Introduction

TRANSCEND

The medium-lived radioactivity in spent fuel mostly consists of Cs-137 and Sr-90, which need to be extracted from nuclear waste streams and ponds. By using ion-exchange materials these radionuclides can be isolated into a solid ceramic phase cost-effectively, easily and consistently. The SIXEP plant at the Sellafield site currently uses the natural zeolite clinoptilolite ("clino") as an ion-exchanger, but this is a finite resource so work is ongoing to find a successor.

A potential candidate is the tin analogue of the natural zirconosilicate mineral umbite. Previously, we have seen that by doping the octahedral tin(IV) sites with elements of a greater charge (V) the materials show enhanced uptake of Cs and Sr cations from solution. Our current research is focused on assessing the applicability of Sb-doped tin umbites in industry, regarding synthesis and ion exchange performance. In particular, we are interested in the selectivity of Cs and Sr uptake at varying pH and against competing cations that are present in nuclear waste streams.

New materials and methods for decontamination of effluent

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> Clinoptilolite (Clino) $Na_{6}[Al_{6}Si_{30}O_{72}](H_{2}O)_{9}$

Tin Umbite $K_2 SnSi_2O_9 \cdot H_2 O$



Figure 1. The structures of clinoptilolite (left) and tin umbite (right). Both viewed down the *c* axis.

Optimising synthesis conditions 2.

To adapt the synthesis of the doped tin umbite to be more appropriate for larger scale production, we have studied the influence of reduced synthesis time and temperature.

The typical synthesis of Sb-doped tin umbite involves heating the reagents under hydrothermal conditions at 200°C for 24 hrs (a) – figure 2 shows the powder X-ray diffraction pattern. By reducing the temperature to 150°C the umbite still crystallise s(b). At 200°C we have reduced the synthesis time to 3 hours, by introducing seeds of previously prepared umbite crystals (5% mass) to the synthesis (c). Without these seed crystals, the product has a much lower crystallinity (d).





Ion exchange performance? 3.

Although we have prepared the doped tin umbite using varied synthesis techniques, we need to ensure that the Cs exchange capacity at low concentrations is retained. To evaluate the ion exchange performance of the Sb-doped tin umbite we performed exchanges with a 10 ppm Cs. Figure 3 shows how the crystalline samples show no significant change in the Cs exchange capacity, irrespective of how the sample was prepared. In contrast, the poorly crystalline sample (200°C 3 hrs) shows a significantly reduced uptake of Cs, however is it still sufficient at 80% Cs removal from solution.











Figure 2. Power x-ray diffraction patterns of samples and SEM micrographs of samples a-d

Poorly crystalline, irregular

"amorphous" aggregates

Crystalline (Sb)-Tin Umbite

Size /µm

1.65 ±0.23

1.09 ±0.15

1.50 ±0.31

Figure 2 also shows SEM images of the samples. The Sb-doped tin umbite grows into regular crystals of approximately 1.5 µm diameter (a-c). The poorly crystalline sample (d) appears as much larger, irregular aggregates, typical of amorphous silica.

These samples were then used for ion exchange experiments, to assess how the variation in synthesis effects the exchange performance. The poorly crystalline sample (d) was tested to observe if the materials need to be crystalline to express selective uptake of Cs and Sr.

Figure 3. Cs Removal % from a 10 ppm Cs solution.

How fast does the umbite exchange?

The rate of Cs uptake was assessed for sample (a) 200°C 24 hrs from a 10 ppm Cs solution. Over 80% uptake was seen in the first 30 seconds of contact, and equilibrium was achieved within approximately 5 minutes (figure 4). This is much quicker than the 6 hours seen for both pretreated and untreated clino . (M.Y. Prajitno et al., J. Environ. Chem. Eng., 2019, 8, 102991; I. Smičiklas et al., Appl. Clay Sci., 2007, 35, 139-144)



Figure 4. Cs Removal % from a 10 ppm Cs solution over time – first 6 mins (left) and over 24 hours (right).

Conclusions and Future Work 5.

Doped tin umbites are promising materials that show enhanced uptake of Cs compared to clino. The umbites show both rapid uptake of Cs and a retention of exchange capacity with reduced synthesis time/temperature. To perform a more pragmatic evaluation of these materials for industrial use, we plan to perform ion exchanges with Sr as the target ion, as well as exchange at different solution pH and in the presence of competitors – K, Na, Mg and Ca. We also intend to run exchange experiments using a column flow setup, to study the breakthrough curves of Cs and Sr. Furthermore, we are undertaking continuing research to find other new candidate materials for waste remediation.

Acknowledgements 6.

We thank the EPSRC for funding under the TRANSCEND project. We thank Norman Day and Chris Stark for help with the ICP-MS measurements. We also thank Ryan George and James Reed for their contribution to this research.



Transformative Science and Engineering for Nuclear Decommissioning





High-fidelity simulation of behavioural modification techniques for nuclear waste transport flows L. F. Mortimer & M. Fairweather

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1. Introduction

- · Multiphase 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.



• We also model a polymeric phase, which can modify both the fluid and solid behaviour. Phenomena such as turbulent drag reduction and flocculation is demonstrated studied computationally.

3. Finitely extensible non-linear elastic dumbbell polymer model



- Polymers are represented as a sequence of beads connected by nonlinear springs.
- Forces are solved for and iterated 1000 times per fluid timestep, as the dynamics of the polymeric phase take place across much smaller scales.

4. Lagrangian particle tracking



- Standard four-way coupled LPT techniques, which accounts for fluid-particle, particle-fluid and particleparticle interactions.
- Extended to account for polymer-particle interactions.

5. Polymeric validation and turbulent drag reduction

Polymers were dispersed in both laminar shear and turbulent channel flows to study the effect of both the fluid on polymer configuration and the polymeric phase on the turbulence properties of the fluid.



5. Adhesion and polymer-particle interaction



- Electrostatic interaction between charged beads and particle surfaces used to predict polymerparticle interaction.
- Upon colliding with a bead, under certain electrostatic conditions the bead will stick to the particle.
- Spring force is then applied to the particle from any bead neighbours which are connected to the 'stuck' bead.
- Particles are then capable of agglomerating with each other with a polymer buffer holding them together.

 y^+

R/l

(Upper-left): Probability density distribution functions of mean polymer extension in shear channel flow simulation for Wi = 1.3, 6.3 and 76. Results are compared with experimental data from *Smith et* al. (1999).

(Upper-right): Mean streamwise velocity normalized by shear velocity, u_{τ} , for turbulent channel flow at Re_{τ} =180.

(Lower-left): Root-mean-square of velocity fluctuations normalized by shear velocity, $u_{ au}$, for turbulent channel flow at Re_{τ} =180.

(Lower-right): Probability density distribution functions of mean polymer extension in turbulent channel flow simulation. Comparison of polymers located within individual flow regions.

6. Conclusions & further work

- DNS-LPT used to study polymer/particle-laden flows and develop understanding behind behavioural modification techniques in such flows.
- Effect of modifying parameters such as pH and temperature will be vital to developing such techniques.
- Polymer and particle-laden turbulent fluids will be simulated to further explore behavioural modification through injection of polymer additives.







Simulation of behavioural modification effects in suspension waste pipe 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 emission, sustainable and affordable electricity. The waste products of most nuclear energy generation are radioactive. Safely disposing of these radioactive materials requires expertise, and implementation of scientifically robust, innovative approaches to decommissioning and waste management. Improved processing methods are vital for both legacy and new build wastes.

Ź

Instantaneous stream-wise particle velocity

0.2 normalized by bulk velocity (U_b) in 3D. 0.0



Motivation and Objective:

The overall aim of this study is to address fundamental difficulties that are encountered by the nuclear industry. Developing and facilitating approaches for safer, cost efficient waste

management and decommissioning is the focus of the research.

Understanding and modelling pond and silo sludge behaviour is essential to the management of radioactive wastes. In the legacy ponds and silos, characterising how sludges and slurries containing dense particulates will behave is vital for post operational clean out (POCO) operations. In this project, we aim to establish a predictive tool to support POCO operations, using first principles mathematical modelling, to improve the flow, mixing and separation of wastes during retrieval and POCO processes. Behavioural modification effects in suspension waste pipe flows will be simulated, i.e. the use of modifications to fluid and solid particle properties to promote a desired outcome such as reducing particle agglomeration, and hence, the likely deposition of particles during processing.

Governing Equations:

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

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

where $Re_b = u_b D/\nu$ is the bulk Reynolds number, u_b is the bulk mean velocity, D the pipe diameter and ν the kinematic viscosity.

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

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

Computational mesh and pseudo-colour visualisation of the instantaneous axial velocity. Panels: (a) is the computational mesh with Gauss–Lobatto–Legendre quadrature points (N = 7) for both simulations at $Re_{\tau} = 180$ and $Re_{\tau} = 361$, (b) & (d) and (c) & (e) are the instantaneous streamwise velocity normalized by the bulk velocity $U_{\rm b}$ of simulations at Re_{τ} = 180 and Re_{τ} = 361, respectively.

Fluid and Particle Results:

The predictions have been validated and compared with literature simulations and experimental datasets. The outcomes are in good agreement with literature results. Using these fully developed multiphase flows, the plan now is to simulate and track different polydisperse and irregular shaped particles.



(a) Inner scaled statistical profiles mean and (b) root mean square of a DNS at $Re_{\tau} = 361$. The axial, z_{rms}^{*} ,

A solution for the unknown p, u, v and w is sought using the continuity equation, $\nabla \cdot u = 0$ and boundary conditions.

The non-dimensional equations of motion is given by:

 $\frac{\partial x_p^*}{\partial t^*} = \boldsymbol{u}_p^*$ $\frac{\partial u_p^*}{\partial t^*} = \frac{3C_D |u_s^*|}{4d_p^* \rho_p^*} u_s^* + g^* (1 - \rho_p^*) + \frac{3C_L}{4\rho_p^*} (u_s^* \times \omega_F^*) +$ Virtual Mass Pressure Gradient Lift Drag Gravity

Methodology:

To solve the descriptive equations in a direct numerical simulation the computational fluid dynamics solver Nek5000 has been used. This solver is based on the spectral element method that is a high-order weighted residual technique. Nek5000 is favourable due to its high accuracy, and low numerical dispersion and dissipation, and is easily and efficiently parallelisable.

To investigate the bulk behaviour of high concentration dispersions, a Lagrangian particle tracker has been developed to model large quantities of dispersed solids which runs concurrently with Nek5000. And then, a fourth order Runge-Kutta method implemented to solve

radial, r_{rms}^* , azimuthal, θ_{rms}^* , and Reynolds shear stress, $\langle u_z | u_r \rangle^*$, as a function of $(1-r)^*$ compared against the following DNS and experimental datasets. — Solid lines are present DNS result, – – dashed lines are El Koury DNS, \circ open circles are Toonder experiment at $Re_{\tau} \approx 315$ and + crosses are Singh DNS $Re_{\tau} \approx$

323.



(a) Inner scaled statistical particle mean velocity profiles of a DNS at $Re_{\tau} = 361$. (b) Statistical particle profiles, root mean square of velocity fluctuations of a DNS at $Re_{\tau} = 361$. The axial z_{rms}^* , radial r_{rms}^* and Reynolds shear stress $< u_z u_r >^*$ are shown. — Solid line and - - dashed lines are current work, and o and + markers are Sarma DNS.

Planned works:

- Investigate the settling and deposition be haviour of suspensions of dense particles
- Modelling and understanding pond and silo sludge behaviour behavioural modification techniques using first principles used to examine effects of flow and solid property changes on particle-laden flow characteristics

the particle equation of motion for each particle within every time-step. The particles are injected at random position within the fully developed fluid flow domain and assigned the mean fluid velocity at that location. Particles collision with the pipe wall considered to be elastic, i.e. the total kinetic energy remains the same and a periodic boundary condition applied in the streamwise direction. Their statistical data gathered for analysis after letting a few response times to adjust to the surrounding fluid.

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- TRANSCEND proposal







Research Aims

TRANSCEN

The aim of this project is to simulate the effects of radiation on sludges. Simulations will be run of the effects of excitons and other particles formed through irradiation (mainly gamma) of metal oxide/hydroxide nanoparticles, on surrounding water media; i.e. the effects on hydrogen production and water radiolysis. The energy transfer across the nanoparticle-water barrier will be calculated and then the resultant chemical changes will be modelled.

Water Radiolysis



Exciton Transfer Figure 1 is lacking the consideration of exciton transfer and it's effects; allowing for this consideration will form a part of this project. Exciton Production





50 nm NP irradiated by 50, 100, 150, 250 and 500 keV photon beams

Secondary particles recorded in phase space file Secondary particles transported





Figure 1 – The three pathways of nanoparticle (NP)/water radiolysis and the subsequent HO[•]. Taken from **[1]**.



50 nm NP

600 nm waterHollow water sphereparticleHollow of 50 nmSphere of 650 nm

50 nm spherical space within 650 nm hollow water sphere

Energy deposit recorded

In the NP the **PENELOPE** physics list was used; meaning that the code list is designed for low-energy models of electrons and photons.

In the water particle and hollow water sphere the **Geant-4 DNA** physics list was used; which specifically looks at simulating water.

Figure 3 – Schematic showing the development and key features of the hollow sphere model used

Research Progress

- Initially a basic simulation method of depositing radiation into a NP, and calculating the subsequent dose deposition was developed using the TOPAS software.
- This was then further developed to be more realistic; depositing radiation into a NP

Figure 4 – Graphs showing the radial dose distributions per incident photon for a) Au, b) AI_2O_3 , c) $Mg(OH)_2$ and d) Water nanoparticles irradiated by 50, 100, 150, 250 and 500 keV gamma beams.

Initial Results

Figure 4 shows the dose distribution produced by Au, Al_2O_3 , $Mg(OH)_2$ and Water nanoparticles per incoming photon. Figure 4a shows that the dose deposited by AuNPs is higher than that of Al_2O_3 , Water and $Mg(OH)_2$ NPs by a factor of 10^3 . The average dose generated by a 50 keV photon is significantly higher than those of greater keV photons for all NPs, suggesting that secondary electrons caused by lower energy kilovoltage photons have the longest range in water. The Al_2O_3 , $Mg(OH)_2$ NPs showed little increase in dose deposition over water at these energies, this could be due to the low density of the NPs resulting in a lower rate of interaction with the radiation.

So far the simulations have only been run once a relatively low number of primaries, by running more simulations at a higher number of primaries and applying Poisson statistics a clearer an more populated view should be produced.

within a hollow water sphere.

• Both simulations were run with various NP types (Au, Al₂O₃, Mg(OH)₂ and Water).

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Future Plans

- Improve noise and population on graphs by running more simulations and applying Poisson statistics.
- Currently developing a scorer to detect the ionisations and excitations caused by electrons in water.
- Incorporate the use of Geant4-DNA chemistry into the model.







Durability of Magnesium Silicate Hydrate Based Cements made from Brucite

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M-S-H is a recently developed cement

 $MgO + SiO_2 + H_2O \rightarrow M-S-H$

Fuel Ponds at Sellafield contain magnesium hydroxide (brucite) – rich sludge which could replace the magnesium component of M-S-H as encapsulating cement and therefore lead to a reduction in waste volume

Aim of the PhD:

- Determine if sludge can be used in cement

- Understand the properties of that cement

11 Magnox powerplants were built at 7 sites over a 20-year

ILW in the UK

Others



period in the UK [1]. The last Magnox reactor (Wylfa) closed in 2015 [2].

Operation and decommissioning of nuclear power plants generates a range of wastes, which are classified according to how much activity it contains.

Intermediate level waste (ILW) is classified as waste whose activity exceeds the upper boundaries of low-level waste without generating significant heat [3]. It includes plant items and equipment, fuel cladding, reactor components and commissioned waste (fig 1) [3].

The UK plans to store ILW in geological disposal facilities [4]. The waste is required to be stored as a solid [4]. To convert ILW into a solid it is mixed into a material such as cement and stored in 500L drums made from steel (fig 2) [3]. Four 500L drums are placed in stillages for handling, transport and storage.

Magnox swarf is generated when uranium fuel is stripped from its cladding (fig 3, 4) [5, 6]. Spent fuel and cladding is removed from reactors [5, 6]. It is then stored in water in the storage silos (fig 5) [5, 6]. The swarf corrodes and forms a brucite sludge [5, 6].



- Activated Metals
- Conditioned Waste
- Contaminated Metals
- Contaminated other
 Materials
 Flocs

Fuel Cladding and
 Miscellaneous Wastes
 Graphite

Mixed Wastes

Plutonium Contaminated Materials

Figure 2: Cut out showing the encapsulation of ILW in a containment drum [3]







Figure 3 (above): Magnox Fuel Rod [14]



What is already known about M-S-H:

- Properties of raw materials control strength and development of M-S-H [7]
- Additives can improve formation rate and M-S-H properties [8]
- Optimum Mg/Si ratio for M-S-H production: 0.67 1 [9]
- Likely final M-S-H composition: M1.4SH2.65 [10]
- Structure: highly amorphous disordered intermediate phases in layered sheets [9]
- MgO dissolves within first 10 days [11]
- MgO + H2O \rightarrow Mg(OH)2 [12]
- Microsilica dissolves during first 28 days [11, 13]
- Brucite forms around silica, creating M-S-H [11]
- Mg(OH)2 + SiO2 → M-S-H [13]

PhD 'Process':

Understand the formation of M-S-HInvestigate three different systems



Figure 6: Compressive strength of 40% MgO/60% silica fume samples (Initial system) – red point indicates results from replication of the system [17]



Figure 4 (left): Magnox Swarf (ILW) [15]

Figure 5 (right): Storage Fuel Pond at Sellafield [16]

Work already done:

- Initial system (MgO-SiO2) has been produced and strength tested (figs 6, 7)
- Research into what is already known about M-S-H
- Planning future work prioritising properties most relevant to encapsulation

Future work to be conducted: Characterisation tests, including:

- Stiffness
- Dimensional Stability
- Setting and Hardening
- Fluidity
- Permeability

Tests to determine how M-S-H behaves in adverse environments

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- Initial System: MgO-SiO₂ (Diamond consortium)
- Second System: Mg(OH)₂-SiO₂ to understand the formation and properties of M-S-H made from brucite
- Third System: CMgS-SiO₂ to understand how the brucite sludge itself may behave when incorporated to form M-S-H

Figure 7: Images showing the external appearance and internal macrostructure of the initial system (before and after compressive strength test)

Transformative Science and Engineering for Nuclear Decommissioning

How does the degree of crystallinity in a glassceramic affect radiation tolerance? Tamás Zagyva¹ Supervisors: Laura Leay¹, Brian O'Driscoll¹, Tracey Taylor² ¹The University of Manchester ²National Nuclear Laboratory Correspondence: tamas.zagyva@postgrad.manchester.ac.uk

1. Introduction

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 the stored highly active liquors resulting in several high-level waste product canisters (Fig. 1) [1,2].

Ca/Zn glass (frit) is planned to be used for the vitrification of high-level nuclear waste with high molybdenum content [1,2].

The different volume changes caused by the swelling of both the crystal and glass phases under irradiation may affect the long-term durability (e.g. cracking) [3]. Therefore, the radiation tolerance analysis of Ca/Zn glass-ceramics is crucial and will be examined in this project.

Ca/Zn glass-ceramic

Ca/Zn borosilicate glass can incorporate more (up to 12 wt%) molybdenum than MW glass via the in-situ formation of a durable molybdate crystal in the glass matrix called powellite [2].

2. Vitrification Test Rig (VTR) samples

VTR is a full scale <u>non-active</u> replica of the Waste Vitrification Plant process lines. It was used for demonstrating the final glass-ceramic waste form (Fig. 2, 3) [1,2]. VTR samples showed several crystalline phases, however the dominant phase was powellite with varying sizes.

3. Ca/Zn glass-ceramic samples

Simple Ca/Zn glass and glass-ceramic (GC) samples (with only powellite crystal phase) have been made at Sheffield Hallam University for later irradiation experiments (Fig. 4). Additional glass-ceramics with different crystal sizes (similar to the VTR samples) will be made.

Next steps

- Heavy-ion irradiation experiments will be conducted on Ca/Zn glass-ceramics (with different crystallized volume fractions and crystal sizes) to simulate α-recoil damage.
- Pre- and post-irradiated samples will be analyzed by several methods (e.g. XRD, SEM, XAS, Raman, EPR spectroscopy).

4. Acknowledgements

Special thanks to Paul Bingham and Prince Rautiyal for the help in glass making, Chetna Tyagi for the XRD measurements and Györgyi Glodán for the help in SEM analyses. I am also grateful to Mike Harrison for the guidance and for the provided Ca/Zn glass frit.

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Transformative Science and Engineering for Nuclear Decommissioning

Process Monitoring and Reducing Emissions During Thermal Treatment of Radioactive Waste A. Stone, A. Holloway, D. McKendrick, A. Nabok, P. Bingham

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Aims

- To develop a system for real time gas analysis from vitrification of intermediate level waste (ILW) from the UK sites.
- Control and constrain emissions by alteration of melt conditions such as temperature, composition and .

The Problem

ILW has many different compositions and can contain a wide range of materials from masonry and cement to sludges and ion exchange resin (IEX). The nature of ILW means that there is a variety of off gases that can be emitted when this waste is heat treated by vitrification, the current preferred method for nuclear waste processing in the UK. Most radionuclides, dioxins and furans are toxic to humans and can contaminate wildlife.

Some combustion gases contribute to climate change and NOx can be very hazardous causing lung disease in humans. Given the hazardous nature of these off gases it is important to limit our emission of these to atmosphere but first we must quantify how much of is produced during the process of vitrification.

Extraction

Glass Technology

Vitrification of nuclear waste is essentially glass and glass-ceramic preparation to temperatures usually over 1000°C. Glass making sessions are vital to understand the off-gases that have been emittted. A glass composition for imitation of ILWs in the UK must be established so as to produce emission spectra similar to that of the actual vitrification tanks in use. Simulant wastes have been formulated to closely mimic some of the common materials in the wasteforms at Sellafield

The Future

Ultimately the end goal will be to test an active vitrification system with a fully validated setup however there are many steps that need to be taken to get here. Firstly a baseline of emissions on a developed test rig must be established. Then a candidate technology must be selected and tested to conform with the previous results. Another avenue of research after this system has been developed will be to alter the melting system to

Volatility

The volatility of the waste components is very important for validating the systems to be used for gas measurement and controlling the escape to atmosphere. A comparison of the ability of radionuclides to remain in glass after vitrification is shown above. The volatility of some species commonly found in the wasteforms is incredibly high especially when considering the high temperatures involved with vitrification. Because of this cesium, iodine and chlorine are of particular interest.

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Transformative Science and Engineering for Nuclear Decommissioning

Vitrification Of Ionsiv as Sodium Titanosilicates

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 Sodium Titanosilicates chosen due to their use in the industry already as ion exchangers from the removal of Cs

TRANSCEND

- The ion exchanger chosen to model glass chemistry off is lonsiv IE-911 due to its prevalence in the literature
- 6 chemistries were made that fell within the Si, Na, Ti phase diagram from Richet et al. 2006 ranging from Ti values of 911 and then decreasing
- IE-911 melt crystallised upon pouring (which isn't too surprising as it sits along the glass forming boundary from Richet et al. 2006).
- The glasses that formed nearest to the Ionsiv IE-911 vitrified but show what looks to be phase separation and in one some localized crystallisation.

CTS structure with Cs exchanged into its tunnel sites created in CrystalMaker from CIF file From Tripathi et al 2003/

Titanosilicate (TS) glass series 1-6 with 1 having the same stoichometry as Ionsiv IE-911

- XRD analysis has been conducted displaying diffuse amorphous scattering for the glass samples and a peaks for the crystallised samples
- RAMAN data has been collected on some of the samples, but the results have yet to be analysed
- The work going forward will involve loading different Cs amounts (0.25, 1 & 2 Mol%) into each glass and seeing the how much loading and retention is possible.

Oxide mol% RMM wt wt.% RMM TiQ2 53.33 79.87 4259.24 59.98 79.87 Na2O 20.00 61.98 1239.58 17.46 108.99 SiO2 26.67 60.08 1602.33 22.56 60.08 TOTAL 100.00 221.56 7101.15 100.00 70.21 Oxide mol% RMM wt wt.% RMM TiO2 8.88 79.87 709.21 9.99 79.87 Na2O 39.72 61.98 2461.80 34.67 108.99 SiO2 51.40 60.08 3088.11 43.49 60.08 TOTAL 100.00 221.56 6259.12 88.14 108.99 SiO2 32.45 79.87 2591.65 36.50 79.87 Na2O 28.62 61.98 1773.84 24.98 108.99 SiO2 38.93 60.08 2338.91 32.94 60.08	IONSIV-IE911						
TiQ253.3379.874259.2459.9879.87Na2O20.0061.981239.5817.46108.99SiO226.6760.081602.3322.5660.08TOTAL100.00221.567101.15100.00100.00TS2Oxidemol%RMMwtwt.%RMMTiO28.8879.87709.219.9979.87Na2O39.7261.982461.8034.67108.99SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.14100.99TOTAL100.00221.566259.1288.14108.99SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.14108.99SiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41108.99SiO252.8060.083172.2244.6760.89TOTAL100.00221.566422.9990.45108.99SiO252.8060.083172.2244.6760.88TOTAL100.00221.566906.6797.26108.99SiO232.0760.081926.7727.1360.08	Oxide	mol%	RMM	wt	wt.%	RMM	
Na2O 20.00 61.98 1239.58 17.46 108.99 SiO2 26.67 60.08 1602.33 22.56 60.08 TOTAL 100.00 221.56 7101.15 100.00 700.01 TS2 Oxide mol% RMM wt wt.% RMM TiO2 8.88 79.87 709.21 9.99 79.87 Na2O 39.72 61.98 2461.80 34.67 108.99 SiO2 51.40 60.08 3088.11 43.49 60.08 TOTAL 100.00 221.56 6259.12 88.14 79.87 Na2O 28.62 61.98 1773.84 24.98 108.99 SiO2 38.93 60.08 2338.91 32.94 60.08 TOTAL 100.00 221.56 6704.40 94.41 79.87 Na2O 29.01 61.98 1798.01 25.32 108.99 SiO2 52.80 60.08 3172.	TiO2	53.33	79.87	4259.24	59.98	79.87	
SiO226.6760.081602.3322.5660.08TOTAL100.00221.567101.15100.00TSUOxidemol%RMMwtwt.%RMMTiO28.8879.87709.219.9979.87Na2039.7261.982461.8034.67108.99SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.1480.00TOTAL100.00221.566259.1288.1499.93SiO232.4579.872591.6536.5079.87Na2028.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.4194.41TIO218.1979.871452.7620.4679.87Na2029.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.4579.87Na2029.0161.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.6697.87Na2024.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TO	Na2O	20.00	61.98	1239.58	17.46	108.99	
TOTAL 100.00 221.56 7101.15 100.00 TS2 Oxide mol% RMM wt wt.% RMM TiO2 8.88 79.87 709.21 9.99 79.87 Na2O 39.72 61.98 2461.80 34.67 108.99 SiO2 51.40 60.08 3088.11 43.49 60.08 TOTAL 100.00 221.56 6259.12 88.14 60.08 TOTAL 100.00 221.56 6259.12 88.14 60.08 TOTAL 100.00 221.56 6259.12 88.14 60.08 TO2 32.45 79.87 2591.65 36.50 79.87 Na2O 28.62 61.98 1773.84 24.98 108.99 SiO2 38.93 60.08 2338.91 32.94 60.08 TOTAL 100.00 221.56 6704.40 94.41 94.91 TiO2 18.19 79.87 1452.76 2	SiO2	26.67	60.08	1602.33	22.56	60.08	
TS2Oxidemol%RMMwtwt.%RMMTiO28.8879.87709.219.9979.87Na2O39.7261.982461.8034.67108.99SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.14100.00TS3Oxidemol%RMMwtwt.%RMMTiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.08233.89132.9460.08TOTAL100.00221.566704.4094.41100.99SiO238.9360.083172.2244.6760.08TIO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TIOTAL100.00221.566422.9990.45108.99SiO252.8060.083172.2244.6760.08TIO213.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TIOTAL100.00221.566906.6797.26108.99SiO232.0760.081926.7727.1	TOTAL	100.00	221.56	7101.15	100.00		
Oxidemol%RMMwtwt.%RMMTiO28.8879.87709.219.9979.87Na2O39.7261.982461.8034.67108.99SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.14TS3Oxidemol%RMMwtwt.%RMMTiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41TiO218.1979.871452.7620.4679.87Na2O29.0161.981778.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45TS5Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26Total100.00221.566906.6797.26Total100.00221.566906.6797.26Total100.0	TS2						
TiO28.8879.87709.219.9979.87Na2O39.7261.982461.8034.67108.99SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.14TOTAL100.00221.566259.1288.14TOTAL100.00221.566259.1288.14TOTAL32.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41TOTAL100.00221.566704.4094.41TiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45TOTAL100.00221.566422.9990.45SiO252.8060.083172.2244.6760.08TOTAL100.00221.566906.6797.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26Cxidemol%RMMwtwt.%RMM<	Oxide	mol%	RMM	wt	wt.%	RMM	
Na2O 39.72 61.98 2461.80 34.67 108.99 SiO2 51.40 60.08 3088.11 43.49 60.08 TOTAL 100.00 221.56 6259.12 88.14 TS3 Oxide mol% RMM wt wt.% RMM TiO2 32.45 79.87 2591.65 36.50 79.87 Na2O 28.62 61.98 1773.84 24.98 108.99 SiO2 38.93 60.08 2338.91 32.94 60.08 TOTAL 100.00 221.56 6704.40 94.41 TS4 Oxide mol% RMM wt wt.% RMM TiO2 18.19 79.87 1452.76 20.46 79.87 Na2O 29.01 61.98 1798.01 25.32 108.99 SiO2 52.80 60.08 3172.22 44.67 60.08 TOTAL 100.00 <	TiO2	8.88	79.87	709.21	9.99	79.87	
SiO251.4060.083088.1143.4960.08TOTAL100.00221.566259.1288.14TS3Oxidemol%RMMwtwt.%RMMTiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41TS4Oxidemol%RMMwtwt.%RMMTOTAL100.00221.566704.4094.41TOTAL100.00221.566704.4094.41TiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.4579.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2679.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2679.87Na2O26.1461.981620.1322.811	Na2O	39.72	61.98	2461.80	34.67	108.99	
TOTAL 100.00 221.56 6259.12 88.14 TS3 Oxide mol% RMM wt wt.% RMM TiO2 32.45 79.87 2591.65 36.50 79.87 Na2O 28.62 61.98 1773.84 24.98 108.99 SiO2 38.93 60.08 2338.91 32.94 60.08 TOTAL 100.00 221.56 6704.40 94.41 Oxide mol% RMM wt wt.% RMM TIO2 18.19 79.87 1452.76 20.46 79.87 Na2O 29.01 61.98 1798.01 25.32 108.99 SiO2 52.80 60.08 3172.22 44.67 60.08 TOTAL 100.00 221.56 6422.99 90.45 90.45 TIO2 43.03 79.87 3436.63 48.40 79.87 Na2O 24.90 61.98 1543.27 21.73	SiO2	51.40	60.08	3088.11	43.49	60.08	
TS3Oxidemol%RMMwtwt.%RMMTiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41TS4VTS4Oxidemol%RMMwtwt.%RMMTiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08SiO234.8460.08209.1929.4860.08	TOTAL	100.00	221.56	6259.12	88.14		
Oxidemol%RMMwtwt.%RMMTiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41TOTAL100.00221.576704.4094.41TOTAL100.00221.566704.4094.41TOTAL100.00221.566704.4094.41TO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45TOTAL100.00221.566422.9990.45TIO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26Coxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TIO234.8460.082093.1929.4860.08	TS3						
TiO232.4579.872591.6536.5079.87Na2O28.6261.981773.8424.98108.99SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.41TS4TS4Oxidemol%RMMwtwt.%RMMTiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45-TS*Oxidemol%RMMwtwt.%RMMTiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45-Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26-Coxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.0820	Oxide	mol%	RMM	wt	wt.%	RMM	
Na2O 28.62 61.98 1773.84 24.98 108.99 SiO2 38.93 60.08 2338.91 32.94 60.08 TOTAL 100.00 221.56 6704.40 94.41 Oxide mol% RMM wt wt.% RMM TiO2 18.19 79.87 1452.76 20.46 79.87 Na2O 29.01 61.98 1798.01 25.32 108.99 SiO2 52.80 60.08 3172.22 44.67 60.08 TOTAL 100.00 221.56 6422.99 90.45 90.45 TOTAL 100.00 221.56 6422.99 90.45 98.7 SiO2 52.80 61.98 1543.27 21.73 108.99 SiO2 43.03 79.87 3436.63 48.40 79.87 Na2O 24.90 61.98 1543.27 21.73 108.99 SiO2 32.07 60.08 1926.77 27.13 60.08	TiO2	32.45	79.87	2591.65	36.50	79.87	
SiO238.9360.082338.9132.9460.08TOTAL100.00221.566704.4094.4160.08TS4Oxidemol%RMMwtwt.%RMMTiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.4590.45Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2697.87Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08SiO234.8460.082093.1929.4860.08SiO234.8460.082093.1929.4860.08	Na2O	28.62	61.98	1773.84	24.98	108.99	
TOTAL 100.00 221.56 6704.40 94.41 TS4 Oxide mol% RMM wt wt.% RMM TiO2 18.19 79.87 1452.76 20.46 79.87 Na2O 29.01 61.98 1798.01 25.32 108.99 SiO2 52.80 60.08 3172.22 44.67 60.08 TOTAL 100.00 221.56 6422.99 90.45 90.45 Oxide mol% RMM wt wt.% RMM TiO2 43.03 79.87 3436.63 48.40 79.87 Na2O 24.90 61.98 1543.27 21.73 108.99 SiO2 32.07 60.08 1926.77 27.13 60.08 TOTAL 100.00 221.56 6906.67 97.26 Oxide mol% RMM wt wt.% RMM TiO2 39.02 79.87 3116.36 43.89 79.87	SiO2	38.93	60.08	2338.91	32.94	60.08	
TS4Oxidemol%RMMwtwt.%RMMTiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.4560.08TSTOxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2660.08Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08SiO234.8460.082093.1929.4860.08	TOTAL	100.00	221.56	6704.40	94.41		
Oxidemol%RMMwtwt.%RMMTiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45-TSTOxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26-Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18-	TS4						
TiO218.1979.871452.7620.4679.87Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45-Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26-Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18-	Oxide	mol%	RMM	wt	wt.%	RMM	
Na2O29.0161.981798.0125.32108.99SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45	TiO2	18.19	79.87	1452.76	20.46	79.87	
SiO252.8060.083172.2244.6760.08TOTAL100.00221.566422.9990.45	Na2O	29.01	61.98	1798.01	25.32	108.99	
TOTAL100.00221.566422.9990.45TUTALID0.00SUSOxidemol%RMMwtwt.%RMMTIO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2697.26TUTALmol%RMMwtwt.%RMMTIO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18100.00	SiO2	52.80	60.08	3172.22	44.67	60.08	
TiS5Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2697.26Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18100.00	TOTAL	100.00	221.56	6422.99	90.45		
Oxidemol%RMMwtwt.%RMMTiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26TSEOxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18	TS5						
TiO243.0379.873436.6348.4079.87Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2697.26Coxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.1850.8	Oxide	mol%	RMM	wt	wt.%	RMM	
Na2O24.9061.981543.2721.73108.99SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.26TSSOxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18	TiO2	43.03	79.87	3436.63	48.40	79.87	
SiO232.0760.081926.7727.1360.08TOTAL100.00221.566906.6797.2697.26Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18100.00	Na2O	24.90	61.98	1543.27	21.73	108.99	
TOTAL100.00221.566906.6797.26SUBLETEROxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18	SiO2	32.07	60.08	1926.77	27.13	60.08	
TS6Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18	TOTAL	100.00	221.56	6906.67	97.26		
Oxidemol%RMMwtwt.%RMMTiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18			Т	S6			
TiO239.0279.873116.3643.8979.87Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.1856.18	Oxide	mol%	RMM	wt	wt.%	RMM	
Na2O26.1461.981620.1322.81108.99SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.18560.08	TiO2	39.02	79.87	3116.36	43.89	79.87	
SiO234.8460.082093.1929.4860.08TOTAL100.00221.566829.6896.1856	Na2O	26.14	61.98	1620.13	22.81	108.99	
TOTAL 100.00 221.56 6829.68 96.18	SiO2	34.84	60.08	2093.19	29.48	60.08	
	TOTAL	100.00	221.56	6829.68	96.18		

Phase diagram edited from Richet et al. 2006 with TS series 1-6 plotted on

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Glass compositions data used for creating the titanosilicates

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

Phase transformations of natural zeolites to improve Cs and Sr uptake from nuclear wastewaters

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Background

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 caesium and strontium radionuclides from effluent. Due to cost effectiveness, simplicity and selectivity, ion exchange materials, such as zeolites, are often employed. The anionic framework of interconnected SiO₄ and AlO₄ tetrahedra forms uniform channels and cavities, which often provides sites to trap cationic radionuclides. Zeolites also have high exchange rates as well as resistance to radiation, further adding to their appeal.^{1,2}

In the Site Ion Exchange Effluent Plant (SIXEP) at Sellafield, a clinoptilolite zeolite is packed in two columns in which effluent is passed through before environmental release (figure 1). The plant treats 100's of m³ effluent per day, selectively removing tiny quantities of radionuclides from within a matrix of competing cations at far higher concentrations.¹

Whilst synthetic zeolites have shown higher affinities for caesium, their high cost, synthesis time, availability and fine particle size lessens their appeal in radionuclide removal. Natural sources are therefore preferred, such the clinoptilolite used at Sellafield, which is mined from Mud Hills region of California.^{1,3} However, this material is only estimated to last decades and may not perform as well at treating different feedstocks.

This work focusses on providing viable alternatives to Mud Hills clinoptilolite by improving cheap readily available zeolites via chemical treatments. This should allows us to develop a toolbox of capable ion exchange materials, helping us meet future decontamination needs.

Figure 1: Schematic of the SIXEP plant (taken directly from 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 and N. Bryan, J. Radioanal. Nucl. Chem., 2018, 318, 2473-2491)

Controlled phase changes

Three natural zeolite sources have demonstrated full phase changes via hydrothermal treatment with sodium hydroxide (figure 2).

Cs and Sr uptake

Ion exchange studies were performed on the natural zeolites, their fully converted forms (figure 2) and the multiphase systems. Both caesium and strontium uptake was tested in a variety of competing cations, under batch conditions.

Figure 2: Observed phase changes of 3 naturally sourced zeolites by treatment with sodium hydroxide. Powder XRD pattern $(\lambda = 1.5406 \text{ Å})$ and SEM images are shown for each material.

These phase changes, among other possible transformations, could be very useful if both the original and new structure have different absorption characteristics, as a material proficient at capturing either of caesium or strontium could be converted to a material capable of absorbing the other. This opens a world where many natural, available zeolites can be used in systems to remove both caesium and strontium, whether this be by mixing phases post treatment or through the use of multiple systems (figure 3). This is important as natural materials capable of selective 'duel' decontamination, such as Mud Hills clinoptilolite, are rare.

Generally, the zeolite P and chabazite structures show superior Sr uptake and this is reflected in the composite materials. This is particularly pleasing for derivatives from Zeoclere and mordenite, as these materials show very poor Sr uptake. Cs selectivity generally decreases upon phase transformation, apart from for Zeoclere and its derivatives. However, Cs uptake was generally good with all the natural zeolites.

All the composite materials show great promise as duel purpose radionuclide removal materials, although column studies must be undertaken in order to gauge whether the physical properties are suitable for industrial use.

Future work

- Test ion exchange capabilities at different pH levels.
- Use simulated effluents to further gauge potential application.
- Test materials ability to work in column systems.
- Explore lower cost routes, such as shorter treatment times and use of microwave irradiation.
- Test materials ability to deal with active effluents.
- Further explore origins of these phase changes . E.g through use of alternative hydroxide sources.

parent zeolite and its alternate phase counterpart.

Multiphase systems

The above treatments have also been tuned for partial conversion of the natural zeolites, resulting in biphasic solids (composites). These materials are exciting prospects as ion exchange materials, as they may be capable of selective caesium and strontium removal with each phase removing one of the species. Furthermore, the biphasic zeolites could work in tandem, with one phase removing a cation species from solution that would compete with a radionuclide removed by the other phase.

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Transformative Science and Engineering for Nuclear Decommissioning

Radiolytic Hydrogen Bubble Formation in Magnox Nuclear Waste Sludge Mimics.

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diamond

TRANSCEND

Introduction

This project investigates hydrogen production and transport mechanisms in magnox waste sludges. Magnox sludges formed from the corrosion of magnox fuel cladding. These sludges are composed of magnesium hydroxide and aluminium oxide. Large volume of these sludges are on the Sellafield site.

X-ray Beam

Method

We irradiated cuvettes filled with magnox sludge mimics at the diamond light source. Then images of the irradiated sludges where taken. The mimics we used where simply water mixed with nano-particles of either magnesium hydroxide or aluminium oxide. We also used corroded magnesium sludge. Magnesium metal corroded in a similar way to actual sludge formation.

Results

To the right you see image of bubbles formed in a corroded magnesium sludge sample. This image was take 40 seconds into an irradiation of the sample with the full synchrotron spectrum (from B16's bender). This image clearly shows hydrogen bubble formation in the sample.

The First Bubble

Below you see a series of images showing the formation of the first bubble to form. The first image in the series shows the region before the bubble forms. The second image shows the

2 mm

first signs of bubble formation around 12 second into irradiation. The final image from around 30 seconds into sample irradiation, shows the bubble fully formed.

Bubble Formation Time Model

We modelled this process using previously measured hydrogen production rate and diffusion coefficients. This model predicts hydrogen concentration over time during these irradiations. The image's irradiation model's predictions are plotted to the right. The black dotted line indicates saturation concentration. The blue curve predicts the hydrogen concentration with slowest hydrogen transport. The red curve predicts the hydrogen concentration with fastest hydrogen transport.

Transformative Science and Engineering for Nuclear Decommissioning

Functionalised SPIONs – Facilitating nuclear waste remediation

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ABSTRACT

SPIONs – Super Paramagnetic Iron Oxide Nanoparticles, are pioneering materials in the field of nanotechnology. They are being used extensively in a wide range of applications such as diagnostics, drug delivery, magnetism and therapeutics. A recent study at Imperial, demonstrated that functionalised SPIONs showed fast sorption of uranium from real waste solutions with strong selectivity and a high capacity. However, the mechanism is not yet fully understood and is believed to be due to chelation mechanism. Building further on this work, a list of hypotheses is being made to attempt specific types of functionalisation on the surface of SPIONs, in order to target selective radionuclides, and understand the mechanism of action. Furthermore, this poster presents a range of studies that could be deployed towards designing functionalised SPIONs towards nuclear waste remediation, stimulating multiple collaborations and cross-disciplinary studies across the TRANSCEND consortium.

TRANSC

• Radionuclides sequestration is a PRIORITY for environmental sustainability.

CLINOPTILOLITE

• Sellafield's legacy ponds \rightarrow Over 140 million litres of radionuclide water needs to be treated every 3 months. ¹

Ion-exchangers target to remove 99.9% of Cs and Sr from SIXEP legacy pools

• Clinoptilolite with Q_{max} up to 55 mg/g for Cs & 30 mg/g for Sr. ^{2, 3} • Over 700 m³ of Clinoptilolite & Sand from filter beds (Lead & Lag). ^{1, 2}

• Column beds are an ageing asset, needs replacement by 2060. Contingency plan to expand facility in action. Reprocessing of MAGNOX fuel is terminated.¹ • Residence time is only 8 min, so max theoretical capacity of 2.2 Meq/g is never reached.²

• Volumes of used Clinoptilolite is building up and require encapsulation & underground storage (no regeneration attempted)

Sellafield's Legacy Ponds

Innovative Solution \rightarrow Regenerateable magnetic nanocomposites

Oraman sequestiation anectly nom spent raci

Oleyl Phosphate groups ^{4, 5} Q_{max} = >1667 mg/g

Oleic acid groups ⁴ $Q_{max} = 909.1 \text{ mg/g}$

Octadecyl CTAB groups ⁴ sulphate groups ⁴ Q_{max} = 178.6 mg/g $Q_{max} = 416.7 \text{ mg/g}$

Magnetic Composites					
Strengths	Weaknesses				
 Low cost to mass manufacture 	 Requires expertise to 				
 Magnetic separation in real time 	functionalise				
 Extremely low cost of treatment 	 Magnetism reduces upon coating 				

Selectivity & high

Capacity for Cs-137 &

Sr-90, with K_D > 5000

and Q_{max} > 100 mg/g

Uranium adsorption, initial concentration of 0.1 to 40 ppm, pH 5.6^{4, 5} Time to reach equilibrium = 24 hours Time to attain >90% magnetic separation = 24 hours

PROPOSED STUDIES

<u>Study 1</u>: Functionalisation of magnetite towards radionuclide remediation & recycling <u>**Reason**</u> \rightarrow Phosphate and oleic acid ligands have been demonstrated in literature ^{4, 5} to show the highest adsorption capacity for uranium reported so far. This needs further exploration for other radionuclides such as of Cs, Sr, Co, as well as exploring softer routes of synthesis. Furthermore, optimising the regeneration & recycling capabilities of these materials still needs to be explored, in order to establish its full potential.

Study 2: Acid stable nanoparticles with high capacity & selectivity

<u>**Reason</u>** \rightarrow Phosphate & Oleic acid functionalised magnetic nanocomposites are not stable</u> under pH 4 due to the iron core getting disintegrated. A protective coating of functionalised silica will stabilise until pH 1, while maintaining a high capacity & selectivity remains a task yet to be achieved.

- Efficient regeneration & recycle
- Ease of handling magnetic powders
- Tuneable surface functionalisation
- Minimum spent waste generation

Imperial college

Stability in pH

ranges of 1 to 13

with gamma

irradiation > 6

Mgy (Structural)

Saturation

magnetisation >

20 emu/g

- **Environment friendly disposal**
- Limited research available on stability & regeneration studies
- Magnetic clustering & thermal disintegration

Regeneration

capacity of >

90%, along with

retaining Q_{max} >

90% over at least

5 cycles

prospective collaborators

Study 3: Analytical and chemical tests to understand mechanism of phosphate groups <u>Reason</u> \rightarrow Chelation and electrostatic interactions are assumed to be the mechanism by Imperial's researchers. Studying of bonding type and charge distribution using densityfunctional studies, NMR, XPS & radiotracer imaging can provide greater insights to the accessibility and reactivity of the functional groups present on the magnetite's surface.

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Transcend Consortium

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