 years to remove Cs and Sr from alkaline liquid effluents². Its selectivity even in the presence of competing cations, such as sodium, makes clinoptilolite an ideal candidate for this purpose.

Strong

In-Situ Cs-Exchange Experiments In-situ ion exchange experiments were

*Figure 1 – the crystal structure of clinoptilolite along the c-axis*¹









[2] A. Dyer, J. Hriljac, N. Evans, I. Stokes, P. Rand, S. Kellet, R. Harjula, T. Moller, Z. Maher, R. Heatlie-Branson, J. Austin, S. Williamson-Owens, M.

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Figure 3 (above) – graph showing selected refined cation occupancies for the Naexchanged Mud Hills sample

Figure 4 (left) – crystal structure of Na-clinoptilolite. The colours of the cations correspond to the graph. The results indicate that Cs is exchanged into the 8-ring initially and the occupancies of the cations in the 10-ring change very little.

undertaken on beamline 111 at Diamond Light Source. Mud Hills clinoptilolite samples, Na-exchanged and untreated, were loaded into a capillary and 0.5 mM CsNO₃ was flown through. XRD patterns were recorded over the course of the exchange. Selected results are presented to the left; the graphs in figure 2 compare the change in *b*-parameter and unit cell volume over time for each sample. Figure 3 shows the change in cation occupancies over the the exchange for the of Nacourse exchanged sample, and the crystal structure in figure 4 highlights the positions of these fitting Rietveld cations. Pawley and refinement were used to elucidate these values – all calculations were performed in the program TOPAS³.



Figure 2 – graphs comparing results of sequential Pawley fitting the Na-exchanged and untreated Mud Hills datasets

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Future Work

Other zeolite structure types, for example chabazite, also have well documented selectivity towards Cs. In future it would be beneficial to repeat the in-situ flow experiments with chabazite to see how it compares to clinoptilolite.

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Particle-laden flow characterisation and prediction

L. F. Mortimer & M. Fairweather

School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT l.f.mortimer@leeds.ac.uk, m.fairweather@leeds.ac.uk

1. Introduction

- · Particle-laden turbulent flows occur commonly in both natural and industrial environments.
- Decontamination of legacy ponds and silos is of great importance and stands as a matter of increasing urgency throughout the nuclear industry. In facilities around the UK, waste suspension flows transport legacy material from historic ponds to other interim locations where they are safely stored.
- The work presented here uses Lagrangian particle tracking (LPT), coupled to a spectral element method based direct numerical simulation (DNS) solver to determine the effect of particle diameter and turbulence structures on important flow characteristics of interacting particle-laden turbulent waste transport flows.

2. Direct numerical simulation

- **DNS** fully resolves all relevant space and timescales associated with the flow.
- This means we are able to take into account the effect that eddies of all sizes have on the particulate phase.
- This is important since **collisions** tend to occur more



- We also introduce modelling of polymer-laden flows, which can modify both the fluid and solid behaviour. Phenomena such as turbulent drag reduction and **flocculation** will be studied computationally.
- 3. Deterministic energy-based particle-particle collisions



- Standard four-way coupled LPT techniques are implemented and extended to model post-collision agglomeration events.
- Upon collision, particles either bounce or stick, depending on whether or not their resultant kinetic energy is enough to overcome the van der Waals attraction.
- Particles which agglomerate form a larger spherical particle with equivalent volume to the two primary particles.
- **Right:** Instantaneous realisation of four-way coupled turbulent particle flow laden with 300,000 particles.

 $\left\| \boldsymbol{u}^{*2}_{P,r} - \frac{\left(1 - e_n^{*2}\right) \left(\boldsymbol{u}^{*}_{P,r} \cdot \widehat{\boldsymbol{n}}\right)^{2}}{\left| \left(\boldsymbol{u}^{*}_{P,r} \cdot \widehat{\boldsymbol{n}}\right) \right|} \leq \frac{H^{*}}{6\delta_0^{*2}} \left| \frac{6\left(1 - e_n^{*2}\right)}{\pi^2 \rho_P^{*} \overline{\sigma}^{*}} \left(\frac{d_{P,1}^{*3} + d_{P,2}^{*3}}{d_{P,2}^{*2} \left(d_{P,1}^{*} + d_{P,2}^{*}\right)} \right) \right|^2 \right\|$

4. Under what conditions to particles agglomerate?



5. Simulating polymer-laden flows

- Polymers are simulated using the finitely extensible nonlinear elastic dumbbell model, representing the polymer as a sequence of beads connected by nonlinear springs.
- Preliminary results show good agreement for important observables such as equilibrium stretch and radius of gyration



- Particle-particle collisions are most frequent close to the wall, where turbulence is strongest. The deviations from chaotic fluid streamlines encourage particles to collide. · Agglomeration is greatest in the bulk flow, away from the walls. This is unexpected, since despite collisions being enhanced close to the wall, particles are undergoing fewer agglomeration events in this region.
- The agglomeration rate (or mean chance for agglomeration given two particles collide at a certain wall distance) correlates strongly with distance from the wall. • This implies that agglomeration is dominated by local favourable flow conditions. • Agglomeration is also favoured by smaller particles since the van der Waals attraction is stronger.





Instantaneous realisation of ensemble of polymer chains (left) and force balance schematic for polymer i (right).

6. Conclusions & further work

- DNS-LPT used to study particle-laden flows and develop understanding behind conditions for aggregation. Effect of density ratio should also be studied to provide insight into inertial effect.
- Polymer-laden turbulent fluids will be simulated to further explore behavioural modification through injection of polymer additives.









Simulation of complex particle flows

Bisrat Wolde

School of Chemical and Process Engineering, University of Leeds

pmbw@leeds.ac.uk

Introduction:

Nuclear energy plays an important role in providing reliable, low pollutant gas emissions such as carbon dioxide (CO_2) and affordable electricity. There are drawbacks on delivering this affordable energy future - the waste product of most nuclear energies are radioactive. Safely disposing these radioactive contaminated materials require expertise and it's an expensive process. Implementing scientifically robust, innovative approach to decommissioning and waste management is essential for legacy wastes as well as future nuclear sites.

Motivation and Objective:

The joined-up approach to nuclear energy research and development across academia, industry and government would benefit the UK economy in a number of ways. The research will also establish UK industry to be a leading global competitors in end to end radioactive waste management and decommissioning, i.e. processing and waste treatment to reduce active radiations, packaging in specially engineered containers for safe transportation, storage for interim place to store certain waste materials and final disposal site where the nuclear waste remain permanently. Developing and facilitating safer, cost efficient waste management and decommissioning is the focus strategy of the research.

Understanding and modelling pond and silo sludge behaviour is essential to the management of radioactive wastes. "In the decontamination of legacy ponds and silos, the provision of a predictive capability to understand how sludge will behave is crucial to successful retrieval and completion of post operation clean out (POCO) operations. This project will establish a predictive tools that support retrieval technology selection: particle-laden flow characterisation and prediction is using first principles of mathematical modelling and complementary experimental work to establish the impact of behavioural modification techniques, implemented using additives, on such flows, enabling improved flow, mixing and separation of wastes during retrieval and POCO activities." Behavioural modification effects in suspension waste pipe flows will be simulated.



Governing Equations:

Cor

A pressure driven incompressible flow in a long straight pipe of circular cross section with internal diameter D – time dependent governing equation of Navier-Stokes can be derived as follows:

iservation of Mass:
$$\frac{d\rho}{dt} + \rho(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}) = \frac{d\rho}{dt} + \rho(\nabla, u) = 0$$

While the density ρ is constant, $\frac{d\rho}{dt} = 0$, for incompressible flow the continuity equation can be simplified to:

$$\rho(V, u) = 0$$

Conservation of Momentum: $\rho \frac{\partial u}{\partial t} = ma = f = f_{body} + f_{surface}$

The Navier Stokes equation can be expressed as follows for constant density:

 $\frac{\partial u}{\partial t}$ + ($u.\nabla$) $u = -\nabla p + \frac{1}{Re_b}\nabla^2 u$, where $Re_b = u_b^{-D}/\nu$, Re_b - the bulk Reynolds number, u_b - the bulk mean velocity, D - pipe diameter and ν - kinematic viscosity.

The velocity vector of u has a Cartesian co-ordinates points of x, y, z with velocity components u, v and w respectively. These unknown components are function of the independent variables x, y, z and t.

For velocity component *u*, the Navier Stokes equation can be expressed as follows:

$$\boldsymbol{\rho}\left\{\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z}\right\} = -\frac{\partial p}{\partial x} + \mu\left\{\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right\}$$

A solution for the unknow p, u, v and w is sought using continuity equation, $\nabla \cdot u = 0$ and boundary conditions. The general equation for bulk Reynolds number Navier Stokes is: $\nabla \cdot u = 0$

$$\frac{\partial u}{\partial t} + (u.\nabla)\boldsymbol{u} = -\nabla p + \frac{1}{Re_b} \nabla^2 \mathbf{u}$$



I – Stream wise pressure, II – Stream wise velocity profile and III – the cross sectional view of a quarter of the computational mesh at Re = 361.

Methods:

To solve the DNS code numerically a computational fluid dynamics solver Nek5000 has been used. This solver is based on spectral element method (SEM) – that is a high order weighted residual technique. Nek5000 is favourable for its high spectral accuracy, very little numerical dispersion and dissipations and parallelisation. The non dimensionalised form of the Navier Stokes equation in Nek5000 is:

$$\begin{aligned} \mathbf{x}^* &= \frac{x}{L}, u^* = \frac{u}{u}, t^* = \frac{t}{L_{/u}}, p^* = \frac{p}{\rho u^2} \text{ for high velocity flow or } p^* = \frac{pL}{\mu u} \text{ for Stokes flow.} \\ \frac{\partial u^*}{\partial t^*} + (u^* \cdot \nabla) u^* &= -\nabla p^* + \frac{1}{Re} \nabla \cdot \tau^*, \text{ where } \tau^* = \nabla u^* + \nabla u^*^T \end{aligned}$$

The high level computational algorithm is:

- Split the controlled volume into small cells(meshing)
- · Numerically integrate the equations throughout the cells
- Solve numerical equations for u, v, w and p in combination with boundary conditions
- · Save the solutions for post processing

Results:

Below result achieved by running the simulation for few days. The result has not been fully developed yet. The solution analysed to check the progress of the computation. Once its fully developed the result will be validated against previous DNS literatures.



The computational mesh of the pipe and pseudo-colour visualisation of the instantaneous axial velocity. (a) – The computational mesh with Gauss–Lobatto–Legendre quadrature points (N = 7) at Shear Reynolds number $Re_r = 361$, (b) – the instantaneous stream wise velocity, (c) – the x –direction which are normalized by bulk

velocity $U_{\rm b}$ of simulations at $Re_{\rm T}$ = 361 and (d) – the velocity direction in the flow

Planned works:

- Developing optimised single phase circular pipe of radius R, axial length 25R in the turbulent flow at shear Reynolds number at Re_{τ} =361 using a direct numerical simulation (DNS) method of computational fluid dynamics(CFD) code Nek5000. The result will be tested and validated against an experimental data and DNS results carried out by EI Khoury. Also which variables differs between in the pipes will be investigated pressure, wall shear stress, velocity fields.
- Develop and validate multiphase DNS in a horizontal and vertical turbulent flow at Re_{τ} = 361. Both polydispersed and irregular shaped particles will be tracked.
- Modelling and understanding pond and silo sludge behaviours behavioural modification techniques using first principles of mathematical modelling
- Potentially, a machine learning algorithms might be used to analyse the data
- generated during simulation such as Neural network modelling.

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- TRANSCEND proposal

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The PhD problem: Ponds at Sellafield

- Contain:
 - Mg(OH)₂ rich sludge



Mercedes Baxter Chinery, Imperial College London m.baxter-chinery19@imperial.ac.uk



• Al, Mg, U

TRANSCEND

- pH 9 10
- How to store/make safe:
 - sludge
- The Opportunity: Magnesium – Silicate – Hydrate cement
- $MgO + SiO_2 + H_2O \rightarrow MSH$ • pH 9.5 - 10.5

The approach:

- Create artificial sludge like material by slow formation and sedimentation of Mg(OH)₂
 Investigate cementation of such sludge by condition and mixing
- Compatible with Al and Mg metal
- Potential for waste volume reduction as sludge could be part of stabilising cement



 Water content and dispersant expected to be key

Study durability of M-S-H cements

Little known to date

Important if to be stored for very

long times

Transformative Science and Engineering for Nuclear Decommissioning





How does the degree of crystallinity in a glassceramic affect radiation tolerance? Tamás Zagyva Supervisors: Laura Leay, Brian O'Driscoll, Tracey Taylor The University of Manchester, Dalton Cumbrian Facility

Correspondence: tamas.zagyva@postgrad.manchester.ac.uk

1. Post operational clean out (POCO)

The nuclear fuel reprocessing activity at Sellafield Ltd is planned to finish by the end of 2020. The storage plants will go through a post operational clean out (POCO) phase which includes the vitrification of all storage tanks which have stored acidic highly active liquors (HALs) since the 1950s. HAL is a nitric-acid based liquid which contains the fission products and residual actinides after the nuclear fuel reprocessing. The vitrification process is required for the immobilization of radioisotopes before the disposal of these high-level wastes into an underground repository. The number of vitrified containers depends on the solubility limit of the molybdenum in the glass, therefore vitrifying the old POCO HALs (with increased molybdenum content) would produce a buge amount of waste packages [1, 2].

2. Solution for incorporating increased molybdenum content

The currently used 'Mixture Windscale' (MW) base glass can incorporate only 3-5 wt% MoO_3 . Above this concentration molybdenum precipitates in the borosilicate glass as a 'yellow phase' containing water soluble molybdate crystals (Fig. 1A) [1,2].

A new 'Ca/Zn' glass has been developed in order to increase the solubility of molybdenum without yellow phase formation. Ca/Zn borosilicate glass can incorporate up to 12 wt% MoO_3 via the in situ formation of a durable crystal in the glass matrix called powellite (CaMoO₄) (Fig. 1B) [1,2].



Fig. 1. Crystalline phases in MW (A) and Ca/Zn (B) glasses [1].

Ca/Zn borosilicate glass-ceramic

3. Different degree of crystallinity in the VTR samples

The Vitrification Test Rig (VTR) is a full scale non-active replica of the Waste Vitrification Plant (WVP) process lines. Using the VTR the final waste form after the vitrification process can be demonstrated [2].



Although powellite in the Ca/Zn based glass-ceramic can incorporate the molybdenum and suppress the formation of the undesirable water soluble alkaline molybdates, the VTR results showed that the degree of crystallinity is different in the outer and middle part of the glass-ceramic composite due to the different cooling rates (Fig. 2.).

irradiation

4. Work planned in this project

Radiation from the incorporated radioisotopes can cause changes in the microstructure like cracking, void formation, amorphization, precipitation of additional phases or ion migration. These processes may affect the long-term durability of the waste forms, therefore the radiation tolerance analysis of Ca/Zn glass-ceramics with different crystallinity is crucial.

- Ca/Zn base glass, powellite crystal and glass-ceramic samples with different degree of crystallinity will be created.
- He ion and heavy-ion irradiation experiments will be conducted for the simulation of α-particle and α-recoil damage.
- Pre- and post-irradiated samples will be analysed by several $_{\alpha \text{ particle}}$ methods (e.g. XRD, SEM, TEM, electron microprobe,





analysis



cracking, voids

ion migration

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Understanding glass melt chemistry in thermal treatment of nuclear waste

Lucas-Jay Woodbridge

University of Sheffield Sir Robert Hadfield Building Mappin Street Sheffield S1 3JD lwoodbridge1@Sheffield.ac.uk

- PhD project aims to provide deeper understanding into the chemistry of glass melt
- Looking at the process of immobilization of radionuclides to create a safe waste form for storage.
- The medium selected for immobilization, in this instance is glass.



- Reading from the literature, alongside guidance from my supervisor Russell Hand, has led to some good initial points of interest.
- One of these is looking at Silicotitanates ability to use ion exchange in immobilizing Cs based wastes in their structure.
- A second line of interest resides in researching the immobilization abilities of modified MW glass (for example using a Barium doped version).



- The research will involve making glasses, loading them with substitute nuclides to test loading capacity and retention with a potential ultimate aim of using active radionuclides.
- The work being undertaken from here onwards will mainly involve batching of potential glass compositions which will then (if successful) be utilized as a medium for waste loading to explore their viability for use in industry.

• Glasses will be characterized using a vast range of analysis techniques from XRD and Raman to AFM or micro-indentation.

• Analysis will allow for the correct compositions of the glass to be determined which will allow determination of success alongside general factors about the waste form.



This image is of a Ba_MW glass being analyzed using a Polar eye viewer which helps to determine stress in the glass

Project supervisors are: 1st – Russell J. Hand 2nd – Neil C. Hyatt Industry – Mike Harrison

In-situ synchrotron X-ray diffraction studies of ion exchange in zeolites

Clinoptilolite

H. A. Parish¹, G. Cutts, C. C. Tang and J. A. Hriljac

¹University of Birmingham - hap431@student.bham.ac.uk

Introduction

Zeolites and related inorganic materials with open framework structures are often used in the clean up of radionuclides from nuclear waste streams. These materials have high stability towards heat and radiation and can also be highly selective towards radioactive cations, even in the presence of other competing ions. ¹³⁷Cs is a common and particularly problematic radionuclide; it is water soluble and harmful to humans. This work will focus on the analysis of zeolite structures in order to determine their ability to act as efficient ion exchangers for radioactive Cs.

Structure and Properties of Zeolites

Zeolites are a class of porous aluminosilicates with the general formula Candidate for Waste Clean-Up

 $M_{x/n}[Al_xSi_yO_{2(x+y)}]$.pH₂O, where M is a cation such as Na, K or Ca and n is the charge on the cation. Their structures are made up of SiO_4 and AlO_4 tetrahedra that are linked by corner sharing of oxygen atoms to form a 3D network of rings and cages. The tetrahedra give the structure an excess negative charge, which is accounted for by cations occupying the pores. Pores in the framework also contain water molecules.

In-Situ Diffraction Cell The flow cell designed by Dr Geoff Cutts for in-situ ion exchange.

Clinoptilolite is a naturally occurring zeolite with ideal formula the $(Na,K,Ca)_6Al_6Si_{30}O_{72}\cdot 24(H_2O)$. The selectivity of clinoptilolite towards Cs is well documented in the literature and it was used during the clean-up after the Chernobyl incident. Furthermore, clinoptilolite from Mud Hills, California, has been used in the SIXEP effluent treatment plant at Sellafield for the past 30 years to remove Cs and Sr from alkaline liquid effluents². Its selectivity even in the presence of competing cations, such as sodium, makes clinoptilolite an ideal candidate for this purpose.

Strong

In-Situ Cs-Exchange Experiments In-situ ion exchange experiments were

*Figure 1 – the crystal structure of clinoptilolite along the c-axis*¹

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Figure 3 (above) – graph showing selected refined cation occupancies for the Naexchanged Mud Hills sample

Figure 4 (left) – crystal structure of Na-clinoptilolite. The colours of the cations correspond to the graph. The results indicate that Cs is exchanged into the 8-ring initially and the occupancies of the cations in the 10-ring change very little.

undertaken on beamline 111 at Diamond Light Source. Mud Hills clinoptilolite samples, Na-exchanged and untreated, were loaded into a capillary and 0.5 mM CsNO₃ was flown through. XRD patterns were recorded over the course of the exchange. Selected results are presented to the left; the graphs in figure 2 compare the change in *b*-parameter and unit cell volume over time for each sample. Figure 3 shows the change in cation occupancies over the the exchange for the of Nacourse exchanged sample, and the crystal structure in figure 4 highlights the positions of these fitting Rietveld cations. Pawley and refinement were used to elucidate these values – all calculations were performed in the program TOPAS³.

Figure 2 – graphs comparing results of sequential Pawley fitting the Na-exchanged and untreated Mud Hills datasets

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Future Work

Other zeolite structure types, for example chabazite, also have well documented selectivity towards Cs. In future it would be beneficial to repeat the in-situ flow experiments with chabazite to see how it compares to clinoptilolite.

Transformative Science and Engineering for Nuclear Decommissioning

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TRANSCE

Advanced radiation-based borehole monitoring

Soraia S. C. Elísio, Malcolm J. Joyce

Lancaster University, Bailrigg, Lancaster LA1 4YW

s.elisio@lancaster.ac.uk, m.joyce@lancaster.ac.uk

-> It is of great importance to monitor underlying soil and groundwater surrounding nuclear facilities to identify and quantify potentially hazardous substances that might be released to the environment.

> The standard method to monitor radioisotopes migration within the groundwater flow system at contaminated sites is through sampling of groundwater from boreholes and further ex-situ laboratory analysis [1,2].

> Well-logging technology has been used for detection of radioactive elements in-situ. The system comprises a prove installed in a water-proof housing on a push-rod cable that is deployed in a borehole/blind-tube (Figure 1). Additionally it is also necessary to provide power and to recover signals [3].

 \rightarrow Borehole probes typically use NaI(TI), plastic scintillators and Geiger-Mueller counters [3,4]. Recent studies have been exploiting different potential probe/sensors for radiation monitoring [5-7].

OBJECTIVES

Develop a resilient detector by which blind-tube measurements might be done, such that the system can be left in-situ.

The system shall yield a degree of spectroscopy to identify principally Cs-137, and potentially Sr-90.

LONG-TERM MONITORING IN-HOLE OF FISSION CONTAMINANTS MIGRATION IN SOIL AND GROUNDWATER

REDUCED NEED FOR HUMAN INTERVENTION

RESEARCH PLAN

Development	of	а	thorough	requirements	specification	for	the
instrument.							

Detailed investigation and analysis of the various candidate sensors that meet the needs of the requirements specification.

Favourable candidates: CeBr3, CLYC, SiC, GAGG, CZT, ...

Set-up a campaign of laboratory-based tests in a soil-filled phantom (Figure 2) with which to compare and identify the best detector.

Detectors/sources can be placed at any x-y tube positions.

Shall be performed temperature, shock and moisture tests.

Set-up an extension of the former to explore its resilience.

Figure 1. Illustration of an in-situ radiationbased borehole monitoring system.

Build of a prototype and proceed outdoor field tests of the system at Sellafield site, comparing it to the existing monitoring method.

Figure 2. Soil-filled phantom to replicate borehole monitoring.

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Predicting Gamma Dose Rates with Limited Information

Luke Lee-Brewin, Dr Caroline Shenton-Taylor, Prof David Read University of Surrey I.lee-brewin@surrey.ac.uk

R

R

Overview of the Project

It is essential that buried and potentially contaminated structures can be quantitatively assessed to facilitate future decommissioning of nuclear sites. This PhD, funded by the Nuclear Decommissioning Authority, will seek to develop a robust methodology to predict gamma dose rates in contaminated underground structures based on limited direct information.

The project objective is to minimise and, where possible, avoid intrusive sampling and analysis whilst still acquiring sufficient information to justify management options for radioactively contaminated underground pipes and other structures at UK nuclear sites.

Use of a waste pipe due for decommissioning at a legacy site in the south of England has already been agreed. This means more intrusive sampling can be taken to increase compare to results being generated through newly developed methodologies.

An example of gamma ray detectors being deployed

Literature Review

0000

The project will begin with a comprehensive literature review with the goal of becoming familiar with all past and current research of the relevant topics. Some research has begun on methods to improve the analysis of any radiation spectrum obtained. Fuzzy logic offers a way of increasing confidence in a measurement by intelligently combining multiple sources of information while wavelet analysis could potentially identify peaks obscured by the Compton continuum or background noise.

The literature review will continue throughout the PhD but will be the primary focus of the first 6 months. Another area to explore is the legal requirements for burying and disposing of waste to better understand what to expect in the pipes when field tests begin.

A

A

A picture of the soil tank provided allowing us to run controlled experiments in a lab environment

Geant4 Modelling and Experimentation

3

Experiments will be conducted using an existing soil tank to determine the appropriateness of various detection methods for future field tests. These experiments will also show us the extent to which soil shields the gamma sources from detection as well as other environmental factors such as the effect soil moisture content has on the levels detected. To test this a soil tank has been provided, by encasing the source in a plastic tube and placing gamma detectors over the tank, we gain significantly more control over environmental factors and can begin to develop methodologies to test in the field. Alongside the soil tank experiments in the lab, testing will be conducted on the waste pipe at the site with the goal of fully characterising the gamma emissions in real life environment.

As well as an experimental component, models will be created of this pipe incorporating decay profile, contaminants and environmental conditions. Use of Geant4 to model radiation transport will be utilised. Standard and enhanced data analysis of both experimental and modelled data sets will be applied, incorporating data fusion methodologies.

Algorithm Development

The final part of this research project will involve taking the data gathered from the lab and the field and developing new methods of detection that can be used in a cost efficient, non-intrusive manner. This will combine all aspects of the project combining techniques learnt in the literature review, the experiments conducted in both the lab and the field and the models constructed using Geant4.

A commonly used standard in industry is "Technology Readiness Level". This is a scale between 1, a basic concept and 9, a design being used operationally in an active facility. This project aims to take the development of this analysis method to level 6, field testing at full scale with a nearly complete design.

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Assessing the strength of biomineral strategies for concrete repairs PhD Student: Athanasios Christos Karampourniotis 5th floor, James Weir Building, University of Strathclyde, Glasgow E-mail address: athanasios.karampourniotis@strath.ac.uk

Professor Rebecca Lunn¹, Dr. Enrico Tubaldi², Dr. Grainne El Mountassir³

^{1,2,3}Department of Civil and Environmental Engineering, Faculty of Engineering, University of Strathclyde, Glasgow, United Kingdom

Problem Introduction

It is a challenge for modern Civil Engineers to monitor and repair deteriorating concrete infrastructure.

Many concrete assets in the UK are past their original design life and have an increased risk of failure.

Microbially Induced Calcite Precipitation

- The biomineralization process that this research will work on is Microbially Induced Calcite Precipitation via urea hydrolysis.
- Firstly, this process depends on a ureolytic bacterium (like sporosarcina pasteurii) that hydreolyzes urea into ammonia and
- The rate of concrete degradation on individual structures is highly variable.
 - Concrete structures
 (ports, roads, bridges,
 buildings) have been
 exposed to a unique
 combination of
 environmental conditions
 resulting in degradation
 and cracking of the
 concrete.

Project aims

- Develop a new biomineral concrete repair strategy at the Department of Civil and Environmental Engineering at the University of Strathclyde.
- Repair degraded concrete samples, taken from Devonport,

- carbonic acid.
- Secondly, what follows is the production of ammonium ions and an increase in the pH around the bacterial cell.
- Then as the pH rises, bicarbonate ions (formed by carbonic acid) create carbonate ions, which in the presence of calcium ions lead to the precipitation of calcite.¹
- MICP has been proposed for soil strengthening², permeability reduction³, sealing fractured rock⁴ and more.
- No research has yet modelled MICP repaired concrete. Such a model could be used to better understand the mechanical behavior of MICP treated concrete and inform treatment strategies.

Mesoscale modelling - FEM

• The mesoscale modelling of concrete makes it possible to understand the behavior of the composite materials under various loading conditions.

Plymouth infrastructure and compare the results with more traditional repair techniques in the laboratory.

Develop a numerical model to simulate the repair of mechanical behavior of repaired concrete. This model will then be used to improve the design of the repair strategy and to provide information for field trials which will be conducted in year-3 of the PhD.

Acknowledgements

This PhD project is funded by Cavendish Nuclear

• The Finite-Element mesoscale model although is mesh-dependent, gives a good representation of the intact concrete as a heterogeneous continuum⁵.

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Transformative Science and Engineering for Nuclear Decommissioning

Introduction

TRANSCEND

Magnox nuclear reactors, using metallic uranium as fuel operated in the UK from the 1960's until just a few years ago. The metallic fuel was encased in a Magnesium alloy 'Magnox' cladding, which along with the U metal, is susceptible to corrosion by water. Until 1992, a significant volume of Magnox waste materials, including spent fuel assemblies, had been accumulated in the storage ponds at Sellafield in Cumbria [1]. These ponds were maintained at a high pH (above 10.5) to minimise corrosion [2]. However, considerable corrosion has still occurred over extended periods, raising concerns about the safe decommissioning of the facilities [3]. Corroded Magnox Sludge (CMS) arising from long-term corrosion of the cladding material is a prevalent residual material amongst others (e.g. fuel fragments and wind-blown debris) [4]. Corrosion of Magnox forms brucite (Mg(OH)₂) and liberates hydrogen. Embedded uranium metal fuel is also expected to have been exposed to water throughout the storage period. Uranium reacts with water to form uranium hydride (UH₃), uranium dioxide (UO₂) and hydrogen, presenting potential uncontrolled thermal hazards during decommissioning.

Flange U rod Sludge

Feasibility trials on uranium corrosion in sludges using in situ X-ray Computed Tomography Haris Paraskevoulakos, Tom Scott HH Wills Physics Laboratory, Bristol, BS8 1TL

cp13846@bristol.ac.uk, t.b.scott @bristol.ac.uk

Figure 1: Experimental Analogue

Experimental Approach

A miniature analogue of storage pond conditions was experimentally replicated to investigate the behaviour of uranium while embedded in CMS (**Figure 1**). Powderised CMS–simulant was diluted in water to produce a thick slurry, resembling pond conditions. The sludge was poured into a cylindrical stainless steel cell. A single uranium specimen (1 mm x 1 mm x 20 mm) was then encapsulated in the CMS and the system was allowed to dry in air for 3 days before being sealed. At distinct time intervals, X-Ray Computed Tomography (XCT) was used to probe the evolving interior state of the sample and investigate the corrosion behaviour. Primary results are shown in **figure 2**. It can be observed that there is a notable change in the morphology around the

embedded uranium specimen, attributed to progressive corrosion. The morphology of the developing corrosion layer at the uranium–CMS interface suggests the formation of UH_3 based on a morphology very similar to experiments performed in uranium–grout systems [5]. The progress of uranium corrosion can also be observed in **figure 3** where the residual metal has been segmented from the rest of the materials.

Figure 2: XCT scans exhibiting uranium corrosion evolution within a CMS environment. The "age" of the sample at each different scan is shown in green letters.

Summary–Future Plans

Feasibility trials have proven that XCT is a powerful non destructive method for investigating complex corrosion systems. Corrosion of the uranium, based on morphology change, has been observed to progress over more than a year since sample preparation. Using relevant software, a quantification of the corrosion percentage over time is now possible. Confirming the phase of the corrosion product (UH₃ versus UO₂) is now of **significant importance** for the project. Synchrotron X-ray Diffraction may provide a method to characterise the interacting materials without breaking the sealed containment. Thus, potential formation and persistence of the pyrophoric UH₃ could be validated.

20 days

50 days

References:

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Figure 3: 3D views of the uranium specimen. Threshold segmentation allowed separation of the non–corroded metal.

Corrosion and Leaching of Carbide Fuels in a Geological Disposal Facility (GDF) Setting

Dimitris Samaras

Interface Analysis Centre, School of Physics, University of Bristol, Bristol, UK

Dimitris.samaras@Bristol.ac.uk

History and Motivation

Uranium Carbide (UC) constitutes one of the exotic fuel types tested in the UK Nuclear Research Programme, utilised by sites like Dounreay, and facilities like CERN. The NDA has ended up with a rather large legacy amount of this material to manage as waste. Uranium Carbide is considered chemically reactive and potentially pyrophoric in water and oxygen; this exotic legacy will eventually have to be disposed in a Geological Disposal Facility, where it will inevitably contact groundwater.

The Samples

The Uranium Carbide sample materials available for this PhD consists of two monocarbide (UC) pellets, with a total mass is 163g and a total activity of 6 MBq. Initial examination and preparation will be conducted inside a glovebox, to avoid any reactions of the pellets with water vapour and oxygen, present in atmospheric air.

Figure 2: Uranium-Carbon Phase Diagram [6]

Future Work

Samples will now be cut and prepared for X-Ray Diffraction (XRD), Electron Microscopy (SEM) and High Speed Atomic Force Microscopy (HSAFM) to determine microstructure and composition. Analyses will be performed with minimal exposure to oxygen and water vapour, to prevent premature degradation. Later, more advanced techniques will be employed, both before and during corrosion simulation (which will happen by enclosing samples in water filled cells); these techniques involve material analysis methods such as XRT, SIMS, EM as well as wet chemical techniques, like ICP-MS, ICP-OES, TRLFS, and Residual Gas Analysis mass spectrometry...

Figure 1: Uranium Monocarbide-vs-Dioxide structures [1]

Corrosion - Oxidation

Uranium Carbide reacts with water, in some cases vigorously [2]. Several studies have examined its hydrolysis properties, observing that uranium monocarbides produce mainly methane gas when hydrolysed, whereas ethane and heavier hydrocarbons are produced from dicarbides and mixtures [3][4]. In addition, oxidation studies have been performed, showing dry oxidation follows a linear rate law [5]. However, it should be noted that the lowest reaction temperature studied was 230°C, which is far and above the temperature expected for a GDF.

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Oxidation of Uranium Oxide (UO₂) at Low Temperatures

YiFeng HUANG (Nigel)^{1*}, Richard WILBRAHAM¹, Prof Colin BOXALL¹, David I. HAMBLEY² ¹ Department of Engineering, Lancaster University, Lancaster, LA1 4YR ² The National Nuclear Laboratory Central Laboratory, Sellafield, Cumbria CA20 1PG * y.f.Huang@Lancaster.ac.uk

Background and Research Motivation

UO₂ is the fuel source for the UK's fleet of Advanced Gas Cooled Reactors (AGR), existing in the form of annular UO₂ ceramic pellets, sealed inside 20/25/Nb stainless steel cladding to give fuel pins.

The four points below sets out the key motivations for this research:

- To underpin the options for pre-disposal storage of SNF and prediction of the behaviour during final disposal.
- Must satisfy safety case requirements for the UK's Geological Disposal Facility and for interim storage options prior to final disposal.
- Concerned with the management of in-reactor or in-pond failed fuels. The loss of fuel pellet integrity can lead to potential release of fission products and radionuclides.

THORP storage ponds

AGR spent nuclear fuel (SNF) reprocessing has historically taken place at THORP, however, since November 2018, THORP is no longer in operation. The fate of reprocessing has shifted the UK towards an open fuel cycle likely to involve long term fuel storage followed by final disposal in a Geological Disposal Facility (GDF).

AGR fuel cladding

Aims & Objectives

Using AGR SIMFuels to understand the oxidation behaviour of the UO₂ matrix in failed AGR spent fuel, at low temperatures and under conditions relevant to UK interim storage and the drying of wet stored SNF.

- Study UO₂ and AGR SIMFUEL oxidation as a function of simulated burn-up and temperatures of < 200°C, in:
 - simulated interim storage pond-waters and repository ground-waters
 - \circ dry air as a function of oxygen partial pressure (P₀₂)
 - \circ damp air as a function of relative humidity (RH) and P₀₂
- Hence determine thresholds for the onset of UO₂ oxidation in AGR SIMFUELS and pure UO_2 .

Much of the existing research on simulant fuels (SIMFuels) are based on the study of Light Water Reactor and CANDU Pressurised Heavy Water Reactor SIMFuels. There is a need for UK specific AGR spent fuel research.

Methods in Literature

Electrochemistry

Various factors can affect fuel corrosion/dissolution such as pH, temperature, groundwater chemistry, fuel matrix dopants and the influence of products derived from water radiolysis. Electrochemistry can be used to probe the anodic and cathodic activity of and the oxidation and reduction reactions taking place on the fuel surface.

μ-Raman Spectroscopy

The use of µ-Raman spectroscopy for surface and structural study of UO₂ has been an increasing method of choice. Enabling analysis of the surface structure in relation to oxidative and reductive activity, the effects of dopants and hyperstoichiometry on its lattice

structure.

Cubic – fluorite lattice

50x magnification of UO₂ surface

AGR SIMFuel pellet encased in resin

Preliminary Results

Fig. 1a/b/c CV of undoped UO₂, 25 and 43 GWd/tU SIMFuels in a range of NaCl concentrations.

Dependence of [carbonate] at pH13 and pH11 (Fig. 2) \rightarrow

- Greater [carbonate] dependence is observed at pH11 than compared to pH13. At both pH's the max current achieved is roughly the same at approx. 0.18 V.
- Carbonate is known for its ability to enhance UO_2 dissolution as it's a strong complexing agent with UO_2^{2+} . At higher pH the [OH⁻] saturates the electrolyte solution and thus reducing the relative concentration of carbonate in the bulk. It is also a possibility that at higher pH, the formation of insoluble surface precipitate schoepite is competing with the carbonate complexation with the uranyl.

 \leftarrow Dependence of [chloride] (Fig. 1)

- As expected, the higher [CI⁻] produce greater currents due to increased ion mobility. The difference is less noticeable with the 25/43 GWd/tU SIMFuels.
- 25 and 43 GWd/tU burn-up SIMFuels also express greater currents than the undoped sample due to decreased resistivity, but also the effect of dopants enhancing oxidation/reduction.

Fig. 3 Raman spectra of (a) undoped UO₂, (b) 25 GWd/tU and (c) 43 GWd/tU SIMFuels (d) comparison of all three samples.

- \leftarrow Raman after 15+ hours in NaCl (Fig. 3)
 - μ -Raman spectra of undoped UO₂ and SIMFuels samples, recorded after open circuit potential measurements in 1 mM NaCl for 15+ hours.
 - 10 scans were recorded at random locations on the sample surface to show an average, outliers were excluded.

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About Me:

Born and raised in Cumbria. I did my MPhys course at the University of Salford and I am now undertaking a PhD at the University of Leeds.

TRANSCEND

BSc Project:

Triangulation of a Point Source of Radiation inside a Shielded, Sealed Container [1]

Characterisation of AGR Fuel and its Behavior During Drying

Thomas O. Bainbridge and Bruce C. Hanson

School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK pmtoba@leeds.ac.uk

Previous Work:

- Drying rig developed as part of a previous project (figure 5) [3].
- Rig capable of performing vacuum and flowed gas drying.
- Investigated methods to crack the samples.

Full Test Piece Sample <4g

- Able to sweep a hemispherical area to locate the point source.
- Able to produce a graphic showing the location of the source in the container.
- Code written in MATLAB, ARDUINO and Processing.
- Rig built and sensor collimator 3D printed.

Figure 1: The mechanism built to drive the motion of the sensor.

Jampie		· •0
Pin holed	0.4-0.5	0.15
Cracked	0.5	0.1-0.04

Table 1: Drying rates for the different samples in mg s⁻¹ at 30°C.

Standard data plot used for the drying tests. This particular experiment was run at 150°C at 20 mBarA with a drying rate of 55 mg min⁻¹.

Figure 5: The drying rig developed as part of a previous PhD.

MPhys Project:

Tomography of a Nuclear Waste Drum [2]

- Able to reproduce layout of the contents of the drum.
- Based on CT and PET scan operations.
- Code written in MATLAB.
- Mock readings from Excel
- Radiation level readings taken from multiple angles.
- Can handle multiple layers at once (figure 2)
- Can resolve low intensity and small footprint areas (figure 3) using different sized regions of high and low attenuation.

Aim:

lacksquare

Leeds.

To prove that cracked Advanced Gas-cooled Reactor Fuel can be dried

Objectives:

- Crack fuel.
- Dry the cracked samples.
- Develop a process model.

Figure 6: SEM and optical image of a crack produced.

Figure 7:

2 hour drying of a test piece at 20°C.

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Introduction

TRANSCEND

- Fuel cladding houses the fuel pellets and retains the fission products, and in AGRs, the cladding is made from 20-25-Nb stainless steel.
- Spent AGR fuel and cladding is stored in the spent fuel ponds at Sellafield.
- The spent fuel cladding suffers from sensitisation and stress corrosion cracking (SCC) induced by irradiation.

Research Methods

Digital Image Correlation: A full-field method that can monitor the development of cracking to gain a better understanding of the initiation of SCC.

Development of micromechanical testing methods for spent AGR cladding to examine effects of sensitisation and stress corrosion cracking

K. Yuan¹*, R. Clark², M. Mostafavi¹

¹Department of Mechanical Engineering, University of Bristol, BS8 1TR ²National Nuclear Laboratory, 102B Stonehouse Park, Stonehouse, Gloucestershire, GL10 3UT

*k.yuan@bristol.ac.uk

- A better understanding of the SCC behaviours and the change of mechanical properties of the cladding materials during transportation and storage is required.
- New testing methods shall be developed to better monitor the cladding to improve the safety.

Fig. 1. Spent fuel pond at Sellafield^[1]

Fig. 2. SEM image of a stress corrosion crack; the crack initiation site is highlighted ^[2]

Traditionally, the average size of the specimens for SCC test is at the scale of at least a few centimetres^[3]. However, due to the nature of the irradiated materials, the size of the sample should be reduced. The challenge of the research would be

Fig. 3. DIC strain mapping of the development of a crack^[2]

- Synchrotron light source at Diamond Light Source can be used to perform XRD, and because of the high intensity of the synchrotron, the sample can be tested in the sample cell.
- Grazing Incidence X-ray Diffraction (GIXD) can be used to test the surface layers of the sample.
- X-ray computed tomography (CT) can also be performed with synchrotron light source,

Fig. 4. Synchrotron XRD at Diamond Light Source, where (A) X-ray source, (B) sample cell, (C) detector, and the red arrows show the X-ray beam^[4]

to keep the sample representative while minimising the size of it.

Aim and Objectives

The overall aim of the research is to better understand SCC including the initiation of cracking and the change on the mechanical properties and behaviours of the AGR spent fuel cladding and further develop new testing methods to monitor the materials. There are several objectives:

Initial tests will be performed on surrogate materials, thermally sensitised 304 stainless steel:

- The current state-of-the-art techniques on SCC will be evaluated.
- Relatively large samples with a large number of grains will be tested using fullfield DIC to study the initiation of SCC.
- With a better understanding of the initiation of cracking, new testing set-ups will be designed with a smaller sample size while keeping relatively complete features of the bulk materials.
- The materials will be modelled at multiple scales, and crystal plasticity will be

and 3D reconstructions can be used for volumetric DIC.

Fig. 5. Sample cell for synchrotron X-ray CT; and the red arrows show the X-ray beam^{[4}

Fig.6. Schematic of a proposed test design

Conclusions

Overall, by performing current tests and developing new testing methods, the SCC phenomenon of AGR fuel cladding would be better understood and the safety of the storage ponds could be improved.

References

The sample size will be minimised and figure 6 shows a proposed test sample design, where SCC is most likely to occur at two corners of the folded centre piece.

introduced to study cracking at grain level.

Finally, the tests will be performed on irradiated cladding materials, and the difference between SCC in 20-25-Nb and SCC in 304 stainless steel will be studied. New testing methods could be developed to monitor the cladding materials stored in the ponds.

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Transformative Science and Engineering for Nuclear Decommissioning

Characterisation of Uranium Species by Time-Resolved Laser Fluorescence and Raman Spectroscopy Victoria L. Frankland^{1*}, Nathan Thompson², Antoni Milodowski¹, Joshua W.G. Bright¹, Neil Hyatt² and David Read^{1,3}

¹ Department of Chemistry, University of Surrey, Guildford, GU2 7XH, UK;
 ² Materials Science and Engineering, University of Sheffield, Sheffield, S10 2TN, UK
 ³ National Physical Laboratory, Teddington, TW11 0LW, UK

*v.frankland@surrey.ac.uk

Introduction

Monitoring the corrosion behaviour of stored spent nuclear fuel (SNF) is required to ensure safety and to inform decisions on future treatment and disposal options. It is possible that this can be achieved using remotely operated techniques, including the laser-base methods of Raman, time-resolved laser fluorescence (TRLFS) and laser-induced breakdown (LIBS) spectroscopy. Characterisation of natural uranium minerals, representing potential corrosion species, provides essential reference spectra for identification purposes whereas real-time corrosion experimental simulation of the corrosion process(es) on thin film surrogates will help validate models of reaction pathways and kinetics.

Characterisation Techniques

Raman spectroscopy is used to observe vibrational, rotational and other low frequency modes. The apparatus (Figure 1) has four lasers (457, 532, 633 and 785 nm) enabling a greater range of Raman modes to be observed. The fluorescence excitation, emission and decay behaviour is explored using the TRLFS apparatus. Chemical composition was confirmed using SEM-EDX and XRD.

Secondary Uranium Mineral Raman Characterisation

The most intense and well defined Raman features were obtained using the 785 nm laser. Good agreement exists with the literature ¹⁻¹⁰ for assigning the Raman modes (indicated using highlighted regions in Figure 3) although not all the features are known. The most intense feature observed in the Raman spectra is the uranyl symmetric stretch

Samples

The mineral samples included here (Figure 1) were loaned by the British Geological Survey (BGS) and the National Museum of Wales. Heated synthetic studtite samples were provided by the University of Sheffield.

Figure 1: From left: vandenbrandeite (CuUO₂(OH)₄); becquerelite (Ca(UO₂)₆O₄(OH)₆·8(H₂O)); vandendriesscheite (Pb_{1.5}(UO₂)₁₀O₆(OH)₁₁·11(H₂O)); Sr-meta-autunite (Sr(UO₂)₂(PO₄)₂·6-8(H₂O); meta-torbernite (Cu(UO₂)₂(PO₄)₂·8(H₂O)); boltwoodite (K₂(UO₂)₂(SiO₃)₂(OH)₂·5(H₂O)); and johannite (Cu(UO₂)₂(SO₄)₂(OH)₂·8(H₂O)).

Fluorescence Spectra of Heated Synthetic Studtite

Excitation and emission spectra (Figure 2) indicate that the fluorescence intensity generally decreases with increasing temperature. The exception to this is the studtite sample heated to 350 °C. The University of Sheffield characterisation results indicate studtite first dehydrates into meta-studtite (100 and 150 °C) before forming an amorphous intermediate. At 535 °C, uranium trioxide forms in two phases (hexagonal

vibration, $v_1(UO_2)^{2+}$. This mode is sensitive to the local environment resulting in the peak position shifting and enabling the calculation of the U-O bond length, d_{U-O} , and bond force constant, k_{U-O} , (equations 1 and 2) ¹¹. For the minerals shown in Figure 4, d_{U-O} and k_{U-O} varies between 1.78 – 1.87 Å and 3.68 – 5.69 millidynes Å⁻¹.

 $\begin{aligned} &d_{U^{-O}}(\text{\AA}) = 106.5 \times v_1 (\text{UO}_2)^{2+} + 0.575 & (1) \\ &k_{U^{-O}}(\text{millidynes } \text{\AA}^{-1}) = [1.08 / (d_{U^{-O}} - 1.17)]^3 & (2) & (1 \text{ millidyne } \text{\AA}^{-1} = 100 \text{ N m}^{-1}) \\ &v_3 (\text{UO}_2)^{2+} (\text{cm}^{-1}) = [91.41 / (d_{U^{-O}} - 0.804)]^{3/2} & (3) \end{aligned}$

The position of the uranyl antisymmetric stretching mode, $v_3(UO_2)^{2+}$, can be estimated from d_{U-O} using equation 3¹². This mode is Raman weak and usually not detectable. However, the observation of the $v_3(UO_2)^{2+}$ mode in some of the minerals shown in Figure 3 suggests a deviation from the linear uranyl ion structure for this species which results in a lower symmetry.

and orthorhombic) but only fluorescence from the hexagonal phase was observed.

Discrepancies with the studtite sample heated to 350 °C were also identified using other characterisation methods. A new sample is being prepared to confirm our findings. However, the detection of medium intensity fluorescence features in Figure 2 suggest the 350 °C sample could exist as a pure, single phase intermediate species.

Figure 3: 785 nm Raman spectra for a range of secondary uranium minerals.

Future Work

Characterisation of uranium mineral and solution samples by TRLFS and Raman spectroscopy will continue. Reference spectra will be compiled into a database as a resource for project partners and the wider community. During the next phase the aim is to run simulation SNF corrosion experiments on thin U phase films with real-time characterisation of the evolving secondary phases.

Figure 2: Fluorescence excitation (left) and emission spectra (right) of heated studtite samples.

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1835

Transformative Science and Engineering for Nuclear Decommissioning

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Atomistic simulation of Am incorporation into PuO₂ William Neilson*, Dr. Samuel T. Murphy Department of Engineering, Lancaster University, Lancaster, LA1 4YR *w.neilson@lancaster.ac.uk

Introduction

This project will use atomistic simulation to understand the defect chemistry of PuO₂, and how incorporation of Am into PuO₂ may contribute to canister pressurisation.

Since sealing, some canisters exhibit signs of becoming pressurised. A possible explanation is the evolution of hydrogen gas from corrosion of the surface by entrained water.
 The conditions do not appear to be sufficiently oxidising to promote corrosion, however studies have indicated the existence of a hyperstoichiometric PuO_{2+x} [1] that could act as the precursor to corrosion.

• Oxidation may be being driven by changes in the defect chemistry of PuO₂ due to radioactive decay, in particular, the accumulation of americium.

• Americium exhibits complex chemistry with multiple oxidation states, some of which may promote the formation of PuO_{2+x}.

1. Predict defect chemistry in PuO₂ as function of environmental variables

i) Will determine formation energies for intrinsic defects in PuO₂

- O''_i, V_o'', Pu_i''', V'''' + variations of these at varying charge states.
- Utilise LDA + U functional in *ab initio* simulation.

ii) Combine DFT data with thermodynamics to predict defect chemistry in PuO_2 as function of environmental variables.

- The vibrational entropy change due to introduction of defects is obtained with empirical calculations, and combined with DFT defect energies.
- With UO₂, this approach led to improved replication of experimental data and the solving of the 'uranium vacancy problem' when combined with interstitial clusters [2].

3. Determine energies of Am incorporation into PuO₂ lattice

The energies of americium incorporation will be determined for all possible oxidation states, allowing prediction of:

2. Considerations

- 2 x 2 x 2 supercells to be used, simulating 96 atoms.
- Magnetic order of PuO₂ to be considered.
- Diamagnetic ground-state traditionally inferred, however Pegg *et al* (2018) propose longitudinal 3k antiferromagnetic ground-state.

4. Study whether the Am incorporation is capable of electrically activating PuO₂

If Am incorporation is found to be capable of electrically

- Its oxidation state.
- The presence of charge compensating defects.

Fig 1: The crystal structure of PuO₂. Am (red) shown incorporated on a plutonium vacancy site.

activating PuO₂, can begin to ask the following questions:

- What is the corrosion rate?
- What is the gas production rate?
- How does this impact the lifetime of the canisters?

Table 1: Lattice parameters & elastic constants of PuO₂. Calculated for this work using the General Utility Lattice Programme (GULP) [6] with the Cooper Rushton Grimes potential [7]. Compared with experimental findings [8,9] and a density functional calculation with the LDA + U model [9].

	Lattice constant (Å)	Bulk modulus	Young modulus	Shear modulus	Poisson's ratio
This work	5.38	225.16	365.92	81.81	0.229
Experiment	5.40 ^[8]	178 ^[9]	268 ^[9]	78* ^[8]	0.28 ^[9]
LDA+U	5.36	232	247	93	0.322

Fig 3: The experimentally obtained phonon density of state of UO₂ [4] and PuO₂ [5] compared with results obtained using the General Utility Lattice Programme (GULP) [6] with the Cooper Rushton Grimes potential [7].

*	Pu ₃₂ O ₆₂	

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Lancaster

University

Gas Generation from the Radiolysis of Water on UO_2 and THO_2

Christopher Anderson The University of Manchester & Dalton Cumbria Facility christopher.anderson-3@postgrad.manchester.ac.uk

<u>Overview</u>

The Radiation induced yields of H₂ present a significant challenge to the storage of radio-emissive material at nuclear sites, It is therefore necessary to secure a suitable surrogate for plutonium to further understand it's behaviour during storage.

Introduction

- Interactions between radiation and water is known to produce several reactive and stable products.
- The production of hydrogen as one of the final stable products is particularly interesting for safety and practical applications.

Preliminary Methods

- A humidity source and the samples will be attached to the manifold using stainless steel vessels (Figure 1).
- The radiolytic decomposition will be achieved using a Co⁶⁰ gamma irradiator.
- The radiolytic decomposition of water adsorbed onto a metaloxide interface may enhance or diminish hydrogen yields.
- Due to it's characteristics thorium presents itself as an explorable option as a plutonium surrogate.
- The resulting gases will be measured using either a gas chromatographer or bespoke manifold utilising H₂ and O₂ probes.
- The BET theory will be incorporated to allow the adsorption to be expressed as the average number of monolayers.

Figure 2 – Path of Surrogate Research

TRANS

Atomistic Simulation of the ageing of PuO₂

Elanor Murray

School of Chemistry, University of Birmingham, B15 2TT

exm350@student.bham.ac.uk

Introduction

The UK has the largest civil stockpile of plutonium in the world, stored at Sellafield. However, ageing mechanisms associated with the storage of PuO₂ are poorly understood. The generation, stability and mobility of fission products, in addition to the role of the surface oxide layer are key factors. Atomistic simulation techniques are ideally suited to provide fundamental insight into the defect chemistry of PuO₂. Interatomic potentials have been used in GULP to replicate PuO₂ accurately and to model a range of intrinsic defects [1]. The calculated defect formation energies were compared to determine which defects are energetically favourable. METADISE was then used to simulate pure surfaces.

•••••	Ageing of Plutonium			
	Frenkel pair:	U range 12 nm	He range 10 μm	\rightarrow
	O Vacancy			

Plutonium is vulnerable to ageing as it is a radioactive element. Pu²⁸⁹ decays principally

by α -decay. The daughter nuclei travel through the lattice initiating a collision cascade. From collisions, plutonium atoms can be displaced, creating numerous vacancies. A displaced plutonium atom may come to rest at an interstitial site, becoming a self-interstitial. Each decay event therefore creates many Frenkel pairs [2].

Defects in the Bulk

Bound	Defect Form	Binding	
Defect	Unbound (eV/Defect)	Bound (eV/Defect)	Energy (eV/Defect)
Schottky Trio	3.545	1.929	-1.616
Oxygen Frenkel Pair	2.668	2.069	-0.599
Plutonium Frenkel Pair	10.029	7.868	-2.161

The Schottky Trio has the lowest bound defect formation energy, therefore is energetically favourable and likely to be present in PuO₂. The surrounding ions distort to accommodate the defect. Oxygen Frenkel pairs are also likely to form.

Table 1: Unbound and bound Frenkel and Schottky
 energies from atomistic simulations of PuO₂ using GULP.

Fig 2: A Schottky defect in PuO₂. LHS: unrelaxed. RHS: relaxed.

Unrelaxed Relaxed Surface Surface Energy Surface (hkl) Energy (Jm⁻²) (Jm⁻²) 100 6.309 2.406 110 3.360 1.791 111 1.670 1.205

Table 2: Surface energies of PuO_2 simulations (n=1).

Surface Simulations

Pure PuO₂ surfaces were simulated using METADISE. The {*n*10}, {*n*11} and {*nn*1} surfaces were simulated, where *n*=1,2,3. It was found that initially unstable surfaces had a higher percentage relaxation than initially stable surfaces. The simulations indicate that the {*nn*1} surfaces are the most energetically stable, with {*n*10} surfaces generally being the least stable. The most stable surfaces simulated were: (111), (221) and (331).

Conclusions and Future Work

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- The most energetically favourable forms of intrinsic defects were found, by calculation, to be Schottky defects and oxygen Frenkel pairs.
- The pure (111) surface was found to be the most energetically stable.

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Future work includes: simulating defective surfaces, and investigating helium migration pathways.

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Dr Mark Read (Supervisor) NDA, NNL and EPSRC

TRANSCENE

Advanced Characterisation of Nuclear Waste Suspensions

Serish Tanya Hussain, Tim Hunter School of Chemical & Process Engineering, Leeds, LS2 9JT

pm14sth@leeds.ac.uk

Rig

Abstract

- Characterisation of nuclear waste is required to be in-situ due to the radioactive nature of all things nuclear.
- This research investigates the use of an ABS (acoustic backscatter system) to characterise non-active nuclear simulants: Honite-22 glass beads.
- ABS can be used in-situ and does not require direct contact with samples. The use of ABS for extracting physical properties is investigated.

Methodology

- **Tank transparent** to prevent acoustic signal interruption.
- Transducer frequency used: 2MHz. Material used: Honite-22 (glass beads)

OVER TIME...

From contamination and corrosion of the fuel cladding, the **composition** of the sludge has **changed**. The plan is to determine **physical properties** of the sludge **in-situ**. [2]

- Transducers **suspended** in the **rig**.
- Transducers were **probed** to ensure **no bubbles** had **formed** on the transducers [1]

Results: In-situ Characterisation

• PSD of all simulants are compared below using the Malvern Mastersizer 2000. • Bi-modal results for Mg(OH)2

- SEM images of nuclear simulants: Honite-16, 22 and Mg(OH)2 from left to right.
- Progressively building towards material which simulates the sludge more precisely.

due to aggregation of material • Simulant size decreases as sludge simulated with higher precision.

Results: Understanding Acoustics

Conclusion

• PSD data determined accurately from Master sizer for glass beads, not Mg(OH)2

• Transducers maintained to prevent air entrainment (submerging samples).

- Signal for concentrations decreases with distance
- Highest concentration, high attenuation
- Increased distance, attenuation increases exponentially with M

 $V = \frac{k_s k_t}{M^2} M^{\frac{1}{2}} e^{-2r\alpha}$ [3]

ψr

 $G = \ln(Vr\psi)$ [3]

Distance from Transducer (m)

UVP system requires calibration from oscilloscope.

Distance (m)

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due to aggregation.

Uranium Oxide Thin Films for Photovoltaic Devices: Characterisation by EXAFS & Future Work

Jarrod C. Lewis – Interface Analysis Centre & Correlated Electron Systems, Centre for Doctoral Training in Condensed Matter Physics H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, BS8 1TL, UK **Email** - jarrod.lewis@bristol.ac.uk

The Many Uranium Oxides

There are many crystallographic forms that uranium oxide systems can adopt. These range from the face-centred cubic fluorite structured uranium dioxide (UO_2) to the orthorhombic triuranium octoxide (U_3O_8) , which are both included as **Figure 1**.

Between these two well defined structures exists a plethora of intermediate oxide crystals. Of these, the widely accepted stable compounds of the uranium oxides are UO_2 , U_3O_7 , U_4O_9 , U_3O_8 , and UO_3 [1].

Extended X-Ray Absorption Fine Structure (EXAFS)

EXAFS is an element specific spectroscopic technique that offers sub-angstrom precision measurements of atomic distances.

By tuning the incident x-ray source at the to the U L_3 absorption edge (at 17.1663keV), the observed EXAFS probes atomic distances relative to the absorbing U atoms. The mechanism behind this is shown in **Figure 5**.

By fitting the resulting absorption signal with **Equation 1**, the atomic distances (R) that arise from multiple scattering mechanisms of the photoelectron can then be used to confirm the crystal structure, and thus the oxide form of the uranium oxide thin film.

The U-O Phase Diagram

The various structural phases of uranium oxide can be described by the general notation of UO_{2+x} compounds, where x denotes the shift in oxygen content from stoichiometric UO_2 . The UO_{2+x} structural phase diagram is shown in **Figure 2**.

This allows the crystal structure of uranium oxide crystals to be tuned by varying oxygen pressure whilst annealing. It is by exploiting this phase diagram that the physical properties of the uranium oxides can be studied as a function of oxide stoichiometry.

Growing and Tailoring UO_{2+x} Thin Films

Nominally stoichiometric UO₂ was grown onto epitaxially matched calcium fluoride (CaF₂) by reactive DC Manipulator

$$\chi(k) = \sum_{j} \frac{N_{j} S_{0}^{2} f_{j}(k) e^{-2R_{j}/\lambda(k)} e^{-2k^{2} \sigma_{j}^{2}}}{k R_{j}^{2}} \sin\left[2k R_{j} + \varphi_{j}(k)\right]$$

Equation 1 – The empirical EXAFS equation [4]. Here the absorption μ is scaled to the absorption edge $\Delta\mu$, to obtain the dimensionless variable χ .

A comparison of the UO₂, U₃O₇, U₄O₉ and U₃O₈ EXAFS fits are shown in **Figure 6**.

Figure 6 – EXAFS spectra (blue) fitted with Equation 1 (red), solved in terms of R for 10 distinct scattering pathways.

The shift in the EXAFS peak locations supports the transition of the thin films through an intermediate structure that is a convolution of the established UO_2 and U_3O_8 structures between these two stoichiometries, with these intermediates nominally denoted as U_4O_9 and U_3O_7 .

These results also support the validity of the thin film fabrication and processing methodology previous discussed for creating UO_{2+x} samples with varying stoichiometries.

Figure 5 – A diagram of the physical mechanism that gives rise to EXAFS. An emitted photoelectron (orange) interferes with the backscattered photoelectrons (blue) from neighbouring atoms. The final signal (blue inset) is the observed sum of these interreferences, with the EXAFS oscillations annotated.

magnetron sputtering, which is depicted in Figure 3. An unprocessed film obtained using this technique is shown in Figure 4A.

The samples were processed to obtain a range of UO_{2+x} single crystals from UO_2 to U_3O_8 ($0 \le x \le 2.67$).

Near-stoichiometric UO₂ was obtained by prolonged annealing at 400K under a vacuum of 1×10⁻⁵mbar. The higher UO_{2+x} oxides were obtained by annealing samples at 400-650K under 120mbar of O_2 , with the temperature and annealing time proportional to x.

The shift towards (or away from) stoichiometric UO₂ was monitored by in-situ x-ray diffraction (XRD). A depiction of the observed XRD peak shifts is shown in Figure 4B.

Figure 3 – Schematic representation of DC magnetron sputtering, omitting the reactive element of O_2 gas required for oxide growth. Adapted from a similar figure found in [3]

Α.

A Tuneable Semiconductor for Photovoltaics

Of particular interest is the observation that UO_2 is a n-type semiconductor when hypostoichiometric, and p-type when hyper-stoichiometric [1]. When coupled to the broadband absorption of UO_2 that spans both the visible and infrared regions of the electromagnetic spectrum [5], this offers exciting possibilities for both optoelectronic devices and photovoltaic cells.

What remains to be studied is how these properties translate to the higher oxide states, as a function of stoichiometry, and with doping with other elements.

To study these properties, the proposed device structure shown in **Figure 7** will be employed. The goal of these experiments will be to determine whether the UO_{2+x} systems are suitable for photovoltaic or optoelectronic applications, and if so, quantify their performance relative to other benchmark systems.

Figure 4 – DC magnetron sputtering output and in-situ off-stoichiometric processing monitoring. (A.) A single crystal UO₂ thin film grown on CaF₂. (**B**.) Depicts the change in XRD spectra for stoichiometric {111} UO₂ when **reduced** to hypo-stoichiometric (x < 0) and **oxidised** to hyper-stoichiometric (x > 0) regimes.

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Figure 7 – This diagram shows a basic outline of a four-point contact set up for a uranium oxide crystal, shown here in green. With the light source inactive, the "dark resistivity" of the sample can be measured. By activating the light source at a specific wavelength, the wavelength dependent photocurrent can be determined from the change in the illuminated resistivity, with a sketch of this included in the **blue inset**.

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Characterisation of single phase uranium silicide thin films Lottie Harding,¹ S. Rennie¹, E. Lawrence Bright¹, D. T. Goddard², R. Burrows³ R. Springell¹ University of BRISTOL

¹ University of Bristol, BS8 1TL, UK, e-mail: lottie.harding@bristol.ac.uk ² National Nuclear Laboratory, Springfields, Preston, Lancs. PR4 OXJ, UK ³ National Nuclear Laboratory, Stonehouse, Gloucestershire, GL10 3UT, UK

Uranium Silicide

Uranium silicide, U₃Si₂, has been identified as a potential ATF, having improved thermal properties and higher uranium density compared with UO₂ [1]. Conducting analysis on \geq this material, is, however, challenging, as, ₹ although progress has been made in synthesising bulk uranium silicide, these materials often exhibit mixed phases and are rich in impurities [2,3].

In this regard, thin films offer significant potential as a method of isolating phases and providing idealised surfaces on which single parameter studies can be conducted.

Structural Characterisation

The films engineered for this project have been characterised using x-ray diffraction and x-ray reflectivity, providing information about the samples thickness, electron density, interface roughness, crystallite size, and stoichiometry. By utilising the uranium-silicon binary phase diagram, provided by Middleburgh et al. [6], a series of high temperature samples have been engineered in order to investigate the crystallisation of uranium silicide phases with a varying uranium deposition rate.

300 ·

200

100 ·

20

Initial calculations predicted a uranium power rating of 10.7 W to be suitable for U_3Si_2 crystallisation. Comparing the diffraction peaks from Figure 6 to the uranium-silicon phase diagram (Figure 5) indicates that the Inte conditions are located within the α + U₃Si region.

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Fuel	ρ (g(U)cm ⁻³)	Tmelt (K)
UO ₂	9.7 [6]	3138 [7]
UN	14.32 [8]	3123 [8]
U_3Si_2	11.3 [6,9]	1938 [6,9]

Table 1: Comparative uranium density and melting temperatures for traditional uranium oxide fuel, compared with ATF candidates uranium nitride and uranium silicide.

400 1200 600 800 1000 1400 1600 Temperature (K)

1: Comparison of the thermal Figure conductivities of UO_2 and U_3Si_2 as a function of temperature. Data taken from [4,5].

Through varying the growth parameters, it is possible to control the stoichiometry, grain size, and crystallographic orientation of the sample. This project looks at the engineering and characterisation of single phase uranium silicide thin films, with particular emphasis on U_3Si_2 .

Thin Films

To synthesise uranium silicide thin films, samples have been engineered through co-deposition of uranium and silicon via DC magnetron sputtering within a dedicated actinide deposition chamber at the University of Bristol (Figure 2). DC magnetron sputtering involves the acceleration of gaseous ions towards a target material. Upon collision with the target material, the ions cause an ejection of sputtered atoms which condense onto a chosen substrate, forming the desired thin film.

2θ (°) 2400 - 6.5W - 5.5W 2000 - 3.5W U₃Si $U_{3}Si_{2}$ (a.u.) α-U Nb Intensity 800 800

Figure 5: Uranium-Silicon binary phase diagram taken from [6].

Figure 6 indicates the crystallisation of U-Si phases when employing three varying uranium deposition powers. The ability to travel through the U-Si phase diagram has come from altering the uranium power rating, and therefore deposition rate. It is

Figure 6: a) U-Si deposited at 500 °C with a uranium power rating of 10.7 W, diffraction scan showed no evidence of U₃Si₂ crystallisation. b) XRD of U-Si thin films grown at 500 °C using varying uranium powers. Strong indication of multiple U-Si phases crystallising with a uranium deposition power of 6.5 W and 5.5 W, whereas 3.3 W only produces α -U. Film deposited at 5.5 W is shown to produce Bragg reflections of the (001), (201), (211), and (002) of U₃Si₂.

2θ(°)

Figure 2: a) Image of actinide deposition chamber at the University of Bristol. b) Schematic showing the process of DC magnetron sputtering. This PVD technique is used to fabricate thin film samples.

By controlling the voltage supplied to the target, the sputtering deposition rate of both target materials can be altered. To determine the deposition rates, calibration samples have been analysed using x-ray reflectivity (XRR), as shown in Figures 3 & 4. Target voltage, and therefore deposition rates can be selected to deposit in the stoichiometry of the desired U-Si phase.

however apparent that the formation of U-Si phases is limited at 3.3 W.

These conditions were trialled on an epitaxially matched substrate, YVO₄. This compound has a 4% lattice mismatch from U_3Si_2 (a,b = 7.33 Å). Figure 7 indicates the diffraction data for the YVO₄ sample. There is a high indication of oxygen contamination with the presence of UO_2 .

Figure 7 (right): U-Si deposited at 500 °C with a uranium power rating of 5.5 W on a YVO_4 (100) single crystal substrate. Diffraction scans indicates the separation of phases alongside oxidation due to the presence of UO_2 .

Future Work

By optimising both the uranium and silicon deposition rates using XRR, there has been some success in the crystallisation of U₃Si₂. However, in order to fully characterise these U-Si phases, considerable work is required in engineering single crystal samples of U_3Si_2 . This will be achieved with an extensive study trialling epitaxial matches with the tetragonal structure of U_3Si_2 .

Figure 3: X-ray reflectivity scan of uranium Figure 4: X-ray reflectivity scan of silicon deposited on a Corning glass substrate. Data deposited on a Corning glass substrate. Data fitted using Gen-X [10]. Deposition rate fitted using Gen-X [10]. Deposition rate calculated to be 0.21 Ås⁻¹. calculated to be 0.14 Ås⁻¹.

Once engineered, the structural, chemical, and thermophysical properties of single phase U₃Si₂ thin films will be characterised using XRD and XPS. This study will then be extended to the remaining U-Si phases. Following this, the effect of irradiation on the thermophysical properties of single phase U-Si thin films will be investigated using ion-irradiation, and measured using an in house 3ω device.

Figure 8: Tetragonal structure of U₃Si₂, uranium represented with green spheres and silicon represented with blue. Image produced using data from [11] in Vesta.

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Computational Studies of Incorporation of Actinides and Ce into Zirconolite

<u>Jonathan Tanti</u>, Nikolas Kaltsoyannis

jonathan.tanti@manchester.ac.uk

Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL

1. Background

A potential long-term solution to the build-up of spent nuclear fuel is to immobilise and safely sequester it, through underground containment/disposal, from the biosphere.

Immobilisation requires the atomistic replacement of constituents of the proposed waste form by radioactive atoms, such as Pu.

Fig 1. The 88-atom unit cell

of zirconolite.

Colour key: dark blue - Ca,

green - Zr, light blue - Ti and

red - 0.

4. Substitution Energies

Substitution energies are calculated as:

 $E_{sub} = E_{An_{Zr}^{x}} + E_{Zr^{4+}} - (E_{Zirconolite} + E_{An^{4+}})$

where $E_{An_{Zr}^x}$ is the energy of the substituted cluster within the PEECM, E_X is the energy of cation X, and $E_{Zirconolite}$ is the energy of the unsubstituted zirconolite cluster.

Strong correlations have been found between the substitution energy and the ratio of ionic radii of the substituent actinide and the substituted ions for both Zr- and Ca-substituted systems. Across the actinide series, the substitution energy is positive and decreases with a reduction of the radius ratio.

The ceramic zirconolite (CaZrTi $_2O_7$), shown in figure 1, has been identified as a candidate waste form for Pu.

Zirconolite is able to accommodate actinides on its Zr and Ca sites, with cations such as Fe³⁺ able to occupy the Ti-site for charge balancing.

Through use of the Periodic Electrostatic Embedded Cluster Method (PEECM) and hybrid DFT, computational analysis of energetic and structural properties can be performed.

In the PEECM, the zirconolite lattice is separated into 3 distinct regions. These regions are the quantum mechanically treated local cluster, the intermediate region and an infinite periodic region of point charges. Using the PEECM allows for the use of hybrid functionals which better describe insulators such as zirconolite compared to GGA functionals such as PBE.

The local cluster (Fig. 2a) is made up of 110 atoms. Within this region, 17 atoms (2 Ca, 9 O, 4 Ti and 2 Zr) are free to move during geometry optimisations.

The intermediate region (Fig. 2b) surrounds the local cluster and is used to prevent over-polarisation of the local cluster. It contains effective core potentials on the cations (Ca²⁺, Zr⁴⁺ and Ti⁴⁺) and (2-) point charges (not shown in Fig 2b.) in place of the oxygen atoms.

The presence of differing oxidation states for Pa, Am and Ce causes a large shift in the radius of said ions compared to the M(IV) state. Defined correlations to not take these outliers into account.

Similarly strong correlations for double substitutions were found. 2x Zr-substitutions: $R^2 = 0.971$, 2x Ca- $R^2 = 0.994$.

5. Redox Behaviour of Oxidised Species

To understand the oxidation behaviour of Pa and U seen from the spin density data, a model system was used in which all but one (or two - for doubly substituted systems) Ti ion is substituted for Ge ion. This remaining site was changed until integer reduction of a Ti ion was found.

Both the cluster and the intermediate region are embedded into an infinite, periodic region of point charges. This region (Fig. 2c) recreates the Madelung potential of the bulk of the system.

TURBOMOLE 7.2 was used in conjunction with the PBE or PBE0 functionals. def2-SVP basis sets on all atoms smaller than Th (inclusive), def-SV(P) for atoms larger than Th. Default small-core ECPs (def2-ecp or def-ecp) have been used for Zr and all larger atoms.

Figures 2a-c. The local cluster, intermediate region and the point charge region of the zirconolite structure. Large spheres represent QM treated atoms, medium spheres represent full-electron ECPs and small spheres represent point charges.

3. Spin Density

While the majority of substituent actinides are present as An(IV), some alteration

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Ti(1) (blue in Fig. 3) was found to have been reduced, while substituent Pa was oxidised. For double substitutions, both Ti(1) and Ti(2) (navy in Fig. 3) were

reduced when both substituent ions (Pa and U) were oxidised. Both of these Ti sites are 5-coordinate with oxygen, with all but one other Ti site being 6-coordinate.

Changing the charge compensating ion in systems with substitutions onto Ca-sites to redox-inactive Al^{3+} gives a clearer understanding of the behaviour of reduced substituents when compared to the use of Fe³⁺.

Spin density data shows that oxygen ions in the centre of the cluster are partially oxidised when Pu, Am and Ce are reduced.

Fig 3. The local cluster of the Ge-containing Zirconolite system. Pink and purple indicate Zr(A) and Zr (B), blue and navy represent the reduced Ti(1) and Ti(2) sites.

6. Conclusions

Small differences are seen in the electronic structure of zirconolite following the

in oxidation state is seen.

Pa is generally oxidised to Pa(V) in most systems and Am is reduced to Am(III) whenever it is substituted onto a Ca site.

Ce and Pu exhibit very similar redox behaviour when substituted onto a Ca site.

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Substituted site	Ce	Th	Pa	U	Np	Pu	Am
Zr (Site A)	-	-	<u>0.00</u>	1.96	2.94	3.96	5.00
2x Zr (Site A)	-	-	<u>0.01</u>	1.95	2.95	3.95	5.00
2x Zr (Site B)	-	-	<u>0.00</u>	<u>1.08</u>	2.91	3.94	4.99
Ca (Site C)	<u>0.99</u>	0.00	0.96	1.98	2.97	<u>4.91</u>	<u>5.91</u>
2x Ca (Site C)	0.02	0.00	0.96	198	2.98	4.02	<u>5.91</u>
2x Ca (Site D)	0.03	0.00	<u>0.04</u>	1.96	2.97	4.00	<u>5.88</u>

Table 1: Spin Density data for single and double substitutions onto Zr and Ca sites.

introduction of f-element defects. This difference is larger for Ca-substituted systems, presumably due to the additional substitution of Fe³⁺ for charge balancing. Introduced f-orbital states decrease in energy across the actinides.

A correlation between the radius of the substituent atom and the substitution energy is seen across the actinides. Redox behaviour of earlier and later actinides has been found and analysed through the use of spin density data.

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