

**Nuclear Decommissioning Authority
PhD Research Seminar for NDA-Sponsored PhD
Projects, 2016**

ABSTRACT BOOKLET

**20th January 2016
Manchester Conference Centre**

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

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Introduction

Rick Short (Research Manager, Nuclear Decommissioning Authority)

In order to successfully deliver our mission NDA needs to ensure that our plans are technically underpinned by sufficient and appropriate R&D and that our estate has the skills and capability to deliver them efficiently and effectively. University research plays an essential role in this delivery through the advancement and transfer of knowledge, the development of appropriate technology and in the training of researchers in key technical and engineering skills. As part of our University Research Strategy NDA funds a number of university research projects through its annual NDA Bursary Programme. This PhD seminar forms a key component of our university research programme and aims to raise the overall impact of the NDA Bursary Programme. It represents an opportunity for industry to learn more about the university based research that NDA is sponsoring and meet the students carrying out the research. For academia it represents an opportunity to meet key industry figures who are developing our strategy and implementing it through our Site Licence Companies. Finally I would like to thank you for attending the seminar.

2016 NDA PhD SEMINAR PROGRAMME		
Day 1: Tuesday 19 th January 2016 - 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 20 th January 2016 - 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 - NDA	
09:00 – 11:08	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	Diletta Invernizzi 2015 Bursary - Decommissioning	Benchmarking Analysis in the Nuclear Decommissioning Sector
09:04 – 09:08	Reece Hall 2015 Bursary - Decommissioning	Zirconium Doped Natisite for the Removal of Radionuclides From Solution
09:08 – 09:12	Mel O'Leary DISTINCTIVE - Decommissioning	Irradiated Sludges
09:12 – 09:16	Valerio Ortenzi 2013 Bursary – Decommissioning	An experimental study of robot control during environmental contacts based on projected operational space dynamics



09:16 – 09:20	Ioannis Tzagkaroulakis 2012 Bursary – Decommissioning	Real Time Nanogravimetric Monitoring Of Corrosion in Radioactive Environments
09:20 – 09:24	Thomas Unsworth 2012 Bursary – Decommissioning	Radioactive Organic Liquid Waste Treatment Using the Arvia Process
09:24 – 09:28	Mohammed Talha 2011 Bursary – Decommissioning	Evaluation of human interface devices for robotic decommissioning
09:28 – 09:32	Jessica Higgins 2014 Bursary – Spent Fuel and Nuclear Materials	Wet Oxidation of Uranium Dioxide in Sealed and Unsealed Enclosures in Radiation Fields
09:32 – 09:36	Jamie Southworth 2013 iCASE - Spent Fuel and Nuclear Materials	Investigation of Anomalous Hydrogen Production from Water Adsorbed to Metal Oxide Surfaces
09:36 – 09:40	Mike Pugh 2014 Bursary – Spent Fuel and Nuclear Materials	AGR Fuel Pin Cracking in Dry Storage
09:40 – 09:44	Benjamin Krawczyk 2013 Bursary – Spent Fuel and Nuclear Materials	Performance Optimisation of THORP Containers
09:44 – 09:48	Robert Shearman 2014 Bursary - Characterisation	Enhancing and improving nuclear decay data
09:48 – 10:20	COFFEE & NETWORKING 	
10:20 – 10:24	Richard Gray 2014 Bursary - Characterisation	Multi-pixel Avalanche Photodiode for the Detection of Ionising Radiation
10:24 – 10:28	Emily Clare Stokes 2013 Bursary – Characterisation	Towards Rapid ⁹⁰ Sr Determination by Improved Liquid Scintillation Counting
10:28 – 10:32	George Rowley 2014 Bursary - Waste Packaging and Storage	Optical detection of corrosion on intermediate level waste containers
10:32 – 10:36	James E. Vigor 2013 Bursary – Waste Packaging and Storage	The Hydration of Highly Substituted Slag Blended Cements: An In-Situ Synchrotron Study
10:36 – 10:40	Eszter Makkos 2013 Bursary – Waste Packaging and Storage	Modelling the interaction of corroded Magnox surfaces with nuclear fission products
10:40 – 10:44	Stephanie Thornber 2013 Plutonium – Waste Packaging and Storage	Glass-Ceramic Wasteforms for Pu Disposition Consolidated by Hot Isostatic Pressing

10:44 – 10:48	Asmi Barot 2012 Bursary - Waste Packaging and Storage	Radiation damage in zirconolite and gadolinium pyrochlores; simulating the effects of grain boundaries
10:48 – 10:52	Jack Clarke 2013 iCASE - Waste Packaging and Storage	A thermal rework strategy for failed cemented wasteforms
10:52 – 10:56	Jamie Purkis 2015 Bursary – Land Quality	Studies of an Unusual Bimetallic Uranium (V) Motif in a ‘Pacman’ Macrocyclic Framework
10:56 – 11:00	Chak-Hau Michael Tso 2014 Bursary – Land Quality	Enhancing the information content of geophysical data applied to nuclear site characterisation
11:00 – 11:04	Adrian Cleary 2014 Bursary – Land Quality	Assessment of natural attenuation and targeted in-situ remediation of radioactively contaminated land
11:04 – 11:08	David Hodkin 2013 Bursary – Land Quality	90Sr and 14C groundwater treatment via carbonate co precipitation reactions
11:08 – 12:00	KEYNOTE INDUSTRY TALK Gerry Thomas – Imperial College ‘Health effects from nuclear accidents – science facts or fiction?’	
12:00 – 13:00	LUNCH AND POSTER SESSION (presenters to stand by posters from 12:30)	
13:00 – 16.55	PhD STUDENT ORAL PRESENTATIONS	
	STUDENT BURSARY YEAR – GROUP	TITLE
13:00 – 13:20	Jaiyana Bux 2011 Bursary – Characterisation	Up-scaling crossflow membrane emulsification & polymerization, and in situ acoustic characterization of the colloidal dispersions
13:20 – 13:40	Benjamin Pearce 2012 Bursary – Characterisation	Remote alpha counting with a radioluminescence detector: moving toward automated, quantitative alpha assessment at distance
13:40 – 14:00	Frances Burrell 2012 Bursary – Characterisation	Development of Robust Automated Techniques for Radionuclide Separation
14:00 – 14:20	Luke Boast 2012 iCASE - Waste Packaging and Storage	Thermal Treatment of Plutonium Contaminated Material (PCM) Waste

14:20 – 14:40	Haris Paraskevoulakos 2012 Bursary - Waste Packaging and Storage	Modelling the Degradation of Intermediate Level Waste Packages Resulted from Internal Metallic Corrosion
14:40 – 15:00	Lorraine Sharp 2012 Uranium– Waste Packaging and Storage	Uranic Interactions in Cementitious systems
15:00 – 15:15	COFFEE & NETWORKING	
15:15 – 15:35	Izaak Fryer-Kanssen 2012 Bursary - Waste Packaging and Storage	Computational Studies of Lanthanide & Minor Actinide Complexes with Industrially Relevant Ligands
15:35 – 15:55	Matthew Nancekievill 2012 iCASE - Decommissioning	Development of a Mechatronic System for Underground Sensor Deployment
15:55 – 16:15	David Cundy 2012 Bursary – Land Quality	Assessment of sorbent materials for the in-situ remediation of radionuclide contaminated groundwater
16:15 – 16:35	Nicholas Laver 2013 Bursary – Land Quality	The sorption of nuclear fission products and transuranic elements from aqueous environments by graphene oxide nano-flakes
16:35 – 16:55	Ronald Clark 2013 Bursary – Spent Fuel and Nuclear Materials	Investigating IGC Initiation in Stainless Steel Fuel Cladding Alloy 20/25/Nb
16:55 – 17:15	– closing remarks & presentation of prizes -	
17:15 – 17:45	COFFEE & NETWORKING – Seminar Ends	



POSTER PRESENTATIONS

Benchmarking analysis in the nuclear decommissioning sector

¹Diletta Invernizzi

¹University of Leeds

Globally the cost estimates for decommissioning projects lie in the range of hundreds of billions of dollars and are characterized by high costs, long schedule and several risks. In many countries, decommissioning projects are even more significant than the nuclear new build. Despite this extremely high relevance there is a huge gap in the literature concerning the benchmarking of these projects. The budgets for these projects keep increasing and the key stakeholders have a limited understanding of the key determinants that engender these phenomena.

Therefore, my research will on a top-down benchmarking approach instead of providing a bottom-up analysis. This analysis aims to find best practices and retrieve guidelines both from the nuclear sector and other industrial sectors, comparing case studies and summarizing key results. In other sectors, such as the oil & gas and the chemical sector, benchmarking has already been used to compare projects in order to identify both successful projects and the reasons for their success. So, best practices and lessons learned could be transferred to the nuclear sector to promote changes in the organization, increase its performance and establish improvement objectives.

Moreover, my research will not only focus on the UK scenario, but will compare UK decommissioning projects performance to international experience.

The key deliverables of the researches in this first stage will be:

1) Critical literature review and summary of the key aspects, where

a. the main topics of the literature review are: national and international experiences of nuclear and non-nuclear decommissioning projects, international benchmarking of nuclear and non-nuclear decommissioning projects, construction benchmarking, knowledge management;

and

b. the main references of the literature review are: WNA, IAEA, OECD/NEA, EPRI, NDA, scientific papers and conference proceedings.

2) Definition of the methodology for the project benchmarking, that is strictly related to the data that I will have access to.

Zirconium doped natisite for the removal of radionucleotides from solution

¹Reece M. Hall and ¹J.E. Readman

¹University of Central Lancashire

Microporous materials are used commercially as ion-exchange materials and are often used to treat nuclear waste. However, their use in the nuclear industry has some problems, as the acidity of some legacy waste pools can lead to a loss of crystallinity limiting the effectiveness of these materials. One such solution could be microporous titanium silicates. These materials display different structural characteristics to zeolites but have similar physiochemical properties [1]. It is hoped that this class of materials can still be as effective as traditional zeolites whilst remaining stable at lower pH's.

Doping different transition metals into existing titanium silicate structures can lead to significant changes in the structure which, in-turn, lead to differences in the ion-exchange chemistry of the materials. One such example being Sitinakite, $\text{KNa}_2\text{Ti}_4\text{Si}_2\text{O}_{13}(\text{OH}) \cdot 4\text{H}_2\text{O}$, whose synthetic niobium doped analogue is currently used as an ion-exchanger for the removal of Cs^+ and Sr^{2+} from nuclear waste.

Natisite, $\text{Na}_2\text{TiSiO}_5$, is a layered titanium silicate with titanium in an unusual 5 coordinate square pyramidal environment.[2] This work focuses on the synthesis of a series of natisite and zirconium doped natisite samples that have been prepared. The inclusion of zirconium in the framework has a considerable effect on the ion-exchange chemistry of the material. It was found that increasing the levels of zirconium increased the affinity towards Cs and it was also found the rate of exchange of Co was increased with increasing Zr content. The materials have a high affinity towards Ce and Nd (used as inactive surrogates for Pu and U respectively) even in the presence of competing ions. A series of ion-exchanges have also been conducted in acid conditions to better replicate real life conditions in order to determine if natisite would be a viable material for use in industry.

X-ray Absorption Spectroscopy (XAS) has been conducted at Diamond Light Source. This has been useful in determining the coordination environment of titanium and zirconium. Also this technique have been useful in determining the coordination states of exchanged cations as well as determining if the exchanged cations preferred sites closer to Zr rather than Ti.

References

- [1] P.A. Wright, Microporous Framework Solids (RSC materials Monographs), The Royal Society of Chemistry, Cambridge, (2008).
- [2] S.Ferdov et al., Powder Diffraction, 17, p.234 (2002).

Irradiated sludges: a joint experimental/theoretical Study

¹Mel O'Leary

¹Queens University Belfast

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. For the investigation of other end products colorimetric assays can be used. 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)

An experimental study of robot control during environmental contacts based on projected operational space dynamics

¹Valerio Ortenzi

¹University of Birmingham

This project is investigating novel uses of automatic vision systems to control robotic arms with multiple degrees of freedom, and theoretical and applied approaches to exploit and control contacts between the robot and other objects, while performing tasks such as those needed for nuclear decommissioning.

There are currently a significant number of robotic manipulators deployed in multiple UK nuclear sites to perform tasks in environments which might be dangerous to humans. These systems are generally powerful and reliable, but lack sensors capable of providing information about their tool position as well as forces and torques. Therefore, they are not able to automatically perform complex tasks, e.g. following a precise trajectory with a fixed stand-off distance for scabbling. Only simple movements are possible, and these must be directly controlled, joint by joint, by a human operator, who may have very limited visibility and situational awareness of the robot and objects e.g. inside a cell or cave. The addition of new electronics is unfeasible, due to certification rules and also the vulnerability of delicate electronics to radiation. Also, the powerful interactions between the tooltip and the environment have to be taken into account, which can perturb the base of the robot with respect to the scene.

Hence we are exploring the possibility to use cameras and range sensors, e.g. depth cameras, to provide an automatic controller with information about the robot, which can be used in a feedback loop to enable it to perform tasks automatically. Cameras and depth sensors are external technology and they do not require any modification of the actual robots, keeping the costs and risks low. For this purpose we are investigating the potential of Computer Vision techniques to estimate in real time the robot's position and orientation in space. To achieve these aims, the work also involves numerical optimisation and image processing techniques. Moreover, the knowledge of the robot CAD model is used in order to have more reliable and precise results.

The project is also theoretically examining the exploitation of contacts in order to take advantage of them, namely to command lower torques to the robot (e.g. during cutting or grinding operations), thus improving reliability and reducing decommissioning costs due to robot maintenance. Therefore we are working on new theories in robot dynamics and, in particular, the operational space formulation of robot dynamics, which allows tasks to be defined in the robot workspace, i.e. Cartesian space, as opposed to in the robot's joint space. We are analysing the use of mathematical methods such as a projection into the space of the physical constraints of the robot, in order to devise a smart control method that potentially can reduce the torques needed to control the robot. We are studying different control methods, such as Projected Inverse Dynamics Control and Optimal Control, and also Robust Control, this last one to counteract the effects of possible uncertainties in the parameters of the robot model and/or the model of the surfaces being contacted.

Real-time nanogravimetric monitoring of corrosion in radioactive environments

¹Ioannis Tzagkaroulakis, ¹Colin Boxall and ²Divyesh Trivedi

¹Lancaster University

²National Nuclear Laboratory

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. 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 ng sensitivity.

Current experiments are concentrating 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 being studied as an Enhanced Chemical Cleaning (ECC) decontamination agent in the decommissioning of high level waste storage tanks comprised of low carbon steel at the Hanford and Savannah River Sites (SRS). The efficacy of the ECC and the corrosion behavior of steels at especially low oxalic acid concentrations are not widely studied and knowledge gaps remain. These gaps afford an ideal opportunity for achieving the twin objectives of device development whilst providing new insights into the behavior of a hitherto unstudied corrosion vulnerable system. Mild carbon steel is composed from about 99% iron and initial experiments have shown that pure iron samples can be used as a surrogate to mild carbon steel samples for corrosion measurements in oxalic acid or in a mixture of oxalic acid and H₂O₂. At this project iron coated QCN crystals have been used as a less resource intensive surrogate to mild carbon steel coated crystals.

Previous work has focused on demonstrating that QCN technology can be used for real time corrosion measurements. Using the iron-coated QCN crystals in oxalic acid containing environments as an exemplar system, we have measured (nano)gravimetric corrosion rates directly using the QCN technology – and compared the rates so-obtained with those obtained using corrosion current measurements. Results show that corrosion rates obtained using the QCN are in excellent agreement with those obtained using corrosion current measurements with the added advantages of real time and potentially in-situ and higher sensitivity measurements. [1, 2]

Extending these findings to measurements in radioactive environments and this is the main objective of the current work [3, 4]. H₂O₂ is widely used as an experimental surrogate to simulate its effects of radiation and especially γ radiation in aqueous environments. We have therefore conducted QCN-based corrosion rate measurement experiments on the Fe/oxalic acid system in the presence of H₂O₂, so allowing for determination of the effect of (simulated) water radiolysis on key Fe/oxalate corrosion processes. Measurements indicate the involvement of Fenton chemistry in the observed Fe oxide formation and dissolution processes, indicating that QCN technology offers an advantageously unique combination of capacities for real time and potentially in-situ corrosion measurements in a complex environment where more than one reaction is observed. A key insight of this work is that for the ECC process, it is observed that at low oxalic acid concentrations and at high simulated radioactive environments, it is possible oxalic acid not to act as a corrosion inhibitor.

To summarize QCN technology prevails over other common corrosion rate measurement techniques in terms of measuring the corrosion rates in real time and its capacity for being

applied in complex systems such as a mixture of oxalic acid and H_2O_2 . In collaboration with Dalton Cumbrian Facility, it is proposed for the first time to test the QCN technology as a corrosion monitor in real radioactive environments and to determine the effect of radiation fields on system corrosion/electrochemistry and on the sensitivity of transducer crystal itself.

References

- [1] I. Tzagkaroulakis and C. Boxall, 3rd PhD Research Seminar for NDA Sponsored PhD Projects, Manchester, January 14, 2015.
- [2] I. Tzagkaroulakis and C. Boxall, *Electrochemical Society Transactions*, 66, (17), p.73-83, 2015.
- [3] I. Tzagkaroulakis, C. Boxall and D. Trivedi 4th PhD Research Seminar for NDA Sponsored PhD Projects, Manchester, January 20, 2016.
- [4] I. Tzagkaroulakis, C. Boxall and D. Trivedi, WM2016, Phoenix, AZ, March 6-10, 2016.

Radioactive organic liquid waste treatment using the Arvia process

¹Thomas J. Unsworth, ²Nigel W. Brown, ¹ Ram Krishna and ¹Simon M. Pimblott

¹University of Manchester

²Arvia Technology Ltd

Radioactive organic liquid wastes, such as scintillation liquids, solvents and contaminated lubricating oils, make up one of the more challenging categories of waste in terms of treatment [1]. Developed by Arvia Technology Ltd. in the mid-2000s, the Arvia organics destruction process is a lower energy, cheaper alternative treatment to conventional incineration and has been successfully trialled at the Magnox Trawsfynydd decommissioning site [2, 3]. The process involves adsorption of organic components followed by electrochemical oxidation on the surface of proprietary adsorbent NyexTM.

The reported research provides a better understanding of the fate and behaviour of radionuclides and the impact of ionising radiation on treatment efficacy. Information about how Nyex performs under gamma-ray irradiation has been gathered using the ⁶⁰Co irradiator located at the Dalton Cumbrian Facility (DCF). Ion beam irradiation of Nyex by 3 MeV H⁺ ions has been carried out using the DCF's tandem ion accelerator. The extent of radiation damage was studied in terms of disorder in the material structure and performance removing organic material from solution.

Analysis of the behaviour of radioactive components in the process began using inactive salts of caesium, an important element due to its highly mobile nature. The interaction between Cs⁺ ions in solution and Nyex has been studied at various pH levels to identify the optimum operational conditions. The ultimate aim of this work is to incorporate the above experiments into a laboratory scale Arvia process unit. This approach involves the destruction of low concentrations of organics in solution in experiments using irradiated Nyex, and the treatment wastes containing Cs⁺ ions and solutions spiked with ¹³⁷Cs.

In conclusion, the research carried out in this project aims to establish the limits under which the Arvia organics destruction process can be operated safely and effectively. This work will support the addition of the Arvia process to the catalogue of treatment methods available in the safe disposal of challenging radioactive wastes at sites across the UK and beyond.

References

- [1] R. O. A. Rahman, H. A. Ibrahim, and Y.-T. Hung. Liquid Radioactive Wastes Treatment: A Review. *Water*, 3(2):551–565, 2011.
- [2] N. W. Brown, A. K. Campen, D. A. Wickenden, and E. P. L. Roberts. On-site destruction of radioactive oily wastes using adsorption coupled with electrochemical regeneration. *Chemical Engineering Research and Design*, 91(4):713–721, 2013.
- [3] H. K. Jeswani, H. Gujba, N. W. Brown, E. P. L. Roberts, and A. Azapagic. Removal of organic compounds from water: life cycle environmental impacts and economic costs of the Arvia process compared to granulated activated carbon. *Journal of Cleaner Production*, 89:203–213, 2015.

Robotic-assisted decommissioning of alpha contaminated environments

¹Mohammed Talha

¹University of Birmingham

This project investigates the use of semi-autonomous telerobotic systems for decommissioning nuclear waste. In particular, a case study problem of legacy glovebox decommissioning is addressed. UK nuclear sites, such as Sellafield, contain large numbers of highly contaminated legacy glove-box labs, some of which date from the 1950s and are in a dangerous state of collapse. Gloveboxes are currently dismantled and placed safely into storage containers by human workers wearing protective suits. The working conditions in these suits can be physically laborious and hazardous, and the suits themselves generate additional secondary waste.

It is proposed to build a telerobotic prototype for decommissioning gloveboxes utilising advanced control interfaces, imaging and visualisation methods, as an alternative to current practices. Using such a system, a robot could be placed inside a hazardous zone and controlled from a safe remote location to carry out decommissioning activities which were previously performed manually. Such robotic decommissioning could remove humans from harm, significantly reduce the generation of secondary waste, reduce costs and accelerate the dismantling of legacy plant.

The past 30 years has seen the development of many telerobotics systems, of varying complexity. However, actual application of such systems has been very limited. In the nuclear industry, teleoperation is still limited to direct position control using multiple joysticks whilst viewing CCTV monitors with limited situational awareness. Reasons such as problem complexity, lack of technological maturity and safety concerns are behind the lack of penetration in the industry. However, the state of technology has since advanced and warrants another attempt at penetrating the nuclear industry with advanced telerobotics systems.

Previous robotics work from the research community, has not yet fully explored the human factors issues that affect the performance of humans working with robots to perform practical tasks. This PhD project aims to carry out, for the first time, principled evaluations of the performance of humans working with a variety of robotic technologies, on representative decommissioning tasks. Standardised tasks (e.g. pick and place or trajectory following) will be designed, and human test subjects will complete the tasks using a variety of different human-robot interfaces and levels of robot autonomy. Task performance will be evaluated using objective performance metrics and subjective questionnaires about the operating experience.

Our first experiment will involve operators carrying out standardised manipulation tasks with a number of different control interfaces, to determine their efficacy. We hope to be able to present initial findings by the time of the January NDA seminar.

Wet oxidation of uranium dioxide in sealed and unsealed enclosures in radiation fields

¹Jessica Higgins, ²Robin Orr, ¹Howard E. Sims and ¹Simon M. Pimblott

¹University of Manchester

²National Nuclear Laboratory

Within both open and closed the nuclear fuel cycles, (used) nuclear fuel comes into contact with water during interim storage in cooling ponds prior to disposition in a waste repository or reprocessing, respectively. The used fuel emits an intense ionising radiation field comprising alpha, beta and gamma radiation.

This project focuses on the radiation chemical behaviour of water adsorbed onto uranium dioxide, UO_2 , powders under gamma, high energy proton and 5.5 MeV helium ions irradiation. Initial studies will examine

1. the radiolytic production of hydrogen as a function of humidity and dose and dose rate, and
2. the oxidation and dissolution of the uranium dioxide surface by the reactive oxygen species produced in water.

The interaction of radiation with liquid water has been widely studied and modelled with the 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.

Recently a number of experimental studies have observed that the gamma radiolysis of adsorbed monolayer water on many ceramic oxide powders gives a higher than expected yield of molecular hydrogen. This enhancement of the yield decreases as the amount of surface water is increased. In addition, the magnitude of the enhancement depends upon the specific elemental composition of the underlying surface oxide.

In an oxidising aqueous environment, the surface structure of uranium oxide cycles between $\text{UO}_2 \rightarrow \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_8$. The formation of the intermediate fluorite-type lattice structures is believed to cause a slight contraction in the overall volume, while U_3O_8 has to have a lower density and therefore there is a volume increase when compared to the original UO_2 material. This expansion and contraction will lead to serious mechanical strain within spent fuel. It is observed as a 'popcorn effect' where localised pockets of the surface have expanded, pushing outwards. The consequence of this is an increase in the overall surface area, further enhancing the production of hydrogen and creating potentially hazardous situations when considering enclosed storage.

Investigation of anomalous hydrogen production from water adsorbed to metal oxide surfaces

¹Jamie Southworth

¹University of Manchester

The long term storage of PuO_2 poses significant challenges to the nuclear industry. Hydrogen production due to the radiolysis of water present in active waste containers can generate potentially explosive levels of hydrogen gas. Certain metal oxides have been found to have a catalytic (enhancing or reducing) effect on the yield of hydrogen relative to the radiolysis of pure water. Due to the hazardous nature of plutonium a metal oxide with similar catalytic behaviour should be found. This is necessary to be able to predict how active waste containers will behave over their projected lifetimes.

To establish methods and experimental procedures initial experiments have investigated the gamma radiolysis of water adsorbed on the surface of monoclinic Zirconia. ZrO_2 is a metal oxide known to have a catalytic enhancing effect on the radiolytic yield of hydrogen. The experiments have measured hydrogen yield as a function of water loading and particle size. The Brunauer-Emmet-Teller method was used to determine the particle surface area and the crystal structure was found using x-ray diffraction. It has been observed that there is a greater catalytic effect at lower water loading, with $G(\text{H}_2)$ values orders of magnitude greater than pure water. The smaller particle size also demonstrated greater $G(\text{H}_2)$ values than the larger particles.

Future work will focus on hydrogen generation from ZnO . H_2 will be measured as a function of water loading, particle size and crystal structure. Using humidity control to adsorb water to powder samples is imprecise, therefore a vacuum line method will be developed which will allow greater control over the water delivered to the sample.

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

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²National Nuclear Laboratory

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 'dry' storage of spent fuel cladding, which has been sensitised during several years' operation in the core of the nuclear reactor, is an option under consideration by the Nuclear Decommissioning Authority (NDA) for future deployment following the closure of the UK's fuel reprocessing facility. Inter-granular cracking at stress concentration points in the cladding has been observed during post-irradiation examination where humidity was present. Because 'dry' storage has an inherent risk of the presence of low and variable levels of humidity a programme of tensile testing of sensitised 20/25/Nb alloy in a controlled environment of relative humidity and temperature is necessary.

Samples of fuel cladding have been sectioned and characterised in terms of their micro-structure and basic mechanical properties. Both dynamic (slow strain rate) and static (u-bend) testing is in progress using novel testing equipment which incorporates the head of a reduced-size slow strain rate test (SSRT) rig into the testing space of a controlled environment cabinet. This allows testing to be delivered over suitable ranges of relative humidity and temperature.

Corrosion propensity of THORP PuO₂ storage container

¹Benjamin Krawczyk and ¹Dirk L. Engelberg

¹University of Manchester

PuO₂ product from re-processed oxide fuel from the THORP (Thermal Oxide Reprocessing Plant) is stored in Type 316L stainless steel containers. A design of several 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 of storage in chloride-containing environment. The aim of the project is to inform about the propensity of THORP storage containers towards localised corrosion and Environment Assisted Cracking (EAC) in HCl and chloride-bearing atmospheric environment. Investigations are 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, X-ray 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. Corrosion product development and attack morphology was characterised by laser surface confocal microscopy and scanning electron microscopy.

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

Atmospheric exposure in chloride-containing atmospheres showed that corrosion product development followed a parabolic growth law. Additional mechanical surface treatment with laser engraving resulted in the most susceptible microstructures, with localised corrosion occurring within or at the periphery of the laser engraved region. A similar trend was also observed by using electrochemical measurements in aqueous HCl environment. Atmospheric exposure tests in HCl vapour are currently being conducted to compare with results obtained in aqueous environment with atmospheric exposure regimes.

Enhancing and improving nuclear decay data

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Nuclear decay data is a crucial dataset, relevant to all nuclear situations. In industry, this is best noted in the modelling of future reactors where evaluated libraries such as JEFF (Joint Evaluated Fission and Fusion file)[1], are used to provide the best possible data for nuclear physics modelling calculations. Furthermore, in the assay of waste; intimate knowledge of particular radionuclides relevant to the fuel cycle is vital to the future storage and management of the decommissioned plants, using accurate and precise decay data is of upmost importance in this task.[2] Despite the clear requirement for these data there are still areas in which it is lacking, and can be improved upon[2]. Beta and gamma-ray decay heat, the residual activity, and its associated heat and radiation emissions from irradiated material is one such area. The poster presented will outline the two experimental programmes in which NPL, Surrey and the NDA, with respect to this PhD scholarship, are improving the problem outlined.

NANA (NAtional Nuclear Array) is composed of 12 LaBr₃(Ce) to be used as gamma-ray coincidence spectrometer [3]. The improved energy resolution of LaBr₃(Ce) compared to other scintillation materials, 3% at 0.662 MeV [4] and fast-timing available from such scintillators will allow NANA to be used to provide a detailed and precise gamma-ray analysis of radionuclides following fission using high-fidelity time-correlated gamma-ray energy coincidences. The poster will show simulated γ and γ - γ spectra from the proposed geometry of the array and actual γ and γ - γ spectra using 2, 3 and 4 detectors. It will also include an evaluation of the work carried out in the implementation of fast-timing techniques used and characterization of the timing response of the LaBr₃(Ce) detectors and the CAEN V1751C digitizer.

The IPN Orsay developed LICORNE (Lithium Inverse Cinematique ORsay NEutron source)[5] was used to study the fast-neutron induced fission of ²³⁸U over an experimental campaign of three weeks. The RF-pulsing and mechanical chopping of the ALTO tandem accelerator beam and the high energy resolution of the MINIBALL HPGe cluster array used, allows for the clean selection of gamma-ray cascades in prompt fission daughters and following the depopulation within isomeric states <50 μ s long. Analysis is ongoing, however preliminary fission-yield calculations and an introduction to the time and energy gating techniques to clean such a vast, convoluted dataset will be presented.

References

- [1] A.J. Koning et al., International Conference on Nuclear Data for Science and Technology 2007, 194 771 (2007)
- [2] A.L. Nicholset et al., AIP Conference Proceedings - International Conference on Nuclear Data for Science and Technology, 769 242 (2005)
- [3] P.H. Regan et al., Journal of Physics: Conference Series 620 012005 (2015)
- [4] K.S. Shah et al., IEEE Transactions on Nuclear Science, 50 2410 (2003)
- [5] M. Lebois et al., Nuclear Instrumentation and Methods, A735 145 (2014)

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

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The reuse and recycling of materials that have been used in the construction of nuclear facilities is an important consideration during the decommissioning process. The level of contamination determines whether a material should be environmentally isolated and managed as radioactive waste, or if there are options for its reuse. Waste disposal is a costly process and metals are finite and expensive resources, therefore reuse is the preferable option. Difficulties arise in the characterisation of metal pipework which is behind walls, submerged in concrete or deposited in other hard to reach locations. Radiological laboratory analysis of this pipework can be a time consuming process, the removal of samples from inaccessible areas poses additional health and safety concerns for workers and the cost of radionuclide identification can be high. It is therefore beneficial to develop our techniques for in-situ measurements in order to optimise the clearance and recycling process, as this will reduce timescales and costs while allowing clearance levels to be better determined before any demolition work has been undertaken.

This project will initially focus on the feasibility of employing multi-pixel Geiger mode avalanche photodiodes to access and characterise this potentially contaminated pipework.

Towards rapid ^{90}Sr determination by improved liquid scintillation counting

¹Emily Stokes, ¹Simon Pope, ¹Ian Fallis, ²Colin Harvey and ³Jeremy Andrew

¹Cardiff University

²National Nuclear Laboratory

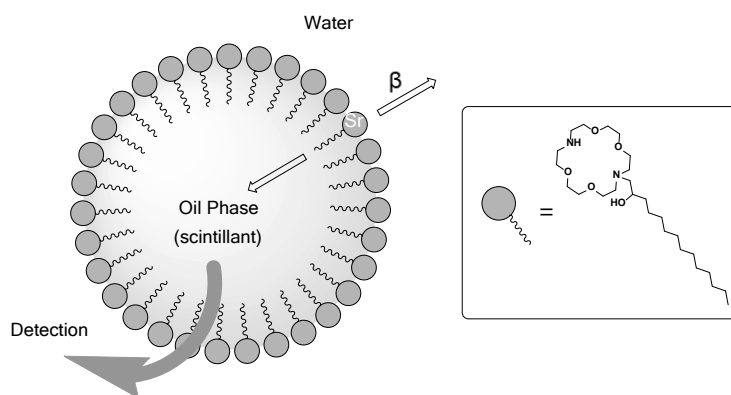
³Dounreay Site Restoration Ltd

The easy incorporation of ^{90}Sr into the biosphere renders its determination a key issue in decommissioning. Current detection methods are both labour and cost intensive, thus the aim of this project is to develop a method for the rapid analysis of ^{90}Sr in groundwater samples by enhancing the sensitivity of direct ^{90}Sr determination by liquid scintillation counting (LSC). Design of ^{90}Sr -specific LSC cocktails through the combination of new Sr^{2+} selective ligands, microemulsions and compatible fluorophores will lead to the systematic development of new protocols for the direct measurement of ^{90}Sr in under 24 hours.

Work to date has involved the synthesis of a range of surfactant-based ligands, namely a 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (N2O4) based system incorporating a hydrophobic dodecyl chain and a multidentate head group capable of binding Sr (pictured below). Surface Tension measurements were performed via Drop Volume Tensiometry to determine the Critical Micelle Concentration (the concentration at which micelles begin to form) of both the free ligand and the Sr complex. These surfactants have been found to form micelles which are capable of solubilising toluene to form an oil-in-water (o/w) microemulsion. Current tests involve investigations to quantify the loading ability of the secondary scintillants into the microemulsion system to create the full LSC cocktail.

Small angle neutron scattering (SANS) was used to probe the structural properties of these ligands within o/w microemulsion systems. The results of these experiments suggest the formation of core shell ellipsoid micelles with the metal species bound to the headgroup and therefore localised on the surface of the scintillation droplet.

The aim with ligands such as these is that they may be employed in the design of LSC cocktails in which the ^{90}Sr is sequestered from the ground water analyte and localised on the surface of the scintillation droplet. It is hoped that preorganising the system in this way will lead to enhanced β -capture, thus increasing the sensitivity of the detection technique.



Sr-localising Microemulsion

Optical detection of corrosion on intermediate level nuclear waste containers

¹George Rowley

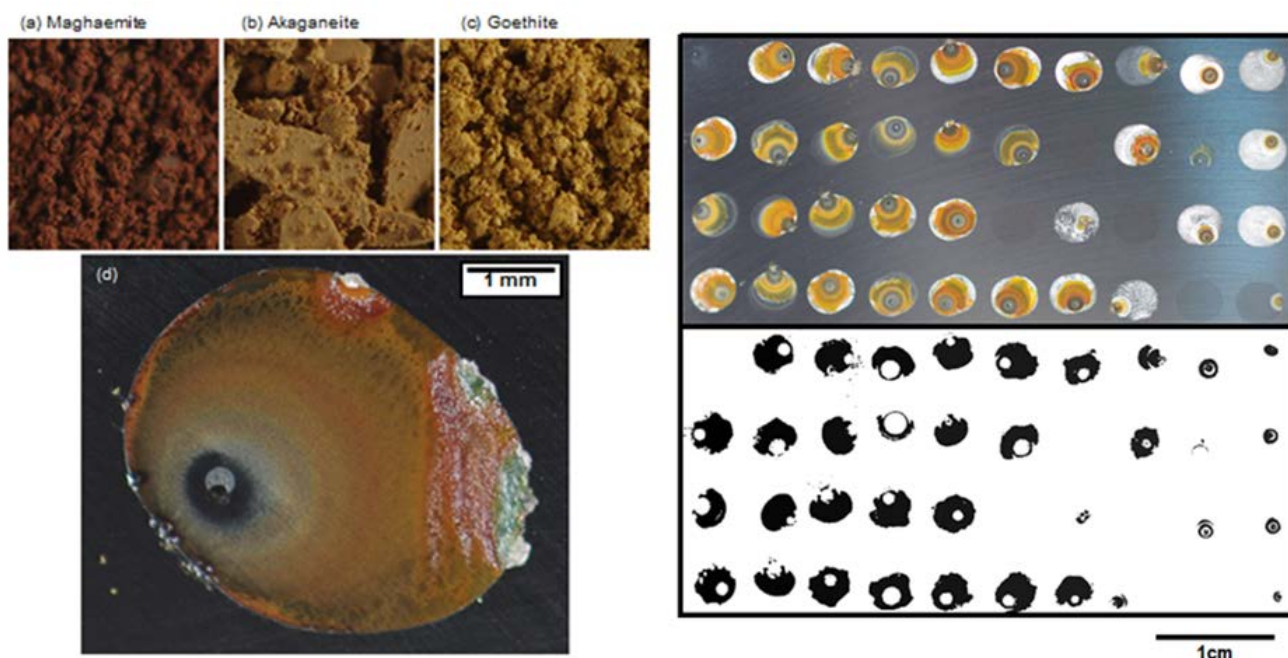
¹University of Birmingham

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, IR, Raman mapping, reflectance and grazing incidence x-ray diffraction (GIXRD) are being 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 that are expected to be present on steels have been synthesised by a colleague. These are being compared with corrosion product formed from atmospheric deposition of chloride salts on 304L and 316L stainless steel in order to find spectrally active wavebands for imaging.

Image processing techniques are also being used on standard colour images of corrosion in order to see if colour and texture analysis can be used 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.



Left: A comparison of colour between synthetic iron oxide phases (a), (b), (c) and rust around a corrosion pit formed on 304L stainless steel (d).

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

In-situ synchrotron x-ray diffraction study of the hydration of highly substituted slag blended cements

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We present results from the analysis of the first 48 hours of the hydration of three high-volume blended BFS-PC systems. This work has been carried out on the I11 beamline of the Diamond Light Source, UK, and is a novel experiment paving the way for a long duration study at the same facility. The application of the 'partial or no known crystal structure' (PONKCS) methodology to a reacting cementitious system with a dominant amorphous content in the cementitious constituent is demonstrated, enabling accurate phase quantification with no internal reference standard. We describe the data acquisition methodology, and the refinement technique developed with a view towards producing quantitative information regarding the phase composition of the material as a function of time during the early stages of reaction. The formation of common crystalline hydrate phases such as portlandite and ettringite is observed, along with the generation of amorphous hydrate components within the system. The consumption of clinker and slag phases, and the reaction of gypsum and anhydrite present within the cement powder, are monitored with unparalleled temporal and angular resolution.

Modelling the interaction of corroded Magnox surfaces with nuclear fission products

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²University of Manchester

³Lancaster University

In the first generation British nuclear power reactors, a Mg-Al alloy, Magnox was used to contain the uranium fuel rods. This cladding, which is now a significant part of nuclear waste, corrodes over time and forms a brucite ($\text{Mg}(\text{OH})_2$) surface. Since the waste is held in water filled storage ponds, the brucite surfaces become highly reactive in their hydrated form and can interact with the aquo and hydroxide complexes of uranium and its main fission products, ^{90}Sr and ^{137}Cs . Therefore, understanding of these interactions is important for creating successful treatment strategies for the waste. Since the monitoring and experimental investigation of the problem is difficult due to its high radiological hazard, computational modelling can provide important information for this challenging task.

In this project, we seek to develop a computational model, using high-level quantum chemical techniques based on density functional theory (DFT), which is able to describe the aquo and hydroxide complexes of strontium and their interactions with hydrated brucite surfaces, aiming to create a general approach which can be used subsequently for the investigation of other radioactive ions/surfaces.

My poster contains the results of a study which we did to find a suitable representation of the brucite surface for studying adsorption reactions. Using the periodic embedded cluster method (PEECM), implemented in the TURBOMOLE code, we have created a quantum chemically treated cluster in an infinite array of point charges and used this model to explore the adsorption of Sr^{2+} and other s block cations such as Ba^{2+} and Cs^+ on bare and hydrated surfaces. The latest results from this work will be shown on the poster, along with those of a parallel project in which we are comparing our PEECM data with those from a periodic DFT study using the CRYSTAL code.

Development of glass-ceramic wasteforms for the disposition of plutonium residues

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²National Nuclear Laboratory

Glass-ceramics are being developed for the disposition of Pu-residues where current vitrification techniques are inapplicable and reprocessing is economically non-viable. These alternative matrices provide dual functioning wasteforms with higher loading capacities, radiation tolerance and leach resistance than their vitrified equivalents, whilst retaining an ease of processing.[1] Zirconolite based glass-ceramics harness the high actinide and rare earth loading capacity of the highly durable ceramic phase, combined with the amorphous protective barrier that immobilises miscellaneous material from the waste-stream. These wasteforms are highly flexible for handling the variety of physically and chemically demanding Pu-residue waste-streams.

This project also utilises hot isostatic pressing (HIPing) for processing these wasteforms, again due to its flexibility to handle a vast range of waste-streams. HIPing has the capacity to process all families of Pu-residues with only minor changes to the processing parameters and wasteform matrix. HIPing applies high temperatures and pressures to produce high density bodies concomitant to reducing the overall wasteform volume. These advantages alone make hot isostatic pressing a promising technique for processing Pu-residue waste-streams.[2]

Samples discussed in this poster investigate the processing and formulation optimisation of zirconolite based glass-ceramic systems. All samples were HIPed at 1250 °C, 100 MPa for 4 hrs. By investigating the effects of; different pre-HIP heat treatments on sample quality and throughput, and glass phase compositions on the crystalline phase assemblage, an optimised method and wasteform composition have been achieved.

References

- [1] P.W. McMillan, Glass-ceramics, 2d ed. Academic Press, London ; New York, 1979.
- [2] Nuclear Decommissioning Authority, Conditioning of Plutonium Residues by Hot Isostatic Pressing and Options for packaging and Disposal (pre-conceptual stage) Summary of Assessment Report. 2009

Radiation damage in 'real' zirconolite and gadolinium pyrochlores; simulating the effects of grain boundaries

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In our current project exploring radiation damage in potential nuclear waste encapsulation materials we have been investigating the effects of grain boundaries in zirconolite, $\text{CaZrTi}_2\text{O}_7$. Simulations have been aimed at seeing how grain boundaries affect damage creation, propagation, and recovery following the energy impulse from a heavy recoil atom. The key focus of this work has been to compare with the damage created within pristine crystalline zirconolite.

The study has extended to include gadolinium pyrochlores which have been proposed as potential materials for high-level radioactive waste storage, due to gadolinium's high absorption of neutrons. We consider two systems $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$, whose cubic structures are shown in Figure 1 and Figure 2 respectively. These structures are based on the fluorite structure, as is the monoclinic zirconolite structure, but with 1/8 of fluorite anion sites vacant. The pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$ is predicted to withstand radiation damage for 30 millions years compared with 800 years for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and therefore want to investigate how the change in behaviour from Ti to Zr withstands radiation damage.

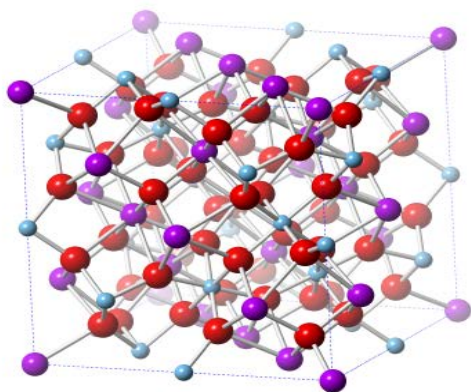


Figure 1: Cubic $\text{Gd}_2\text{Ti}_2\text{O}_7$

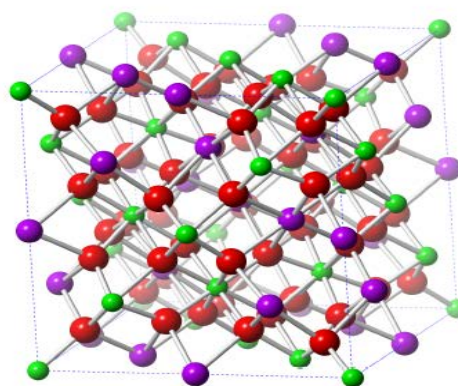


Figure 2: Cubic $\text{Gd}_2\text{Zr}_2\text{O}_7$

We are interested in understanding the stability of these pyrochlores over transformation to the monoclinic zirconolite structure. We have simulated radiation damage in perfect cubic structures of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ induced by 80 keV uranium recoils, in systems of just over one million atoms. The simulations were carried out at different recoil directions to obtain reasonable statistics. They will be compared with the prior results for zirconolite.

Previously, with zirconolite we have created and analysed with two types of interfaces, (i) a thin interface of two slabs on top of each other with random orientations, and (ii) a thick interface between spherical nanoparticles of random orientation, with one at the origin and one at the centre of the configuration. We constructed these grain boundary interfaces by annealing the structure at high temperature and pressure to resemble the industrial process of hot isostatic pressing. Then, we aim to simulate collision cascades in the polycrystalline gadolinium pyrochlores for 8 directions of recoil in a system of over a million atoms. The aim is to compare the results with those from the perfect starting material, particularly to see whether the enhanced disorder in the polycrystalline materials affect the size or recovery of the damaged region.

A thermal rework strategy for failed cemented wasteforms

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²National Nuclear Laboratory

The UK's baseline technology for ILW treatment is cementation. One of the plants that cements waste is the Magnox Encapsulation Plant (MEP) that encapsulates Magnox swarf in a blend of Ground Granulated Blast furnace Slag (GGBS) and Ordinary Portland Cement (OPC). When a sample of these drums were monitored, in interim storage, it was observed that several of them had expanded due to $H_{2(g)}$ generation from metal corrosion.

Here we present findings on the possibility of the reworking of these problematic drums into a stable wasteform, using vitrification. We utilise the glass-formers present in the waste as well as the addition of readily-available glass-formers: sand, boron oxide and sodium carbonate. Different waste loadings are utilised including 100%, 90%, 72%, 46% and 36%. Wasteforms are characterised by different techniques including SEM/EDX, XRD, DTA, Mössbauer, density and mass balance measurements.

Results show that vitrification is a feasible solution- oxidising reactive metals, evaporating the water content and showing the possibility of volume reduction. Wasteforms at higher waste loadings show crystallisation of mineral phases as well as evidence of porosity whereas at lower waste loadings a homogenous, vitreous wasteform is produced.

Studies of an unusual bimetallic uranium (V) motif in a 'Pacman' macrocyclic framework

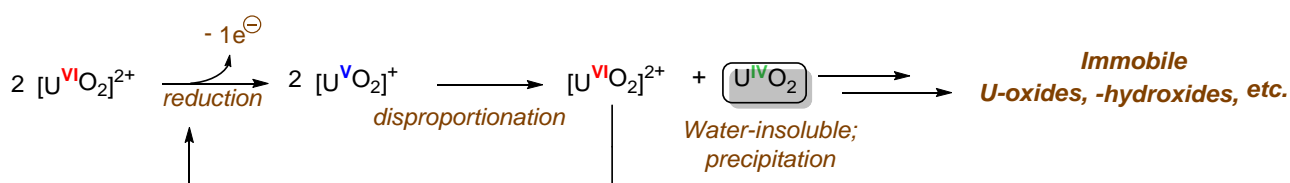
¹Jamie M. Purkis, ¹Polly L. Arnold, ¹Jason B. Love, ¹Nicola L. Bell, ²Roberto Caciuffo, ¹Bradley E. Cowie, ¹Guy M. Jones, ²Nicola Magnani, ³Georg Schreckenbach

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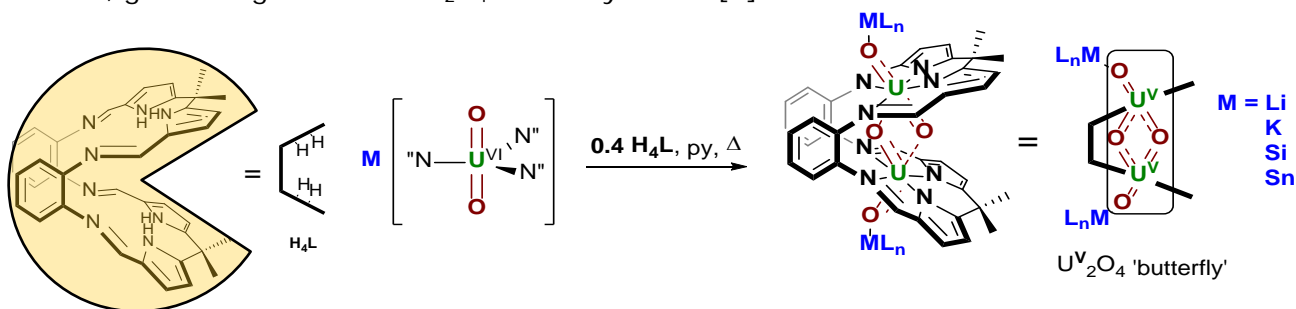
The uranyl dication, $[\text{UO}_2]^{2+}$, is the predominant and therefore most relevant form of uranium (**VI**) in aqueous environments. Microbial- or mineral-induced *in-situ* one-electron reduction to afford *f*^I uranium (**V**) in $[\text{UO}_2]^+$ is a reasonably facile redox process ($E^\circ \approx -0.7 \text{ V vs. Fc/Fc}^+$). [1]



However, $[\text{U}^{\text{V}}\text{O}_2]^+$ is inherently unstable, readily disproportionating back to uranium (**VI**) in $[\text{UO}_2]^{2+}$ and insoluble uranium (**IV**) precipitates in water. This leads to eventual immobilisation and, significantly, removal of uranium contaminants from aqueous environments; an understanding of uranyl oxo-group chemistry is therefore paramount.

The $\text{O} \equiv \text{U} \equiv \text{O}$ bonds in $[\text{UO}_2]^{2+}$ are also chemically inert, and so reactivity at uranium (**VI**) commonly occurs in the equatorial plane. [2] We have shown that by rational ligand design (to inhibit equatorial reactivity) it is possible to stabilise one-electron reduction to the $[\text{U}^{\text{V}}\text{O}_2]^+$ ion, using the sterically-congested 'Pacman' macrocyclic framework. [3]

Using this Pacman we have also elicited new oxo-group reactivity around adjacent uranium (**V**) centres, generating the novel $\text{U}^{\text{V}}_2\text{O}_4$ 'butterfly' motif: [4]



Unusually for two adjacent uranium (**V**) centres, our system does not disproportionate; indeed, silylation of *exo*-oxo groups in the $\text{U}^{\text{V}}_2\text{O}_4$ butterfly renders the motif inert to oxidation and hydrolysis, even at elevated temperatures.⁴ Given the importance of uranium (**V**) in the environment, we will present our efforts to understand bonding and reactivity of this unusual $\text{U}^{\text{V}}_2\text{O}_4$ motif.

References

- [1] J. Am. Chem. Soc., **2013**, 135, 3841; Coord. Chem. Rev., **2009**, 253, 1973
- [2] J. Chem. Phys., **2002**, 117, 8008; J. Phys. Chem. A, **2012**, 116, 12373
- [3] Inorg. Chem., **2004**, 43, 8206; Nature, **2008**, 451, 315; Nat. Chem., **2010**, 2, 1056; J. Am. Chem. Soc., **2013**, 135, 3841
- [4] Angew. Chem. Int. Ed., **2012**, 51, 12584; Chem. Eur. J., **2013**, 19, 10287

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

¹Chak-Hau Michael Tso, ¹Andrew Binley and ²Oliver Kuras

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²British Geological Survey

Cross-hole electrical resistivity has been identified as the ‘best available technology’ for in-ground detection and volumetric monitoring of potential leakage from waste storage facilities. Previous studies have demonstrated that ERT can provide valuable subsurface information (including the tracking of solute plumes) which would be impossible to obtain through other means (e.g. boreholes). This capability addresses key regulatory requirements and directly underpins the decommissioning of legacy ponds and silos at nuclear sites, which is a priority task for the NDA. However, as the performance of ERT strongly depends on the geological setting, parameter contrasts, environmental conditions, indirect petrophysical relationships, and sensor array geometry at each specific site, it is critically important to understand the capabilities and limitations of the technique specific to the nuclear context. A vital ingredient to success is the incorporation of ancillary environmental data into the ERT interpretation in order to maximise value and impact of the geophysical data. It has been shown recently in published work how information content in geophysical data can be quantified alongside the value of additional (e.g. hydrogeological and geochemical) data in enhancing the worth of geophysical surveys. Whilst this recent work focussed on relatively simple (2D) geophysical models, the proposed project aims to build on these achievements in the context of characterising nuclear sites.

This project, which started in October 2015, begins with a literature review of uncertainty estimation and image appraisal in hydrogeophysics and other related disciplines. In particular, we focus on approaches that allow fusion of datasets under uncertainty, such as hidden Markov models. The review aims at summarizing and categorizing different popular approaches, as well as identifying the key strengths and limitations of existing methods. We will then develop new methods for quantifying uncertainty in near-real-time 4D geoelectrical imaging and for conveying this information to nuclear engineers, decision makers and regulators. Specifically, we will first theoretically investigate the utility of ancillary environmental data that may improve our estimation. Subsequently, we plan to develop an improved geophysical inversion method to allow the different ancillary environmental data to contribute to the estimation under uncertainty. Efficient algorithms will also be developed and implemented to allow near-real-time and reliable detection of contaminant migration so that the 4-D images can turn to robust tools to assist decision-making of a nuclear facility. Finally, we will demonstrate the capabilities of the new method using 4-D cross-hole electrical resistivity data at NDA’s Sellafield site collected by BGS’s ALERT system.

Assessment of natural attenuation and targeted in-situ remediation of radioactively contaminated land

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²National Nuclear Laboratory

³Sellafield Ltd

Nuclear fuel cycle operations over the last 60 years have led to a legacy of radioactively contaminated land at NDA sites such as Sellafield and Dounreay. ⁹⁹Tc and ⁹⁰Sr are amongst the priority radionuclides present at elevated concentrations in groundwater within these sites. This project aims to assess the potential of natural attenuation and targeted in-situ strategies to immobilise these contaminants within the subsurface. In order to accommodate the long half lives of these radionuclides and the long site lifetimes at e.g. Sellafield it is necessary for these strategies to be resilient to environmental perturbations over the long term.

The dominant control on ⁹⁹Tc mobility within groundwater is its oxidation state. Under oxic conditions it exists as the highly mobile pertechnetate ion, Tc(VII)O₄⁻. Following reduction to Tc(IV), it may form insoluble TcO₂ or TcS₂ mineral phases or become sorbed to sediments at very low concentrations. This project will focus on biogeochemical processes leading to reducing conditions with for example Fe(III)- and sulfate-reduction as target biogeochemical processes and with amendments such as nano zero-valent iron and Fe(II) bearing nano materials also being explored.

⁹⁰Sr is present in the environment as Sr²⁺ and sorbs to surfaces at high pH via weak outer shell complexes. Although high pH levels will encourage sorption of Sr²⁺, an increase in ionic strength of groundwater will result in strontium release as smaller cations are preferentially sorbed. In order to ensure long term stability of ⁹⁰Sr it is necessary to encourage uptake into mineral phases. Work discussing the potential for ⁹⁰Sr and ⁹⁹Tc co-treated in the subsurface by addition of agents which promote bioreduction and pH / mineral control will also be discussed.

It will be necessary to assess the long term stability of reaction products by reoxidation experiments and post reaction manipulation of the ionic strength. Also the coordination environment and oxidation state of these radionuclides will be analysed by X-ray absorption spectroscopy.

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

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²National Nuclear Laboratory

Treatment of radioactive effluents and groundwaters containing ⁹⁰Sr at low molar concentrations is traditionally achieved by cation exchange. However, the effectiveness of the process is reduced by competing ions present in groundwaters (e.g. Ca²⁺, Na⁺) and anionic radionuclides are not removed (⁹⁹Tc, ¹⁴C). Inorganic precipitation of ⁹⁰Sr and ¹⁴C 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 Ca²⁺ and CO₃²⁻ and crystallization pathways on the removal of Sr and ¹⁴C from solution.

The crystallization pathways occurring between aqueous ions of Ca²⁺ and CO₃²⁻, and thermodynamically stable calcite appear to be an important control on the removal of ¹⁴C from solution. If the precipitate undergoes recrystallization ¹⁴C and ⁹⁰Sr will become remobilized to the solution. This is of minimal importance for the Sr, which is reprecipitated into the newly formed crystal lattice. ¹⁴C however undergoes mixing with ¹²C derived from CO₂ in-gassing and becomes diluted, reducing its removal efficiency. Solution Ca:CO₃ ratios were found to be important for ¹⁴C removal, due to the effects of dilution by excess CO₃²⁻. Sr removal however was not significantly affected, as atmospheric CO₂ in-gassing was able to provide sufficient CO₃²⁻ for full Ca²⁺, and thus Sr²⁺ removal.

Future work for this project will involve researching the importance of groundwater ionic composition and seed crystal concentration on the removal of ¹⁴C and ⁹⁰Sr. The project will also seek scale up the most promising reaction conditions to column scale to develop methods applicable to flowing systems and large volume treatment. A full cost-benefit analysis will also be performed for an installed engineered treatment system versus likely alternative methods.

RECENT STARTERS

The following section provides abstracts of NDA-funded PhD students who started their PhD projects within the last six months.

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

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¹Lancaster University

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. This includes verifying existing sources that are known and locating sources that are unknown (due to limited legacy record keeping or unanticipated contamination). This has two purposes: the safety of workers handling the contaminated materials and the correct removal and storage of the contamination. Both of these also have associated cost implications, which is not a trivial consideration in nuclear decommissioning.

As a part of this process, Plutonium-Contaminated Material (PCM) has to be identified and treated appropriately. Current assays in contaminated facilities are primarily based on total alpha counting. Most conventional alpha detection systems are only effective at relatively short range, or if the detection is based on alpha-induced air-fluorescence, then generally only under dark conditions. Such systems also have the disadvantages of, for example, lengthy counting times, which substantially increase the time take to characterise, and significant uncertainties in measurements, which would increase the risk to operators from the alpha activity as the majority of alpha decommissioning is done manually using hand-held tools.

Alpha particles excite the nitrogen in the air and, as a result, ultraviolet (UV) photons are emitted by nitrogen molecules. These UV photons have a long range in air, considerably larger than that of alpha particles. Large numbers of UV photons per alpha decay (depending on the alpha energy) will allow high detection efficiency even under a strong gamma radiation field. However, generally, current alpha induced UV detection systems are only accurate in dark conditions (or operate in a sodium lamp room) since natural UV radiation generated by the sun causes interference.

The aim of this project is to develop a scanning based optical imaging system to detect alpha-induced air fluorescence under daylight conditions from long distances. The system will contain a UV detector mounted on to a scanning platform, where it will be operated remotely to collect UV photon events corresponding to a user specified area. The scanning process will also enhance the location accuracy of the alpha-induced air fluorescence against background UV, whilst the optical collimator will improve the field of view of the system. Alpha induced air-fluorescence yield will also be investigated to determine the corresponding radioactive isotope. In order to further advance the detection range of the system, other filtering and relevant techniques will also be developed and employed.

Enhance nuclear waste assay

¹Kevin Tree, ²Beth Ripper, ¹Laura Harkness-Brennan, ¹Paul Nolan, ¹Dan Judson, ¹Carl Unsworth, ³Gary Bolton, ⁴A.S. Adekola, ⁴J. Colaresi, ⁴J.F.C. Cocks and ⁴W.F. Mueller

¹University of Liverpool

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⁴Canberra Industries Inc.

Assay of nuclear waste is a problem for both legacy waste sites (decommissioning) and for newly developing monitoring solutions for existing facilities and new build. A common assay method is to use gamma-ray spectroscopy to both identify and quantify the waste. This project aims to increase the sensitivity of these measurements, using advanced algorithms and novel detector technology. The expected outcomes are significantly reduced counting times and improved isotope identification in the presence of large backgrounds.

High-resolution germanium gamma-ray detectors are an important tool in nuclear waste assay. The detectors can be coupled with digital electronics to extract, with a high degree of accuracy, the total energy deposited by gamma-rays in the detector, thus allowing radionuclides to be identified and quantified. However, in nuclear waste assay, the relative activities or location distributions of radionuclides is not necessarily known and the radionuclides of interest may be masked by the presence of others. Long measurement times can therefore be required to quantify the relative activities. By improving the spectral response of Broad Energy Germanium (BEGe) detectors, techniques to optimise and evaluate digital Compton suppression algorithms, aimed at reducing the measurement time in nuclear waste assay, will be developed.

These techniques will be based upon distinguishing low energy gamma rays that are absorbed near the outer surface of the detector, from Compton events arising from higher-energy gamma rays, which interact throughout the whole volume of the detector. This technique is not only applicable to assay solutions, but can also offer significant improvements of spectroscopic performance for environmental measurements.

This work will derive from the measurement of the relationship between the gamma-ray interaction position in the crystal and the shape of the charge pulse. Simulations will be used to model the electric field within the bulk of the detector to understand the charge collection process. The models will be validated by comparison with an experimental database of pulse shapes for known positions of single gamma-ray interactions in BEGe detectors of differing geometries.

The digital Compton suppression technique relies on a detailed characterisation of the position dependent response of the detector to gamma irradiation, for which the University of Liverpool has well-established facilities. The systems being considered will be modelled using simulation codes such as ADL, MCNP or GEANT. Realistic industrial performance tests will be conducted using the developed algorithms to evaluate the proposed solutions. These will take place at Canberra (Harwell) using their facilities that include waste drum analogues. Measurements will also be made at the National Nuclear Laboratory (NNL) Central Laboratory, through support from the Nuclear Decommissioning Authority (NDA), for verification of the algorithms.

The effective models for engaging and supporting SMRs in delivering technological innovation in nuclear decommissioning

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The last decade has seen a growing application of the idea of “open innovation” across a range of industrial sectors and organisations. Open Innovation (OI) is the idea that effective technological innovation comes not only through internal R&D within an organisation but also through its effective engagement with other external sources of intellectual property. The project critically and systematically reviews academic literature to determine (i) how OI is variously defined and what research has been published on the implications and impacts of OI, specifically in relation to comparison with more traditional forms of innovation and (ii) the implementation of OI in complex organisations/sectors where supply chain partners, academia and customers on a local and national level collaboratively innovate and on a global level utilise OI technologies/platforms to innovate across organisational and geographic boundaries (particularly in sectors such as aerospace, defence and oil and gas exploration).

For an innovation or innovative idea to successfully navigate through the innovation process from basic principle to diffusion and adoption, differing players within the supply-chain (vertical) or knowledge creation and exchange (horizontal) networks will require complementary, may be sometimes contrasting, attributes. Particularly relevant to the project is the Absorptive Capacity of Lead Firms to identify a novel solution to a problem and through either exploitative or explorative capabilities, engage with other players to deliver a successful outcome. The term Small and Medium Size Enterprise (SME) is used to describe a sole trader, through micro-businesses (0-9 employees) up to firms with 250 employees. Findings of previous research have suggested that the capability and capacity for innovation can be impacted by SME size, the project will review how firm size might determine the engagement strategies of Lead Firms to most effectively benefit from SME innovation. Working with the Nuclear Decommissioning Authority (NDA), through the development and evaluation of case studies on how OI and engagement with the supply chain can be done effectively, the project will identify and disseminate effective practices for the engagement and support of SMEs in delivering technological innovation.

ORAL PRESENTATIONS

Up-scaling cross-flow membrane emulsification and polymerization, and *in situ* acoustic characterization of the produced colloidal dispersions

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Initially we report on the up-scaled production of stable mono-disperse latex emulsions via cross-flow membrane emulsification (XME). A two-step process was adopted where the monomer was emulsified in the micron size range via XME [1] and subsequently encapsulated via interfacial polymerization in a heated reactor. Pressure and flow rates were adjusted to produce several liters of stabilized emulsions in the desired micron size range. Due to the operating parameters of the XME, it was necessary to adjust the emulsion from the original latex formulation, which subsequently had implications on attempts to polymerize the emulsions on a 2 L volume scale. A systematic study was conducted where physical parameters and formulation content were adjusted to achieve successful polymerization. In particular, issues regarding addition of Hydroquinone inhibitor content are discussed.

Additionally we report on the *in situ* characterization of the resulting colloidal dispersions. Characterization is typically a non-trivial process, and *in situ* measurements removing sampling restrictions are preferable in numerous laboratory and industrial applications. Ultrasonic measurement is a superior approach for the characterization of concentration and particle size in colloidal systems, especially where the emulsions are optically opaque. Traditionally this involves measurement of acoustic velocity or attenuation, and relating to these physical properties using theories describing ultrasonic propagation in emulsions. Here, phenomenological methods are utilized to characterize density concentration with an acoustic backscatter system (ABS). Specifically, the acoustic response of emulsified monomer, the corresponding polymerized latex dispersions and aggregated dispersions coagulated through salt addition are compared. The attenuation-concentration relationship for each emulsion type is elucidated and the corresponding scattering and attenuation coefficients are quantified. Essentially, the need for the application of complex theoretical theories is removed, and a convenient technique for true *in situ* deployment in concentrated emulsions demonstrated.

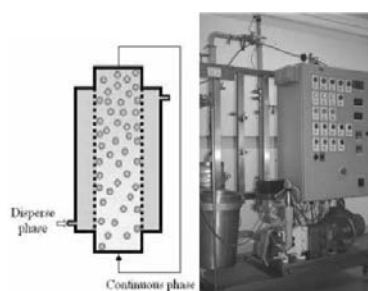


Figure 1. Mechanism of XME and a pilot rig [1]

References

[1] Q. Yuan, R. Hou, N. Aryanti, R. A. Williams, S. Biggs, S. Lawson, H. Silgram, M. Sarkar, R. Birch, *Desalination* 224 (2008) 215-220.

Remote alpha counting with a radioluminescence detector: moving toward automated, quantitative alpha assessment at distance

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The emission of brief, weak flashes of light induced when alpha particles collide with and ionise nitrogen in air is being explored as a mechanism to detect and quantify alpha-emitting radionuclides remotely. Of the 20 ultraviolet photons emitted per MeV of decay energy in this process approximately 30% are emitted with a single wavelength, 337nm, which allows fine filtering of backgrounds from other sources in this region of the electromagnetic spectrum. In air, photons of 337nm have a scattering length of 11km (Abbasi, 2008) at STP, by comparison to the centimetres of alpha particles, and this fact means that detection of such interactions can be achieved far beyond the path length of the alpha particle itself.

The possibility of remote detection is of significance to the UK's nuclear decommissioning legacy; in 2013 a Nuclear Decommissioning Authority report identified that all but three facilities on the Sellafield site had a need for robust, remote alpha detection techniques. (S. J. Palethorpe, October 2013) This is especially important for radionuclides with low energy or low intensity gamma emissions such as Am-241 and various isotopes of plutonium, contaminants in constrained geometries (e.g. pipes) where conventional mechanisms cannot easily be employed, and areas where analysis is problematic in-situ (e.g. glove boxes and hot cells). While a number of devices have been developed in the past, most are focused on the imaging (Lamadie, 2005) (Sand, 2015) of contamination for decontamination or detection (Sand, 2005) for nuclear security and forensics although these often rely on UV light sensors which are typically very costly and complex. This work is focused on the ability to quantify contaminants from radioluminescence signals using relatively simple, inexpensive equipment with which most industry end-users will be familiar. It has been demonstrated that the developed device is appropriate and useful for decommissioning environments, offering low detection limits (surface emission rates $<10\text{s}^{-1}$), fast response (Am-241 of S.E.R. 105s^{-1} detected in 2.2s to 99% confidence level) and the ability to quantify amounts of radioactive surface contamination present. Additionally the ability to detect materials at distance has been demonstrated, with detection of a 33kBq Am-241 source demonstrated at over a metre; for more active materials (e.g. Pu) this would be possible at significantly greater distance.

As such this presentation and the project at large focus on the design, development, calibration and testing of a remote alpha detection device suitable for end users in nuclear decommissioning. A variety of novel methods are presented in relation to the modelling and calibration of such radioluminescence-sensitive devices with modelled and empirical detection limits presented over distance for Am-241. Finally developments are presented in relation to the construction of an automated assessment system for alpha-contaminated materials for use in the classification of waste, the locating of contaminants using remotely deployed systems (e.g. Wall Rover) and scanning systems.

Bibliography

Abbasi, R. et al., 2008. Air fluorescence measurements in the spectral range 300–420nm using a 28.5 GeV electron beam. *Astroparticle Physics*, 29(1), pp. 77-86.

Lamadie, F. et al., 2005. Remote alpha imaging in nuclear installations: new results and prospects. *IEEE Transactions on Nuclear Science*, 52(6), pp. 3035-3039.

Mort, P. et al., October 2013. *Technical challenges, needs and opportunities in decommissioning of the Sellafield Site*: Sellafield Ltd.

Sand, J. et al., 2005. Remote optical detection of alpha radiation. *IEEE Transactions on Nuclear Science*, Volume 52, pp. 3035-3039.

Sand, J. et al., 2015. Imaging of alpha emitters in a field environment. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, Volume 782, pp. 13-19.

Development of robust automated techniques for radionuclide separation

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Quantitative radiological characterisation of a wide range of sample types is essential in underpinning environmental, health physics and decommissioning programmes within the nuclear industry. The measurement of alpha and beta-emitters typically requires multiple steps to separate the analytes from the bulk matrix and other species that may interfere with detection (either by radiometric or mass spectrometry methods). These procedures are time consuming and require significant analyst input.

Column-based ion exchange and extraction chromatography techniques are widely used for both preconcentration and isolation steps and have already been thermodynamically characterised in terms of sorption and desorption potentials for a large range of resins, analytes and matrices. Automation of chromatographic techniques is possible using fluid handling systems and has many advantages including a reduction in radiological risk to the analyst, an improvement in reproducibility of data and a lowering of cost via shorter analysis time, less volume of reagent and reduced labour demand.

Automated systems using peristaltic or syringe pumps can deliver flow rates much greater than those produced under gravity. Elevated flow rates, however, lead to changes in elution peak width, shape and timing and can subsequently affect the collection volumes needed and the achievable decontamination factors. Existing automated systems have chosen flow rates based on basic empirical findings or practical reasons. Greater understanding of the impact of column parameters such as flow rate, bed length and particle size is needed. This can then be combined with analyte specific reaction and mass transfer kinetics and distribution constants at equilibrium to create a predictive separation model.

Several equations have been assessed for their applicability to describe column elution for a range of sorptive materials used in the nuclear industry. Recommendations on the tests needed to derive input parameters for an uncharacterised material or analyte have also been made.

A final aim is to apply this predictive model to a bespoke automated radioanalytical system incorporating user-friendly graphical software and validate it using simulated and real wastes arising from decommissioning. By predicting and implementing the appropriate flow rate, column length and reagent volumes the analyst can meet the required decontamination levels whilst maintaining a high throughput. This easy adjustment of column and reagent parameters will also support the future use of the system as a method development tool.

The sorption of nuclear fission products and transuranic element from aqueous environments by graphene oxide nano-flakes

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One of the main technological challenges facing the nuclear industry is the containment, management and remediation of waste radioactive material in aqueous environments. The creation of contaminated liquid effluent is not solely from power production. Activities such as uranium mining yield large volumes of naturally occurring radioactive materials (NORMs) and technologically enhanced naturally occurring radioactive materials (TENORMs), which can easily contaminate surrounding ground water and require decontamination.

The main focus of the research carried out here is for the remediation of legacy nuclear sites. Legacy nuclear waste contains significant volumes of manmade transuranic elements and long lived fission products. Remediation of contaminated waste water is essential but at present a very time consuming and costly process. A recent report published by the UK government [1] projected that the full decommissioning of Sellafield alone would cost approximately £67 billion and take up to a century to complete.

Recent experimental research [2-5] in the area of graphene oxide (GO) has shown it to be an extremely effective material for the removal of transuranic elements and fission products from realistic simulated environments. It has been shown to be effective across a wide pH range and under a variety of laboratory conditions through surface absorption. Complementary research has also shown that the interaction between GO and cations caused the formation of nanoparticulate aggregates through coagulation[3,6]. Such aggregates may be easily removed and reprocessed.

The project to date has comprised a wide scale investigation of the surface and edge properties of GO nano-flakes using density functional theory (DFT), in order to form a coherent model in computational chemistry and advance experimental understanding. Current work is investigating the interaction between a variety of common radionuclides, and GO surfaces and functionalised edges, to better understand the nature and strength of binding that occurs. The understanding obtained will be used to investigate the potential for optimisation of the absorption process through manipulation of the nature and degree of GO surface and edge oxidation. It is proposed that, through such optimisation, radionuclide selectivity maybe be possible, leading to new materials suitable for radioactive waste recycling.

References

- [1] Parliament UK, 2012 Statement from PAC chair on Nuclear Decommissioning Authority: Managing risk reduction at Sellafield
- [2] Y. Sun *et al.*, Environ. Sci. Technol., 2012, **46**, 6020-6027
- [3] A. Y. Romanchuk *et al.*, Phys. Chem. Chem. Phys., 2013, **15**, 2321-2327
- [4] G. Zhao *et al.*, Environ. Sci. Technol., 2011, **45**, 10454-10462
- [5] N. Pan *et al.*, J. Radioanal. Nucl. Chem., **298**, 1999-2008
- [6] S. T. Yang *et al.*, J. Colloid Interface Sci., 2010, **351**, 122-127

Thermal treatment of plutonium contaminated material wastes

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The projected UK plutonium contaminated material (PCM) waste volume is $>30000 \text{ m}^3$ with 70% arising at Sellafield. The current baseline treatment is supercompaction / cement encapsulation. Thermal treatment, i.e. in-container or plasma vitrification has been identified as the main alternative. Key drivers for the application of thermal treatment processes include the reduced volume, improved passive safety, and superior long term stability, of the vitrified wasteform products. Although proof of concept studies by Sheffield University and others have demonstrated PCM compatibility with thermal processes, a fundamental understanding of waste incorporation reactions and the impact of waste inventory on product quality remains to be established. This generic understanding is clearly critical to successful technology deployment.

Laboratory scale experiments (Fig 1) using mock ups of PCM waste (using Ce as a Pu surrogate) and glass forming additives have been performed in order to understand the reactions / processes of waste digestion and incorporation during thermal treatment.



Fig1: (Left) Laboratory scale PCM mock up drums, with addition of 1.04 wt% CeO_2 , as a Pu surrogate. (Center) Addition of glass forming frit at a 1:1wt% ratio with waste simulants. Thermal treatment 1560°C Melting temperature for 4 hours. (Right) example of vitrified waste product, masonry in this case.



Melting behaviour showed no violent reactions between the waste simulant and glass additive. A metallic fraction resulted for the vitrified metal type. PVC and masonry waste types were composed of 100% glass waste form. Glass in masonry and metallic feed exhibited little crystallinity. Glass derived from PVC and Mixed were partially crystalline throughout. Cl presented in the PVC was volatilised at high temperature.

Time resolved investigation of the melting process through *post mortem* characterisation of the product phase assemblage, microstructure and composition have been performed. It was found that PuO_2 (CeO_2 surrogate) from the PCM is physically and chemically immobilised in the resulting materials, i.e no residual PuO_2 (CeO_2) remains after processing. All of the analysis indicated that Ce was incorporated into the oxide phase in all samples. Estimated volume reductions of ca. 80–95% were demonstrated, against a baseline of un-compacted 200 L PCM waste drums.

The project will contribute to accelerating the acquisition of knowledge and experience required to support NDA in deploying thermal technologies as a national asset for ILW treatment.

Modelling the degradation of intermediate level waste packages resulted from internal metallic corrosion

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One of the most common ways in order to manage nuclear waste is to encapsulate it in cementitious materials. However, even when encapsulated, the waste can potentially cause problems that should be taken into consideration. One of these problems is that of metallic corrosion, which, due to volumetric expansion associated with arising corrosion products can cause mechanical distortion or even failure of the encapsulating system. This increasing internal pressure can lead to extensive grout cracking, when its strength (tensile and compressive) is exceeded. Furthermore, the transmitted stresses throughout the whole volume of the grout cause strains which are finally imposed on the encasing steel canister causing the formation of bulges.

A useful tool for studying this problem is Finite Element (FE) modelling. Simulating the pressure developed during the metal–water corrosion reactions can provide a rough estimation of how the waste package will evolve. The models employed in this study are all subjected to some simplified, though reasonable assumptions in terms of corrosion simulation and materials mechanical properties and general behaviour. The main target of the modelling work is to be able to correlate the level of corrosion with the magnitude of grout and steel degradation as the phenomenon evolves.



Figure 1: Miniaturised ILW drum system being corroded in the lab.

Experimental work has been also carried out in order to validate the numerical results. Miniaturised ILW canisters with encapsulated magnesium mini rods were produced (figure 1) and allowed to react in presence of sodium chloride to accelerate the corrosion process. The embedded metal, acting as a working electrode, is connected through a wire to a potentiostat so that current flow is allowed to activate corrosion. The outputs of the FE analyses indicate that the grout's failure may occur very rapidly for low levels of metallic corrosion. This is validated from the experimental work.

Migration of the cracks to the external surface of the grout is also occurring very rapidly. Steel distortion is not observed throughout the experiments conducted. This can be attributed to the geometry of the experimental set up as the drum's diameter compared to external diameter is limited and thus decreasing the slenderness of the system. Besides FE analyses performed showed that for this specific set up, steel yielding initiates when the level of lateral distortion is less than 100 μm , a displacement which is not easily detected and measured. Corrosion extent is measured after opening up the systems correlating the amount of metal loss with the degradation of the system, in terms of grout cracking. SEM/EDX analyses showed that no migration of the corrosion products occurs either through the cement pores or the corrosion – induced cracks.

Similar systems are going to be investigated using uranium instead of magnesium. Additional experimental work is going to be performed focused on reproducing a more realistic mini ILW drum where several metallic bits are corroding all around the grout volume as well as deliberately causing distortion on the external surface of a mini drum. A detailed investigation of the behaviour of a corroded ILW miniaturised system is planned to be conducted using high energy X-rays in Diamond Light Source, provided

that the relevant proposal for the upcoming session is accepted. Detection of cracking network (orientation, width, length), characterization, profiling and thickness of the corrosion products, steel distortion are some of the problem's aspects that can be studied, taking advantage of the synchrotron's facilities.

Uranic interactions in cementitious systems

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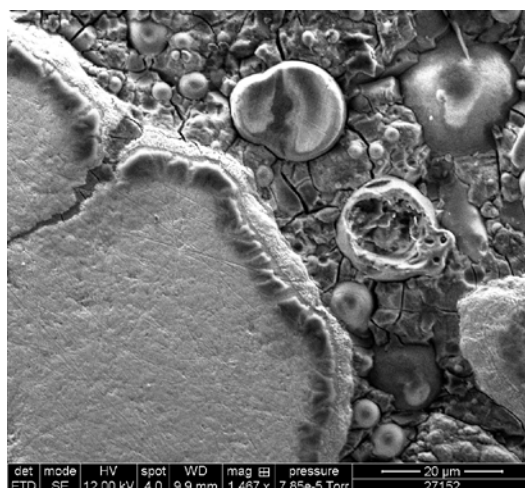
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Nuclear waste is a huge challenge faced by the nuclear industry. The Nuclear Decommissioning Authority (NDA) has an inventory of uranics consisting of thousands of tonnes of UO_2 , UO_3 , U_3O_8 and UF_6 , held in storage. There are a number of strategic options for the management of these materials, one of which is to classify the inventory as waste. If this strategy is adopted it is likely that the materials must be immobilised in a suitable encapsulation matrix. Ordinary Portland cement (OPC) is commonly used to encapsulate nuclear waste[1], however uranics are known to interact with free water in the high pH system. An alternative immobilisation matrix to OPC is magnesium phosphate cement (MPC). MPCs have been used in preliminary trials at National Nuclear Laboratory (NNL) which indicate their suitability to incorporate high loadings of a range of uranic powders. Their near neutral pH and chemically bound water in the crystal structure leaves less water available for interaction with the encapsulated waste[2,3].

Encapsulation of uranic oxide powders in MPC is being investigated. Two formulations with varying water/cement ratios of 0.44 and 0.48 were used. Blank matrix and loadings of 10 and 20 wt% UO_3 , U_3O_8 and UO_2 were investigated for both formulations. CeO_2 and WO_3 mixes were also investigated for non-active experiments in order to assess their validity as surrogates for UO_2 and UO_3 respectively. Mixes were cast into cubes and cured at 20°C for periods of 3, 7, 28, 90 and 360 days, at which times testing was carried out. Ultrasonic Pulse Velocity (UPV), compressive strength testing, XRD, FT-IR, Raman, SEM and TGA were also carried out on samples.

F1 20% UO_3 360 Day SEM micrograph



References

- [1] M. Atkins, F. P. Glasser *Waste Manage.* **1992**, 12, 105-131.
- [2] Hayes, M. and Godfrey, I.H., *Development of the use of alternative cements for the treatment of intermediate level waste.* **2007**.
- [3] A. Covill, N. C. Hyatt, J. Hill, N. C. Collier *Advances in Applied Ceramics* **2011**, 110, 151-156.

Computational studies of lanthanide and minor actinide complexes with industrial relevant ligands

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An important problem in the nuclear power industry is associated with the separation of two radioactive components of spent nuclear fuel. These components are characterised as long-lived minor actinides (Np, Am, Cm) and short-lived lanthanide species. Our work aims to improve our understanding of the basic underlying processes which govern the successful separation of trivalent actinides and lanthanides. The chemical bonding in actinide systems is believed to be subtly different to that of their lanthanide counterparts due to the greater spatial extent of the 5f orbitals in the former. This leads to greater covalent character in An-ligand bonds and allows carefully selected ligands to preferentially bind the An(III) ion [1,2,3].

This study focuses on N-donor ligands such as terpyridine, BTP, BTBP and BTPhen, due to their relative softness and adherence to the CHON principle. Reaction energies for the formation of the tris-BTP complexes of several Ln and An complexes (Ln = La, Lu, Gd, Eu, An = Cm, Am) have been calculated, indicating a slight energetic preference for the formation of the An complexes over their Eu analogues. Additionally, the nature of the M-N bonding in the tris-BTP complexes has been investigated using QTAIM (Quantum Theory of Atoms in Molecules) methods. A greater electron density (ρ) and delocalisation index (δ) at the M-N bond critical points in the An complexes may indicate an enhanced covalent interaction between the An ions and the BTP ligands.

References

- [1] Verboom, W. *et al.*, *Chem. Soc. Rev.*, **2007**, 36, 367-377
- [2] Harwood, L.M. *et al.*, *Synlett*, **2011**, 18, 2609–2632
- [3] J.-H. Lan *et al.*, *Coord. Chem. Rev.*, **2012**, 256, 1406– 1417

Development of a mechatronic system for underground monitoring and sensor deployment

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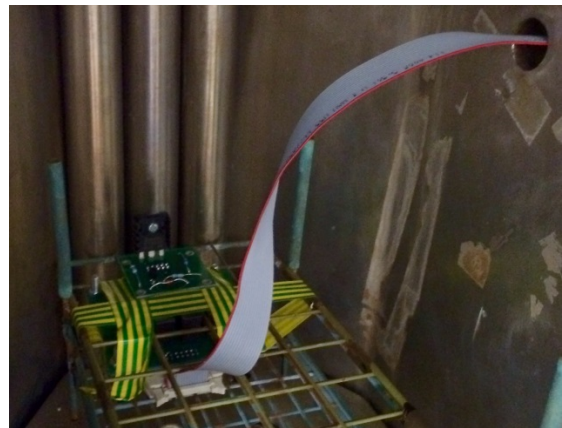
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The aim of the project is to develop a robotic tool able to autonomously burrow underground, where it will then be able to take measurements using sensors transported within it. Current technology is not capable of completing a full underground survey of the earth around the legacy nuclear storage ponds at the Sellafield site. Leakages need to be quickly and accurately detected and located. The continuous monitoring of sub soil activity is important to avoid hazardous exposure to the environment and pollution that will affect local communities.

The effects of radiation exposure to critical components of a robotic tool have been investigated. It has been found that voltage regulators show a drop in output voltage with an increased gamma radiation dose. This happens at different rates for different load currents. Among other results a discrete voltage regulator has been designed to try and mitigate some of the degradation due to gamma exposure. Initial results show mixed success in achieving this. Understanding the failure mechanisms of critical components will aid in the component choice of a final design.

Burrowing techniques are varied with current technologies concentrating on boring at great depths. A collaboration of existing technologies and ideas needs to be investigated to improve manoeuvrability. 3D printing is being used to quickly design and prototype options with aid from the University's mechanical workshop.

Broad research on the geological environment highlighted the superficial surface deposits are mainly clay, silt, sand and gravel and work is being completed to create a test-bed that is indicative of the likely sub-soil environment around Sellafield.



Assessment of high efficiency sorbent materials for application in the remediation of radionuclide contaminated groundwater

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Decades of leaks and spills at the Sellafield nuclear site have contaminated the underlying soil and groundwater with radionuclides. The key radionuclide groundwater contaminants are tritium, the highly conservative ⁹⁹Tc and the less mobile ⁹⁰Sr. Traditionally contaminated groundwater is treated by removing it from the aquifer, treating it and then either returning the treated groundwater to the aquifer or disposing of it off site. As the financial cost of 'pump and treat' primarily depends on the volume of groundwater being treated and not on the concentration of contaminants, remediation is expensive for legacy sites. *In-situ* treatment in the form of a permeable reactive barrier (PRB) may therefore provide a lower cost alternative to 'pump and treat' as groundwater is forced through the PRB's treatment zone by the natural hydraulic gradient of the aquifer. A barrier's material can be selected to remove ⁹⁰Sr or ⁹⁹Tc (but not tritium) from groundwater. In order to select a material for use in a PRB it is crucial to demonstrate the material's ability to rapidly remove the target radionuclides from groundwater without creating a secondary source of groundwater contamination. As sorption behaviour is dependent on groundwater chemistry (pH, Eh, ionic strength, competing ions, complexants) determining the radionuclide uptake mechanism is necessary in order to predict the material's performance with changes in groundwater chemistry. This presentation reports on the sorption kinetics of Tc on zero valent iron (ZVI) using a synthetic groundwater based on the typical groundwater composition of a monitoring well within the Separation Area at Sellafield. At low concentrations, Tc uptake follows pseudo first order kinetics with a distribution coefficient (K_d) of 50,000 ml g⁻¹ and a sorption half-life of 1 h. At high Tc concentrations uptake time remains well below the typical residence time of a barrier ($t_{1/2} = 7$ h) and Tc uptake by ZVI remains high with a K_d of 1,400 ml g⁻¹. Future work will be discussed.

A scanning probe investigation of inter-granular corrosion in sensitised stainless steel nuclear fuel cladding

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Spent Nuclear Fuel (SNF), originating from British advanced gas-cooled nuclear reactor stations is investigated by advanced imaging techniques. UO₂ pellets are encapsulated in an austenitic, stabilised-stainless steel cladding; which is currently subjected to pond storage, pending reprocessing. With UK due to cease reprocessing operations in the coming years, the fuel will be managed safely in a dry or wet storage environment, until the UK geological disposal facility is sited. The stainless steel cladding composition: 20% Chromium (Cr), 25% Nickel (Ni), stabilised by Niobium (Nb) is susceptible to high levels of neutron radiation within the core. This may lead to small quantities of cladding becoming sensitised by the mechanism of Radiation-Induced Segregation (RIS). High energy neutrons create vacancies, voids and dislocations; which diffuse toward Grain Boundaries (GB), causing a redistribution of alloying elements within the cladding. Counter diffusion of Cr atoms causes discrete areas to become depleted of the passivating element; such that these areas of the stainless steel can become susceptible to localised attack within a corrosive environment. In a chloride environment it is possible that a small quantity of Cr-depleted, sensitised, cladding may be affected by intergranular corrosion (IGC).

This effect can be simulated by a series of heat treatments; drawing Cr away from GB regions to form Cr carbide precipitates, hence sensitising the cladding. A combination of high-resolution scanning probe techniques has been used to characterise the cladding alloy in the as-received and thermally sensitised condition. In order to image the cladding before and after heat treatments Atomic Force Microscopy (AFM); is used to provide highly resolved topographical maps of the specimen surface. In order to identify possible IGC initiation locations we compliment AFM maps with a micro-scale scanning Kelvin probe to produce spatially resolved, topographically independent, surface potential maps. Scanning Kelvin Probe Force Microscopy (SKPFM) is capable of mapping the relative nobility of inclusions, such as niobium carbides present within the as-received alloy and Cr carbides at GB in the sensitised alloy. An in-situ time lapse microscopy experiment is also displayed to the audience; displaying the initiation, development and propagation of IGC within the sensitised stainless steel AGR cladding.

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