Institution: University of Bristol

Unit of Assessment: 9 - Physics

Title of case study: Uranium storage – ensuring nuclear safety

1. Summary of the impact

Research at the University of Bristol's Interface Analysis Centre has been used to make storage of uranium and uranium carbide safer.

Our research into uranium corrosion has been used to predict the state of uranium present in 'intolerable' legacy wastes at Sellafield and has shaped the way that Sellafield Ltd intends to safely recover and repackage it for prolonged storage. Our research has also similarly influenced the operations of the Atomic Weapons Establishment (AWE) in relation to improving the safety of stored materials. Our research has also been used to implement treatment processes for uranium carbide wastes arising at CERN.

2. Underpinning research

Dr. T. Scott, Professor Geoff Allen and their interdisciplinary research unit based in the School of Physics, the Interface Analysis Centre (IAC), have been working closely with the nuclear industry on prediction and assessment of risks for storage of nuclear waste – specifically uranium. Scott joined Physics in 2009 and became the IAC director in 2009 (a position which he still holds at present), taking over from Allen who had founded and directed the IAC from 1989 onwards (and has since stayed as an emeritus Professor of Materials Science and academic coordinator for the Bristol-AWE strategic partnership). Their research focuses on different aspects of uranium research from metallurgy and alloying through to corrosion and environmental geochemistry [1-6]. A significant spotlight has been on establishing the mechanisms that control uranium corrosion, from initiation to cessation [1,3,5]. A primary focus has been on understanding the corrosion of uranium in storage environments containing varying quantities of hydrogen alongside other gases. The resulting corrosion product – uranium hydride (UH_3) is pyrophoric and consequently poses a significant operational safety risk in almost all storage environments.

This work has enabled identification and better understanding of many of the significant factors controlling the onset (initiation) of hydride formation, including the influence of different cover gases, micro-scale anomalies in the metal itself and structure of the protective surface oxide layer [1,2,5]. This understanding has allowed better prediction of when and if hydrogen corrosion will occur and to implement preventative measures that will delay or even prevent such an occurrence [2]. As an inherent impurity in the metal, uranium carbide has also been studied in our corrosion research in relation to (i) how it offsets apparent corrosion rates of the parent metal [3] and (ii) methods for its deliberate and controlled oxidation [4].

The approach to research has been to combined sophisticated surface analysis techniques with specialist isotope-spiked corrosion cells in which the storage environment (pressure, temperature & gas composition) is precisely controlled and monitored to provide not only real-time corrosion. Of additional significance is that we have also been able to determine the actual mechanisms of uranium corrosion, demonstrating that in mixed gas atmospheres containing both oxygen and water vapour (e.g. air), the latter is the driver for corrosion, with the surface oxide facilitating the concurrent combination of released hydrogen with free oxygen to form 'new' water. A strong recommendation from our research is that uranium is best stored in an environment where significant accumulation of hydrogen gas may be prevented.

The Interface Analysis Centre is recognised as world-leading in the field of uranium research, to the extent that Sellafield Ltd, through the auspices of the Office for Nuclear Regulation (ONR) nominated the University as both a Centre of Excellence and a strategic partner.

Over the current REF period, uranium research funding to the IAC group has exceeded £1.5M, coming from the AWE, CERN and Sellafield, in addition to Research Council funding as part of consortia projects on nuclear materials (e.g. EP/I003207/1 and EP/I003207/1). The Centre has produced some 14 technical reports, in support of the AWE activity, 2 in support of Sellafield Ltd and 5 in support of CERN.

The Bristol-AWE partnership was formalised in 2009, with the establishment of a strategic alliance agreement that was instigated in response to a broadening IAC research activity with the company [a]. In 2010, the IAC was funded by CERN for a 2-year research project to develop a process for the controlled chemical conversion of their uranium carbide fission targets into an acceptable waste form [c]

In 2011, Sellafield Ltd embarked on a national search to identify and evaluate academic expertise related to the corrosion of uranium and other reactive metals. The reason for this search was to establish a Sellafield sponsored link between the internal SL Centre of Expertise (CoE) on Uranium and Reactive Metals and a suitably qualified UK University that would provide expert advice and research to support Sellafield particularly in relation to the behaviour of uranium in wastes [c].

During this period, the IAC was identified as having a 'substantial and leading international expertise for research on uranium and its corrosion products', 'accumulated over a period of approximately 10 years in close collaboration with the UK Atomic Weapons Establishment (AWE)'.

Subsequently in early 2012, after a national tendering process, Bristol was successfully awarded the CoE-university link. Sellafield have acknowledged that the IAC's prior research conducted with the AWE 'directly impacted the company's decision on which University to work with' and gained £500K direct funding from the company over a 5 year period.

3. References to the research

[1] *Jones, CP, **Scott, TB**, Petherbridge, JR and Glascott, J. (2013) A surface science study of the initial stages of hydrogen corrosion on uranium metal and the role played by grain microstructure. Solid State Ionics 231,81-86, doi:10.1016/j.ssi.2012.11.018

[2] *Harker NJ, **Scott TB**, Jones CP, Petherbridge JR, Glascott J. (2013) Altering the hydriding behaviour of uranium metal by induced oxide penetration around carbo-nitride inclusions. Solid State Ionics, 241;46-52, doi:10.1016/j.ssi.2013.04.004

[3] ***Scott, TB**, Petherbridge, JR, Harker NJ, Ball RJ, Heard PJ, Glascott, J and **Allen, GC** (2011) The oxidative corrosion of carbide inclusions at the surface of uranium metal during exposure to water vapour. J.Haz. Mat. 195;115-123, doi:10.1016/j.jhazmat.2011.08.011

[4] **Scott, T**, Harker, NJ, Jones, C, Hallam, K, Heard, P & Catherall, R (2012) Controlled conversion of uranium carbide fission targets using water vapour. in: KR Hallam (eds) *42èmes Journées des Actinides (42nd JdA) conference, Bristol, UK*.

[5] **Scott, TB**, Findlay, I, Glascott, J, **Allen, GC** (2006).UD_3 formation on uranium: evidence for grain boundary precipitation. Phil. Mag. 87;02; 177-187, doi:10.1080/14786430600919294

[6] **Allen GC**, Brown IT and Harris SJ (1994) The matrix dependence of ion emission from uranium oxides. Nuclear Instruments and Methods in Physics Research Section B, Volume 88, Issue 1-2, p. 170-173, doi:10.1016/0168-583X(94)96099-2

4. Details of the impact

Regardless of the civil or military setting, the occurrence of a storage incident is likely to have significant national and international impact. The work of Scott, and others within the IAC, is part of the effort to make uranium storage safer and better understood in terms of reactive chemistry. As demonstrated by the three examples, the IAC has broad reach, connecting with national and international partners. All efforts translate detailed, focused scientific research into tangible outputs and advice for the industry. Our advice has been taken up by both the AWE and Sellafield and this has led to changes to protocols, be it from changing the way uranium (and daughter products) are stored (i.e. the safest environmental conditions or storage configurations) through to improved understanding of the reactive chemistry of uranium in different possible storage environments. For CERN we have not only provided underpinning research but we have also developed and implemented, from scratch, a processing route for fission target wastes.

Beneficiaries of impact

The nuclear industry, including the AWE, CERN and Sellafield in particular have performed extensive programmes of targeted research work to assess the corrosion of uranium in conditions which reflect those which are expected to present in the storage areas. For the AWE, the data feeds directly into the programme for the safe storage, maintenance and management of the UK's nuclear deterrent. For Sellafiled, the data feeds directly into programmes of work for the retrieval and treatment of the legacy wastes.

Atomic Weapons Establishment (AWE)
The AWE plays a crucial role in the defence of the United Kingdom, responsible for the manufacture and maintenance of warheads for Trident, a submarine-launched ballistic missile.
Since 2004, the AWE has collaborated closely with the IAC, Bristol in relation to research directed at better understanding and predicting the corrosion of uranium and its alloys. To date, research has been primarily focused on determining the factors influencing the initiation of hydrogen corrosion on uranium surfaces. This research has had a direct feed-through to the safe storage of uranium and associated materials within the MoD estate, considered to account for a significant proportion of the operational cost of Trident and the cost of running Aldermaston (AWE expenditure between 2008 and 2011 was about £2.6bn)[d].

"*Over the past 9 years, extensive experience and valuable data relating to the corrosion of uranium metal has been accumulated by the Bristol group. This knowledge has furthered our understanding of some uranium corrosion processes (particularly the reaction between uranium and hydrogen) and helped to validate and quantify some important predictive uranium corrosion models developed at AWE. For example, the fundamental relationship between oxide thickness and the severity of hydride attack, which is an underlying mechanistic assumption within several corrosion models applied at the AWE, was directly verified by Bristol in a 2006 technical report. The use of such models enables corrosion predictions which are used unequivocally to reduce the need for physical examination, intervention and measurements of stored materials; all of which account for a heavy financial burden on the UK Government*."[a]

The potential magnitude of the problems being addressed by Bristol are best coined by a further quote from the AWE: "*The storage of uranium in all but the driest of atmospheres can inevitably lead to the generation of hydrogen gas and the later formation of uranium hydride. This presents serious safety hazards during the long term or even medium-term storage of metallic waste (prior to eventual treatment/disposal) with explosions and fires being a risk on the eventual exposure of the payload to the atmosphere.*"[a].

Consequently although no specific details may be supplied, the AWE are strongly voiced in their opinion that The "*contribution to the AWE [from Bristol], and by association the UK, has been significant and much needed*."

Sellafield Ltd (SL)
One of the primary missions of the Sellafield Site is the characterisation, retrieval, treatment and safe interim above ground storage of the legacy wastes which were produced from the earlier operations of the UK nuclear industry. These waste streams contain substantial quantities of uranium metal (from spent nuclear fuel) along with components of the fuel cladding such as Magnox and aluminium. The wastes have been stored under conditions which have lead to the formation of corrosion products such that their characteristics are expected to be significantly different from those of the materials originally consigned to the plants for storage. Unanswered questions pertaining to the state of uranium in storage are key to the safe retrieval and treatment of the legacy wastes [b].

Whilst the research relationship between Bristol and SL. is relatively new, the technical input provided to date, has had a positive influence on several Sellafield programmes which predate the formation of the link, providing late-stage but valuable supporting data and expert advice that have reinforced and influenced decisions relating to waste retrieval and treatment programmes' such as Magnox swarf storage silos (MSSS), the silos direct encapsulation plant etc. The Bristol research has allowed SL to "*better predict the current state and residual reactivity of uranium and reactive metal bearing wastes across a number of the legacy plants on the Sellafield site*".

More specifically, SL (and by association the National Nuclear Laboratory who are performing the package of experimental work for Sellafield) has used the specialist uranium research facilities at the University of Bristol to perform contract measurements (ongoing since April 2012) in relation to determining the proportions of alpha- and beta-UH_3 forming at different temperatures and formation rates [b].

We recommended to SL that spent uranium fuel should be stored in a semi-dry and open containment system such that the potential for significant hydrogen accumulation is prevented. SL has contracted the UK company Croft Ltd to manufacture a series of test storage casks, to provide a full-scale demonstration of such a storage concept. SL has so far investing approx. £1M in this project.

The work on hydride formation has affected the SL safety case for recovery of legacy wastes by reducing uncertainty in quantifying the risk associated with the occurrence of thermal excursions. We have helped to confirm that there is not a significant safety issue posed by uranium hydride in the recovery of legacy waste from SL storage silos. SL is now continuing with the MSSS (£387M) and other legacy retrieval projects including the solis direct encapsulation plant (£1.28B) and pile fuel cladding silo project (£341M); projects worth a total of ~£1.9 billion [e]. Our work on encapsulation of uranium metal in cement (using synchrotron X-rays) has proven that hydride can be a developing corrosion product. SL will use this information to inform its safety case for waste encapsulation. Correspondingly our research has had "*a direct bearing on UK national level programmes for the safe and cost effective remediation of the Sellafield site*" [b].

CERN (ISOLDE Facility).

The safe disposal of radioactive waste arising from experimental fission studies at CERN is a key objective for the organisation; *"As a by-product of our experimental activities at the ISOLDE on-line isotope mass separator facility, the site has a stockpile of spent uranium and thorium carbide targets from which we have produced fission product gases. These wastes have historically been stored on site and have gradually accumulated, awaiting the development of a suitable processing route for conversion of the material into a waste form that is acceptable to the Swiss authorities"* [c]. In 2010, CERN instigated IAC funding for a 2-year research project to develop a process for the controlled chemical conversion of their uranium carbide fission targets into an acceptable waste form. Scott's research has solved this specific problem; *"It is considered that the work conducted by Dr Scott and his team has allowed us to develop and implement (from scratch) a processing route for our radioactive fission target wastes. This has had a direct and positive bearing on the operations at the ISOLDE facility and at CERN in general"* [c]. This method for processing ISOLDE fission wastes has ***"****constituted the building of a specialist hot-cell facility for handling waste targets and a gas treatment system for converting the targets. This investment was in the order of 1.4 million Euros"* [c]. Indirect beneficiaries of this programme includes other EU research facilities such as the SPIRAL2 project at GANIL, Caen, France and the SPES project at INFN, Italy. According to CERN: *"Members of these facilities are already enquiring about the work done by the University of Bristol in order to assume the elimination pathway of their actinide material".*

Other indirect beneficiaries include the UK public and the US public through trans-Atlantic sharing of information between AWE and the Department of Defence. Impact, as a pull-through, is garnered through the uptake of advice and change to protocols; be it from changing the way uranium and uranium carbide are stored or processed through to improved understanding of the reactive chemistry of uranium in different possible storage environments.

5. Sources to corroborate the impact

[a] Letter of support from AWE (TS), Dr David Geeson, Head of Materials Science. Supports all claims made related to research and research findings with the AWE. National security sensitivities dictate that they cannot disclose more detailed and specific information.

[b] Letter of support from Sellafield (TS); Ed Butcher, Technical Lead for the Sellafield CoE in Uranium and Reactive metals. Supports all claims relating to the Bristol-SL relationship; including the research being conducted and fit with the various legacy programmes.

[c] Letter of support from Dr Richard Catherall, Technical Lead for the ISOLDE facility at CERN, Geneva. Support claims regarding development of thermal processes for fission wastes arising at CERN.

[d] Britain's nuclear spending soars amid defence cuts. The Observer. Sunday 2nd October 2011. Jamie Doward. http://www.theguardian.com/uk/2011/oct/02/ministry-of-defence-nuclear-spending-project-pegasus. Supports claims about the cost of running the Aldermaston activity.

[e] National Audit Office. Managing risk reduction at Sellafield. Nuclear Decommissioning Authority.Report by the Comptroller and Auditor General. Ordered by the House of Commons (2012). Supports claims relating to the intolerable nuclear risks posed by the Sellafield site.