Universities

Imperial College London

Lancaster University

Queen's University Belfast

University of Birmingham

University of Bristol

University of Leeds

Manchester 1824 The University of Manchester

The University Of Sheffield.

University of Southampton

University of Strathclyde Glasgow

University of Surrey

Project Partners

LLW Repository Ltd

National Nuclear Laboratory

Radioactive Waste Management

Sellafield Ltd

AWE

cavendish nuclear

NDA

TÜV SÜD Product Service

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

1st Annual Meeting

Apex City of Bath Hotel, Bath

3rd - 4th April 2019

transcendconsortium.org

EPSRC Engineering and Physical Sciences Research Council | UK Research and Innovation

Energy For a Low Carbon Future

A university consortium funded by:

Thank you to our key project partners for their support and significant contributions to the programme:

Welcome

On behalf of the TRANSCEND Leadership Team, I welcome you to the Apex City of Bath Hotel, Bath, for the 1st Annual Meeting of the Consortium.

The TRANSCEND (Transformative Science and Engineering for Nuclear Decommissioning) consortium was formed following a successful application to a Nuclear Consortia Follow-on Funding call for proposals on "Decommissioning, Immobilisation and Management of Nuclear Waste" by the Engineering and Physical Sciences Research Council in January 2018. I would like to take this opportunity to acknowledge funding from the EPSRC-UKRI Energy Programme (EP/S01019X/1). I would also like to thank our key project partners, AWE, Cavendish Nuclear, LLW Repository Ltd., NNL, NDA, Radioactive Waste Management, Sellafield Ltd. and TÜV SÜD Nuclear Technologies for their support and significant contributions to the project.

The programme follows on from the highly successful DISTINCTIVE and DIAMOND Consortia. Again, TRANSCEND is led by the University of Leeds, and our partners now include Imperial College London, Lancaster University, Queen's University Belfast, and the Universities of Birmingham, Bristol, Manchester, Sheffield, Southampton, Strathclyde and Surrey. This broadened academic collaboration strengthens the UK's nuclear research capability, and increases the multi-disciplinary nature of the project group.

Over the next two days you will gain an improved personal knowledge of the individual research projects and their importance to the UK's nuclear decommissioning programme. Please take the opportunity to foster existing relationships, and to form new ones by interacting with representatives from academia, industry, government and the regulatory authorities.

I look forward to introducing you to our Keynote Speakers, Charlie Scales (National Nuclear Laboratory), Trevor Chambers (Imperial College London), Prof. David Shoesmith (University of Western Ontario, Canada) and Helen Steele (Sellafield Ltd) and thank them for contributing to this event.

I hope that you enjoy the meeting.

Prof. Michael Fairweather

Principal Investigator

www.transcendconsortium.org

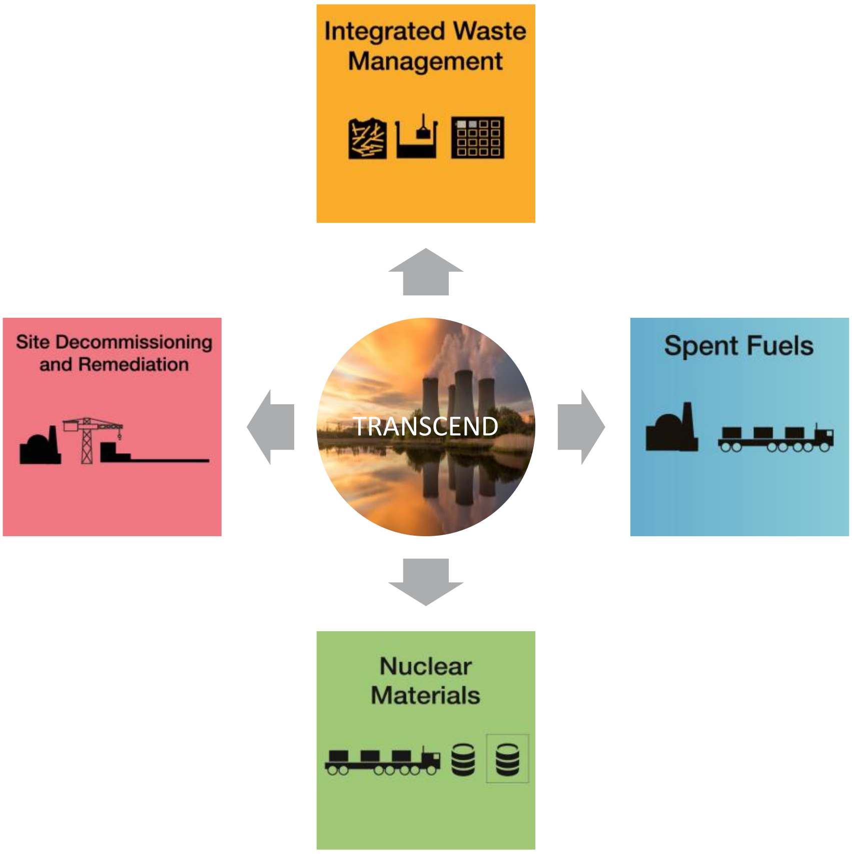
Programme Overview

TRANSCEND (Transformative Science and Engineering for Nuclear Decommissioning) is a collaborative research consortium of 11 universities and 8 industry partners. The £9.4million research programme comprises 40 projects which will address some of the key challenges within the areas of nuclear decommissioning and waste management.

The work of the consortium continues, rationalises and extends that previously undertaken on DISTINCTIVE (Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories) with increased breadth, particularly in bringing together the academic and industrial communities to take more of a whole lifecycle approach to decommissioning and waste management.

The consortium's strategic aims in the area of decommissioning, immobilisation and management of nuclear waste are to:

- Carry out internationally leading science and engineering research
- Undertake fundamental and applied research that leads to innovative technology developments that can be applied in industry
- Develop new multi-disciplinary research and innovation partnerships between academic and industry researchers
- Train the next generation of UK researchers with relevant skills and experiences that can be applied in the sector
- Provide a focus for all stakeholders, including government, industry and academics, through which current and future research and innovation requirements can be discussed
- Provide a route for public understanding of research and development needs, opportunities and solutions.



Theme 1: Integrated Waste Management

The management of radioactive waste includes mobilisation, processing, packaging, storage, transport and final disposal.

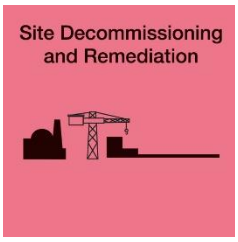
The research in this theme focuses on underpinning science and engineering in three areas of relevance to hazard reduction and decommissioning: removal of radionuclides from effluent; enhanced characterisation and modelling of the behaviour of sludges in the Sellafield ponds and silos; and development and evaluation of new wasteforms.

Aim: To develop an enhanced understanding of the materials, processes and wasteforms used in hazard reduction and decommissioning to underpin new technologies for safe and efficient management of legacy waste.

Objectives:

- Develop new materials for effluent decontamination
- Demonstrate predictive modelling of sludge/slurry removal, underpinned by experimental data
- Transform understanding of radiation-driven processes in nuclear waste sludges
- Provide underpinning studies to develop innovative processes and wasteforms

Theme 2: Site Decommissioning and Remediation



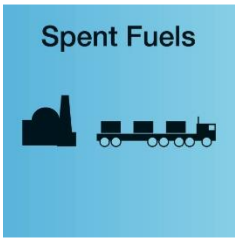
Decommissioning nuclear sites involves waste retrieval, decontamination, and deconstruction and, where necessary, containment and/or remediation of the remaining structure and surrounding land. Critical to management of these processes is limiting radiation exposure for the workforce, restricting the spread of radionuclides in groundwater, surface water and airborne particulates, and minimising the volume of contaminated waste for disposal.

Aim: To develop new technologies for monitoring, remediation and containment that serve to minimise the volume of radioactively contaminated waste for disposal, for application prior to, during and after retrieval, deconstruction and decontamination operations.

Objectives:

- Develop soil/infrastructure grouting strategies, for application prior to and during decommissioning, that minimise airborne and waterborne hazards and environmental risk
- Develop viable in-situ and ex-situ wasteforms for silica-grouted soils/cements such that the silica is redeployed within the vitrified or cementitious wasteform.
- Adapt and develop low-energy ex-situ and in-situ electrokinetic remediation/waste volume minimisation approaches, already proven on some legacy wastes, to other UK nuclear sites, and to combine these with silica-based in-situ grouting/vitrification
- Develop rapid non-invasive geophysical techniques for the assessment of radiological soil contamination and structural degradation (including reinforcement)

Theme 3: Spent Fuels



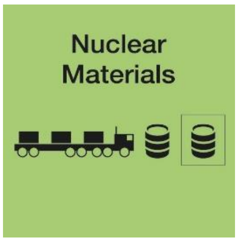
Spent nuclear fuel is a major concern for the UK as we have a large and complex inventory, due to the accumulation of waste from Magnox, AGR, PWR and prototype reactors. Retrieval and relocation operations for legacy fuels are imminent and any measurements or models that enhance our understanding of spent nuclear fuel evolution will mitigate the risks associated with fuel management and inform future decisions for long-term storage or disposal.

Aim: To provide a better understanding of the properties of bulk corrosion products arising from the degradation of waste and of pressing fuel barrier corrosion issues, as well as techniques for in-situ identification of materials and their surface corrosion products coupled to predictive tools for long-term spent fuel behaviour.

Objectives:

- Develop a better understanding of the properties and reactivity of bulk corrosion products arising from the degradation of legacy metallic and exotic spent nuclear fuel
- Develop a deeper understanding of pressing fuel barrier corrosion issues facing the UK
- Develop a series of spectroscopic and radiometric techniques that provide rapid and in-situ identification of nuclear fuel materials and their surface corrosion products
- Develop a predictive tool for long-term spent nuclear fuel behaviour under a range of environmental conditions

Theme 4: Nuclear Materials



The UK's civil inventory of nuclear materials contains significant stocks of separated Pu from the reprocessing of Magnox and AGR spent fuels. The preferred option for the 140 t of Pu is re-use as mixed oxide fuel, although 5% is not suitable for re-use and is recommended for direct disposal. However, it will take >15 years to implement re-use, requiring that the Pu be kept in its current state for that period, i.e. as PuO_2 powder in inert steel storage cans at Sellafield.

Aim: To provide technical underpinning to ongoing option development for the UK civil Pu stockpile.

Objectives:

- For interim storage, to understand how the surface structure and properties of pristine and radiation damaged PuO2 change with time in the absence and presence of water
- For disposition, to understand the mechanisms of incorporation of Pu into ceramic and glass-ceramic wasteforms, as well as the effect on these of self-induced radiation damage

Introducing the Invited Speakers

Charlie Scales (National Nuclear Laboratory, UK)

Charlie Scales is a specialist with 25 years' experience in the field of nuclear waste immobilisation and is based at NNL's facilities at Sellafield and Workington. He has prepared and subsequently led a number of R&D immobilisation programmes with emphasis on developing both vitreous and ceramic wasteforms suitable for storage and ultimate disposal.

Charlie is the NNL technical lead for an NDA initiated Integrated Project Team on Thermal Treatment which is exploring credible options for the immobilisation of ILW across the NDA estate. He has recently been responsible for the technical delivery of a melt demonstration programme carried out on the Geomelt ICV currently installed in the NNL Central Lab at Sellafield exploring the generic potential of thermal treatment for NDA estate ILW using radioactive surrogates.

Charlie is also NNL technical lead for the NDA funded PuO2 immobilisation project supporting the disposition of UK owned PuO2 unsuitable for MOX fabrication. He is supporting the development of a small scale active ceramic immobilisation line for installation in the NNL Central Lab capable of fabricating zirconolite wasteforms for the immobilisation of Sellafield stored PuO2 using hot isostatic pressing.

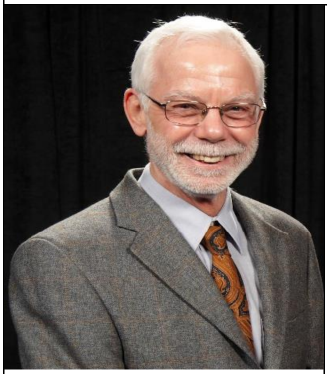
Trevor Chambers (Imperial College, UK)

Trevor has spent the majority of his working life employed by the United Kingdom Atomic Energy Authority at Harwell. His early nuclear experience was in the design of radioactive facilities, later becoming responsible for the operation of the High Active shielded facilities at the Harwell site. During this period he was engaged with the Post Irradiation Examination of a variety of reactor fuels and cladding materials, and the production of medical sealed sources. Later as a Senior Project Manager on the Harwell site, he undertook the full decommissioning of a major α, β, γ shielded facility, at the time the first facility of its type to be decommissioned in the UK.

For the past ten years Trevor has been Head of Reactor Centre at Imperial College London. In this role he has managed the re-commencement of reactor critical operations, and more recently final shutdown, defuel and decommissioning of the reactor. He has also assisted with the introduction of the Imperial College MSc in Nuclear Engineering, and lectures to and supervises MSc and PhD students.

Trevor holds the title of European Engineer, and is a Chartered Engineer, a Chartered Scientist, a member of the Nuclear Institute, a member of the Institution of Mechanical Engineers, a member of the Institute of Physics, a member of the Association for Project Management and Fellow of the Chartered Management Institute.

Professor David Shoesmith (University of Western Ontario, Canada)



David Shoesmith is a Professor in the Department of Chemistry at Western University (London, Canada), Director of Surface Science Western, and a Fellow of the Royal Society of Canada. His research interests are on the electrochemistry and corrosion of materials with a special emphasis on the corrosion of uranium dioxide (nuclear fuel) and high level nuclear waste container materials. From 2000 to 2016 he held the Canadian Natural Sciences and Engineering Research Council and Nuclear Waste Management Organization (NSERC/NWMO) Industrial Research Chair in Nuclear Fuel Disposal Chemistry. He has on-going collaborations with universities and nuclear research organizations in Canada, Sweden, Finland, Switzerland, and South Korea. He has served as an international reviewer of waste disposal programs in the USA, France, Germany, Sweden, and Switzerland. His research is also funded by automobile, chemical processing and oil and gas transmission companies.

Dr Helen Steele (Sellafield Ltd., UK)

Dr Helen Steele is a chartered chemist, with nearly 15 years of nuclear industry experience. She graduated from the University of Manchester with a PhD in quantum mechanics, focussing on actinide and heavy metal surface interactions. Subsequently, she has worked at a number of European nuclear research institutions; including as the recipient of a European Marie Curie Research Fellowship, based at CEA Marcoule. For the last 4 years she has worked for Sellafield Ltd., on the Sellafield site in West Cumbria; technically managing the Special Nuclear Materials (SNM) Science programmes, to deliver the underpinning science and technical justification to support the safe consolidation of all UK owned civil plutonium. She represents Sellafield SNM Value stream with the nuclear regulator ONR (Office for Nuclear Regulation), BEIS (UK government Department for Business, Energy and Industrial Strategy) and international partners including US-DOE (United States Department of Energy).

She has been strongly involved with PhD. students and PDRA’s as part of the Distinctive research consortium and wishes to continue this involvement through Transcend.

Agenda

Wednesday 3rd April		
Time	**Title**	**Presenter**
10:00	Registration / Poster Board set up / Refreshments	
10:40	Introduction and Housekeeping	Prof Michael Fairweather University of Leeds
Session 1 Integrated Waste Management *Chairs: Dr Claire Corkhill, University of Sheffield & Dr Joe Hriljac, University of Birmingham*		
10:50	**Keynote: Thermal treatment as a credible option for the immobilisation of ILW on the NDA estate**	Charlie Scales NNL
11:20	**Theme Overview**	Dr Claire Corkhill University of Sheffield
11:45	Particle-laden flow characterisation and prediction	Lee Mortimer University of Leeds
12:05	Generation and transport of radiolytic hydrogen in magnox sludge mimics	Dr Mel O'Leary The University of Manchester
12:25	Ongoing development of heavy ion irradiation experiments on glassy waste forms	Dr Laura Leay The University of Manchester
12:45	Ultrasonic backscatter for characterising nuclear slurries and suspensions: Perspectives and future work	Dr Tim Hunter University of Leeds
13:05	Lunch & Poster Session	
Session 2 Site Decommissioning & Remediation Chairs: Prof Rebecca Lunn, University of Strathclyde & Prof Luc Vandeperre, Imperial College		
14:05	**Keynote: From Fission to Final Site Clearance – Decommissioning the CONSORT reactor**	Trevor Chambers Imperial College
14:35	**Theme Overview**	Prof Rebecca Lunn University of Strathclyde
15:00	Inhibiting Radionuclide Migration during Deconstruction and Decommissioning using Colloidal Silica Grout	Dr Matteo Pedrotti University of Strathclyde
15:20	Calcite Biomineralisation for the Repair of Damaged Concrete	Ronald Turner University of Strathclyde
15:40	Refreshments & Poster Session	
16:10	Realising the potential - electrokinetics and decommissioning	Prof Andy Cundy University of Southampton
16:30	Predicting Gamma Dose Rates from Buried Pipelines based on Limited Information	Dr Caroline Shenton-Taylor University of Surrey
16:50	Break	
19:00	Drinks & Canapés Reception	Roman Baths & Pump Room
20:00	Dinner	Roman Baths & Pump Room

Thursday 4th April		
Time	**Title**	**Presenter**
08:30	Registration / Poster Board set up / Refreshments	
09:00	Introduction and Housekeeping	Prof Michael Fairweather University of Leeds
Session *3* Spent Fuels *Chairs: Prof David Read, University of Surrey & Prof Tom Scott, University of Bristol*		
09:10	**Keynote: Developing Models for the Corrosion of Spent Nuclear Fuel inside a Failed Waste Container**	**Prof David Shoesmith Western University, Ontario**
09:40	**Theme overview**	Prof Tom Scott University of Bristol
10:05	Evaluating the mechanical properties of corium	Dr Haris Parasevoulakos University of Bristol
10:25	The Oxidation of Uranium Oxide Spent Fuel at Low Temperatures	Prof Colin Boxall University of Lancaster
10:45	Refreshments & Poster Session	
11:15	Characterisation of Uranium Mineral Phases by Time-Resolved Laser Fluorescence and Raman Spectroscopy	Dr Victoria Frankland University of Surrey
11:35	Building the foundations of a predictive tool for spent fuel behaviour	Angus Siberry University of Bristol
Session 4 Nuclear Materials *Chairs: Prof Colin Boxall, Lancaster University & Prof Nik Kaltsoyannis, University of Manchester*		
11:55	**Keynote: Positioning ourselves to deal with todays and tomorrows Plutonium safe storage challenges; with a look back over our shoulder, to see how we got here**	Helen Steele Sellafield Ltd
12:25	**Theme overview**	Prof Colin Boxall Lancaster University
13:00	Lunch and Poster Session	
14:00	Investigating the Interaction of water with plutonium oxide and analogues: three methods	Dr Dominic Laventine Lancaster University
14:20	Atomistic simulations of the ageing of PuO2	Elanor Murray University of Birmingham
14:50	Synthesis of zirconolite ceramics incorporated with cerium and aluminium for plutonium disposition	Dr Shikuan Sun University of Sheffield
15:10	Atomistic simulation of Am incorporation into PuO2	Dr Samuel Murphy Lancaster University
15:30	Refreshments & Poster Session	
Session 5 Links to ongoing research *Chair: Prof Michael Fairweather*		
16:00	TRANSCEND links to EPSRC-funded grants on robotics	Profs Tom Scott University of Bristol
16:20	ATLANTIC programme overview	Prof Bruce Hanson University of Leeds
16:40	TRANSCEND links to EPSRC-funded extreme environment grants on sensors	Prof Tom Scott University of Bristol
17:00	Closing remarks	Prof Michael Fairweather University of Leeds

All presentations will be made available to download from our consortium website: transcendconsortium.org

Posters

The following posters will be presented throughout the event:

	Researcher	Poster title	University
1	Mel O'Leary	Generation and transport of radiolytic hydrogen in magnox sludge mimics	Manchester
2	Hannah Parish	In-situ synchrotron X-ray diffraction studies of ion exchange in zeolites	Birmingham
3	Lee Mortimer	Particle-laden flow characterisation and prediction	Leeds
4	Matteo Pedrotti	Inhibiting Radionuclide Migration during Deconstruction and Decommissioning using Colloidal Silica Grout	Strathclyde
5	Nigel Huang	The Oxidation of Uranium Oxide Spent Fuel at Low Temperatures	Lancaster
6	Victoria Frankland	Characterisation of Uranium Mineral Phases by Time-Resolved Laser Fluorescence and Raman Spectroscopy	Surrey
7	Haris Parasevoulakos	Feasibility trials on uranium corrosion in sludges using in situ X-ray Computed Tomography	Bristol
8	Angus Siberry	Multi scale modelling utilising thin film experiments: Aqueous phase corrosion of spent fuel’	Bristol
9	Elanor Murray	Atomistic simulations of the ageing of PuO_2	Birmingham
10	Dominic Laventine	Electrochemical studies of plutonium oxide and analogues	Lancaster
11	Shikuan Sun	Structural destabilisation induced by trivalent cations in zirconolite-2M	Sheffield
12	James Eales	Understanding composition-structure-property-phase relations in high-Fe_2O_3 radioactive waste glasses for the Hanford site	Sheffield Hallam
13	Katrina Love	Phosphate solubility and impacts on properties of radioactive waste glasses for the Hanford site	Sheffield Hallam
14	Jessica Rigby	Understanding REDOX reactions in the cold cap got nuclear waste vitrification at the Handford site	Sheffield Hallam
15	Jonathan Collard	Modelling the Thermal Desorption of HCl from PuO_2 Surfaces	Manchester

16	Jiali Chen	Theoretical study of plutonium americium mixed oxides surfaces	Manchester
17	Jonathan Tanti	Computational Studies of Incorporation of Pu and Ce into Ceramic Matrices Such as Zirconolite	Manchester

Attendee List

First Name	Surname	Organisation
Phoebe	Allan	University of Birmingham
Geoffrey	Allen	University of Bristol
Victoria	Anderson-Matthew	Innovative Physics
Mike	Angus	National Nuclear Laboratory
Federico	Antonelli	University of Leeds
Antony	Banford	National Nuclear Laboratory
Mark	Bankhead	National Nuclear Laboratory
Martyn	Barnes	Sellafield Ltd
Paul	Bingham	Sheffield Hallam University
Brad	Bowan	Atkins / SNC Lavalin
Colin	Boxall	Lancaster University
Frankie	Brookes	Department for Business, Energy and Industrial Strategy
Anthony	Burnett	Cavendish Nuclear Ltd
David	Burt	Frazer Nash
Ed	Butcher	National Nuclear Laboratory
Colin	Campbell	Environment Agency
Gavin	Cann	National Nuclear Laboratory
Tom Carey	Carey	National Nuclear Laboratory
Trevor	Chambers	Imperial College London
Jiali	Chen	The University of Manchester
Ronald	Clark	National Nuclear Laboratory
Jonathan	Collard	The University of Manchester
Claire	Corkhill	University of Sheffield
Michelle	Cowley	Radioactive Waste Management Ltd
Andy	Cundy	University of Southampton
Fred	Currell	DCF, Manchester
Adrian	Davis-Johnston	Nuvia Limited
Carlos	De La Fontaine	TUV SUD Nuclear Technologies
Jonathan	Dodds	National Nuclear Laboratory
James	Eales	Sheffield Hallam University
Nick	Evans	CEFAS
Michael	Fairweather	University of Leeds
Victoria	Frankland	University of Surrey
David	Geeson	AWE plc
James	Graham	National Nuclear Laboratory
Antonio	Guida	Wood
Keith	Hallam	Interface analysis Centre, University of Bristol
David	Hambley	National Nuclear Laboratory
Bruce	Hanson	University of Leeds
Martin	Hayes	National Nuclear Laboratory
Joe	Hriljac	University of Birmingham
Yifeng	Huang	Lancaster University

Timothy	Hunter	University of Leeds
Malcolm	Joyce	Lancaster University
Nikolas	Kaltsoyannis	The University of Manchester
Dominic	Laventine	Lancaster University
Laura	Leay	Dalton Cumbrian Facility	The University of Manchester
Bryony	Livesey	Costain
Katrina	Love	Sheffield Hallam University
Becky	Lunn	University of Strathclyde
Kevin	Malone	URENCO Nuclear Stewardship
Tom	McMillan	Sellafield Ltd
Alessandro	Mirabella	National Nuclear Laboratory
Sean	Morgan	Sellafield Ltd
Lee	Mortimer	University of Leeds
Samuel	Murphy	Lancaster University
Elanor	Murray	University of Birmingham
Mel	O'Leary	DCF
Robin	Orr	National Nuclear Laboratory
Cristiano	Padovani	Wood
Haris	Paraskevoulakos	University of Bristol
Hannah	Parish	University of Birmingham
Matteo	Pedrotti	University of Strathclyde
Ian	Pegg	The Catholic University of America
Geoff	Randall	Sellafield Ltd
David	Read	University of Surrey/NPL
Joanna	Renshaw	University of Strathclyde
Jessica	Rigby	Sheffield Hallam University
Charlie	Scales	National Nuclear Laboratory
Tom	Scott	University of Bristol
Caroline	Shenton-Taylor	University of Surrey
David	Shoesmith	University of Western Ontario
Rick	Short	Nuclear Decommissioning Authority
Angus	Siberry	University of Bristol
Ross	Springell	University of Bristol
Helen	Steele	Sellafield Ltd
Shikuan	Sun	University of Sheffield
Jonathan	Tanti	University of Manchester
Tracey	Taylor	National Nuclear Laboratory
Frank	Taylor	LLW Repository Ltd
Lois	Tovey	University of Leeds
Divyesh	Trivedi	National Nuclear Laboratory
Ronald	Turner	University of Strathclyde
Luc	Vandeperre	Imperial College London
Deborah	Ward	Nuclear Decommissioning Authority
Robert	Winsley	RWM

Master Project List

Title	Leading Institution	Researcher	Academic Supervisor	Type
Theme 1: Integrated Waste Management				
New Materials and Methods for Decontamination of Effluent	Birmingham		Joe Hriljac	PDRA
Nanotechnology for effluent treatment and radionuclide assay	Imperial		Luc Vandeperre	PDRA
Scoping studies of new ion exchange materials	Birmingham		Joe Hriljac	PhD
In situ ion exchange studies of zeolites	Birmingham	Hannah Parish	Joe Hriljac	PhD
Particle-laden flow characterisation and prediction	Leeds	Lee Mortimer	Mike Fairweather	PDRA
Radiation Induced CHanges in Effluents/Sludges (RICHES)	Manchester	Mel O'Leary	Fred Currell	PDRA
Simulation of behavioural modification effects in suspension waste pipe flows.	Leeds		Mike Fairweather	PhD
Advanced characterisation of waste pipe flows with polymeric behavioural modifiers.	Leeds		Tim Hunter	PhD
Modelling nanoscale radiation physics/chemistry processes in sludges	Manchester		Fred Currell	PhD
Durability of magnesium silicate cements	Imperial		Luc Vandeperre	PhD
Radiation effects on wasteforms	Manchester		Laura Leay	PhD
Conditioning and encapsulation of mercury contaminated wastes	Sheffield		Neil Hyatt	PhD
Novel approaches to encapsulation of low level waste	Strathclyde		Joanna Renshaw	PhD
Characterisation of thermal treatment products	Sheffield		Claire Corkhill	PhD
Process monitoring of thermal treatment of nuclear wastes	Sheffield Hallam		Paul Bingham	PhD
Understanding glass melt chemistry in thermal treatment of nuclear waste	Sheffield		Russell Hand	PhD

Theme 2: Site Decommissioning & Remediation				
Inhibiting Radionuclide Migration during Deconstruction and Decommissioning using Colloidal Silica Grout	Strathclyde	Matteo Pedrotti	Rebecca Lunn	PDRA
Electrokinetic ground remediation, and combination with colloidal silica grouting for minimisation of soil contamination and in-situ vitrification	Southampton		Andy Cundy	PDRA
Electrokinetic remediation application to soils, concretes and other site and process wastes (including EDTA-containing wastes)	Southampton		Andy Cundy	PhD
In-situ groundwater monitoring to improve identification of ground/soil contamination volumes and associated contaminated in-ground infrastructure that may remain at the Site End State	Lancaster		Malcolm Joyce	PhD
Predicting Gamma Dose Rates from Buried Pipelines based on Limited Information	Surrey		Caroline Shenton-Taylor	PhD
Muon Tomography for Monitoring Civil Nuclear Assets	Strathclyde		Marcus Perry	PhD
Field deployment of biomineral technologies for treatment and repair of concrete nuclear infrastructure	Strathclyde		Rebecca Lunn	PhD
Theme 3: Spent Fuels				
Assessing the properties and release behaviour of products arising from metallic and exotic fuel corrosion	Bristol	Haris Parasevoulakos	Tom Scott	PDRA
An investigation of corrosion and leaching of carbide fuels in a Geological Disposal Facility (GDF) setting	Bristol		Tom Scott	PhD
The Oxidation of Uranium Oxide Spent Fuel at Low Temperatures	Lancaster	Nigel Huang	Colin Boxall	PhD
Characterisation of perforated AGR fuel and its behaviour during drying	Leeds		Bruce Hanson	PhD
Development of micromechanical testing methods for spent AGR cladding to examine effects of	Bristol		Mohammed Mostafavi	PhD

sensitisation and stress corrosion cracking				
In-situ Identification of Surface Corrosion Products on Spent Nuclear Fuels	Surrey	Victoria Frankland	David Read	PDRA
Predicting the Corrosion of Spent Nuclear Fuels	Surrey		David Read	PhD
Building the foundations of a predictive tool for spent fuel behaviour	Bristol		Ross Springell	PDRA
Building the foundations of a predictive tool for spent fuel behaviour	Bristol	Angus Siberry	Ross Springell	PhD
Theme 4: Nuclear Materials				
The Surface Chemistry of Plutonium Dioxide under Conditions Relevant to Interim Storage	Lancaster	Dominic Laventine	Colin Boxall	PDRA
Atomistic simulation of Am incorporation into PuO_2	Lancaster		Sam Murphy	PhD
Quantum chemical modelling of PuO_2 surface chemistry	Manchester		Nik Kaltsoyannis	PDRA
Gas generation from the radiolysis of water on uranium oxides and ThO_2	Manchester		Fred Currell	PhD
Computational Modelling of PuO_2: Ageing and Storage Phenomena	Birmingham	Elanor Murray	Mark Read	PhD
The Recombination of Hydrogen and Oxygen on Metal Oxide Surfaces	Lancaster		Colin Boxall	PhD
Underpinning plutonium immobilization in advanced ceramic wasteforms	Sheffield	Shi-Kuan Sun	Neil Hyatt	PDRA
Disposability of wasteforms for plutonium immobilisation and efficacy of surrogates	Sheffield	Clemence Gausse	Claire Corkhill	PDRA

Project Descriptors

The following pages contain the project descriptors (in master project list order).

Full project information and updates will be posted on our website:

transcendconsortium.org

Theme 1: Integrated Waste Management

New Materials and Methods for Decontamination of Effluent

University of Birmingham

The objectives of the project are to:

(1) continue and expand our work from DISTINCTIVE on developing new ion exchange systems for Cs and Sr removal (e.g. $K_{1.75}[Sn_{0.75}Nb_{0.25}Si_3O_9]{\bullet}H_2O$) from effluent under realistic legacy pond and decontamination conditions;
(2) develop our work on producing magnetized inorganic ion exchange materials in collaboration with the NNL and SL who have produced a test rig for magnetic retrieval post use;
(3) investigate new means to deploy ion exchangers such as *via* the production of monoliths or pellets that avoid problems using fine powders in applications.

Nanotechnology for effluent treatment and radionuclide assay

Imperial College

This project will build on the work done in the Distinctive consortium, where it was shown that phosphate functionalised paramagnetic iron oxide particles showed a surprisingly large capacity and selectivity for uranium sorption. A first set of research objectives is to clarify further why what appears to be a multi-layer structure has such a large capacity. A second objective is to widen the same approach to other radionuclides of interest. A third objective is to develop particles that can act in acidic environments.

Scoping studies of new ion exchange materials

University of Birmingham

The aim of this project is to develop a better understanding of the key structural and chemical features needed in inorganic ion exchange materials for the effective removal of strontium and caesium from effluent. Materials will be tested for ion exchange performance against the Mud Hills clinoptilolite used in SIXEP in a variety of simulated effluent streams. Mineral sources will include clinoptilolite samples from other locations and also other zeolites such as mordenite and chabazite. Synthetic materials may include IONSIV, Cs-Treat and Sr-Treat depending upon availability. Materials will be characterised in Birmingham using the large suite of available techniques (powder XRD, XRF, electron microscopy, porosimetry) and selected samples studied at the Diamond Light Source using high resolution X-ray powder diffraction. Materials will be tested in as-received forms and also after pre-treatments to assess performance changes and also whether it is possible to control radionuclide uptake levels to control ultimate activity after use. Testing will utilise the Rapid Ion Exchange Test Method developed at the NNL in collaboration with SL and the NDA and in the latter stages of the project the most promising materials will be used in column trials. Where feasible (i.e. when suitable atomic pair potentials are available), atomistic modelling and molecular dynamics simulations will be used to understand the key structural and chemical features.

In situ ion exchange studies of zeolites

University of Birmingham

The project will involve structural studies of zeolites and other porous inorganic solids that can act as ion exchange media for the safe removal of radionuclides from the environment. The aim is to further the understanding of the ion exchange mechanisms at the atomistic level and provide accurate structural details for computer modelling studies. The research will entail analysis of powder diffraction data using both Rietveld and Pair Distribution Function techniques and the data will come from synchrotron X-ray sources, in particular Diamond Light Source, whenever possible. Atomistic computer modelling of the processes will be done as long as suitable atom-atom potentials can be obtained or derived. Systems for study will include at least two different clinoptilolites (Mud Hills being one), mordenite and synthetic umbites developed at Birmingham under DISTINCTIVE.

Particle-laden flow characterisation and prediction

University of Leeds

Decontamination of legacy ponds and silos is of great importance and stands as a matter of increasing urgency throughout the nuclear industry. In facilities within the UK, waste suspension flows transport legacy material from historic ponds to other interim locations where they are safely stored. However, at present these processes are not as efficient as they might be due to a lack of understanding of the multiphase flows involved. It is also possible that the current transportive systems may be subject to problems if used for long periods of time, wherein issues such as blockages and poor flow conditions may develop downstream. In order to perform successful POCO operations, it is crucial that knowledge surrounding the behaviour of transportive waste sludges is developed in order to provide accurate predictive capabilities for use in design. This project will establish computational tools, with some complementary experimental work, to study the characterization of particle-laden flows which will support the development of efficient and effective retrieval technology. The project will also provide insight into the issues and problems that current waste processing techniques may encounter.

Particle-laden flow simulation techniques using first principles mathematical modelling have been developed at Leeds in order to explore the fundamentals of multiphase flow dynamics. With an increase in available computing power, these high-fidelity methods provide the means to model multiphase fluid dynamics processes with extreme accuracy, such as particle-particle interaction, turbulence modulation and agglomeration events. These mechanisms are fundamental to understanding the aggregation conditions and properties of waste slurries. Direct numerical simulation will be used throughout, and various flow conditions and geometries (channels, pipes and ducts) relevant to waste management will be examined. Focused regions of homogeneous isotropic turbulence will also be simulated. The solid phase will be modelled using two techniques. To establish relevant bulk properties of large ensembles of particles such as collision, aggregation and deposition rates, Lagrangian particle tracking (LPT) will be used, with four-way momentum coupling and deterministic agglomeration mechanisms. To study the particle- and turbulent eddy-scale dynamics an immersed boundary method (IBM) will be employed.

Often in particle-laden flow simulations, the solid phase is represented by point-spheres. In practice this is likely not the case, with morphologies in nuclear slurry flows ranging from disc-like to needle-like, and including many other complex shapes. In practice there are very few studies that consider the way in which drag and lift coefficients are calculated, and work using the IBM will be performed to develop such correlations, comparing with present experimental studies. Although work has been performed studying large numbers of non-spherical particles using LPT techniques, there is little or no detail surrounding the agglomeration mechanisms behind these, even in theoretical models. There is significant challenge in determining the way in which two or more non-spherical particles interact and produce larger structures. The way in which large particles in flows behave is highly dependent on their shape and fractal dimension, and therefore assumptions that larger particles are spherical leads to inaccuracies in the predicted behaviour. We aim to use the IBM to study non-spherical particle aggregation under a range of conditions relating to turbulence level, particle and fluid material and chemical properties and initial interaction energy. Sensible choices will be made surrounding the range of parameters studied based on those present in typical industrial flows. In particular, the work will focus on behavioural modification techniques implemented through material and chemical property changes that can be used to improve flow, mixing and separation of wastes during retrieval and POCO activities.

Another current key research topic in particle-laden flows is developing understanding of the ways in which particles modulate the local turbulence field, which has consequences for the resulting particle interaction dynamics. For instance, microparticles are capable of dampening the turbulence, especially at high volume fractions and particle-fluid density ratios. This leads to fewer collisions in the turbulent regions of pipes, channels and duct transportive flows. It is not fully understood how these processes occur, and whether current LPT two-way coupling methods are fully accurate for large (> Kolmogorov length scale) particle diameters. As such, work will be carried out to generate further understanding behind the particle-turbulence interaction mechanisms and to test the various coupling regimes presently used.

For spherical and non-spherical particles in flows, the potential for aggregation is not only based on the types of turbulence encountered, but also the chemical and mechanical properties of both phases. As noted, by using certain behavioural modification techniques, such as the addition of additives, we are able to tune the properties of the waste flow in order to achieve the desired outcome. For example, reduced deposition, increased aggregation and improved mixing or separation. The effect of such tuneable parameters will be studied in order to establish these techniques. This work will be supported by two PhD projects which will complement the present study by exploring the application of the above techniques in a waste pipe flow, through both modelling and experimentation.

Radiation Induced CHanges in Effluents/Sludges (RICHES)

The University of Manchester

External beams of radiation can be used to accelerate radiolytic processes inevitably occurring in sludge wasteforms. At the Diamond Light Source (DLS) we have pioneered a new technique to follow the full creation and transport dynamics of key products (e.g. hydrogen). We can perform a full study of the radiolytic yield and diffusivity of hydrogen using this approach for a given sludge in typically a few hours – results show elevated yields and reduced diffusivity in brucite-water systems. Furthermore, we characterize the energy transfer between these two phases using Monte Carlo simulation [e.g. DOI:10.1038/srep00018 (2011)]. Using DCF-based irradiator systems coupled to a GC system we can make complimentary measurements of the total product yield (gas products or volatiles). Together these techniques allow us to assess the overall importance of radiation driven processes and then to develop a mechanistic picture of the processes at work. For zeta-potential measurements, we will use the technique of Nakuta et al [DOI:10.1016/j.apt.2015.01.017], developing a similar apparatus, additionally incorporating our small irradiator system, thereby allowing us to assess changes in zeta-potential due to the effects of radiation. As a final summative aspect of the project, we will radiolytically generate hydrogen (closed cell) and then examine the formation of bubbles.

Simulation of behavioural modification effects in suspension waste pipe flows

University of Leeds

In nuclear facilities around the UK, waste suspension flows transport legacy radioactive material between, e.g., historic ponds and interim storage facilities as part of decontamination processes. The waste treatment programme relies heavily on the retrieval of legacy sludges, often performed using circular cross-section pipelines which transport solid-liquid suspensions over significant distances. Presently, these systems suffer from lack of design data, which can potentially result in problems such as blockages and poor mass-transfer conditions. As such, these processes are performed using conservative process conditions as correcting issues downstream is extremely expensive and time consuming. These operations generally use high flow rates to avoid the potential for aggregate build-ups and blockages. However, this process leads to increased turbulence levels within the flow which increases wall deposition and particle-particle collision rates, and the need to process more waste material. In order to perform POCO operations successfully, it is crucial that these types of flows are understood and, as a result, better controlled. This project will investigate the application of behavioural modification techniques to suspension waste pipe flows.

First principle mathematical modelling techniques have been developed at Leeds to predict particle-laden flows with extreme accuracy. The use of Lagrangian particle tracking (LPT) coupled to direct numerical simulation provides a high accuracy predictive capability for studying waste transport systems. They also show great promise in generating knowledge surrounding the development and application of behavioural modification techniques in flows. For instance, the addition of polymer additives to slurries can help obtain desired flow conditions such as reduced agglomeration and/or deposition rates. Alternatively, to enhance downstream sedimentation, the addition of flocculation agents can also be employed.

With all these methods, however, there remain uncertainties of the long-term behaviour of both the fluid and particle phase, and work needs to be performed to generate understanding. This project will study these techniques for a range of simulated multiphase pipe flows with relevance to nuclear waste transport, such as empty pipes and pipes with bends and deposited beds. To predict potential issues and develop knowledge surrounding these flows, properties such as particle dispersion, flow rate, turbulence modulation and collision rates will be investigated to determine the way in which the modifications techniques affect the bulk properties of the system.

A further complication is that particles present in nuclear slurry flows are distributed widely in terms of diameter and shape. Sizes generally range between 1µm to 1mm, with previous studies exhibiting a range of different particle-fluid and particle-particle interaction mechanisms depending on size. Moreover, the particles are not necessarily spherical, with morphologies ranging from needle-like to disc-like, and other complex shapes. Advances in LPT techniques allow for methods of predicting both polydispersed and ellipsoidal particles, and calculations will be performed as part of the project to investigate their influences on the resulting flow dynamics and aggregation properties.

Finally, to study the addition of polymer additives at a more fundamental level, this project will use an established immersed boundaries method (IBM) to simulate binary or low-particle number interactions. The effect of polymer structurants on the particle-scale dynamics will be investigated to feed back to LPT agglomeration and collision models, improving their accuracy. This work will be supported by another PhD and a PDRA, which will complement the present study by providing both experimental data for validation purposes as well as knowledge from IBM simulations to aid in the development of LPT modelling.

Advanced characterisation of waste pipe flows with polymeric behavioural modifiers

University of Leeds

Waste suspension flows are encountered across the nuclear sector, and their characterisation is of great importance to the safe transport of radioactive material. A waste treatment program that has received high priority in recent years, is the retrieval of legacy waste sludge from historical ponds to safe interim storage facilities. Suspension transfer via pipeline has encountered several problems resulting from a lack of relevant design data. As such, operations are often run with extreme caution and not necessarily at their optimum, which may cause further downstream problems. For example, to mitigate the potential for radioactive particles to block pipes, high flowrates are employed, leading to shear breakdown of aggregates that reduces waste consolidation rates downstream in the interim stores. This project seeks to understand these issues and overcome pipeline transportation problems in two ways – the development of an online acoustic backscatter technique for remote characterisation of particle size and concentration online, and the use of polymer additives to modify slurry characteristics enabling safe and efficient slurry transport.

Acoustic backscatter systems have been previously developed at Leeds as an *in situ* technique to characterise suspension wastes and they show great promise as a technique to measure slurries in pipe-flows non-invasively online. In particular, ultrasonic backscatter strength can help determine particle size or concentration, while simultaneously, speed of sound can also be used to correlate the aggregation state of slurries. There are still significant challenges however, in the use of ultrasonic measurements to characterise particle properties in pipes. While there is potential to extract size and aggregate data from acoustic backscatter parameters, information is highly convoluted, and currently quantification only extends to spherical dispersions that are unlike the wastes encountered. There is also a lack of theoretical models that may be used to predict size from backscatter and velocity parameters. As a further complication, the turbulent nature of pipe flows may alter aggregate size and structure over time, and the influence of particle aggregation states (in regards to backscatter and speed of sound measurements) also requires investigation. We will therefore initially aim to classify acoustic behaviour in a small well controlled variable shear cell (of similar dimensions to a full pipe) with various disperse and aggregated test materials of relevance to nuclear waste flows, before moving into full pipeline implementation. Other characterisation techniques (e.g. focused beam reflectance measurements and particle image velocimetry) will also be used to correlate key properties of the slurries. Focus on the project will be to deconvolute acoustic backscatter and speed of sound parameters by extending current acoustic theory to be able to extract size and aggregation information from backscatter measurements. The influence of large particle size distributions will be another important consideration. Artificial Neural Networks (ANN) and other machine learning techniques may also be applied to match acoustic response patterns to systems of different particle sizes and distributions.

A second major aim of the research project will be to understand the influence of polymer additives to modify slurry flow behaviour under various shear regimes, and the resulting effect on acoustic backscatter response. Polymer flocculation agents may be added inline to aggregate waste streams for enhanced sedimentation downstream. However, such additives will also affect slurry rheology and pipeline behaviour. Ultimately, the addition flocculation agents and other polymer structurants may result in highly aggregated paste type flows that will have very different deposition and flow behaviour to the non-flocculated wastes . Work will focus on firstly characterising the structure-property relationships of the polymer-particle slurries (e.g. through rotational rheometry and measurements in the shear cell) before their behaviour in full pipeline conditions will be examined.

Modelling nanoscale radiation physics/chemistry processes in sludges

The University of Manchester

Using a combination of kinetic Monte Carlo radiation transport and (if necessary) atomistic simulation approaches, this investigator will investigate the energy transfer processes at work when brucite is irradiated in water. The description of the energy spectrum of particles thus transferred from the brucite to the water will be augmented with description of the energy spectrum of particles created directly by ionisation of the surrounding water. These spectra will be used to predict the resultant heterogenous chemical kinetics using newly developed codes (inc. with input from the student involved), thereby providing a comparison to the measurements being made.

Durability of magnesium-silicate-hydrate based cements made from brucite

Imperial College

Magnesium silicate hydrate (M-S-H) based cements are a new type of cement that exploits the strength generated when magnesium oxide is made to react with a soluble silica source to form a mostly amorphous hydrated gel of magnesium silicate (M-S-H gel). It is a perfect candidate for reducing the volume of waste from the fuel ponds in Sellafield as the solids in these ponds are mostly magnesium hydroxide, which can be converted to M-S-H gel under the right circumstances. Therefore, the waste would effectively be a large component of the binder in which it is immobilised.

Hydrated magnesium silicate gels have been known for a long time as a by-product of magnesium sulphate attack on conventional Portland cement-based materials. However, much less is known about the durability and long-term behaviour of M-S-H gel. Therefore the project would explore (i) how sludges should be pre-treated to enable the production of a suitable wasteform as too much water will reduce the mechanical properties substantially and (ii) the durability, i.e. long term stability of the wasteform made from such cements to ascertain whether it is likely to remain stable especially during the initial above ground storage of the waste.

This project will first involve pre-treating simulated waste sludges and processing them to form M-S-H based binders. It is envisaged that several types/formulations of waste sludges will be considered as each may require a different processing approach. Selected products from the most promising approaches will then be characterised using a range of techniques available at the Department of Materials and Department of Civil & Environmental Engineering. The workability, setting behaviour and the heat of hydration (isothermal calorimetry) will be determined. The hardened wasteform will be cured and conditioned to several regimes and then tested as a function of age for mechanical properties (e.g. strength, stiffness), dimensional stability (shrinkage), mass transport properties and resistance against degradation processes such as leaching/frost. The composition, phase assemblage and microstructure will be investigated using electron microscopy, X-ray microanalysis and thermal analyses. XRD will be used to characterise any crystalline phases formed. The pH and composition of pore solution and leachate will be analysed using ICP-OES.

Radiation effects on wasteforms

The University of Manchester

This project will focus on determining how the degree of crystallinity would affect cracking of vitrified High Level Waste (HLW). Radiation is known to affect glass in a variety of ways, for example causing a volume change. This volume change can induce strain which can lead to cracking. Historic work on active glass showed that crystalline inclusions could halt crack propagation. The new glass formulation being used to vitrify HLW is known to form Ca-Mo crystals although there is little information on how radiation affects the growth of these crystals.

There are various factors that affect degree of crystallinity, including cooling rate and glass composition. It would be particularly relevant to industry to look at glass generated from Post-Operational Clean Out (POCO) waste versus normal HLW. Although HLW contains over 30 elements, a simple 6-7 component glass can be developed, this could be based on the International Simple Glass, ensuring that the results are relevant to the international community as well as the UK.

Irradiation of inactive samples can be carried out at the Dalton Cumbrian Facility (DCF), and active glasses could be made in a fume hood at NNL Central Lab which could be used as a comparison. In addition, active glass produced during the UK's original development work is available on Sellafield Site, and could be analysed as a comparison to the fresh active glass.

Conditioning and encapsulation of mercury contaminated wastes

University of Sheffield

Contaminated mercury is a problematic orphan waste arising across the NDA, LLWR, AWE and MOD estates. EU restrictions on mercury import / export mean that there is an excess of market supply, which is a barrier to decontamination and reuse; the alternative is conditioning for disposal. The aim of this project is to develop a simple one-pot process for conversion of contaminated mercury to cinnabar and encapsulation in a phosphate cement matrix.

The objectives are to demonstrate: 1) An efficient process for conversion of Hg metal to HgS, via phosphoric acid digestion and sulphide precipitation; 2) An optimised cement formulation to achieve one pot encapsulation of HgS in a phosphate cement, with no secondary waste generation; 3) The acceptability of the wasteform for storage and disposal. This approach will be developed alongside an evaluation of conventional OPC encapsulation and potential high temperature alternatives.

Characterisation of Thermal Treatment Products

University of Sheffield

A programme of synthesis of a range of model (lab-scale) thermally treated simulant waste materials will be initiated with the addition of active (e.g. U, Th) or inactive (e.g. Cs, Ce for Pu etc.) radionuclide surrogates. We will liaise with NNL to also obtain products of full-scale Geomelt trials (active or inactive) for appropriate waste streams. A suite of characterisation techniques will be applied to understand the thermal, mechanical and chemical properties of the materials, for example, as a function of additives and redox conditions. A particular focus of the work will be to determine the partitioning and local chemical environment of "radionuclide" species within the wasteform materials. Additionally, a series of long term (2.5 year) durability tests will be initiated on selected samples, to understand the influence of key parameters on the durability of the thermal treatment waste products. Finally, a study of the response of selected thermal treatment waste form materials to irradiation will be performed, to assess the effect of dose and dose rate on their mechanical and chemical behaviour.

Process monitoring of thermal treatment of nuclear wastes

Sheffield Hallam University

A considerable proportion of the UK's LLW and ILW radioactive waste inventories arise in a range of physical and chemical forms with varying degrees of radioactive / toxic hazard. They include PCM, IEX resins and decommissioning wastes such as concrete, bricks, sludges and contaminated soils. These wastes are considered unsuitable for treatment using existing vitrification and cementation technologies at Sellafield, owing largely to their heterogeneity and variable organic / inorganic compositions. Consequently, alternative thermal treatment technologies to form glass / glass-ceramic / glass-composite wasteforms are being considered and developed to treat these wastes. These include the GeoMelt technology currently being trialled by NNL; also plasma and other technologies. A key issue thermal treatment processing is the (currently) limited ability to (a) monitor off-gas emissions in real-time; and (b) control, constrain or inhibit emissions. In particular, emissions of volatile radionuclides (e.g. ^{137}Cs, ^{129}I, ^{36}Cl, ^{99}Tc, ^{106}Ru) and toxins (e.g. dioxins, furans, flammables) must be minimised and monitored, in order to provide maximum safety and control. Monitoring is currently carried out post-treatment through analysis of gas filtration media, with off-gas calculations performed retrospectively. From the perspective of safety and process control, on-line, real-time monitoring of off-gas emissions, in addition to other thermal treatment parameters such as melt temperature / viscosity, melt pool conditions and melt rate, are key developments needed to present the most robust methodology for safe thermal treatment of UK LLW / ILW.

This PhD project will address these issues in two ways. The primary objective is to develop new, more responsive methods for on-line, real-time monitoring of off-gas emissions. The secondary objective will be to develop new methods of controlling, limiting or inhibiting off-gas emissions of volatile compounds during thermal treatment. The student will carry out a thorough desktop survey and investigate a range of potential on-line monitoring technologies, which may include recently developed THz (Okhoshi et al, Sci. Rep. 7 (2017) 8088) and γ-spectroscopies (Maekawa & Oshima, J. Nucl. Sci. Technol. 55 (2018) 181-189) in addition to more established chemical / process / biological engineering routes. Design and development of new or modified technologies will be carried out at desk-scale then at lab-scale. The multidisciplinary approach taken will be reflected in the supervisory team, comprising experts in radioactive waste vitrification, (bio) chemical and process engineering; and instrumentation and data processing. On-line gas monitoring technologies used in the nuclear industry will be considered; also expertise from across manufacturing, chemical, bio-chemical and food industries will be enabled through the team's existing industrial links. New developmental technologies will also be considered and modest budget has been included for rental of on-line off-gas sensing technologies for benchmarking and to aid technology development and testing.

The student will establish selection criteria for candidate technologies, and will use them to down-select candidate technologies for development and testing. Lab-scale testing will be carried out in parallel with lab-scale development of methods for reducing off-gas emissions (expected to include glass melt chemistry manipulation, temperature control, physical and chemical controls and addition of inhibitors such as barrier layers). Following initial development and testing at lab-scale, it is envisaged that the most promising candidate technologies, addressing both primary and secondary objectives, will be up-scaled and trialled using inactive and then active facilities. The preferred active facility is the NNL Central Laboratory GeoMelt test facility, where it is expected that the student will receive training and access to active areas to prepare for, and execute, active trials. In addition, discussions are underway with Veolia to access its' inactive GeoMelt facility in Richland, USA. Other candidate thermal treatment technologies including plasma vitrification will also be explored, to provide further diversity and risk mitigation for management of the project. Close consultation with key stakeholders including RWMD, NDA, NNL, Sellafield Ltd and TRANSCEND consortium members and associates, will be maintained to ensure the wastes, technologies and approaches used provide tangible scientific and process engineering advances and increase the TRL of thermal treatment of UK LLW / ILW. The first 18 months of the project will prepare and train the student with the skills and clearance needed for active area access, and the second 18 months of the project will include preparation, execution and data analysis from full-scale inactive / active trials. A target of 3 experiments at the NNL active laboratory is envisaged (the first for benchmarking and the second and third for trials of candidate technologies and materials), averaging one active experiment per year throughout the project. However, it is acknowledged that any active experiments will need to align with other experiments and demands upon the active facility, so flexibility will be maintained throughout. Close communication with stakeholders will ensure all trials are well-planned in advance.

Understanding glass melt chemistry in thermal treatment of nuclear waste

University of Sheffield

This project is intended to develop a deeper understanding of how glass chemistry can be used to maximise waste incorporation while minimising volatilisation. Specific aims are to understand the waste incorporation reactions and radionuclide incorporation mechanisms for a variety of representative wastes. These aims will be addressed by undertaking 1) investigations of quenched melts produced at various time intervals; 2) investigations of the final equilibrium glass composition and 3) real time measurements of the off-gas from the melts.

While borosilicate glasses are most commonly used for nuclear waste immobilisation such glasses have limited compatibility with, for example, wastestreams with significant halide, molybdate or actinide contents. Thus the project will look at the different behaviours of conventional borosilicate, aluminosilicate (calcium aluminosilicates have a greater capacity for chloride containing wastes) and titanosilicate (potentially attractive for high soda and molybdate wastes) melts. Incorporation of specific species into a glass is determined both by the final glass structure and the role of specific species within that structure (both of which are related to the melt structure) as well as kinetically favoured species that are formed during the melt process, which if volatile, lead to notable losses from the melt. Thus the intention of this project is to study 1) the final glass using a range of structural analysis techniques including Raman and FTIR spectroscopies (existing facilities) and NMR and XAS (national facilities), chemical analysis techniques including XRF and EDS (existing facilities); 2) the evolved gas species by melting in a controlled environment with a dedicated off-gas line. At the moment these facilities rely on analysis of the species that either plate-out or end up in washing solutions, which may not be identical the actual forms that are evolved from the glass melts. *In-situ* Raman analysis, requiring a portable Raman system with a specialist cell is required for this element of the project and has been included in the project costs.

Inhibiting Radionuclide Migration during Deconstruction and Decommissioning using Colloidal Silica Grout

University of Strathclyde

Research will focus on the use of colloidal silica to treat surface soils as a risk mitigation measure for inhibiting airborne and waterborne radionuclide migration, which poses a severe hazard to workers and the environment. Under DISTINCTIVE, we demonstrated that colloidal silica can penetrate low permeability materials (including cement) for hydraulic barrier formation, improved sorption capacity, structural repair and erosion inhibition. It can be injected at surface using extremely small (potentially gravity-driven) fluid pressure, without the need for borehole drilling. Here, research will investigate:

- optimisation of sorption/desorption grout properties by addition of other materials (such as biominerals formed in-situ);
- the feasibility of redeploying the silica grout in the form of in- and ex-situ vitrification of grouted soils, thus minimising waste volumes via redeployment of the silica as an integral component of the final wasteform;
- colloidal silica as a strategy for repair of existing degraded cementitious waste packages;
- combining colloidal silica grout containment and in-situ vitrification with the electro-kinetic technique in WP2.2.

Electrokinetic Remediation, and combination with silica grouting for minimisation of soil contamination / in-situ vitrification

University of Southampton

Despite a range of existing soil and water remediation, and waste clean-up, techniques available to nuclear site managers, effective in-situ and ex-situ remediation remain a common technical challenge, particularly at sites with complex or low permeability soils / subsurface geology, and on working sites or sites with considerable surface and subsurface infrastructure. This research builds on emerging sustainable remediation ideas and previous proof-of-concept work at the AWE Aldermaston site to develop novel ex-situ and in-situ low-energy electrokinetic based approaches that can be flexibly applied to different site materials and work around existing site infrastructure, providing new and flexible approaches for complex site materials (including low-permeability soils) at working (and legacy) nuclear sites. Electrokinetic (EK) techniques use a low voltage DC current to control migration of, remove, or degrade contaminants in soils. This PDRA-led project has the overall aim of developing EK techniques for novel applications in nuclear wastes, site soils and groundwater management (supporting site decommissioning and remediation). The project will use electrokinetic test cells containing simulated nuclear site materials at the lab and intermediate-scale (m-scale) to (a) remove, focus or degrade soil-bound contaminants (*remediation or waste minimisation*), and (b) direct subsurface water, chemical and colloid flow (*fencing/containment or forced migration*). Specifically, the work will: (1) adapt low-energy *ex-situ* electrokinetic remediation and waste volume minimisation techniques already proven on AWE legacy wastes (Agnew et al, 2011) to other UK nuclear legacy wastes and sites; (2) develop *in-situ* low-energy electrokinetic fencing (for groundwater) and remediation (for soils and sediments), to limit the spread of active contaminants, and minimize soil volumes for subsequent treatment, and (3) combine EK with colloidal silica grouting techniques (with TRANSCEND partner Strathclyde) for wastes or infrastructure treatment (e.g. concrete repair) or to minimise soil contamination for in-situ vitrification. Simulated pipes, foundations and other subsurface infrastructure will be incorporated into the test designs to simulate on-site conditions, and numerical and physicochemical models of EK and contaminant processes will be developed to inform full-scale on-site application by nuclear site holders.

Electrokinetic remediation application to soils, concretes and other site and process wastes (including EDTA-containing wastes)

University of Southampton

Despite a range of existing soil and water remediation, and waste clean-up, techniques available to nuclear site managers, effective in-situ and ex-situ remediation remain a common technical challenge, particularly at sites with complex or low permeability soils / subsurface geology, and on working sites or sites with considerable surface and subsurface infrastructure. This research builds on emerging sustainable remediation ideas and previous proof-of-concept work at the AWE Aldermaston site to develop novel ex-situ and in-situ low-energy electrokinetic based approaches that can be flexibly applied to different site materials and work around existing site infrastructure, providing new and flexible approaches for complex site materials (including low-permeability soils) at working (and legacy) nuclear sites. Electrokinetic (EK) techniques use a low voltage DC current to control migration of, remove, or degrade contaminants in soils. This project will use electrokinetic test cells containing simulated nuclear site materials at the lab and intermediate-scale (m-scale) to (a) remove, focus or degrade soil-bound contaminants (remediation or waste minimisation), and (b) direct subsurface water, chemical and colloid flow (fencing/containment or forced migration). This PhD project, supporting the PDRA work undertaken within TRANSCEND at Southampton on in-situ and on-site EK system design, and combined EK approaches with colloidal silica grouting, will examine EK application to soils, concretes and other wastes (including EDTA-containing wastes). Specific objectives are: (1) To adapt low-energy *ex-situ* electrokinetic remediation and waste volume minimisation techniques already proven on AWE legacy wastes (Agnew et al, 2011) to other UK nuclear legacy wastes and site scenarios; (2) To develop *in-situ* low-energy electrokinetic fencing (for groundwater) and remediation (for soils and sediments), to limit the spread of active contaminants, and minimize soil volumes for subsequent treatment. Simulated pipes, foundations and other subsurface infrastructure will be incorporated into the test designs to simulate on-site conditions, and numerical and physicochemical models of EK and contaminant processes will be developed to inform full-scale on-site application by nuclear site holders.

An in-situ, resilient blind tube instrument for soil contamination assay

Lancaster University

The blind tube measurement of radiation to determine dose rate as a function of depth in contaminated land is performed currently with Geiger-Müller (GM) tubes on a push-rod cable. The former is installed in a water-proof housing and detects gamma radiation with which to infer the dose, whilst the latter is necessary to provide power and to recover signals, and also as the means by which the detector is deployed in a given measurement site (borehole/Blind Tube).

The sensitivity of the GM tube in this application is satisfactory and it is a robust, tried & tested technology. However, it is not sufficiently resilient to be left in-situ for long periods of time, either for the purposes of continuous monitoring or until such time that it might need to be used. Further, the relatively high cost of the system somewhat precludes a significant number of these devices being deployed at different sites at the same time. GM tubes, whilst sensitive, do not afford any spectroscopic functionality and hence, whilst the main constituent of the isotopic inventory is ^{137}Cs, sensitivity to alternatives is not possible; neither is a relative measurement of the attenuation of the detected photons by the surrounding water when the instrument is submerged.

In this project the objective is to explore an alternative means by which blind tube measurements might be done that is more resilient, such that systems can be left in-situ for longer thus reducing the need for human intervention. Also we would like to consider a counter which yields a degree of spectroscopy to provide greater analytical insight of the measurement environment. We shall perform the following in this study: A thorough requirements specification for the instrument to be developed; an options study of the various candidate detectors that meet the needs of the requirements specification (for example, cerium bromide, silicon carbide, etc.); a campaign of laboratory-based tests in our dedicated soil tank with which to identify the best candidate; an extension of the former to explore its resilience for long-term use, in-situ. Finally, we shall construct a prototype with the intention of carrying out field tests of the system on site, comparing it to the existing system. The selection of exemplar detector materials cited above is not exhaustive: cerium bromide is suggested because it is radiation-tolerant and yields good energy resolution, particularly in the range needed for ^{137}Cs. Silicon carbide is suggested because, whilst it might not yield spectroscopic information to match cerium bromide, it's relatively cheap to produce, has a small form factor and is likely to be more resilient for high-dose applications for land quality assessment.

Predicting Gamma Dose Rates from Buried Pipelines based on Limited Information

University of Surrey

The PhD project will seek to develop robust algorithms to predict gamma dose rates in contaminated pipelines based on limited direct information. The objective is to minimise and, where possible, avoid intrusive sampling and analysis while still acquiring sufficient information to justify management options (e.g. excavation, capping, leaving *in situ*) The focus will be on underground discharge pipes, initially at Winfrith, where the algorithms developed will be used to infer the distribution and activity concentrations of selected gamma-emitting isotopes. The results will be compared to currently available proprietary packages.

Gamma spectrometry will be used to measure the surface gamma emission for known sources inside mild steel and cast iron pipes, supplementing work already underway at licensed sites. A complementary experimental validation facility will be developed at UoS using gamma radioisotope sources (^{137}Cs, ^{60}Co) buried in an environmental tank containing soil and underground structures of known geometry. Modelling methods will use Geant4 Monte Carlo to model radiation transport, which will be run on the University's local HPC cluster with data analysis performed in Matlab or Python. Algorithms will then be used to correct for attenuation from soil, concrete and other underground features to determine the source activities. Their spatial distribution will be estimated using *inter alia* the Parley method to obtain consensus across a sparse network of surface measurements, combined with triangulation algorithms and data fusion methods applicable to hybrid quantitative and qualitative datasets.

Muon Tomography for Monitoring Civil Nuclear Assets

University of Strathclyde

Muons are fundamental charged particles, produced in the atmosphere by cosmic rays. Every second, hundreds of high velocity muons shower each square meter of earth, providing a highly penetrating, naturally abundant, and safe particle source that can be used for passive imaging. One such imaging technique is Muon Scattering Tomography (MST), which uses sandwiches of detectors to measure statistical changes in the scattering angles of muons as they pass through an object. This provides a 3D map of the object's density.

Passive MST has already been used to image the internal structure of ancient pyramids, voids in active volcanoes, encapsulated nuclear waste, and fissile materials concealed in shipping containers [1,2]. As muons arrive at earth from all angles, near-horizontal imaging is also possible [3]. Passive MST has an imaging rate and resolution that is defined by the background muon flux (~10^2 Hz/m^2) and the strength of the interaction between the muons and the imaged object. As such, MST works well when there are large contrasts in the atomic numbers of the particles that comprise the object: for example, a 5 cm^3 block of uranium can be discriminated from surrounding tungsten with over 80% confidence after one hour, and with over 95% confidence after four hours [1].

While MST systems for monitoring civil infrastructure have been proposed [4], this area is in its infancy. Field work to date has focussed on the geological structures surrounding tunnels [5,6], while proof-of-concept MST systems for concrete slab thickness have been limited to lab demonstrations [7]. Real applications of MST for reinforced concrete and steel structural health monitoring remain highly promising, but undeveloped.

The aim of this project is to develop an MST system for passively monitoring the structural health of reinforced and steel concrete assets. The work will be conducted in collaboration with:

- the Particle Physics group (led by Dr Jaap Velthuis) at the University of Bristol (UoB), and;
- Cavendish Nuclear (part of Babcock International).

Field deployment of biomineral technologies for treatment and repair of concrete nuclear infrastructure

University of Strathclyde

Nuclear sites comprise huge volumes of concrete assets, which are exposed to differing environmental conditions resulting in variable mechanisms for, and rates of, concrete degradation. For example, external concrete building facades may be exposed to freeze-thaw and high salinity, whereas some internal concrete structures may be exposed to high temperatures and high levels of radiation. This project will develop novel field deployment techniques for biomineral technologies, being developed at Strathclyde, that are designed for repair and treatment of concrete nuclear infrastructure. Field-based treatment of concrete is a significant challenge. Damage can extend several cms into the concrete and surfaces include overhangs and vertical walls. Specifically, the project will explore the feasibility of applying these techniques to dock sides and caissons, where saltwater ingress has led to concrete damage 50-70mm into the structures. The project will include development of a monitoring system for assessment of the structural repair.

Theme 3: Spent Fuels

Assessing the properties and release behaviour of products arising from metallic and exotic fuel corrosion

University of Bristol

Aim: To develop a better understanding of the properties and reactivity of bulk corrosion products arising from the degradation of legacy metallic and exotic SNF.

Research will develop understanding of the fundamental properties and reactivity of bulk corrosion products arising from the degradation of legacy metallic and exotic nuclear fuel materials. Such research will allow better prediction of the pyrohporicity, and therefore risk posed by such actinide corrosion products present in nuclear storage that might represent a hazard during repackaging or transport to a disposal facility. A recent (22nd Jan 2018) meeting between RWM, Sellafield, NNL, Magnox and Bristol permitted the following specific objectives to be defined:

- A targeted study using advanced X-ray imaging, tomography and diffraction methods to understand the corrosion behaviour of spent metallic fuel sealed ‘partially wet’ inside metal storage cans. Small-scale simulants will be utilised to understand the relative mass, type and distribution of the arising corrosion products.

- Corrosion study using isotopic labelling to establish the fundamental mechanisms and rates for oxidation/pyrophoricity of fuel corrosion products in water versus dry oxygen and air. The extent and rate of heat release during oxidation will be determined to aid prediction of possible future thermal excursions during legacy waste repackaging.

The PDRA will use cutting edge materials analysis techniques to provide a nano to micro to millimetre scale observation of carbide corrosion behaviour. Techniques will include X-ray tomography (XRT), high-speed atomic force microscopy, secondary ion mass spectrometry, high-resolution electron microscopy and X-ray diffraction. The techniques are all routinely used and available at the IAC in Bristol. To compliment the materials analysis, residual gas analysis mass spectrometry will be used to examine the gases produced by corrosion and their rate of production; thereby indirectly yielding a corrosion/oxidation rate.

An investigation of corrosion and leaching of carbide fuels in a Geological Disposal Facility (GDF) setting.

University of Bristol

Uranium carbide (UC) is considered an exotic fuel material which has arisen from the UK nuclear test reactor programme. This material has served as both a fuel at sites like Dounreay, Scotland and as a fission target material in facilities such as CERN.

The NDA has an inventory of irradiated uranium carbide as part of its legacy waste exotic fuel materials within its estate and therefore carries the liability for its safe management and ultimately its disposal. Uranium carbide is considered a reactive and potentially pyrophoric material with a reactivity comparable to uranium metal.

Geological disposal is considered the ultimate fate for this unique material and the current PhD project will investigate its corrosion and leaching behaviour under conditions analogous to a GDF facility both (i) pre-closure and (ii) post-closure.

Experimental Approach:

Utilising virgin Uranium carbide fuel material provided by the NNL, Springfields laboratory, the current studentship will use cutting edge materials analysis techniques to provide a nano to micro to millimetre scale observation of carbide corrosion behaviour. Techniques will include X-ray tomography (XRT), high-speed atomic force microscopy, secondary ion mass spectrometry, high-resolution electron microscopy and X-ray diffraction. The techniques are all routinely used and available at the IAC in Bristol. To compliment the materials analysis, leaching studies will utilise solution analysis techniques such as ICP-MS and ICP-OES to determine evolving U concentrations in different GDF-analogous groundwater solutions (oxic and anoxic). In addition, the project will also utilise the unique TRLFS instrument available at the University of Surrey which is being developed for aqueous actinides analysis as part of the main TRANSCEND project.

The project will setup a series of enclosed cells experiments, using sealed, water-filled glass housings to hold small uranium carbide 'stick' samples in a fixed position. These special cells will permit periodic measurement of the evolving water chemistry using TRLFS and also the corrosion progression using X-ray tomography. These analysis techniques will enable a detailed study of corrosion and leaching behaviour but without disrupting the experimental system. The lower density of the oxide (10.97 g/cc) which forms from corrosion of the carbide (13.66 g/cc) means that rates of oxidation under different conditions (temperature, dissolved O_2 and water chemistry) can be determined by measuring the evolving thickness of the oxide using XRT.

Isotopic labelling of water saturated corrosion systems will also be used to determine the mechanisms for corrosion of the carbide. Residual gas analysis mass spectrometry will be used in conjunction with such experiments to determine the arising gases under GDF conditions.

The Oxidation of Uranium Oxide Spent Fuel at Low Temperatures

Lancaster University

The expected remaining lifetime of the UK's Advanced Gas-cooled Reactors (AGRs) will result in the generation of ~6600t of Spent Nuclear Fuel. The Nuclear Decommissioning Authority's preferred option for this spent fuel is pre-disposal interim storage – currently in ponds at Sellafield – prior to final disposal by consignment to a geologic disposal repository in or around 2075. AGR fuel pins consist of UO2 pellets sealed inside steel cladding tubes.

Whilst in-reactor, some of the cladding can be rendered susceptible to in-pond corrosion, potentially leading to through-wall cladding failure. This may result in pond water contamination by the spent fuel (which now contains fission products and actinides as well as UO2) and inter-granular corrosion of the pellets themselves with loss of pellet integrity. Consequently, a transition to dry storage has been proposed – including the drying of wet stored spent fuel. Both actions may carry further unknown risks that need to be understood before implementation.

Using novel spent fuel simulants (SIMFUELs), we will seek to develop a molecular level understanding of the oxidation behaviour of the UO2 matrix in spent AGR fuel at low temperatures <200oC and under conditions relevant to proposed UK dry storage. Sited within Lancaster's new state-of-the-art nuclear chemistry / chemical engineering facility (UTGARD Lab, funded by the Dept of Business, Energy & Industrial Strategy), this project will use coupled electrochemical, thermogravimetric and spectroscopic methods to elucidate the products, kinetics and thus mechanisms of the oxidation processes that obtain in both the gas an solution phase.

The project is 100% funded by EPSRC through the Next Generation Nuclear Centre for Doctoral Training. Industrial supervision will be provided by subject matter experts from the UK National Nuclear Laboratory.

Characterisation of perforated AGR fuel and its behaviour during drying

University of Leeds

A recently completed PhD project tested and proved the feasibility of drying AGR fuels that had been stored for long periods in a caustic environment. The project successfully developed a drying process and proved that end points can be identified.

During the project, drying of perforated fuels was simulated in the main using pin holes, but a method to produce characteristic stress corrosion cracks in AGR cladding was used and these samples were used in some drying tests. A joint report to the NDA highlights that perforated cladding may have water ingress into the fuel and should be investigated.

This project will build on the previous knowledge by:

- Further development of the preparation methodology to simulate SCC in AGR fuel cladding. Where possible the samples will be compared to "real" cladding so that the characteristic perforations can be validated. Further use of micro-CT scanning will confirm the size and extent of cracking.

- Development of the process to characterise and investigate drying through “cracked cladding”.
- Development of the process to include the effects of “wet” fuel pellets within the cladding. A simulant fuel pellet will be developed that can be inserted into the prepared AGR cladding samples and then the combined test piece will be treated so that is represents long stored fuel. Further tests will then be carried out to prove that the cladding and fuel can be dried.

The project will use a combination of experimental testing (making use of the existing drying rig developed and installed at Leeds) and modelling of flow through the perforated cladding to inform experimental procedure and assist in prediction of process performance. The model will be validated using results from the drying rig.

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

University of Bristol

There is a need to understand the stress corrosion cracking and mechanical properties of stainless steel 20-25-Nb AGR cladding material before and after irradiation to underpin predictions of structural integrity during transport and in storage and disposal environments. This PhD project aims to utilise real spent fuel clad materials recently provided to Bristol from the NNL Central Labs. However, as the first step, the methodology to observe and quantify cracking will be developed using surrogates such as stainless steel 304. The studentship will undertake in-situ corrosion experiments on the Bristol’s unique characterisation techniques such as high speed atomic force microscopy and high resolution digital image correlation using specially developed loading rigs to examine the aqueous corrosion behaviour of metallic systems. This will be complimented by work to develop a comprehensive, reliable, and safe technique to characterise the full mechanical behaviour of irradiated materials from micromechanical samples.

In-situ Identification of Surface Corrosion Products on Spent Nuclear Fuels

University of Surrey

The PDRA project will seek to develop laser-based methods for characterisation of degraded spent nuclear fuel materials *in situ*. The techniques, including time-resolved laser fluorescence (TRLFS), Raman and laser-induced breakdown (LIBS) spectroscopy, provide direct speciation, structural and compositional information on uranium-containing compounds and solutions. Moreover, they offer the potential for ‘hands-off’ deployment, which is essential in high dose environments.

The corrosion of spent nuclear fuel leads to poorly defined, amorphous and non-stoichiometric solid phases together with colloidal suspensions and actinide-containing solutions, typically of high pH, as is the case with Magnox ponds. Fluorescence spectra and decay lifetimes of uranium (and several other species, such as europium and curium) are hypersensitive to the type and number of ligands surrounding the actinide ion, enabling identification of the species on thin films or in solution down to millimolar concentrations. State of the art TRLFS and Raman systems have been established at UoS and a LIBS capability is being developed. The set-up is sufficiently flexible to allow corrosion or mixing experiments to be conducted online and in real time. Substantial effort is now required to compile a comprehensive database that will provide a characterisation profile unique to each species. Type mineral samples on loan from national reference collections together with bespoke samples prepared at UoS and partner laboratories are being used to derive the necessary data.

The feasibility of *in-situ* deployment will be explored in collaboration with the University of Bristol who have extensive experience with miniaturised fibre-optic coupled probes. The Bristol group (Scott/Springell) is also capable of supplying single-crystal thin films of U phases with a precisely defined surface orientation.

Predicting the Corrosion of Spent Nuclear Fuels

University of Surrey

The PhD project will seek to investigate, experimentally and computationally, the corrosion mechanism(s), including intermediates, products and reaction rates, of spent nuclear fuel (SNF) in oxidative environments. The objective is therefore, to be able to predict quantitatively the degree of corrosion and product formation as a function of time and temperature by using a combination of experimental techniques (fluorescence, Raman, EXAFS) and computational techniques (density functional theory, DFT). The focus will be on understanding the surface chemistry of nuclear fuel, modelling the formation and dissolution of the surface oxides exposed to wet environments.

Hubbard-corrected density functional theory (DFT+U) and dynamical mean-field theory (DMFT) will be employed to provide an accurate description of structure and electronic properties of the material surface and the reactive species, predict the geometry and energetics of the local and global minima as well as the activation energies for reactions occurring on the surface of the materials investigated. Experimental validation will allow us to calibrate and benchmark the theoretical results against state-of-the-art measurements including laser fluorescence and Raman spectroscopy, as well as X-ray spectroscopy at synchrotron facilities (EXAFS). The project will also benefit from parallel experimental work at the University of Bristol (Scott/Springell), capable of supplying single-crystal thin films of U phases with a precisely defined surface orientation.

Building the foundations of a predictive tool for spent fuel behaviour

University of Bristol

The overall aim of the PhD project and associated PDRA position is to construct the basis for a predictive tool for spent fuel behaviour; to model spent fuel in aqueous environments, across length-scales, using results from atomistic simulations, using physical and chemical kinetics, combining radiolysis models with molecular dynamics. We plan to close the loop between experiment and theory, by designing experiments that mimic and test the idealized scenarios implicit in these models. This project will bring the theorists and experimentalists together on a joint venture; retaining, building and developing knowledge-base for future generations.

Later, we plan to increase the complexity of the model; adding defect impurities, lattice damage, modifying the crystallography and the stoichiometry. We plan to vary the physical and chemical environment; mimicking the fuel in the spent fuel pool, in long-term storage and in operation, during an accident scenario. In the longer term, this approach will be extended to exotic fuels (nitrides, silicides for example), linking to work in the ATLANTIC consortium.

The PhD project will focus on building the model, collaborating with international partners (CEA) and within the UK (Lancaster, Bath) to better understand the fundamental behaviour of water at the surface of spent fuel. We plan to develop FACSIMILE + COMSOL models in collaboration with NNL, moving towards real-world systems. We will then design experiments that mimic these idealised scenarios and test them. This will involve the deposition and control of actinide-based surfaces, using the dedicated actinide deposition system run at UoB.

The PDRA will focus on experimental aspects of the project, using facilities such as the DCF and Surrey Ion Beam Centre to mimic radiation damage from specific fission product species. Further, we have a collaboration with the KURRI and CLADS facility in Japan, which will enable us to irradiate thin film fuel samples with high neutron fluxes. These samples will be investigated for their dissolution properties and compared to (and provide input to) model calculations. Our methodology is ambitious and at the cutting edge of what is possible today but utilizes some of the unique facilities that the UK possesses, and more importantly combines knowledge pools across the UK and, more widely, across the world, to input into the foundations of a predictive tool for SNF behaviour.

Theme 4: Nuclear Materials

The Surface Chemistry of Plutonium Dioxide under Conditions Relevant to Interim Storage

Lancaster University

Approximately 125 tonnes of separated Pu is in long term storage at Sellafield as calcined PuO_2 powder in nested, sealed steel storage cans. Under certain circumstances, gas generation may occur with consequent storage package pressurisation. In practice, this is rarely seen and empirically derived criteria are used to ensure safe storage conditions remain and account for the release of known gases into the package . Fundamental mechanisms that could lead to pressurisation must be understood. The 5 main routes suggested are:

(i) Helium accumulation from α decay;

(ii) Decomposition of polymeric packing material;

(iii) Steam produced by H_2O desorption from hygroscopic PuO_2 due to self-heating or loss of cooling in stores;

(iv) Radiolysis of adsorbed water; and,

(v) Generation of H_2 by a postulated chemical reaction of PuO_2 with H_2O.

Mechanisms (i) and (iii)-(v) are currently under study by the EPSRC-funded TRANSCEND Consortium, with the last 3 mechanisms (iii)-(v), all involving PuO_2/H_2O interactions, being especially complex, inter-connected and poorly understood. The PDRA project is focussed on those three mechanisms.

The physico-chemical state and amount of the water ad-/absorbed at the surface, or wettability of the surface, will be determined not only by the PuO_2 crystal faces presented at the surface of the powders, but also radiation damage to the surface and (bulk) defect structure. Such radiation damage will also affect the susceptibility of the PuO_2 to corrosion - potentially by mechanism (v) but more likely by hydroxyl radicals/hydrogen peroxide generated by the radiolysis of water at or close to the plutonium dioxide surface.

Pre-DISTINCTIVE, we developed a contact angle technique for measuring metal oxide surface wettability – effectively a measure of chemisorbed OH group concentration at the oxide surface.

Experimental work in DISTINCTIVE focussed on the use of direct nanogravimetric measurements to quantify the total amount of physisorbed H_2O and associated enthalpies of water sorption on unirradiated single element CeO_2, UO_2 and ThO_2 in Lancaster's UTGARD Lab and PuO_2 in Central Lab.

Work in DISTINCTIVE has also involved preliminary studies of PuO_2 electrochemistry and corrosion behaviour at JRC Karlsruhe. Parallel computational work has focussed on the bulk electronic structures of UO_2 and PuO_2, and the geometric structure and energetics of water adsorption on stoichiometric surfaces.

Thus, using a combined experimental and computational approach, this WP will concentrate on unravelling the surface phenomena underpinning mechanisms (ii)-(v) and the effects on these processes of (bulk) defects and surface radiation damage. Specific tasks will include the following.

1. Using ThO_2 as a surrogate and unirradiated PuO_2 systems, we will use combined nanogravimtric and spectroscopic techniques to determine the extent, nature and speciation of surface-sorbed water and the effect of heat treatment on same.

2. Surrogate samples will be irradiated at the Dalton Cumbrian Facility to study the effect of radiation damage-derived surface defects on water sorption and data compared with computational results – focussing on consequences for wettability (assessed by contact angle measurement and Raman spectroscopy), balance between non-dissociative (physi-) & dissociative (chemi-) sorption and surface MO_2OH formation as a putative route to hydrogen production via a surface specific embodiment of mechanism (v).

3a. The preliminary electrochemical studies at JRC-Karlsruhe referenced above have indicated that the direct chemical reaction of plutonium dioxide with H_2O to generate hydrogen is thermodynamically forbidden – at least at room temperature. However the same studies indicate that PuO_2 may be susceptible to attack by radiolytically generated hydroxyl radicals / peroxide, so suggesting the possibility of radiolytically promoted corrosion reactions at the PuO_2 surface. Thus ,in an analogous series of active experiments conducted in NNL's Central Laboratory we will use thin PuO_2 films made from low activity Pu-242 and higher activity Magnox Pu to study the effects of self irradiation and Am in-growth on putative PuO_2 corrosion reactions. The latter particularly may influence not only the radiation chemistry of the system but potentially also the matrix conductivity of the PuO_2 itself and thus the material's capacity to couple corrosion half-reactions reactions at its surface.

3b. These studies will be complemented by experiments designed to assess not only the corrosion susceptibility of PuO_2 and its surrogates in the presence of deliberately added radiolysis simulants H_2O_2, HO_2● and OH● (produced via Fenton Chemistry) but also how the target metal oxide surface ages in the presence of these species. Radiolysis simulant induced changes to the PuO_2 and PuO_2 surrogate surfaces will be assessed by a combination of electrochemical, nanogravimetric, spectroscopic, microscopic and surface wettability (contact angle) studies with particular focus again being paid to the generation of M-OH sites at the metal oxide surface.

As Sellafield are already funding work in this area directly at NNL, it is envisaged that work within the active laboratories would be performed in parallel, with associated benefits relating to knowledge transfer and reducing NNL's partnering/supervision costs.

Atomistic simulation of Am incorporation into PuO_2

Lancaster University

The UK currently holds the world's largest stockpile of plutonium. For storage the Pu was converted into PuO_2 and sealed in inert steel canisters under argon. Since sealing, some canisters exhibit signs of becoming pressurised raising concerns over their viability over anticipated lifetimes. A possible explanation for this pressurisation is the evolution of hydrogen gas from corrosion of the surface by entrained water.

Conditions in the canisters may not appear sufficiently oxidising to promote corrosion, at least not by water. However, recent experiments suggest the existence of a hyperstocihiometric PuO_{2+x} phase that may act as a precursor to corrosion. Oxidation may be driven by radiolysis of water or by changes in the defect chemistry of PuO_2 due to radioactive decay, in particular accumulation of Americium.

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

This project will employ density functional theory (DFT) to understand the defect chemistry of PuO_2 and how incorporation of Am will influence reactions at the surface. The first objective will be to determine formation energies for the intrinsic defects in bulk PuO_2. The DFT data will be combined with simple thermodynamics to generate Brouwer diagrams that will facilitate prediction of the defect chemistry in PuO_2 as a function of key environmental variables including temperature and oxygen partial pressures present in the canisters.

Finally, the energies for americium incorporation into PuO_2 lattice will be determined for all possible oxidations states. This will allow a prediction of the mode of Am incorporation, its oxidation state and the presence of any charge compensating defects. This detailed description of the defect chemistry of the Am bearing PuO_2 will facilitate a prediction of the corrosion rate and hence the gas production rate. This information will prove critical to understanding the extent of future pressurisation in the canisters and allow a realistic assessment of the service life of the existing canisters.

Quantum chemical modelling of PuO_2 surface chemistry

The University of Manchester

Quantum chemical calculations (DFT), in both the embedded cluster and periodic boundary condition (PBC) framework, will be employed to study:

- Non- and dissociative adsorption of water on stoichiometric and substoichiometric ThO_2 surfaces – comparison with our previous work on water adsorption on other AnO_2 (An = U-Cm).
- Evaluation of the effects of the size of the chemical model, *e.g.* the slab thickness in PBC calculations.
- Surface chemistry of water radiolysis products (HO· and H·) on stoichiometric and substoichiometric ThO_2 surfaces, in the presence and absence of water. Extension to PuO_2.
- Surface chemistry of other small molecule species (NO_x, ozone) on stoichiometric and substoichiometric ThO_2 surfaces, in the presence and absence of water. Extension to PuO_2.

The work will align with and support experimental studies at Lancaster, and link with other computational work in WP 4.1.

Gas generation from the radiolysis of water on uranium oxides and ThO_2

The University of Manchester

This PhD will involve measuring the radiolytic hydrogen yield from water adsorbed surrogate materials for PuO_2 and plutonium-uranium mixed oxides. Measurements will be made under gamma and helium ion irradiation. The effect of irradiation on the oxide surface will be characterised.

Powders of UO_2, U_3O_8, UO_3 and ThO_2 oxides, and possibly $(U,Th)O_2$ will be prepared (either at DCF, or at other UoM facilities and transported to DCF for irradiation). Controlled amounts of water will be adsorbed onto the surface. The hydrogen (and oxygen) production under gamma and helium ion irradiation as a function of water content will be measured. Variables that might affect the yield, such as specific surface area, radiation damage, co-adsorption of surface impurities (e.g. HCl or NO_x) will be investigated. The surface of the oxide will be characterised before and after irradiation to better understand the changes occurring during irradiation. For example using XPS, Raman and IR spectroscopy.

Computational Modelling of PuO_2: Ageing and Storage Phenomena

University of Birmingham

Until the UK Government arrives at a decision regarding the final treatment and disposition of Pu, the NDA remain responsible for the "safe and secure storage". However, ageing mechanisms associated with the storage of PuO_2 are poorly understood. The generation, stability and mobility of fission products in addition to the role of the surface oxide layer being key factors. Atomistic computer simulation techniques remain complementary to experimental methods and are ideally suited to provide fundamental insight into the defect chemistry.

The scope of this study is to focus on investigating the defect chemistry of PuO_2 associated with ageing phenomena, in particular the incorporation and entrapment of helium. Radiogenic helium gas generation naturally occurs in the ageing of PuO_2 due to the spontaneous alpha decay of Pu isotopes, creating self-radiation damage to the lattice. Helium gas bubbles can form in the matrix, causing swelling and accumulation along grain boundaries can cause embrittlement.

Computational modelling techniques would employ robust interatomic potentials derived from empirical fitting to experimental data to predict bulk and surface structures and their defect chemistry. Relative thermodynamic stabilities of fission products and Helium atom incorporation/aggregation would be calculated and compared with bulk and surface sites in order to predict migration pathways and mechanisms. Extended defects such as grain boundaries and their role in fission product/helium migration would be simulated using surface simulation techniques. These simulations would be extended through the application of molecular dynamic techniques to model the effect of radiation damage on the lattice structure and subsequent effect on fission product and trapped helium atom mobility. The combination of these modelling techniques would provide valuable insight into furthering the understanding of ageing mechanisms associated with PuO_2 at the atomic scale relevant to storage.

Additional points

- This project would employ surface simulation techniques which would have wider applicability within the nuclear field (*e.g.* waste form dissolution).
- This project would help to build stronger links between the UK central facilities and nuclear researchers.
- This project would be best formulated in collaboration with researchers in other Universities in the consortium.

The Recombination of Hydrogen and Oxygen on Metal Oxide Surfaces

Lancaster University

Approximately 125 tonnes of separated Pu is in long term storage at Sellafield as calcined PuO_2 powder in nested, sealed steel storage cans. Under certain circumstances, gas generation may occur with consequent storage package pressurisation. In practice, this is rarely seen and empirically derived criteria are used to account for the release of known gases into the package and so ensure safe storage conditions. The purpose of this proposed PhD project is to contribute to a fundamental understanding of the factors influencing the empirical criteria.

There are a number of fundamental mechanisms that could lead to pressurisation, and all must be understood. The 5 main routes suggested are:

(i) Helium accumulation from α decay;

(ii) Decomposition of polymeric packing material;

(iii) Steam produced by H_2O desorption from hygroscopic PuO_2 due to self-heating or loss of cooling in stores;

(iv) Radiolysis of adsorbed water; and,

(v) Generation of H_2 by a postulated (hydrothermal) chemical reaction of PuO_2 with H_2O.

Mechanisms (i) and (iii)-(v) are currently under study by the EPSRC-funded TRANSCEND Consortium. The last 3 mechanisms (iii)-(v), all involve PuO_2/H_2O interactions and are especially complex, inter-connected and poorly understood.

The scope for this PhD is focussed on mechanisms (iv) and (v). Previous experience has shown that packages sealed in storage cans under uncontrolled or none ideal conditions can potentially have headspace atmospheres that are hydrogen rich but rarely flammable i.e. contain hydrogen and oxygen.

Small scale studies of PuO_2 packages at Los Alamos National Laboratory suggest that gaseous hydrogen and oxygen may be formed in such packages. However, the study also found that the pressure is limited by a recombination process. This may be through a gas phase recombination process of molecular hydrogen and oxygen, or hydrogen and a surface oxygen species on the PuO_2 surface, and could be thermally or radiolytically driven processes.

If the hydrogen is produced primarily by the radiolysis of water, i.e. mechanism (iv), the comparative absence of oxygen in the can headspace raises questions as to whether this is due to PuO_{2+x} formation, i.e. mechanism (v) or some other oxidative process. Gas phase recombination, with or without PuO_2 acting as a catalyst, could prevent the coincident observation of the two gases and limit the extent of package pressurisation, but not fully explain why a number of packages have been shown to contain hydrogen.

Preliminary studies conducted at the Dalton Cumbria Facility indicate that irradiation of gas phase mixtures of hydrogen and oxygen with helium ions or gamma rays can lead to loss of hydrogen, presumably through radiation-induced reaction with oxygen to form water. This loss of hydrogen is found to be accelerated by the presence of zirconium and cerium oxides. Other radiolytic reactions also remove oxygen such as its reaction with nitrogen, although the potential role of metal oxide surfaces in promoting this reaction is not clear.

Thus, questions arise as to whether this putative catalysis exists on PuO_2. Sellafield Ltd have started a programme of work at NNL to investigate what conditions would challenge any catalytic performance of the PuO_2 surface. For instance, is it possible that surface saturation by moisture or adsorbed gases can reduce the PuO_2 catalytic efficacy? Further, does aged PuO_2 material behave in a similar way to fresh material in terms of its putative catalytic performance.

The proposed PhD, which will involve a significant period of placement at NNL's Central Laboratory, will be working to address these questions. The student will work alongside NNL to further the understanding of the efficacy of PuO_2 as a catalyst, and understand dependencies of the composition of the gas-phase on the surface activity of the metal oxide.

Parallel/preliminary work at the University will focus on method development for the on-line sampling of both hydrogen and oxygen and potentially other species as a function of T, P, water content, dose rate, specific surface area, co-adsorbed species etc. during recombination / catalytic reaction studies.

As Sellafield are already funding work in this area directly at NNL, it is envisaged that PhD work within the active laboratories would be performed in parallel with this ongoing research, with associated benefits relating to knowledge transfer and reducing NNL's partnering/supervision costs.

Underpinning plutonium immobilization in advanced ceramic wasteforms

University of Sheffield

Key outcomes are to underpin and enable immobilization of the plutonium stockpile through: Pu partitioning data, and verified computational models, to guide wasteform design; and new understanding of mechanisms of crystalline to amorphous phase transition in ceramic wasteforms and its potential deleterious effect on dissolution kinetics. Impact will arise through uptake of research by NDA, through integration with our EPSRC / NDA IIKE project, to inform government decision making on stockpile management.

The objectives are 1) to understand the plutonium incorporation mechanisms in ceramic and glass-ceramic wasteforms, for immobilization of the UK plutonium stockpile; and 2) to understand the effect of cation disorder on the crystalline to amorphous phase transition in model ceramic wasteforms for plutonium immobilization. The research will develop the fundamental understanding required to deliver immobilization of the UK Pu stockpile, in terms of formulation design, radiation damage, and dissolution mechanisms. The methodology is novel and ambitious is undertaking a programme of Pu research and utilizing unique national facilities.

Disposability of wasteforms for plutonium immobilisation and efficacy of surrogates

University of Sheffield

This project aims to reduce the key uncertainties pertaining to zirconolite ceramic/glass-ceramic waste form dissolution. The key objectives are to:

- Understand the effects of relevant geochemical parameters on the kinetics of HIP-ed ceramic/glass-ceramic zirconolite materials, using Ce and U as surrogates for Pu;
- Develop an understanding of the dissolution mechanisms of HIP-ed ceramic/glass-ceramic zirconolite materials;
- Perform selected experiments to understand the dissolution of ^{239}Pu-doped ceramic/glass-ceramics, fabricated by University of Sheffield PhD student Steph Thornber at ANSTO in 2017;
- Establish a series of long-term (1 – 3y) dissolution experiments with ^{239}Pu-doped samples, to be periodically sampled.