Key Findings of DISTINCTIVE to Date

Ian L. Pegg

The Catholic University of America
Vitreous State Laboratory
Washington, DC

DISTINCTIVE

- World-class multi-disciplinary science and engineering R&D program aligned with the strategic needs of the UK industry in the area of nuclear waste management and decommissioning
  - Innovation, partnerships, collaboration, training, communication

- 10 Universities
- 3 Industrial partners: NNL, NDA, and Sellafield Ltd
- 53 research projects

- Theme 1 - AGR, Magnox and Exotic Spent Fuels
- Theme 2 - PuO_2 and Fuel Residues
- Theme 3 - Silo Ponds and Legacy Wastes
- Theme 4 - Structural Integrity

- Cross Cutting: Active Research Projects
- Cross Cutting: Outreach and Public Engagement

Acknowledgements

- DISTINCTIVE management and Theme Leads and researchers for providing information on key findings to date

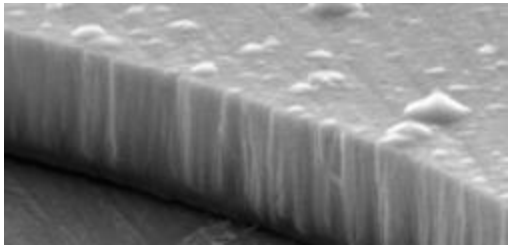
Theme 1: AGR, Magnox and Exotic Spent Fuels

Novel Approach - Thin films as SNF surfaces

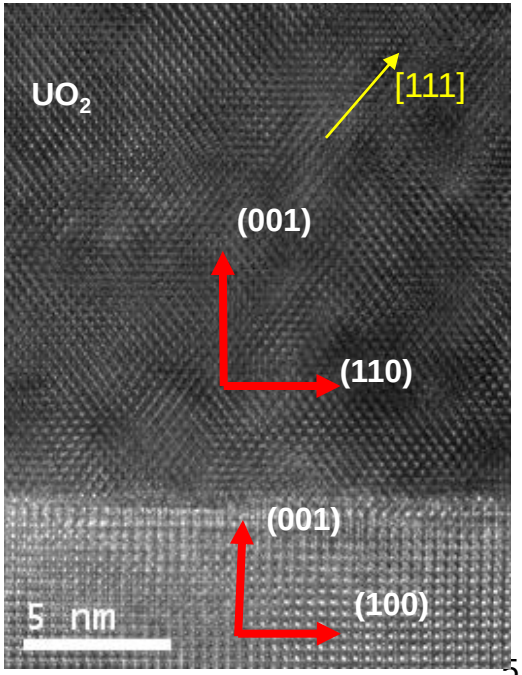
Scott, Springell, Hallam, Darnbrough, Costelle, Rennie (Bristol)

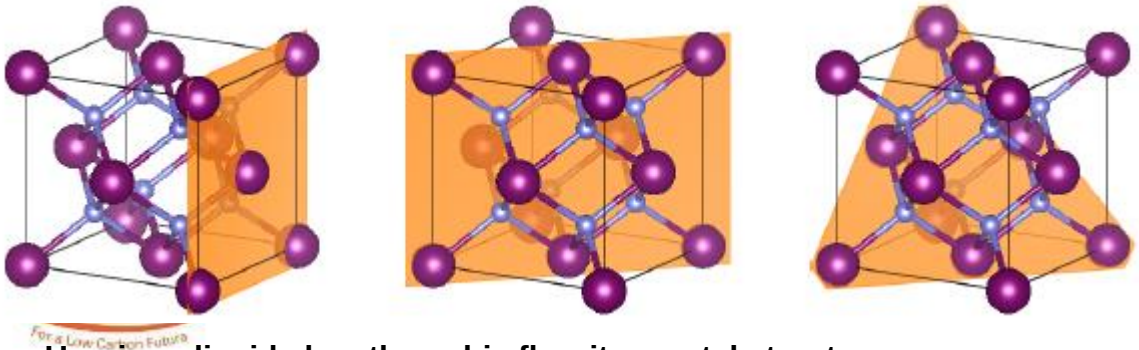
- Small sample masses (<mg) such that **radioactivity is extremely low**
- Control of crystal growth to control thickness/mass
- Single crystal - orientation, strain, phase, stoichiometry
- Can be doped and irradiated
- Model surfaces/interfaces to mimic real life scenarios
- Proven to be the same as surfaces of bulk equivalents

Section through a UO_2 thin film



TEM of UO_2 on LSAT





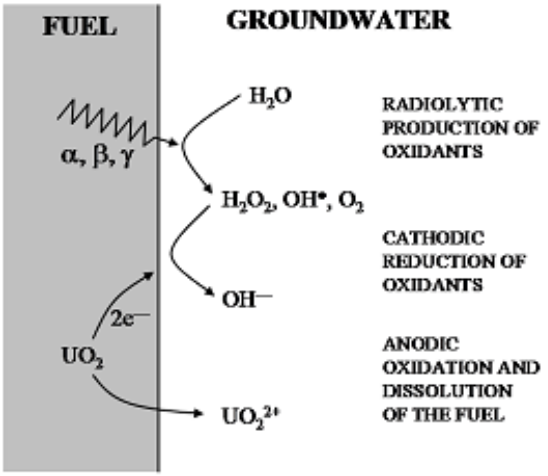
Uranium dioxide has the cubic fluorite crystal structure, space group

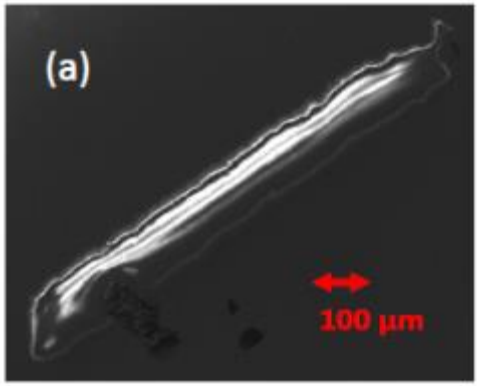
Fuel Materials Research (U-oxide)

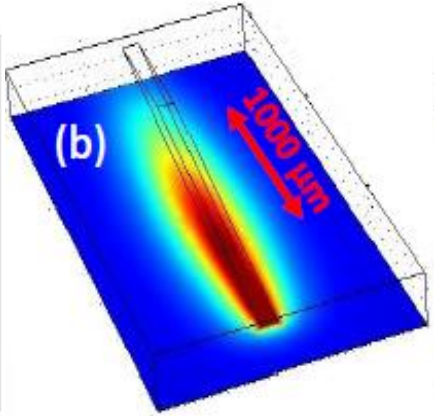
Springell, Scott, Darnbrough, Rennie, Hallam (Bristol)

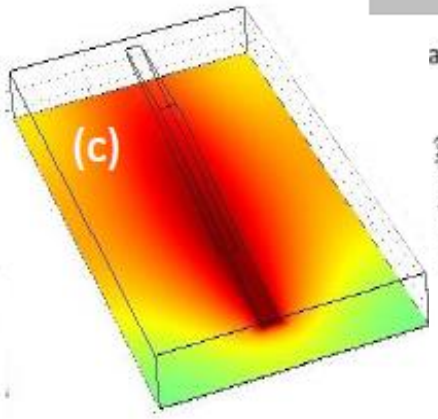
Thin film experiments allowed in situ and real-time observation of radiolysis driven dissolution of UO_2 surfaces in water (driven by X-ray beam)

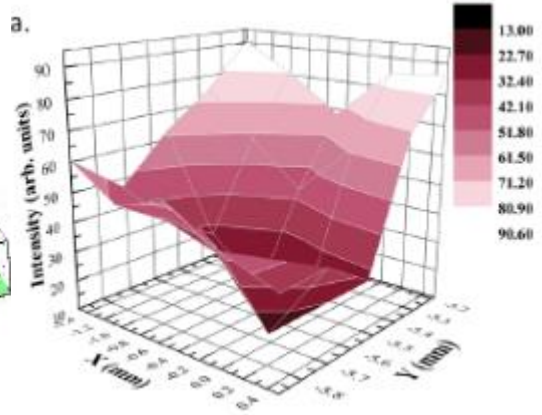
Early experiments show short-lived species, confined to the radiolysis volume in the beam path indicating diffusive transport of H_2O_2 is limited. After long exposure times dissolution/corrosion stopped.











Most recent work on radiation damage effects via thin film doping and ion damage. Prolific use of Synchrotron facilities (I07and XMaS for X-ray reflectivity experiments).

Fuel Materials Research (U-oxide)

Springell, Scott, Darnbrough, Rennie, Hallam (Bristol)

The work on uranium dioxide has focused on dissolution of the material in an aqueous environment in the presence of a radiation field, in this case mimicked by the high energy x-ray source from a synchrotron.

- Combined XRD and XPS analysis of pristine UO_2 films clearly shows that thin film surface are directly comparable to surfaces found on bulk crystals.
- When exposed to near-neutral pH conditions UO_2 will corrode/dissolve faster in the presence of the x-ray beam. At high pH, UO_2 dissolution rates under a photon irradiation field are negligible.
- UO_2 dissolution in this case appears to be a surface mediated effect; I.e. the dissolution is very local to the beam position suggesting either the Oxide surface is activated or the dissolution is enhanced by short-lived radiolytic products. The effect seen is far more reactive than initially considered based H_2O_2 experiments.
- A significant dependence of UO_2 crystallographic orientation on aqueous dissolution rates was also observed.
- It has also been shown that UO_2 films can reproduce reactor irradiation damage structures by using light and heavy ion irradiation. Illustrating the initial lattice changes under proton irradiation and the apparent substitutional uptake of daughter fission products into the lattice.

Energy
For a Low Carbon Future

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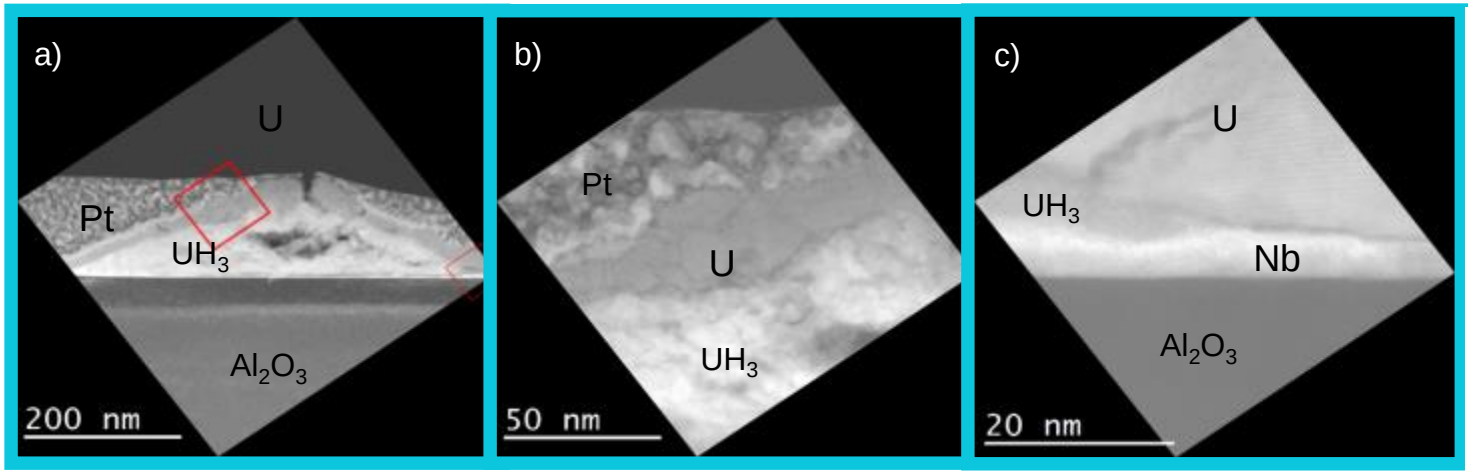
Fuel Materials Research (U-metal)

Springell, Scott, Darnbrough, Rennie, Hallam (Bristol)

New observations of U corrosion mechanisms by H_2O and H_2

- Thin film analogues of Magnox uranium with a thin oxide formed over a metal film shows H2 corrosion forms hydride at the oxide:metal interface.
- The rate of consumption of U metal, with a uniform oxide layer, appears to be dependent on the crystallographic orientation of the metal.
- When U metal forms hydride in thin film samples no crystalline material is observed
- U corrosion in air shows (using APT) formation of a thin ~10nm hydride layer at the oxide:metal interface.



High Resolution Scanning Transmission Electron Microscopy Annular Dark Field Images depicting the formation of a blister of lower density material in a uranium metal thin film showing no effect on the buffer layer a). The large volume expansion leads to cracks in the uranium metal b) region selected from centre left of a). Atomic resolution images of the blister tip show that the hydride formation is initially in an amorphous form c) region selected from right of a). TEM foil produced via Focused Ion Beam using Pt protective layer to protect the sample during milling.

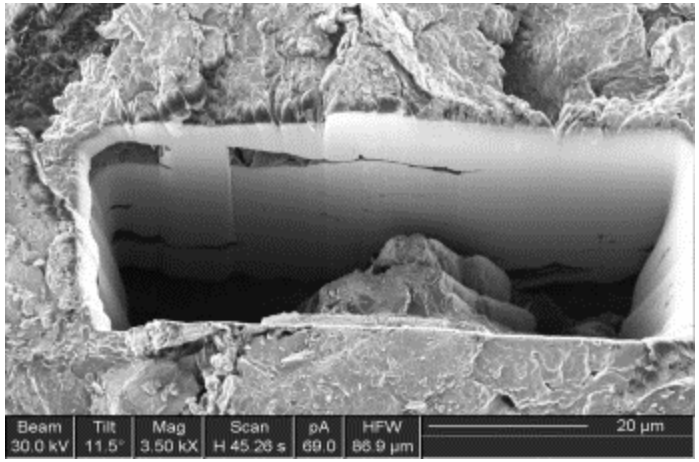
Fuel Materials Research (U-carbide)

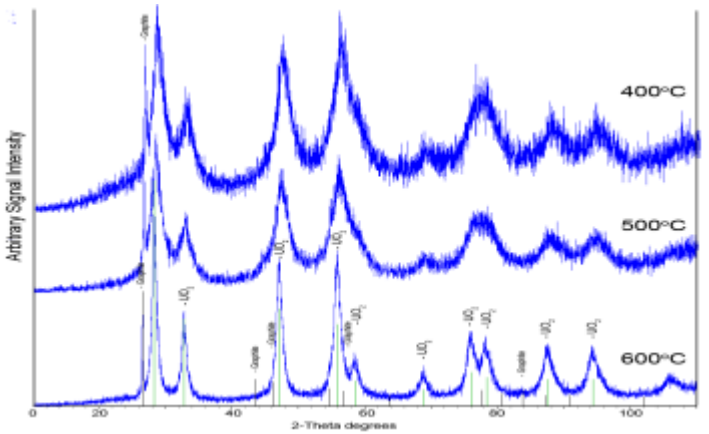
Lee and Gasparini (Imperial)

In situ observation of oxidation/corrosion

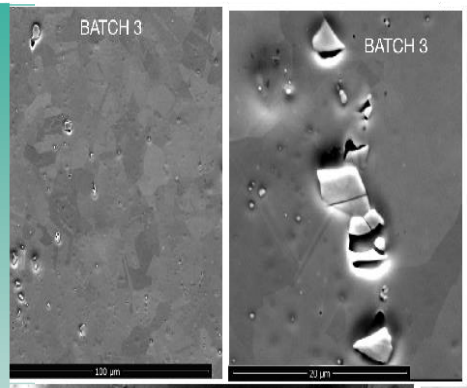
Focus on virgin UC pellets and ZrC (as an analogue) to simulate exotic fuel material from Dounreay

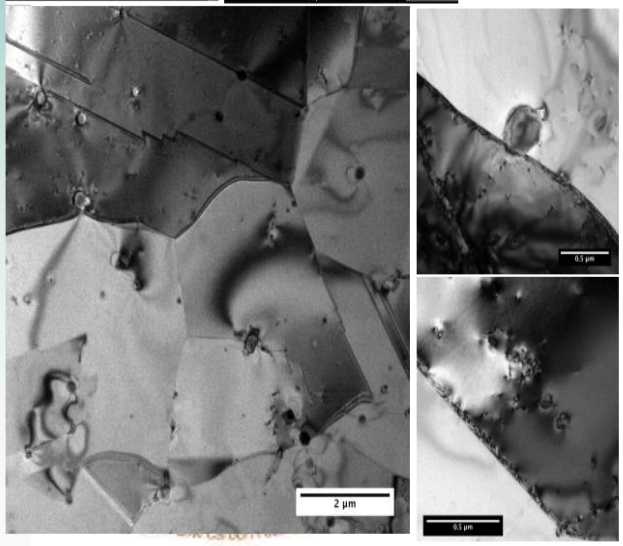
- Work has demonstrated controllable conversion of the carbide to oxide using thermal treatments in low partial pressures of air and water vapour. This is a much preferable waste form due to its much lower chemical reactivity.
- Work on carbide has yielded some amazing *in-situ* results which will help to quantify the volume expansion of the material during oxidation. This is a key consideration and will underpin the engineering design for scale-up of carbide processing.





XRD spectra of UC after controlled oxidation in water vapour at different temperatures.





Novel experiments at the University of Manchester have used the facility at the DCF to irradiated with intense beam of protons or heavy ions virgin cladding samples to reproduce the damage structures seen by the NNL in real irradiated clad via Post-irradiation examination at the Central Laboratory. Work is now focused on quantifying the extent and distribution of the microstructure damage using a suite of complementary materials analysis techniques.

Main Findings:

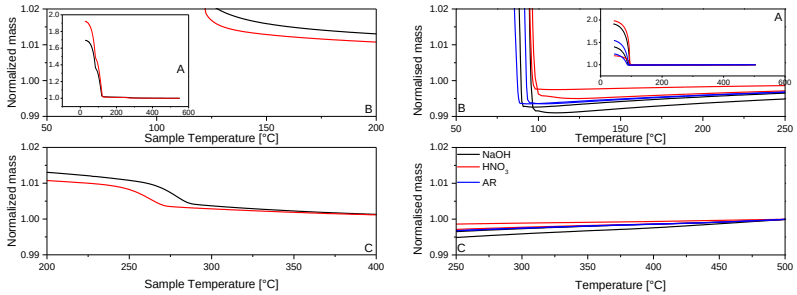
- Three different batches of 20Cr25Ni Nb-stabilised stainless steel have been so fare characterised. Work has been done in order to obtain similar microstructures in order to have a common starting point for accessing the effects of irradiation in the AGR cladding material.
- 12 samples have been irradiated with protons or iron ions using different conditions of temperature and damage.
- A set of fours samples, two irradiated with proton and two with iron ions, have been tested with nano-indentation in order to access the effects of ions irradiation on the mechanical properties of 20Cr25Ni Nb-stabilised stainless steel. The results show a radiation hardening effect on the material. The phenomenon is greater for proton irradiated specimen in respect to iron irradiated ones at the same conditions of dose and temperature.

Cladding Research (Drying processes)

James B. Goode, David Harbottle and Bruce C. Hanson (Leeds).

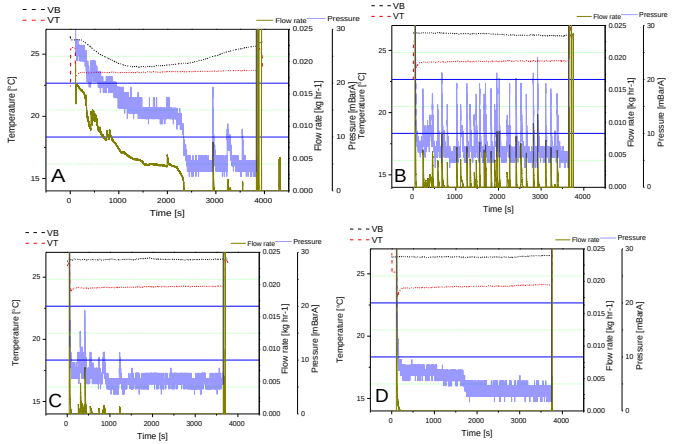
With UK reprocessing due to cease in 2018 dry storage is being considered as an interim storage option for AGR fuel. While this has been used successfully for Zircaloy clad LWR fuel the stainless steel cladding on AGR fuel will require a new safety case. **This work is looking at whether AGR fuel can be dried sufficiently to allow dry storage of AGR SNF.**

- TGA analysis of corroded SS has shown no moisture loss during heating indicating that the quantity of bound water on the surface is negligible. This means that water trapped within a failed pin is the major concern.



The TGA plot of corroded aluminium (left) shows a mass change around 270 C as the oxide dehydrates. The same is not observed for corroded SS indicating that there is minimal bound water.

- Experiments with a sample simulating a cracked fuel pin shows a change in drying behaviour as the mass of water inside the pin is reduced.



The four plots show how the drying behaviour changes as the mass of water is reduced. The initial high rate drops at a steady rate indicated by the drop in flow rate and pressure. This is followed by an erratic period with spikes in P and flow. The final drying behaviour is seen with a relatively constant pressure. The flow rate is below the LOD. Once all free water is removed there is a final drop in pressure.

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Theme 2: PuO_2 and Fuel Residues

PuO_2 during Interim Storage

Interim storage of PuO_2 involves sealing in inert steel containers. Under certain circumstances, these gas cans may pressurise; must be avoided in practice.

"*worker performing general housekeeping and relocating storage cans in the interim storage vault noticed plutonium bearing storage can was* ***bulging on both ends*** " – Lawrence Livermore National Laboratory 1994

5 routes to gas production have been suggested:

(i)Helium accumulation from α decay;

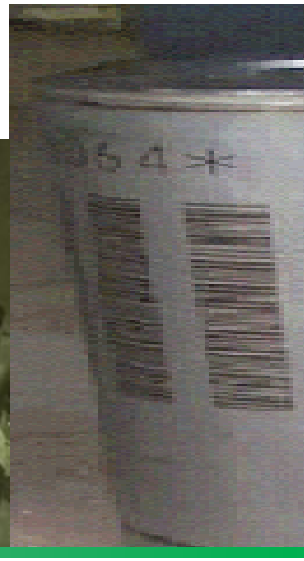
(ii)Decomposition of polymeric packing material;

(iii)H_2O desorption (steam) from hygroscopic PuO_2;

(iv)Radiolysis of adsorbed water;

(v)Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

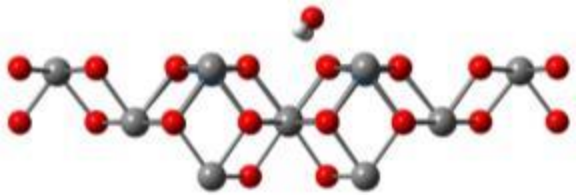
Last 3 all involve PuO_2/H_2O interactions and are complex, inter-connected & poorly understood.



Modelling water adsorption on UO_2 & PuO_2 - Nik Kaltsoyannis, Manchester

The interaction of water with the low index {111}, {110} and {100} surfaces of UO_2 and PuO_2 are modelled quantum mechanically using density functional theory at the embedded cluster (**Joe Wellington** – UCL) and periodic boundary condition (**Bengt Tegner** – Manchester) levels.

- Mix of molecular and dissociative water adsorption is the most stable on the {111} surface
- Dissociative water adsorption is most stable on the {110} and {100} surfaces ⇒ fully hydroxylated monolayer
- Water desorption temperatures at various pressures increase in the order {111} < {110} < {100} ⇒ alternative interpretation proposed for the two experimentally determined temperature ranges for water desorption from PuO_2



Water adsorbing molecularly on PuO_2 {110} surface

Outputs:

J.P.W. Wellington, A. Kerridge, J.P. Austin and **N. Kaltsoyannis** *J. Nucl. Mat.* **482**, 2016, 124 (DOI: 10.1016/j.jnucmat.2016.10.005).

B.E. Tegner, M. Molinari, A. Kerridge, S.C. Parker and **N. Kaltsoyannis** *J. Phys. Chem. C* 2017 (DOI: 10.1021/acs.jpcc.6b10986).

Highlighted in 'Nuclear power in the 21st century' by **N. Kaltsoyannis** and S.T. Liddle. *Chem* **1,** 2016, 652–662. Invited *Catalyst* article – see also reaction pieces by Dame Sue Ion and Dr Robin Taylor.

Chosen as a case study in the annual report to EPSRC of the Materials Chemistry High Performance Computing Consortium.

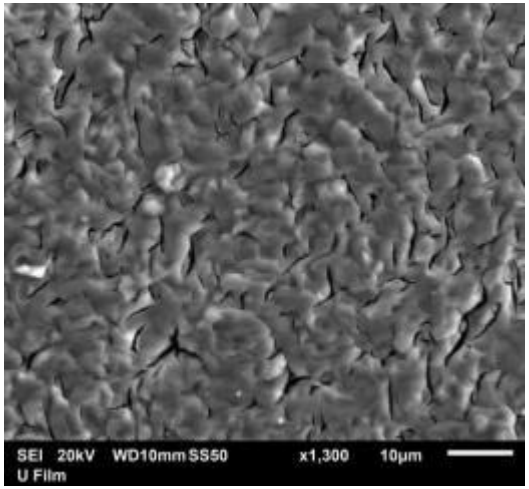
Measuring water adsorption on UO_2 & ThO_2 as PuO_2 surrogates – Colin Boxall, Lancaster

- The **Quartz Crystal** Nanobalance (QCN) measures in-situ mass changes at the surface of a piezoelectrode. Changes in mass, due to oxide formation or dissolution at the electrode surface or adsorption / desorption of gases, result in resonant frequency changes of the quartz crystal.
- Changes in frequency can be related to changes in mass through the Sauerbrey equation:

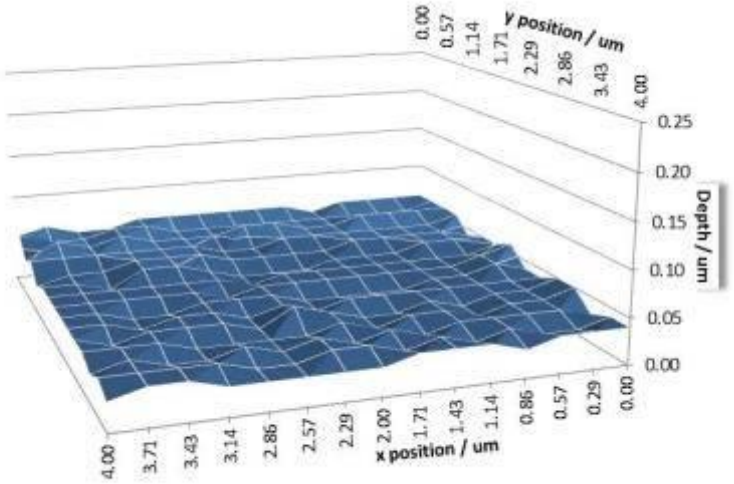
$$\Delta f = -\left(\frac{n{f_0}^2}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

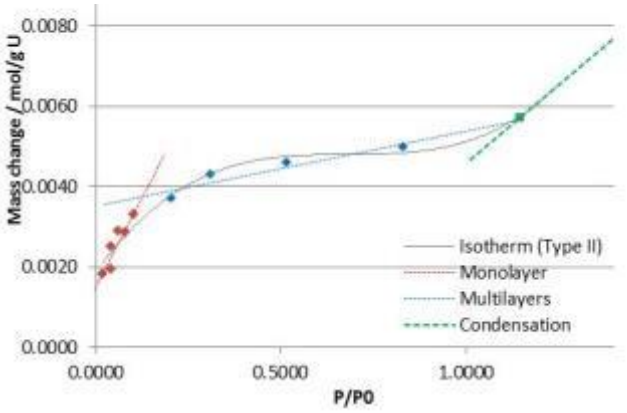
- Knowing the surface area of the metal oxide layer and the mass of water absorbed allows the number of layers to be accurately calculated.
- The differences in temperature at which water absorption/desorption occurs allows the thermodynamics to be determined, indicating which layers are chemi- or physio-sorbed.
- Studies of water adsorption at the surfaces of UO_2, ThO_2 and CeO_2 layers as PuO_2 surrogates being conducted by **Dom Laventine** – Lancaster
- Work about to move to Central Lab for studies on real PuO_2 samples

Measuring water adsorption on UO_2 & ThO_2 as PuO_2 surrogates



- UO_2 samples shown as example
- Data processed using BET Theory

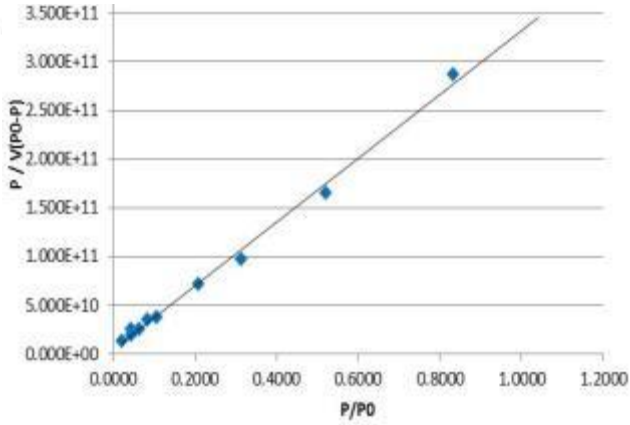




$$1/\left[Va\left(\frac{P0}{P}-1\right)\right] = \left(\frac{C-1}{V_M C}\right)\left(\frac{P}{P_0}\right)+\frac{1}{VmC}$$

V_m (UO_2)= 3.0 x 10^{-12} m^3

ΔH_{abs} (UO_2) = 54 $kJmol^{-1}$



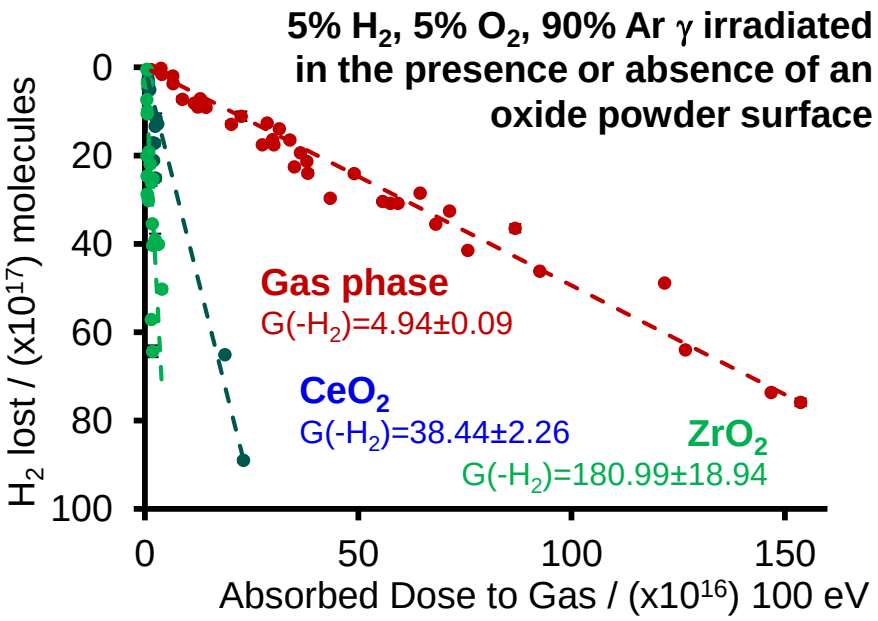
Outputs

- "Direct mass analysis of water absorption onto ceria thin films", D.Laventine, C.Boxall in "The Scientific Basis of Nuclear Waste Management", N.C.Hyatt, R.Ewing, Y.Inagaki, C.Jantzen (Eds), Cambridge University Press, Cambridge UK, MRS Advances., 6 pages (2017) DOI: 10.1557/adv.2016.671
- "Direct Mass Analysis of Water Absorption onto Ceria Thin Films" D.Laventine, C.Boxall, IChemE Sustainable Nuclear Energy Conference (SNEC) 2016, East Midlands Conference Centre, University of Nottingham, 12th–14th Apr 2016.
- "Direct mass analysis of water absorption onto ceria thin films" D.Laventine, C.Boxall, ATALANTE 2016, Le Courm, Montpelier, France, 5th–10th Jun 2016.

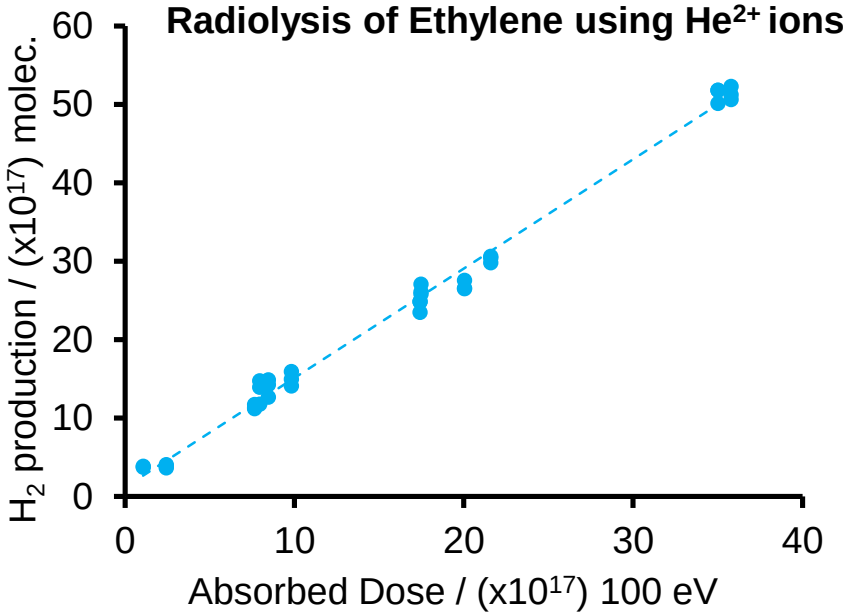
Understanding the behaviour of stored PuO_2 Effect of oxide surface on gas phase chemistry

- Studies of gas phase and surface chemistry of surrogate materials using He ion or gamma irradiation.
- Atmosphere and moisture content controlled.
- Analysis using gas chromatography.
- Experiments with PuO_2 powders in progress.

Luke Jones



- Oxide surface enhances H_2-O_2 recombination



- Radiolytic decomposition of gaseous organic.

Ceramics for actinide disposition – Sheffield PDRA, Shi Kuan Sun

Betafite $CaUTi_2O_7$ is a candidate ceramic for Pu disposition

Synthesis is difficult, yield <80%, and requires average U oxidation state >U^{5+}, e.g. by Ca excess $Ca_{1+x}U_{1-x}Ti_2O_7$

This is undesirable for geological disposal due to higher solubility of U^{5+}/U^{6+}

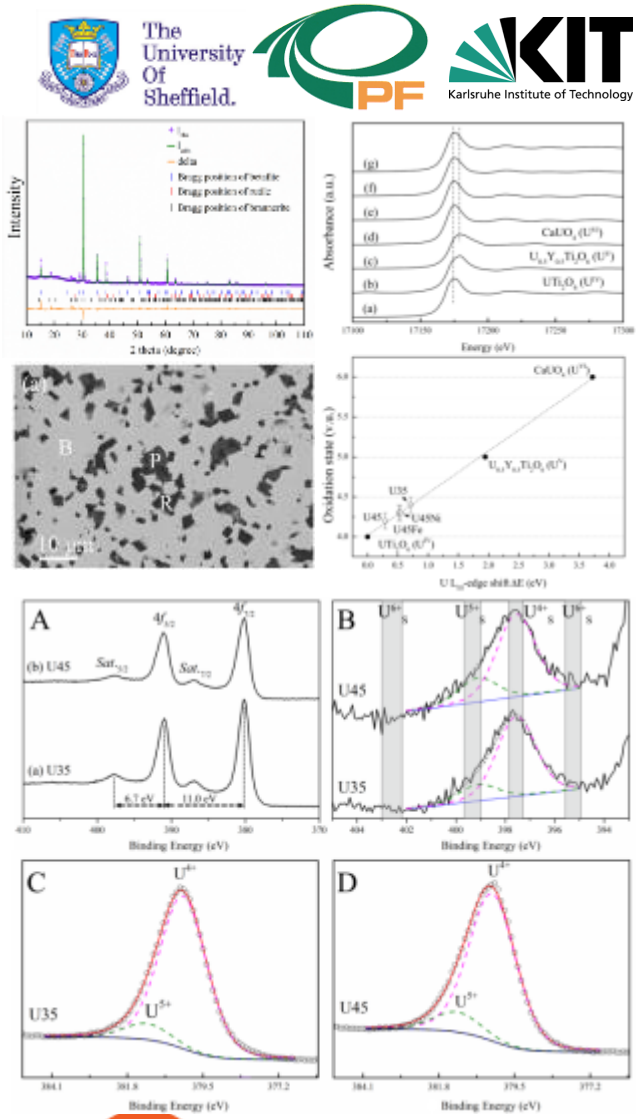
New approach, stabilisation of structure by ZrO_2 solid solution, with average U oxidation state close to 4+

- $Ca_{0.96}U_{0.48}Zr_{0.18}Ti_{2.20}O_7$ – yield 85%, av. $U^{4.3+}$
- $Ca_{0.87}U_{0.67}Zr_{0.16}Ti_{2.01}O_7$ – yield 96%, av. $U^{4.2+}$

Average U oxidation state determined by UL_3 XANES at NSLS and Photon Factory

Contribution of U^{4+}/U^{5+} solved uniquely by U 4f XPS studies at ITU Karlsrhue – possibility of U^{6+} definitively *excluded*

This research has optimised a leading Pu ceramic wasteform for disposal by control of U oxidation state



Publication: S. Sun *et al.*, *RSC Advances*, in submission, 2017

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Plutonium waste treatment options – Sheffield PhD projects

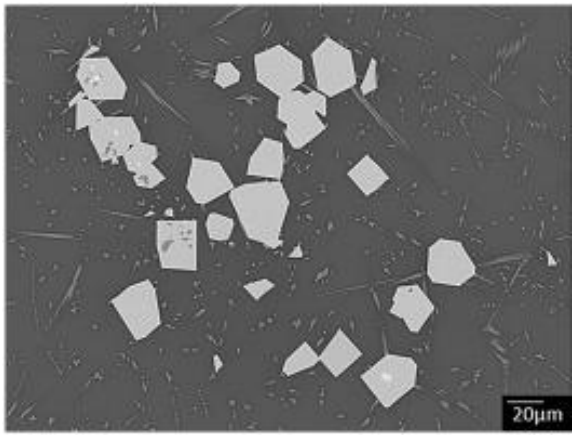
1: Hot isostatically pressed glass-ceramics for plutonium disposition; Steph Thornber

New formulation development – eliminated CaF_2 addition due to concerns regarding α,n reaction on ^{19}F

Optimised phase assemblage in favour of zirconolite, through ceramic / glass ratio

Determined mechanisms of Ce / U partitioning between ceramic / glass phase; NDA funding to undertake Pu studies at ANSTO

Publications: J. Nuclear Mater., 485 (2017) 253; 456 (2015) 461.

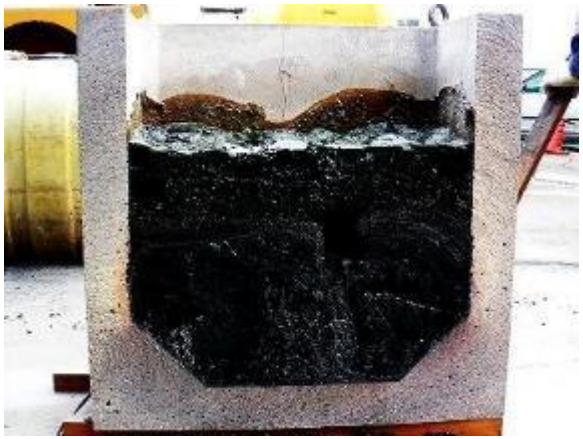


2: Processing and performance of vitrified higher activity wastes; Luke Boast

Successful vitrification of plutonium contaminated materials using recycled bottle glass

Vitrified products show very slow dissolution kinetics in simplified hyperalkaline fluid of cementitious disposal facility

Pilot scale vitrification studies performed at NNL in collaboration with Kurion using Geomelt system



UK Plutonium disposition strategy – Sheffield, Neil Hyatt

UK plutonium management policy states: *any remaining plutonium which is not converted into MOX fuel, or otherwise reused, will be immobilised and treated as waste for disposal*

Is MOX as technically mature as assumed?

US MOX fuel fabrication facility (MFFF) is projected to be at least $6 billion over budget and 15 years late

UK MOX scenario utilises same MELOX reference design as MFFF and could be vulnerable to similar difficulties

- Additional need for plutonium pre-treatment
- Unrealistic design assumptions; inadequate review / challenge
- Substantive design variation during build
- Inadequate supply chain capability

Conclusion: UK Strategy would be significantly de-risked if stockpile immobilisation option developed in parallel

Analysis presented at House of Commons, All Party Parliamentary Group on Nuclear Energy.

Publication: N.C. Hyatt, Energy Policy, 101, 303-309, 2017.

The University Of Sheffield.

Image: Shaw Areva MOX Services

Energy Policy

Plutonium management policy in the United Kingdom: The need for a dual track strategy

Neil C. Hyatt

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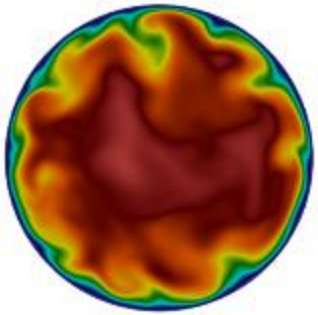
Theme 3: Legacy Ponds and Silo Wastes

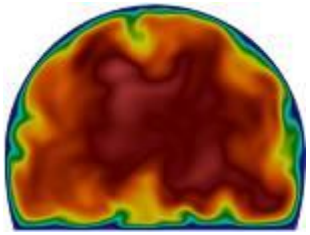
Sludge Mobilisation and Transport – Leeds PDRAs

Project: Measurement and Modelling of Sludge Mobilisation and Transport (D Njobuenwu and H Rice)

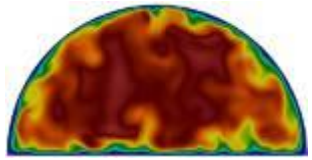
- **Experimental programme with horizontal critical deposition velocity (CDV) and vertical in-line rheometry (ILR) pipe flow measurements completed; results to form two papers**
- **CDV: extension of existing model [1] to intermediate solid fractions, including bed packing and interparticle effects using seven test materials**
- **ILR: validation of velocimetry-pressure drop method, including rheological modelling with three test materials (barite, calcite, $Mg(OH)_2$)**



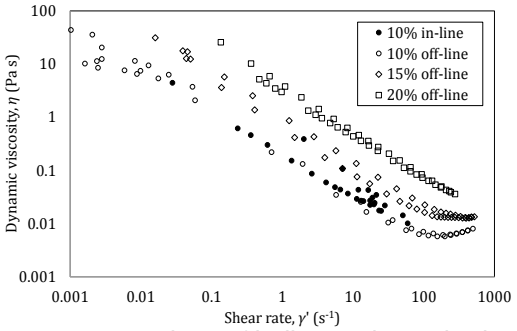
LES of full pipe flow
With Re = 53,000



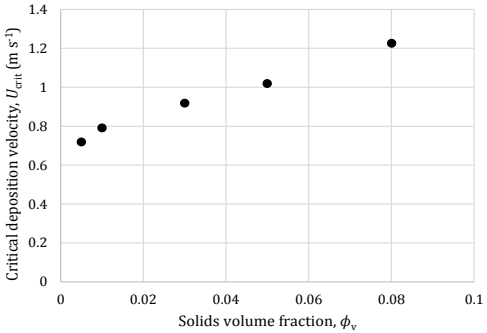
LES of pipe flow with
a quarter bed height



LES of pipe flow with
a half bed height



Comparison of in-line and standard off-line rheometry with calcite



Critical deposition velocity of non-spherical plastic particles

- **Large eddy simulation (LES) of pipe flow with variable bed heights to mimic flows with stationary homogeneous beds performed**
- **Discrete particle simulation (DPS) CFD code with capability to predict particle transport, collision, agglomeration, deposition and breakup developed and verified in turbulent channel flows.**
- **Implementation of developed LES-DPS code on fully-developed pipe flow with variable bed heights in progress, with validation against experimental measurements underway**

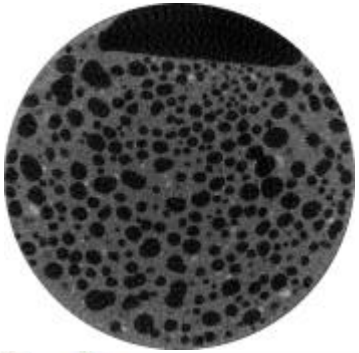
[1] Rice HP, Fairweather M, Peakall J, Hunter TN, Mahmoud B, Biggs SR, 2015, *Constraints on the functional form of the critical deposition velocity in solid-liquid pipe flow at low solid volume fractions.* Chem Eng Sci, 126. 759-770.

DISTINCTIVE

Gas retention and sludge characterization – Leeds PhDs

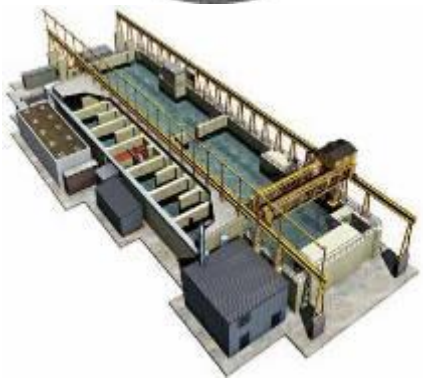
Project: Gas retention and release from nuclear legacy waste (M Johnson)

- Used x-ray computed tomography to characterise the growth and release of hydrogen bubbles within consolidated beds of nuclear cladding and fuel corrosion products in order to mitigate against large periodic gas releases



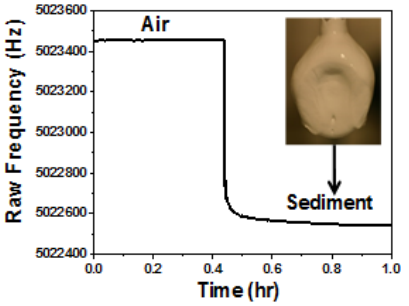
Project: Characterisation of flocculated dispersion using acoustic backscatter systems (A Tonge)

- Determined concentration profiles in flocculated systems using ultrasonic backscatter so that sludge settling and transport operations can be performed with greater efficiency



Project: Quartz crystal microbalance as a tool to measure sludge rheology (A Botha)

- Air-to-sample frequency and resistance shift of quartz crystal microbalance measured and compared to shear yield stress of sludge suspensions using vane viscometry. This will ultimately allow *in-situ* rheological measurements to be made on site.



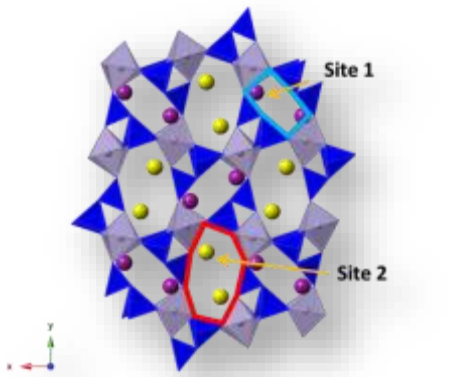
Energy
For a Low Carbon Future

DISTINCTIVE

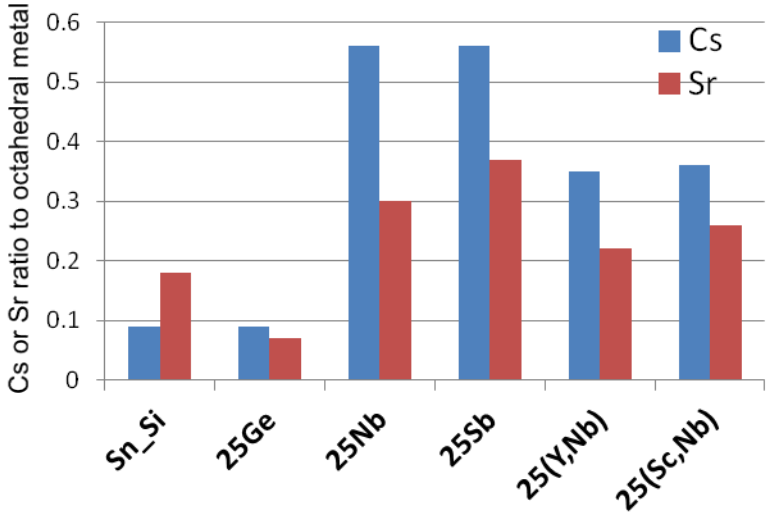
New ion exchange materials – Birmingham PDRA & PhD

Project: New Ion Exchange Materials (T-Y Chen and R George)

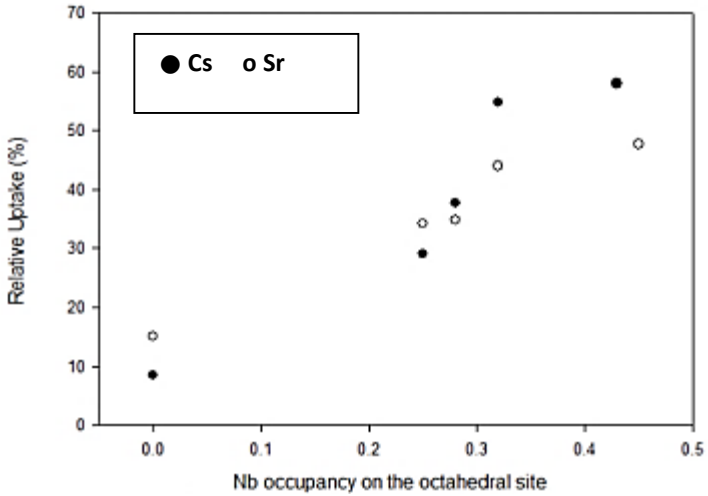
- **Preliminary exploration of a range of metal silicates and germanates, testing for Cs^+ and Sr^{2+} uptake especially in the presence of competing cations**
- **Strong focus on umbite materials such as $K_2[SnSi_3O_9]\cdot H_2O$ and $K_2[ZrGe_3O_9]\cdot H_2O$ which should thermally transform into dense wadeite phases suitable as long-term immobilisation ceramics**
- **Complementary atomistic modelling started by T-Y Chen based on industrial placement at NNL with Mark Bankhead**



Umbite structure for $M_2[M'X_3O_9]\cdot H_2O$ where M (sites 1 & 2) is an exchangeable cation, e.g. K^+, M' (grey) is an octahedral metal , e.g. Zr^{4+}, and X (blue) is a tetrahedral metal, e.g. Si^{4+}



Cs and Sr uptake in batch tests. The materials (left to right) are the parent $K_2[SnSi_3O_9]\cdot H_2O$, 25% Ge for Si, 25% Nb for Sn, 25% Sb for Sn, 12.5% each Y and Nb for Sn and 12.5% each Sc and Nb for Sn



Uptake of Cs or Sr for K in $K_{2-x}(Sn_{1-x}Nb_x)Si_3O_9\cdot H_2O$

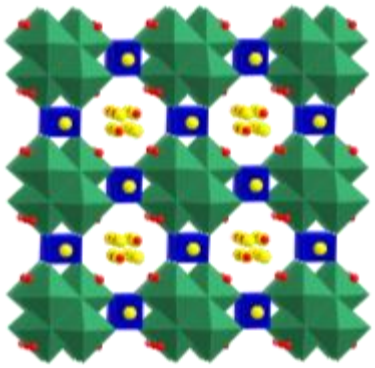
A manuscript for the tin silicate work is in preparation, the germanium work has been published: R George and JA Hriljac, "Umbite Type Zirconium Germanates for Cs Removal", Scientific Basis for Nuclear Waste Management, MRS Advances, 2017

DISTINCTIVE

Ceramic waste forms for spent ion exchange media – Birmingham PhD George Day

Project: Studies of ceramics formed by HIPing Cs and/or Sr-exchanged IONSIV IE-911

- IONSIV IE-911 is a mixture of Nb-doped CST ($Na_{0.4}(H_3O)(Ti_{1.4}Nb_{0.6})O_3SiO_4 \cdot 2H_2O$) and a $Zr(OH)_4$ binder, it has been used in the UK, US and Japan for Cs and Sr removal
- Previous work of T-Y Chen showed HIPing Cs-exchanged IONSIV produces a mixed ceramic with $Cs_2TiNb_6O_{18}$ as the Cs phase up to 6 wt% loading



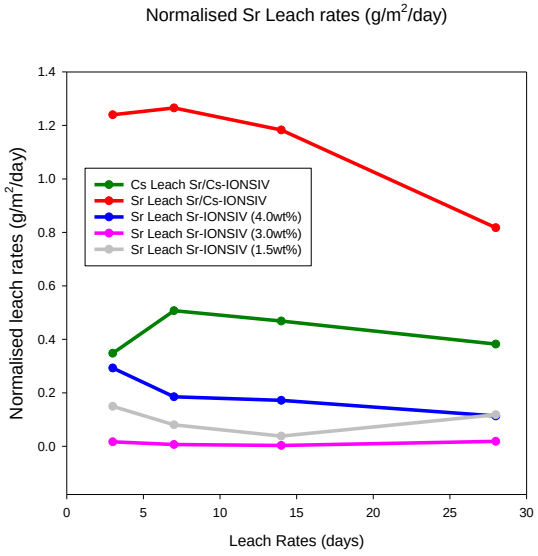
CST

Study 1

- *Will $Cs_2TiNb_6O_{18}$ retain Ba^{2+} formed by transmutation of Cs^+ via reduction of some Ti^{4+} to Ti^{3+} or Nb^{5+} to Nb^{4+}?*
- Extensive experimental doping studies have so far failed to conclusively show Ba^{2+} incorporation
- New potentials have been derived for atomistic modelling of these systems and predict the experimental results as well as stability of Ba^{2+} in hollandite, hence can guide future work

Study 2

- *What phases form from Sr-exchanged or Sr- and Cs-exchanged IONSIV?*
- Sr predominantly partitions into a perovskite of formula $(Na,Sr)NbO_3$
- $Cs_2TiNb_6O_{18}$ still forms even in mixed systems
- All systems show low Sr leach rates

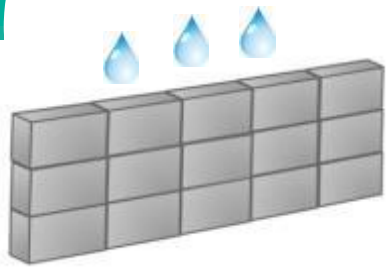


- A potential wasteform for Cs immobilisation: synthesis, structure determination, and aqueous durability of $Cs_2TiNb_6O_{18}$, T.-Y. Chen, E. R. Maddrell, N. C. Hyatt and J. A. Hriljac, *Inorg. Chem.* **55**, 12686 (2016).
- The solubility of Ba in a new Cs waste form, $Cs_2TiNb_6O_{18}$, G. Day, G. L. Cutts, T.-Y. Chen, J. A. Hriljac and Y. Guo, *MRS Advances* (2017)

DISTINCTIVE

Theme 4: Structural Integrity

Cementitious materials for nuclear industry



“Low-pressure silica injection for porosity reduction in cementitious materials”

R. Maddalena, A. Hamilton. Journal of Construction and Building Materials, 2016

*In the first research article we describe a new technique to “**heal**” cracks in concrete structures and reduce the water flow, using silica nano-particles.*

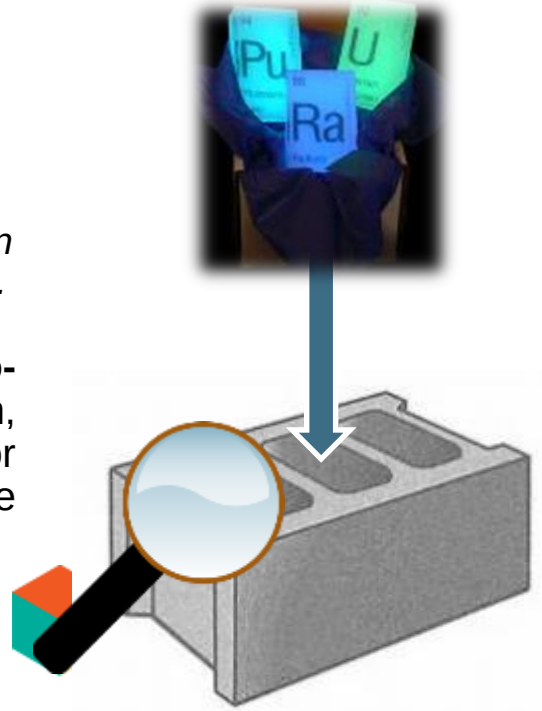
In structures housing radioactive waste, ‘impermeabilisation’ of building materials is an important feature in order to contain waste and **prevent leaking** into the environment.

“A novel synthesis process for calcium silicate hydrate gel (C-S-H) with tobermorite-like structure”

R. Maddalena, A. Hamilton. In submission, 2017

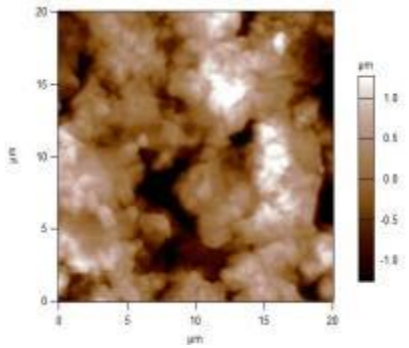
In this research article we describe a novel synthesis process for the production of C-S-H gel, a mineral phase responsible for strength in cement and concrete.

Using different analytical techniques it is possible to study at the **micro-scale** the interaction between **radionuclides** (e.g. Plutonium, Uranium, Caesium etc) and the building material structures, such as cement or concrete. Therefore materials can be **tailored** in order to enhance mechanical and physical properties

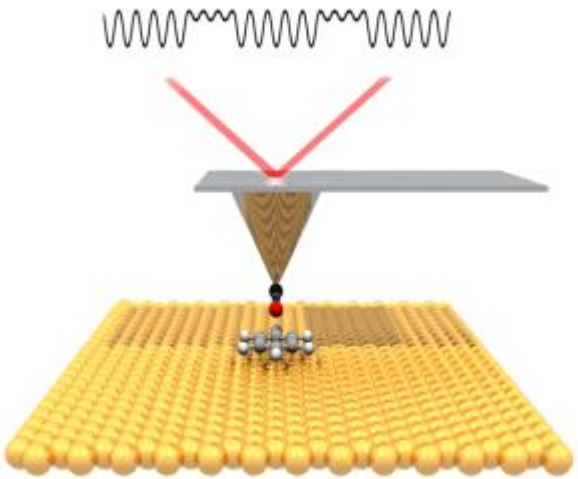


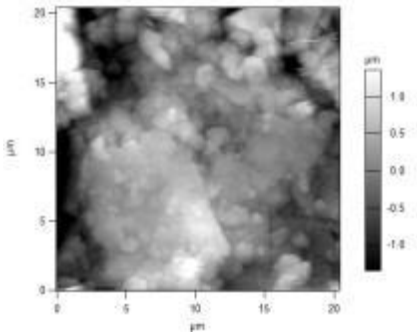
Investigation of cement properties at micro-nano scale

AFM characterization

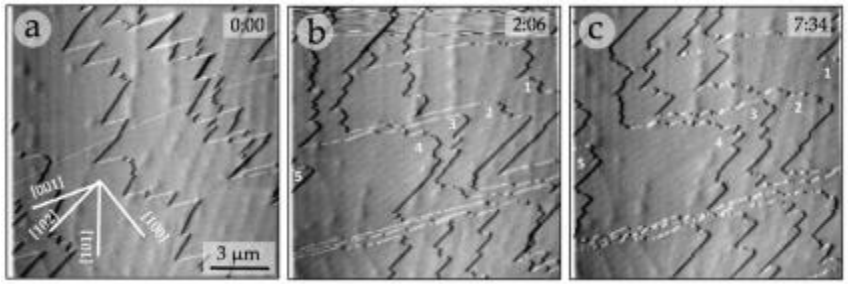


Surface characterization at the atomic level to study reaction effects in situ (hydration, carbonation, ionic substitution).





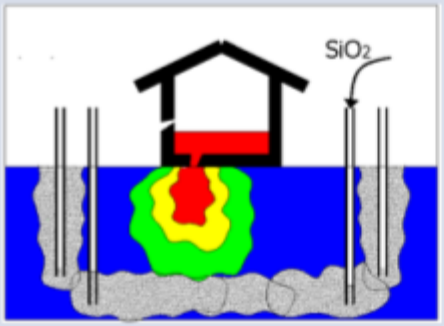
Crystal growth and dissolution of mineral phases contained in the cement (Portlandite,Calcite,Ettringite) examining behaviour in different environments.



Use of colloidal silica grout for ground barriers in decomissioning

THE PROBLEM

Colloidal silica based grouts for formation of **ground barriers**.

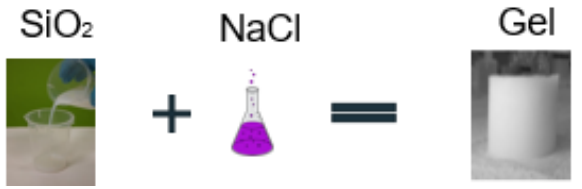


SITE APPLICATIONS

- Vertical hydraulic barriers
- Horizontal hydraulic barriers
- Ground sealing
- Combined hydraulic & mechanical improvement

"An analytical model for the control of silica grout penetration in natural groundwater systems" (Under review)

Colloidal silica hardens when an accelerator is added.

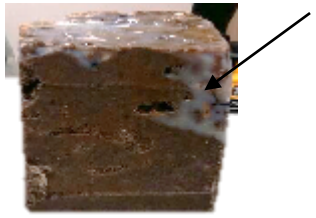


We are now able to **tailor the accelerator** to mix with colloidal silica to achieve the required hardening time under different environmental conditions (e.g. saline water)

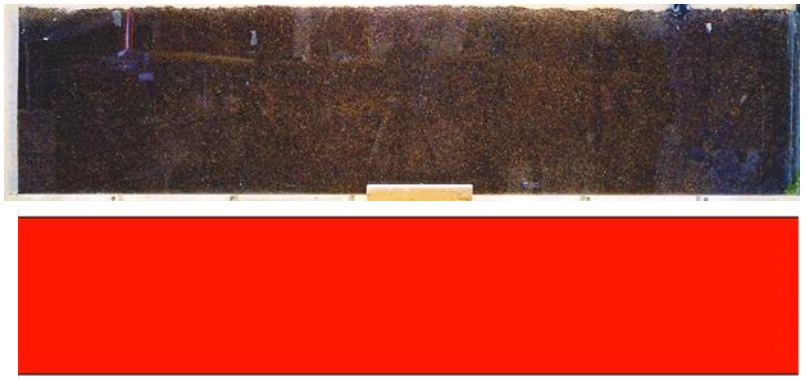
"Colloidal silica injection as ground mechanical-improvement technology" (Under review)

"Hydraulic characterisation of colloidal silica-grouted sand upon dry-wetting cycles" (Draft)

Mechanical characterization and evolution of **permeability** of grouted soil under different environmental conditions.



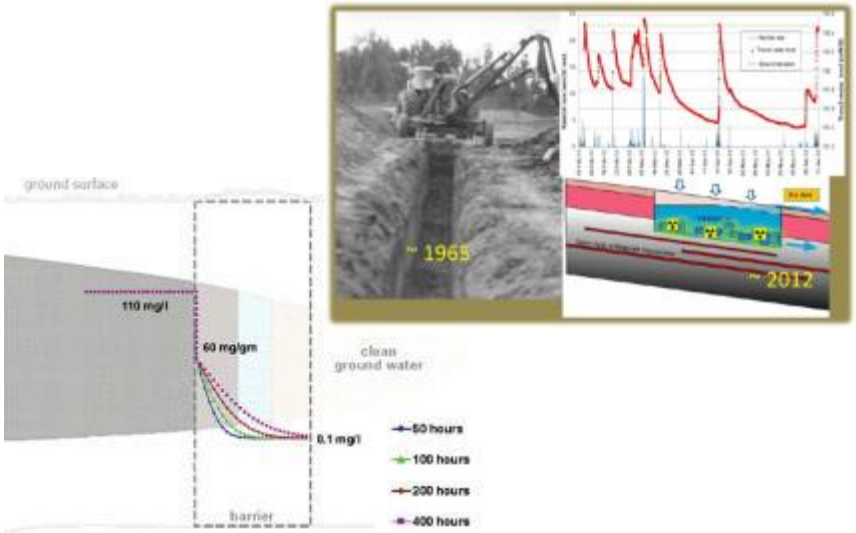
"Numerical simulation of laboratory-scale injections of colloidal silica into sandy soil" (Draft)



DISTINCTIVE

Use of colloidal silica grout for ground barriers in decomissioning

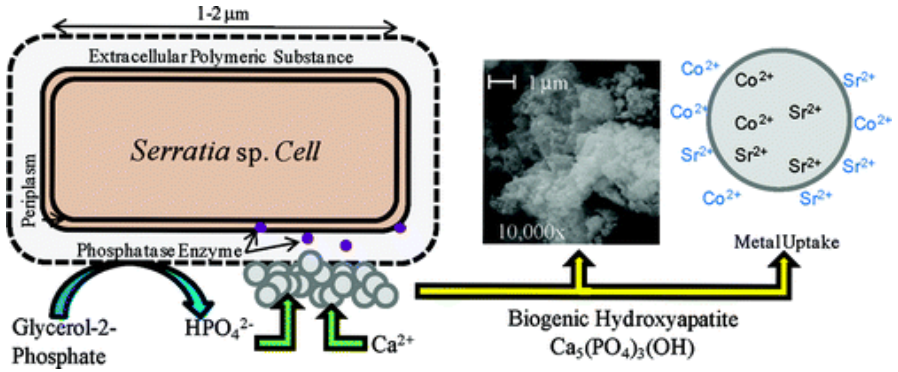
Behaviour of radioactive elements in soil, waste and colloidal silica grout



Radioactive elements in soil and waste will be affected by grout injection

How do these behave in soil and waste before and after grouting?

Improving the retention of radionuclides in colloidal silica grout



Microbes make minerals with high adsorption capacity and incorporate radionuclides in structure

Can we promote such (bio)mineralisation within colloidal silica grout after gelling?

DISTINCTIVE

Summary

- Program is well matched to the strategic needs of the UK industry in the area of nuclear waste management and decommissioning
- Well planned and organised
- High quality science and engineering R&D linked to real-life waste management issues
- Network of effective partnerships and collaborations
- Active facilities and materials
- Impact, visibility, communication
- Training the next generation
- With cleanup programs spanning many decades, the UK needs a supporting coordinated R&D effort like this well into the future

Sellafield Ltd

Impact of the DISTINCTIVE programme on work at Sellafield

Andrew Cooney, Technical Manager, Sellafield Ltd

Why we work universities?

- Innovation, to reduce the cost and risk of decommissioning.
- Mitigate risk/uncertainty, gaps in knowledge related to our operations
- Pipeline of future technical personnel, especially specialists.
- Peer review capability, perhaps for where we have singleton expertise.
- Engaging our workforce with academics.
- Academic advocacy, senior academics often act positively on our behalf.

Background

- SL work with NNL to supervise relevant projects.
- One of a number of methods of commissioning work with Universities.
- Perhaps 60 relevant projects
- We contribute perhaps £0.5m directly plus resources into an £8m programme across all the themes.
  - Theme 1 - AGR, Magnox and Exotic Spent Fuels
  - Theme 2 - PuO2 and Fuel Residues
  - Theme 3 - Silo Ponds and Legacy Wastes
  - Theme 4 - Structural Integrity

Effluent Treatment

- The industry tends to be Plan A, delivering mission focussed
- Working with Universities, low SRL research work, enables us to look more broadly. Looking perhaps 5 to 10 years into the future.
- Effluent work established by Simon, Like and other's in Theme 3 will support work we are planning now to address how we will deliver the effluent management challenges arising during the POCO phase.

Plutonium Dioxide – Theme 2.

- Understanding the Interfacial Interactions of Plutonium Dioxide with Water – Luke Jones, (Manchester / DCF) is now working with real material in B170 with NNL doing measurements on H2 generation / recombination relevant to how we will open cans for SRP or similar plant and whether we need to worry about flammable / explosive atmosphere's as we do so.
- Understanding surface species and interactions between adsorbed chloride and water on stored PuO2 – Sophie Sutherland-Harper, Manchester - Sophie has been in B170 taking real measurements on our Cl contaminated material that will feed into SRP or similar process for stabilisation. She has now moved onto ITU in Germany where she'll being doing similar work but with a wider range of analytical equipment. NGN, not DISTINCTIVE but its all really part of the same effort.
- Modelling the surface chemistry of PuO2 at the molecular level – Bengt Tegner, is helping to understand the experimental findings from the others using his modelling.
- Computational modelling of PuO2 ageing and fuel residues- Nathan Palmer, Birmingham - Nathan will produce useful results for us on helium in PuO2 but is 1 year behind the rest.

Acoustic Back Scattering technique – Theme 3

- Evolved from a Diamond project to monitor gravity settlers in real time in an Innovate UK partnership with University of Leeds and MMI taken to TRL 5.
- Now prototype being installed in legacy fuel storage pond
- Supported by a DISTINCTIVE PhD at Leeds exploring the acoustic behaviour of suspensions of different waste materials (Alastair Tonge).
- Maximising the success of this approach requires the ability to model the system and Leeds (Derrick Njobuenwu) have been collaborating with MMI as commercial modellers as part of the process.
- monitoring and controlling gravity settlers is only on part of sludge and slurry processing challenge, understanding what is happening in pipes is also vital and work on pipe flows (Hugh Rice) is also underway at Leeds with a view to developing techniques to reliably measure critical transport velocities and solids deposition in pipes.
- A single pipe blockage can take several weeks to recover …. order of £50m.
- The technology could accelerate 7 year hazard reduction (emptying of the tanks) by more than 1 year, savings in the order of £10m

Conclusions

- Looking forward to building on Distinctive.
- Increase alignment between our needs and academic programmes drive for industrial outcomes
- Recruitment leaflet

So what next, what have you observed?

- Thanks to
  - Geoff, Martyn and Paul for insight into projects they supervise
  - Lois for data
  - You guys for the opportunity to talk and taking part in this programme.

Actinide Research at Bristol

York 2017

T.B. Scott, S Rennie, A Banos,
H Paraskevoulakos, K Wyness, L Costelle,
J.E. Darnbough, R.S. Springell

IAC

University of BRISTOL

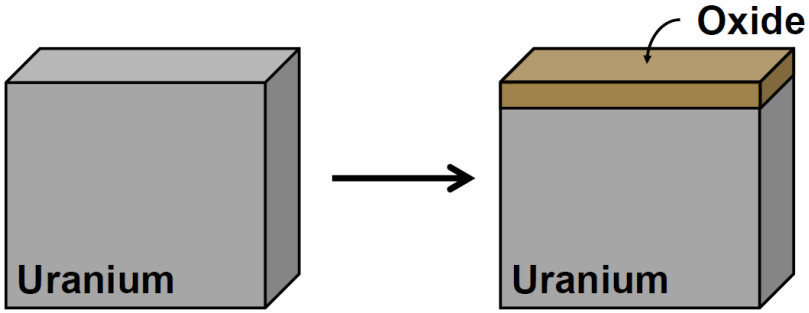
DISTINCTIVE

Bristol DISTINCTIVE Topics

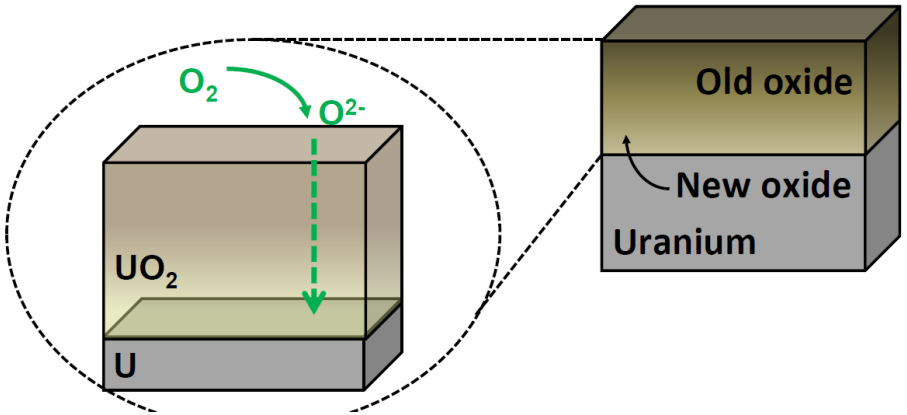
- Uranium hydriding in aqueous environments
- Corrosion of Uranium in grout (Harris 14:40 Tomorrow)
- Investigations into Radioactive Sludge (Kate 9:50 Tomorrow)

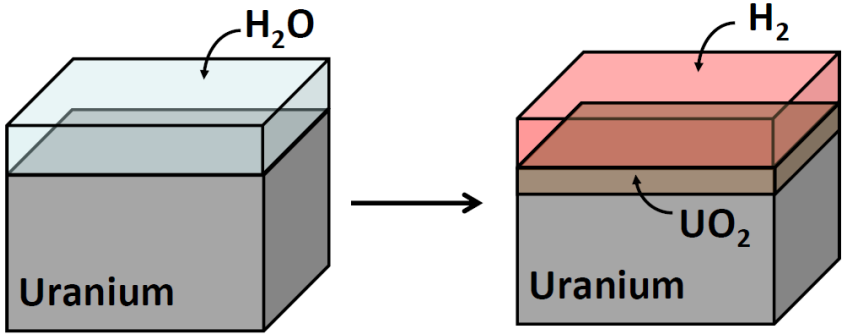
- Uranium Dioxide thin films
- Electrochemistry of uranium corrosion
- The initiation of uranium hydriding under oxide layers
- Actinide thin films

Uranium Metal Corrosion

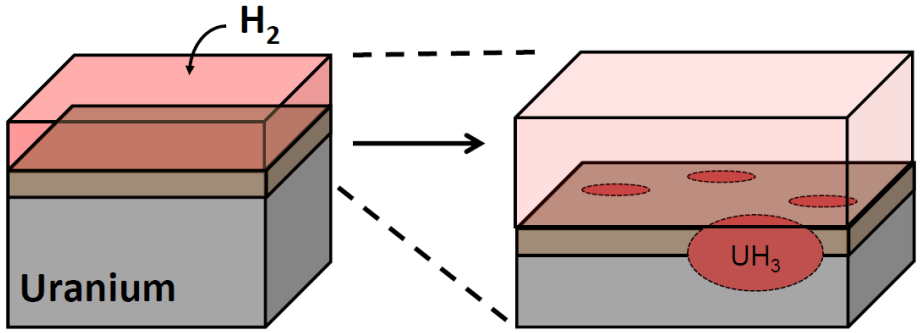


$$U + \left(\frac{2+x}{2}\right) O_2 \rightarrow UO_{2+x}$$

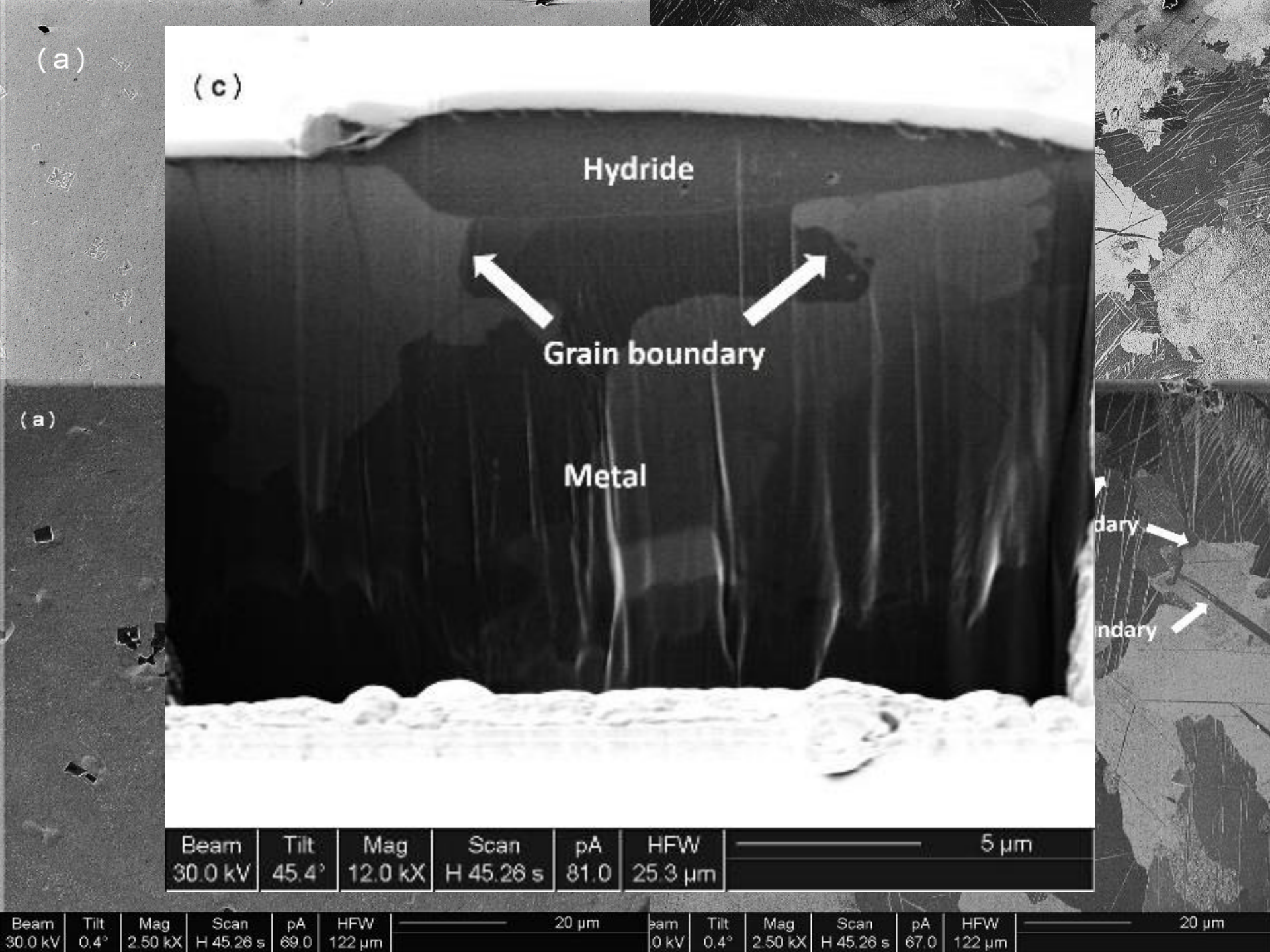




$$U + H_2O \rightarrow 2UO_2 + H_2$$

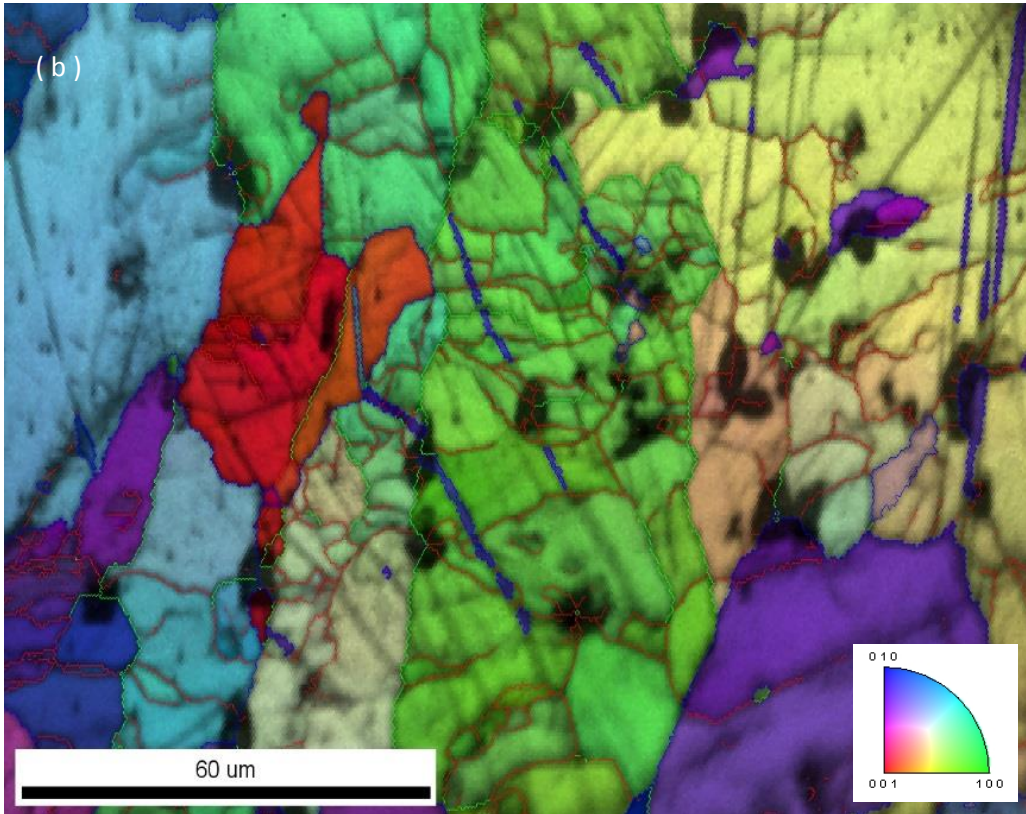


$$2U + 3H_2 \rightarrow 2UH_3$$


(a)
(c)
Hydride
Grain boundary
Metal
(a)
dary
ndary
Beam 30.0 kV
Tilt 45.4°
Mag 12.0 kX
Scan H 45.26 s
pA 81.0
HFW 25.3 µm
5 µm
Beam 30.0 kV
Tilt 0.4°
Mag 2.50 kX
Scan H 45.26 s
pA 69.0
HFW 122 µm
20 µm
eam 0 kV
Tilt 0.4°
Mag 2.50 kX
Scan H 45.26 s
pA 67.0
HFW 122 µm
20 µm

Bulk Uranium Hydriding

- Blisters at Triple points and high angle grain boundaries
- High diffusion paths
- Free surfaces with lower density than crystalline material

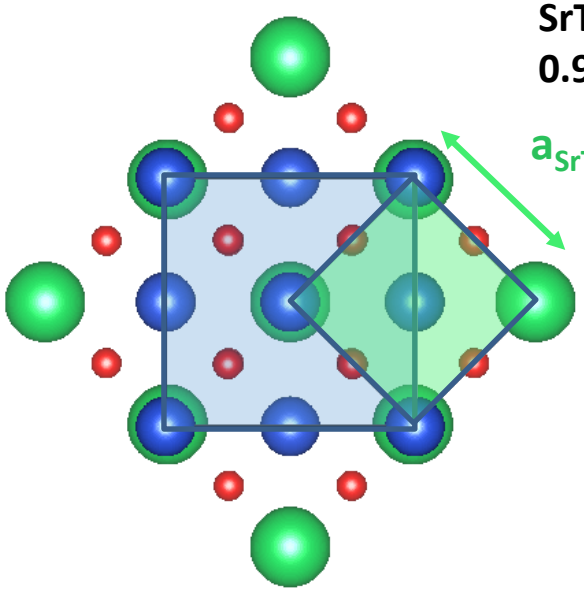


Utilisation of thin films for Actinide Investigation

- Uranium Dioxide Investigations
  - Epitaxial single crystals, Epitaxial matched poly-crystalline or Nano-crystals
  - Corrosion behaviour in radioactive environments
  - Effect of Irradiation
    - Protons, alpha, Xe and Cs
  - Irradiation damage effect on corrosion

DC Magnetron Sputtering

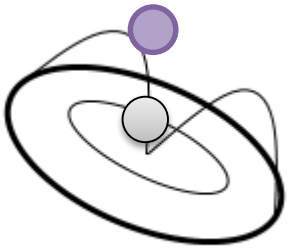
- Reactive sputtering in a partial pressure of oxygen at temperature on a matching substrate



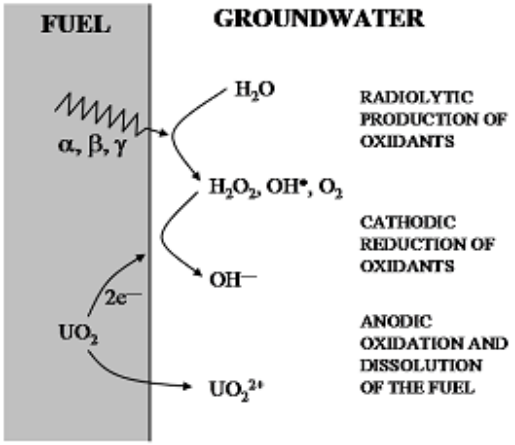
$SrTiO_3$ [001]:UO_2 [001]
0.97% Mismatch

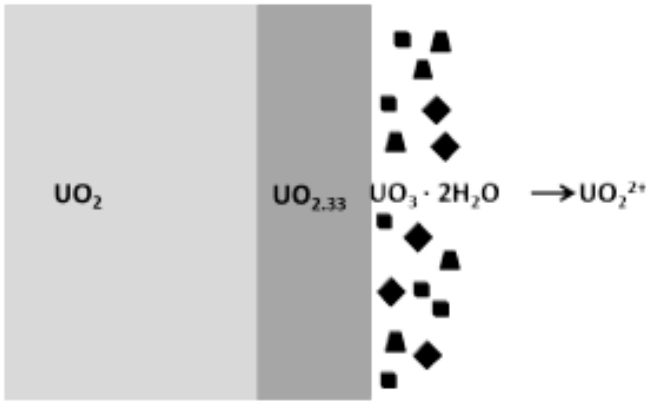
a_{SrTiO3} = 3.91 Å

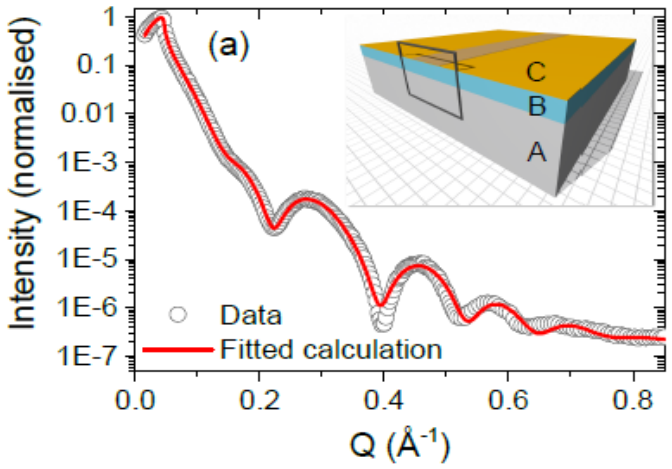
a_{UO2} = 5.47 Å

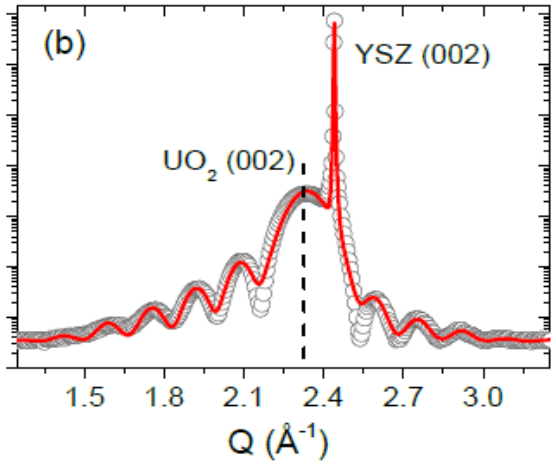


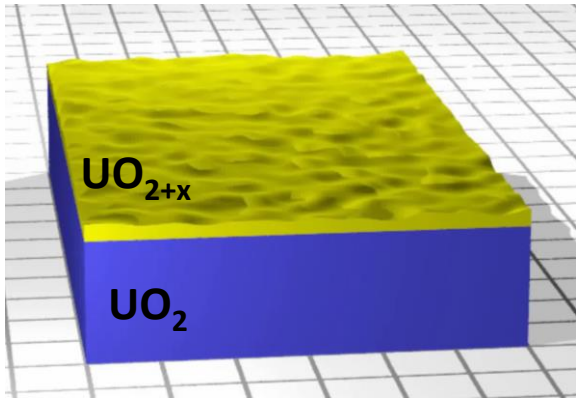
Corrosion of UO_2 thin films

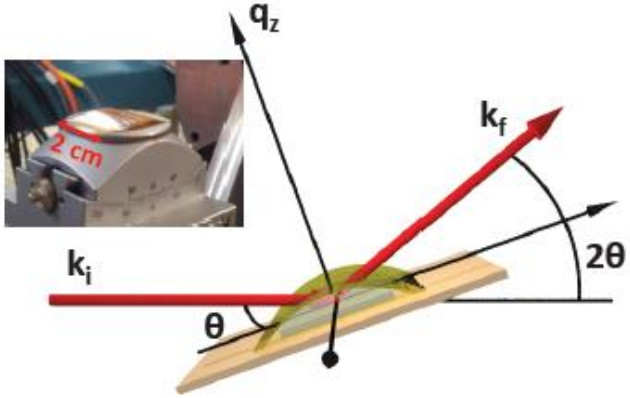










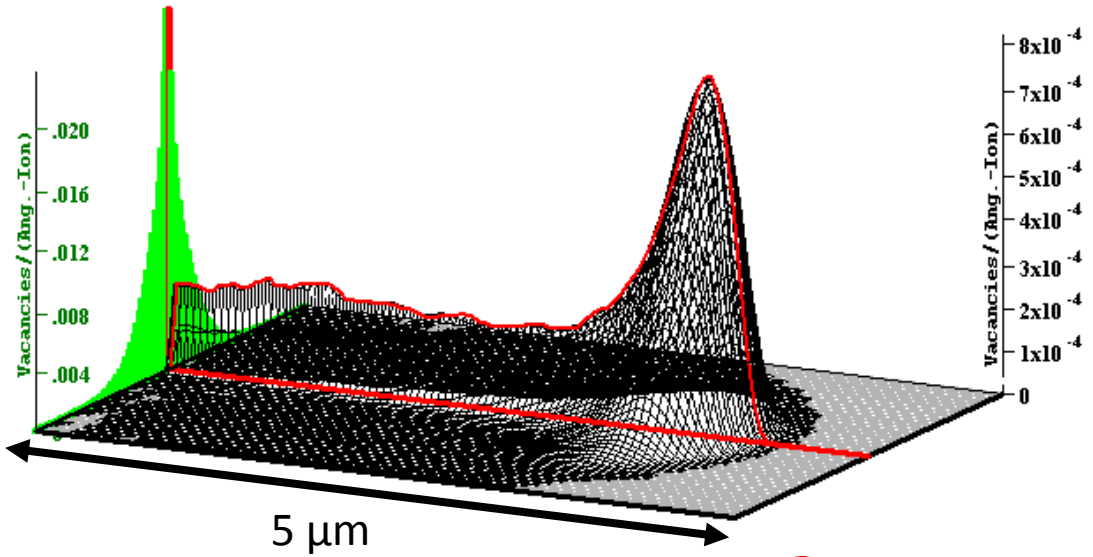


Reflectivity 1) electron density as a function of depth.
2) total thickness
3) interfacial roughnesses

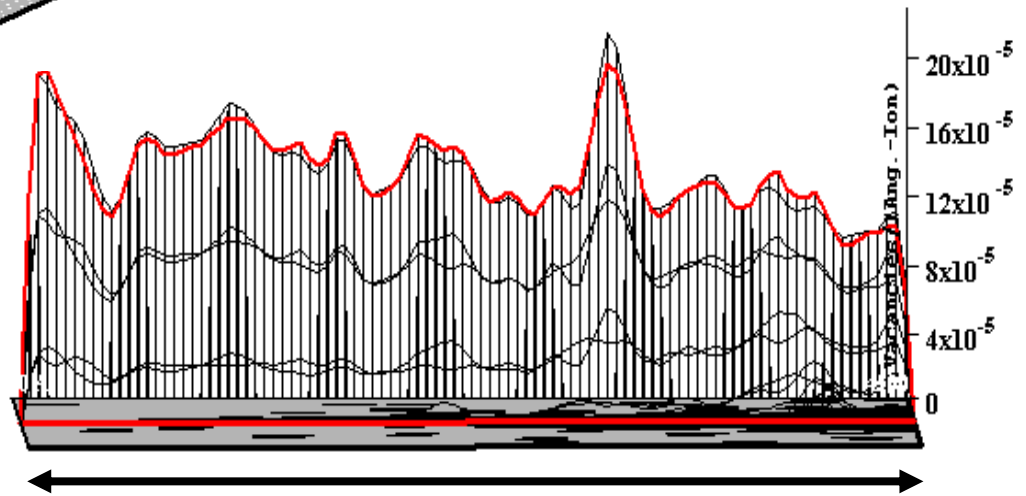
High angle 1) number of lattice planes contributing (i.e. thickness of crystalline material)
2) total thickness
3) surface roughness

1×10^{12} photons/s, at 17.116 keV

He^{2+} damage profile

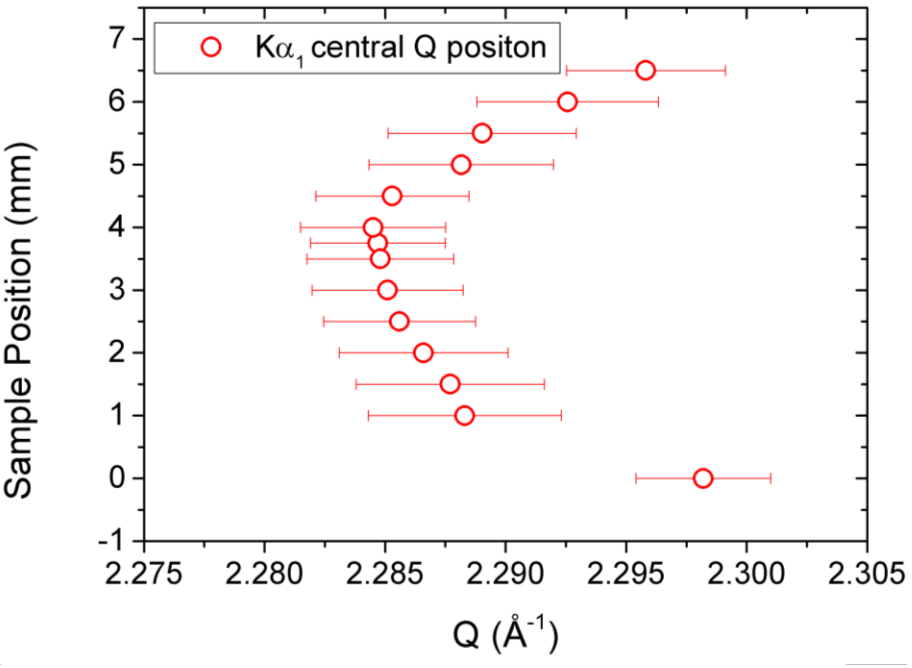


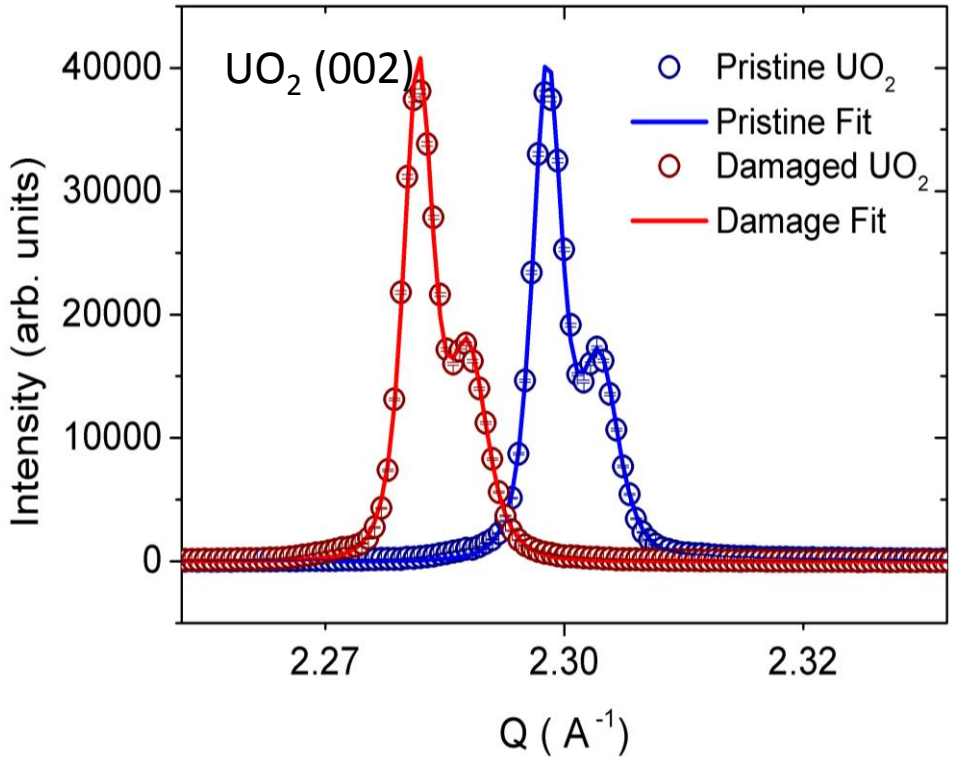
5 µm



450 nm

He^{2+} damage profile



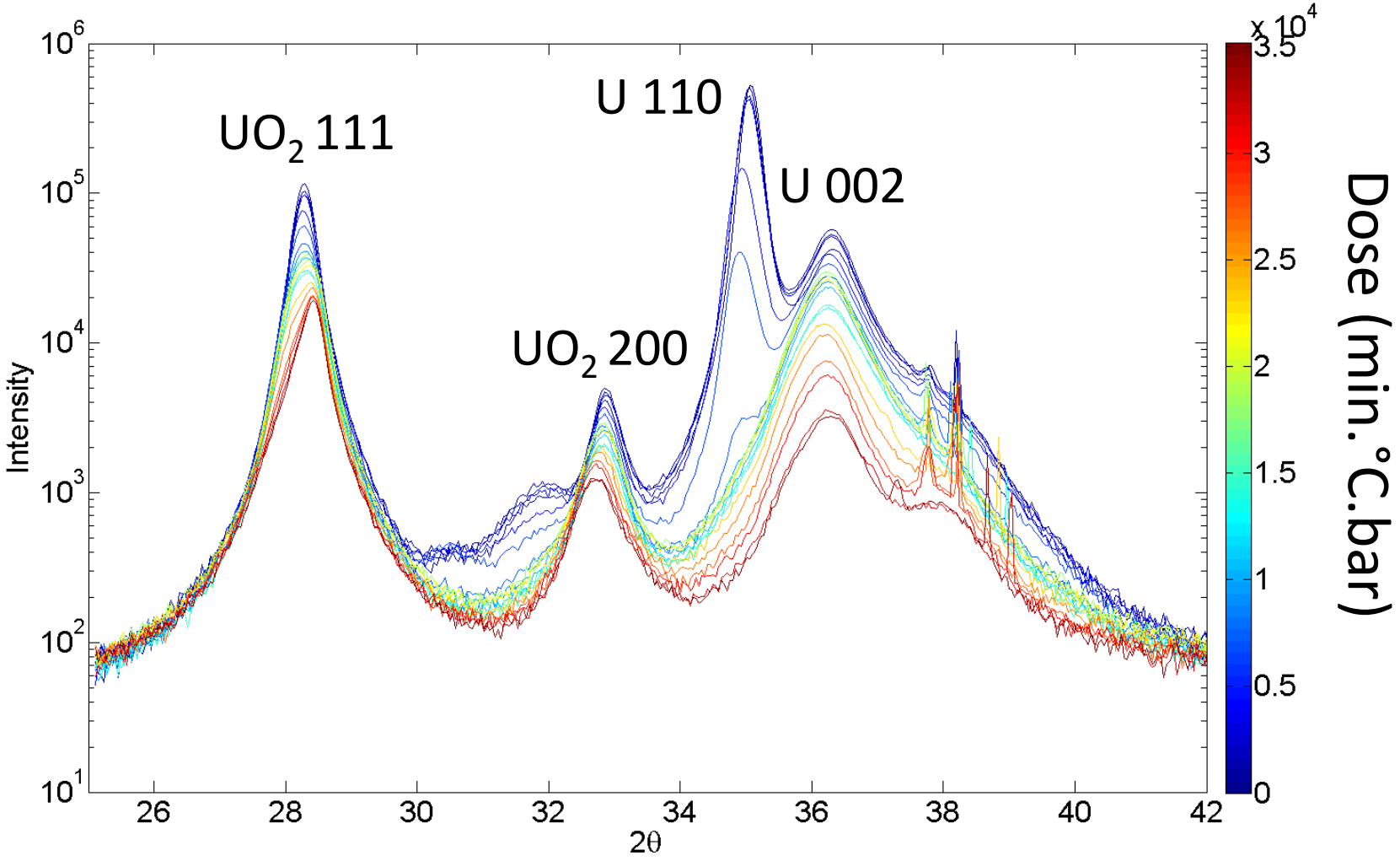


Shift in Bragg Peak: 0.0135 $Å^{-1}$ (~0.59%)

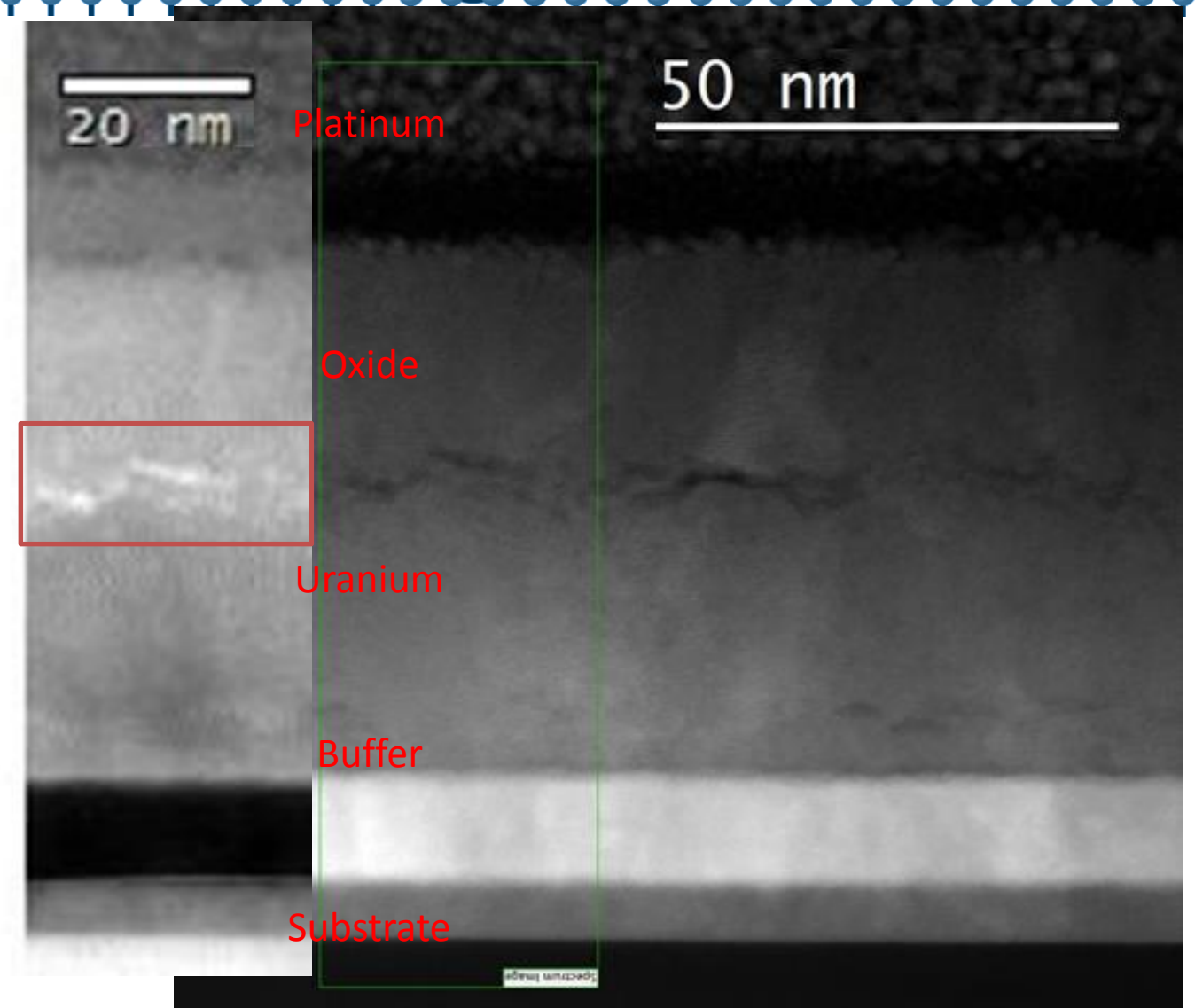
Thin films for corrosion at buried interfaces

- Low partial pressure of H_2 and low temp can corrode crystalline U
- Different crystal orientations consumed at different rates
- Oxide types effect the rate of the corrosion
- Uranium hydriding initiation under oxide layers
- Hydriding of thin films does not lead to crystalline UH_3

High angle Diffraction



STEM
High Annular Dark Field



The new frontier of thin films

- UN (& U_2N_3)
- UX (Mo, Nb, Zr)
- Th, ThO_2 and U-Th, U-ThO_2
- Uranium Silicide

Thank you for your attention

And thanks to all these people:

DCF A. Smith, S. Pimblott, J. Schofield

R. Burrows

G. H. Lander

N.Harker, P. Thompson & D. Wermeille

J. Rawle & C. Nicklin

Water Layers on Actinide Oxide Surfaces

Bengt Tegner
School of Chemistry
The University of Manchester

DISTINCTIVE 3rd Annual Meeting
5 - 6th April 2017
York

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Outline

- Motivation
- Summary of Previous Work
- Results and Discussion
- Conclusions and Future Work
- Acknowledgements

Motivation

- The UK's stock of civil plutonium is stored as PuO_2 powder in multi layer steel cans in Sellafield.
- Under certain circumstances, gas generation may occur within the cans, with consequent pressurisation.
- Several proposed routes to gas production, including:

(i) steam produced by H_2O desorption from hygroscopic PuO_2 due to self-heating

(ii) radiolysis of adsorbed water

(iii) generation of H_2 by reaction of PuO_2 with H_2O, producing a "postulated" PuO_{2+x} phase

All involve PuO_2/H_2O interactions and are complex, inter-connected and poorly understood

$\Rightarrow$Model the interaction of water on PuO_2 surfaces at the atomic level

- method development
- initial results

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Summary of Previous Work

- Results on the stoichiometric UO_2 (111), (110) and (100) surfaces suggest mixed adsorption on the (111) surface and dissociative adsorption on the (110) and (100) surfaces.
- Using these results we calculate water desorption temperatures for the most stable configurations on each surface at various pressures.
- These results have been written up and published in the Journal of Physical Chemistry C.

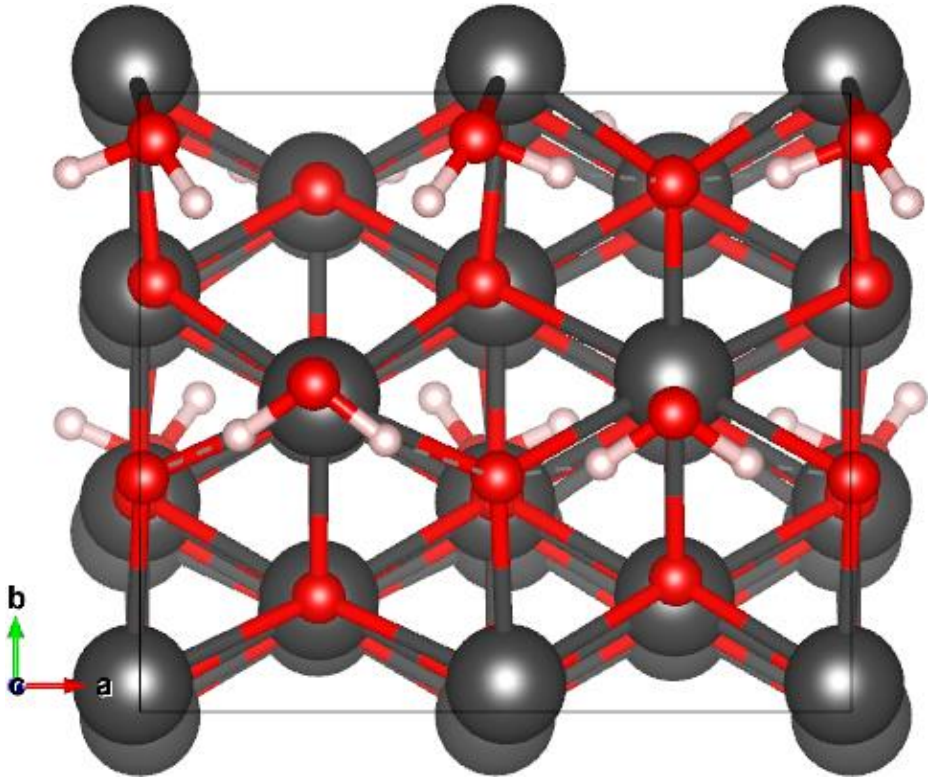
Results: UO_2 Surface Oxygen Vacancies

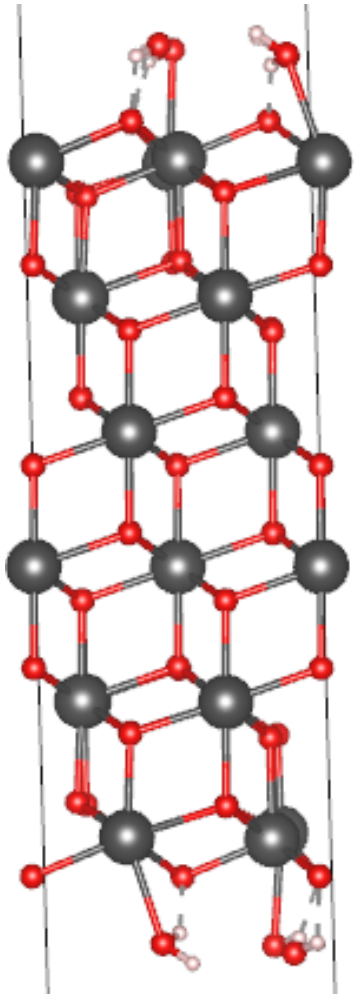
Surface	(111)	(110)	(100)
UO_2	6.45	5.69	5.93
UO_2 [1]	5.95 (-0.50)	5.38 (-0.31)	N/A

Oxygen vacancy formation energies in eV.

[1] T. Bo, J-H. Lan, C-Z. Wang, Y-L. Zhao, C-H. He, Y-J. Zhang, Z-F. Chai and W-Q. Shi, *J. Phys. Chem. C* **118** (2014) 21935–21944.

Results: Water on Reduced UO_2 (111)





Molecular

100% Coverage = 1 ML

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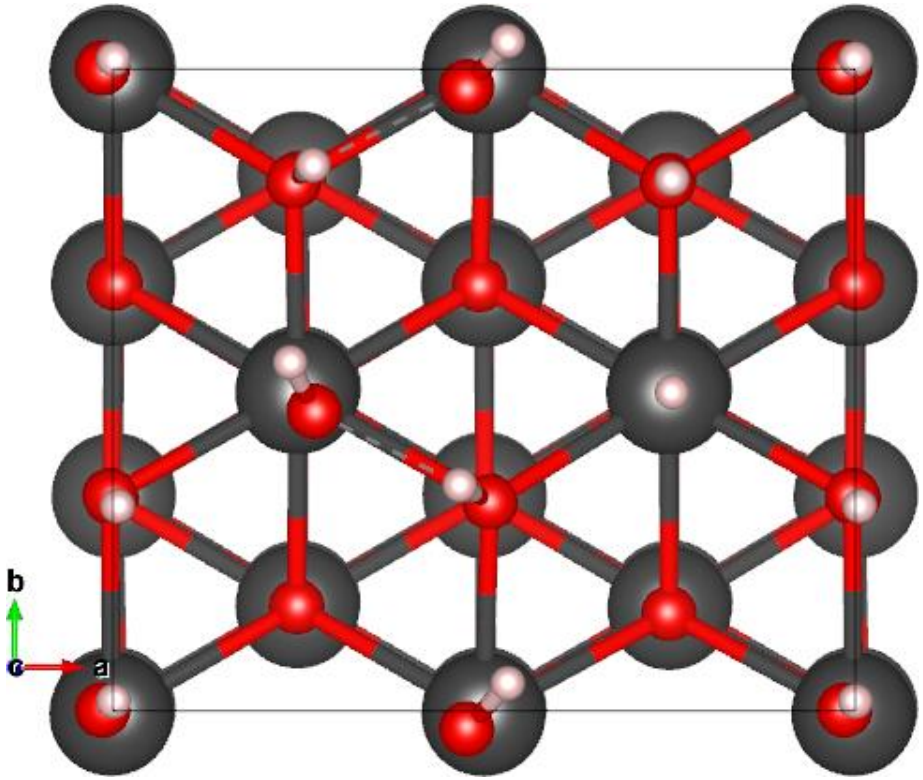
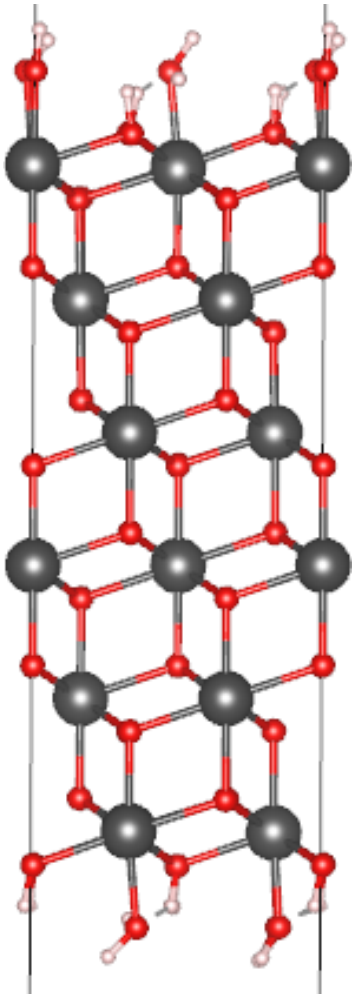
Results: Water on Reduced UO_2 (111)





Dissociative
100% Coverage = 1 ML

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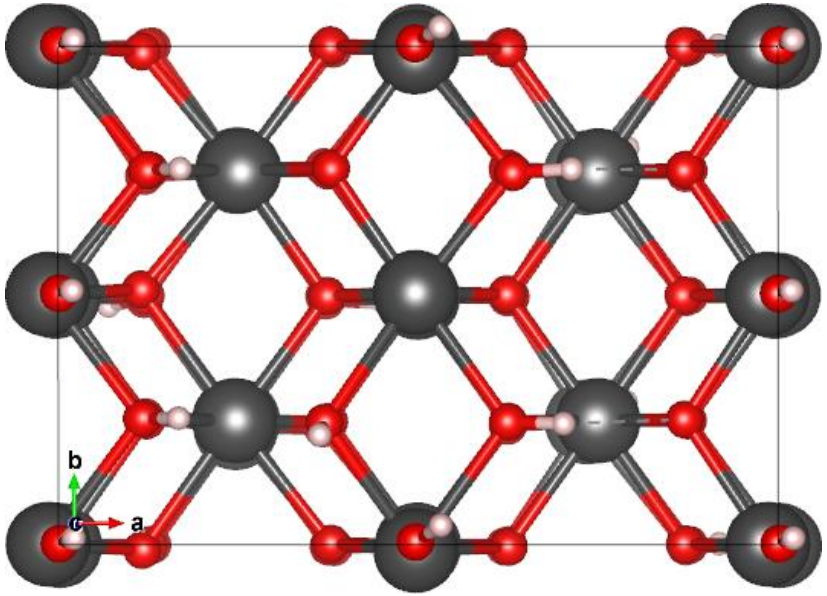
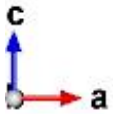
Results: Water on Reduced UO_2 (111)

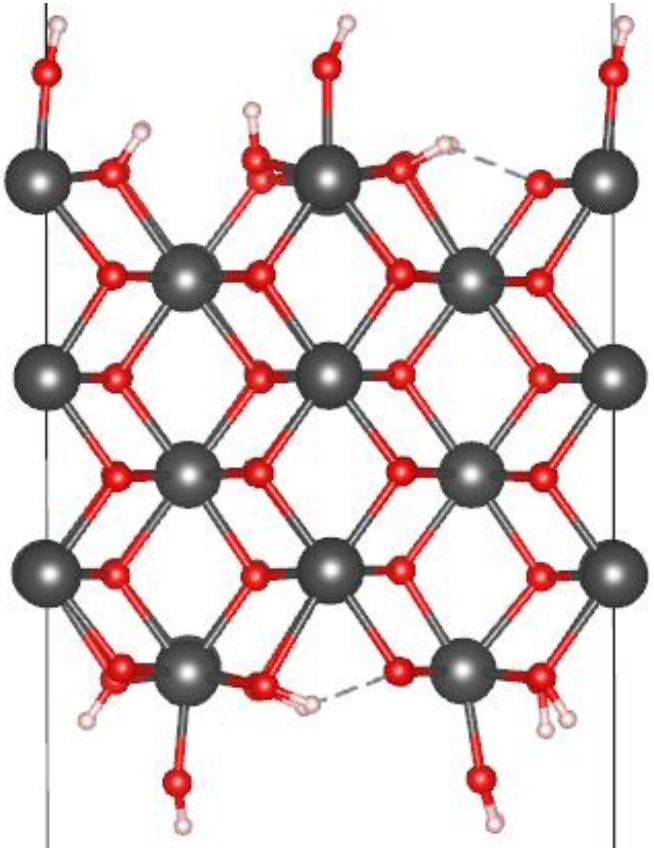
System	0.25 ML	1.0 ML
Stoichiometric UO_2 + H_2O	-0.53	-0.49
Stoichiometric UO_2 + OH + H	-0.50	-0.15
Reduced UO_2 + H_2O	-0.90	-0.66
Reduced UO_2 + OH + H	-2.23	-0.91

Adsorption energies in eV per water molecule.

Results: Water on Reduced UO_2 (110)







Dissociative

100% Coverage = 1 ML

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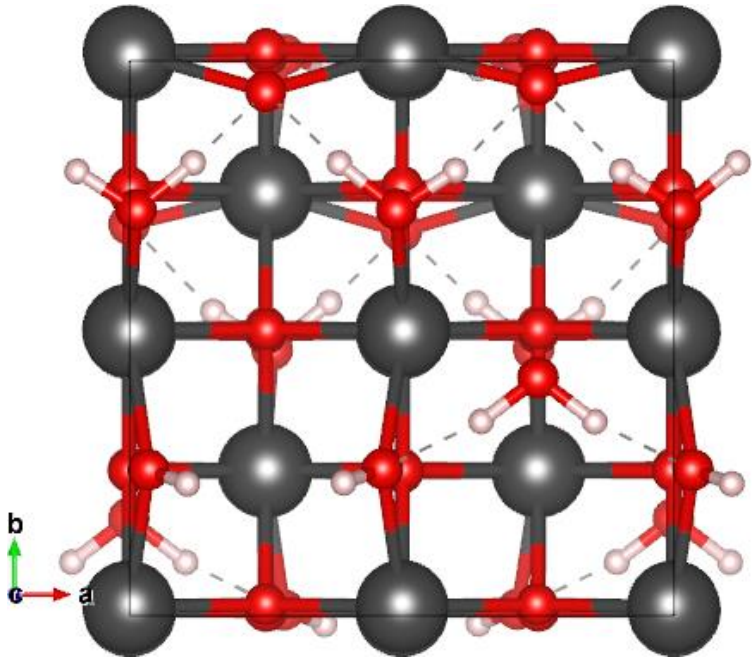
Results: Water on Reduced UO_2 (110)

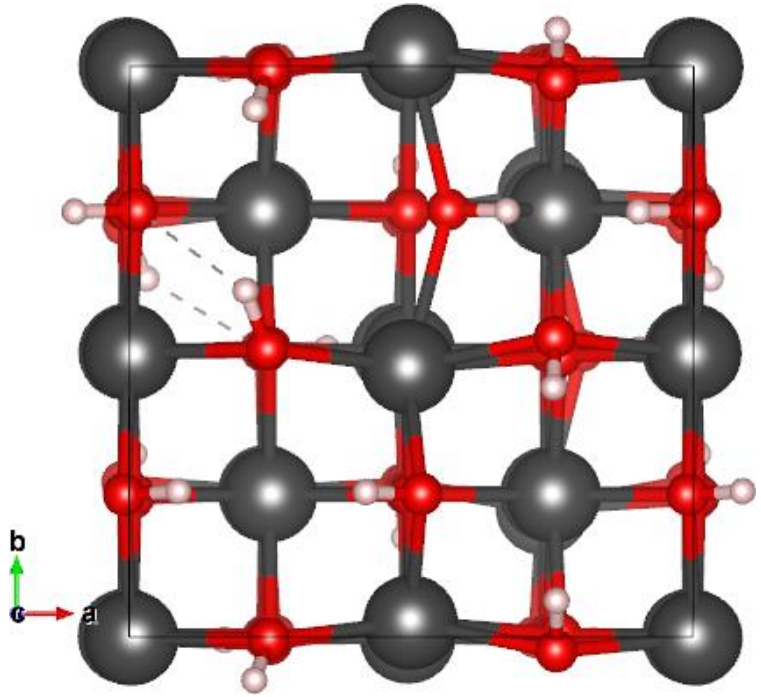
System	0.25 ML	1.0 ML
Stoichiometric UO_2 + H_2O	-0.93	-0.65
Stoichiometric UO_2 + OH + H	-1.39	-1.00
Reduced UO_2 + H_2O	-0.82*	-0.74
Reduced UO_2 + OH + H	-1.50	-1.01

Adsorption energies in eV per water molecule.

Results: Water on Reduced UO_2 (100)



Molecular



Dissociative

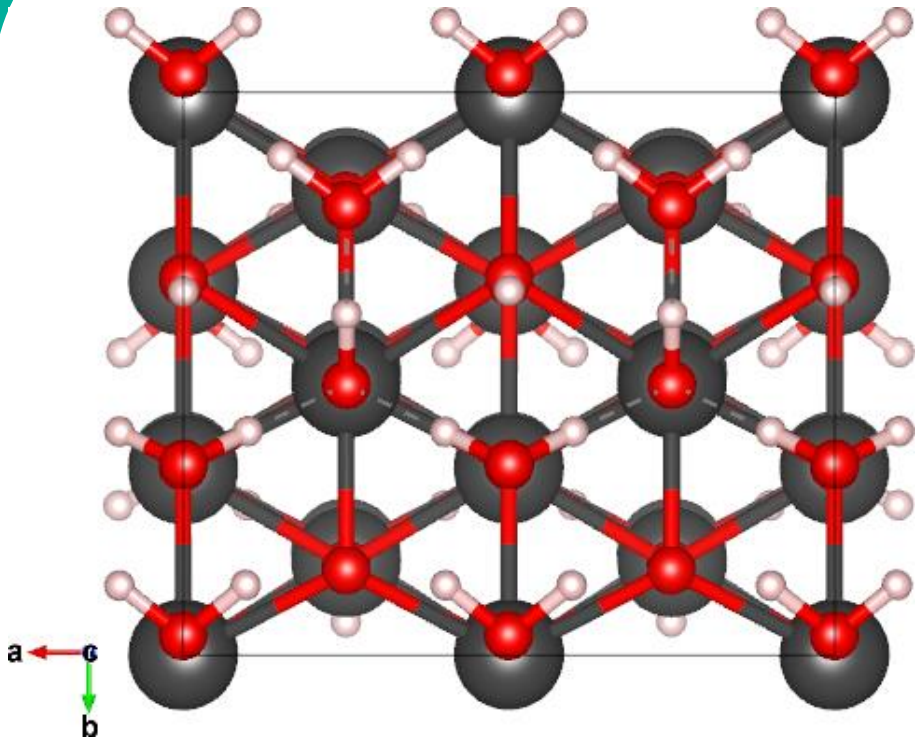
100% coverage = 1 ML

Results: Water on Reduced UO_2 (100)

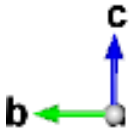
System	0.25 ML	1.0 ML
Stoichiometric UO_2 + H_2O	-0.97	-0.86
Stoichiometric UO_2 + OH + H	-1.55	-1.01
Reduced UO_2 + H_2O	-1.62	-1.12
Reduced UO_2 + OH + H	-2.43	-1.78

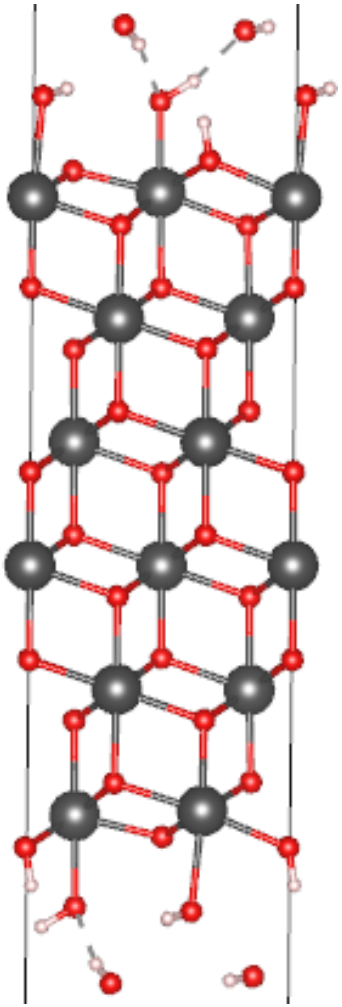
Adsorption energies in eV per water molecule.

Results: More Water on Wet UO_2 (111)



Mixed 50% Molecular and 50% Dissociative + 1 extra ML
Total Coverage = 2 ML



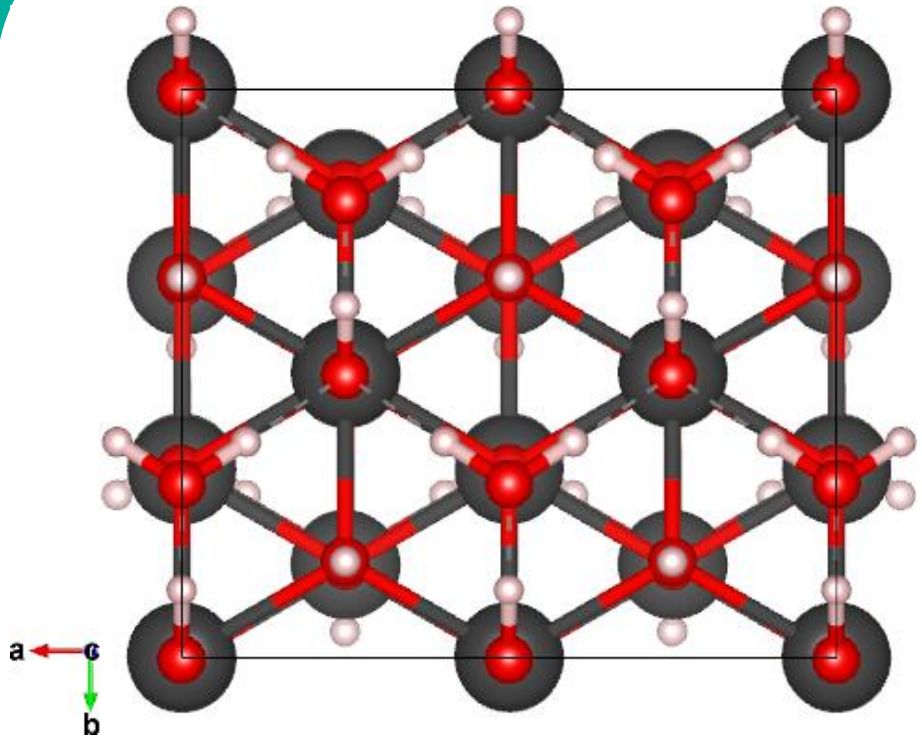


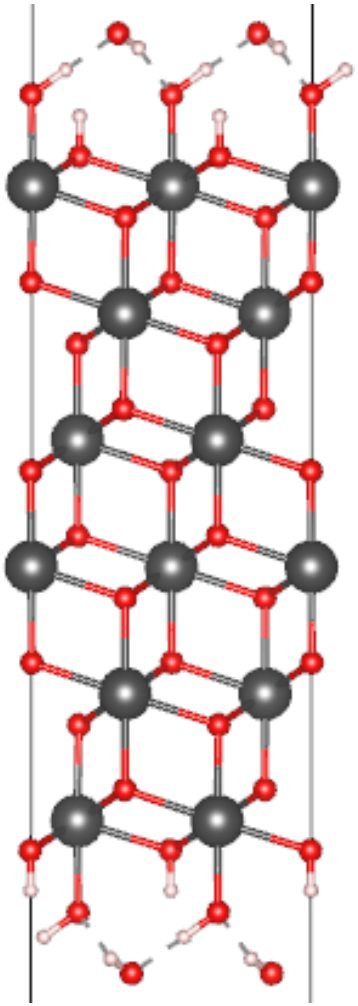
Results: More Water on Wet UO_2 (111)

System	1st Layer: 100% H_2O or 50% / 50% H_2O / OH + H	2nd Layer: 100% H_2O
$UO_2 + H_2O$	-0.59	-0.46
UO_2 + 50% H_2O + 50% OH + H	-0.73	-0.07

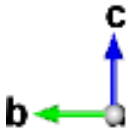
Adsorption energies in eV per water molecule.

Results: More Water on Wet UO_2 (111)





100% Dissociative + 1 extra ML
Total Coverage = 2 ML



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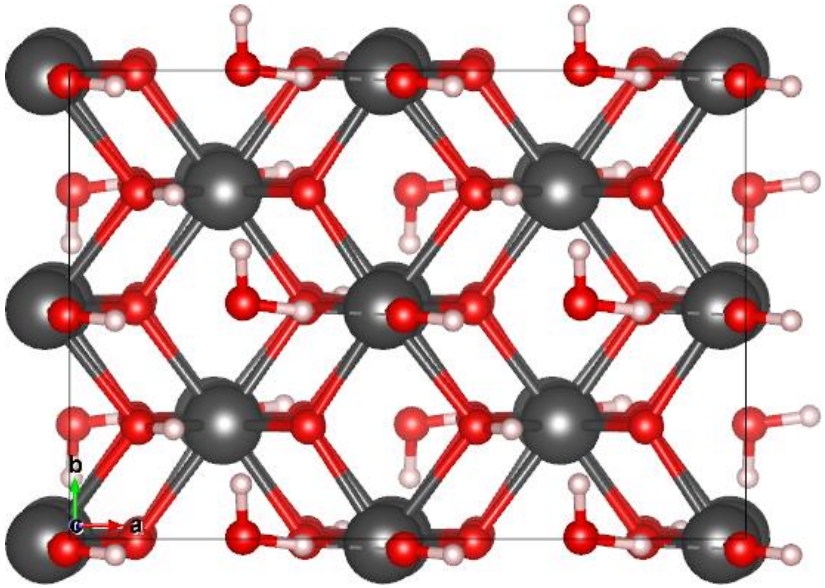
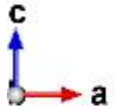
Results: More Water on Wet UO_2 (111)

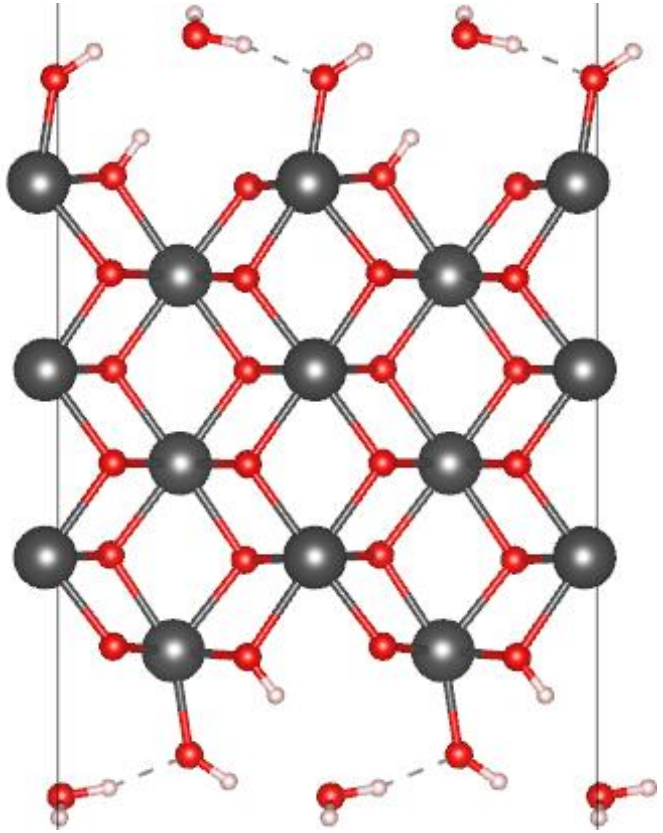
System	1st Layer: 100% H_2O or 100% OH + H	2nd Layer: 100% H_2O	3rd Layer: 100% H_2O
$UO_2 + H_2O$	-0.59	-0.46	-0.43
UO_2 + OH + H	-0.32	-0.65	-0.28

Adsorption energies in eV per water molecule.

Results: More Water on Wet UO_2 (110)







100% Dissociative + 1 extra ML

Total Coverage = 2 ML

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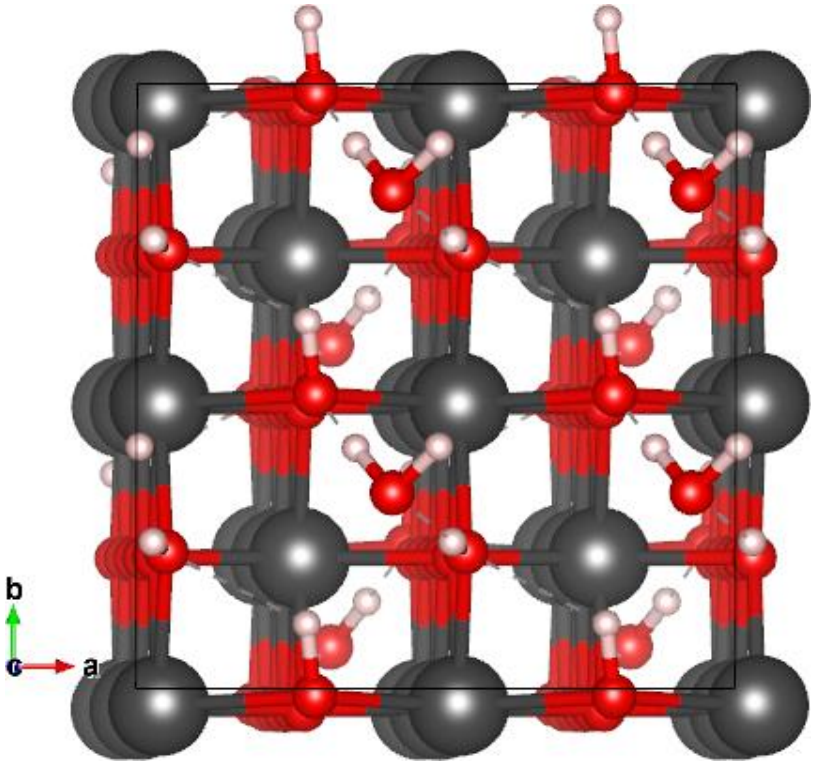
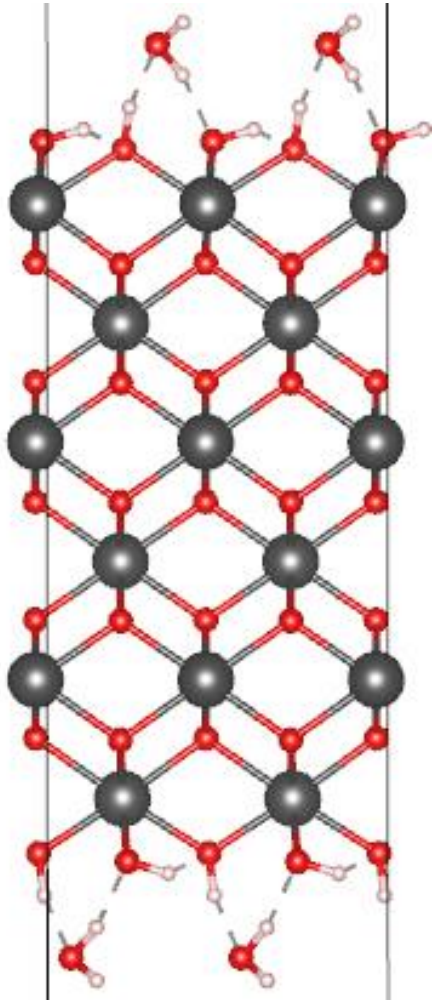
Results: More Water on Wet UO_2 (110)

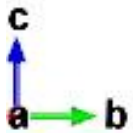
System	1st Layer: 100% H_2O or 100% OH + H	2nd Layer: 100% H_2O	3rd Layer: 100% H_2O
$UO_2 + H_2O$	-0.65	N/A	N/A
$UO_2 + OH + H$	-1.00	-0.57	-0.41

Adsorption energies in eV per water molecule.

Results: More Water on Wet UO_2 (100)







100% Dissociative + 1 extra ML
Total Coverage = 2 ML

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Results: More Water on Wet UO_2 (100)

System	1st Layer: 100% H_2O or 100% OH + H	2nd Layer: 100% H_2O
$UO_2 + H_2O$	-0.86	N/A
$UO_2 + OH + H$	-1.01	-0.78

Adsorption energies in eV per water molecule.

Conclusions and Future Work

- Results on the UO_2(111), (110) and (100) surfaces suggest mixed adsorption on the (111) surface and dissociative adsorption on the (110) and (100) surfaces.
- Adsorption at defects suggest a strong preference for dissociative adsorption.
- Adsorption of additional water layers on UO_2(111) surface suggest a hydrogen bond network forming after just a few layers.
- Future work will focus on adsorption of additional water layers on all three surfaces.

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Acknowledgements

Nik Kaltsoyannis, The University of Manchester

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Jeff Hobbs and Helen Steele, Sellafield Ltd

Robin Orr and Howard Sims,

National Nuclear Laboratory

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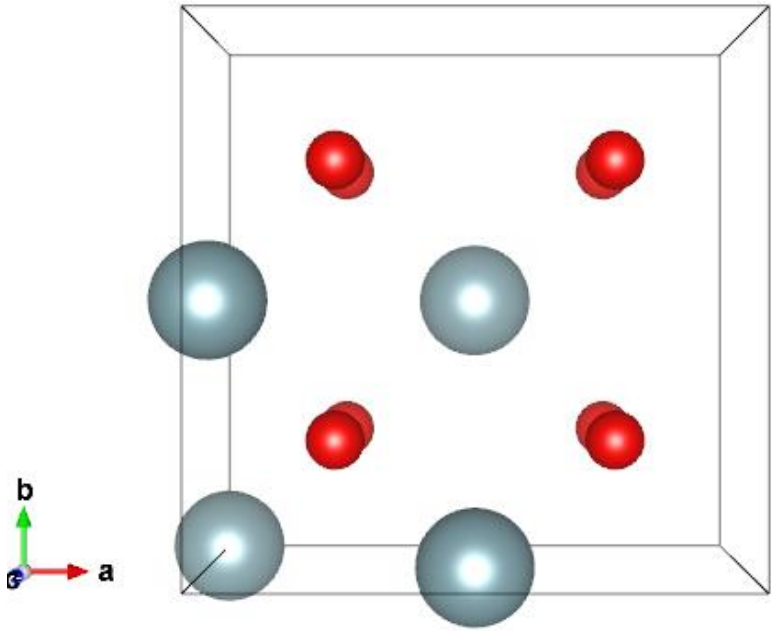
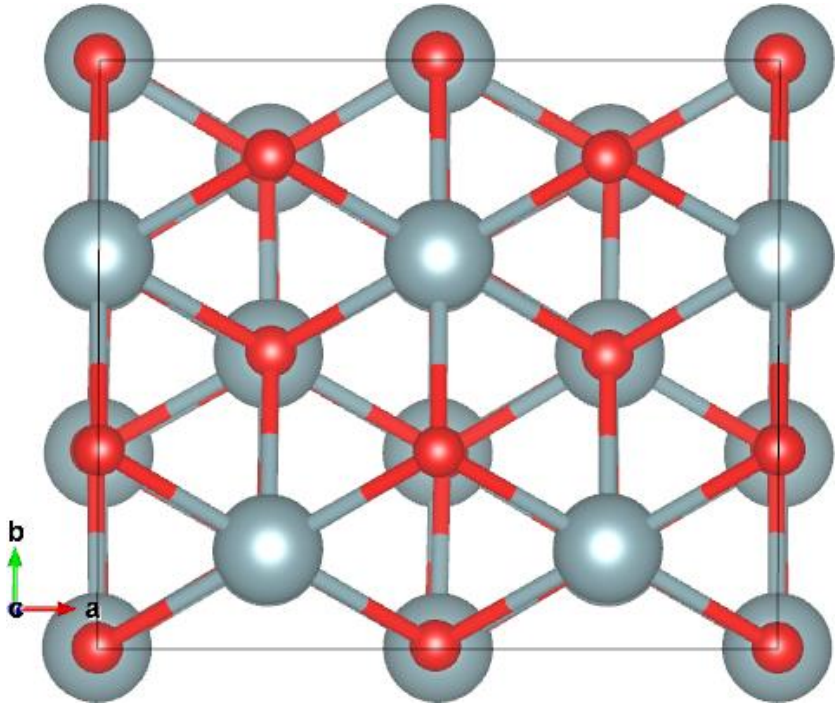
Computational Method

- Density Functional Theory
- VASP 5.4.1
- PAW-pseudopotentials
- Plane wave basis set
- k-point sampling of 1st BZ
- Spin-polarised
- DFT+*U* = PBE+*U*
- $U_{eff} = (U - J) = 4.0$ eV



Computational Method

- Surfaces are modelled using a repeating slab of 24 UO_2 units with 18 Å of vacuum between each slab.
- Water is adsorbed on both sides of the slab to ensure the system has no net dipole moment.



A DISTINCTIVELY academic career*

*Other academic careers are available

Dr. Claire Corkhill

University of Sheffield

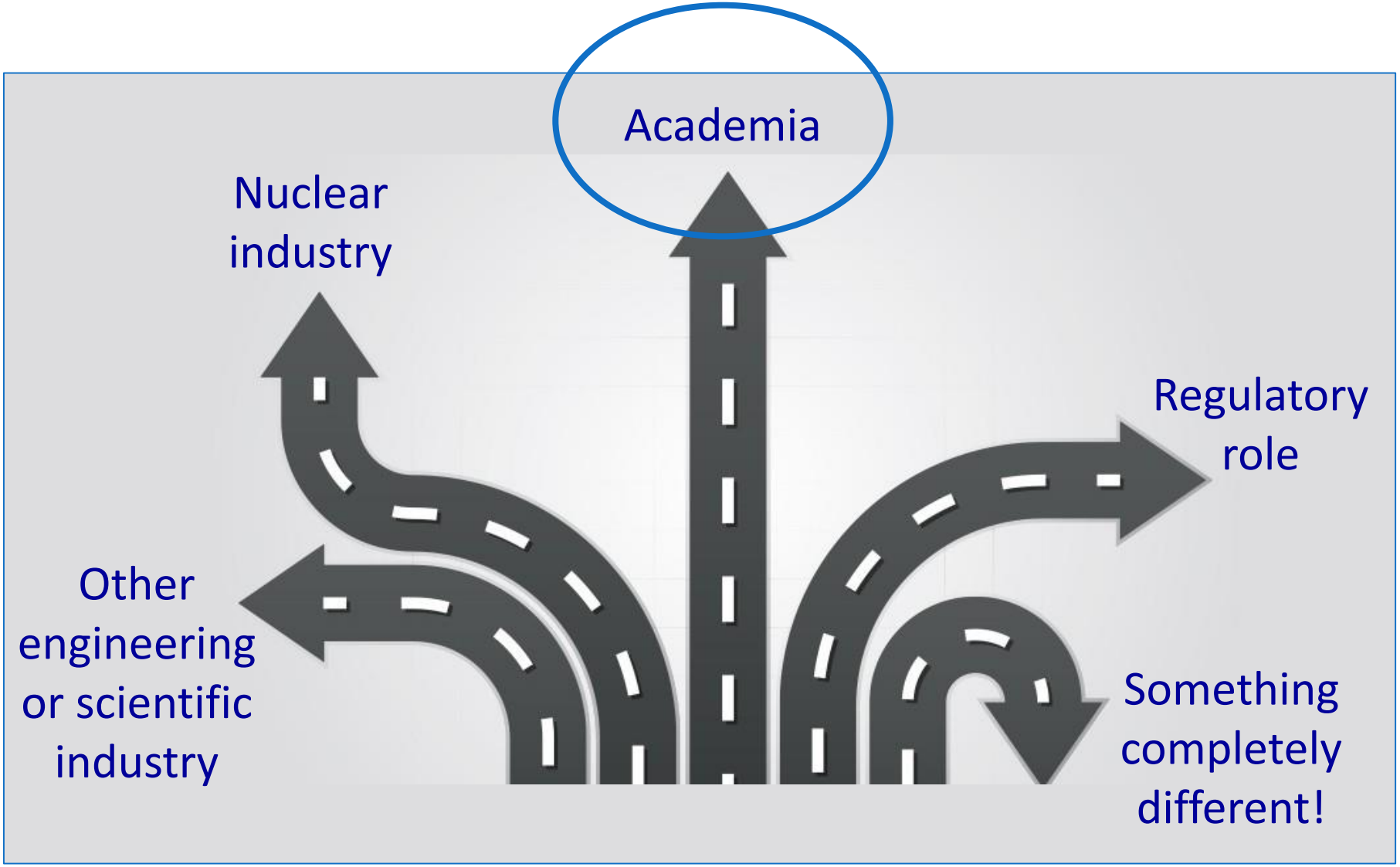
DISTINCTIVE annual meeting, York, April 2017

@clairecorkhill
@ISL_Sheffield

Careers after DISTINCTIVE?

The University Of Sheffield.

NucleUS
Immobilisation Science Laboratory



My career path

The University Of Sheffield.

NucleUS
Immobilisation Science Laboratory

2005
MEarthSci
Geology

2009
Research Associate
(3 months)

2010 - 2011
Postdoc
DIAMOND

2013 - 2016
Vice Chancellor's
Research Fellowship

2009
PhD Applied
Mineralogy &
Geochemistry

2009 - 2010
Analytical
Geochemistry unit
technician

2011 - 2013
Postdoc
REDUPP

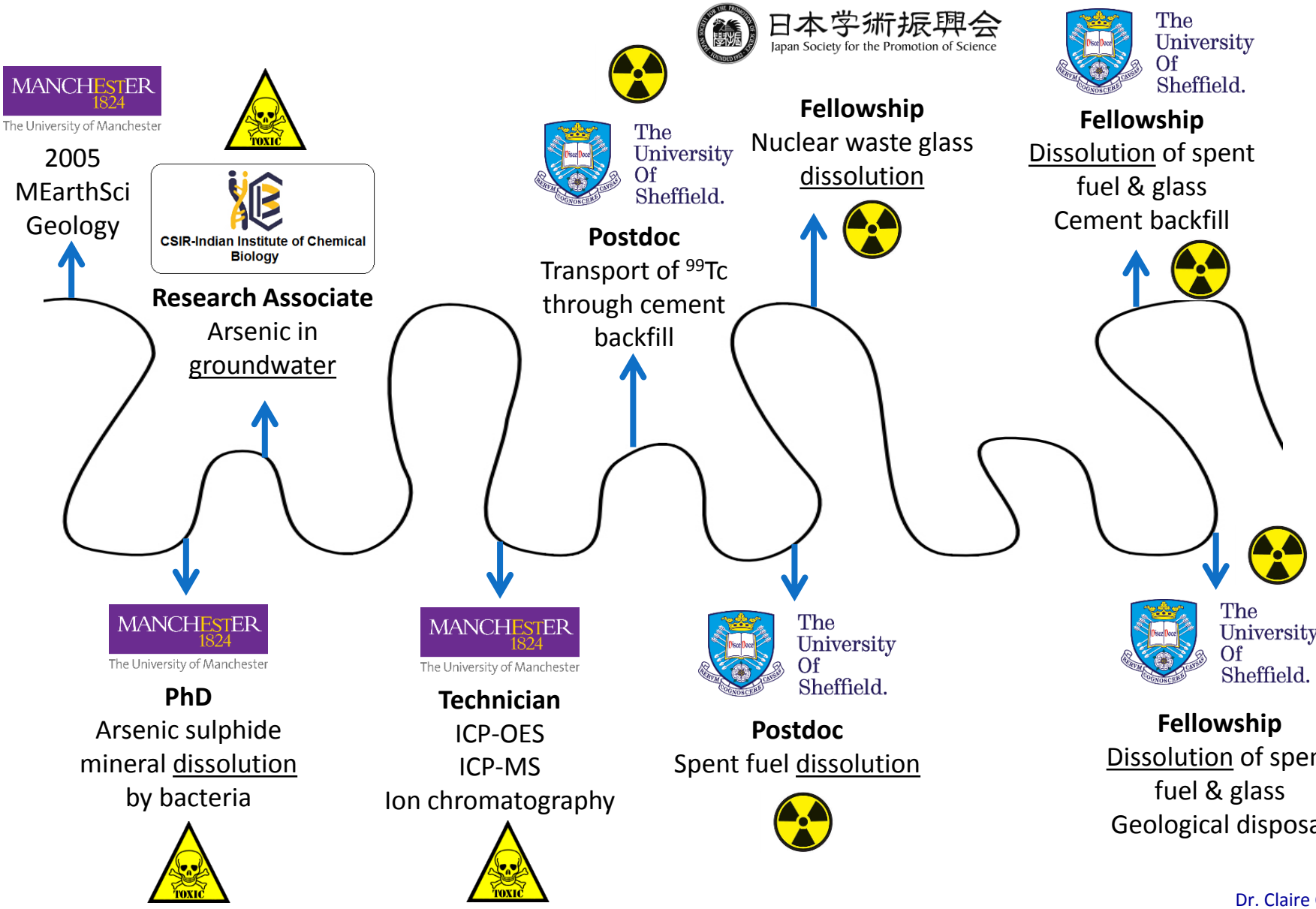
2016 - 2021
EPSRC Early Career
Research Fellow &
Senior Lecturer

Secondment through
JSPS fellowship to U.
Kyushu

My wiggly career path

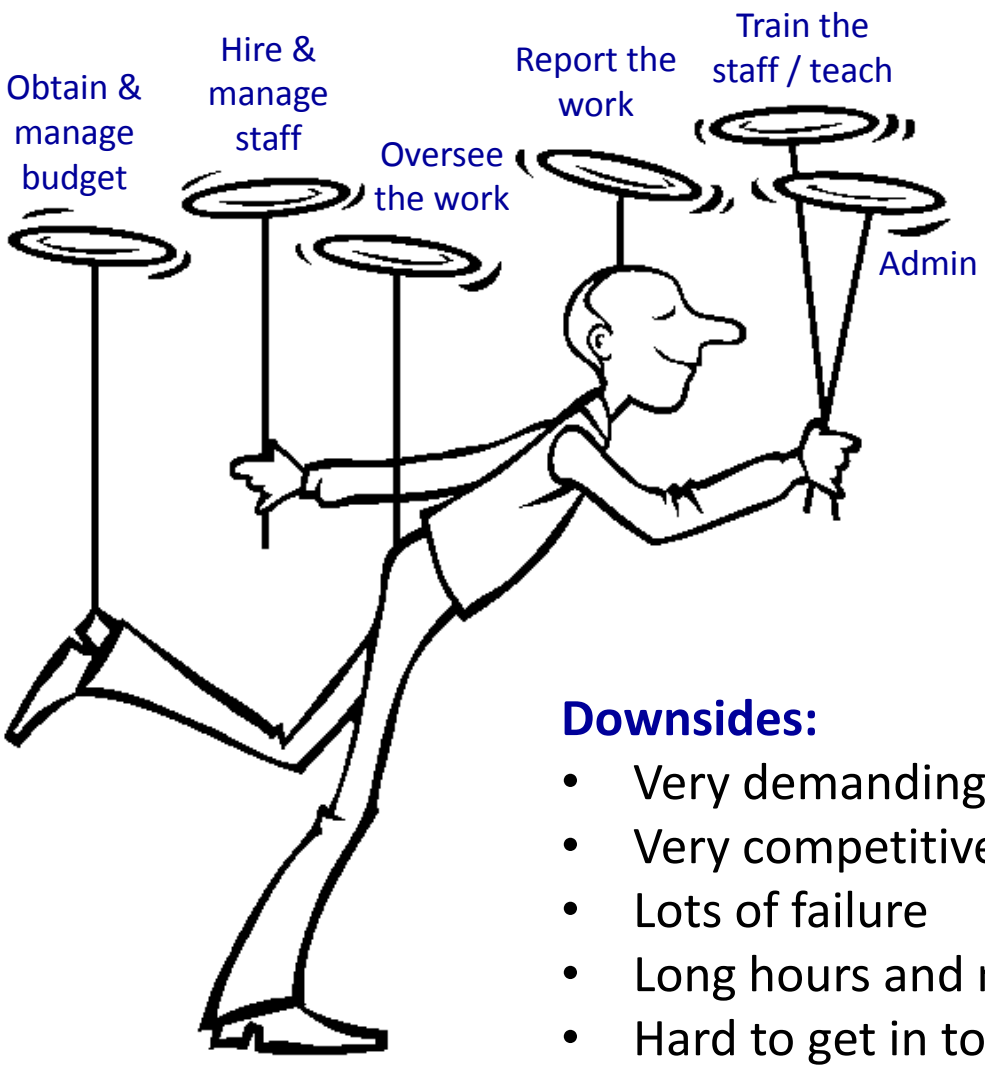
The University Of Sheffield.

NucleUS
Immobilisation Science Laboratory



Dr. Claire Corkhill

What is an academic job like?



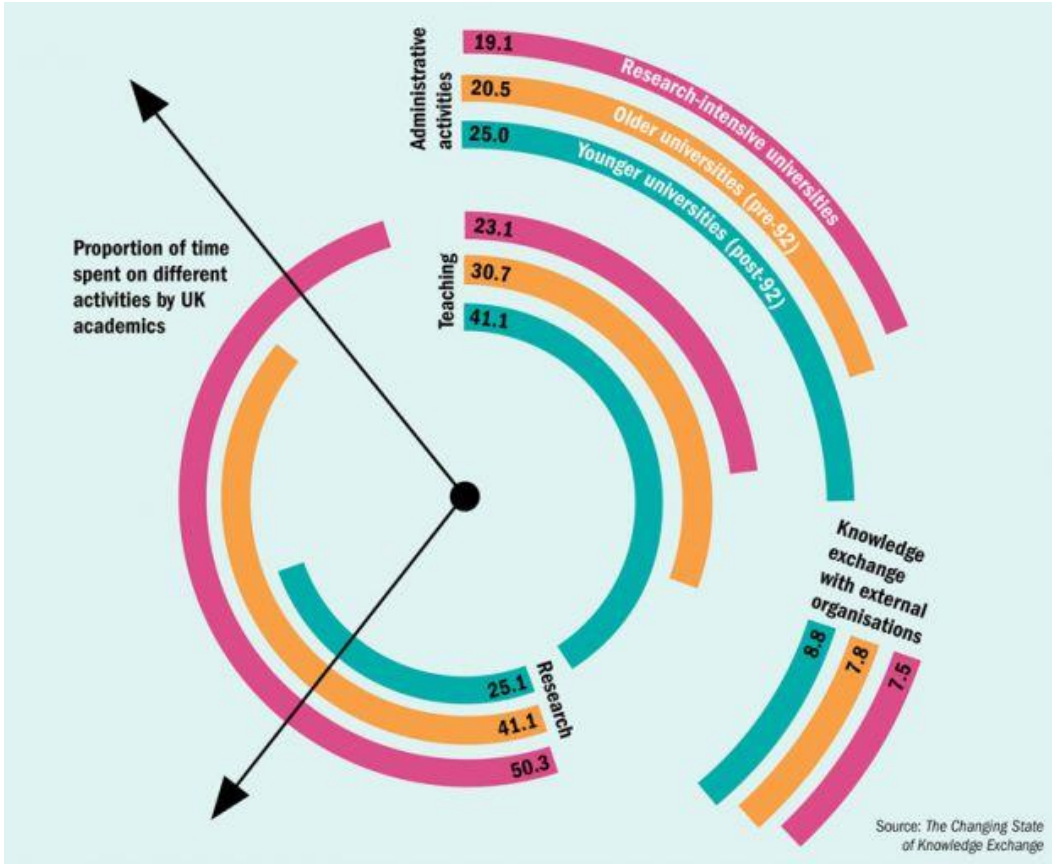
Upsides:

- Do all of the roles of a small business
- Challenging
- Freedom and flexibility
- Varied
- Fairly well paid

Downsides:

- Very demanding
- Very competitive
- Lots of failure
- Long hours and much to do
- Hard to get in to

What does an academic do?



https://www.timeshighereducation.com/news/infographic-how-scholars-spend-their-time

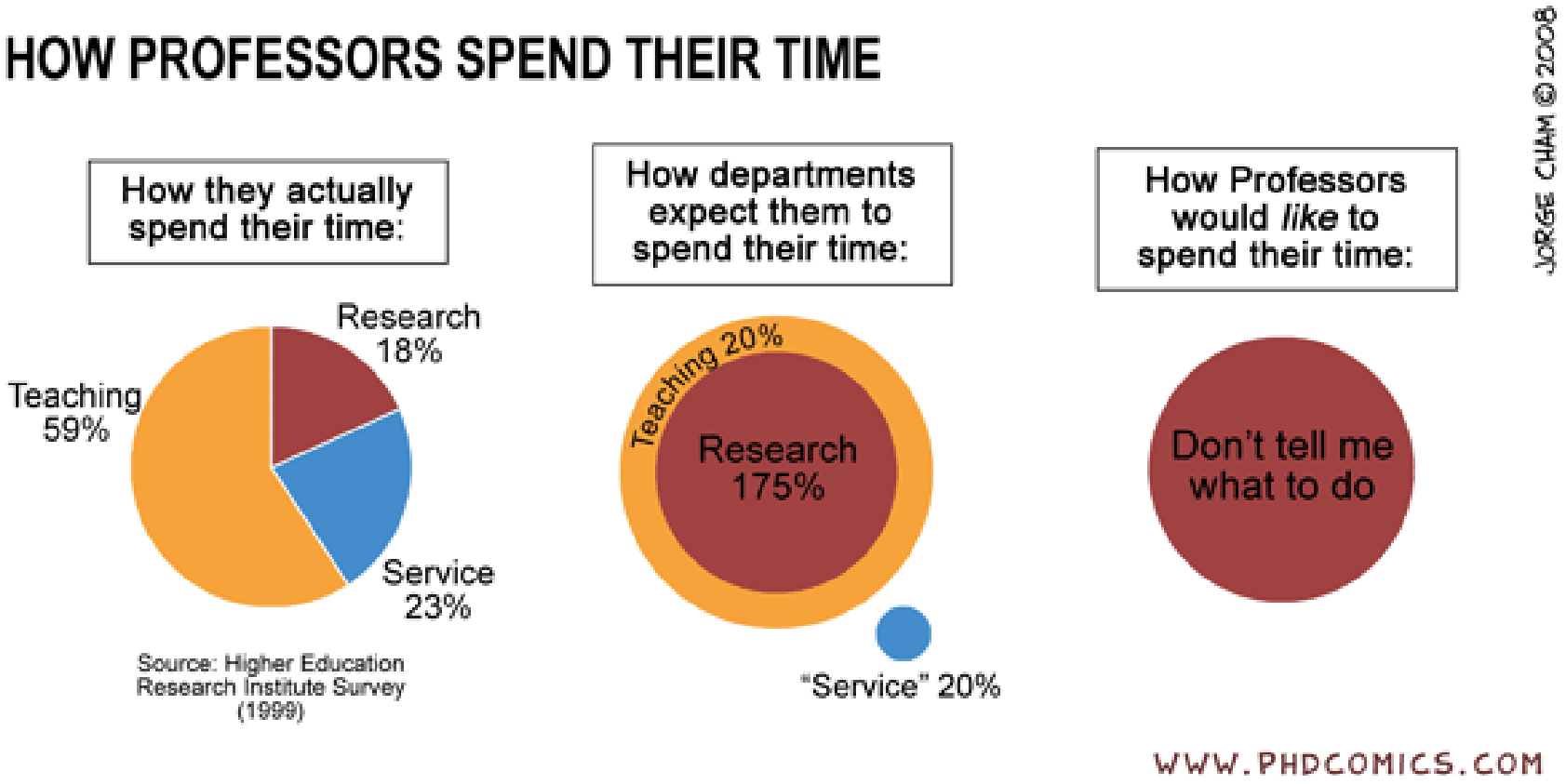
- 50 – 70 hours per week (including weekends)
- **Research management** (25 - 50% of time)
- **Teaching** (23 – 41% of time)
- **Admin** (19 – 25 % of time)

(almost) all of this is a lot of fun!

What does an academic do?

The University Of Sheffield.

NucleUS
Immobilisation Science Laboratory



My top 3…

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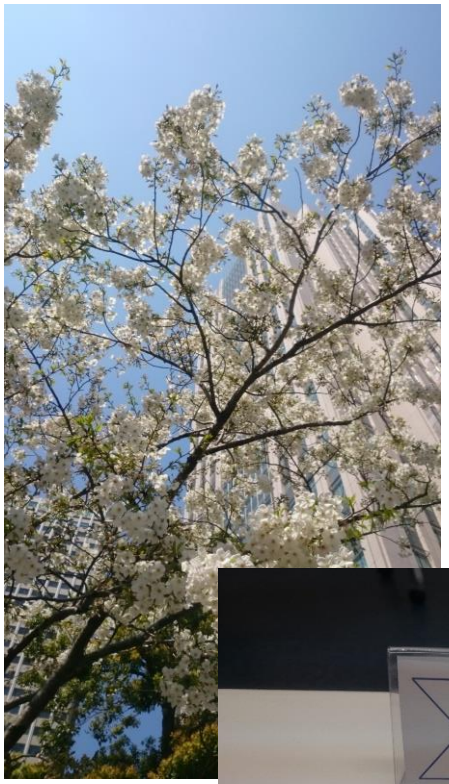
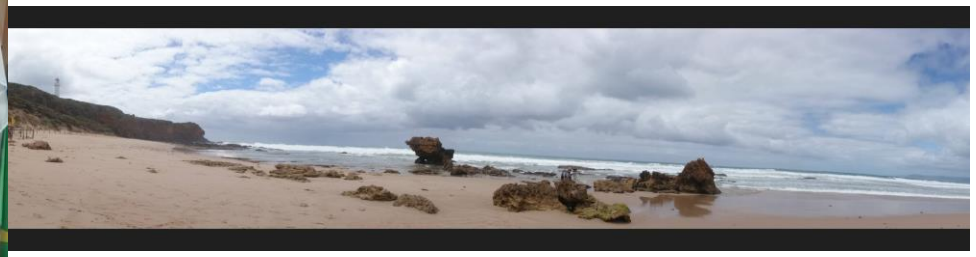
1. **Travel** (conferences, project meetings, collaboration visits)

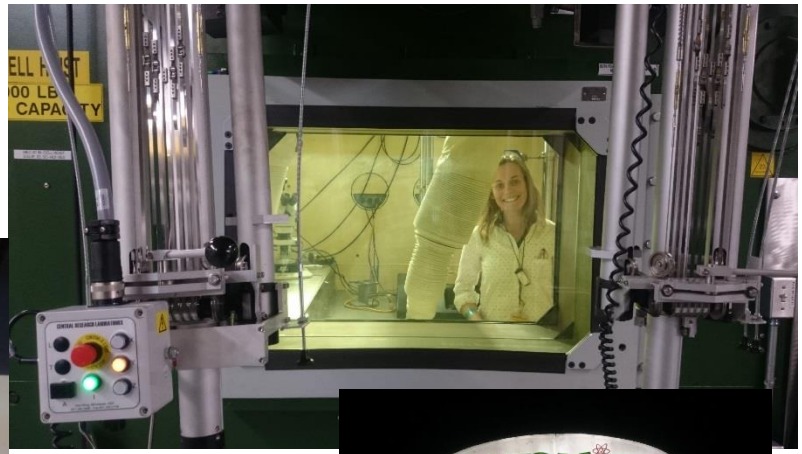
Boston (USA)



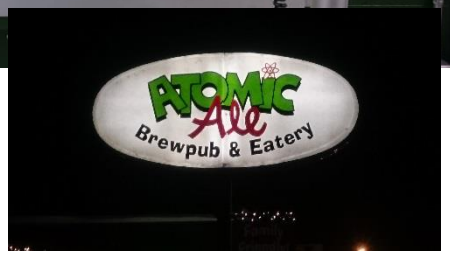
Tokyo & Fukushima (Japan)

Melbourne & Sydney (Australia)



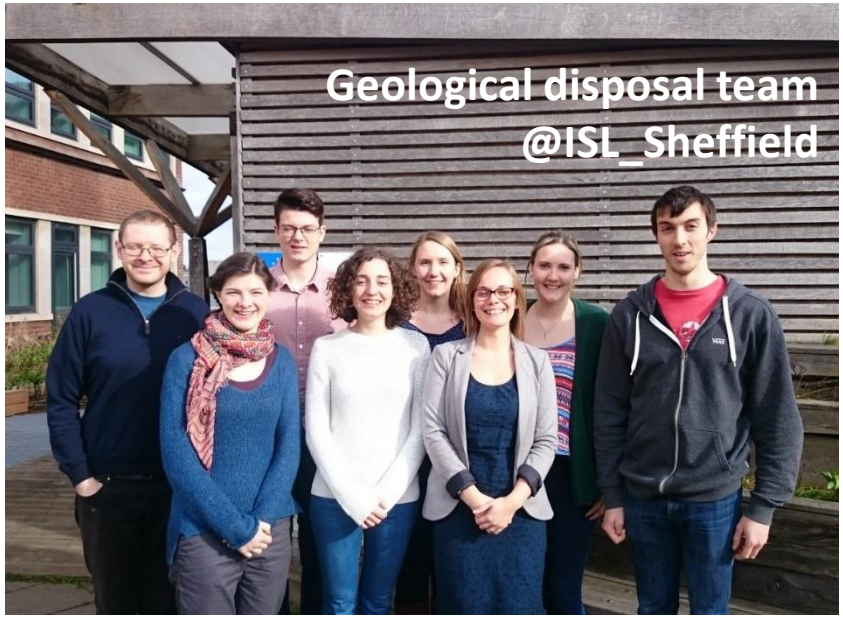


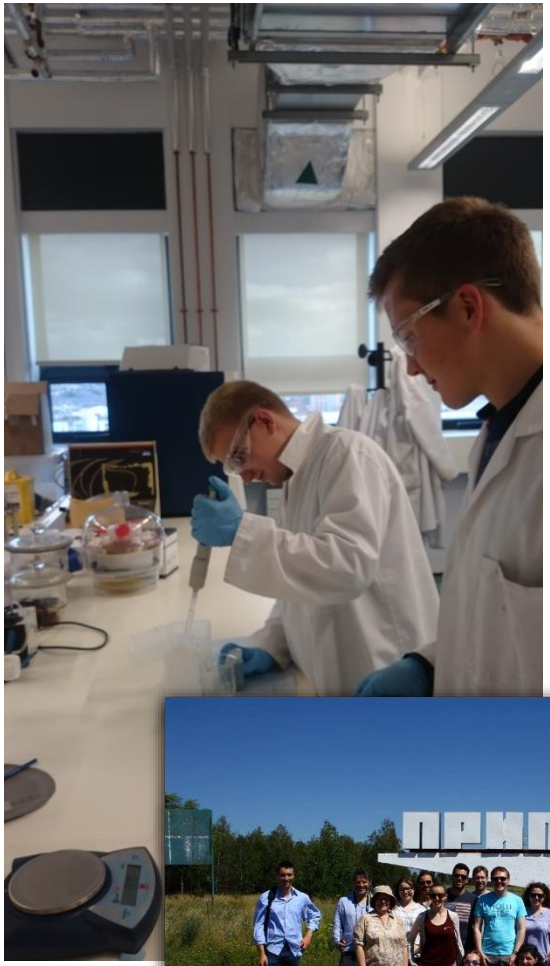
Hanford (USA)

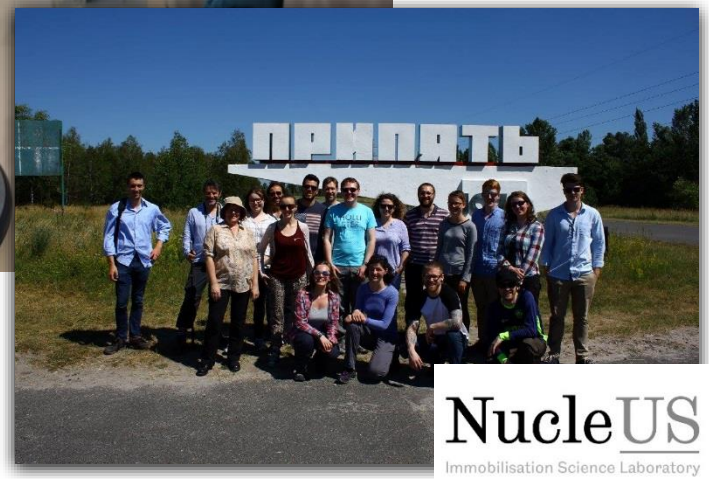


My top 3…

1. **Travel** (conferences, project meetings, collaboration visits)
2. **My team** – Doing super cool science with my PhD students and postdocs







My top 3…

1. **Travel** (conferences, project meetings, collaboration visits)
2. **My team** - Doing super cool science with my PhD students and postdocs
3. **Talking to the public** about my research

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Nuclear waste
The Observer

Britain leads race to make nuclear waste safe for 100,000 years

My 3 least favourite things…

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1. **Not being in the lab as much as I'd like**
2. **The highly competitive nature of academia can be a little bit overwhelming**
3. **Trying to get the work-life "blend" right is pretty hard**

Academia and family life

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- Balancing work and family life has it's challenges in many professions
- Hours worked in academia are long, but flexible (they also don't necessarily need to be long…)
- Requires excellent prioritisation skills!

https://royalsociety.org/~/media/Royal_Society_Content/about-us/equality/2011-06-15-Mothers-in-Science.pdf


The superwoman fallacy: what it really takes to be an academic and parent

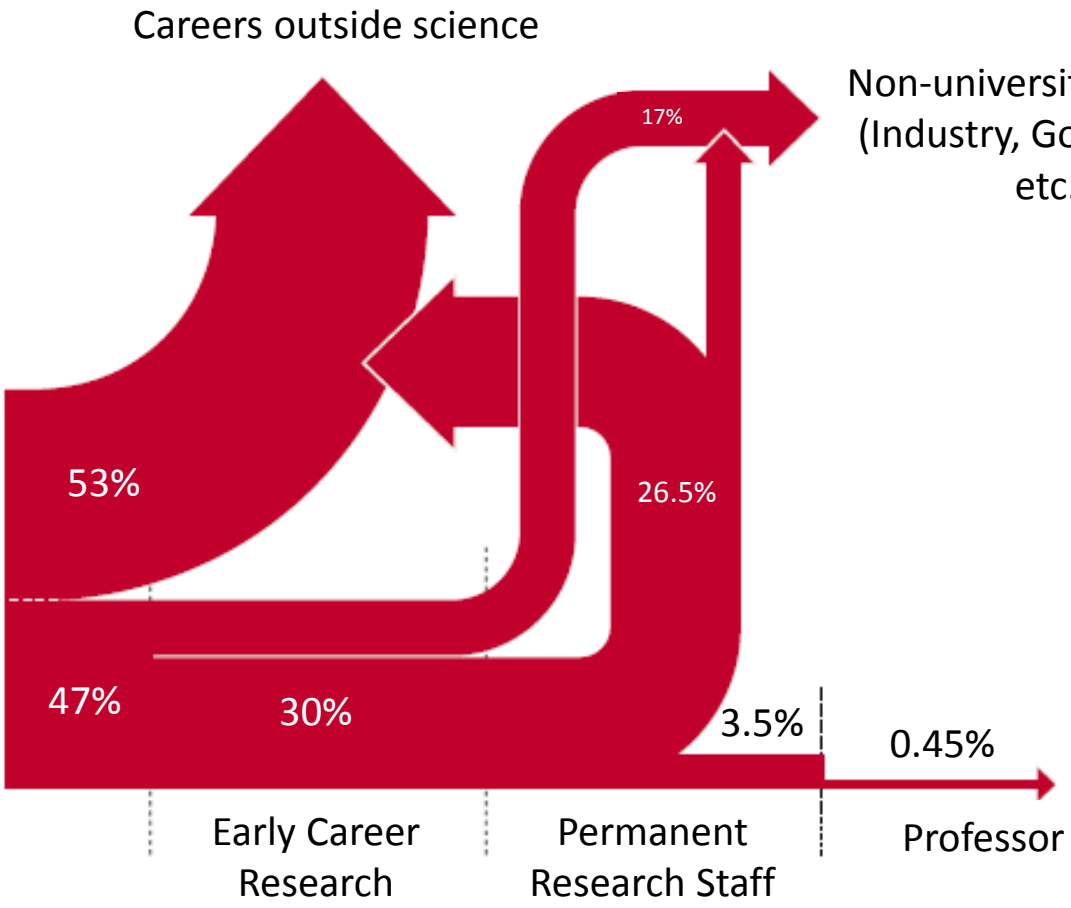
Melissa Terras is tired of being called superwoman because she has three young children and a job. Here she takes apart the myth and says there's no such thing as 'work-life balance'

Work-life balance: as fictional a construct as Superman or Woman. Photograph: Ronald Grant Archive

https://www.theguardian.com/higher-education-network/blog/2012/aug/17/academic-careers-work-life-balance

http://www.sciencemag.org/careers/2015/07/balancing-career-and-family

How do I become an academic?



Be prepared to:

(a) Be persistent

(b) Be tenacious

(c) Fail

https://royalsociety.org/~/media/royal_society_content/policy/publications/2010/4294970126.pdf

How do I become an academic?

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Step 1.

During your PhD and postdoc(s) you must:

- Publish good quality papers
- Obtain funding wherever you can, no matter how small
- Present your research at national and international conferences
- Start to build a network of academic and industrial collaborators
- Talk about your research (public events, media, blog etc.)

Publish, get funding & network

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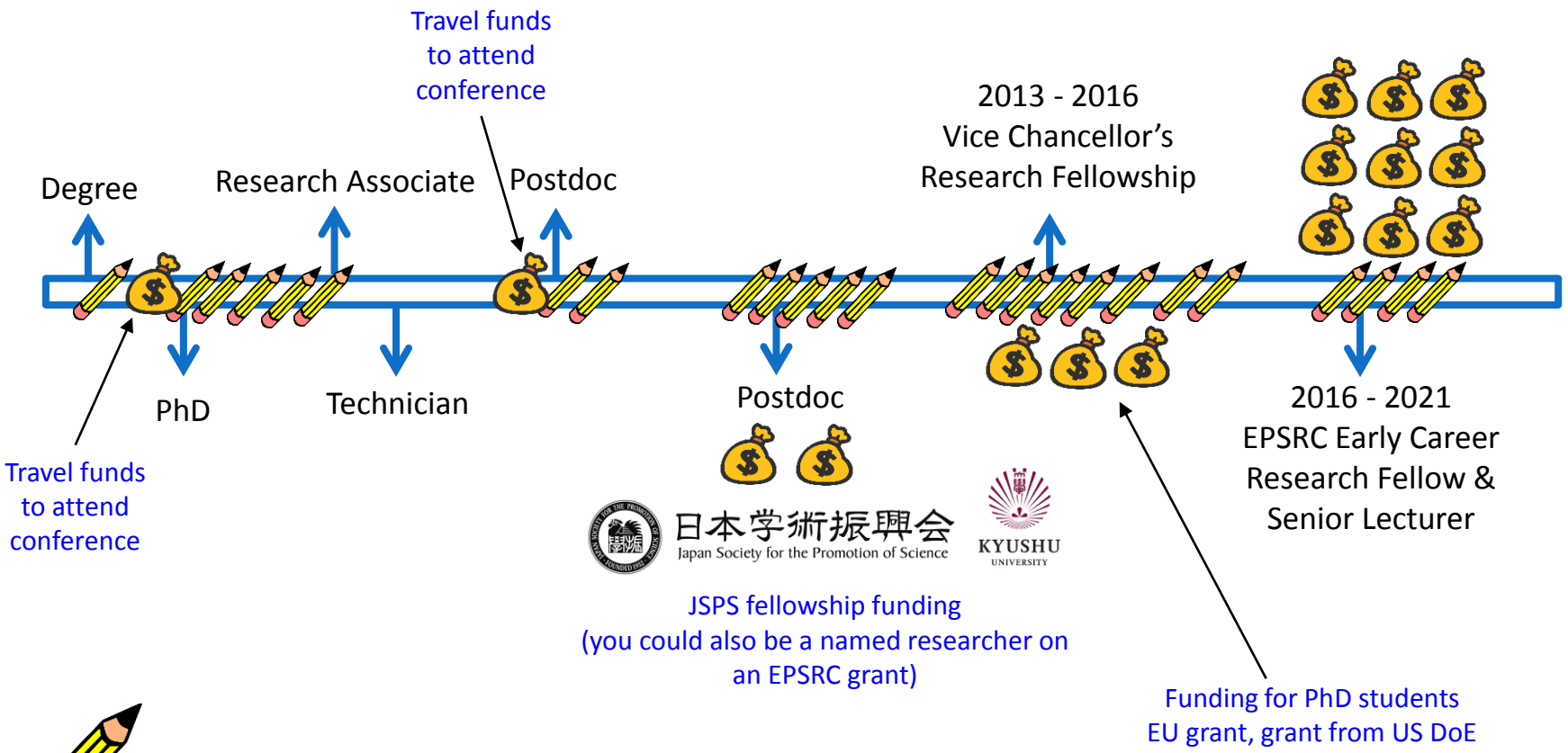

Publication

Funding

Radioactive Waste Management

DISTINCTIVE

U.S. DEPARTMENT OF ENERGY

NDA Nuclear Decommissioning Authority

EPSRC Engineering and Physical Sciences Research Council

HORIZON 2020

Sellafield Ltd

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- Talk about your research (public events, media, blog etc.)

Step 2.

Develop:

- A fantastic research idea that will get funded!
- An understanding of how your idea will lead to impact
- A totally unique skill set that sets you apart from everyone else

How do I become an academic?

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Things that will help:

- Think ahead & develop a plan
- Decide which route to follow:
  - Fellowship?
  - Industry then academia?
  - Straight to lecturer?
- Get a mentor and consult them

Fellowships:

- Tend to be 1 – 5 years
- Some have a time limit for application
- Give you freedom to develop your research independence

EPSRC
Engineering and Physical Sciences Research Council

Postdoctoral (3 years) & Early Career (5 years) – undersubscribed in Nuclear Fission theme!

ROYAL ACADEMY OF ENGINEERING

5 year fellowship
Limited to +4yrs of PhD

THE ROYAL SOCIETY

5 year fellowship (+3 yrs)
Limited to +8yrs of PhD

The Leverhulme Trust

MARIE CURIE ACTIONS

ROYAL COMMISSION EXHIBITION OF 1851

Thank you for your attention