



### Nuclear Decommissioning Authority PhD Research Seminar for NDA-Sponsored PhD Projects, 2017

**ABSTRACT BOOKLET** 

18th January 2017 Manchester Conference Centre

# Nuclear Decommissioning Authority PhD Research Seminar for NDA-Sponsored PhD Projects

### 18th January 2017

### Introduction

#### Rick Short (Research Manager, Nuclear Decommissioning Authority)

A key part of NDA's R&D strategy is to ensure that we have the appropriate skills and capabilities available over the timescales necessary to carry out the decommissioning of the UK civil nuclear legacy. University research plays a major role in the maintenance of these skills, and the NDA PhD Bursary programme helps to provide the next generation of technical specialists required to support the NDA mission. Our aim is that students who are supported by NDA bursaries go on to contribute to the clean-up effort by becoming members of the Estate, the Supply Chain or by staying in academia and educating subsequent generations about the challenges faced by the decommissioning industry.

An important aspect of the bursary programme is to promote the transfer of knowledge between academia and industry. The annual Bursary Seminar provides an opportunity for that transfer to happen. The attendees from industry get to learn of the breadth of decommissioning related research that is being undertaken in academic institutions across the UK and about new tools and techniques that might be applicable to their site challenges. The academic attendees get the chance to talk to the industry experts who have first-hand experience of tackling those challenges and can help direct academic research to make it as relevant as possible. So, I'd like to thank you for attending the seminar and hope that you make the most of this opportunity to learn from each other throughout the day.

2017 NDA PhD SEMINAR PROGRAMME					
Day 1: Tuesday 17 <sup>th</sup> January 2017 - Early registration and poster drop off, hotel check in, informal meal					
16:00 - 18:00	EARLY REGISTRATION and POSTER DROP OFF				
19:00	Informal meal out in Manchester (NNL convening)				
Day 2: Wednesday 18 <sup>th</sup> January 2017 - Seminar Day					
08:00 - 08:40	REGISTRATION - Posters put up COFFEE & NETWORKING				
08:40 - 08:50	WELCOME & INTRODUCTORY REMARKS				
08:50 - 09:00	NDA UNIVERSITY PROGRAMME Rick Short & Michelle Cowley - NDA				
09:00 - 11:28	PhD STUDENT POSTER INTRODUCTIONS (each 'poster presenter' will provide an oral introduction to their poster - max 4 minutes each)				
	STUDENT BURSARY YEAR - GROUP	TITLE			
09:00 - 09:04	Jamie Southworth 2013 iCASE – Spent Fuel & Nuclear Material	Investigation of anomalous $H_2$ production from water absorbed on metal oxides			
09:04 - 09:08	Jessica Higgins 2014 Bursary - Spent Fuel & Nuclear Material	Wet oxidation of uranium oxide within sealed and unsealed environments subject to radiation fields			
09:08 - 09:12	Nathan Palmer 2014 iCASE & DISTINCTIVE - Spent Fuel & Nuclear Material	Computational modelling of $PuO_2$ ageing and fuel residues			

09:12 - 09:16	Cara Mulholland 2015 iCASE – Decommissioning	Creating social value for the NDA
09:16 - 09:20	Diletta Invernizzi 2015 Bursary - Decommissioning	Do you know what makes your decommissioning project successful?
09:20 - 09:24	Dobromil Duda 2015 Bursary - Decommissioning	Autonomous mobile robotic systems for remote handling and decommissioning
09:24 - 09:28	Kate Lawrence 2014 iCASE - Decommissioning	Effective models for engaging and supporting Small and Medium-sized Enterprises (SMEs) in delivering technological innovation in nuclear decommissioning
09:28 - 09:32	Jack Clarke 2013 iCASE - Waste Packaging & Storage	Conditioning of legacy radioactive wastes requiring additional treatment
09:32 - 09:36	Daniel Geddes 2016 Bursary - Waste Packaging & Storage	Geopolymers as an alternative cement for problematic UK wastes
09:36 - 09:40	Adrian Cleary 2014 Bursary – Land Quality	Enhanced in-situ treatment of strontium in sediment systems by stimulation with glycerol phosphate
09:40 - 09:44	Chak-Hau Michael Tso 2014 Bursary – Land Quality	Enhancing the information content of geophysical data applied to nuclear site characterisation
09:44 - 09:48	David Hodkin 2013 Bursary - Land Quality	Co-treatment of mixed radionuclides in large volumes of contaminated water by carbonate coprecipitation reactions
09:48 - 09:52	Emma James 2016 Bursary –Land Quality	Assessment of the impact of leak zone processes in the natural attenuation of radionuclides
09:52 - 09:56	Jamie Purkis 2015 Bursary – Land Quality	Towards catalytic uranyl hydrocarbon C-H bond cleavage
09:56 - 10:00	Gianni Vettese 2015 Bursary – Land Quality	Optimising bioremediation end-points for the safe and effective long-term stewardship of UK radwaste impacted land
10:00 - 11:00	COFFEE & NETWORKING	
11:00 - 11:04	Anita Crompton 2015 Bursary - Characterisation	Long-range scanning based detection of Alpha-Induced Air Fluorescence even under daylight conditions

11:04 - 11:08	Ikechukwu Ukaegbu 2015 Bursary - Characterisation	Radiological characterisation of hard to access areas: Integrated Mixed Field Imaging and Surface Penetrating Radar approach.
11:08 - 11:12	Kevin Tree NGN - Characterisation	Enhance nuclear waste assay
11:12 - 11:16	Mel O'Leary DISTINCTIVE - Characterisation	Irradiated sludges, a joint theoretical/experimental study
11:16 - 11:20	Richard Gray 2014 Bursary - Characterisation	Development and industrial testing of multi-radiation systems for the characterisation of nuclear facilities
11:20 - 11:24	Robert Shearman 2014 Bursary - Characterisation	The development of a novel gamma-ray detection system for fission fragment decay data measurement and evaluation
11:24 - 12:00	KEYNOTE INDUSTRY TALK Tom Scott – University of Bristol 'Investigating claims of nuclear waste dumping in Somalia'	
	LUNCH AND POSTER SESSION (presenters to stand by posters from 12:30)	
12:00 - 13:30	<b>LUNCH AN</b> (presenters to st	and by posters from 12:30)
12:00 - 13:30 13:30 - 16:10	LUNCH AN (presenters to st PhD STUDENT	ID POSTER SESSION and by posters from 12:30)       Image: Constant of the second sec
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<b>12:00 - 13:30</b> <b>13:30 - 16:10</b> 13:30 - 13:50	LUNCH AN (presenters to st PhD STUDENT STUDENT BURSARY YEAR - GROUP Ioannis Tzagkaroulakis 2012 Bursary - Decommissioning	ID POSTER SESSION   and by posters from 12:30)     CORAL PRESENTATIONS     Image: Display the image:
<b>12:00 - 13:30</b> <b>13:30 - 16:10</b> 13:30 - 13:50 13:50 - 14:10	LUNCH AN (presenters to st PhD STUDENT STUDENT BURSARY YEAR - GROUP Ioannis Tzagkaroulakis 2012 Bursary - Decommissioning Reece Hall 2015 Bursary - Decommissioning	<b>POSTER SESSION</b> and by posters from 12:30) <b>ORAL PRESENTATIONS EXAMPLE</b> Real-time nanogravimetric monitoring of corrosion in radioactive environments     Natisite- a layered titanium silicate for use as an ion-exchanger within the nuclear industry

14:30 - 15:30	COFFEE & NETWORKING	
15:30 - 15:50	Benjamin Krawczyk 2013 Bursary – Spent Fuel and Nuclear Materials	Performance characterization and optimization of THORP storage cans
15:50 - 16:10	Mike Pugh 2014 Bursary - Spent Fuel & Nuclear Material	Susceptibility to cracking of sensitised stainless steel nuclear fuel containment under simulated storage conditions
16:10 - 16:30	- closing remarks & presentation of prizes -	
16:30	– Seminar Ends – Coffee is available	

### **POSTER PRESENTATIONS**

## Investigation of anomalous H<sub>2</sub> production from water absorbed on metal oxides

<sup>1</sup>Jamie Southworth, <sup>1</sup>Sven Koehler, <sup>1</sup>Simon M. Pimblott, <sup>2</sup>Robin Orr and <sup>2</sup>Howard Sims

<sup>1</sup>University of Manchester

<sup>2</sup>National Nuclear Laboratory

Legacy plutonium in the UK is currently stored in sealed canisters at Sellafield, West Cumbria. Certain  $PuO_2$  canisters have become pressurised over time, and a major component of the gas was determined to be  $H_2$  [1]. The presence of a metal oxide can vastly alter the product distribution during the radiolysis of water. Most notably, for the radiolysis of water on  $ZrO_2$ , this includes an increase in the yield of  $H_2$  by up to three orders of magnitude [2].

The  $\gamma$ -ray radiolysis of water adsorbed on the surface of ZnO as a surrogate for PuO<sub>2</sub> was investigated to establish the evolution of gas from the  $\gamma$ -radiolysis of adsorbed water. Surprisingly, both O<sub>2</sub> and H<sub>2</sub> were produced in similar quantities. This is unexpected as previously, either none or negligible volumes of O<sub>2</sub> are typically observed for water radiolysis on other oxides [1].

 $O_2$  was observed during the radiolysis of both wet and dry ZnO, indicating the source of some of the  $O_2$  to be the bulk oxide. The production of  $H_2$  due to the radiolysis of water adsorbed on ZnO was observed to be an order of magnitude greater than for pure water for water adsorbed to the surface of the oxide. This could be attributed to an energy transfer process from the oxide to the adsorbed molecules. The yield of  $H_2$  was also observed to increase linearly with dose and decrease with increased water loading.



References [1] LaVerne. J. A, Tandon. L, J. Phys. Chem. B, 2002, 106, 380-386 [2] Sims. H. E, Webb. K. J, Brown. J, Morris. J, Taylor. J. R, J. Nuc. Mater.,2013, 437, 359-364

### Wet oxidation of uranium oxide within sealed and unsealed environments subject to radiation fields

<sup>1</sup>Jessica Higgins

<sup>1</sup>University of Manchester

During several stages of both the open and closed nuclear fuel cycles, spent uranium oxide fuel comes into contact with water; either during interim storage, reprocessing or final deposition. The used fuel emits an intense ionising radiation field comprising of alpha, beta and gamma, capable of imparting a significant dose to surrounding materials. This project focuses on the radiation induced chemical behaviour of water adsorbed onto the surface uranium oxide powders under gamma, high energy proton and 5.5 MeV helium ions irradiation. Initial studies will examine:

- 1. The oxidative dissolution mechanisms of the uranium oxide surface induced by reactive species produced in the radiolysis of water;
- 2. Quantification of these radiolytic products, in particular hydrogen, as a function of humidity, dose, dose rate, and stoichiometry.

The interaction of radiation with liquid water has been widely studied and modelled, with the predominant stable products being hydrogen peroxide and gaseous molecular hydrogen. The yields of these products depend upon radiation quality, i.e. the radiation type and its energy. In addition, an enhancement to the yield of molecular hydrogen has been shown to exponentially increase with decreasing quantities of adsorbed water.

Under a gaseous atmosphere, UO<sub>2</sub> has been shown to oxidise through a mechanism of oxygen inclusion at the interstitial sites, elongating the fluorite type cubic lattice structure. At high enough temperatures and/or oxygen gaseous concentrations, UO<sub>2</sub> can be induced to form UO<sub>3</sub> by the following pathway; UO<sub>2</sub>  $\rightarrow$  U<sub>3</sub>O<sub>7</sub>/U<sub>4</sub>O<sub>9</sub>  $\rightarrow$  U<sub>3</sub>O<sub>8</sub> $\rightarrow$  UO<sub>3</sub>, where UO<sub>3</sub> is the thermodynamically favoured product but not the kinetically favoured one.

However, under aqueous conditions, rather than forming the intermediate lattice structure, a soluble uranyl ion is produced in a two-step electron transfer process. This interaction occurs between the uranium surface and adsorbed radiolytic products and can be summarised as;

 $UO_2 \rightarrow UO_{2+x} \rightarrow UO_2{}^{2+} \rightarrow UO_3 \bullet yH_2O.$ 

As the formation of the aqueous uranyl ion reaches supersaturation, deposits of studtite/metastudtite ( $UO_3 \bullet yH_2O$ ) are believed to precipitate out of solution, building up to form a protective layer on the surface of any remaining  $UO_2$ . The rate of formation and speciation as a function of dose within the  $UO_2 \rightarrow UO_3 \bullet yH_2O$  system can be studied and reaction kinetics obtained. In situ spectroscopic analysis of the liquors can be used to calculate dissolution kinetics, while surface characterisation of remaining uranium solids will reveal oxidative changes to the surface.

### Computational modelling of PuO<sub>2</sub> ageing and fuel residues

#### <sup>1</sup>Nathan Palmer

<sup>1</sup>University of Birmingham

Computational modelling of  $PuO_2$  is required to understand the complicated ageing of the  $PuO_2$  stockpile at Sellafield, UK. Atomistic simulations are a powerful and versatile tool to probe the detailed defect chemistry of the bulk and surfaces of  $PuO_2$ . Hence, robust interatomic pair potentials have been used in GULP (General Utility Lattice Program) [1], [2] to replicate the bulk accurately and to model a range of intrinsic defects and including helium atoms. Understanding helium behaviour in  $PuO_2$  is important as it is produced from the alpha decay of plutonium and is considered to contribute to gas build up in storage cans. The simulations have shown it is energetically favourable for helium atoms near bound defects to migrate to and reside in lattice vacancies. Hence, helium can be accommodated easily in the defected structure of bulk  $PuO_2$ . Furthermore, METADISE (Minimum Energy Techniques Applied to Dislocation, Interface and Surface Energies) [3] has been used to model a range of  $PuO_2$  surfaces, to predict their structure and stability.

Regarding the bulk simulations of  $PuO_2$ , the interatomic potentials by Read et al. (2014) [4] have been used, predicting a range of structural and mechanical properties in agreement with experiment. Using these potentials in GULP has also enables calculation



region strategy for defect energy calculations.

of a range of intrinsic defect energies using the Mott-Littleton method [5]. In this method, the crystal is separated into two spherical regions, centred on the defect, as shown in Fig.1. The inner region, region I, is relaxed explicitly whilst the outer region IIa is treated as a dielectric continuum and is polarised by the influence of the defect. In addition to point defects, bound defects such as anion and cation Frenkel pairs and Schottky defects have been simulated. The simulations have clearly shown that oxygen Frenkel pairs and Schottky defects are the preferred forms of intrinsic defects in PuO<sub>2</sub>. To model helium from plutonium alpha decay, the potentials by Grimes et al. (1990) [6] has been used, predicting defect energies with helium atoms located in vacancies. The simulations have shown it is typically preferable for this to occur, rather than for the helium atoms to reside in octahedral sites.

Finally, modelling of surfaces has been underway using METADISE, transferring the  $PuO_2$  potentials applicable to surface modelling. The choice of surfaces follows from the atomistic study of grain boundaries in UO<sub>2</sub> by Williams et al. (2015) [7]. These include the {nn1}, {n11} and {n10} sets of surfaces, where n = 1, 2 and 3. Early results have shown that the relaxed structures of the {nn1} set are most stable. In addition, the less stable surfaces have a significant relaxation, reducing their energy significantly. Of the low index surfaces, the (111) surface is most stable, followed by the (110) and (100) surfaces as expected structurally. The relaxed (111) surface is shown in Fig.2.



Fig.2. Views of the relaxed (111) surface of  $PuO_2$  for (i) top-down view and (ii) side view showing an apparent hexagonal arrangement of the ions.

#### References

[1] Gale JD. GULP: A computer program for the symmetry-adapted simulation of solids. Journal of the Chemical Society, Faraday Transactions. 1997;93(4):629-37.

[2] Gale JD, Rohl AL. The General Utility Lattice Program (GULP). Molecular Simulation. 2003;29(5):291-341.

[3] Watson GW, Kelsey ET, de Leeuw NH, Harris DJ, Parker SC. Atomistic simulation of dislocations, surfaces and interfaces in MgO. Journal of the Chemical Society, Faraday Transactions. 1996;92(3):433-8.

[4] Read MSD, Walker SR, Jackson RA. Derivation of enhanced potentials for plutonium dioxide and the calculation of lattice and intrinsic defect properties. Journal of Nuclear Materials. 2014;448(1–3):20-5.

[5] Mott NF, Littleton MJ. Trans Faraday Soc. 1938:485.

[6] Grimes RW, Miller RH, Catlow CRA. The behaviour of helium in UO<sub>2</sub>: Solution and migration energies. Journal of Nuclear Materials. 1990;172(1):123-5.

[7] Williams NR, Molinari M, Parker SC, Storr MT. Atomistic investigation of the structure and transport properties of tilt grain boundaries of UO<sub>2</sub>. Journal of Nuclear Materials. 2015;458:45-55.

### Creating social value for the NDA

<sup>1</sup>Cara Mulholland and <sup>1</sup>Paul Chan

<sup>1</sup>University of Manchester

Nuclear energy is a current topic in British politics as plans are made for the future of UK energy. The government wants to ensure the social sustainability of the work - social value becoming a prominent policy concern with the Public Services (social value) Act 2012. This often encourages assigning monetary values when measuring social impacts. However, it may not be desirable to view social value outcomes as concrete objects to be measured and which can be monetised. It is possible to view measurement as not necessarily the whole solution when wanting to encompass social value; it is a tool through which the concept of social value is created. This research looks at how social value is being brought into organisations and what this means for the future of nuclear, by reviewing the literature and critiquing current thoughts, practices and emerging trends.

The NDA is already giving energy and momentum towards this movement, highlighting socio-economics and stakeholder engagement, among others, as critical enablers which encompass social value in the 2016 NDA Strategy. At an early stage it is interesting to see how the organisation will evolve the concept in practice. A shift could allow space for the acceptance of intangible ideas to influence decisions within a technical field. With no clear definitions of social value, and many experts advocating a bespoke method for each project, social value is a concept allowing space for intangible discussions. There is scope to change how social value is viewed, depending on the motives behind the work. The outputs of identifying, measuring and classifying social value have practical significance. However, the usefulness of understanding social value as a conceptual outcome that has been created in the process of measurement allows for more robust systems throughout the sector. Viewing social value from this perspective allows for an increased understanding when using it in practice.

Next stages of research will observe different stakeholders who are taking part in the conversation creating social value, and critiquing measurement methods and systems to understand how they could be useful for the NDA's socio-economic work.

## Do you know what makes your decommissioning project successful?

<sup>1</sup>Diletta Invernizzi

<sup>1</sup>University of Leeds

Project management literature has, until now, mainly focused on new built and only in the last decades the issues of decommissioning (mega) projects came up. Therefore, in the future, project management will need to focus more and more extensively on the challenges imposed by decommissioning projects. Within other projects, such as the Oil&Gas and the chemical ones, Nuclear Decommissioning Projects and Programmes (NDPs) are characterized by the highest costs, longest schedule and several risks. Additionally, the budget for these projects keep increasing and, due to NDPs complexity and variety, key stakeholders lack a full understanding of the key determinants that engender these phenomena. Benchmarking involves "comparing actual or planned practices to identify best practices, generate ideas for improvement" [1] and offers significant potential to improve the performance of project selection, planning and delivery. However, even if benchmarking is the envisaged methodology to investigate the NDPs characteristics that impact on the NDPs performance, until now, it has only been partially used. Despite this extremely high relevance, there is a huge gap in the literature concerning benchmarking NDPs. This research adapts a top-down benchmarking approach to highlight the NDPs characteristics that mostly impact on the NDPs performance. This is exemplified by a systematic quantitative and qualitative cross-comparison of two major "similar-but-different" NDPs: Rocky Flats (UK) and Sellafield (UK). Main results concern the understanding of the alternatives of the owner and/or the contractors in relation to (1) the physical characteristics and the end state of the nuclear site, (2) the governance, funding & contracting schemes, and (3) the stakeholders' engagement. This paves the way for developing the methodology presented in [2] to analyse the statistical correlation and causation between NDPs characteristics and NDPs performance.

#### References

[1] PMBOK. (2013). A Guide to the Project Management Body of Knowledge - Fifth Edition.

[2] Brookes, N. J., & Locatelli, G. (2015). Power plants as megaprojects: Using empirics to shape policy, planning, and construction management. Utilities Policy, 36, 57–66.

## Autonomous mobile robotic systems for remote handling and decommissioning

<sup>1</sup>Dobromil Duda, <sup>1</sup>C. James Taylor, <sup>1</sup>Allahyar Montazeri and <sup>1</sup>Steve D. Monk

#### <sup>1</sup>Lancaster University

In areas of significant radioactive contamination, it is necessary to use teleoperated mobile robots. These provide an invaluable option for the safe retrieval and disposal of contaminated materials in high-hazard legacy facilities, whilst safeguarding the environment and minimising radiation exposure to operators. This PhD bursary will develop novel autonomous systems to support teleoperation, based on e.g. object depth perception and force feedback, and improved operation via a touch screen controller interface. The demonstrator system is a BROKK-40 decommissioning robot, consisting of a moving vehicle with a single 5 degree-of-freedom manipulator, hydraulic tank and remote control device. Attached to the BROKK are two HydroLek seven-function manipulators, i.e. each with six rotary joints and a gripper. The manipulators in this project have to interact with objects of varying dimension, position, appearance and weight, and these objects may have initially unknown and potentially time-varying (e.g. during a dismantling task) location and orientation. To support the operator, the supervisory control system has to combine information from multiple (sometimes redundant) sensors, for which the data are typically noisy and ambiguous. Nonetheless, when the robot is used to undertake a realistic task such as welding or pipework dismantling, exact knowledge of the location of the joint or pipe in 3 dimensions relative to the robot is essential. This involves the use of cameras located at two different locations on the robotic platform, and will utilise stereoscopy to produce a 3D image from these two 2D images. This approach will be coupled to the use of haptic sensors to provide feedback to the gripping mechanism, so that the robot can successfully pick up objects without crushing them due to the application of excess pressure. The touch screen will allow the operator to select the target and where on the target to approach with the gripper.

### Effective models for engaging and supporting Small and Mediumsized Enterprises (SMEs) in delivering technological innovation in nuclear decommissioning

<sup>1</sup>Kate Lawrence

<sup>1</sup>University of Manchester

The potential of an innovative idea or invention is realised once it has successfully navigated its path through concept, testing and commissioning to final deployment and/or commercialisation. Once in operational use, the innovative idea or invention is recognised as an 'innovation'. Collaborations between the public and private sector play a vital role in bridging the gap between the 'idea' and 'commercialisation' of new technologies. Governments and the public sector rarely commercialise new or novel knowledge through exploiting an innovation for commercial gain. However, promoting innovation (for example, through investing in research grants; sponsoring innovation competitions; supporting alliance and innovation networks etc.) is a public sector strategy to achieve social, political, economic and environmental 'added value' at local, regional and national levels. In particular, accessing an innovative or novel idea from a small firm is of strategic importance to the UK Government, who recognises the important contribution that SMEs make, not only to the economy, but also to the UKs innovation infrastructure.

The NDA has expressed an interest in learning from analogous public bodies in respect of the challenges and opportunities associated with accessing technological innovation through engaging with SMEs. Encouraging innovation supports the efficient delivery of the NDAs complex and challenging decommissioning mission. In terms of time, costs and safety, the adoption of emerging technologies (in particular, from SMEs outside of the decommissioning sector) provides opportunities to improve on established technologies and ultimately deliver the NDAs decommissioning mission more effectively.

Through a critical review of the academic literature, private sector engagement with SMEs to access technological innovation is more widely discussed than public sector engagement with SMEs. The review also highlighted opportunities to extend current research. Firstly, in respect of the routines and practices of public bodies when addressing issues such as (i) relationship asymmetries with SMEs and (ii) the cross-boundary search for innovations. Secondly, in respect to how public bodies judge the success of engagement instruments in delivering technological innovation with SMEs. Hence, through a theory building, multiple case study research strategy, we will be questioning 'How do Public Bodies engage with SMEs to access technological innovation?'

In accessing technological innovation, the research project will consider why a Public Body would choose to engage with SMEs. How a Public Body then operationalises an SME engagement strategy and the mediating impact of Absorptive Capacity capabilities on a Public Body's engagement decisions. Absorptive Capacity is described as the "ability of a firm to recognise the value of new, external information, assimilate it, and apply it to commercial ends" [1] and has been linked to the successful commercialisation of new knowledge. Other questions for review include, which SME engagement instruments a Public Body would use (whether across vertical supply chains or horizontal knowledge transfer relationships). For example, ideas competitions, co-creation, consortia, intermediaries, venturing, strategic alliances, networks, research grants etc. Also, which characteristics determine engagement outcomes (for example, prior experience, type of boundaries, technology state, sector, size, culture and resources etc.) and finally, how a Public Body measures engagement success with SMEs.

#### References

[1] Cohen, W.M. and Levinthal, D.A., 1990. Absorptive capacity: a new perspective on learning and innovation. Administrative Science Quarterly, 35(397), pp.128-152 (p. 128).

## Conditioning of legacy radioactive wastes requiring additional treatment

<sup>1</sup>Jack Clarke

<sup>1</sup>University of Sheffield

Intermediate level waste (ILW) (i.e. that which contains >4MBq kg<sup>-1</sup> a or >12MBq kg<sup>-1</sup>  $\beta/\gamma$  but generates <2kW m<sup>-3</sup> of heat) covers a wide range of waste materials found at nuclear sites. Thermal treatment offers several benefits for certain ILW streams including waste volume reduction and utilising the natural glass-formers present in the waste (such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>). This poster shows results from laboratory-scale vitrification of two different ILW streams- problematic cemented Magnox fuel cladding and ion exchange resins. Various analytical techniques are used to characterise the resulting glassy wasteforms- including SEM/EDX (to study microstructure), XRD (for phase analysis), thermal analysis (to determine glass transition temperatures) and PCT-B (to study the durability of the glass).

### Geopolymers as an alternative cement for problematic UK wastes

#### <sup>1</sup>Daniel Geddes

<sup>1</sup>University of Sheffield

Portland cement-based materials have been used extensively to immobilise nuclear wastes in the UK. However, the compatibility of certain wastes with Portland cement matrices can pose issues regarding short term gas generation and setting characteristics, in addition to long term product evolution, with resultant potentially significant restrictions to the waste loadings that can be achieved. As a result, an alternative has arisen in the form of geopolymers. Geopolymers are attractive as their aluminosilicate chemistry and tailorable pore structure can be used to produce a matrix to encapsulate intermediate level oily organic problematic wastes. This is key as the UK has a large inventory of problematic oil based waste that is difficult to encapsulate using the current methods. Geopolymers can also be used with corrosion inhibitors, to immobilise reactive metals that would otherwise corrode in cements at the high pH environment encountered in conventional cements.

In this project, bespoke solutions based on geopolymer materials will be developed and organic release rates will be examined. Tests will be developed to assess the performance of the geopolymer systems in relation to material integrity and the release of organics and radionuclides, compared to baseline UK Portland cement grouts. Hydrogen evolution measurements and microstructural analysis will also be used to analyse the resistance to corrosion of the encapsulated reactive metals.

## Enhanced in-situ treatment of strontium in sediment systems by stimulation with glycerol phosphate

<sup>1</sup>Adrian Cleary, <sup>1</sup>Laura Newsome, <sup>1</sup>Jonathan Lloyd, <sup>1</sup>Sam Shaw, <sup>2</sup>Genevieve Boshoff, <sup>2</sup>Divyesh Trivedi, <sup>3</sup>Nick Atherton and <sup>1</sup>Katherine Morris

<sup>1</sup>University of Manchester

<sup>2</sup>National Nuclear Laboratory

#### <sup>3</sup>Sellafield Ltd

Nuclear fuel cycle operations over the last 60 years have led to a legacy of radioactively contaminated land at sites such as Sellafield and Dounreay in the UK and Hanford and Oak Ridge in the USA. <sup>90</sup>Sr is often considered one of the priority mobile radionuclides present at elevated concentrations in groundwater within these sites but may also be present with other contaminants in groundwaters. In-situ bioremediation treatments are capable of immobilising several radioactive contaminants within the subsurface, including U, <sup>99</sup>Tc and <sup>90</sup>Sr. It is important that the products of remediation are resilient to environmental perturbations and also that these remediation strategies consider treatment of likely co-contaminants present at nuclear licensed sites.

The dominant control on  ${}^{90}$ Sr mobility in the environment is sorption as the Sr<sup>2+</sup> ion although Sr removal to solids may be increased through addition of sorbent materials such as hydroxyapatite, or by increasing the pH through nitrate bioreduction. The co-precipitation of Sr into stable mineral phases is also another pathway which has the potential to ensure the long term removal of  ${}^{90}$ Sr from groundwater.

The focus of this study is co-precipitation of Sr with stable phosphate minerals using an in-situ biomineralisation treatment previously shown to treat soluble uranium [1]. In the current work, a pure culture biomineralisation experiment with soluble  $Sr^{2+}$  was conducted anaerobically using glycerol phosphate as the electron donor to stimulate growth of a Serratia isolate [2] and in a synthetic freshwater minimal media containing  $Sr^{2+}$  and  $Ca^{2+}$  (0.7 and 16 mM). Following the biodegradation of glycerol phosphate, inorganic phosphate was released to solution and a decrease in Ca2+ and Sr2+ concentrations was observed. These data will be discussed in terms of aqueous and solid phase analyses.

Additionally, a series of sediment microcosms were stimulated with glycerol phosphate under anaerobic conditions to examine the impact of this on Sr behaviour. Here, results show that sediments treated with glycerol phosphate removed  $90 \pm 2\%$  Sr from solution compared to only  $44 \pm 1.2\%$  removal from untreated sediments. Ongoing work is examining the nature and stability of strontium phases that are responsible for the enhanced removal using a range of direct and sequential extraction processes. Overall, these data suggest that enhanced removal of Sr from solution during biostimulation by glycerol phosphate may occur through the formation of phosphate biominerals. This opens up new routes for the co-treatment of strontium and other redox active radionuclides such as technetium and uranium. The latter has been shown to be reduced in sediment systems in the presence of glycerol phosphate to form a recalcitrant U(IV)-phosphate[1].

References

[1] L. Newsome, K. Morris, D. Trivedi, A. Bewsher, J. R. Lloyd Biostimulation by glycerol phosphate to precipitate recalcitrant uranium(IV) phosphate. Environ. Sci. Technol., 49, 11070-11078. 2015

[2] L. Newsome, K. Morris, J. R. Lloyd. Uranium biominerals precipitated by an environmental isolate of Serratia under anaerobic conditions. PLoS One, 10, e0132392. 2015

## Enhancing the information content of geophysical data applied to nuclear site characterisation

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Large volumes of hazardous wastes are stored worldwide in surface and underground tanks or buildings [1]. They are prone not only to a loss of stored inventory but also contamination to soil and groundwater. Detection of leaks from such stores is challenging because it is expensive and hazardous to emplace sensors in the potentially contaminated subsurface. Moreover, the heterogeneous finger-like structure of contaminant transport in the subsurface would require numerous sensors around a storage facility to ensure a reliable detection of leaks.

Geophysical tomography, which reconstructs the subsurface distribution of geophysical properties using a limited number of sensors, is a more realistic option to detect leaks, particularly at nuclear sites. One of the geophysical methods, cross-hole electrical resistivity tomography (ERT), has been identified by the NDA as the 'best available technology' for inground detection and volumetric monitoring of potential leakage from waste storage facilities after a field trial at Sellafield [2]. Previously, the US DOE reached similar conclusions for its underground storage tanks at the Hanford and Savannah River sites. Recent improvements in the ERT method, such as a permanently installed remote monitoring system, better modelling of metallic structures and improved inversion methods, has made the method more readily available for leak detection.

There remains much room for improvement for ERT leak detection. It is now recognized that throughout the hydrogeophysical workflow, different sources of uncertainties contribute to the final reliability of leak detection. This PhD studentship considers three sources of uncertainties in the workflow and proposes methods to improve each of them. A major goal of the PhD is to rank these improvements through total sensitivity analysis in order to decide the relative importance of each of the improvements to the final reliability of leak detection, and the steps needed to reduce such uncertainty. The first part of the PhD, "improved characterisation and modelling of measurement errors in ERT", has been completed and is summarized in the poster. This element of the work has scrutinised existing ERT data collected at the Sellafield site and has resulted in a new approach for treating ERT measurement errors, thus improving the efficiency and reliability of ERT.



Figure 1: Conceptualization of a subsurface leak at Sellafield detected by ERT (modified after [2])

#### References

[1] Ramirez et al. (1996) Journal of Environmental & Engineering Geophysics doi: 10.4133/JEEG1.3.189
[2] Kuras et al. (2016) Science of the Total Environment doi:

[2] Kuras et al. (2016) Science of the Total Environment of 10.1016/j.scitotenv.2016.04.212

## Co-treatment of mixed radionuclides in large volumes of contaminated water by carbonate coprecipitation reactions

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Treatment of radioactive effluents and groundwaters containing <sup>90</sup>Sr at low molar concentrations is traditionally achieved by cation exchange. However, the effectiveness of the process is reduced by completing ions present in groundwaters (e.g.  $Ca^{2+}$ ,  $Na^+$ ) and anionic radionuclides are not removed (<sup>99</sup>Tc,<sup>14</sup>C). Inorganic precipitation of <sup>90</sup>Sr and <sup>14</sup>C as insoluble carbonate offers a lower cost alternative, producing a solid residue that is readily grouted in cement wasteforms. Work has been carried out to understand the importance of initial concentrations of  $Ca^{2+}$  and  $CO_3^{2-}$  and crystallization pathways on the removal of Sr and <sup>14</sup>C from solution.

The crystallization pathways occurring between aqueous ions of  $Ca^{2+}$  and  $CO_3^{2-}$ , and thermodynamically stable calcite appear to be an important control on the removal of <sup>14</sup>C from solution. If the precipitate undergoes recrystallization <sup>14</sup>C and <sup>90</sup>Sr will become remobilized to the solution. This is of minimal importance for the Sr, which is reprecipitated into the newly formed crystal lattice. <sup>14</sup>C however undergoes mixing with <sup>12</sup>C derived from  $CO_2$  in-gassing and becomes diluted, reducing its removal efficiency. Solution  $Ca:CO_3$  ratios were found to be important for <sup>14</sup>C removal, due to the effects of dilution by excess  $CO_3^{2-}$ . Sr removal however was not significantly affected, as atmospheric  $CO_2$  in-gassing was able to provide sufficient  $CO_3^{2-}$  for full  $Ca^{2+}$ , and thus  $Sr^{2+}$  removal.

Current work for this project involves researching the importance of the Sr:Ca ratio in solution on strontium's incorporation mechanism into calcite (as preliminary data suggest that higher Sr:Ca solution ratios can produce significantly higher  $D_{sr}$ ). The project will also seek to test the final treatment method on groundwater currently being pumped from site. A full cost-benefit analysis will also be performed for an installed engineered treatment system versus likely alternative methods.

## Assessment of the impact of leak zone processes in the natural attenuation of radionuclides

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The NDA recognise that if decommissioning practices are not carefully implemented, environmental contamination is possible. Therefore, land quality management is key in elevating risk to people and the environment [1]. The NDA have identified that in some situations, the use of *in situ* remediation techniques such as natural attenuation/monitored natural attenuation (NA/MNA) may be appropriate when managing contaminated ground. However, in contaminated land assessments, the NA processes occurring close to the leak point in "leak zones" are often not considered as:

- 1. these areas are heavily contaminated and difficult to sample;
- 2. soil volumes in leak zones are relatively small and their contribution to NA could be interpreted to be negligible.

As a result, when model predictions of contaminated land risk/liabilities are made, these often assume that NA processes in leak zones are the same as those occurring further down-gradient. However, an ongoing study into the fate of C-14 in a historical alkaline leak at Sellafield [2], has indicated that the NA leak zone processes –i.e. the precipitation of carbonate minerals - are having a profound effect on C-14 attenuation, and are still controlling the site distribution of this radionuclide 35 years after the leak ceased.

This study will investigate the effect of leaks with varying chemistries (pH, ionic strengths, and organics) on the NA processes and radionuclide behaviour. A combination of batch alteration, sorption and column experiments coupled with electron microscopy, X-ray and synchrotron based XAS analysis, will be used to determine the fate of <sup>90</sup>Sr, U and <sup>137</sup>Cs when released into several different sediments and groundwater types found across the NDA estate. Experimental results will then be used to inform both thermodynamic models of radionuclide speciation and reactive transport models to assess the extent that near-field chemistry must be considered in MNA programmes at NDA sites.

References

[1] Nuclear Decommissioning Authority. Strategy, Effective from April 2016. 2016

[2] Boylan A. A., Stewart D. I., Graham J. T., Trivedi D. and Burke I. T. Mechanisms of inorganic carbon-14 attenuation in contaminated groundwater: Effect of solution pH on isotopic exchange and carbonate precipitation reactions. Submitted to Applied Geochemistry.

### Towards catalytic uranyl hydrocarbon C-H bond cleavage

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Depleted uranium (DU) is a widely untapped resource, with approximately 1.3 million tonnes stored globally in 2008. This has helped trigger a renaissance in uranyl chemistry, with recent years having witnessed numerous, seminal advances [1].

The irradiation of uranyl  $(U^{VI}O_2^{2^+})$  compounds with visible or UV light to affect chemical transformations – uranyl photocatalysis – is one such area, and its efficacy has been proven, in the destruction of aqueous organic pollutants or the fluorination of inert C-H bonds, for example [2].

In aqueous solution, the photoexcited state of the uranyl ion becomes highly reactive and can effect C-H bond cleavage by H-atom abstraction. We recently reported the first examples of hydrocarbon C-H bond cleavage via a thermal pathway [3].

However, and since the aqueous systems are generally poorly understood and indiscriminate, we are currently extending our studies to target the photo-activation of the uranyl ion for controlled and selective C-H bond cleavage in organic systems.



Figure 1: C-H bond oxidation using visible or UV light and a uranyl catalyst

We will therefore present our efforts towards the use of well-defined uranyl complexes (Fig. 1) in uranyl photo-catalysis.

References

[1] Arnold et al., Nature, 2008, 451, 315; Liddle et al., Science, 2012, 337, 717.

[2] Krishna et al., J. Phys. Chem. C., 2008, 112, 15832; West et al., Angew. Chem. Int. Ed., 2016, 55, 8923.

[3] Arnold et al., Nat. Chem., 2010, 2, 1056.

[4] Wang et al., Inorg. Chem., 1995, 54, 6034; Yong et al., Sci. China Chem., 2013, 56, 1671

### Optimising bioremediation end-points for the safe and effective long-term stewardship of UK radwaste impacted land

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Microbial processes play a significant role in controlling the long-term fate of radionuclides in radioactively contaminated land environments. This PhD will make, for the first time, detailed comparisons of the long-term stability of radionuclides (<sup>99</sup>Tc, <sup>90</sup>Sr, <sup>14</sup>C & <sup>238</sup>U) removed from solution via several contrasting mechanisms relevant to the UK's radioactively contaminated land legacy. These include:

- 1. enzymatic and Fe(II)-mediation bioreduction in sediments stimulated by optimal electron donors,
- 2. biostimulation of phosphate biomineralisation,
- 3. carbonate formation linked to urease activity and bioreduction,
- 4. sulfidation reactions mediated by sulfate-reducing bacteria,
- 5. the application of novel engineered bionanomaterials e.g. functionalized biomagnetite.

These will be compared to natural attenuation processes and the applications of state of the art invasive treatment strategies, e.g. using nano and micron-scale ZVI.

Radionuclides will be looked at singly and in combination, to understand the optimal remediation strategies for a wide range of scenarios, and in some cases treatment strategies will be combined to give optimal end-points for stable, long-lived immobile For example, combining bioreduction of U(VI) and Tc(VII) with the phases. biomineralisation of Sr(II) as a phosphate or carbonate (the latter tackling <sup>14</sup>C also). The main focus of this PhD will be to subject a range of end-member phases from these experiments to a comprehensive series of long-term batch and column experiments, and to explore the impact of perturbations including aeration, nitrate, pH and chelating agent introduction. These experiments will help identify the optimal (bio) remediation endpoint(s), and identify approaches that could be used to design out inherent instabilities, e.g. making minor modifications to groundwater chemistry or the further application of timed remediation agents. Again, these modifications will be tested in batch and column studies. Current work focuses on U(VI) reduction in laboratory incubations containing pure cultures of the subsurface metal-reducing bacteria Geobacter and Shewanella to examine fundamental mechanisms of reductive precipitation in model systems.

### Long-range scanning based detection of Alpha-Induced Air Fluorescence even under daylight conditions

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As part of the nuclear decommissioning process it is important to characterise plant and equipment to determine sources and types of radiation emitting contamination in order that correct treatment and disposal can be planned. A very wide range of materials can be contaminated with alpha radiation emitting radionuclide, ranging from discrete concentrated materials in gloveboxes or hot cells to diffusely distributed contamination on building surfaces. Characterising material can be challenging, from potentially missing "hotspots" to assuring radiation safety of workers in locations with unknown levels of contamination. Additionally, being able to quickly scan an area at a location and identify areas of contamination might result in significant cost savings compared to taking many samples for expensive laboratory analysis.

Current assays in contaminated facilities are primarily based on total alpha counting. Most conventional alpha detection systems are only effective at relatively short range. Recently, detectors are starting to become available based upon alpha-induced airfluorescence. However these only operate under dark conditions which impose obvious constraints on the ability to characterise contaminated materials. There is therefore a significant benefit in developing instrumentation that is able to scan an area of alpha activity from several metres distance under daylight conditions.

Alpha particles cause ionisation in the air and as a result ultraviolet (UV) photons are emitted. These UV photons have a long range in air, considerably larger than that of alpha particles. This provides an avenue to detect alpha contamination from a distance and through translucent materials. However, the intensity of this UV light is exceedingly small in comparison to natural daylight, making detection difficult in the field. Although the majority of emitted photons are in the 300 to 400 nm wavelength range, it may be possible to detect those in the UVC range (180 – 280 nm) using 'solar blind' detectors. As the atmosphere absorbs light from the sun in the UVC range this removes the interference from background light in daytime conditions.

UVC light detection is already used in the discovery of fires and corona discharge from high voltage power lines. In the first experimental stage of this project, a group of such detectors are undergoing a series of tests to determine the performance characteristics of these detectors and if these are suitable for detecting UVC emissions from alpha particle induced air fluorescence. A range of environmental conditions will be used, including gaseous atmosphere (e.g. nitrogen, argon, xenon), on-site materials (reflection and transmission), light levels and type (e.g. sun, fluorescent, LED, incandescent) to ascertain the effect on UVC detection. Preliminary results will be shared at this conference.

### Radiological characterisation of hard to access areas: Integrated Mixed Field Imaging and Surface Penetrating Radar approach.

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The recent development of mixed field imaging (MFI) systems have enabled the simultaneous localisation and discrimination of neutron and gamma sources. However, their application is limited to radioactive wastes located on visible surfaces and they provide no information on the distance of the waste from the point of observation. These limitations make it difficult to characterise radioactive wastes located underground or behind barriers (e.g. walls) without having recourse to destructive techniques. This increases the risks of exposure to radiation and leads to the generation of secondary wastes. Therefore, this research proposes to improve the effectiveness of MFI systems in characterisation using surface penetrating radar by employing multi-sensor data fusion paradigm. This will improve the radiological characterisation process through automated non-destructive stand-off determination of: three dimensional location of the radioactive waste in or behind barriers; radiation type and activity level of the waste; expected quantity of waste; and material type of waste i.e. liquid, plastic, metal, concrete etc.

#### Enhance nuclear waste assay

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Broad Energy Germanium detectors are routinely used for gamma ray spectroscopic analysis of nuclear waste streams to ascertain the type and relative activity of radionuclides. Challenges arise when low activity radionuclides of interest are obscured by the presence of higher activity radionuclides. A key example is when Compton scattered gamma rays from <sup>137</sup>Cs in the spectrum conceal the presence of low energy gamma rays from <sup>241</sup>Am. The Compton scattering events manifest in a continuum within the spectrum, elevating noise. Current methods to overcome this problem involve the use of Compton suppression systems that use a central broad energy germanium detector surrounded by a guard ring of bismuth germanium oxide scintillator detectors. Any gamma-rays which Compton scatter from the germanium detector energy spectrum using timing coincidence methods.

In this project, algorithms have been developed to perform digital Compton suppression, alleviating the requirement for scintillator detectors. This has been achieved by distinguishing low energy gamma rays that are absorbed near the outer surface of the germanium detector, from Compton scattering events that are as a result of higher energy gamma rays interacting throughout the bulk of the detector. The digital Compton suppression algorithm significantly reduces counting times with improved low energy isotope identification when in the presence of large backgrounds, without the requirement for Compton suppression shielding. It also allows for a "one detector"system to be utilised. The technique exploits the knowledge of how the detector signal varies as a function of gamma-ray interaction position, characterised by position-dependent charge collection times.

Databases of experimental and modelled detector signals have been produced for known (x,y,z) gamma-ray interaction positions in the germanium detector. The modelled signals were produced using the AGATA Detector Library and the experimental signals were collected through precision scanning of the detector. A 1GBq <sup>137</sup>Cs source calibrated into a 1mm beam was mounted on a software controlled (x,y) scanning table below the germanium detector. As the collimator was moved, the detector was thus irradiated at known (x,y) positions. To determine the depth of interaction within the germanium detector, scintillator detectors were positioned behind collimators at various known z depths alongside the germanium detector. The position dependence of charge collection times could then be investigated.

In this paper, the background to the project together with its aims will be presented. Presented results will include the dependence of charge collection times on both radius and depth (z) within the Broad Energy Germanium detector. Additionally, the results of the optimised Compton suppression algorithm will be presented. The results show that the Compton suppression algorithm is successful and has enabled a reduction in the Minimum Detectable Activity of the detector. This reduction will enable waste producers to re-characterise some of their low level waste as very low level waste. Very low level waste can be diverted to licensed land fill sites rather than being sent to the low level waste repository.

### Irradiated sludges: a joint experimental/theoretical Study

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This project aims to identify production mechanisms for important radiolytic products, especially gaseous products for example molecular hydrogen gas, from Magnox sludges stored at Sellafield. This involves irradiating materials that mimic properties of the sludges and determining and quantifying the effects of irradiation. Early sludge mimics are simple mixture of magnesium hydroxide and water, but more realistic sludge mimics will be used later in the project. For the irradiation of these sludge mimics, a sample chamber has been developed specifically for irradiating sludge mimics. At first these irradiations will take place on the Q14 radiation platform. Q14 is a general purpose irradiator, with a design based on a previously developed irradiation apparatus [1]. In the future a new radiation platform will be used, which is in development. This irradiator will use a novel ring design, and is being designed to produce high dose rates (~100 Gy/s). After irradiating a sample by one of these methods, measurements are taken of the type and amount of what is produced during the irradiation. This involves using a variety of methods to determine and quantify end products of irradiation. The headspace of the sample chamber is removed and analysed by gas chromatography, to determine and quantify gases produced by irradiation like hydrogen gas. Gas chromatography can also be used to separate and analyse volatile organic compounds; with this the effects of irradiation on biodegradation products in the sludges will be investigated. Diffusion of hydrogen through sludge mimics will be used to validate these simulations, which will use an experimental method that exploits the spatial coherence of the synchrotron, to measure diffusion over a few micrometers. These results will then be compared to the predictions of simulations made in the Atomistic Simulation Centre. Through this comparison details about the mechanisms occurring in the sludges can be deduced.

References

[1] C Polin et al. Rev. Sci. Instrum. 86 035106 (2015)

### Development and industrial testing of multi-radiation systems for the characterisation of nuclear facilities

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The monitoring of potentially contaminated pipework poses significant challenges for the clearance process.

Two requirements for high resolution gamma-spectrometry by scintillation counting are detector surface area and volume. These properties are apparent in traditional detectors which employ High Purity Germanium or metal halides coupled to photomultiplier tubes. For navigating industrial pipework, we require small scale detectors that are capable of deployment in narrow, difficult to access environments. We must, therefore, develop detectors which are not reliant on volume. To accomplish this we look to Silicon Photomultipliers (SiPM) coupled to novel, high density scintillators.

By doing so, we can considerably reduce the size of our detectors and perform radionuclide identification in confined spaces.

I present an outline of this maturing technology along with some early data taken with the j-series SiPM from SensL coupled to LYSO, LUAG, BGO and GAGG.

## The development of a novel gamma-ray detection system for fission fragment decay data measurement and evaluation

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Gamma-ray spectroscopy is of fundamental importance when considering nuclear science. Through the normal operation of nuclear power to nuclear waste assay and decommissioning. This can be through the guise of measuring and improving the internal nuclear decay data of key radionuclides produced in fission which can later be fed into key models of reactors, to acquiring spectra from waste to identify the constituent radionuclides non-destructively.

The National Nuclear Array [1-3] is a gamma-ray coincidence array housed at the national physical laboratory (NPL). Comprising 12 LaBr<sub>3</sub> scintillators at full capacity, the array has an improved time resolution compared to conventional solid state detectors, and an improved light output and energy resolution compared to other solid non-organic scintillators [4,5]. The array is therefore capable of providing fundamental decay data, by the measurement of extremely short (<1 ns) mean lifetimes of excited discrete levels within the atomic nucleus [6]. Through coincidence gamma-ray spectrometry it can also be utilized to enhance and identify weaker emissions within a complicated mixed matrix of several gamma-emitting radionuclides.

The poster will show much of the commissioning tests undertaken at NPL of NANA, with comparisons with Monte Carlo GEANT4 simulations of the device [7,8]. The poster will also describe how the peak to total of weak gamma ray signatures are enhanced using coincident spectrometry and will identify other ways in which the array can be beneficial to this community such as calculating the activity of cascade-emitting nuclei.

#### References

- [1] Regan, P.H., et al., Journal of Physics: Conference Series. 620(1), (2015)
- [2] Lorusso, G., et al., Appl. Radiat. and Isot., 109, (2016)
- [3] Regan, P.H., et al., Journal of Physics: Conference Series, 763(1), (2016)
- [4] Rosza, C.M, et al., Performance summary: BrilLanceTM scintillators LaCl3 and LaBr3,
- Saint Gobain crystals, available at <www.detectors.saint-gobain.com>
- [5] Anil Kumar, G., et al., Nucl. Inst. and Meth. A, 609, (2009)
- [6] Régis, J-M., et al., Nucl. Inst. and Meth. A:, 763, (2014)
- [7] Agostinelli, S., et al., Nucl. Inst. and Meth. A, 506, (2003)
- [8] Matta, A., et al., Jour. Phys. G., 43(4), (2016)

### ORAL PRESENTATIONS

## Real-time nanogravimetric monitoring of corrosion in radioactive environments

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Monitoring and understanding of corrosion on nuclear sites plays a key role in safe asset management (predicting plant life, assessing efficacy of corrosion inhibitors for plant lifetime extension) and supporting informed choice of decontamination methods for steels due for decommissioning. Commonly used techniques for monitoring corrosion include: the measurement of bulk macroscopic mass changes on corrosion coupons; the measurement of material electrical resistance; and the measurement of material linear polarization resistance during sample immersion in the putatively corrosive environment. However the former is unsuitable for real time measurements, the medial and latter are not suitable for measuring corrosion rates or pitting corrosion.

Recent advances in Quartz Crystal Nanobalance technology offer a means to monitor corrosion *in situ* in radiologically harsh environments, in real time and with high sensitivity. The QCN measures minute changes in frequency of a quartz crystal resonator with weight gain/loss. Using the Sauerbrey equation, the drop in frequency observed during corrosion testing can be converted to an instantaneous corrosion rate with nanogram sensitivity. QCN technology is suitable for measuring uniform and pitting corrosion rates.

Previous work has compared the corrosion rates of steels and steel measured using QCN technology and  $I_{CORR}$  measurements. Whilst overall corrosion rates are in agreement,  $I_{CORR}$  measurements suffer from being peturbative (the potential is swept separately from cathodic and anodic extremes in recording i-V curves to a previously identified  $E_{CORR}$  prior to calculation of the  $I_{CORR}$ , necessarily changing the nature of the surface under study) and being conducted in non-real time. QCN based corrosion monitoring is non-peturbative (it simply involves sample immersion), provides direct access to two import corrosion parameters (mass change with the afore-mentioned nanogram sensitivity and  $E_{CORR}$ ) and can be conducted in real time – the latter two features allowing for the study of changes in corrosion rate on the sub-second timescale and thus the elucidation of the mechanism of the corrosion process under study [1].

Experiments have concentrated on determining corrosion rates in acids and complexants used in chemical decontamination processes, particularly methods involving the commonly used cleaning agents nitric acid and oxalic acid (e.g. the CORD-UV process). Oxalic acid is currently being studied as an Enhanced Chemical Cleaning (ECC) decontamination agent in the decommissioning of high level waste (HLW) storage tanks at the Hanford and Savannah River Sites (SRS). Oxalic acid has the twin ability to act as a rust remover and as a corrosion inhibitor [2, 3]. Therefore it is preferred over bulk nitric acid [4]. The tanks are comprised of low carbon steel; thus the decontamination process must be carefully monitored to avoid over-aggressive decontamination that may result in a loss of asset structural integrity. To avoid this, the oxalic acid concentration being used has been reduced to 1 wt% from the 4-8 wt% range typically used during decontamination campaigns [5].

Using the QCN the rates of corrosion of mild carbon steel surrogates have been measured in the presence of these oxalic acid-based decontamination solutions, and

have directly observed both the removal by oxalic acid of iron oxide corrosion product and the formation of a protective layer of ferrous oxide at the metal surface [6].

Studies have recently extended to newer decontamination solution formulations including basic and acid permanganate solutions and oxalic acid / nitric acid blends. In the case of the former, preliminary results indicate that, counter intuitively, base concentrations of > 10 mol dm-3 will lead to a loss of HLW storage tank structural integrity. This is currently the subject of further study [7].

References

[1] I. Tzagkaroulakis and C. Boxall, "Real time nanogravimetric monitoring of corrosion for nuclear decommissioning," ECS Trans., vol. 66, no. 17, pp. 73–83, 2015.

[2] S. Rahfield and B. Newman, "Composition for rust removal and method of use thereof," Patents US4828743 A, 1989.

[3] M. A. Streicher, "Corrosion – inhibition of oxalic acid," Patent US 2793190 A, 1957.

[4] N. Davis, E. Ketusky, R. Spires, R. Beatty, S. Jones, J. Remark, and P. Wotjaszek, "Enhanced Chemical Cleaning: A New Process for Chemically Cleaning Savannah River Waste Tanks-9100," WM2009, March 1-5, 2009.

[5] E. Ketusky, K. Subramanian, and B.Wiersma, "Savannah River Site Tank Cleaning: Corrosion Rate for One Versus Eight percent Oxalic acid Solution - 11413," WM2011, Phoenix, AZ, 2011.

[6] I. Tzagkaroulakis, C. Boxall, and D. Trivedi, "Real time nanogravimetric monitoring of corrosion for nuclear decommissioning in simulated radioactive environments – 16170," in WM2016, March 6 – 10, 2016.

[7] I. Tzagkaroulakis, C. Boxall, and D. Trivedi, "Real-Time Nanogravimetric Monitoring of Corrosion in Radioactive Decontamination Systems," in MRS2016, November27-December 2, 2016.

## Natisite- a layered titanium silicate for use as an ion-exchanger within the nuclear industry

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Unlike zeolites which contain  $SiO_4$  and  $AlO_4$  tetrahedra, microporous titanium silicates display  $SiO_4$  in tetrahedral coordination and  $TiO_6$  octahedra and therefore display a wider range of possible structures which can result in different properties [1]. Doping different transition metals into existing titanium silicate structures can lead to significant changes in the structure which lead to differences in the materials ion-exchange chemistry. Sitinakite,  $KNa_2Ti_4Si_2O_{13}(OH)\cdot 4H_2O$ , and the synthetic niobium doped analogue (IONSIV-911) is one example of a doped titanium silicate which is used as an ion-exchangers for the removal of  $Cs^+$  and  $Sr^{2+}$  from nuclear waste.

Natisite, Na<sub>2</sub>TiSiO<sub>5</sub>, crystallises in the tetragonal space group P4/*n m* and is a layered titanium silicate with titanium in an unusual 5 coordinate square pyramidal environment [2,3]. Little previous work has been conducted on this material, with any published work focusing on synthesis and characterisation of the structure. No work to date has been conducted on the modification of the framework or any tests on natisite's ion-exchange chemistry. Preliminary results have found that increasing the levels of zirconium doping has significant effects on the materials ion-exchange chemistry. Such differences include a faster rate of exchange for Co, increased affinity for Sr and Cs and, a slight increase in the level of exchange with respect to Ce and Nd (used as inactive surrogates for Pu and U respectively). Cerium ion-exchanges shows the formation of CeO<sub>2</sub> nanoparticles between the layers. X-Ray diffraction shows that the layers themselves are still intact but the stacking has been disrupted by the introduction of these CeO<sub>2</sub> nanoparticles with X-Ray Absorption Spectroscopy (XAS) used to identify the Ce phase.

The work presented here will focus on the differences between 0, 10% and 20% Zr doped natisite and the effect this has on the materials ion-exchange chemistry both with single and competitive ion-exchanges. These results will be compared to clinoptilolite which is used as the industrial standard material for treatment of radioactive liquid waste via the SIXEP process. Clinoptilolite sourced from Sellafield has undergone both single and competitive ion-exchanges with the selectivity and capacity directly compared to natisite.

Results have shown that natisite has superior performance towards Ce, Nd, Co, both single and in the presence of competing ions such as Ca, Mg and K. Also natisite has a comparable exchange capacity towards Cs and Sr to that of clinoptilolite.

References

[1] 1P.A. Wright, Microporous Framework Solids (RSC materials Monographs), The Royal Society of Chemistry, Cambridge, (2008).

[2] D.G. Medvedev et al., Chem. Mater., 16, p.3659 (2004).

[3] S.Ferdov et al., Powder Diffraction, 17, p.234 (2002).

## Optical detection of corrosion on intermediate level nuclear waste containers

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Intermediate Level Waste (ILW) containers are currently stored above ground and must be periodically inspected for signs of atmospherically induced stress corrosion cracking (AISCC) by a human operator via robot – a time consuming and costly process. A novel method for automatic detection of pitting corrosion, a known precursor to AISCC, is being explored with the aim of developing an effective method to direct conservation action.

UV-VIS, FTIR, Raman mapping and x-ray diffraction have been used to characterise the products of pitting corrosion to aid the development of a hyperspectral imaging system which will automatically assess pitting on the 304L and 316L stainless steel used in the construction of intermediate level waste containers.

High-purity standard samples of iron oxide phases have been compared to iron oxide corrosion product gathered by controlled corrosion of 304L and 316L stainless steel in stores-relevant conditions in order to make associations between visible phases and corrosion site chemistry.

Image processing techniques are also being used on standard colour images of corrosion in order to see if colour and texture analysis are able to identify substances on the surface of ILW containers without the computational expense of hyperspectral imaging. A system has been developed which uses principal component analysis to isolate regions of rust on stainless steel for closer inspection by the high data rate hyperspectral system.



Left: Comparison of colour between synthetic iron oxide phases and rust around a corrison pit formed on 304L stainless steel.

Right: Comparison between (a) a colour image of an array of corrosion pits and (b) labeled rusted regions after analysis.

## Performance characterization and optimization of THORP storage cans

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 $PuO_2$  product from re-processed oxide fuel from the THORP (Thermal Oxide Reprocessing Plant) is stored in Type 316L stainless steel containers. A design of nested cans is currently used, with the outer container providing the safety case containment barrier. There are two potential corrosion threats during storage: (i) the environment inside the cans due to the potential formation of HCl, and (ii) the outside as a result chloride contamination from the environment. The aim of the project is to inform about the propensity of THORP storage cans towards localised corrosion and Environment Assisted Cracking (EAC) in HCl and chloride-bearing atmospheric environment. Investigations have been carried out on surface treated 316L coupon specimens to assess and quantify the corrosion propensity as a function of microstructure, environment, and surface condition.

Surface treated specimens were characterised using analytical microscopy techniques, Xray Diffraction (XRD) phase analysis, and XRD residual stress measurements. Corrosion screening was carried out using both atmospheric and electro-chemical polarisation tests under a wide range of chloride and acid concentrations, and elevated temperatures.

Electro-chemical polarisation in aqueous HCl environment informed about the corrosion morphology as a function of acid concentration, microstructure, temperature, and applied electrochemical potential. Three corrosion morphologies were identified, including uniform corrosion, both uniform corrosion followed by pitting corrosion, and pitting corrosion only. The transitions from pitting to mixed mode uniform/pitting corrosion, and from uniform/pitting to uniform corrosion only were not affected by mechanical surface treatments. Corrosion morphology maps have been introduced, to indicate the most likely form of degradation as a function of environment.

Atmospheric exposure to chloride-containing atmospheres at 50°C and 30% relative humidity resulted in localised corrosion within 24 hours, with increasing corrosion attack after longer exposures and higher MgCl<sub>2</sub> deposition densities. It is shown that laser engraving as a surface finish/tagging method, became susceptible towards atmospheric induced stress corrosion cracking after 2 weeks of exposure. This observed cracks dimensions were in good agreement with the maximum depth of introduced tensile stresses of ~200 $\mu$ m. In contrast, aqua blasted surfaces showed localised corrosion only, due to the presence of compressive near-surface stresses. Atmospheric corrosion tests at 110°C using a wide range of humidity and HCl concentrations indicated cracking within 90 minutes of exposure. The results indicate the influence of humidity and HCl concentration, with the corrosion morphology and type changing from SCC, to pitting corrosion, to no corrosion at all. Chloride deposition densities of 1.5 $\mu$ g/cm<sup>2</sup> are adequate to cause local corrosion spots.

## Susceptibility to cracking of sensitised stainless steel nuclear fuel containment under simulated storage conditions

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Advanced Gas-cooled Reactor (AGR) fuel cladding consists of a stabilised austenitic stainless steel containing nominally 20% Cr, 25% Ni and 0.5% Nb (designated 20/25/Nb). The investigation of corrosion in this alloy has had dependency upon its sensitisation by thermal process to simulate the effects of irradiation which segregates the alloying elements resulting in depletion of Cr at the grain boundaries and hardening of the microstructure.

The thermal sensitisation of 20/25/Nb has been shown to be ineffective for the study of stress corrosion cracking due to the design of the alloy cladding which has a primary requirement for ductility under heat exposure in order to accommodate the contained fuel pellets swelling and contraction during reactor operation, and also due to the low availability of carbon for significant sensitisation of its microstructure.

However, McGurk J C, 2011, NNL, speculated 'a possible mechanism in the case of cracking of AGR fuel pins is radiation enhanced hydrogen embrittlement'. This hypothesis has been investigated and it has been found that the un-irradiated 20/25/Nb alloy is susceptible to multiple intergranular cracking when thermally charged with hydrogen in an autoclave. A source of atomic hydrogen has been identified in ionized cooling pond water and also in similarly ionized water vapour which can occur in the 'dry storage' environment of spent fuel pins.

It has also been established that an electrolytic oxalic acid etch can give an impression of the presence of carbide sensitisation occurring at grain boundaries of 20/25/Nb alloy under optical examination. However, SEM/EDX analysis exposes that actually trenching and pitting at the boundaries are caused by that etch.



SEM image of failed slow strain rate test specimen of tube 20/25/Nb alloy.



SEM/EDX image of the result of electrolytic etch of 'sensitised' 20/25/Nb