updates from DISTINCTIVE

EDITION 1 | July 2015

# Welcome to the 1st Newsletter

By Prof. Michael Fairweather, Consortium PI, University of Leeds

**DISTINCTIVE is a multi-disciplinary collaboration of 10 universities and 3 key industry partners from across the UK's civil nuclear sector. Our world-class programme focuses on the area of nuclear decommissioning and waste management, with a special focus on the UK's needs.**

It's been 18 months since the programme kick-started in February 2014 - and we've been very busy in this time! We have held two Industry Road Shows, a series of Theme Meetings, our first International Advisory Group meeting and our first Annual Conference.  We've assigned at least one researcher to each of the ten post-doctoral projects, and gained an additional 16 PhD students, including two from our associate partner Queens University Belfast.

There are also a number of exciting activities in the pipeline. Various DISTINCTIVE supported public outreach events will be held as part of the 2015 Bristol European Green Capital Programme, and the Consortium hopes to produce a radio documentary with BBC Radio 3 in 2016 that explores our nuclear past and future. I encourage you to regularly check our website (**www.distinctiveconsortium.org**) for updates on any upcoming activities.

The newsletter will summarise progress made by the Consortium in a digestible format. It will also contain key messages from our various management groups. Going forward, the newsletter will be published every six months and will track the key outcomes and outputs during that period.

This edition focuses on the industrial applications of the individual projects. Some feedback from our International Advisory Group (IAG), which can be found hereinafter, was that we must ensure that our research is aligned with the needs of the UK civil nuclear industry. To encourage our PhD students and PDRAs to think about the challenges that the industry is facing, and how their results could potentially be used, they were asked to answer the question "So What?". These statements can be found inside.

I hope that you enjoy reading the first newsletter!

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# A Message from the International Advisory Group

By Prof. Ian Pegg, International Advisory Group Chair, Catholic University of America

The International Advisory Group (IAG) for the DISTINCTIVE Consortium held its first meeting immediately prior to the first annual meeting, which was held in Sheffield in April this year. I was honored to be invited by the Leadership Team to take on the role of Chair of the IAG and, particularly as a proud graduate of one of the member universities (Sheffield), it was my great pleasure to accept that position.

I look forward to working with the many talented individuals in the IAG and the Consortium to help make the DISTINCTIVE programme as successful as possible.

The IAG is composed of 22 members from organisations in the UK, USA, and the European Commission as well as 10 senior academic members from the Consortium. The group includes representatives from industry, academia, government, and regulatory agencies who together bring a wealth of experience and perspectives as well as detailed knowledge of the issues and challenges associated with nuclear waste management, immobilization, and decommissioning.

The primary objectives of the IAG are to advise on the education and research strategies of the Consortium, ensure current industrial relevance of the on-going research programme, inform on the socio-economic and environmental impact of the research activities, and to promote and strengthen links to the industrial community. It is anticipated that this may include advice on areas such as relevance of programmes of study, gaps in research within the overall programme, knowledge transfer, emerging research trends, opportunities for access to industrial facilities, industrial collaboration in the supervision of PhD students, career opportunities for students and graduate training schemes, and student visits, placements, projects, and prizes.

During the first IAG meeting the members of the DISTINCTIVE Leadership Team provided valuable overviews of the programme including information on background and objectives, summaries of each of the four Themes into which the present 48 projects are organized, and descriptions of the two cross cutting themes, which cover active research projects and outreach and public engagement.

This provided an excellent introduction for the IAG members in advance of the two-day annual meeting that followed, with about two dozen presentations and some 36 posters providing more detailed information on and results from individual projects. The meeting also provided valuable opportunities for the IAG to interact with members of the Consortium, including students and PDRAs involved in the ongoing research activities.

In the remainder of this brief note, I would like to summarise some of the feedback and general impressions that I have received from the IAG members following the meetings. The feedback was uniformly positive regarding the overall programme importance, concept, approach, focus, and objectives. Several members were involved in similar predecessor programmes and noted that it was clear that valuable lessons had been learned and very well implemented, particularly with respect to the general approach, planning, and coordination.

The meeting format and content were found to be very effective and the use of introductory presentations from industry partners for each Theme session was particularly welcome and very helpful in putting the subsequent research presentations into appropriate perspective. The importance of such connections was a recurring theme in the feedback – "how best to keep the academics aligned with industry needs" – and efforts to further improve in this area were encouraged. There was a good balance of attendees between academics and industry and lots of evidence of good discussions between students and industry delegates, especially around the posters. The one-day Theme-specific meetings held several months earlier, which a few IAG members attended, were also noted as a valuable means of communication between researchers and the various stakeholders.

Most students and PDRAs seemed to have a reasonably good awareness of industry challenges but it was felt that ways to improve the depth and breadth of that awareness should be considered. Secondments, site visits, and themed workshops were some of the suggestions. The challenges associated with finding suitable industry placements for the PDRAs that need to do them, and making those placements useful for both the PDRAs and industry, were recognized, as was the training time necessary before any useful work can be done on most nuclear sites. Possible options, including other, non-site licence companies, therefore should also be considered. In addition, although there are nominated industry mentors and supervisors for all of the projects, it is not clear that all students and PDRAs are getting the same level of industry involvement and ways to improve the community of interest for each project should be considered.

Many projects are still in the early stages and, considering the time to recruit students and PRDAs, some are obviously off to faster starts than others. However, especially at this early stage, it is important to ensure that the researchers are becoming familiar with the relevant international literature in order to help guide and expedite their projects but also to avoid duplication. Some weaknesses were noted in this area, particularly with respect to related projects in the US. In view of the strong US representation on the IAG and as part of the overall UK/US collaboration strategy, it seems clear that the IAG could help in making connections between DISTINCTIVE projects and related projects and/or researchers in the US; similar efforts could then be undertaken for other countries. As a first step in this direction, Rod Rimando, Laurie Judd, and I have met (since, conveniently, we are all located in Washington, DC) to discuss how that might work and the facilitating role that the US DOE could play. This has also provided a valuable opportunity to discuss the broader role of the IAG in the success of the programme as well as how these connections might become collaborations.

There were several thoughts on potential adjustments to the meeting format, including panel discussions for each Theme with strong end-user representation, break-out sessions for more in depth discussions in each area, and time after the main meeting for the IAG to discuss and review the received information. However, these would likely lead to a longer meeting. Other suggestions included broadening the attendance to bring in others from the decommissioning arena such as Magnox, RSRL, Dounreay, Devonport and perhaps even EDF, since the nuclear new build companies will have to plan their decommissioning activities now.

The EPSRC funding for this programme is especially valuable to the industry because of the ability to significantly leverage the amount of research work that industry could otherwise support. So, last, but certainly not least, is the importance of providing evidence to stakeholders and funding agencies of the value and impact that the programme is generating. This, and the related issue of the development and implementation of appropriate metrics, is an area in which the IAG should be able to provide ideas and suggestions. The outreach and public engagement plan, which appears to be well thought-out and very promising, will certainly provide another critical component in addressing this need.

In summary, DISTINCTIVE is a timely and important programme that is clearly off to a very strong start. On behalf of all of the members of the IAG, we look forward to working with the Consortium to ensure its greatest possible success.

# Long Term Degradation Behaviour of Vitrified Intermediate Level Nuclear Waste

## By Dr Rama Krishna Chinnam, PDRA, Imperial College London

Vitrified intermediate level nuclear waste (ILW) canisters disposed into repositories will be vulnerable to the physical and chemical changes. Much work is being published in this field and most related to the surface degradation of simulated ILW glass composite materials (GCM). At the Centre for Nuclear Engineering, Imperial College London studies are being carried on various physical and chemical changes that the glass and simulated vitrified ILW will undergo in contact with water.

The aim of these studies is to understand the rate of GCM dissolution with respect to the physical changes that occurs in the material over time. The experimental data generated will thus be incorporated into the computational models to determine the long term stability of vitrified ILW. Inline with our long term goals, research was carried on the degradation of cracks in International Simple Glass at our Centre.

These findings were presented to the glass research audience at ACers-DGG GOMD conference held in Miami, USA in May 2015. Our work was appreciated and received constructive comments. Efforts to collaborate with the researchers dealing with the nuclear waste forms within the DISTINCTIVE Consortium was fruitful and in the near future we have plans to widen our collaborative network.

Dr. Chinnam's PDRA project is titled "Durability of Heterogeneous ILW Glass/Ceramic Wasteforms from Complex Wastestreams". His lead supervisor is Prof. Bill Lee (**w.e.lee@imperial.ac.uk**).

# 1st Annual Meeting - Sheffield 2014

By Abby Ward, Programme Manager, University of Leeds

The Consortium held its 1st Annual Meeting at the Millennium Gallery, Sheffield, on Wednesday 15th and Thursday 16th April 2015.

The event brought together academics and researchers involved in the programme, as well as representatives from industry, research institutes, governing bodies and regulatory authorities, to share the research advances made in the field of nuclear waste management and decommissioning since the programme started in February 2014.

The objectives of the event were to:

• Facilitate knowledge transfer.

• Enable our researchers to engage with industry experts and potential employers.

• Provide networking opportunities .

• Promote the uptake of DISTINCTIVE research into industry.

• Generate new collaborative research ideas.

Twenty-one oral presentations were given by our researchers across four technical sessions: AGR, Magnox and Exotic Spent Fuels, $PuO_2$ and Fuel Residues, Silo Ponds and Legacy Wastes and Structural Integrity. These sessions were opened and chaired by invited experts from our key industrial partners (Danny Fox (NDA), Howard Sims (NNL), Cristiano Padovani (RWM NDA) and John Riding (Sellafield Ltd), respectively). Thirty-six posters were also presented by our researchers during the coffee and lunch breaks. Consequently, the event gave our researchers the opportunity to raise awareness of their projects within the community, and to receive the support and guidance that they need to progress their projects over the duration of the programme.

Technical presentations were given throughout the two-day event

Poster inspired discussion during one of the coffee breaks

Delegates also received keynote presentations from three international representatives of academia and governance: Prof. Eric McFarland (University of Queensland, Australia), Prof. Ian Pegg (Catholic University of America, US) and Rodrigo Rimando (U.S. Department of Energy). These speakers offered an international perspective on issues being addressed by the Consortium, and introduced research activities that the UK R&D community can learn from.

In a session titled Cross-Cutting Themes, Prof. Neil Hyatt (University of Sheffield) provided an update on a number of proposed outreach activities. This includes a radio-documentary that is currently being led by Frances Byrnes (University of Sheffield) and Matthew Thompson (Rockethouse). Both took the opportunity to give an overview of this project, and to request the support of our academics in forming a proposal to submit to the BBC later this year.

A priority of the NDA is to maintain the key skills and capability within this sector. To support this mission, the NDA sponsored two PhD awards; one for the best oral presentation and one for the best poster presentation.

**The winners of the prizes were voted for by industry delegates, and we would like to congratulate Stephanie Thornber (University of Sheffield) and Conrad Johnston (Queens University Belfast) who received these awards.**

Overall, the event proved to be a great success with over 115 delegates from the UK, USA, Germany and Australia in attendance; over 50 of these delegates were from outside of the consortium!


Rick Short, NDA, presenting the 2015 PhD Student Awards

Those who attended left with a better understanding of the individual research projects and their importance to the UK's nuclear decommissioning programme. There was a great deal of interaction throughout the two days, and a number of new relationships were formed which will ensure the success of the projects, and the Consortium as a whole.

We would like to thank our key project partners NNL, NDA and Sellafield Ltd. for their ongoing support.

Material from the event, including copies of the oral presentations, can be downloaded from our website: **www.distinctiveconsortium.org**

# Save the Date

We will be holding the 2nd Annual Meeting of the DISTINCTIVE University Consortium in Bristol on Tuesday 19th and Wednesday 20th April 2016.

More details will be announced shortly. Please check the website (**www.distinctiveconsortium.org/events/**) for regular updates.

Sponsorship packages, including exhibition spaces, are now available. Please contact Abby Ward(**A.M.E.Ward@leeds.ac.uk**) to discuss this opportunity.

Our DISTINCTIVE PhD researchers at the 1st Annual Meeting

# Hot Isostatic Pressing: A Consolidation Technique for Glass-ceramic Wasteforms

By Stephanie Thornber, PhD Student, University of Sheffield.

Steph won the NDA "Best PhD Oral Presentation" award at the 1st Annual Meeting in April

Hot isostatic pressing (HIPing) is a proposed technique to process glass-ceramic wasteforms for the immobilisation of plutonium residues at Sellafield.[1] Originally developed for the diffusion bonding of fuel element assemblages in nuclear reactors, HIPing has found its place in many different industries with multiple applications on a range of different materials.[2] HIPing is now considered a potential consolidation technique for nuclear waste streams where cementation and vitrification are not suitable, such as plutonium residues and fuel debris. Plutonium residues are categorised as high level waste with higher plutonium contents than intermediate plutonium contaminated material (PCM) waste but are not economically viable for plutonium recovery. The nature of these waste streams, and the variation and complexity of their compositions and physical form, makes them difficult to vitrify. Such wastes include powders, green pellets, MOx fuel material and sludges, all with varying levels of Pu.[3] The HIP has the potential to process all variations of the waste in a single machine, in the same canister design, using the same HIP cycle with different precursors optimised for each waste stream. Glass-ceramics are being studied for low purity Pu waste containing glass formers, full ceramics for high Pu concentrations and MOx residues, and metallic matrices for metallic waste.

The HIP works by applying high temperature and high pressure to the workpiece to produce high density materials (>97% of theoretical density). The precursors and feed are mixed together and packed into stainless steel HIP cans, evacuated and sealed. The canister itself provides containment to the waste form, but a suitable overpack is required for transport and storage. It has been found that the rate limiting step of the HIP process is the canister preparation time for evacuation. The canister is first evacuated at room temperature before high temperature bake-out to remove volatiles from inside the waste feed. Research conducted at The University of Sheffield has shown this can take up to 20 hours per sample. To improve the efficiency of the process and throughput of samples, the pre-HIP waste treatment parameters were investigated with the aim of reducing the time taken to evacuate and seal each canister, thus improving process throughput. It was concluded that the addition of a calcination step is essential to improve the efficiency of the process whilst maintaining sample quality. Table 1 summarises the final material densities and the time taken to prepare each sample. The overnight calcination was done at 600 °C, a temperature representative of that used in industry to calcine waste prior to thermal treatment.[4] Calcining the whole batch has the potential benefit of making the HIP process a semi-continuous method of wasteform fabrication at an industrial scale by maintaining a constant flow of precursor and reducing the time taken to fabricate each HIP canister. Table 1 shows the canister evacuation time was reduced by a third with the addition of the overnight calcination.

Table 1. Summary of material and canister densifications.

| Sample | Total can evacuation time (mins) (±2.5) | Packing density (g/cm$^3$) (±0.04) | Pycnometry density (g/cm$^3$) | Monolith density (g/cm$^3$) | Material densification (%) (±5) | Canister internal volume densification (%) (±5) | Overall canister densification (%) (±5) |
|---|---|---|---|---|---|---|---|
| A (300°C bake out) | 960 | 1.66 | 2.7907 ±0.0021 | 2.7177 ±0.0252 | 97.38 | 40.91 | 33.39 |
| B (600°C bake out) | 480 | 1.57 | 2.744 ±0.0035 | 2.7758 ±0.0058 | 101.16 | 31.80 | 28.77 |
| C (600°C calcine + 300°C bake out) | 150 | 1.37 | 2.7792 ±0.0027 | 2.7584 ±0.0190 | 99.25 | 49.19 | 33.64 |
| D (600°C calcine only) | 45 | 1.38 | 2.8287 ±0.0022 | 2.7802 ±0.0147 | 98.29 | 46.51 | 31.95 |

Figures 1 and 2 show the microstructures and phase assemblages of the HIPed glass-ceramic materials respectively. Both figures show the consistency of the phase assemblage formed across all samples and that the high temperature heat treatments have no detrimental effects to the structure or phases formed.

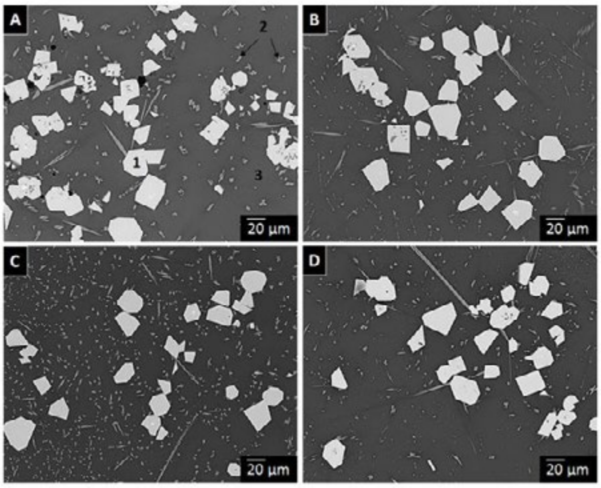


Figure 1. BSE micrographs of the HIPed glass-ceramic materials showing similar microstructures for all samples. 1) Zircon, 2) Rutile, 3) Glass phase.

Hot isostatic pressing has many advantages for processing nuclear waste including minimal off-gas production. The only off-gases produced are from the pre-treatment of the waste and precursors and canister preparation. The applied pressure means lower temperatures can be used resulting in a finer grain structure, subsequently increasing the strength and durability properties. Radionuclides are seen to be uniformly incorporated into the wasteform and the overall volume of waste can be reduced significantly compared to other processing routes. The volume of a single HIP canister can be reduced by up to 50% of its initial volume.[5]

The research taking place at The University of Sheffield is making strong advances in the development and understanding of glass-ceramic wasteforms for actinide immobilisation. Whilst optimising sample formulations and wasteform properties is important, it is also essential to maintain an ease of processing, which is achieved through the use of Hot Isostatic Pressing. The HIP facility in the Materials Science & Engineering Department at Sheffield is being enhanced to accommodate uranium containing samples, making it the only active research scale HIP in the UK. This will allow for further advancements in understanding the wasteforms long-term properties and actinide behaviour within the material.

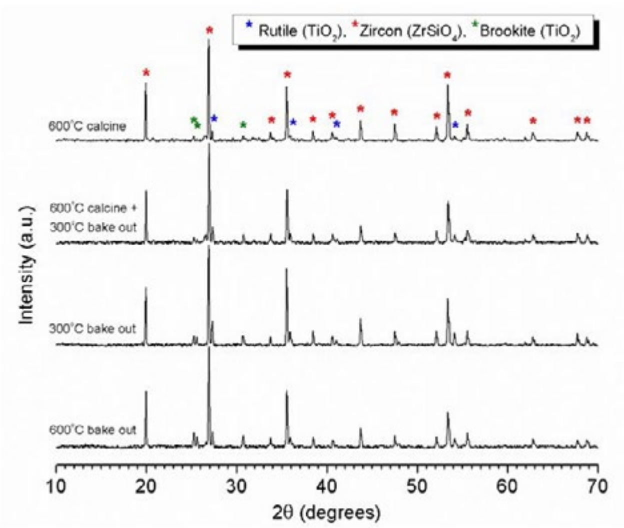


Figure 2. XRD patterns showing the crystalline phase assemblage of each sample.

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4 M.I. Ojovan, An introduction to nuclear waste immobilisation, 1st ed. Elsevier, Amsterdam ; Boston, 2005.

5 E.R. Vance, M.W.A. Stewart, and S.A. Moricca, "Progress at ANSTO on SYNROC," J. Aust. Ceram. Soc., 50 [1] 38–48 (2014).

Stephanie's PhD project is titled "Current glass-ceramic formulations for Pu disposition" . It sits within the $PuO_2$ and Fuel Residues theme of DISTINCTIVE. Her lead supervisor is Prof. Neil Hyatt (**n.c.hyatt@sheffield.ac.uk**).

# Site Visit to Fukushima Daiichi

## By Dimitri Pletser, PhD Student, Imperial College London

On Monday 9th of March 2015 Imperial College London's Centre for Nuclear Engineering Director Professor Bill Lee and PhD student Dimitri Pletser were given the opportunity to visit the site at Fukushima Daiichi, just days before the 4 year anniversary of the 2011 Tohoku earthquake and subsequent tsunami, which caused the accident at Fukushima Daiichi. The visit was organised by Imperial's industrial partner Hitachi Ltd.

The day started early at Iwaki, where we had met up with the Hitachi delegation the day before, from where a taxi was taken to J-Village. J-Village was the former headquarters of the Japanese national football team, its build at the time sponsored by TEPCO. This centre was used as the staging point for all response efforts during the immediate aftermath of the tsunami and is now the departure point for all visits to the site.

We were received by TEPCO and were given an in-depth briefing of the current situation, including the progress of decommissioning and remediation efforts and had our itinerary explained to us. After a whole body count, we were shepherded onto a bus and driven through the abandoned exclusion zone towards the actual site. This 20 km zone is currently uninhabited and only accessible during day time, giving it a very surreal ghost town feel.

Upon arrival at the Fukushima site, we were taken to the seismic isolation building which houses the main control centre. Here we kitted up in multiple layers of PPE, including Tyvek suits, respirators and safety helmets. Once fully suited up we were driven around on-site to visit various parts of the facility. Our first stop was at the Hitachi-run High Performance Advanced Liquid Processing System (HP-ALPS), where we were shown the current set-up used to treat effluent cooling water and the various other adsorbent systems.

Prof. Bill Lee and Dimitri Pletser visiting the Hitachi HP-ALPS


The next stop on the tour was Unit 4. Unit 4 was one of the four hardest hit units located near the seafront. The removal of its fuel was completed recently, on the 22nd of December 2014, and we were very fortunate to be allowed to visit inside the containment building. Once inside the structure the magnitude of the task became clear, as a cantilevered structure containing a colossal 100-tonne rated heavy-lifting crane was built against the side of the reactor building, ensuring that no weight leans on the battered reactor building. This crane was then used to lift the removal cask into the spent fuel pool, into which the fuel debris was transferred using the fuel handling machine. Once the fuel debris was fully loaded into the cask, the cask sealed and then remotely removed using the cantilevered crane.

> The complexity and scale of this operation was staggering and serves to illustrate just how much work has already been done and how much work still remains as this process will be repeated with the other three units on the seafront.

We were then driven across the site to witness various parts of the site and its clean-up. These sites included among others the ever-increasing amounts of water storage units, in all their variations, the ground water bypass system, used to avoid ground water ingress into the basements, the intended site of the frozen soil walls, and finally the restored Shallow Draft Quay, which ensures vital access by sea. Upon our return to the seismic isolation centre we met with Site Superintendent Akira Ono and were shown around the central control centre.

Professor Lee then addressed the workers in the control centre, thanking them for their dedication and hard work and expressing his hope for future UK-Japan collaborations to aid in the remediation of the site.

Prof. Lee addressing the central control room

It is difficult to truly appreciate the scale of the operation without being able to witness the site first-hand, since images and news reports do not do it justice. Currently more than 7000 people work on-site every day, often in difficult or hazardous conditions, making their achievements all the more impressive. Being able to first-hand see the devastation that the tsunami and the accident had wrought on the site aided in putting things into perspective. Despite occasional media coverage suggesting otherwise, an astonishing amount of work has already been done under very difficult circumstances, but the task ahead for all parties involved is of epic proportions. This visit proved to be a humbling experience, one that is sure to inspire for years to come.

Dimitri's PhD project is titled "Glass Composite Materials for Fukushima ILW Immobilisation" . It sits within the Legacy Ponds and Silo Wastes theme of DISTINCTIVE. His lead supervisor is Prof. Bill Lee (**w.e.lee@imperial.ac.uk**).

# Leeds Students to Present Latest Research

Two PhD students from the University of Leeds will be presenting their research at the 35th annual Cement and Concrete Science conference in Aberdeen this August. DISTINCTIVE's Toby Lord will be presenting his preliminary results looking at the reuse of scabbled concrete fines in cementitious grouts. Meanwhile, Josh Hawthorne, in the third year of his PhD, will be presenting his work on the susceptibility of ILW encapsulation grouts to changes in slag composition.

This annual conference has, in recent years, become a key event in the field of cement and concrete, often featuring a number of presentations on nuclear waste encapsulation. With over 100 international experts present, the conference will offer Josh and Toby the opportunity to discuss their results with some leading players in the field.

For more information about these projects, contact Dr Leon Black (**l.black@leeds.ac.uk**)

# Recent Achievements by the University of Bristol

## Presentations on the topic of spent fuel dissolution:

Dr Leila Costelle (PDRA) - Journee des Actinides 2015 in Prague - oral contribution.

Sophie Rennie (PhD) - Plutonium Futures 2014 conference in Las Vegas - poster contribution.

Sophie Rennie (PhD) - TMS 2015 conference in Orlando, Florida - oral contribution.

Dr Ross Springell (Academic Supervisor) - Faraday Discussions on Corrosion 2015, Royal Society of Chemistry - oral contribution.

## Beamtime Awarded at International Facilities:

I09 beamline at the Diamond Light Source - XPS measurements on uranium oxides.

Dalton Cumbria Facility - Effect of damage on behaviour of $UO_2$.

I07 beamline at the Diamond Light Source - Surface diffraction measurements to study the corrosion of $UO_2$.

BM28, XMaS beamline at the European Synchrotron Radiation Facility - x-ray diffraction measurements to probe the formation of uranium hydride at the $UO_2$/U interface.

PolREF beamline at the ISIS neutron spallation source - neutron reflectivity, used to study the formation of uranium hydride at the $UO_2$/U interface.

## Collaborations:

New collaborations with Queen's University, Belfast and with the GANIL accelerator facility in Caen, France on the topic of fuel dissolution and the effect of radiation damage.

# Keeping Nuclear Waste Safe

By Dr Ross Springell and Sophie Rennie (PhD Student), University of Bristol

This article was published in the July edition of the ESRF newsletter, and this work will also appear in the Diamond newsletter in the near future.

By bombarding thin films of uranium oxide with X-rays in the presence of water, users are exploring the long-term effects of storing spent nuclear fuel in geological repositories.

Nuclear power is a reliable, readily available, carbon-free energy resource and therefore presents an attractive solution to the increasing demand for electricity and the global drive toward low-carbon energy technologies. Today, more than 400 commercial nuclear reactors operate in 31 countries, providing 11% of the world's electricity. With these facilities together producing around 12,000 tons of high-level radioactive waste each year, it is essential that a safe and efficient storage strategy for such material is found.

Although there is no long-term radioactive waste storage facility currently in operation, many governments are considering adopting a "multi-barrier" approach whereby waste is encapsulated and then buried in a deep geological repository. Since the waste must be stored over timescales of tens of thousands of years, however, there is still a very real possibility that the stored fuel will one day come into contact with groundwater.

With uranium dioxide ($UO_2$) being the predominant component of nuclear fuel, the presence of groundwater would not normally be a cause for concern because it is insoluble in its stable state. However, once the fuel has been used during reactor operation, the presence of highly radioactive fission products results in extremely strong radiation fields that are able to cause radiolysis of the water. This process yields highly oxidising species that can transform $UO_2$ at the surface into the readily soluble $UO_2^{2+}$ ion. In other words, this mechanism has the potential to cause dissolution of the spent fuel and release harmful radionuclides into the environment.

**Source-probe experiment**

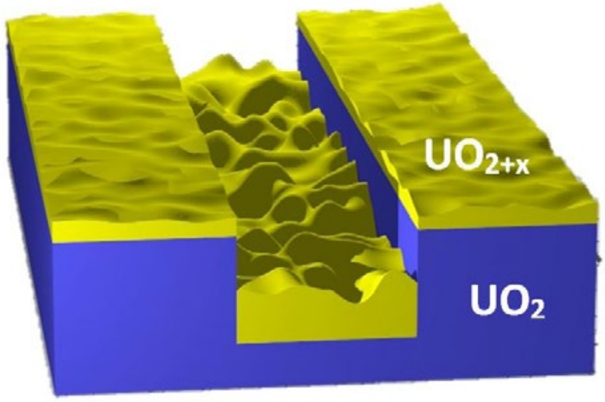
Detailed studies of the structure of spent fuel in such an extreme environment are prohibitively complicated, but there are other experimental routes that might shed light on fuel behaviour. We have used an intense, monochromated beam of X-rays to mimic the radiation fields present in a geological repository, with the aim of investigating their effect on a $UO_2$/water interface (D01: 10.1039/C4FD00254G).

This was first achieved on the ESRF's UK operated XMaS beamline in a joint project carried out between XMaS and Diamond Light Source in the UK, by exposing single crystal $UO_2$ thin films to ultra-pure water in the presence of a 15 keV X-ray beam.

As well as initiating radiolysis, the beam was also used to measure X-ray diffraction and reflectivity so that we could probe crystalline structure, surface morphology, oxide layer density and, ultimately, the dissolution of $UO_2$ as a function of exposure time. Modelling the reflectivity and diffraction data revealed a loss of crystalline $UO_2$, an increase in the $UO_{2+x}$, hyperstoichiometric layer, a surface roughening, and eventually a loss in material due to dissolution (see figure).

These measurements help to refine predictive models of the spent fuel/water interface. Using engineered interfaces that are particularly sensitive to any change in surface structure, for instance, it is possible to investigate the role of individual variables. This information is important for validating theoretical models that attempt to predict the behaviour of fuels in contact with ground water over long timescales. Further complexity can now be introduced, for instance reproducing the effects of radiation damage, lattice deformation and fission product implantation. This research programme will take us towards a more complete understanding of the corrosion behaviour of spent nuclear fuel.

Along the X-ray beam path, the study found a loss of $UO_2$ material (blue) accompanied by an increase in thickness of a hyper-stoichiometric surface layer ($UO_{2+x}$) (yellow)




Sophie's PhD project is titled "$UO_2$ Surface Reactivity and Alteration". It sits within the AGR, Magnox and Exotic Spent Fuels theme of DISTINCTIVE. Her lead supervisors are Dr Tom Scott (T.B.Scott@bristol.ac.uk) and Dr Ross Springell (phrss@bristol.ac.uk).

# Imperial College Attendance at the UHTC Conference

By Claudia Gasparrini, PhD Student, Imperial College London

Between 12 and 16 April 2015, the Imperial College London Director of the Centre for Nuclear Engineering Prof. Bill Lee and a couple of PhD students from the CNE attended an ECI (Engineering Conferences International) conference which was held in Australia in the beautiful setting of Surfers Paradise, Gold Coast. The four day conference was attended by experts in the field of UHTC (ultra - high temperature ceramics) from industry and academia and PhD students coming from all over the world.

The talks and poster presentations covered a variety of topics including: synthesis and processing, characterization, incorporation of fibres, production of composites and the use of UHTC ceramics as coatings and barriers. The plenary sessions also covered innovative applications for which this family of materials is being developed. One of these in particular described the potential use of these ceramics in the manufacturing of scramjet combustors. The talks given by Imperial College attendees included the processing and characterization of (Ta,Hf)C; the modelling of oxidation and melting of $HfB_2$ due to laser jet exposure; the generation of quaternary phase diagrams in the system boron – carbon – hafnium – zirconium via CALPHAD approach and the investigation of the mechanism of oxidation of zirconium carbide, which is the preliminary study performed on carbide materials in order to understand the oxidation of a legacy of exotic carbide fuels in the framework of the DISTINCTIVE. The relatively small audience consisted of lecturers, researchers, people from industry and students. This enabled the success of the event as discussions were prolonged during coffee breaks, lunches and dinners. Everyone had the opportunity to talk with everyone in a casual atmosphere and the impeccable organization further helped the socialization aspects thanks to a planned trip to Springbrook National Park and a surfing lesson organized on the last day of the meeting. Definitely a great experience and it will be a pleasure to have the group reunited in 2017 in UK for the fourth meeting on UHTC.

Claudia's PhD project is titled "Options for Exotic Carbide Fuels" . It sits within the AGR, Magnox and Exotic Spent Fuels theme of DISTINCTIVE. Her lead supervisor is Prof. Bill Lee (**w.e.lee@imperial.ac.uk**).

Delegates enjoying the surfing lesson on the last day of the conference

## Our Website

The DISTINCTIVE University Consortium website was launched in August last year.

The website will act as a respository and showcase for key information and outcomes of the Consortium.

**You can use the website to:**

- Learn more about the framework and objectives of the programme.
- Find up-to-date research project descriptions and details of publications.
- Be notified of upcoming events and how to participate.
- To read latest annoucements including calls for the Active Research Fund (PDRAs only).
- Download materials from past events .
- To contact members of the consortium.

www.distinctiveconsortium.org

# Engaging with Industry

Engagement with key industry stakeholders remains a priority for the Consortium. Collaboration ensures that our research is relevant to the requirements of the civil nuclear industry. We continue to seek support for our on-going work. Below, our key partners explain why they're involved in the programme.

## National Nuclear Laboratory

## By Mike Angus, Corporate Chief Technologist

The government's Nuclear Industrial Strategy sets out a mission to deliver a successful and sustainable nuclear industry by increasing UK delivery of our national programmes and growing international engagement through export of technology and inward investment. Integral to this mission is a growth in nuclear R&D to deliver innovation and an expansion of nuclear skills at all levels. The NNL's vision is "to deliver the best nuclear science and technology solutions in the world". Fundamental to the delivery of this vision is a drive for continual improvement in the quality of our Science and Technology (S&T). This in turn supports the government strategy.

Our collaborations with universities support this vision and hence NNL's contribution to the government strategy. Effective research output on these projects is important to us and to ensure we get the best out of the research, we are;

• Encouraging and supporting closer collaboration including where appropriate, secondments into our facilities – talk to your industrial supervisor about using our facilities.

• Sharing the information needed by the students so the research project can provide the most effective impact – so ask your industrial supervisor if you need more information or advice.

• Encouraging healthy teamworking within the projects we supervise, allowing adequate time for the industrial supervisor to assist the project and to work with the DISTINCTIVE researchers to prepare joint publications.

• As an R&D organisation, we are ourselves funding in-house research that aligns well with many of the projects and so increases the opportunities to collaborate

• We host National Nuclear User Facility equipment and are keen to encourage its use by academic researchers

• Offering short (2-day) industrial familiarisation courses at Workington, dates for which will be advertised shortly – if you want to take part, contact **dominic.rhodes@nnl.co.uk**.

## NNL Bursary Annoucement

To encourage increased collaboration, we are offering a £2000 bursary to support the attendance of a student or postdoctoral researcher at Waste Management 2016 conference to be held from March 6-10, 2016 in Phoenix, Arizona. The bursary will be awarded for the best joint paper with an NNL and university author. The paper will be presented in the DISTINCTIVE dedicated oral presentation session.

To be considered for this bursary, please submit your abstract to Abby Ward (A.M.E.Ward@leeds.ac.uk) by Friday 14th August. Check the WM2016 website for more information.

## Nuclear Decommissioning Authority

## By Rick Short, Research Manager

The NDA's mission of decommissioning the civil nuclear sites in the UK is going to take many decades and thus require several generations of technical experts and industrial leaders with skills and experience that are difficult to obtain from outside of the nuclear arena. To address this challenge, one of the main objectives of the NDA's University R&D programme is to develop and maintain the key skills and capabilities that will be required to carry out our mission. An essential part of this is knowledge transfer. The DISTINCTIVE project provides great opportunity for two-way knowledge transfer between the nuclear industry and the academic community; academics are kept abreast of the current and upcoming challenges on the nuclear sites, and industrial experts learn about cutting edge materials, computing and engineering solutions to their problems. Furthermore, through this two-way communication, a new generation of well informed and well educated PhD graduates with nuclear industry experience will be created to take up future positions supporting our mission and potentially as leaders on the nuclear sites and in the supply chain companies.

## Sellafield Ltd.

### By Debbie Keighley, Head of Technical Capability

Sellafield Ltd. is the company responsible for safely delivering nuclear decommissioning, reprocessing, and waste management at the Sellafield site in Cumbria. Sellafield is home to a wide range of interdependent nuclear facilities and operations. Our challenges range from short term hazard and risk reduction, to long term nuclear waste management. Our site plan extends for decades into the future, and requires resolution of varied and complex science and engineering challenges. To achieve this we need high calibre nuclear specialists, and access to novel and innovative solutions. The DISTINCTIVE programme aims to provide routes to innovative technology, multi-disciplinary research partnerships, and to train the next generation of nuclear specialists, hence this programme provides clear opportunities to help Sellafield achieve its mission. Nuclear activities have been ongoing at Sellafield since 1947 and over that period we have recognised the importance of aiding public understand regarding the benefits and challenges of the nuclear industry. Consequently, we are highly supportive of the public engagement aspects of DISTINCTIVE, and the wide academic network which has been established as part of the programme. We are therefore delighted to be an industrial partner in the DISTINCTIVE project.

### There are a number of ways in which your organisation can get involved:

- Provide access to specialist facilities
- Hosting of secondments/placements
- Industrial project supervision
- Provision of training opportunities for researchers
- Equipment funding/loaning
- Attendance/participation at DISTINCTIVE events (Annual/Theme Meetings, Impact)
- Sponsorship of DISTINCTIVE events

To discuss this opportunity, please contact Abby Ward (**A.M.E.Ward@leeds.ac.uk**)

# CONGRATULATIONS TO DISTINCTIVE'S...

**Prof. Rebecca Lunn (Co-I at the University of Strathclyde)** who has been officially honoured alongside prominent figures from the fields of science, law, politics and arts as part of an inaugural 'Outstanding Women of Scotland' list.

She recieved the accolade at an awards event launched by the by the Saltire Society to coincide with International Women's Day, on 8 March.

Members of the public were invited to submit nominations for inclusion in the list during 2014 leading up to St Andrew's Day, on 30 November. The key criterion for consideration was that those nominated should be living contemporary examples of Scottish women who have made a significant contribution to Scottish culture and society.

Prof. Rebecca Lunn (centre) being presented with a limited edition print.

**Dr Tom Scott (Co-I at the Universty of Bristol)** who has been awarded the Vickerman Prize 2015.

The award, from the UK Surface Analysis Forum (UKSAF), is presented to researchers whose work is anticipated to have a major impact in the field of surface analysis. It is intended as a recognition of high-quality independent research at an early career stage

Tom was presented with the award at the UKSAF Summer Meeting that was held at the University of Chester Thornton Science Park on Wednesday 1st July.

Source: University of Bristol

Dr Tom Scott (left) being presented with a bottle of Glenmorange!

# So What?

To achieve impact it is essential that our researchers can communicate the long-term objectives and outcomes of their projects to a variety of non-academic beneficiaries.

For this edition of the newsletter, we encouraged our researchers to think about the industrial applications of their projects by answering the question "So What?". We hope that these statements will enable representatives from industry to identify projects that are relevant to their organisation.

These statements, as well as brief summaries of project progress made to-date, can be found on the following nine pages.

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## Modelling the Surface Chemistry of $PuO_2$ at the Molecular Level

DR BENGT TEGNER
PDRA, UCL

The short answer is the UK has a lot of civilian plutonium, about 100 tons in fact, mostly in the form of plutonium oxide powder, stored in stainless steel cannisters.

Recently, some of these cans have started to bulge, leading us to suspect that gas build-up is behind the increased pressure. This have lead us to look at water on plutonium oxide surfaces to see if hydrogen is produced. As we don't want to open these cannisters, we are using computer simulations to study the behaviour of water on these surfaces to gain insight into what's going on.

**Progress:**

- Developed a model to study these oxides using computational chemistry.First results on stable uranium dioxide and plutonium dioxide surfaces suggests strongly bound molecular water.
- Attended a Nuclear Workshop at UCL.

## Crack Sealing and Water Transport

RICCARDO MADDALENA
PhD Student, University of Strathclyde

Novel cementitious materials are being investigated as crack-healing agents. The cementitious materials used included nanoparticles such as nano-silica, silica fume and metakaolin. Several composites were chemically and mechanically tested, and a comparison was made between the composite and Portland cement characteristics. Continuing work includes an evaluation of the interaction between nanoparticle cement and existing concrete, and the mobilization of nanoparticles into cracks. Experiments will be assembled to simulate electro-migration, electro-deposition or localized injection through cracks. Numerical modelling will be also used to predict the water-flow permeability of the materials and their durability.

**Progress:**

- Synthesis of C-S-H gel.
- Analysis of C-S-H gel and understanding of its microstructure.
- Investigation on mechanical and hydraulic properties of novel cementitious binders.

## Measurement and Modelling of Sludge Mobilisation and Transport

DR HUGH RICE
PDRA, University of Leeds

We aim to develop a suite of novel, simple, safe, cost-effective ultrasonic methods to measure the flow properties of solid-liquid suspensions and slurries that are analogous to those encountered by the nuclear industry in storage, resuspension and transport operations. We believe such ultrasonic methods have not been exploited for nuclear applications and, in a new flow laboratory at the University of Leeds, we are developing in-line rheometry, time-domain velocimetry and multi-frequency attenuation measurements, along with the corresponding data processing algorithms, to allow industrial operators to robustly characterise the physical and flow properties of nuclear waste slurries.

**Progress:**

- New fluid-flow laboratory being commissioned at the University of Leeds, to contain flow loops with several diameters.
- Novel ultrasonic methods will be combined with laser-based and physically pumped measurements to investigate flow behaviour of complex suspensions.
- We aim to provide capability to measure horizontal, vertical and inclined flows so that effect of gravity/buoyancy/segregation can be isolated.
- Based on existing expertise at Leeds, we aim to develop in-line pipe rheometry (for viscosity measurement), time-domain velocimetry (flow velocity) and multi-frequency attenuation measurement (particle concentration profiles).
- Laboratory to be complete by July 2015.
- Preliminary results of ultrasonic methods available by August 2015 .

## A Life Cycle Approach as a Decision Tool

ANDREA PAULILLO
PhD Student, UCL

The environmental impact of nuclear industry has always been a rather controversial and complex topic. A life cycle assessment (LCA) approach may accomplish this purpose. It could serve as a tool to help decision-making processes within the nuclear field and improve public perception of the nuclear energy. Our long term goal is to evaluate environmental burdens of current nuclear fuel cycle options, identify critical stages and propose alternatives. For instance, we aim to address questions such as: *Is an open cycle (i.e. Spent Fuel disposal) more environmentally sustainable than a closed cycle (i.e. Spent Fuel reprocessed)? Which is the best long-term storage option for spent nuclear fuel?*

**Progress:**

- Literature review of radiological impact assessment methodologies.
- Literature review of nuclear fuel cycle and waste management options.
- Literature review of UK and overseas performance assessments of nuclear waste repository.
- Establishment of a consistent data inventory.
- Modelling the spent nuclear fuel reprocessing cycle.

## One Step Extraction and Quantification of Radionuclides

LAURA MAYNE
PhD Student, Loughborough University

We have developed a range of ligands with the capacity to selectively bind trace radioactive contaminants from solutions containing abundant major cations. These ligands will be immobilised onto silica-coated superparamagnetic beads which can be quickly removed from solution using a magnetic field. Tunable Resistive Pulse Sensing (TRPS) is a technique which allows for the characterisation of nanoparticles based on their charge, size and concentration. Using TRPS, the radionuclides will be detected and quantified by studying the changes on the nanoparticles surface. TRPS is beneficial due to the quick analysis time and the ability to perform particle-by-particle analysis.

**Progress:**

- Silica nanoparticles modified with a ligand (3-aminopropyl) triethoxy silane, which contains a nitrogen donor atom.
- Copper successfully extracted from solution using the functionalised silica nanoparticles, extraction also successful with competing alkali metals eg $K^+$. The concentrations of the copper solutions were analysed using ICP-OES.
- Tunable resistive pulse sensing (TRPS) used for the charge analysis of the silica nanoparticles.
- Bare silica, functionalised silica and functionalised silica with bound copper all analysed using TRPS. Measurements performed in a range of pH and ionic strength to optimise the signal.
- Charge analysis allows small differences between each variety of the particles to be detected.

## Gas Hold-Up in Sludges

MICHAEL JOHNSON
PhD Student, University of Leeds

The First Generation Magnox Storage Pond and Magnox Swarf Storage Silos have reached the end of their working lifetimes and decommissioning these Magnox-era legacy buildings accounts for roughly a quarter of Sellafield's £1.5 billion annual budget. The transport and temporary storage of corroded Magnox sludge is potentially complicated by waste swell due to trapped gas in the consolidated bed and the periodic release of flammable gases formed through corrosion and radiolysis. Understanding the mechanisms for retention and release of gas is fundamental to prescribing a safe waste management strategy until a deep geological facility becomes available.

**Progress:**

- A methodology has been outlined for assessing bed swell due to gas retention using a magnesium hydroxide test material and decomposition of hydrogen peroxide to simulate gas generation.
- The vane method has been used to study the yield stress and shear modulus of the magnesium hydroxide test material.
- A Langmuir-Blodgett trough, bubble column and a film floatation test have been used to assess stable interactions between solid, liquid and bubble which might impact the mechanisms by which gas is retained by the waste.
- A methodology is being tested for using x-ray tomography to capture 3D images of trapped gas within soft sediments.

## Current Glass-ceramic Formulations for Pu Disposition

STEPHANIE THORNBER
PhD Student, University of Sheffield

Immobilising plutonium wastes in glass-ceramics will reduce the overall volume for geological disposal in the future. Glass-ceramics can accommodate higher waste loadings of plutonium than glass thus fewer wasteforms will be produced, which will save on volume and cost. Glass-ceramics act as double barrier systems and have shown to have better properties than glass for immobilising plutonium.

Hot isostatic pressing can be used on many different types of high level and intermediate level wastes and can process glass, ceramics, glass-ceramics and metals. Applying this method to processing plutonium containing wastes will again reduce total wasteform volume and cost.

**Progress:**

- Processing parameters have been investigated to optimise sample quality and throughput showing a two-step heat treatment during sample preparation is the best route.
- Phase formation has been seen to vary as a function of the glass phase composition. Higher aluminium concentration in the glass phase has been seen to increase the formation of zirconolite as the ceramic phase.
- Current work aims to determine an optimum formulation with maximum zirconolite formation, which appears to be dependent on the glass to ceramic ratio as well as the glass composition.

## The Interaction of Water with $PuO_2$ Surfaces

JOSEPH WELLINGTON
PhD Student, UCL

More than 100 tonnes of separated plutonium are stored at Sellafield in the UK as $PuO_2$ powder in sealed steel cans. Under certain circumstances, gas generation may occur in these cans, with consequent pressurization. Of the mechanisms potentially leading to gas production, those involving $PuO_2/H_2O$ interactions are less well understood.

The long-term goal of this project is to study water adsorption on $PuO_2$ surfaces through the use of density functional theory (DFT) with an embedded cluster method. As $UO_2$ has generally been studied in more detail, both experimentally and theoretically, it is useful to study as a benchmark for results.

**Progress:**

- The electronic structure of $AnO_2$ clusters representing the bulk was investigated with the composition of the valence and conduction bands agreeing well with experiment.
- Water adsorption geometries and energies have been calculated on the (111) and (110) surfaces of $UO_2$ and $PuO_2$ with 1 to 4 molecules adsorbing on the cluster dissociatively or molecularly.
- A second layer of water is being built up on the (110) surface of $UO_2$ and $PuO_2$.

## Irradiated Sludges

CONRAD JOHNSTON & MEL O'LEARY
PhD Students, Queens University Belfast

Legacy sludges represent one of highest priority targets for risk reduction at the Sellafield site. Future storage and disposal of these sludges is complicated by in situ hydrogen gas generation, due to radiation chemistry. In a poorly designed closed environment, such as a disposal container, this could lead to a pressurised, explosive atmosphere. Underlying mechanisms responsible are poorly understood, preventing prediction about the quantity of gas that can be expected. Through experimental irradiation of sludge mimics, and computer simulation of chemical processes, this project seeks to identify the key factors affecting gas production, and underlying chemistry.

**Progress:**

- Developed analytical capability for quantification of hydrogen.
- Developed analytical capability for determining radio-reconfiguration of biodegradation products.
- Prepared interface for these analytical tools with the Q14 radiation research platform.
- Performed characterizing measurements on the Q14 radiation research platform.
- Initiated design work on a new, high dose rate (>50 Gy/s) flexible small-sample radiation research platform.
- Continuing simulation work is being carried out on gaseous $MgOH_2$ to provide a benchmark for solid phase systems.

## Autonomous Systems for Nuclear Decommissioning in Extreme Radiation Environments

OLUSOLA AYOOLA
PhD Student, University of Manchester

Monitoring the sludge characteristics for physical, chemical and biological changes provides data inputs to the decision making process on sludge retrieval. The usefulness of such data lies in their consistency and reproducibility.

This research investigates the limitations of various techniques and sampling procedures used in monitoring particle size distribution of sludge in the ponds. Sludge samples used at the central lab at Sellafield will be tested against existing records to allow for a validation of the current sampling procedures and provide recommendations on appropriate adjustments.

An understanding of how radiation source in the ponds can be mapped will be provided.

**Progress:**

- Literature review of some relevant techniques has been conducted while others are in progress.
- Modelling and simulation of acoustic backscattering technique has been conducted.
- Access to NNL Workington Lab has been granted.
- An experimental validation of acoustic backscattering technique is in progress.
- Application for access into NNL Central lab is in progress.

## Novel Ceramic Wasteforms for Cs and Sr Encapsulation

GEORGE DAY
PhD Student, University of Birmingham

A previous study revealed that Cs2TiNb6O18 is the major Cs-containing phase produced when Cs-loaded IONSIV, a commercial ion exchanger, is hot isostatically pressed (HIPed). $Cs_2TiNb_6O_{18}$ demonstrates excellent chemical durability which compares well to the Cs containing phase hollandite in SYNROC and therefore has the potential to be an excellent waste form for long term immobilisation, for example in a Geological Disposal Facility. It is not yet known however how the material will respond to the radioactive decay of $^{137}$Cs+ to $^{137}$Ba2+. In order to determine if $Cs_2TiNb_6O_{18}$ can retain Ba, a number of Ba substituted samples have been synthesised and characterised.

**Progress:**

Preparation of a range of samples with different Ba levels using sol-gel and ceramic routes has been completed. These are undergoing analysis using a range of techniques such as powder X-ray diffraction, X-ray fluorescence and electron microscopy to confirm if Ba has been incorporated and, if so, any changes to the structure or leach rates of the material.

## Grain Boundary Damage Mechanisms in Strained AGR Cladding Under Irradiation

CHIARA BARCELLINI
PhD Student, University of Manchester

The long-term aim of this PhD project is to link the radiation-induced atomic scale changes in the crystal lattice of the Advanced Gas-cooled Reactor (AGR) cladding material to its mechanical integrity and its susceptibility to localised corrosion. Simulating the neutron damage with ions under controlled conditions of dose and temperature is a fast way to get the information needed to improve the existing models for radiation damage and the predictive tools. The data collected will be, therefore, useful for the power station operators who need to understand the behaviour of the claddings in order to guarantee their integrity in both core and storage conditions.

**Progress:**

- Literature review on the microstructure of the un-irradiated AGR cladding material.
- Prepared un-irradiated samples with high quality surface finish for characterisation with electron microscopy.
- Familiarising with the basis of scanning and transmission electron microscopy.
- Initial characterisation of precipitates in un-irradiated sample with SEM.
- Completed the specific training on principles of operation and health and safety related to the use of a tandem ion accelerator at the Dalton Cumbrian Facility.
- Accepted at MATRAC 1 Summer School about the application of neutrons and synchrotron radiation in engineering materials.
- Poster contributions at PGR Student Conference and at National Student Conference in Metallic Materials.

## Thermal Treatment of PCM and ILW

LUKE BOAST
PhD Student, University of Sheffield

My project addresses the common UK R&D need for "treatment techniques for wastes with no confirmed disposal route" and "alternative techniques to encapsulation" as identified by NDA. More broadly, the project will contribute to developing the technical maturity of thermal treatment processes for ILW across the NDA estate.

The primary economic benefit from the research is to underpin estate wide deployment of thermal treatment processes for PCM, enabling potentially significant savings to be realised through accelerated hazard reduction. In this respect, NDA consider that wider application to the national ILW inventory, could save hundreds of millions of pounds.

**Progress:**

Optimisation studies have been performed in developing vitrified PCM wasteforms, now the project aims to develop an understanding of product stability with respect to generic ILW disposal concepts, through accelerated dissolution experiments

## The Interaction of Brucite Surfaces with Uranium and its Fission Products

ESZTER MAKKOS
PhD Student, UCL

The used fuel elements of the first generation of British nuclear reactors are stored in water filled ponds. During the decades, the cover material of the fuel rods corroded and formed brucite ($Mg(OH)_2$). Since this new material is known to be highly reactive and it coexists with radioactive ions in the water, it is important to understand which kind of interactions exist between its surface and the ions to create successful strategies for the further treatment of the storage ponds. This project is focusing on the fundamental understanding of these interactions by using computational methods.

**Progress:**

- Developed a reliable computational model and investigated the hydrolysis of $Sr^{2+}$ ion water with it.
- Identified the most stable $Sr^{2+}$ hydroxide and aqua complexes in the solution.
- Developed a suitable surface model for the brucite surface.
- Carried out a basic adsorption study for different ions ($Sr^{2+}$, $Cs^{+}$, $Ba^{2+}$, $Rb^{+}$, $Mg^{2+}$, $Na^{+}$) and simple $Sr^{2+}$ hydrates.
- Currently focusing on benchmarking: verifying the computational parameters and carry out adsorption simulations with an independent method.

## In-situ Ground Contaminant Containment (Physical Barrier)

CHRISTOPHER WONG
PhD Student, University of Strathclyde

Hydraulic ground barriers are an established technology for use on contaminated sites, as a method of pollutant migration control. However traditional techniques of cement based grouts, soil-bentonite slurries and chemical grouts pose several limitations such as excavation requirements, high pH leachates and presence of toxic components.

Colloidal silica is a new grout material that has the potential for application at Sellafield including for example the formation of horizontal hydraulic barriers. The site presents many different scenarios where this technology could be applied. Colloidal silica poses several favourable characteristics an initial low viscosity, small particle size, and non-toxic nature.

**Progress:**

- Effect of background groundwater pH on grout gelling behaviour.
- Effect of electrolyte concentration on grout gelling behaviour.
- Influence of soil presence on the grout gelling behaviour.
- Characterisation of colloidal silica grouts.

## Understanding Surface Species and Interactions Between Adsorbed Chloride and Water on Stored $PuO_2$

SOPHIE SUTHERLAND-HARPER
PhD Student, University of Manchester

5% of more than 100 tonnes of plutonium dioxide ($PuO_2$) stored in cans at Sellafield in Cumbria, which were produced in 1975, have become contaminated with chloride from the lining of the cans and water from exposure to the atmosphere. This project aims to make $PuO_2$ particles (and less toxic substitutes) with a range of sizes then contaminate and test various decontamination heat treatment methods. This work will form the basis of a decontamination plant to purify the $PuO_2$ and make it safe for either reuse in Mixed Oxide (MOX) fuel or disposal in a Geological Disposal Facility (GDF).

**Progress:**

- A literature review of the analytical techniques which will assess the extent of contamination on PuO2 and its analogues ($CeO_2$, $ThO_2$ and $UO_2$) is undergoing editing.
- X-Ray Diffraction of $CeO_2$ shows that chloride does not incorporate itself into the structure when it is contaminated, as the peak positions do not change.
- X-Ray Photoelectron Spectroscopy shows high specific surface area (HSSA) $CeO_2$ particles adsorb and desorb more chloride than low (LSSA) ones.
- Synthesis of $CeO_2$ of varying crystal sizes will begin as soon as the chemicals arrive.

## Understanding the Interfacial Interactions of Plutonium Dioxide with Water

DR DOMINIC LAVENTINE
PDRA, Lancaster University

More than 100 tonnes of Pu are stored in the UK, typically as plutonium dioxide (PuO2) powder contained within nested stainless steel cans. Under some conditions, these cans could pressurise due to production of gas within the can. This would make the cans difficult to store or handle and must be avoided. A number of chemical and radiological processes that involve moisture in the cans have been suggested as causes of gas production. We aim to study the fundamental surface chemistry of water adsorbed on PuO2 to help predict conditions that could lead to gas generation during long storage. Initially this involves precisely measuring absorption / release of gases including water vapour from PuO2 surfaces using highly accurate piezoelectric crystal nanobalances.

**Progress:**

- A high temperature nanobalance sensor system has been constructed, allowing measurements up to 600ºC, covering the full range of storage can temperatures.
- The system responds both to mass change and temperature; thus in the first instance, the temperature-response dependence and maximum operating temperature of the nanobalance have been measured.
- The nanobalance crystal transducers have been modified by coating with ceria (as a PuO2 surrogate) and europium doped ceria (to mimic americium impurities) layers of different thicknesses; layer thicknesses and roughness have been measured by SEM and AFM.
- Temperature-response dependence studies of the modified, coated crystal transducers have been undertaken (up to 300ºC), showing the coated crystals retain piezoelectric properties and can be employed as nanobalance sensors.
- The absorption/desorption of H2O onto/from ceria-coated crystal transducers up to 175ºC has been measured with studies up to 300ºC ongoing.

## New Ion Exchange Materials for Effluent Clean-up

RYAN GEORGE
PhD Student, University of Birmingham

Caesium and strontium radionuclides are important targets when designing materials for nuclear waste treatment and environmental remediation. The main aim of my project is to create new materials for effluent treatment this in mind, focusing on open framework ion exchange materials. The long term aim of this project is to synthesise a material with high selectivity for caesium and strontium over competing ions such as sodium, potassium and calcium that could then be readily converted into a dense ceramic form with potential long term storage and disposal being the final goal.

**Progress:**

- Initial studies on the synthesis and ion exchange studies of magnesium aluminophosphate materials.
- Synthesis of novel germanate materials.

## Novel Ion Exchange Materials

DR EVIN (TZU-YU) CHEN
PDRA, University of Birmingham

The main aim of this project is to develop new ion exchange materials based on known and stable minerals such as zirconium or tin silicates for effluent clean-up, especially for Sr and Cs. These materials are chemically and thermally stable during the ion exchange process, and can be modified to work efficiently under acidic conditions, where current systems are not very effective. These features make them promising for the treatment of contaminated environmental media. The focus is not only on the ion exchange properties, but also making materials that can be thermally converted to dense ceramic wasteforms via easy conversion routes, such as Hot Isostatic Pressing, for long-term geological disposal.

**Progress:**

- Ion exchange with $^{85}Sr$ in realistic simulated conditions, such as low concentration of $Sr^{2+}$ and a large amount of $Na^{+}$ and $K^{+}$ as completing cations.
- Kinetic studies on natural zeolites (Clinoptilolite and mordenite).
- Investigation of potential ceramic wasteforms for Cs and Sr immobilisation from Tin silicates.

## Enhanced shear Micro- and Ultra-Filtration Without Recycle Pumping

KEITH SCHOU
PhD Student, LOUGHBOROUGH UNIVERSITY

Enhanced shear microfiltration has the potential to increase the rate of flow of a liquid across a membrane, enabling smaller, more portable filtration units. The possibility for such units can allow for a single unit servicing multiple legacy ponds, and as such reducing the capital cost for treatment of medium and low level waste which is distributed around the country. The efficiency gains should also increase the rate at which the waste is processed, making time savings. The technology in development applies to all microfiltration, as such it can be used in a wide range of process applications.

**Progress:**

- Preliminary testing with a rudimentary test setup.
- Development of a more thorough testing setup.
- Development of a comparison between particle retention, flux and shear.
- Attended UNTF conference, attended, and presented a poster, report and presentation at DISTINCTIVE 1st annual conference.
- Experimental regime investigating the effect of shear to cake thickness and flux ongoing.
- Experimental regime investigating the effect of azimuthal and axial oscillations ongoing.
- Created a video promoting nuclear technologies (WNU Olympiad) (available on YouTube “Enhanced shear microfiltration”).

# In-situ Ground Contaminant Containment (Physical Barrier)

DR MATTEO PEDROTTI
PDRA, University of Strathclyde

Hydraulic ground barriers are an established technology for use on contaminated sites, as a method of controlling contaminant migration. However traditional techniques pose several limitations.

Colloidal silica based grouts are increasingly being considered as a potential grouting technology, because it has initial low viscosity, small particle size and it is chemically and biologically inert. Colloidal silica can be destabilised by the addition of a salt accelerator compound and or changes to pH, resulting in a rapid increase in viscosity (i.e. gelation) and formation of a rigid solid gel.

This behaviour allows for low injection pressures to be used during grouting.

**Progress:**

- Fundamental understanding of the factor controlling colloidal silica gelation.
- Development of an analytical model capable of predicting colloidal silica gelation time.
- Experimental calibration and validation of the analytical model.

# $UO_2$ Surface Reactivity and Alteration

SOPHIE RENNIE
PhD Student, University of Bristol

Safe disposal of spent nuclear fuel requires long-term storage over a time scale of thousands of years, during which the storage facility is subject to environmental changes. One possible scenario is the ingress of water into the facility, which has the potential to drive corrosion at the fuel surface, releasing harmful radionuclides into the environment. The project aims to study this process by inducing radiation driven dissolution at a model fuel/ water interface. Synchrotron x-ray diffraction and electrochemistry techniques will be applied to probe the induced structural and chemical changes; information that is important to modelling long-term nuclear waste behaviour.

**Progress:**

- Thin film UO2 samples have been grown and characterised at the University of Bristol.
- Radiation induced dissolution experiments were performed at the ESRF and Diamond Light Source, using XRD to probe the sample structure.
- Analysis of these results provide information on the change in electron density, surface roughness and thickness of the $UO_2$ thin film as the dissolution progresses. (R. Springell, S. Rennie et al., Faraday Discussions 180, 301–31 (2015).)
- Further experimental time has been granted at the Diamond Light Source, for a continuation experiment to investigate the effect of radiation damage on $UO_2$ dissolution.

# An Investigation of Wasteform Evolution During Wet-recovery and Drying of SNF

DR JAMES EDWARD DARNBROUGH
PDRA, University of Bristol

Safe storage of uranium metal is of paramount importance for security, health & the environment. Pyrophoric species have been seen to evolve at the metal & oxide interface. Investigation of crystal structure, environment & engineered surfaces (including multilayers) will allow probing of buried interfaces. To do this a range of thin film depleted uranium samples are produced with a strict control of important variables for analysis via a range of techniques, from in laboratory characterisation to neutron & X-ray experiments at international facilities. This will allow us to identify safe storage environments & atmospheres for uranium.

**Progress:**

- Completion of initial foundation work on preparation of film & layer structures.
- Program of damage completed in collaboration with Dalton Cumbria Facility.
- Successful application for funds to develop an instrument for thermal conductivity measurement of thin films.
- Successful application for beam time at XMAS (Grenoble) to investigate in-situ development of hydride at the uranium-uranium dioxide interface, utilising thin films. Commencing December 2015.

## Computational Simulations of Storage Pond Sludge Disturbance

OLIVIA LYNES
PhD Student, Lancaster University

Across the UK are 35 sites producing radioactive waste. Since the 1950s, much of this has been kept in external waste ponds. Corrosion of the waste, as well as variation in external conditions, has led to a fine particulate sludge lining the base of the ponds. This sludge has to be reprocessed, hence understanding its composition is key. Computational methods are being used to investigate the composition of the sludge and the particulates in the pond water removing the inherent risks associated with nuclear waste. This will allow us to refine the reprocessing methods, to fully reprocess the storage ponds.

Progress:

- Modelling of strontium hydrates using TURBOMOLE to investigate their coordination number.
- Initial investigations into the dynamics of strontium hepta-hydrates using TURBOMOLE.
- Investigations into the coordination of strontium, magnesium, and calcium ions with bulk water using CP2K. Coordination numbers of 8, 6 and 6 have been established respectively.
- Molecular dynamics of the strontium hydrates from the CP2K calculations in bulk water.

## An Investigation of Wasteform Evolution During Wet-recovery and Drying of SNF

DR LEILA COSTELLE
PDRA, University of Bristol

In the present project, we synthesise thin film samples of uranium dioxide-based materials and expose their surfaces to a range of chemical conditions and radiation fields in order to closely mimic the environments expected to be found at the surface of spent nuclear fuel. We use a range of techniques in order to probe the dynamic changes to the fuel's structural integrity and to measure the dissolution products. The arising experimental results will be used as important parametric input for calculations of the likely long-term degradation of Spent Nuclear Fuels in variety of potential storage and disposal scenarios.

Progress:

We designed microelectrodes to study the localised corrosion behaviour of uranium based materials. Conventional macro-electrodes are not suited for the study of these mechanisms as they tend to dilute the responses evident in the localised processes. However, the use of microelectrodes enabled us to isolate the effect and investigate it without the parallel response of a surface undergoing an entirely different reaction. This is very relevant to pitting corrosion, which involves localised chemistries and very high current densities often on extremely small fractions of the surface while the entire remaining surface may be passive. The results will be published soon.

## Determination of Optimum Drying Conditions for AGR Fuels

JAMES GOODE
PhD Student, University of Leeds

The UK is due to cease reprocessing of spent nuclear fuel in readiness for direct disposal to a GDF around 2075. Experience has shown that SS clad fuel can be safely stored in caustic for 25 years although beyond this point behaviour is unknown. In many parts of the world dry storage is being used however there is no safety case for dry storage of SS clad fuel. This PhD is intended to provide some of the basic science to support such a safety case specifically in relation to the removal of both free and bound water (the drying phase).

Progress:

- Method developed to produce simulant fuel samples representative of real fuel by reproducing the conditions experienced by fuel during its life.
- Identification of a number of methods suitable for characterisation of oxide layers on simulant fuels such as SEM, EDX and XPS.
- Initial planning for characterisation of oxides on real AGR fuel cladding samples.
- Outline plan for development of drying methods.

# Publications

The following peer-reviewed papers and articles have been published since the programme started in February 2014.


Makkos E., Kerridge A., & Kaltsoyannis N., *The importance of second shell effects in the simulation of hydrated Sr2+ hydroxide complexes.* **Dalton Transactions,** vol. 44, pp. 11572-11581.2015.
DOI: 10.1039/c5dt01110h

Maddrell E., Thornber S., & Hyatt N. C., *The influence of glass composition on crystalline phase stability in glass-ceramic wasteforms.* **Journal of Nuclear Materials,** vol. 456, pp. 461-466.2015.
DOI: 10.1016/j.jnucmat.2014.10.010

Springell R. et al. (incl. Rennie S., Costelle L., Darnbrough J., Sims H E., & Scott T.) *Water corrosion of spent nuclear fuel: radiolysis driven dissolution at the $UO_2$/water interface.* **Faraday Discuss.**, vol. 180, pp. 301-311.2015.
DOI: 10.1039/c4fd00254g

Frankel G. et al. (incl. Springell R.) *Localised corrosion: general discussion.* **Faraday Discuss.**, vol. 180, pp. 381-414.2015.
DOI: 10.1039/c5fd90046h


# Events

## Theme Meetings - 2015

Attendance at these meetings is restricted. Please contact the listed academic for more information.

Theme 1 - University of Bristol - 21st October
Tom Scott (T.B.Scott@bristol.ac.uk)
Theme 2 - Lancaster University - 12th November
Colin Boxall (c.boxall@lancaster.ac.uk)
Theme 3 - University of Birmingham - 17th November
Joe Hriljac (j.a.hriljac@bham.ac.uk)
Theme 4 - University of Strathclyde - 6th October
Andrea Hamilton (andrea.hamilton@strath.ac.uk)

## Annual Meeting - 2016

19th - 20th April 2016
We will be holding the 2nd Annual Meeting in Bristol. More details will be annouced soon, but please ‘Save the Date’.

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