

Vacuum Drying of AGR Fuel Through Cracked Cladding

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Project Aims Experimental: Computational: Produce a code to determine the **To produce representative** dimensions of a defect. defects.

- **Determine the flow rate through** the produced defects.
- **Conduct drying trials using the** defects.
- Create a process model of the drying set up.
- Validate the model against drying trials.

Why Dry Spent Fuel?

With the current strategy being to wet store the spent AGR fuel pending possible disposal to a GDF in 2075, consideration must be given to preparing the spent fuel for disposal [1].

A small portion of the cladding is known to have failed allowing water from the ponds to come into contact with the fuel where it can become trapped. If this water is not removed prior to disposal or indeed dry storage then radiolysis can lead to the production of H_2 and H_2O_2 – the latter product accelerating corrosion of the cladding contributing to fission product release in addition to increased H₂ production.



Corrosion Results - DET

One sample of 316 stainless steel was found to have failed after a week of exposure in the DET rig. Upon examination we observed multiple fissures present on the surface of the sample.



Fig 1. AGR fuel assembly [2]

Producing Defects - DET

Adjusted from a method used to produce stress corrosion cracks in stainless steel for offshore oil and gas facilities.

The sample is stressed and kept wetted with 4M MgCl₂ which is dripped slowly onto the sample.



Fig 2. Drop evaporation test rig



This level of damage was not seen on any other sample. The current theory is that crevice and galvanic corrosion occurred while the sample was under experimental conditions.



Fig 4. Section of failed sample

Reduced Temperature Results

With the DET rig producing inconsistent results, which was attributed to a flow rate which washed away the concentrated solution, a new set up was devised.

This new method lowered the temperature of the tests and also the rate of solution replenishment to allow for greater chloride concentration.

Fig 6. Failed AGR cladding [3]

Vacuum Drying

Multi-Stage Vacuum:

The updated drying rig showed, in initial trials, a large drop in the temperature of the sample which was deemed to be a major contribution to the slower than expected drying rate.

To rectify this a method described by S. Saha et al [4]. To lower the pressure in stages to allow the temperature of the sample to recover.



Samples

Two types of stainless steel: 304 and 316 has been treated and were subjected to the testing.

Element	% Present			
Element	304	316		
С	0.08	0.08		
Mn	2.00	2.00		
Р	0.045	0.045		
S	0.03	0.030		
Si	1.00	1.00		
Cr	18.00 – 20.00	16.00 - 18.00		
Ni	8.00 - 10.50	10.00 - 14.00		
Мо	-	2.00 – 3.00		
Fe	Bal.	Bal.		

When comparing 304 to 316 stainless steel we see that the key difference is the 2% Mo added to improve corrosion resistance.

Potassium Tetrathionate

A second attempt to produce representative defects using acidified potassium tetrathionate $(K_2O_6S_4)$.

A 0.1M solution of K2O6S4 is made up and altered to pH 1 using sulfuric acid.

Once prepared the samples were placed into a drying cabinet at 65°C with MgCl2 added periodically to prevent the sample fully drying out.



Fig 8. Cracked corrosion pit

Samples of 316 stainless steel and mild steel have been tested with 304 underway.







References

[1] NDA, Strategy Guide. 2021

experimental work also.

ousenuclear.com/blog/the-art-of-innovation-wes 3] Kyffin, J. (2015). Technological Development to Support a Change in the United Kingdom's Strategy for Management of Spent AGR Oxide Fuel. Proceedings of the International Conference on Management of Spent Fuel from Nuclear Power Reactors, IAEA, Vienna [4] Saha, S., Khan, J., Knight, T. and Farouk, T., 2022. A Global Model for Predicting Vacuum Drying of Jsed Nuclear Fuel Assemblies. Nuclear Technology, 208(3), pp.414-427.

Transformative Science and Engineering for Nuclear Decommissioning





TRANSCEND

Developing an M-S-H mortar from corroded magnesium sludge simulant

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Background

Ponds at Sellafield contain a magnesium hydroxide (Mg(OH)₂) rich sludge Potential to reduce the volume of waste required for encapsulation by using the sludge as a raw material in a magnesium- silicate – hydrate (M-S-H) cement mortar

- Determine if this is feasible
- Understand the behaviour of the resulting mortar
 - Mechanical, transport properties, characterisation
 - Durability testing within different environments

MgO and Mg(OH)₂ powders both used to develop reference mortars to understand the changes in behaviour: MgO powder is more reactive magnesium source. Mg(OH)₂ powder as a more consistent magnesium hydroxide source.

Producing an M-S-H mortar from CMgS sludge

When using the same proportions as the Mg(OH)₂ powder (43.3 wt% CMgS, 6.7 wt% MgO, 20.4 wt% SiO₂, 29.6 wt% silica sand, 1 wt% NaHMP, w/s 0.35):

- The resulting mortar was not fluid enough
- Increased the water/solid ratio to 0.375 0.4
 - Mortar with the required fluidity
 - Strength reduced below that desired





Figure 1: (a) the compressive strength development of the MgO and Mg(OH)₂ based reference mortars over the course of one year. (b) the evolution of porosity observed for the same mortars of the course of one year. The mix proportions for the MgO-based M-S-H were 20 wt% MgO, 5 wt% MgCO₃, 25 wt% SiO₂, 50 wt% silica sand, w/s 0.35, 1 wt% NaHMP. The mix proportions for the Mg(OH)₂-based M-S-H were 23.4 wt% Mg(OH)₂, 9.1 wt% MgO, 27.5 wt% SiO₂ and 40 wt% silica sand, w/s 0.35, 1 wt% NaHMP.

Characterising the CMgS sludge

CMgS sludge is purely magnesium hydroxide, with a water:solid ratio of 3:2 The particle diameter is more varied than the MgO and Mg(OH)₂ powder, as



Figure 4: The strength characteristics for a sludge-based M-S-H mortar with various w/s ratios.

Improving the mortar properties:

- Increase in the MgO proportions
 - Reduced CMgS proportions to 40 %
 - Mixes trialled with up to 50 % of the filler replaced for CMgS sludge
 - 30 % sludge replacement produced greatest strength gain in 28 days
 - M-S-H peaks observed within 14 days
 - Total incorporated CMgS is 46.6 wt%

Table 1: Mix proportions of the sludge based mortars

Mix (proportion of sludge substituted as filler)	CMgS wt% solids	MgO powder wt% solids	SiO ₂ powder wt% solids	Silica sand wt% solids	Added water per 100g solids	w/s ratio
20%	<mark>40.0</mark>	<mark>8.7</mark>	<mark>21.0</mark>	<mark>30.4</mark>	<mark>10.8</mark>	<mark>0.35?</mark>
30%	46.6	8.1	20.2	25.2	0	0.388
40%	52.8	7.66	19.1	20.4	0	0.463
50%	58.3	7.28	18.2	16.3	0	0.537





Figure 5: The change in complex viscosity for the sludge-based M-S-H mortars at various water/solid ratios

the powders have been ground, whilst the particles within the sludge are the product of metal corrosion.



Figure 2: (a) The XRD pattern for the magnesium hydroxide powder and dried sludge. (b) The particle size distribution of the magnesium hydroxide powder and dried sludge. The sludge was dried at 105 °C for 25 hours before testing.

When dried at 600 °C, the sludge became a magnesium oxide powder. Drying for 2 hours produced the maximum peak, which did not increase over the next 4 hours of drying.



Figure 6: The strength characteristics for sludge-based M-S-H mortars with various filler substitutions

Figure 7: The porosity of the sludge-based M-S-H mortars with various filler substitutions over 90 days

Increasing the CMgS proportions

- Replaced the MgO powder with CMgS powder
- Total proportion of CMgS incorporated is 54.7 wt% (66.9 wt% when include water removed to create powder)
 21 3
 - Strength of 19.6 MPa within 28 days
 - M-S-H peaks observed by 28 days



Figure 8: The strength characteristics for the sludge-based M-S-H mortar with the sludge MgO powder substituted for the MgO

Conclusions

Figure 3: The XRD pattern for the magnesium oxide powder and sludge. The sludge was placed in a furnace at 600 °C with small proportions of the resulting powder removed every hour for testing.

- MgO powder, Mg(OH)₂ powder and CMgS can all be used to produce an M-S-H cement mortar
- Magnesium oxide powder is required to produce early strength characteristics
- A mortar has been developed which achieves strengths over 10 MPa and has a proportion of over 50 wt% CMgS
 - M-S-H is formed within 28 days in this cement mortar
 - Higher water/solid ratio is needed as some water is already incorporated in the sludge







Thermodynamic modelling of Nirex Reference Vault Backfill (NRVB)



Thomas Budd, Imperial College London, Prof Hong Wong & Dr Rupert Myers, Imperial College London

Introduction

NRVB is a reference material for backfilling the vaults of the Geological Disposal Facility (GDF), and is required to perform as a barrier material for 100s – 1000s of years.

able 1: Percentage const	ituents within NRVB (4sf
Constituent	Wt %

9.850

26.10



Discussion



Hydrated lime	28.56
Water	35.48

CEM 1

Limestone Flour

Thermodynamic modelling can be used to predict the solid phase composition, porosity and pore solution chemistry of cement. To ensure that the thermodynamic modelling software (GEMS) will be able to accurately predict the solid phases over the lifetime of a GDF, the models outputs must first be validated against existing experimental data.

Table 2: X-Ray Fluorescence (XRF) composition data of the experimental NRVB (Vasconcelos 2019) versus the composition data used for NRVB modelling (±0.1%)

Compound	Experimental compositions		Experimental compositions Compositions used for modelling		odelling	
Compound	Cem 1 52.5N	Limestone flour	Hydrated lime	Cem 1	Limestone flour	Hydrated lime
CaCO₃	-	-	-	-	100	-
Ca(OH) ₂	-	-	-	-	-	100
NaO_2	0.3	0.2	<0.1	0.24	-	-
MgO	1.2	1.6	0.5	2.35	-	-
Al_2O_3	5.2	1.9	<0.1	5.45	-	-
SiO ₂	19.7	5.4	0.5	21.13	-	-
$P_{2}O_{5}$	0.2	0.1	<0.1	-	-	-
K ₂ O	0.5	0.3	<0.1	0.70	-	-
CaO	64.1	48.1	73.9	65.11	-	-
Fe_2O_3	2.1	1.7	<0.1	2.69	-	-
SO ₃	-	893ppm	-	2.33	-	-
LOI	3.5	39.6	23.2	-	-	-





Davs

Figure 3: graphs showing the percentage of individual solid phases from both modelling and experimental data over 1000 days. Graph a) shows the Monocarboaluminate phase, b) Ettringite, c) Portlandite and d) Calcite

Figures 3 and 5 show that the difference between the modelled data and experimental results decreases over time. The largest average difference between experimental and modelled phase weight percentage is observed at 2 days, and lowest at 365 days.

Figure 5 highlights the differences between the modelled and experimental data.



Figure 4 shows the percentage of modelled monocarboaluminate versus observed hemicarboaluminate and monocarboaluminate over

Figure 1: Semi quantitative analysis of XRD patterns of NRVB over 1000 days (adapted from Vasconcelos, 2019)



Percentage difference between modelled and experimental results (Figure 6) is largest at early ages of NRVB development. After 70 days, the average difference falls to less than 20% for all phases.

As NRVB ages it gets closer it's final equilibrium state. GEMS thermodynamic modelling predicts phases at equilibrium for a given composition. The older the cement being modelled, the greater the accuracy of the modelling.







Figure 6: percentage difference between modelled and experimental results for individual solid phases over 1000 days.

Conclusions

Figure 2: Weight percentage of solid phases of NRVB using GEMS thermodynamic modelling over 1000 days. The CSH phase has been removed as a phase after modelling for direct comparison to Vasconcelos' experimental data.

Uncertainties

- Differences in the composition of NRVB constituents.
- Phase variation in experimental sampling sites.
- GEMS modelling calculates phases at equilibrium, the metastable phase hemicarboaluminate converts to monocarboaluminate over a span of days and therefore is not calculated by the modelling software.
- Thermodynamic modelling can be used to predict the solid phases in NRVB.
- The model is able to more accurately predict the weight percentage of each phase in the system as NRVB age increases.
- Metastable phases are missed in thermodynamic modelling.
- Further work is needed to match the modelling composition to the experimental composition.
- Further experimental results are needed at ages of over 3 years to validate the use of modelling for phase prediction over decades and centuries.

References

Vasconcelos. The Influence of Groundwater on the Mineralogy of Cement for Nuclear Waste Disposal (PhD Thesis). s.l. : The University of Sheffield, 2019.

Acknowledgements

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University of Southampton

RANSCE

Electrokinetically enhanced migration of soil contaminants into silica grouting

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What is Electrokinetic Remediation?

The use of electricity to migrate and **concentrate pollutants** around an electrode in order to **minimise the volume** of contaminated material.



 $\frac{\text{Electromigration:}}{\text{Cations} \rightarrow \text{cathode}}$ $Anions \rightarrow anode$ $\frac{\text{Electrophoresis:}}{\text{Electrophoresis:}}$

+ charged particles → cathode - charged particles → anode

Experimental Set-up

The experimental design was perfected at the

University of Strathclyde including the optimum

gel mould design and sampling strategy. The

final design includes a cylindrical gel block

(right) with a central hollow to site the graphite electrode cathode. This hollow was also filled with the starting solution and sampled from at regular intervals over the electrokinetic trial.

Two additional sampling wells were installed at

equal distances from the electrodes. When

sampling, only 10-20 µL was taken from each

well and any evaporative loss overcome by

adding MQ water to the outer reservoir.

 $\frac{\text{Electro-osmosis}}{\text{Water} \rightarrow \text{cathode}}$

The advantages of electrokinetic remediation include its **adaptability** to different waste matrices and the **potential to be combined** with other waste minimisation techniques such as bio/phyto remediation, in-situ barrier formation or colloidal grouting.

Graphite electrodes

Arianna (Gea) Pagano, University of Strathclyde/Glasgow

Results and Challenges

Although movement of Cs/Sr towards the cathode was observed (see graph on right), this result was not reproducible across all experiments. This could be due to:

Effect of pH

Colloidal silica grouting is known to be stable over a wide pH range but begins to dissolve above pH 10. During electrokinetics, an alkaline pH front forms at the cathode. At 0.25 V/cm, the solution in sampling well C reached pH > 10 after ~48 hours whereas at 0.5 V/cm, it had reached pH > 10 by the 24 hour sampling time. The silica gel block appeared to show some resilience to these high pH conditions with only some slight discolouration around the sampling well after 14 days exposed to 0.5 V/cm. At the higher voltage gradient of 1 V/cm, however, dissolution was observed after only 2 days.

Loss of analytes by precipitation or sorption

The change in caesium or strontium concentration in each sampling well with time was determined via ICP-MS measurement of the 10 μL sampled aliquot diluted with 2% HNO_3 (10 mL). This relies on the analyte being present in a soluble state.

For experiments conducted with caesium, the starting concentration in wells A and B was lower than expected (\sim 25 % – 50 %). This could be due to uptake to cation exchange sites on clays present within the substrate.

In all experiments, precipitates were also observed on the surface of the solution in sampling well C and deposited on the surface of the graphite cathode. The elemental composition of this precipitate is to be determined by XRD and ICP-MS. This loss of soluble analyte could affect the mass balance of the system.

> UK Research and Innovation



What is Colloidal Silica Grouting?

We have been working with the University of Strathclyde to combine electrokinetics with their expertise in the use of colloidal silica grouting to penetrate contaminated soil, safely containing radionuclides and generating a waste form suitable for in-situ or ex-situ **vitrification**.



Colloidal silica is a suspension of **nanoscale** silica particles. When mixed with a **salt** solution (accelerator), the hydroxyl groups on the surface of these particles undergo **condensation** to form siloxane bonds leading to a **hydrogel** structure. This structure gains viscosity and strength over time.

When forming a silica hydrogel, the gelation speed and subsequent strengthening rate is easily **controlled** by altering the salt concentration and volume ratio.



- Experimental conditions trialled:
- With or without silica gel block at well C
- Soil matrix = sand
- Analytes added: Cs and Sr
- Applied voltage density = 0.25 1 V/cm
- Electrolyte = 0.17 M CaCl₂
- EKR experimental duration up to 2 weeks



The initial concentration of both analyte and electrolyte (0.17 M CaCl₂) was uniform throughout the silica gel block (if present), the sampling wells, the sand and the outer reservoir.

Future Development

Effect of pH

The system could be designed to be more tolerant to the alkaline pH front formed at the cathode by introducing more buffering capacity into the silica gel block. This could be achieved by incorporating sand/clay as either an inner layer between the silica grouting and the cathode or by mixing with the colloidal silica prior to gelation.

Loss of analytes by precipitation or sorption

The sand substrate may need to be equilibrated with the starting solution for a longer period of time prior to commencing the electrokinetic trial to allow for full uptake to occur. This may reduce the mobility of the analyte in the system but is more representative of a real world scenario. This is particularly important if looking to increase the complexity of the experimental set-up by incorporating clays and/or organics.

If precipitation is affecting the aqueous concentration data from well C, then it may be worth focusing on the sampling wells further from the electrodes (A and B). As concentration change in these locations has been shown to be slower, the experimental duration may need to be extended.

Introducing further complexity

In addition to incorporating sand/clay into the silica grouting and adding clays/organics into the sand, the experimental trials will be extended to explore differently charged analytes (in particular U, linking to the recently initiated Horizon Europe project SURRI on remediation of former U mining sites), as well as increasing the complexity of the electrolyte (e.g. using simulated Sellafield groundwater). This will help to validate the technology for real-world applications.

Transformative Science and Engineering for Nuclear Decommissioning





Advanced Characterisation of Irradiated Acoustic Probes

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Background & Introduction

Ultrasonic (US) backscatter is a proposed characterisation method for legacy nuclear wastes suspensions and slurries in the UK.

The technique relies on US transducers probes that will be exposed to radiation during operation.

The effect of irradiation on these US probes is relatively unknown, as such this study looks to ascertain what differences, if any, irradiation of US probes will have.

Research Aims

- Size Characterisation of virgin vs. sieved size fractions and bimodal size fraction mixtures of spherical glass particles.
- Development of Machine Learning code to characterise size and concentration of spherical glass particles.
- Application of aforementioned research to flocculated systems.



The hydrophone beam plotting facility at the National Physical Laboratory, was used where the following tests were completed on two US transducer: □ Electrical impedance measurements.



Axial beam-profiling.

TRANS

- Detailed 2D raster scans, carried out at the last-axial maximum and close to the transducer face (< 3 mm).
- **Q** Reporting of the pulse-echo response of the transducer using a standard reflecting target.

acoustic beam axis to find the last axial

(*right*) Pulse-echo response measurement of the transducer probe using a standard

The probes were sent to the Dalton Cumbria Facility where they were irradiated with 1MGy of γ-radiation from a Cobalt-60 source.

Both probes were then retested using the same techniques to identify if the irradiation had caused any physical or performance degradation.

Testing of the probes on well established calibration suspensions is also to be completed at the University of Leeds. The backscatter performance and key acoustic parameters will be compared to the values reported in Tonge, et al. (2021) for the same probes, to determine if irradiation has altered them in any way.

Results & Discussion

Detailed 2D hydrophone Fig 2 raster scans close to the transducer face for before and after irradiation of the two US transducer probes tested.



- When comparing the before and after scans for transducer #9, a decrease in the intensity of the scan is clearly identifiable.
- The decrease in intensity is uniform

When comparing the before and after scans for transducer #8, it is clear that there has been no change. The intensity of both scans shows very little difference and both scans have the same shape.

The 'flat edge' on the right side of the before scan can be identified on the left side of the after scan, showing that no change in the shape -2 of the profile has been caused by -4 irradiation.

The capacitance measurements also confirm, that probe #8 experienced no change due to irradiation as there was little to no deviation between before and after measurements.

Fig 3 – Capacitance results for a range of frequencies for probe #8 – *left* and probe #9 – *right,* from the impedance measurements, before and after irradiation.



across the probe, evident from a mostly unchanged shape of scan. This suggests that the piezoelectric crystal within the transducer has not been damaged.

Combined with a decrease in capacitance after irradiation shown in Fig 3, a preliminary conclusion that a change in the epoxy/glue within the probe is responsible.

A positive from this is that because the scan shows a uniform and symmetrical profile, this probe can still be considered useable.

However, the use of this probe would be limited to comparative measurements rather than absolute values.

The impedance measurements are relatively quick compared to the raster scans so this could be used as a check to determine whether probes in use are deteriorating from radiation.

Conclusions & Further work

- One transducer probe showed degradation from exposure to 1MGy of γ radiation, this was identified by a decrease in intensity in 2D raster scans, as well as in the impedance measurements.
- The change is likely down to a change in the epoxy/glue within the probe, \bullet but the profile remained uniform and symmetrical, thus useable.

References

- Impedance measurements could be used as a check to determine whether probes in use are deteriorating from radiation.
- \succ Quantify the changes in acoustic performance from the data gathered at NPL.
- Carry out US backscatter testing with the irradiated probes and compare performance and parameters to values before irradiation.

TONGE, A. S., PEAKALL, J., COWELL, D. M. J., FREEAR, S., BARNES, M. & HUNTER, T. N. 2021. Experimental validation of acoustic inversions for high concentration profiling of spherical particles, using broadband technology in the Rayleigh regime. Applied Acoustics, 180.

Transformative Science and Engineering for Nuclear Decommissioning





University of Southampton

Electrokinetic remediation of difficult-tomeasure radionuclides at nuclear sites

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What is Electrokinetic Remediation (EKR)?

- Clean-up of the UK's nuclear legacy is estimated at ~ £200 billion over 100 years
- There is an urgent need to reduce decommissioning costs could new approaches to remediation help?
- Technique must work in different materials AND be site-scalable, cheap, energy efficient and sustainable

EKR involves decontamination by electrocution, concentrating pollutants within cell or at electrodes. It is an adaptable and low-energy waste minimisation technique



Figure 1: A typical electrokinetic cell. C⁺ are cations and A⁻ are anions

Cements Work

- Collaborative work with University of Leeds and the NNUF-EXACT facility (Southampton) into whether EKR can remediate cement containing ²³⁶U, ¹³⁷Cs, ¹²⁹I, ⁹⁰Sr and ³H
- Cement was chosen instead of concrete to simplify the system. Consequently, only cement and water were added, in a 2:1 ratio
- Cement cores were contaminated in 2 different ways:
 - Homogeneous Set radionuclides were added as the cement and water were mixed (RNs are homogeneously distributed throughout core, simulating concrete biosheilding)
 - Soaking Set cores were left to harden (known as curing) for 28 days and, afterwards, placed in a bath containing radionuclides (RNs are bound to the surface or near-surface, simulating storage pond concretes)
- Core treatment occurred for 41 days. Afterwards, the core was cut into sections for analysis (figure 2)

Summary of Results

- ¹³⁷Cs shows high rates of mobility in the Homogeneous-Set when EKR is applied (see below)
- ²³⁶U, ¹²⁹I and ⁹⁰Sr all show little to no mobilisation in all cores (See below for ¹²⁹I). This is expected for ²³⁶U and ⁹⁰Sr but surprising for ¹²⁹I as it is commonly mobile in cementitious pore waters
- ³H data are inconclusive due to notable loss of tritium in all cores
- For all radionuclides, a greater degrees of mobilisation is seen in the Soaking-Set compared to the



Figure 2: **Left** - trial cement core undergoing electrokinetic treatment. **Right** - schematic showing how the core was cut, and the naming convention for each section



Homogeneous-Set is likely to have contamination contained within cement mineral phases



Figure 3: **Left** - ¹³⁷Cs data from Homogeneous-Set cores and ¹²⁹I data from all cores. For schematic of where each section was positioned, see figure 2 (**right**)

Sediment Core - Commencing May 2023

120

360

- Evaluation of whether electrokinetics can migrate the radionuclides present in a 55 cm sediment core from the Ravenglass saltmarsh (~9 km south east of Sellafield)
- Sellafield discharges into the Irish Sea have accumulated in the saltmarsh
- Historical discharges are buried over time by new 240 sediment, creating a discharge profile in the core
 Badionuclides may have been remobilised
- Radionuclides may have been remobilised over time due to changes in conditions
- Itrax XRF scan shows stable element composition throughout the core. Key elements are:
 - S indicates whether the sulphidic zone of respiration has been reached
 - Mn and Fe mark sub-oxic zone of respiration
- Radionuclide analysis will follow soon



30000 60000 0 250000 500000

Figure 4: Optical image, radiograph and Itrax XRF scan of key stable elements in the Ravenglass sediment core before EKR treatment

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Investigating the uranium metal – magnox sludge system using x-ray and neutron tomography

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Figure 1: A view of the first generation magnox storage pond at Sellafield [1].

Introduction

Over several decades, a substantial inventory of spent metallic uranium fuel has slowly degraded and become encapsulated in compacted magnox sludge, whilst stored in Sellafield's first generation magnox storage pond (FGMSP). Safe decommissioning of the FGMSP requires an understanding of any physical and chemical changes to the uranium metal that have occurred during this prolonged wet storage. The shift from a standard wet storage environment to sludge encapsulated conditions changes the possible corrosion reactions that spent uranium metal fuel can undergo. It is suspected that UH₃ formation can occur in encapsulated conditions, as well as a build up of H₂ gas in the sludge matrix. Both these materials pose a potential safety hazard during decommissioning if the materials are present in large enough quantities.



What is Magnox sludge?

Comprising of fine insoluble $Mg(OH)_2$ particulate, water, and partially corroded magnox swarf. Magnox sludge can take the form of anything from a cloudy liquid to a clay-like soft sediment; the consistency of magnox sludge depends mainly on its water content, as well as age, and degree of compaction. Magnox sludge has a relatively high yield strength, which has been shown to facilitate the entrapment of hydrogen gas [2]. Entrapment of hydrogen gas in the FGMSP is expected to impact the corrosion behaviour of encapsulated metallic uranium.

Sample Design

In this work 5 mm lengths of 0.5 mm diameter natural uranium wire has been encapsulated in corroded magnox simulant sludge (CMS). The wire is held in place using a custom 3D printed mounting system, and the sample is sealed in an airtight container. The samples were prepared in atmospheric conditions and have been stored at room temperature for the duration of this corrosion study. This study is a continuation of a feasibility study [3].



X-ray Imaging

X-ray imaging provides a suitable technique for monitoring the corrosion behaviour of metallic uranium encapsulated in magnox sludge; monitoring the uranium metal – sludge environment is challenging due to interference with the sludge and the systems opacity. Periodic XRT scans of a long term corrosion sample have been conducted, and corrosion rates have been extrapolated from volumetric measurements.



Figure 3: Diagram of corrosion sample used in this study, adapted from [3].

Figure 4 shows the corrosion rates from two long term corrosion samples. The contrast in initial corrosion behaviours was caused by the initial oxide layer on the uranium used in this study, compared with the polished metal used in the feasibility study. However, after 100 days the corrosion rates of both samples slow, and settle at similar rates. Figure 2: Left: Sludge taken from the FGMSP [1]. Right: Corroded magnox simulant sludge (CMS) provided by NNL.

Neutron Imaging

Neutron imaging has been used as a complementary technique to x-ray tomography, exploiting differences in the x-ray and neutron absorption cross-section of materials. Corrosion samples were prepared in neutron transparent containers and imaged on the IMAT beamline at ISIS. The aim of this study was to assess the feasibility of using neutron tomography of the uranium – sludge system. Focus was put on identification of persistent UH_3 , and on imaging the sludge matrix at the metal – sludge interface.



Sellafield Ltd



Figure 4: Corrosion behaviour of uranium – sludge system from this study and [3].

X-ray imaging can also be used to identify the type of corrosion occurring on the metal. Figure 5 shows the progressive corrosion of a wire segment over time. The most prominent visible feature is a large, rapidly developing corrosion pit, characteristic of hydriding: producing UH₃ [4]. Uniform corrosion of the metal surface becomes the prominent mechanism after 100 days of corrosion, further study is required to determine the caustic mechanism. Identification of corrosion pits indicates formation of UH₃ can occur in this system, however it cannot be used to study UH₃ persistence.





Figure 6: Inverted neutron tomography slices of dried corrosion sample with Xray image of uranium wire overlayed (right).

Figure 7: Sample mounting on IMAT beamline at ISIS

Initial attempts at imaging corrosion samples failed due to the high neutron absorption of water in the sludge. Water was removed from the samples by overnight drying at 40 °C, figure 6 shows slices of the resulting neutron tomography. The uranium wire can be located by a faint outline, it is unclear whether the outline is a result of neutron attenuation in metal, corrosion product, or Mg(OH)₂ adhered during drying. A distinction between persistent UH₃ and UO₂ corrosion product was expected to be notable by a contrast in pixel intensity at corrosion pit sites, however this was not observed. The sludge at the metal – sludge interface was successfully imaged, supporting the use of this technique to complement x-ray imaging, despite the disruption to the corrosion environment caused by sample drying.

Future work

• A proposal for a joint I12 – IMAT experiment has been submitted. This

Figure 5: X-ray tomography slices of corrosion sample at different over time.

experiment will further probe the corrosion and drying behaviour of the uranium metal – magnox sludge system.

 Chemical immobilisation of partially and fully corroded samples. This process will non-destructively halt the corrosion process by fixing the system in resin, allowing the application of additional characterisation techniques.





TRANSCEND

Tomography of stress corrosion cracking from an in-situ tensile corrosion synchrotron experiment

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Introduction

Aim and background

To develop a new small punch test (SPT) setup for spent AGR cladding (20/25/Nb stainless steel) with surrogate material (thermally sensitised 304 stainless steel) that can initiate SCC (stress corrosion cracking) of stainless steel in a short period time with DIC (Digital image correlation) observation.

The in-situ corrosion experiment was proposed to compare SCC propagation in 3D with surface propagation by using tomography from a synchrotron x-ray source.



Experimental Procedure

Four samples were planned to test:

Sample	1	2	3	4
Material	304	304	20/25/Nb	20/25/Nb
Surface finish	Rough	Mixed	Mixed	Mixed
Solution	Corrosive	Corrosive	Corrosive/ inhibitor	Corrosive
Duration (hours)	10	18	12/6	18 (only 9 hours tested)



Fig. 5. Setup on the turning table

Fig. 1. DCT (diffraction contrast tomography) image showing the propagation of SCC in 3D *

Experimental Plan



Fig. 2. Imaging camera and diffraction detector of DIAD

Experimental methods Tensile Rig

- in-situ corrosion tensile An experiment was granted to carry out at Diamond to develop SCCs on both thermally sensitised 304 and 20/25/Nb stainless steel.
- DIAD beamline enabled point diffraction to be taken during tomography scans.
- FIB milling after the tests to find the relationship between the crack path and grain boundary properties.



All solutions were heated to 70°C and all samples were held at 90% of yield stress. Tomography was taken every 30 minutes and point diffraction was taken between each tomography.

Results



Fig. 6. slice and top views of the sample 2 (mixed 304): (a), (b) after 3 hours and (c), (d) after 16 hours

- Two layers of polycarbonate tubes are X-ray transparent.
- The tensile sample is loaded in the inner polycarbonate tube by turning the bolt on top and the load can be monitored by the load cell.
- The corrosive solution is injected into the inner tube and heated by a heating element.

Fig. 3. Tensile testing rig

Stress corrosion cracking is caused by a combination of following three factors: **Susceptible material:** both 304 and 20/25/Nb has been thermally sensitised:

- 304: aged at 600 °C for 50 hours and cooled in air;
- 20/25/Nb: annealed at 1050 °C in argon for 30 minutes and quenched in water then aged at 600 °C for 50 hours and cooled in air.

Corrosive environment: a corrosive solution with 1000 ppm thiosulphate and 1440 ppm Cl⁻ solution at 80 °C was previously found to develop SCCs in 7 hours. **Mechanical driving force:** the yield strengths of two materials were found: 304: 180 MPa, 20/25/Nb: 190 MPa. A load giving 90% yield stress was applied accordingly.

In addition, an inhibitor solution (1000 ppm thiosulphate, 1440 ppm Cl⁻ and corresponding NaOH to increase pH to 11.4) will also be used to find out if it can reduce the rate of crack growth.



Fig. 7. slice and top views of sample 3 (mixed 20/25/Nb with solution change): (a), (d) after 1.5 hours; (b), (e) after 12 hours; (c), (f) after 18 hours

Sample 2 successfully developed IGC/IGSCC during the experiment. Most cracks initiated on two rough surfaces, especially near the corner of the sample. Cracks started to initiate at the early stage of corrosion.

Sample 3 doesn't show obvious crack development, only some pitting corrosion on the surface of the sample.

Conclusions and Plans

Sample preparation

Different surface combinations were prepared:

- Rough sample: 600 grit for both the faces and the edges
- Fine sample: 1µm on the faces, 1200 grit on the edges
- Mixed samples with rough and fine surfaces



Fig.4 Tensile sample

IGC/IGSS successfully developed during the in-situ corrosion synchrotron experiment. The surface roughness has strong effects on SCC development. 20/25/Nb is more resistant to SCC than 304 and further analysis is needed to confirm if 20/25/Nb has corroded. Digital volume correlation will be used to track the crack growth rate and FIB milling can tell the relationship between the crack path and grain boundary properties.

References

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GAME ON! Addressing the nuclear skills shortage through a radioactivity card game for school pupils

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NUCLEAR SKILLS SHORTAGE

- To address the current and future nuclear skills shortage, investment in multi-level training opportunities through apprenticeships, undergraduate and doctoral training is required.¹
- To support this workforce expansion, collaboration between; schools, academic institutions, and industry is needed to engage students and cultivate interest in these career paths is vital.²
- The following sectors; new nuclear, decommissioning, healthcare and radiopharmaceuticals, all require

Game 1 applies & reinforces examined components of KS4 science.	Price and danger rating were used to support	Southampton Science or RAD RATINGS GAME 1	"RADIATION" is very simple, meaning a material (a chemical element in this case) that gives off, or radiates, something as either particles or energy. Certain elements, like uranium only have unstable isotopes, whilst other elements like	ALPHA (q) radiation: Heavy, slow moving particles made of 2 protons and 2 neutrons. Because they are slow moving they are easily blocked by most things but can be dangerous if inside the body. Stopped mostly by a few cm of air, paper, etc. BETA (β) radiation: Lighter, faster moving particles made of just 1 electron. Harder to shield against but are generally less dangerous.
PROTONS 95 NEUTRONS 146 HALF LIFE 430 YEARS PRICE £ £ £ £ £ DANGER RATING \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	understanding context of uses in everyday life.	<text><list-item><list-item><list-item><list-item><list-item><list-item><list-item><list-item><list-item></list-item></list-item></list-item></list-item></list-item></list-item></list-item></list-item></list-item></text>	carbon have isotopes that can be stable or unstable. Unstable isotopes (collectively called radionuclides or radioisotopes) are radioactive, meaning the number of neutrons and protons in their nucleus is unbalanced, and they want to become stable. They mostly do this by emitting alpha, beta and gamma radiation (other types of radiation such as neutron radiation and positron radiation do exist but are quite rare).	<image/>

workforce expansion over the next 5-20 years.³

AIM & METHODS

AIM: To evaluate the effectiveness of gamification through an interactive card game as a curriculum-enriching activity for engaging KS4 (age 14-16) students with the topics of radioactivity and radiochemistry.

METHODS: We developed an interactive card game that aims to complement and support key concepts of radioactivity and radiochemistry in KS4 curricula while also highlighting the role of radioactivity in everyday life, potential career paths, and general interest in nuclear science.

To evaluate the effectiveness of the card game, we collected written feedback from teachers, administered questionnaires to students, and conducted classroom observations.





'...I was interested in learning about radioactivity and its uses'



CLASSROOM OBSERVATIONS

• Game 1 was suitable for students with limited working knowledge on radioactivity, however, this



 Student feedback demonstrated increased interest in learning about radioactivity and its uses after playing 'RAD Ratings' this was supported by teacher feedback.

- Feedback established that Game 1 was easy to implement in the classroom setting to support KS4 curriculum to support existing lesson plans.
- Feedback from teachers and classroom observations highlighted that conducting both Game 1 and Game 2 was not possible within a standard lesson slot even with prior coverage of radioactivity.

only offers limited opportunity for expanding on key curriculum concepts.

- To effectively engage with and benefit from
 Game 2, KS4 pupils required prior knowledge and
 a double lesson slot
- To increase the accessibility of Game 2 a
 PowerPoint presentation with answers and accompanying lesson plan was developed.
- This enabled both Games to be used in the same lesson slot.

	9 5 points	3 points	1 points
	Americium-241	Californium-252	Uranium-235
	Radium-226	Thorium-232	Uranium-238
ctors	work by a	, = = = =	

Find out more & download RAD Ratings here



Smoke detectors work by a radionuclide emitting particles which ionise the air.

Which is the best radionuclide to use for this purpose and why?



CONCLUSIONS

- 170 card packs have been distributed to 13 schools, reaching >400 students within the first year.
- 70 card packs have been distributed to industry linked STEM Ambassadors (3 public sector, 4 private sector).
- For STEM ambassadors that support school engagement activities with in-person visits, preprepared card games reduces the time commitment of preparation and barrier to participation.

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3 https://www.petnetwork.org.uk/training

WHAT NEXT?

- To continue engagement with schools, academic and industry, RAD Ratings is available online as a free downloadable education resource available through uni4me.
- To develop RAD Ratings for harder to reach audiences and under-served outreach populations the game is currently being developed as a single player for hard to reach audiences.
- Interest from the public sector to develop specific card sets for themes including healthcare and defence have been highlighted, indicting industry appetite to support outreach and engagement with students and to support cross industry learning at different levels.

This work was supported by the Royal Society of Chemistry Schools and Outreach small grant under the project title "Repairing radiochemistry's reputation, isotope by isotope". The project was also supported by NNUF EXACT and TRANSCEND Consortium.



Langevin dynamics simulation of polymer-particle interactions for flocculation process behavioural modification

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1. Introduction

- Decontamination of legacy nuclear waste storage 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 addition of small amounts of high-molecular-weight polymers to particle-laden flows to separate non-settling fine solids from aqueous suspensions is a promising technique to instigate settling.
- The potential to use polymers in sensitive systems such as nuclear waste processing flows depends upon on the development of a better understanding and demonstrable effectiveness.



2. Polymer-induced flocculation

Adsorption of polymers onto particle surfaces causes destabilization through bridging or charge neutralization.



(a) Non-settling dispersed regime. Polymers and particles advected by flow.

(b) Adsorption of polymers
 onto particle surfaces
 through electrochemical and
 hydrophobic interaction

(c) Bridging of polymers
 between particles as
 hydrodynamic forces cause
 particles to collide
 (d) Floc formation and
 subsequent settling

This study aims to elucidate the fundamentals of polymer-particle interaction and adhesion within settling tanks and flows, as well as the way in which chemical or bulk properties affect the dynamics of adhesion, bridging and subsequent flocculation.

3. Finitely extensible non-linear elastic (FENE) polymer model



 Langevin dynamics simulation including spherical particles and bead-spring polymers, which are represented as a sequence of beads connected in a chain through FENE bonds.

$$\frac{d^2 r_i^*}{dt^{*2}} = -\nabla V_i^* - \frac{1}{D} \left(\frac{d r_i^*}{dt^*} - u_{F,i}^* \right) + \sqrt{\frac{2}{D}} \eta_i^*(t^*)$$
$$V_{i,FENE}^*(\delta r^*) = -\frac{K_F^* R_0^{*2}}{2} \ln \left[1 - \left(\frac{\delta r^*}{R_0^*} \right)^2 \right]$$

$$V_{i,WCA}^{*}(\delta r^{*}) = 1 + 4\left[\left(\frac{1}{\delta r^{*}}\right)^{12} - \left(\frac{1}{\delta r^{*}}\right)^{6}\right]$$

$$V_{i,BEND}^*(\theta_i) = K_B^* (1 + \cos(\theta_i))$$

4. Polymer chains in turbulent channel flows



• Conformation is highly shear-dependent, and with polymerparticle interaction shown to depend highly on conformation. Flocculation behaviour will be greatly modified by local shear rate.

5. Polymer-particle adhesion dynamics under shear

• The equations above are solved for each monomer bead using a Verlet-velocity integration scheme and constant timestep $\delta t^* = 0.005$.



- To study multi-polymer adsorption onto a stationary particle within a flow, the domain is a 60×30×30 computational channel cell in all cases.
- Before the first timestep, 15 polymer chains are injected into the upstream region $x^* < 20$, with the particle of diameter $d_P^* = 10$ fixed stationary at $x^* = 30$.
- To quantify the adsorption events, we consider a monomer to have adsorbed onto the particle if its distance from the particle surface is less than the monomer bead diameter ($dr^* < 1$).



6. Adsorption conformation



Instantaneous snapshots of flocculation events. Each shade of grey represents a different polymer.

• As the rigidity is increased, the inability to flatten out onto the particle leads to more cluster-like polymer conformities forming on the particle, and longer structures leading to longer tails. These also tend to form parallel to the streamwise direction.

We observe that for low bending rigidity, more monomers are capable of adsorbing onto the particle surface. As the potential is increased, the longer conformities present means that full adsorption onto the surface is less energetically favourable, and so the percentage is reduced.

Effect of bending rigidity potential strength on the temporal evolution of percentage of adsorbed monomers (left) and monomers in adsorption region $(1 \le dr^* \le d_P^*)$.

6. Conclusions

- A novel potential-based particle-polymer simulation adsorption simulation technique has been developed in order to explore the fundamentals of flocculation and polymer-surface interaction. Monte-Carlo simulations of shear flows in the presence of a single stationary particle were also performed to determine mechanisms for adsorption.
- Simulations of multi-polymer particle adsorption events have been performed using Langevin dynamics. A study into the effect of the Kratky-Porod bending rigidity potential indicates that polymer species with low bending rigidities tend to adsorb fully onto the particle surface, whereas increasing the rigidity leads to long tail-like structures forming and lower adsorption leaving further surface for more interactions to occur.

Transformative Science and Engineering for Nuclear Decommissioning





TRANSCEND

Radiation effects on nuclear waste forms: How does the crystallinity of glass composite affect radiation tolerance? Tamás Zagyva¹, Robert Harrison¹, Tracey Taylor², Mike Harrison², Laura Leay¹, Brian O'Driscoll³ ¹The University of Manchester ²National Nuclear Laboratory ³The University of Ottawa

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1. Introduction

Molybdenum-rich radioactive waste streams generated during postoperational clean-out (POCO) operations in the UK will be vitrified into highlevel waste (HLW) glass composite products containing powellite (CaMoO₄) crystals [1]. The vitrified HLW will be buried underground in a geological disposal facility (GDF) and exposed to self-irradiation for thousands of years.



2. Materials & Methods

- Mo-rich non-active waste simulant glass composites were produced by National Nuclear Laboratory in the Vitrification Test Rig (VTR).
- Nickel and gold ion irradiation experiments were performed to induce changes similar to alpha recoil nuclei. The average total dose was ~1.4 displacements per atom (dpa) in powellite, equivalent to 1.0-1.3 GGy dose.



Goal of research: Characterise Mo-rich nuclear waste simulant glass composites and evaluate their long-term radiation tolerance by performing heavy ion irradiation experiments.

• X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM) (with *in situ* Ar & Xe irradiations) were used for characterisation.

3. Radiation tolerance of glass composites

The main crystal phases in the waste simulant samples were powellite, zircon, cerianite, zincochromite and ruthenium dioxide. Microcracks formed around large powellite and zircon crystals, presumably due to a thermal expansion mismatch between the glass and these phases.





4. TEM with *in situ* Ar and Xe ion irradiation on powellite

- Ar, Xe and Pb irradiations published in the literature suggest that powellite is highly radiation-tolerant as it remains crystalline at high fluences [2-4].
- However, our in situ Ar and Xe ion irradiation experiments show that amorphisation could occur depending on the temperature and ion type.



Powellite and zircon swelled considerably after Ni and Au irradiation. The radiation damage was greater in the Au irradiated sample.



TEM analysis above -80 °C was not possible because of the electron beam-induced recrystallisation.

2.5×10¹⁴ Ar ions/cm

Bright-field (A,B), diffraction (D-G) images and thickness map (1 λ = 159 nm) of Ar-irradiated powellite. Diffraction pattern with bright spots represents crystalline structure, diffuse rings correspond to amorphous material.

5. Conclusions

- We have shown the first evidence of ion irradiation-induced amorphisation in powellite and electron beam-induced recrystallisation in amorphous powellite.
- In contrast to previous findings our results indicate that powellite is susceptible to amorphisation by alpha recoils in high-level wastes; however, the relatively high temperature and the ionisation-induced annealing caused by alpha particles and beta irradiation may cause significant defect recovery and may prevent the complete amorphisation.
- The irradiation-induced swelling might be significant enough to cause further cracking at places where there are large powellite and zircon crystals (e.g., middle of the high-level waste canister).

6. Acknowledgements

Special thanks to Anamul Haq Mir for the TEM measurements at the MIAMI irradiation facility and to Samir de Moraes Shubeita and the DCF ion beam accelerator team for the nickel and gold irradiation experiments. This project has received funding from the EPSRC TRANSCEND consortium under grant agreement number EP/S01019X/1.

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