# Models for the Corrosion of Spent Nuclear Fuel Inside a Failed Waste Disposal Container

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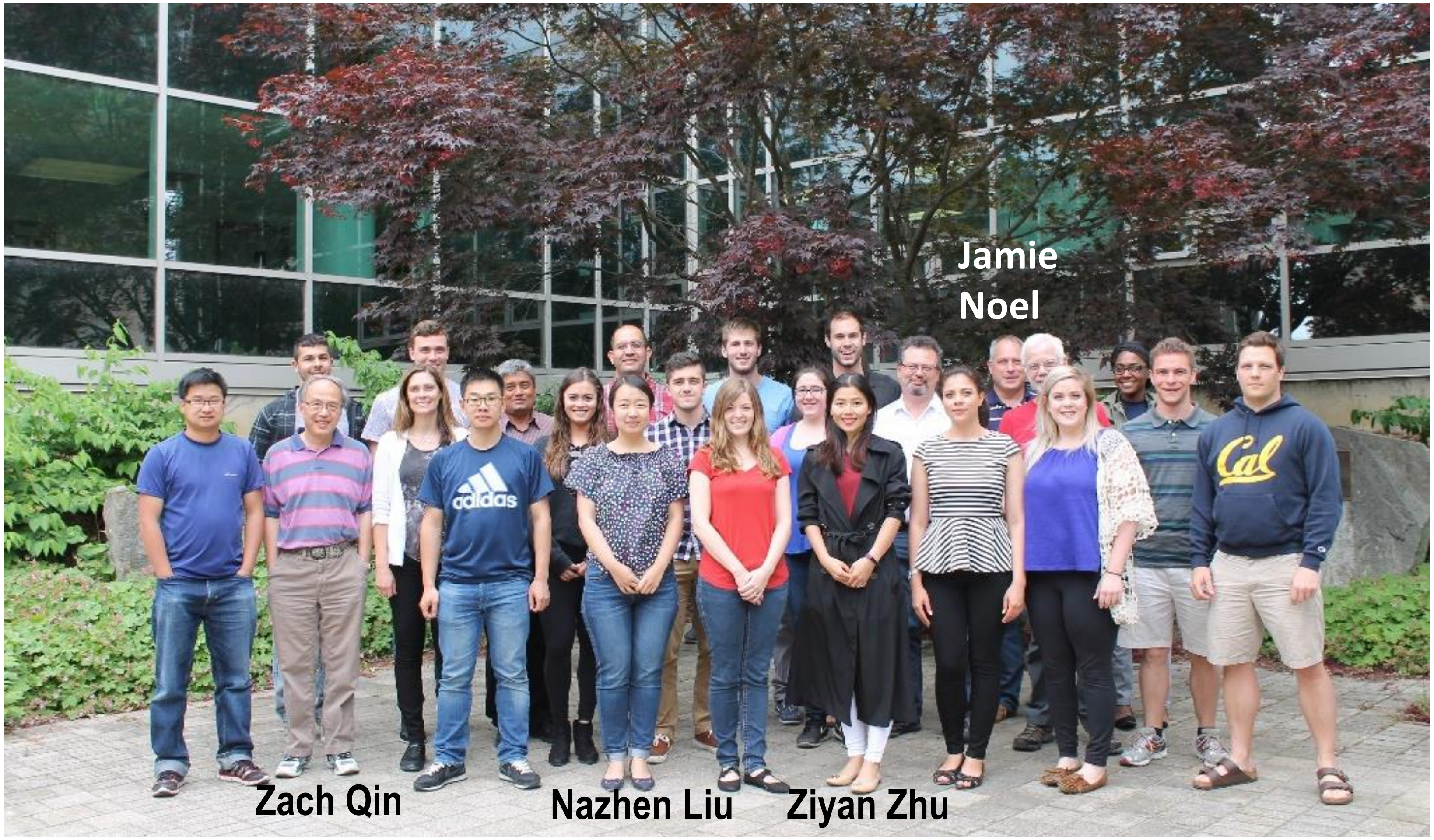
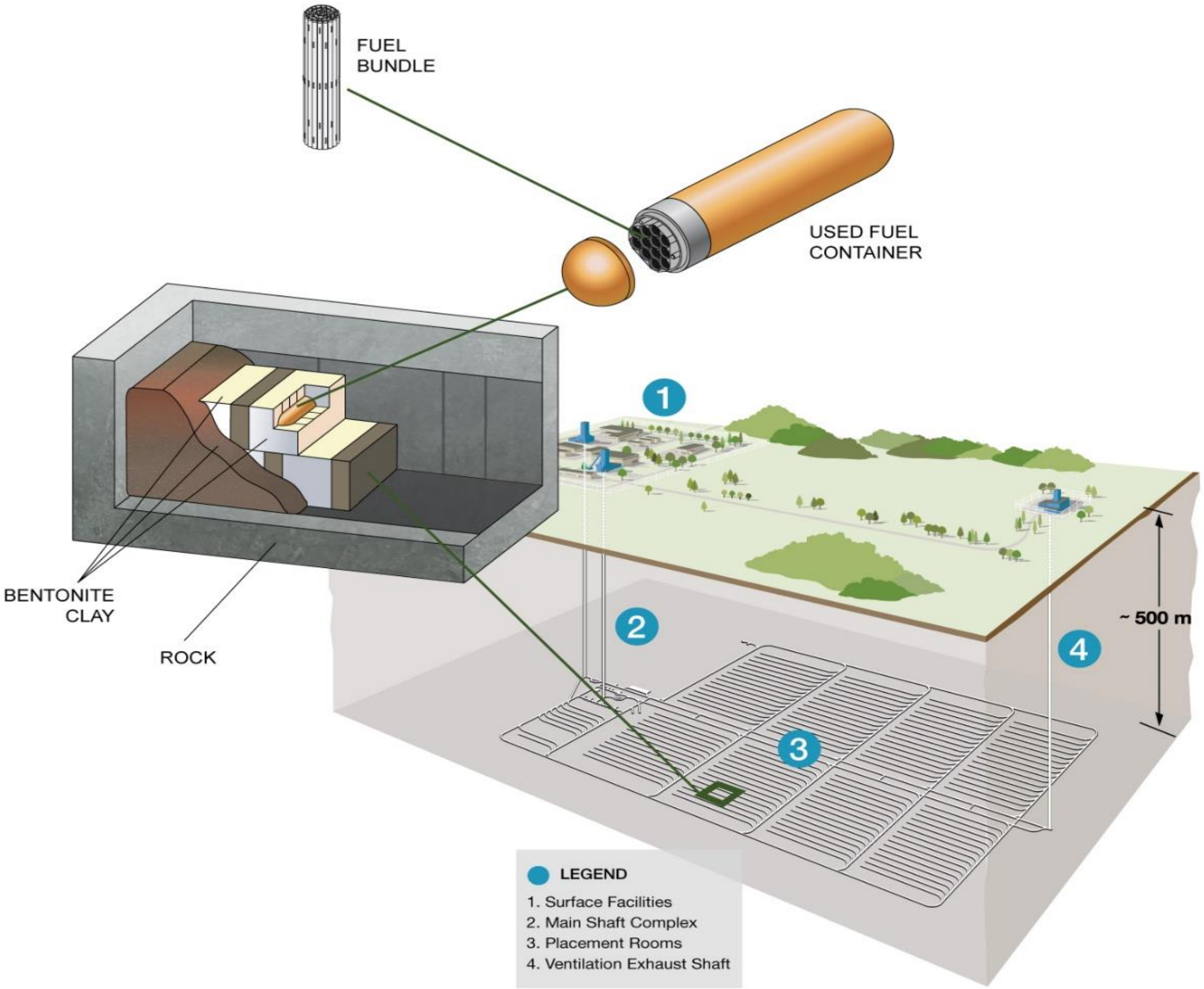


**Linda Wu**

**This research is funded by the Canadian Natural Sciences and Engineering Research Council and the Canadian Nuclear Waste Management Organization**

# THE GENERAL CONCEPT OF GEOLOGIC DISPOSAL IS BASED ON THE PRINCIPLE OF MULTIPLE BARRIERS



● LEGEND
1. Surface Facilities
2. Main Shaft Complex
3. Placement Rooms
4. Ventilation Exhaust Shaft

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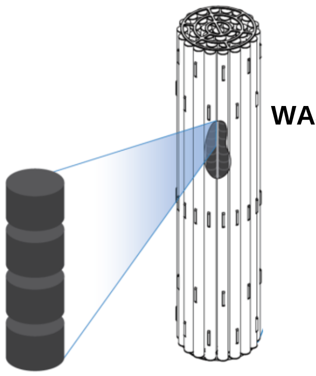
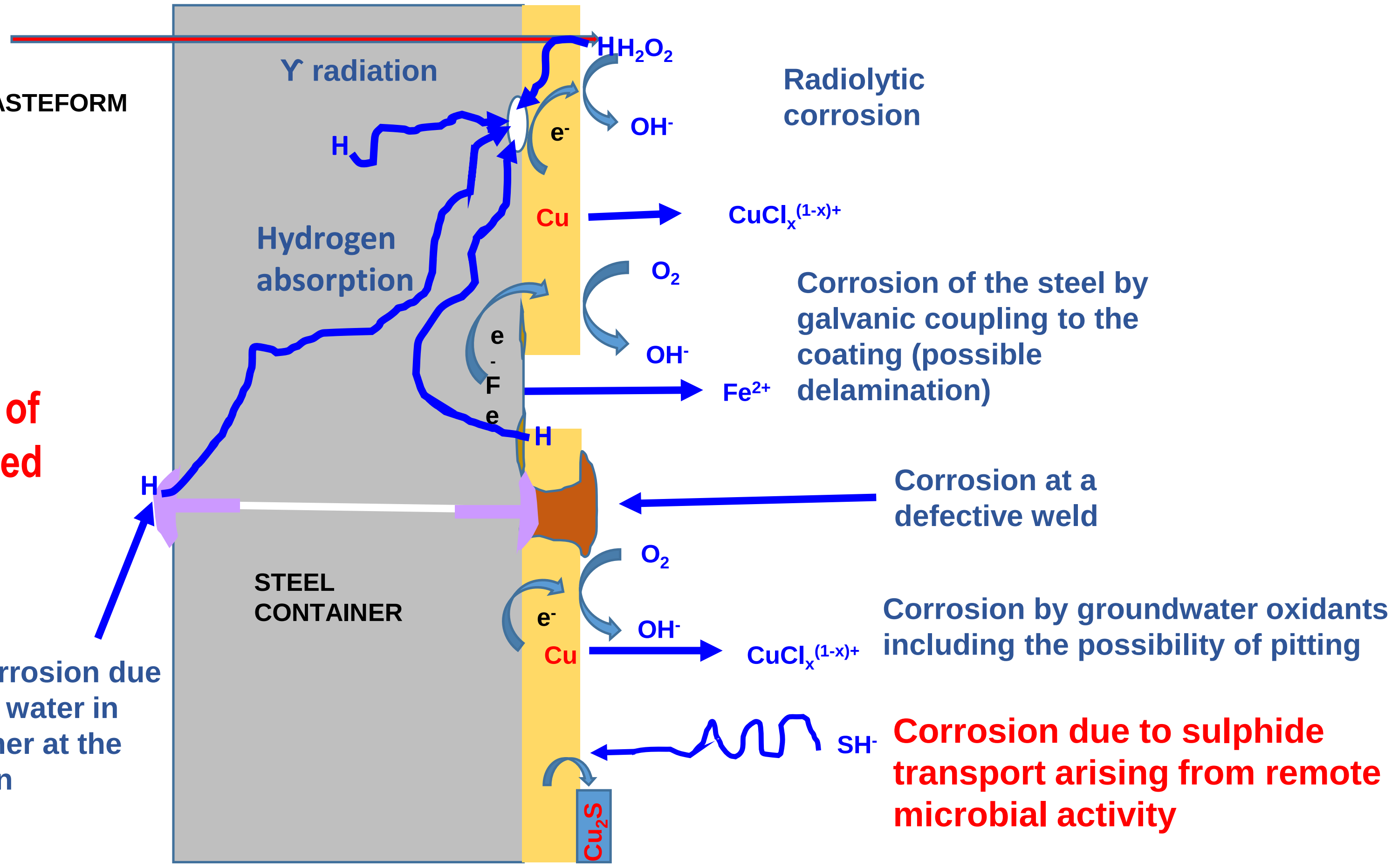
# Possible Corrosion Processes in Anticipated Repository Groundwaters





Radiolytic corrosion

Corrosion of the steel by galvanic coupling to the coating (possible delamination)

Corrosion at a defective weld

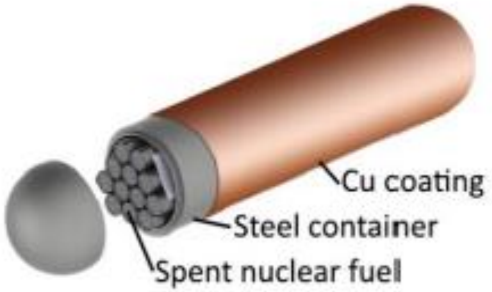
Corrosion by groundwater oxidants including the possibility of pitting

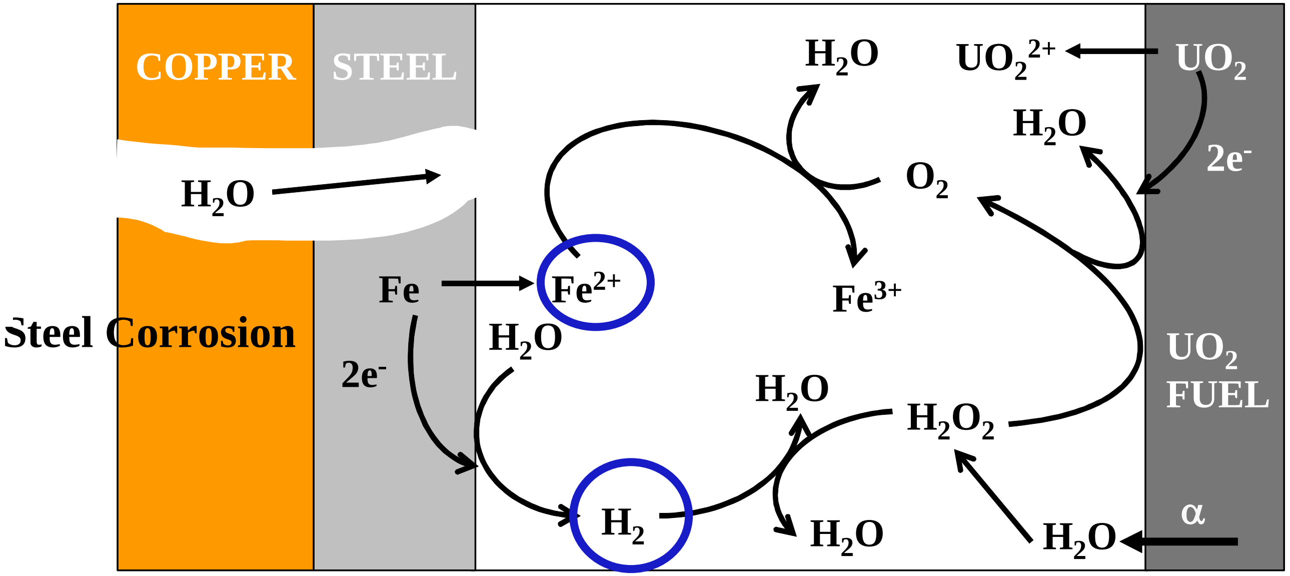
Corrosion due to sulphide transport arising from remote microbial activity

Corrosion performance of nuclear fuel within a failed waste container

Crevice corrosion due to residual water in the container at the weld region

# The Redox Conditions Inside a Failed Container will Determine the Fuel Corrosion Rate



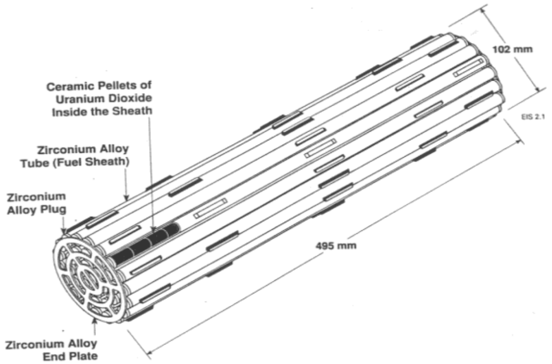


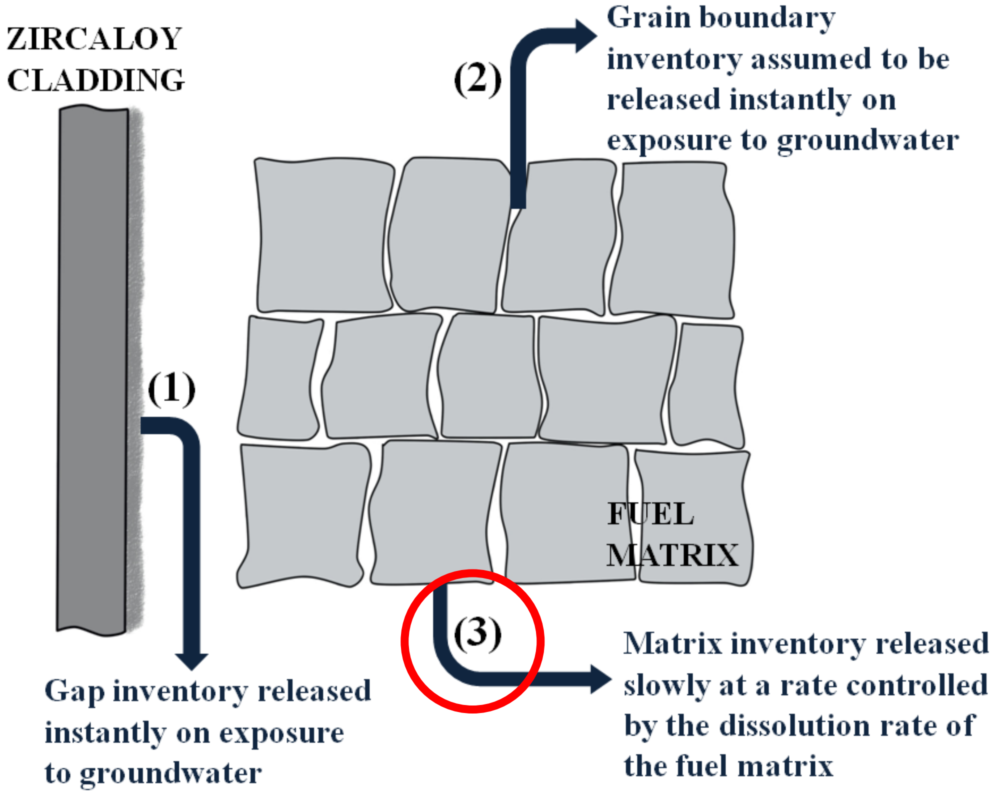
Anoxic Corrosion of the carbon steel liner

Radiolytic Corrosion of the uranium dioxide

**Steel corrosion products expected to scavenge radiolytic oxidants thereby limiting fuel corrosion**

# Some radionuclides could be released independently of the corrosion of the fuel matrix (The Instant Release Fraction). The remainder (> 90%) will be released as the fuel corrodes and dissolves





Grain boundary inventory assumed to be released instantly on exposure to groundwater

Gap inventory released instantly on exposure to groundwater

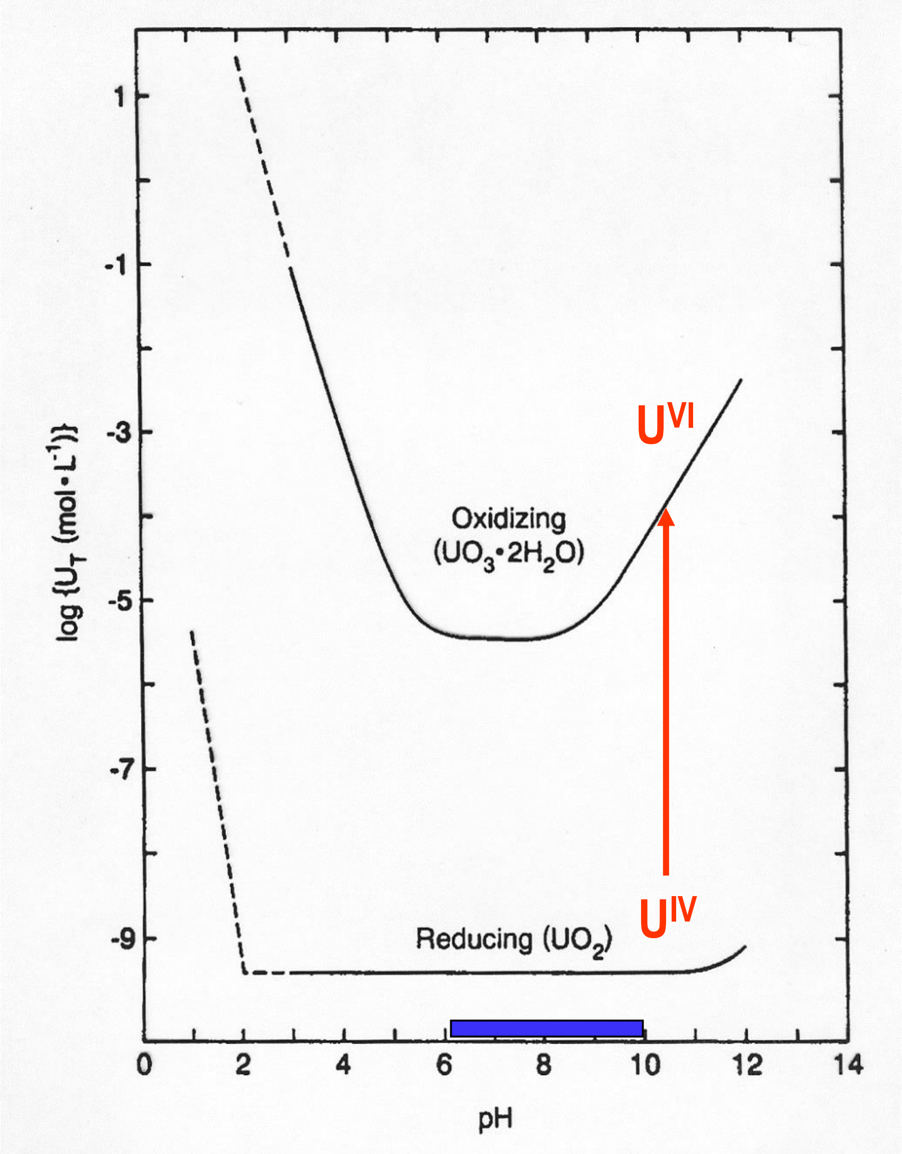
Matrix inventory released slowly at a rate controlled by the dissolution rate of the fuel matrix

The rate of release of the matrix inventory (3) will be determined by the properties of the fuel and the groundwater composition

# Solubility increases on oxidation from $U^{IV}$ to $U^{VI}$ especially in the presence of groundwater anions such as $HCO_3^-/CO_3^{2-}$

Dissolution as $U^{VI}O_2^{2+}$ is corrosion

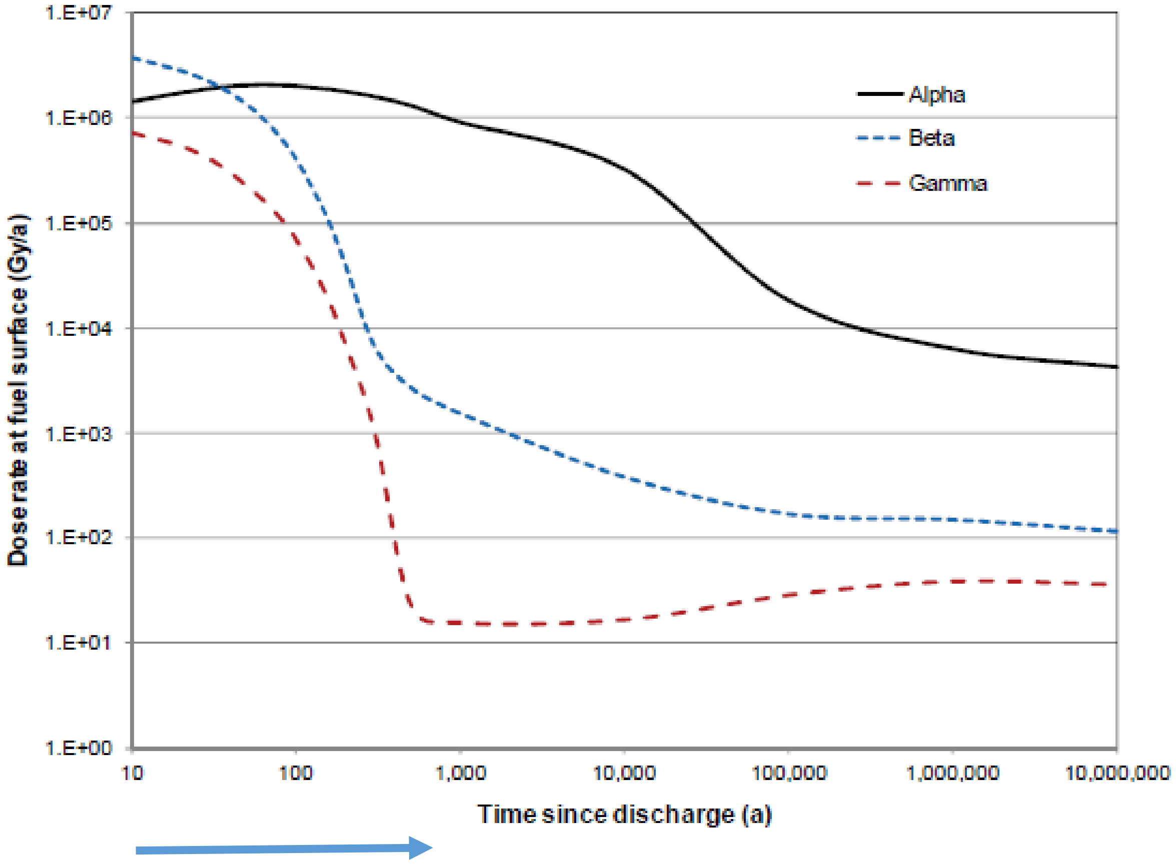
Dissolution as $U^{IV}$ is dissolution



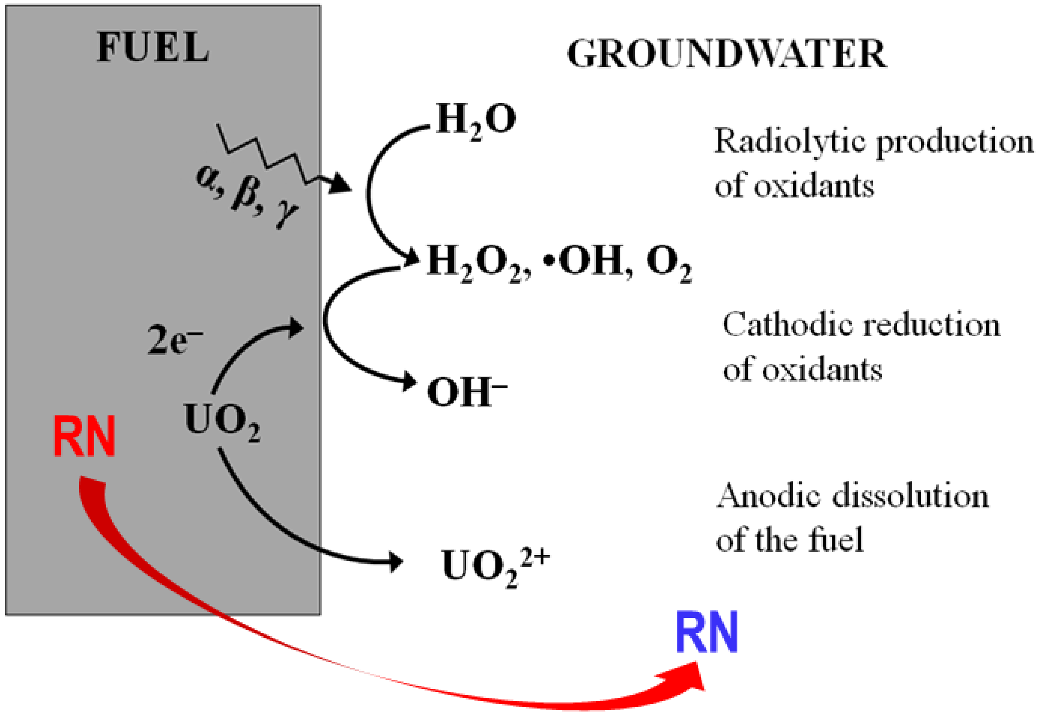
Fuel expected to corrode under oxidizing conditions

# Providing short term containment is achieved, only alpha radiolysis of water will lead to fuel corrosion/radionuclide (RN) release

Radiation decay profiles in the fuel
(Typical CANDU fuel bundle)



Minimum period of containment



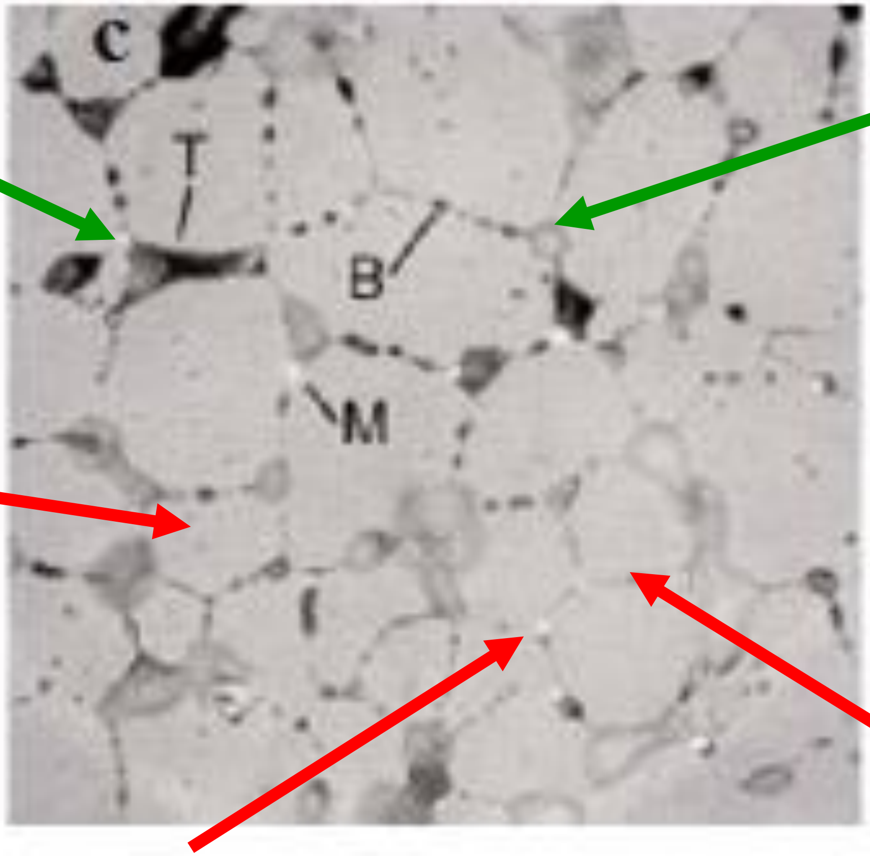
Radiolytic production of oxidants

Cathodic reduction of oxidants

Anodic dissolution of the fuel

Only Alpha Radiation considered in most models

# In-Reactor Fission will Cause many Changes in the Properties of the Fuel (*$UO_{2.001}$ prior to in-reactor irradiation*).



Grain boundary tunnels

Grain boundary fission bubbles

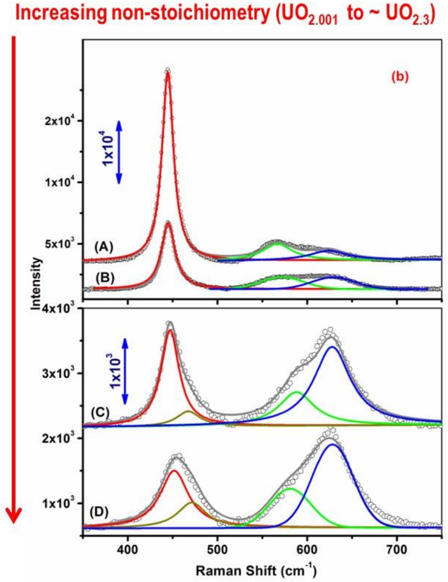
Rare earth-doped grains

Noble metal (Ru, Pd, Mo) particles

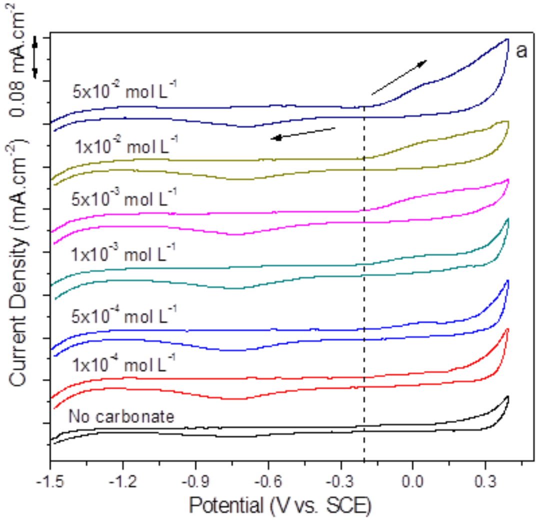
Residual non-stoichiometry in grain boundaries

The features in red can be simulated in custom-fabricated SIMFUELs which avoid the radiation fields associated with spent fuel

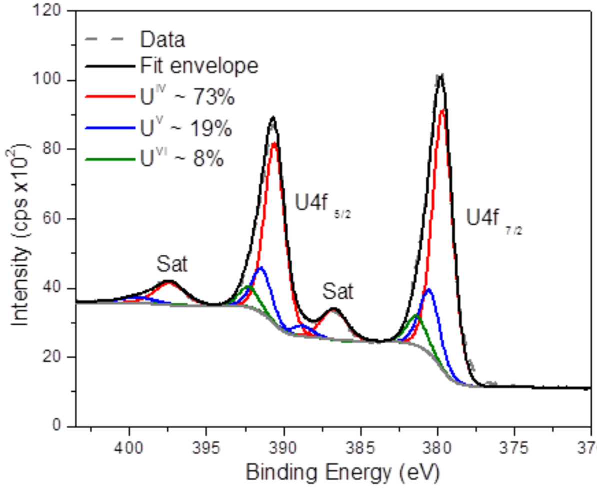
# Electrochemical/Spectroscopic/Microscopic Studies of Simulated Fuel Properties



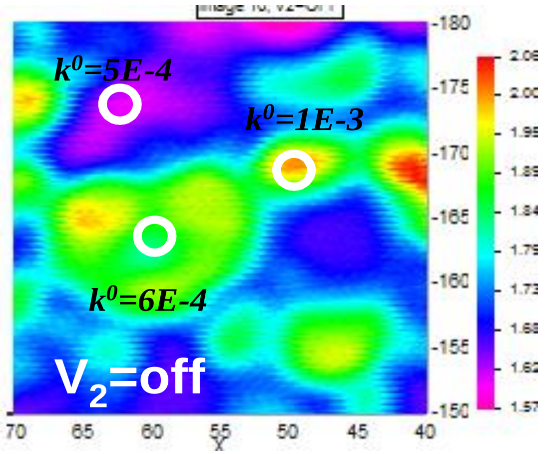
MicroRaman spectroscopy used to determine the influence of doping on the $UO_2$ matrix



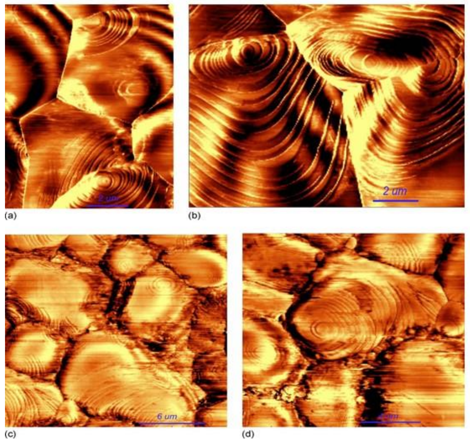
Electrochemical methods used to study $UO_2$ reactivity and the kinetics of oxidant reduction reactions



X-ray photoelectron spectroscopy used to determine surface composition



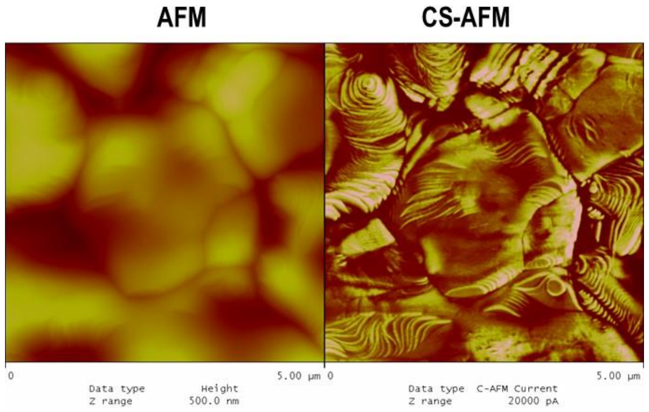
Scanning Electrochemical Microscopy (SECM) used to determine lateral variations in reactivity



Before Corrosion

After Corrosion

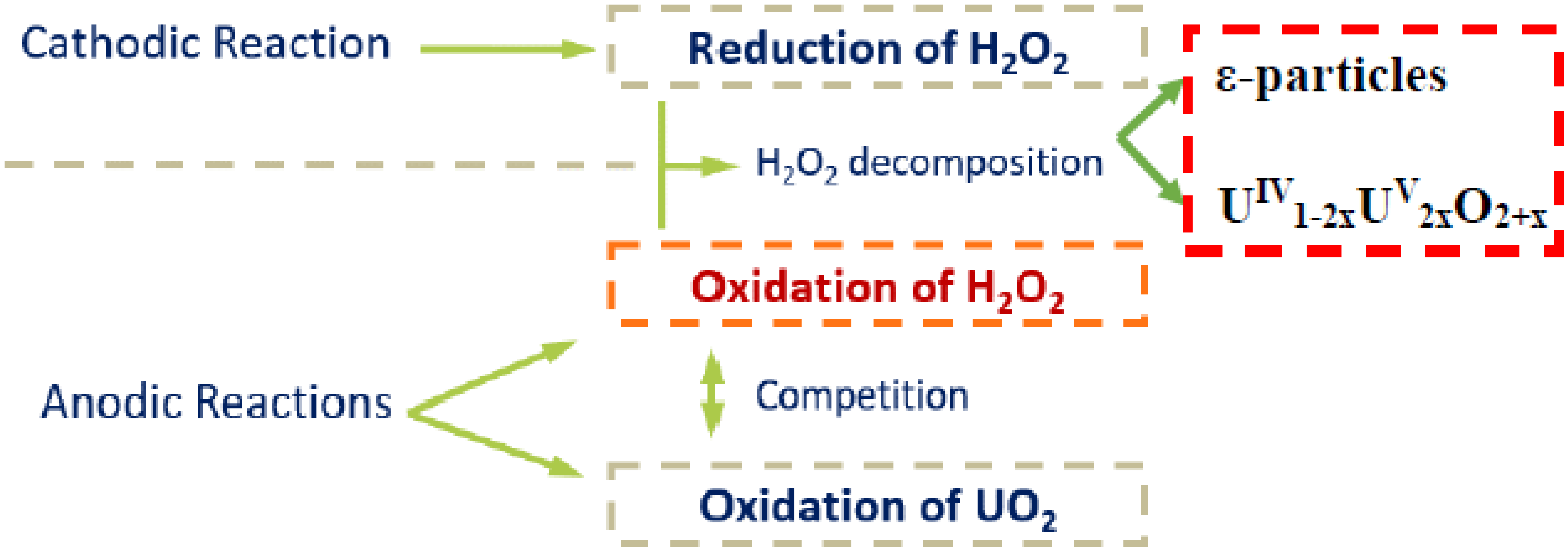
Atomic Force Microscopy (AFM) used to detect corrosion damage



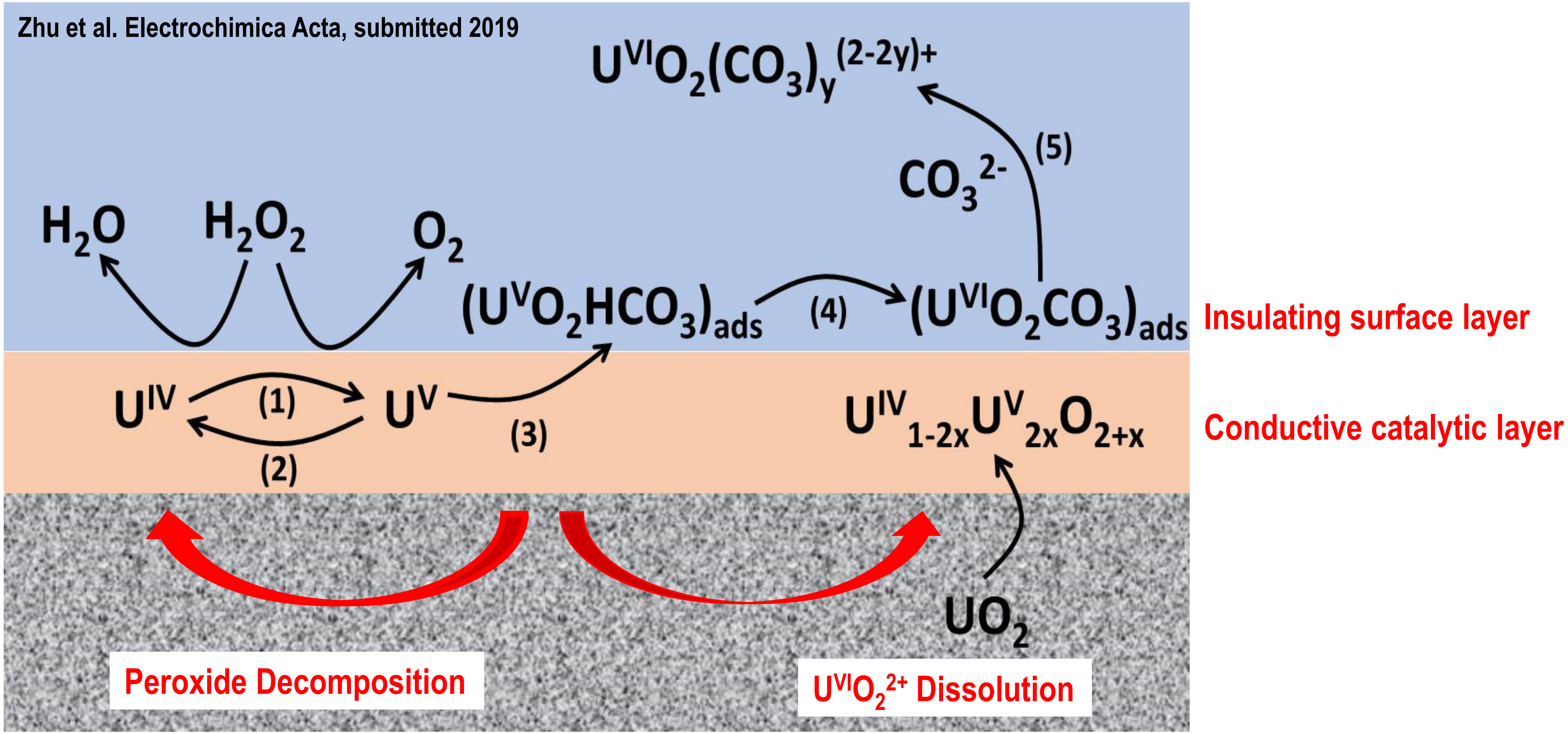
Current sensing AFM used to relate surface conductivity to composition

# One Example of Mechanistic Detail

# THE FATE OF THE KEY RADIOLYTIC OXIDANT ($H_2O_2$)



- Which reaction is the most important?
- What is the function of the ε-particles?
- Does the rare earth doping of the $UO_2$ change the balance between reactions?
- Can we evaluate the parameters required for a model?



Zhu et al. Electrochimica Acta, submitted 2019

$U^{IV}O_2$ -- ~14% of the $H_2O_2$ consumed by dissolution
$U^{IV}_{1-y}RE^{III}_yU^VO_2$ – 0.3% to < 4% consumed by dissolution
$U^{IV}_{1-y}RE^{III}_yU^V_y(\varepsilon)O_2$ -- 0.3% to < 4% consumed by dissolution

$H_2O_2$ reduction catalyzed by $RE^{III}$ doping but not further catalyzed by noble metal (ε) particles

$O_2$ could be the dominant oxidant

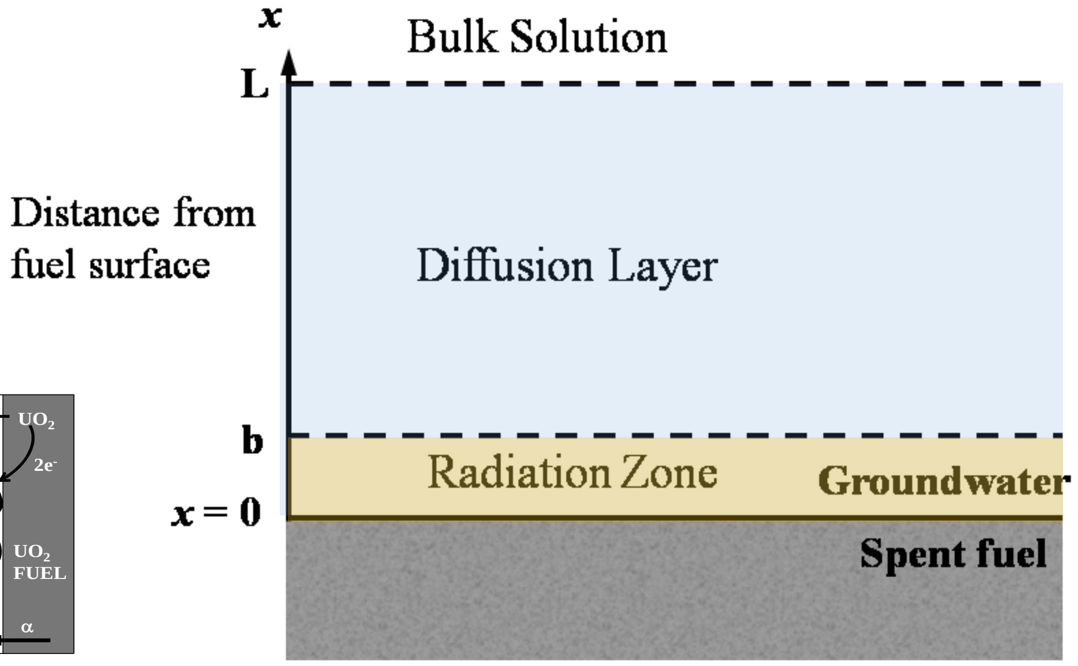
# MODELS FOR FUEL CORROSION

- **De Windt et al. - J. Contam. Hydrology; 61, 303-312 (2003)**
- **Poulesquen and Jegou – Nucl. Technol. 160, 337-345 (2007)**
- **Grambow et al. - European Commission Final Report for the MICADO Project, EUR 24597 (2010)**
- **Shoesmith et al. - Corrosion 59, 802-816 (2003)**
- **Eriksen et al. - J.Nucl. Mater. 420, 409-423 (2012)**
- **Jerden et al. - J.Nucl. Mater; 462, 135-146 (2015)**
- **Liu et al. - Corrosion 75, 302-308 (2019)**

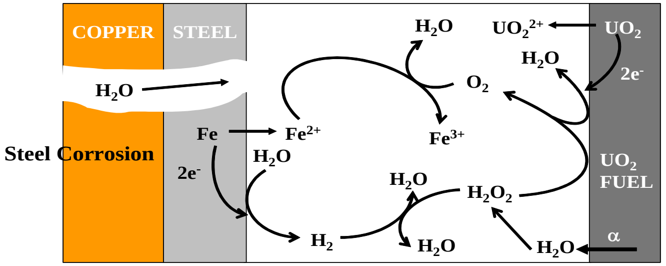
# A Model for the Radiolytic Corrosion of Used Nuclear Fuel Inside a Failed Waste Container

- Wu et al. Corrosion Science 61, 83-91 (2012)
- Wu et al. Corrosion Science 84, 85-95 (2014)
- Wu et al. J.Electrochem.Soc. 161, E3259-E3266 (2014)
- Liu et al. Environ. Sci.Tech. 50, 12348-12355 (2017)
- Liu et al. J.Nucl.Mater, 494, 87-94 (2017)
- Liu et al. Corrosion 75, 302-308 (2019)

# One Dimensional Alpha Radiolysis Model



Separation between the source of redox scavengers and the source of radiolytic oxidants



Anoxic Corrosion of the carbon steel liner

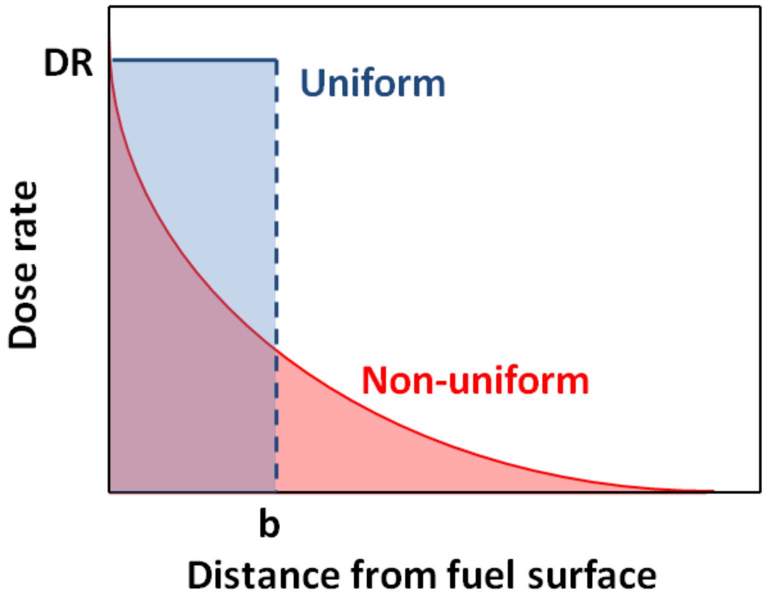
Radiolytic Corrosion of the uranium dioxide

Diffusion-reaction equation at steady state

$$D_i \frac{\partial^2 c_i(x)}{\partial x^2} = -\sum_k R_k(i)$$

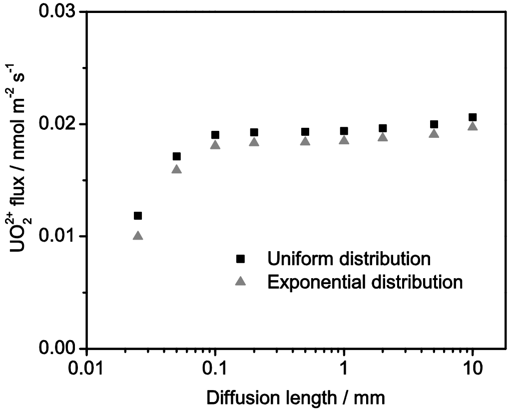
**Model solved numerically using COMSOL Multiphysics (Dilute species transportation and chemical engineering modules).**

# Simplification of the Alpha Dose Rate Distribution



- Uniform distribution:
  - $D(x)=DR$, $0 \leq x \leq b$.
  - DR is average dose rate.
  - b is length of radiation zone, 13 µm.

- Non-uniform distribution:
  - $D(x)=A[\exp(-x/B)+C]$, $0 \leq x \leq \delta$.
  - Values of B and C are obtained from the α-dose rate profile calculated by Nielsen et al.
  - δ is the maximum penetration length of α-radiation.

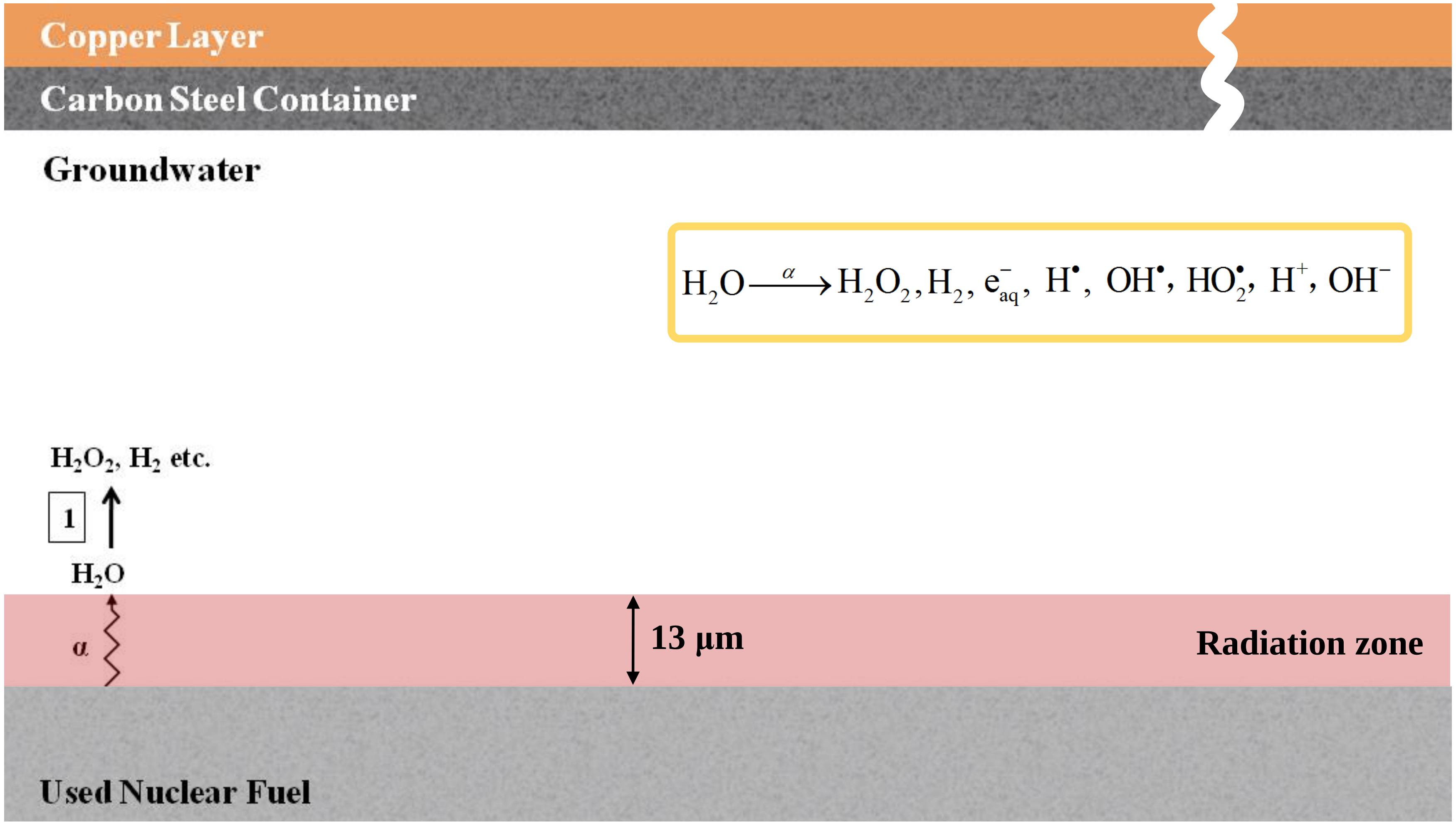


Model calculations indicate this simplification leads to minimal error

# Reactions Occurring Inside a Failed Container Assumed Flooded with Groundwater

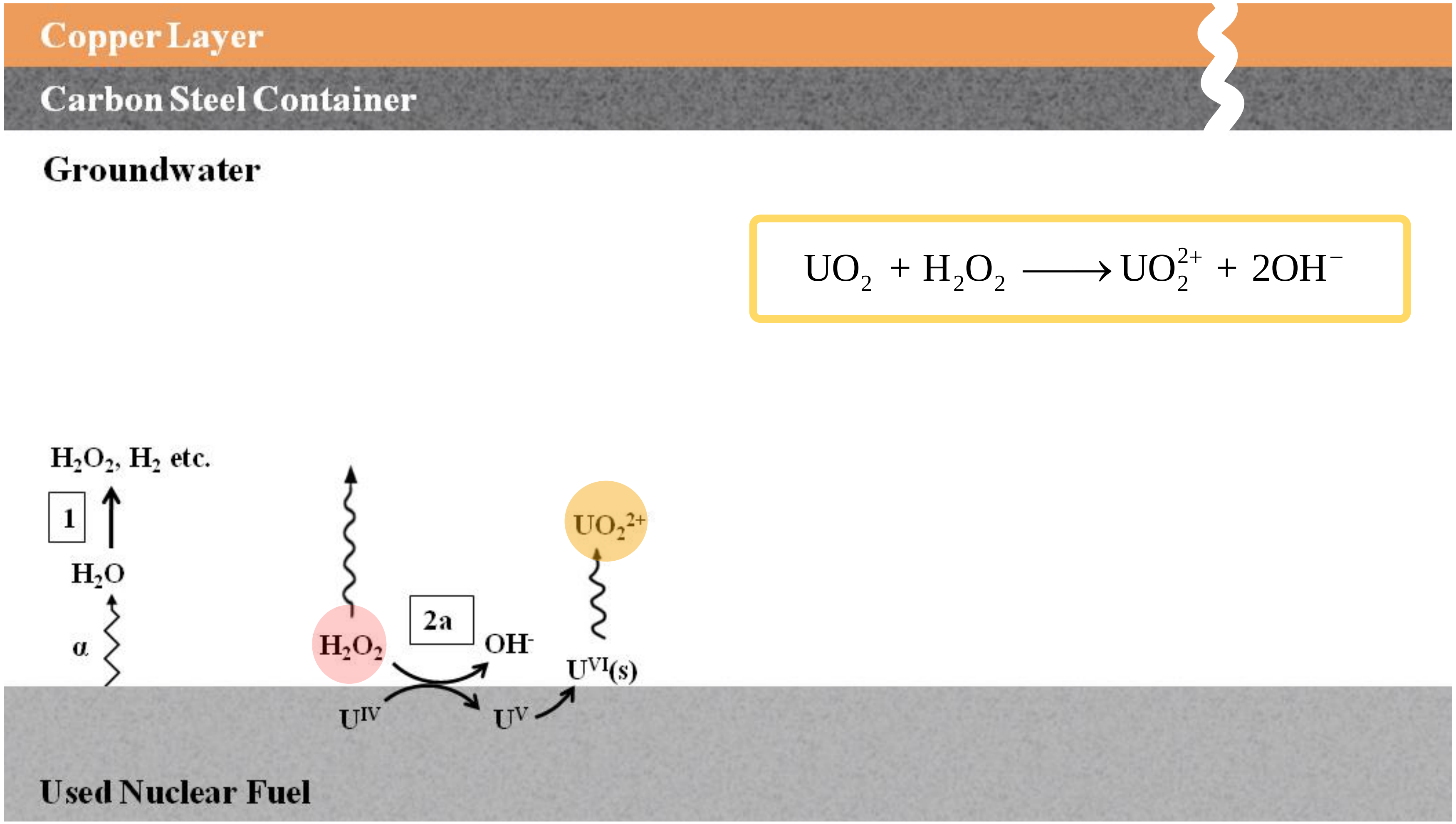
# Reactions Inside a Failed Container

# Reactions Inside a Failed Container



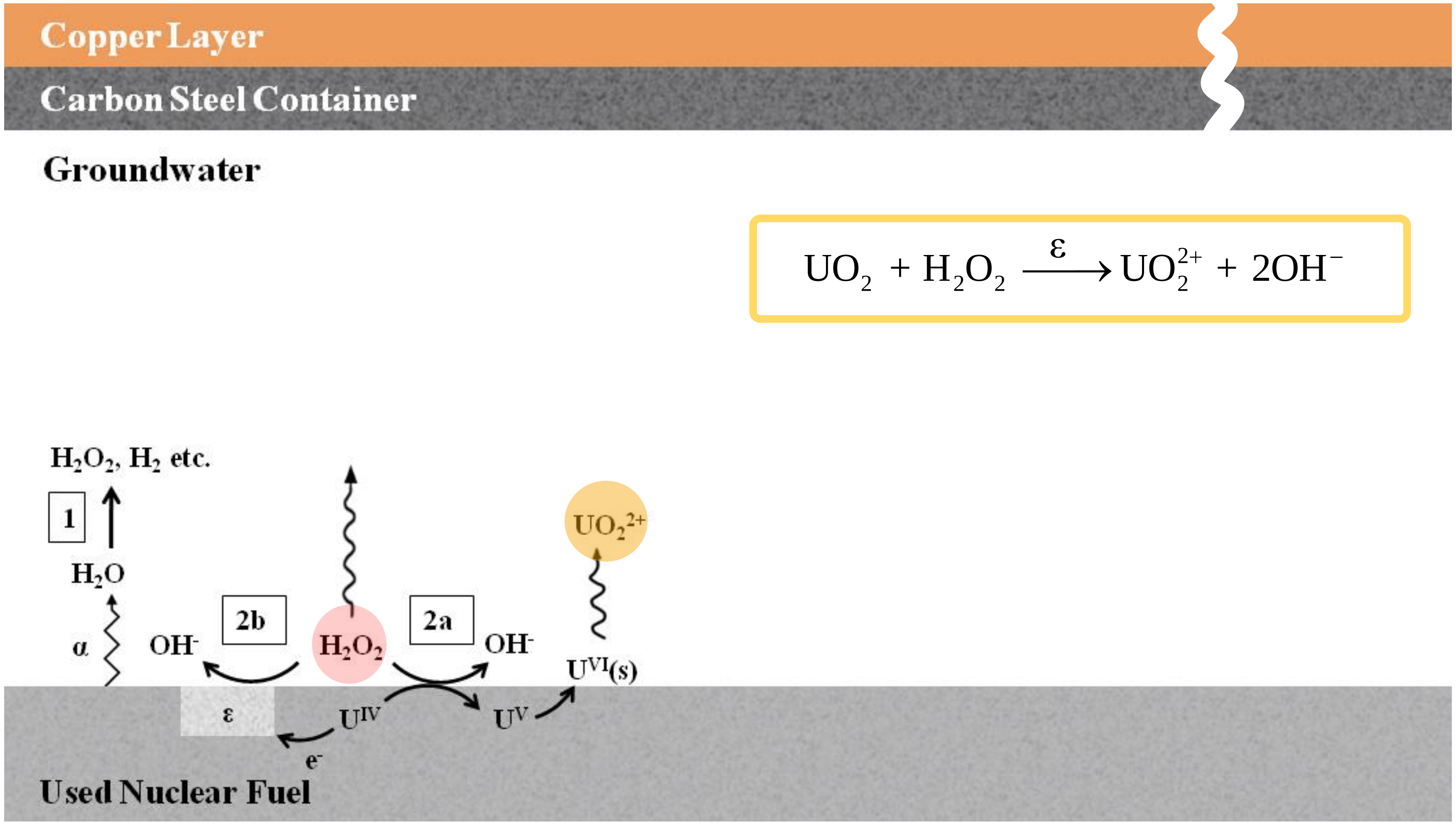
$$H_2O \xrightarrow{\alpha} H_2O_2, H_2, e^-_{aq}, H^\bullet, OH^\bullet, HO_2^\bullet, H^+, OH^-$$

# Reactions Inside a Failed Container



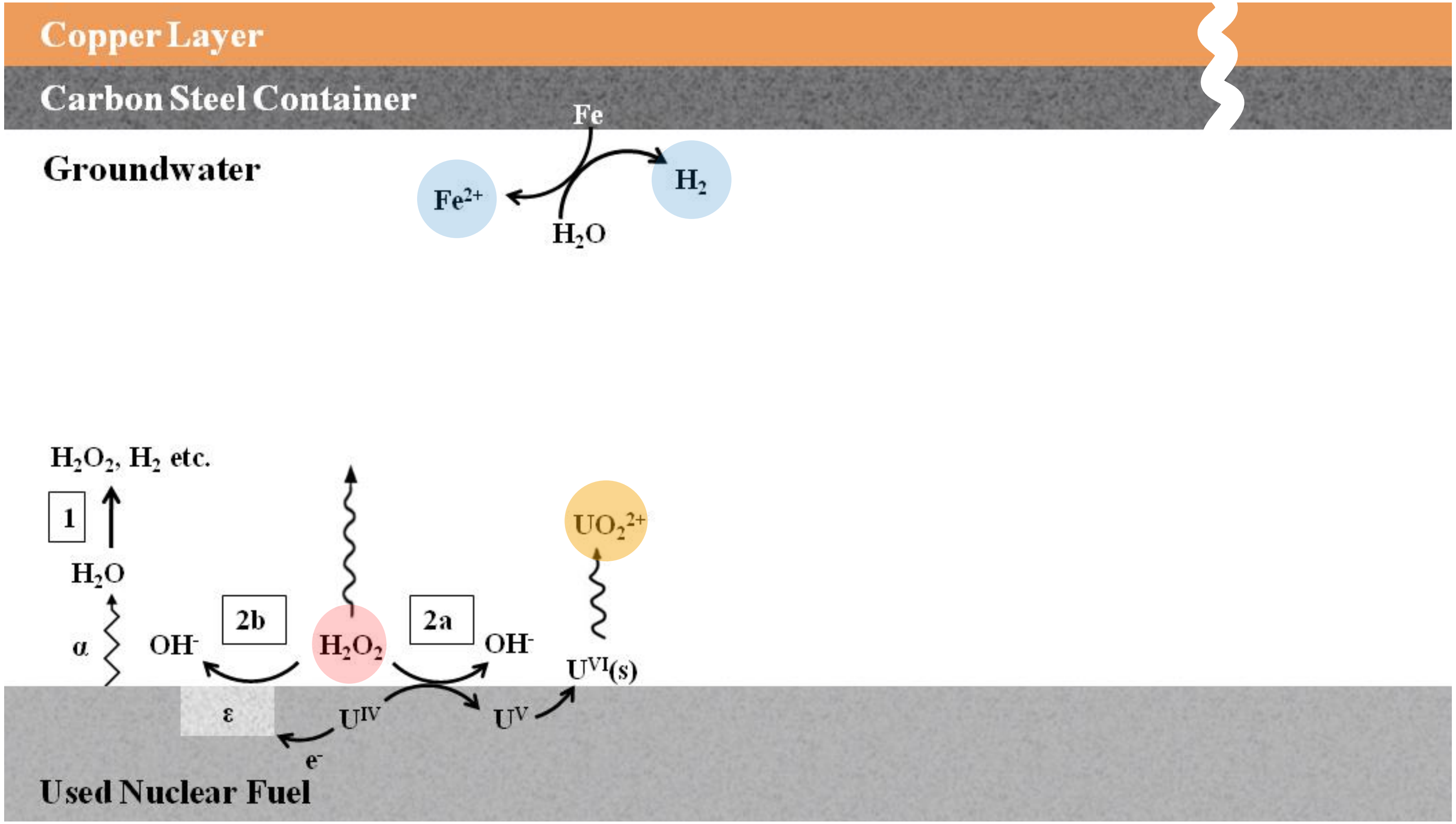
$$UO_2 + H_2O_2 \longrightarrow UO_2^{2+} + 2OH^-$$

# Reactions Inside a Failed Container

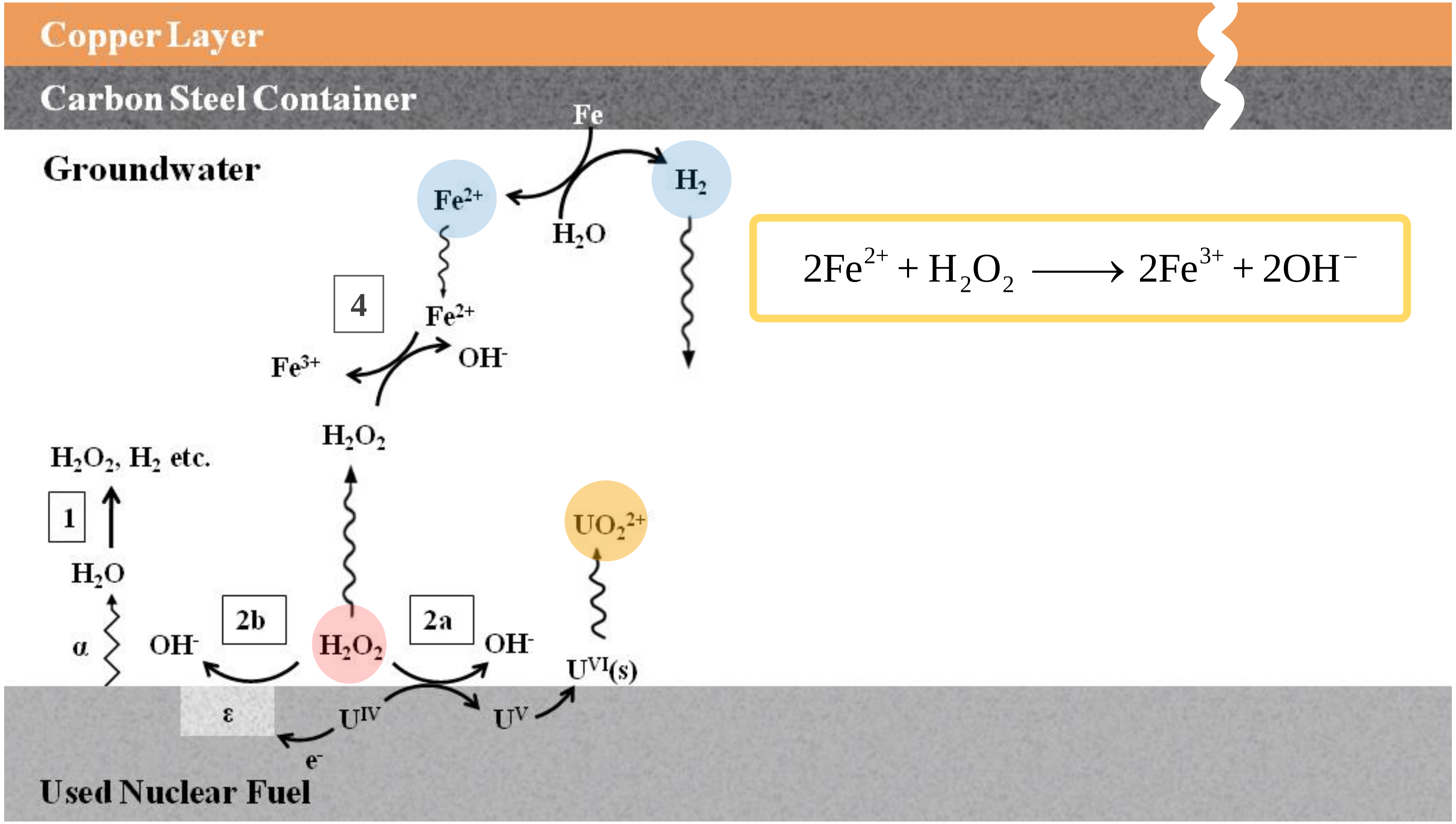


$$UO_2 + H_2O_2 \xrightarrow{\varepsilon} UO_2^{2+} + 2OH^-$$

# Reactions inside a Failed Container



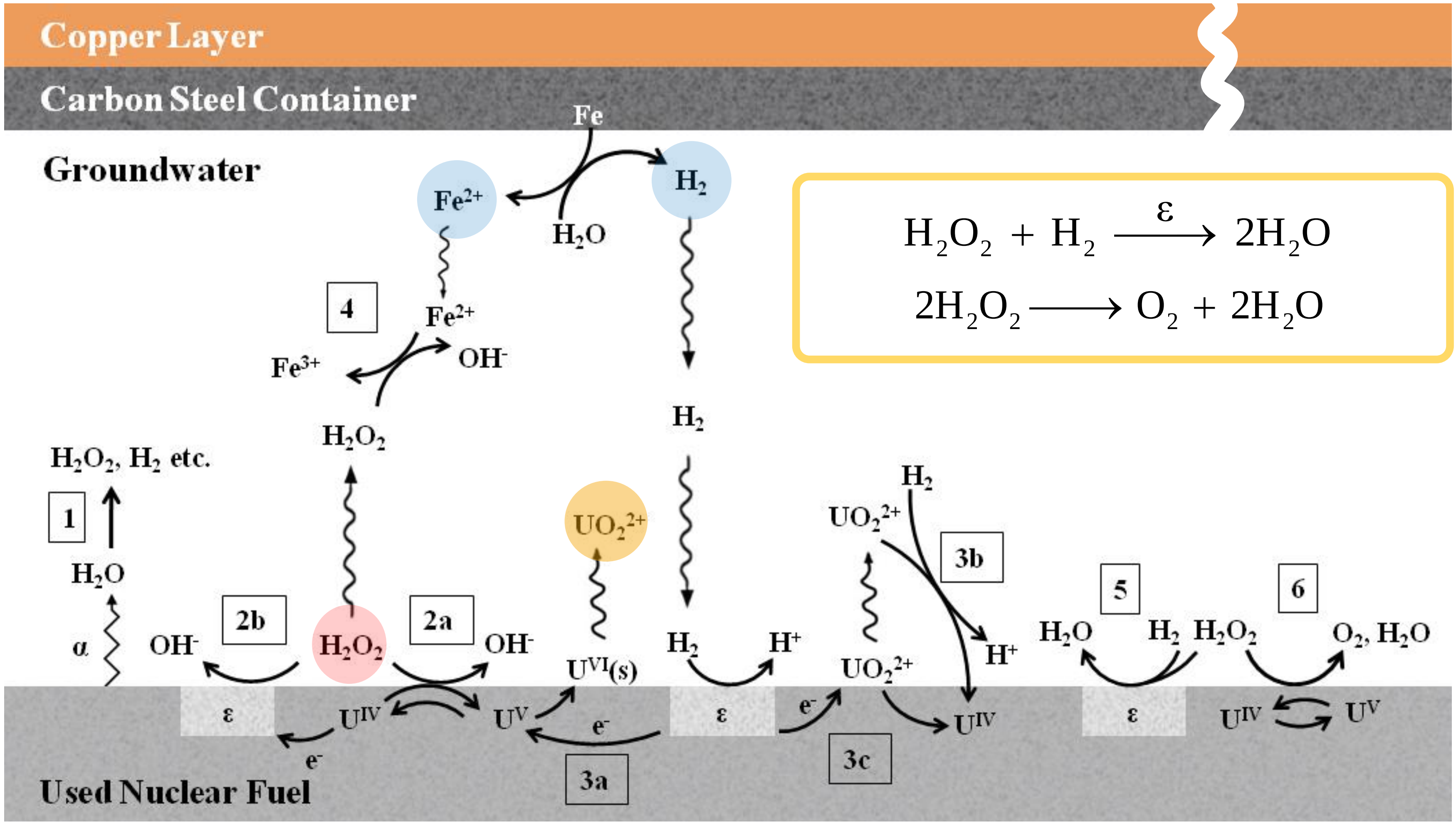
# Reactions Inside a Failed Container



$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$

F.J. Millero, and S. Sotolongo, *Geochim. Cosmochim. Acta* 53 (1989) 1867.

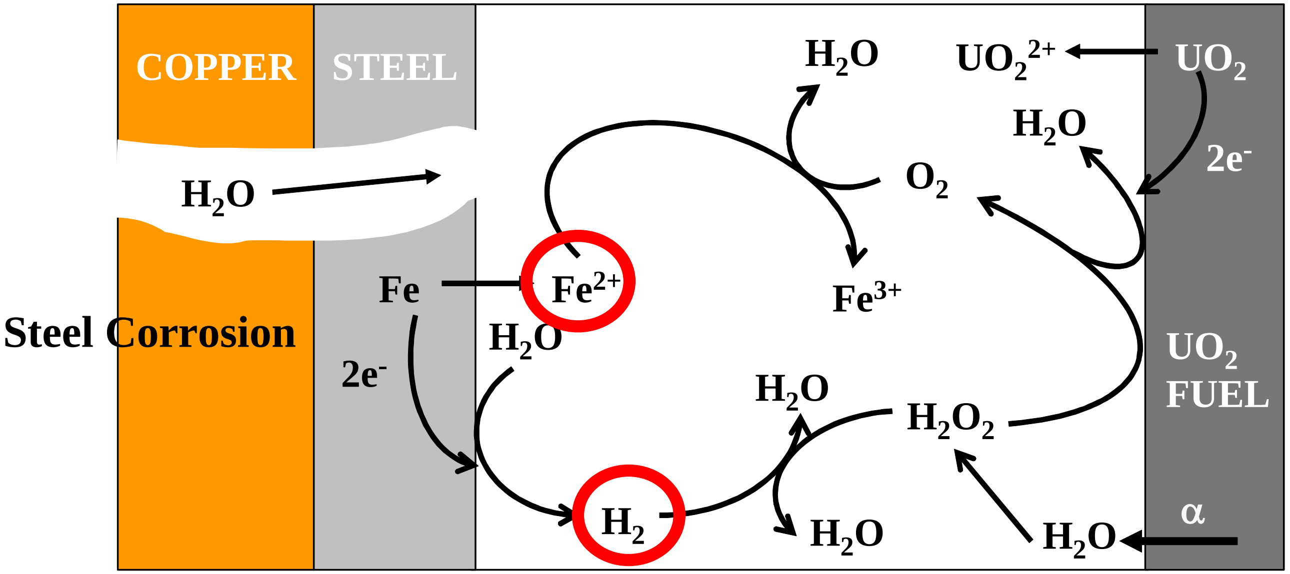
# The Key Reactions Controlling Fuel Corrosion/Dissolution Inside a Failed Container



$$H_2O_2 + H_2 \xrightarrow{\varepsilon} 2H_2O$$

$$2H_2O_2 \longrightarrow O_2 + 2H_2O$$

# The Influence of Redox Scavengers on the Fuel Corrosion/Radionuclide Release Rate



Anoxic Corrosion of the carbon steel liner

Radiolytic Corrosion of the uranium dioxide

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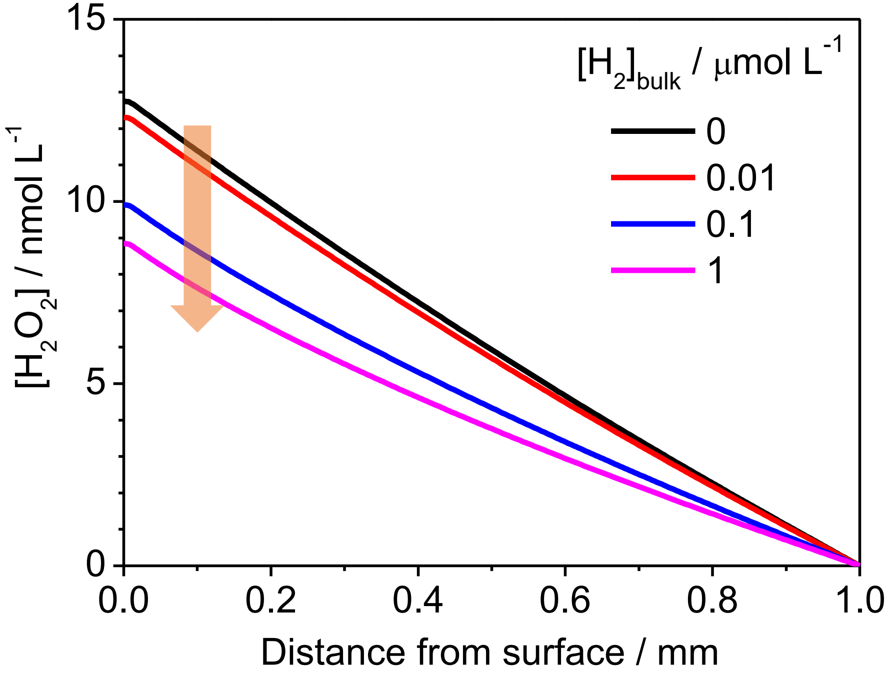
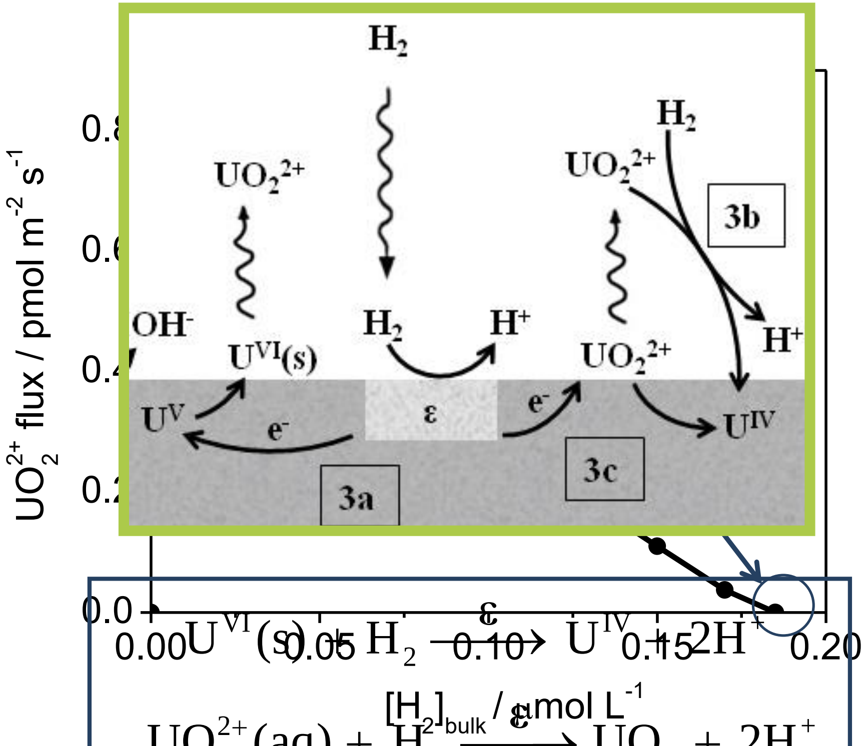
# The influence of $H_2$



From steel corrosion

Steady-state $[H_2O_2]$ profiles at various bulk $[H_2]$, $[Fe^{2+}]_{bulk}$ = 0.01 µmol $L^{-1}$.



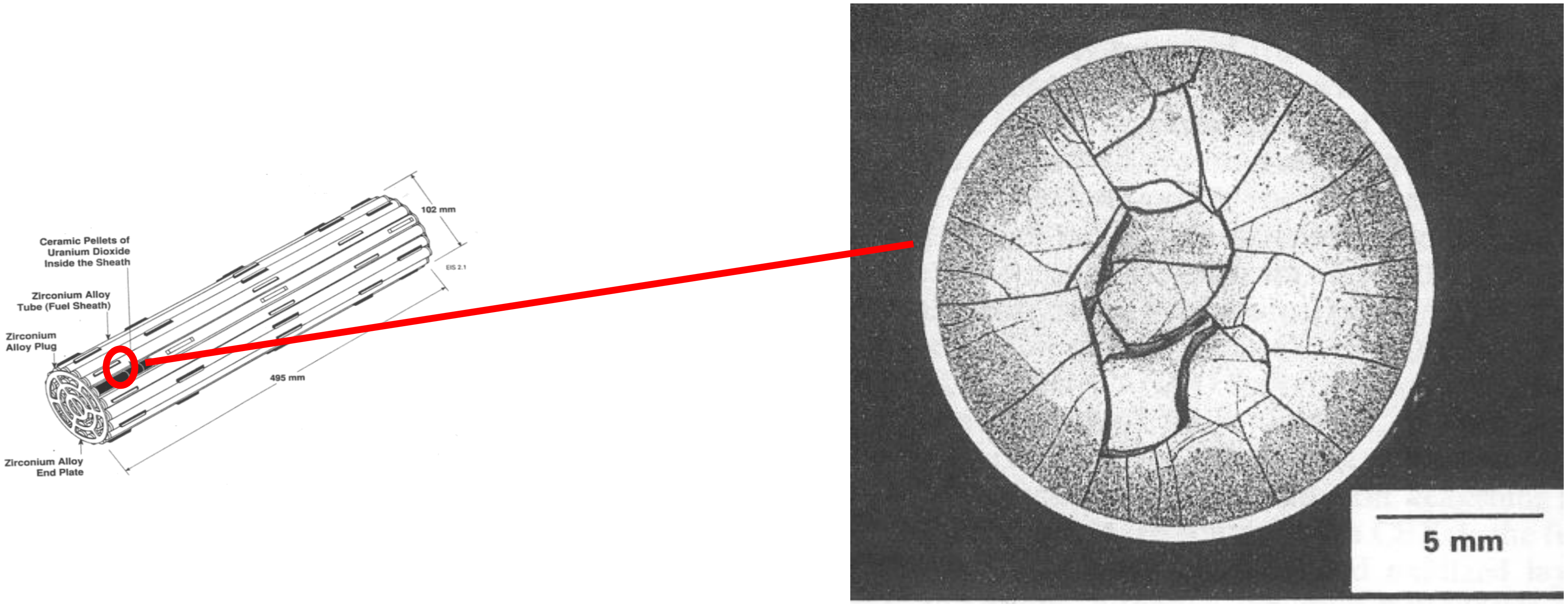
$$U^{VI}(s) + H_2 \xrightarrow{\varepsilon} U^{IV} + 2H^+$$

$$UO_2^{2+}(aq) + H_2 \xrightarrow{\varepsilon} UO_2 + 2H^+$$

$UO_2^{2+}$ flux (equal to the $UO_2$ corrosion rate) as a function of $[H_2]_{bulk}$.

**$H_2$ can suppress fuel corrosion by lowering $[H_2O_2]$ and reducing $U^{VI}$ species.**
**In a sealed repository $[H_2]$ can reach millimolar levels**

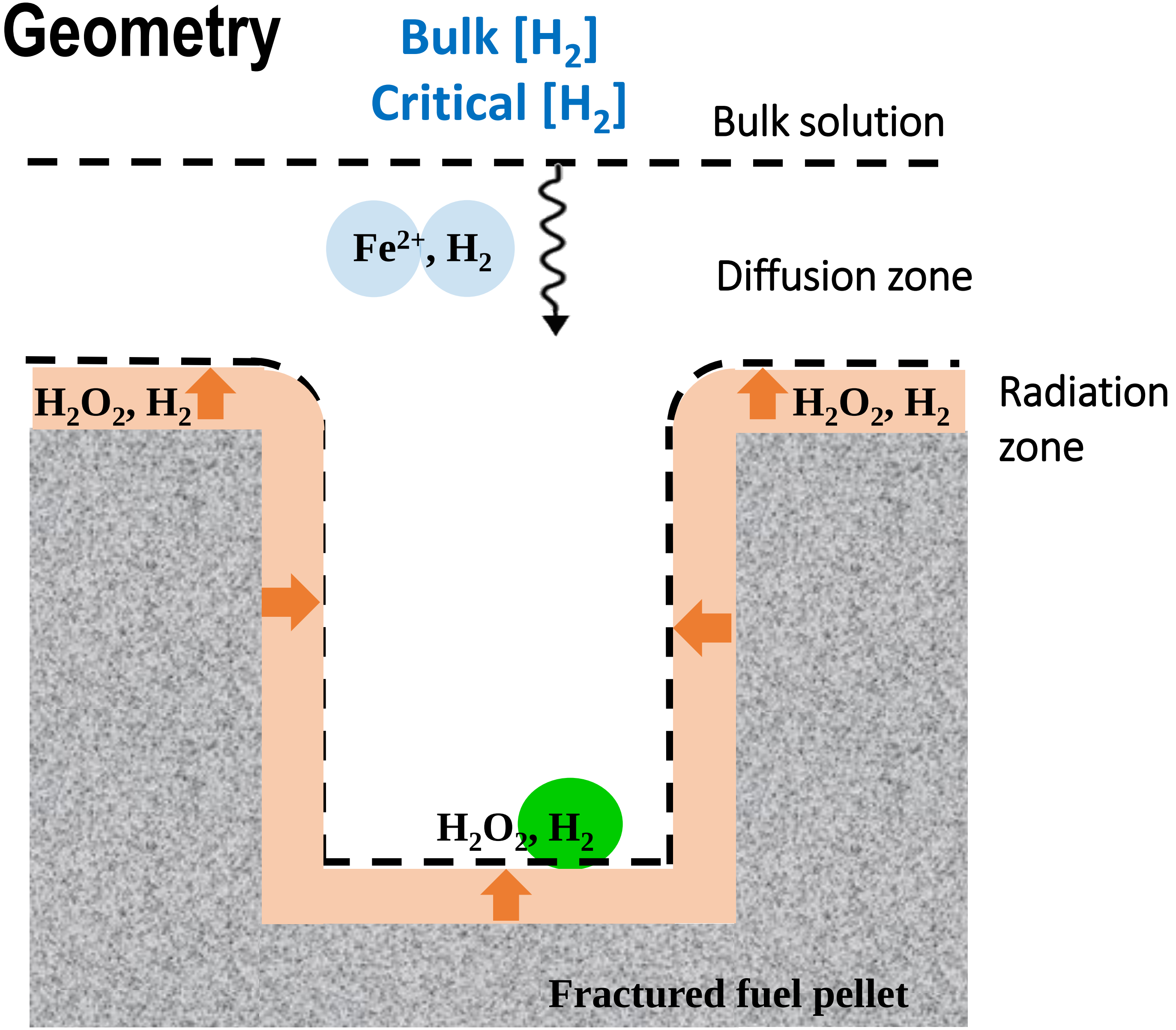
# Due to the Fractured Nature of the Fuel a Two Dimensional Model is Required



Cross section of used CANDU fuel pellet after 15 years of storage in humid air

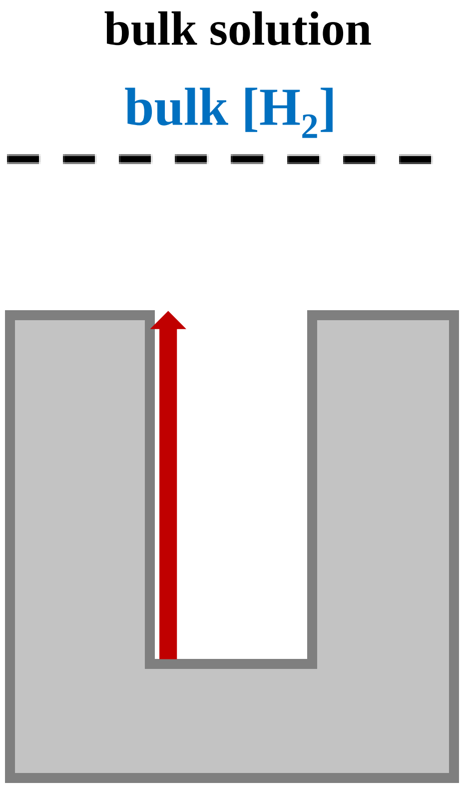
**Fractures allow groundwater access to the internal structure of a pellet.**
**Will the redox scavengers be effective at locations within the fuel?**

# Effect of Geometry

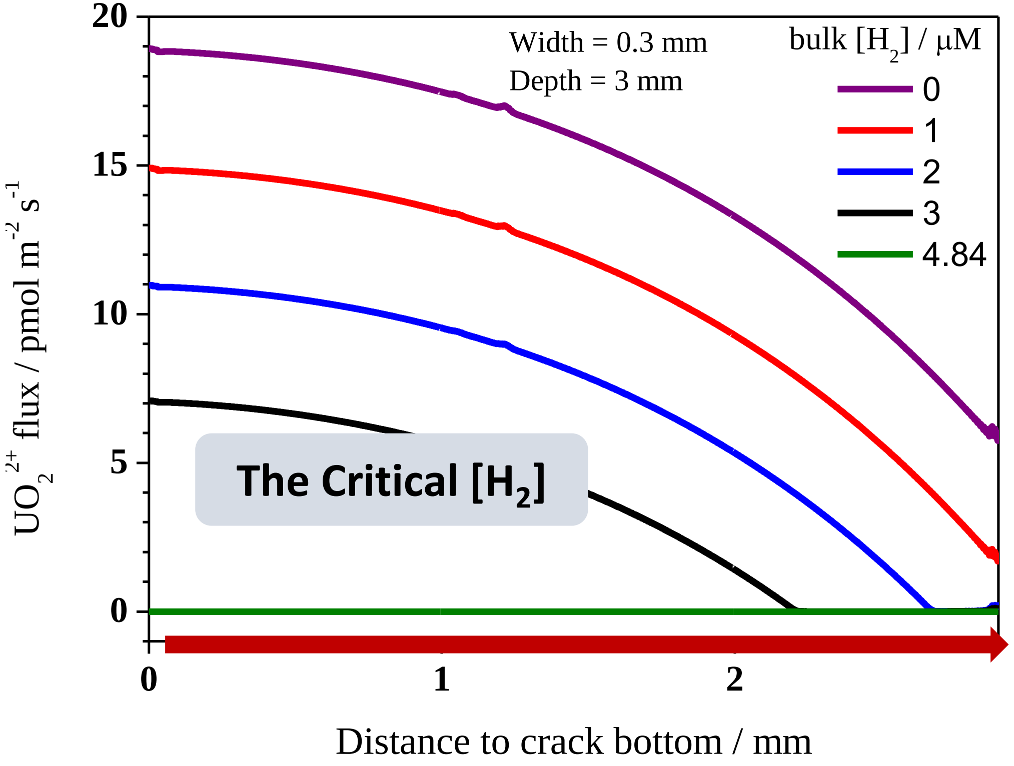


# The Influence of Hydrogen on the Corrosion Rate Inside a Fracture

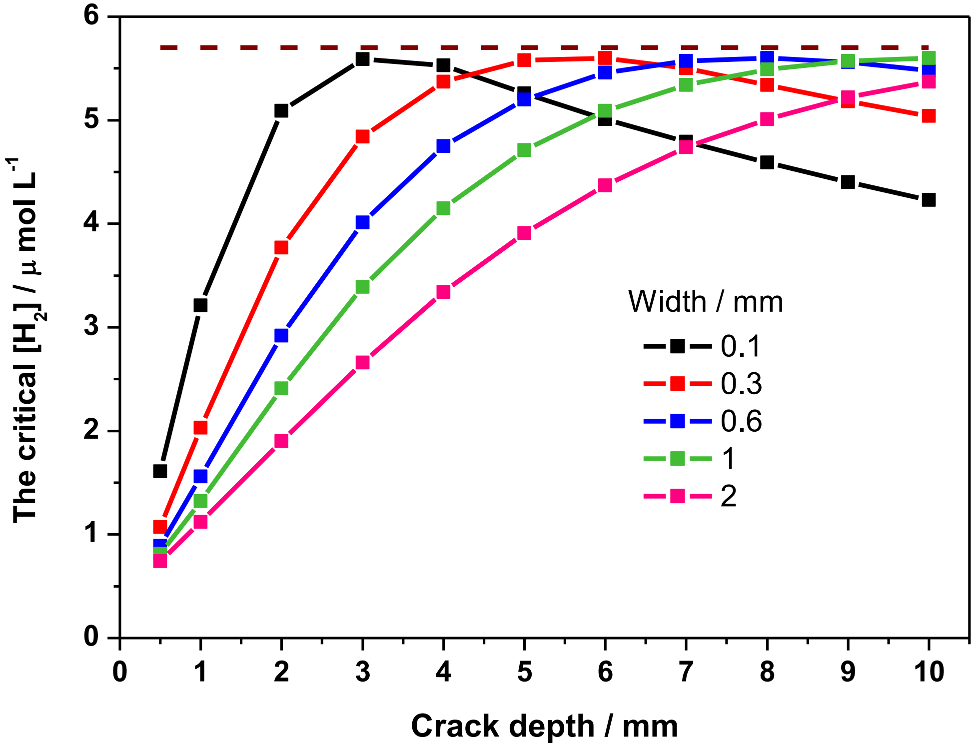
**The critical [$H_2$] is defined as the minimum bulk [$H_2$] (from carbon steel corrosion) required to completely suppress fuel corrosion.**



**As the bulk [$H_2$] increases fuel dissolution becomes progressively more suppressed**



# The Influence of Crack Geometry on the Critical [$H_2$]



**The calculated critical [$H_2$] in cracks with different widths and depths, with α dose rate = *9.03 × $10^5$* Gy $a^{-1}$.**

**There exists an upper limit (5.7 μmol $L^{-1}$ indicated by the dashed line) for the critical [$H_2$] for the anticipated range of possible crack geometries.**

**These calculations suggest a significant role for radiolytic $H_2$ in the suppression of corrosion in narrow and deep fracture locations**

# Separation of Internal and External $H_2$ Effects

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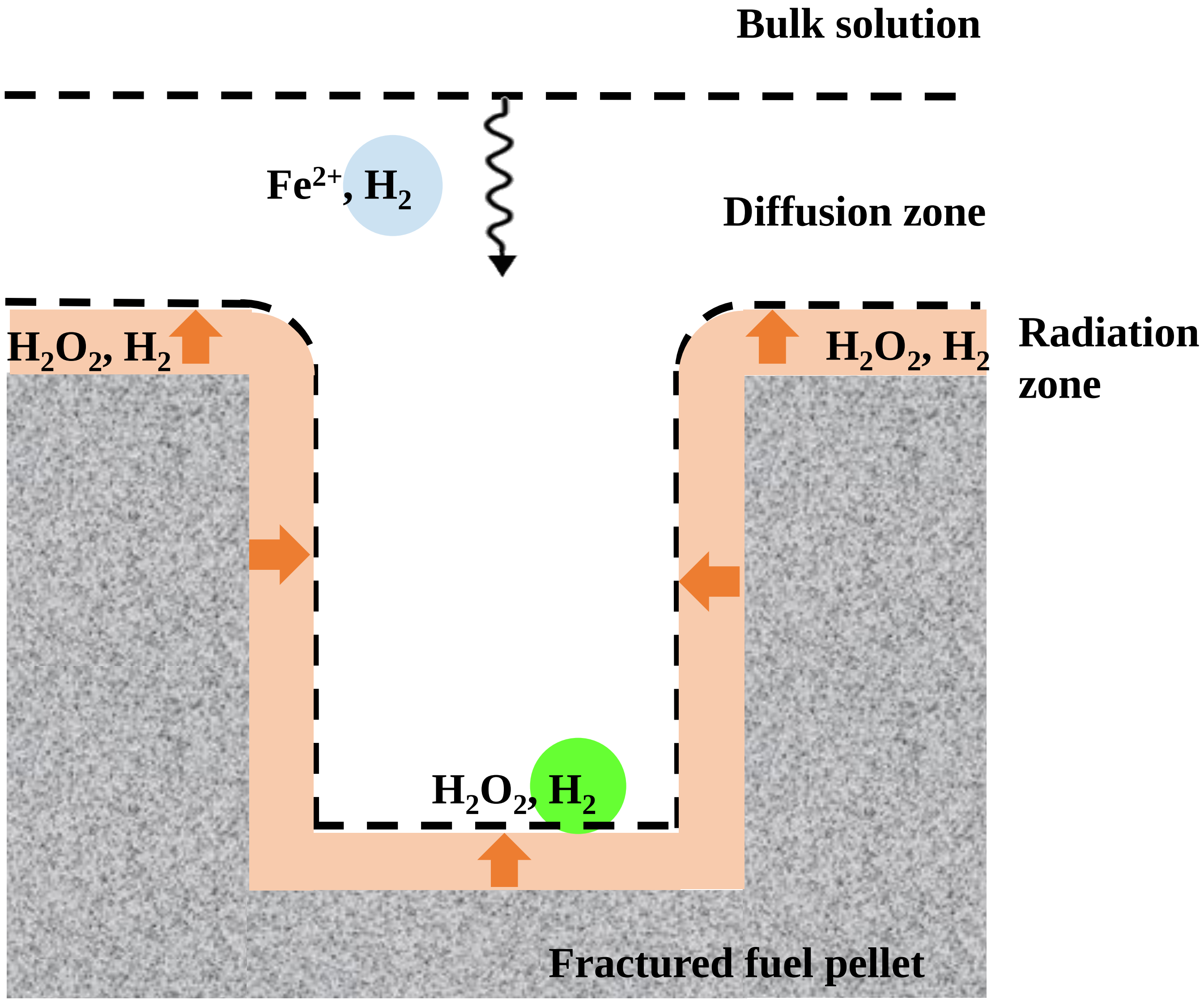
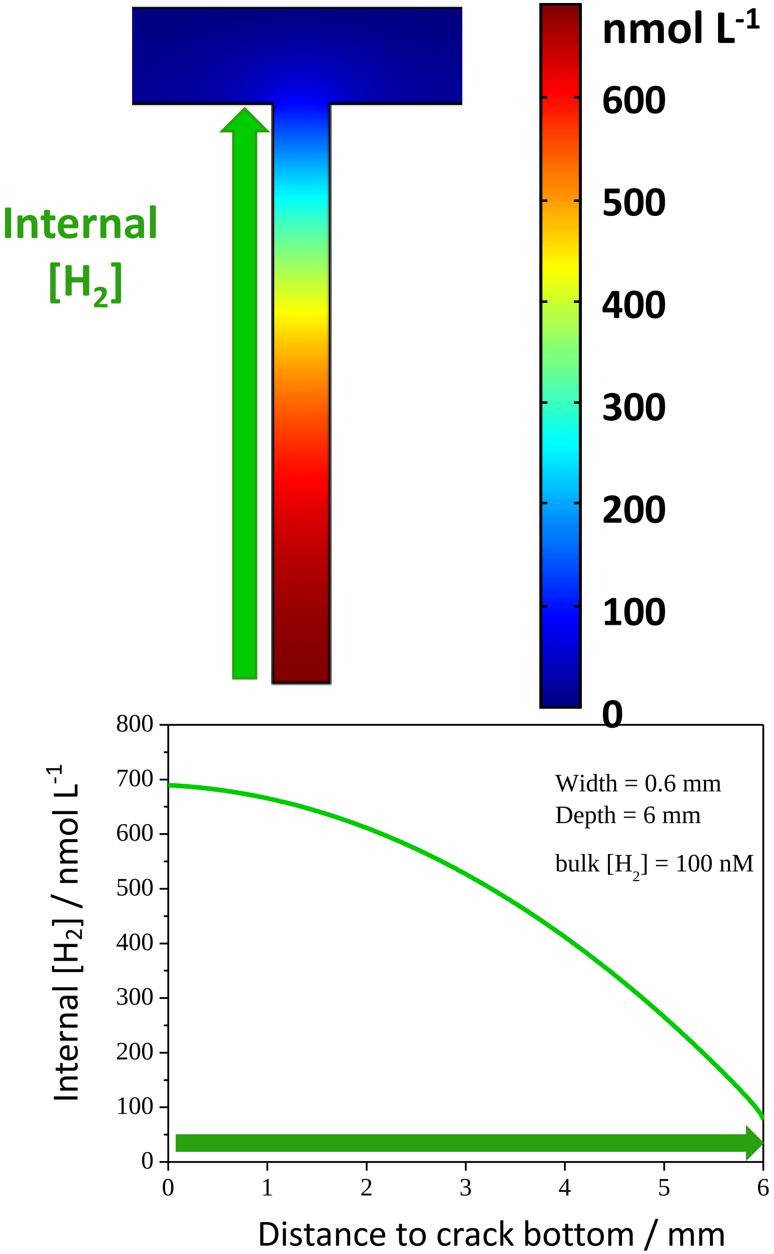
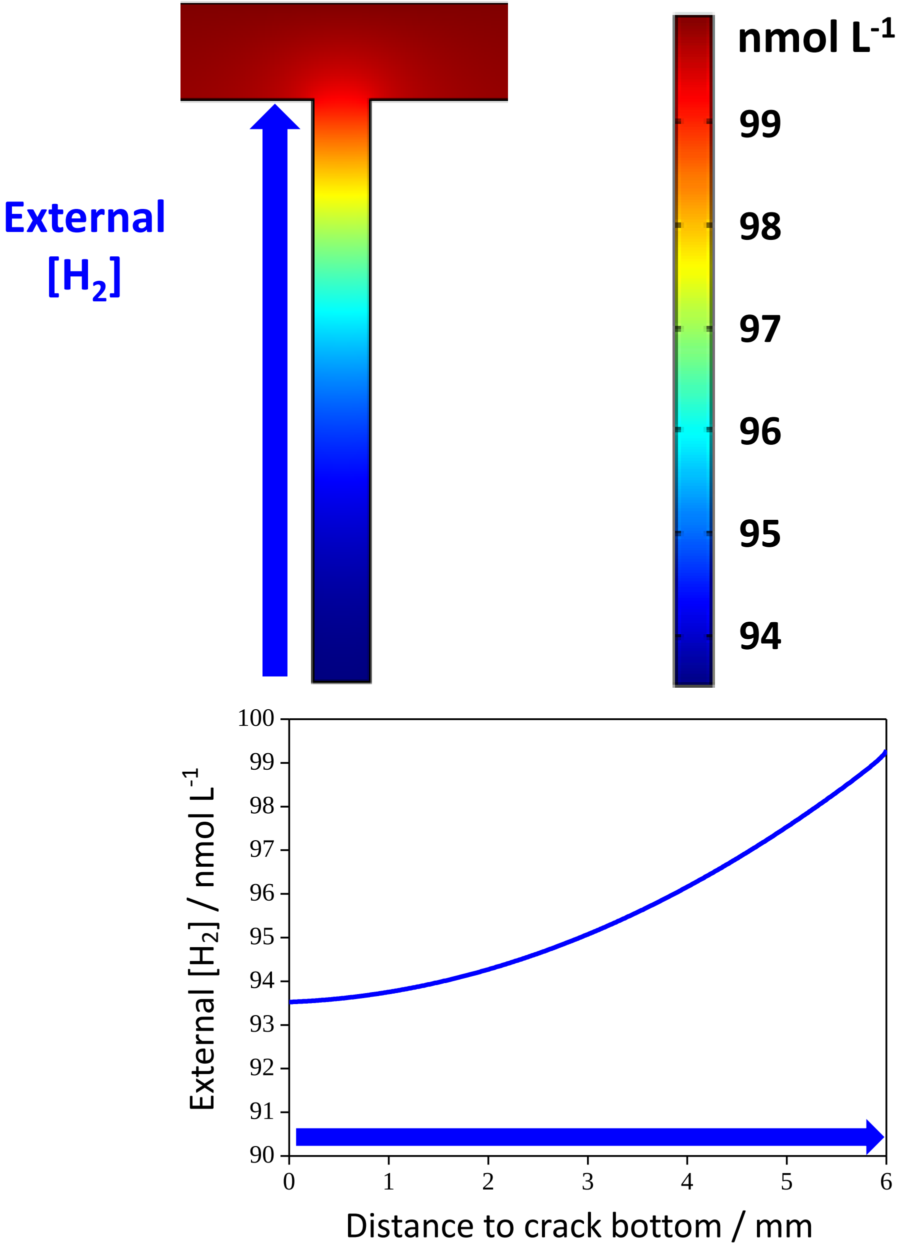


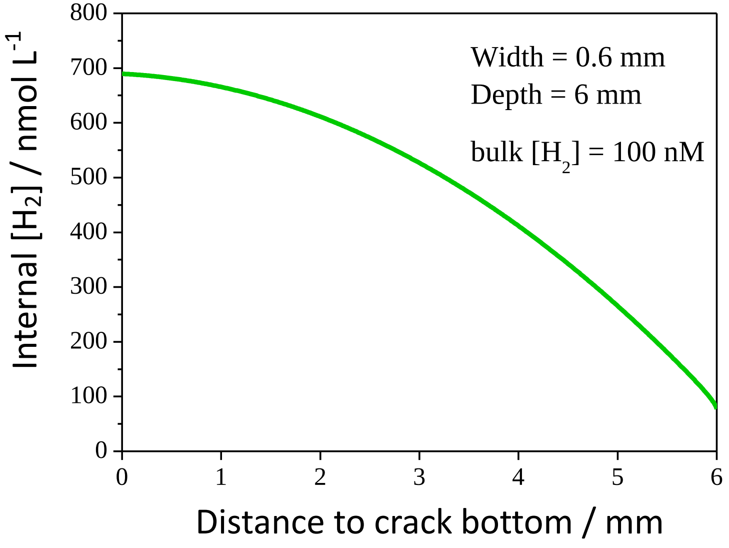
The effects of radiolytic (internal) $H_2$ and $H_2$ from steel corrosion are separated by calculating the ratio of their concentrations at specific locations

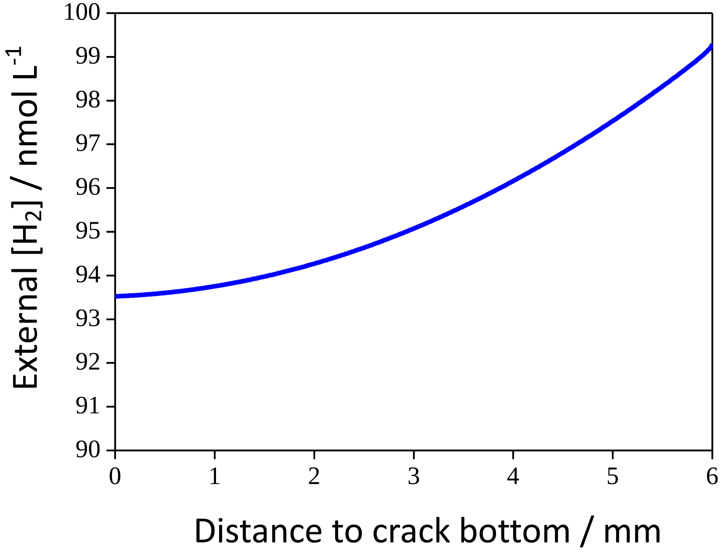
# Separation of Internal and External $H_2$ Effects





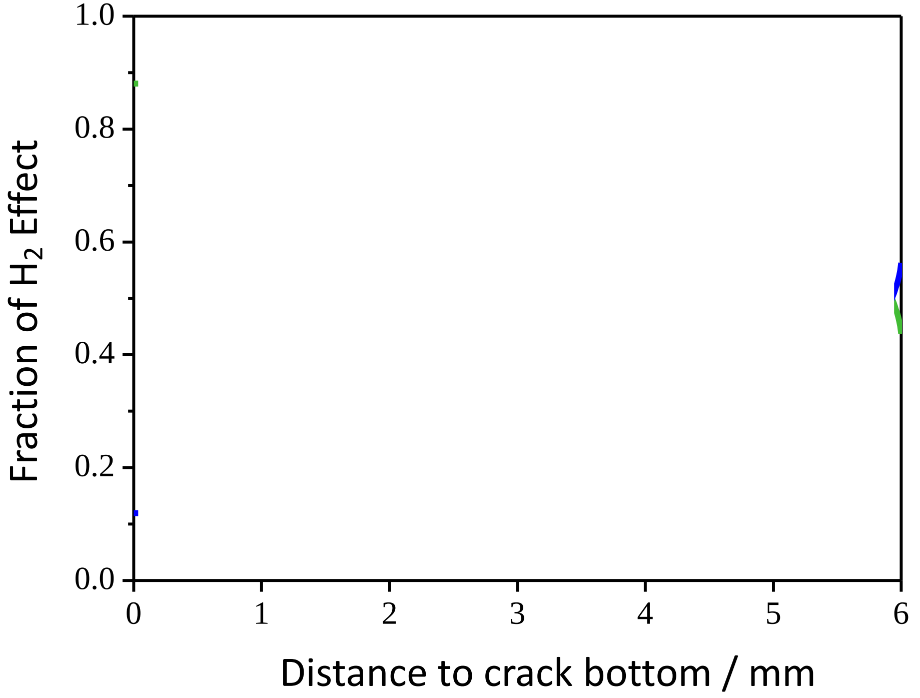
# Separation of Internal and External $H_2$ Effects





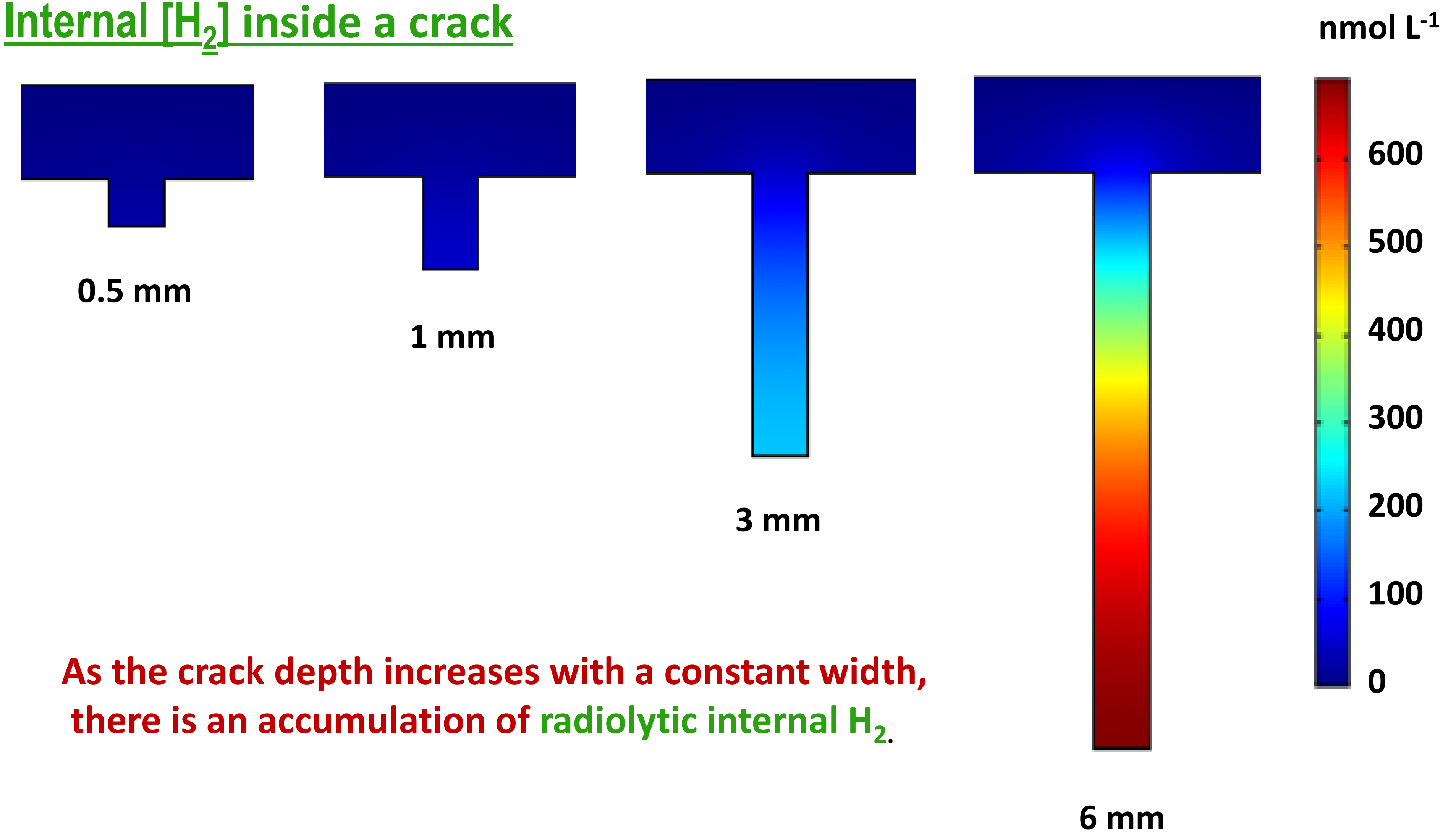
**Fraction of internal $H_2$ effect :**

$$\frac{\text{internal } [H_2]}{\text{internal } [H_2] + \text{external } [H_2]}$$



# Separation of Internal and External $H_2$ Effects

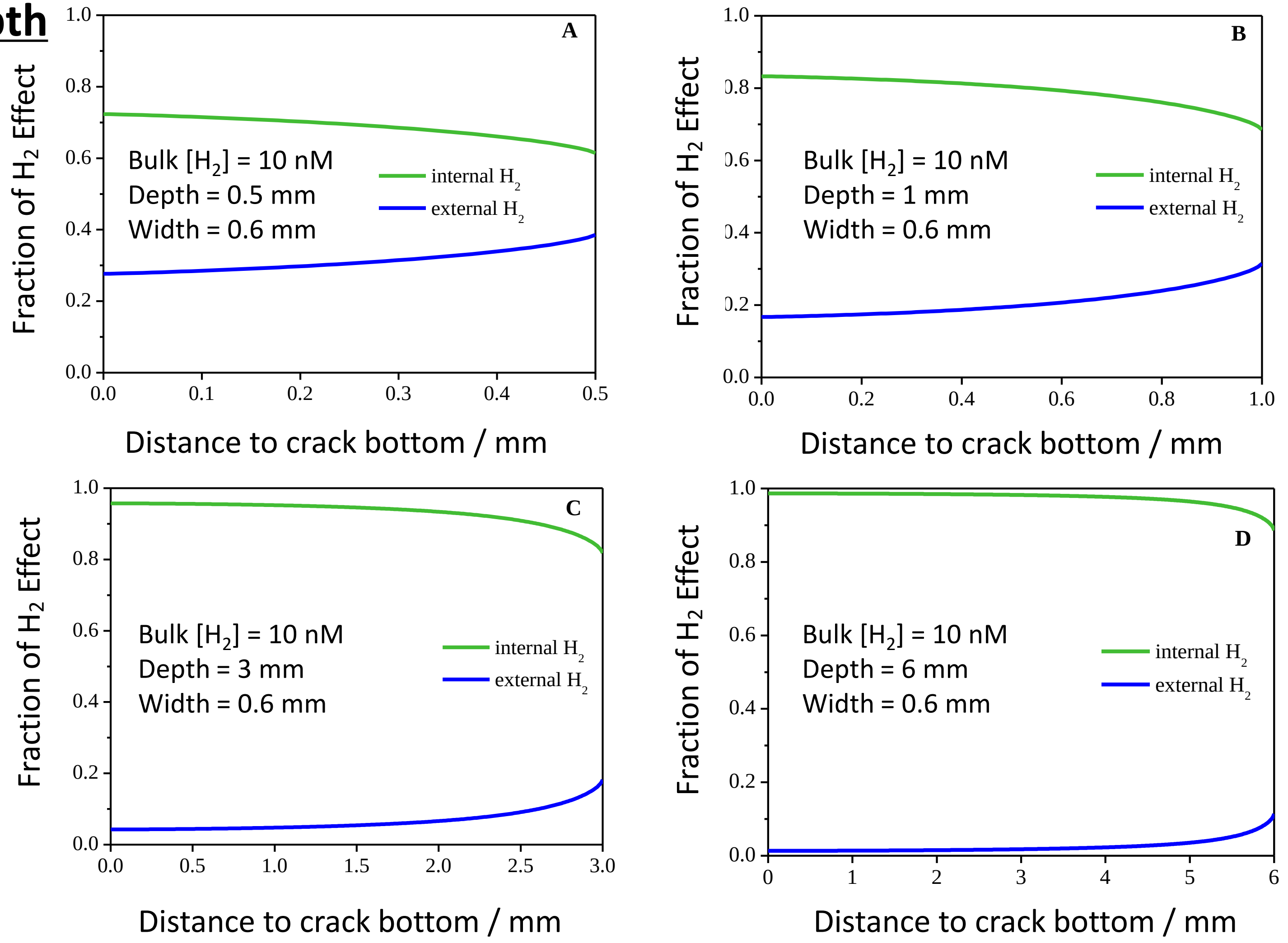
## Internal $[H_2]$ inside a crack



As the crack depth increases with a constant width, there is an accumulation of radiolytic internal $H_2$.

# Separation of Internal and External $H_2$ Effects

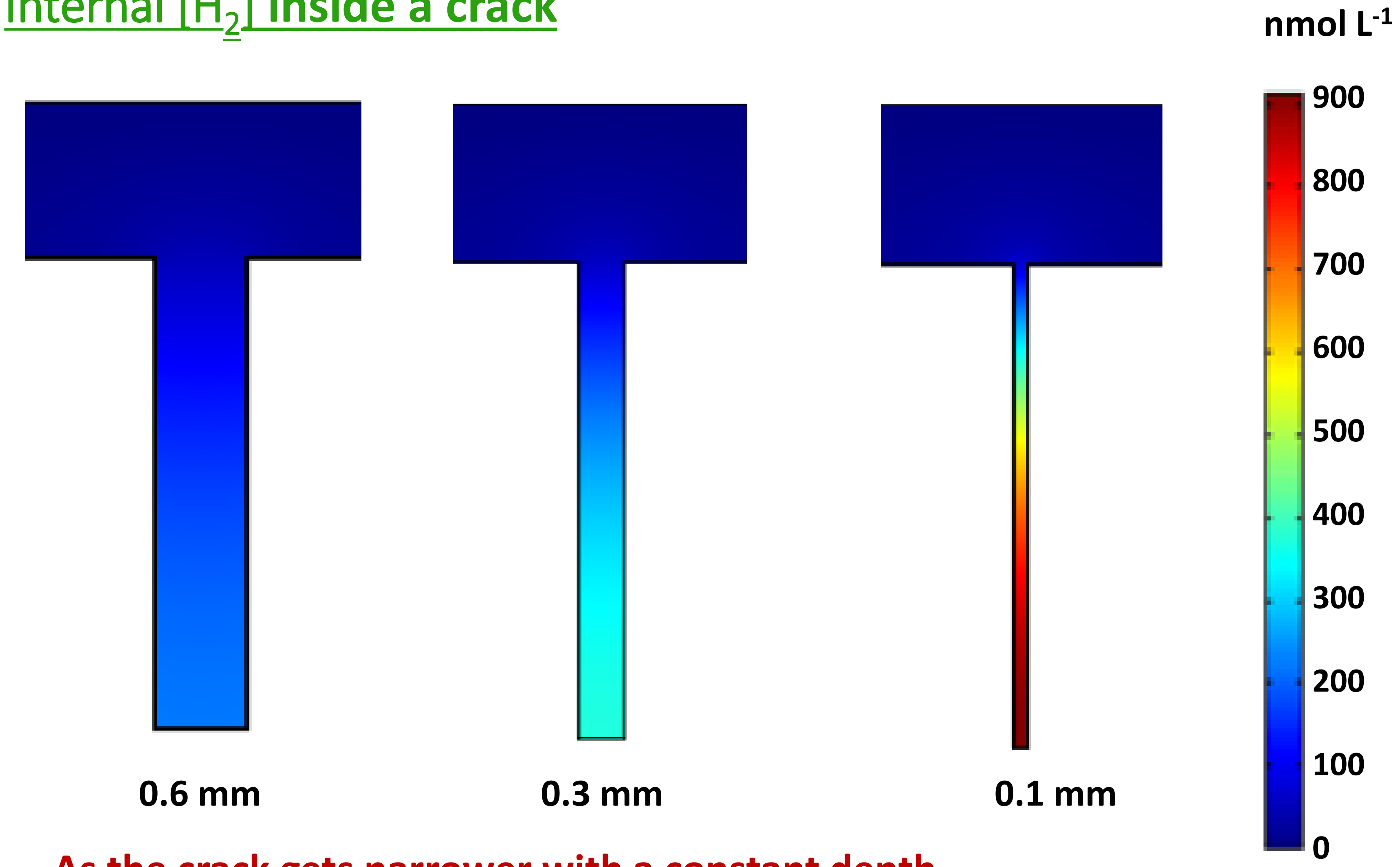
**Fracture depth**



**As the fracture depth increases for a constant fracture width, the fraction of $UO_2$ corrosion suppressed by internal $H_2$ increases.**

# Separation of Internal and External $H_2$ Effects

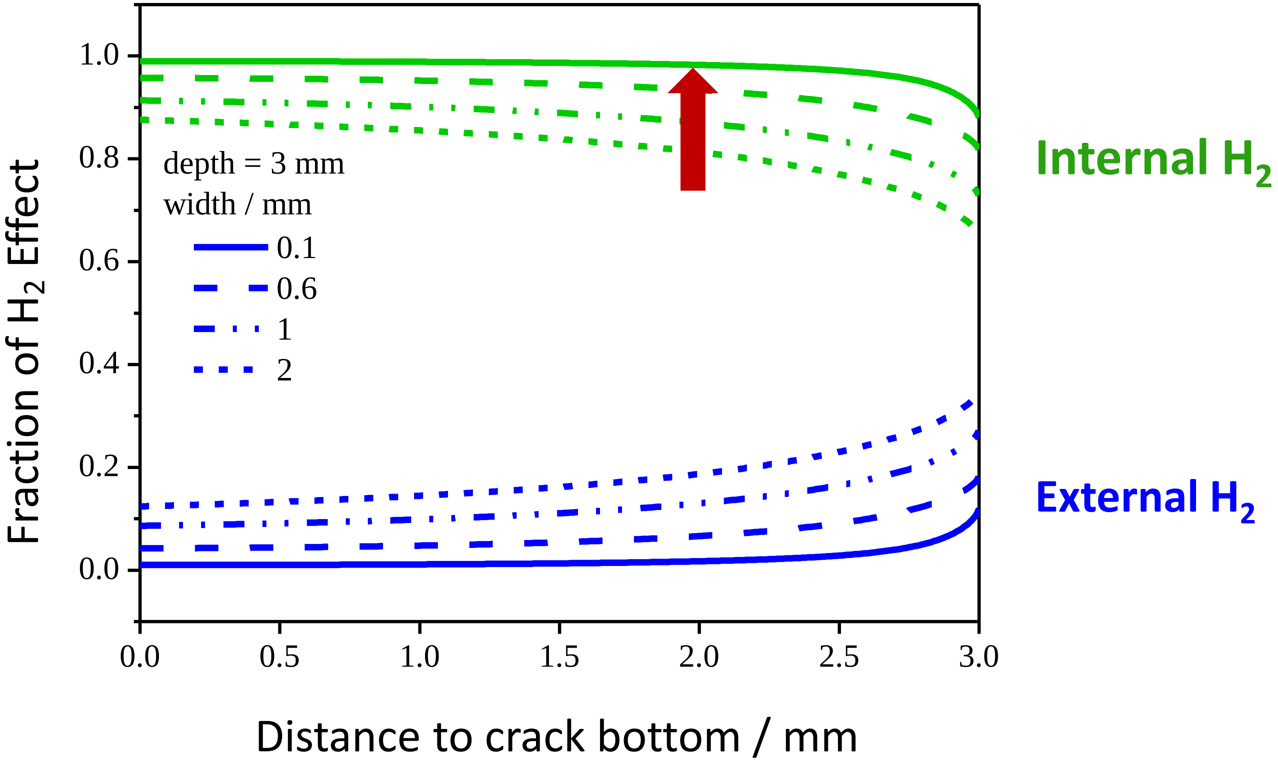
Internal $[H_2]$ inside a crack



As the crack gets narrower with a constant depth, there is an accumulation of radiolytic internal $H_2$.

# Separation of Internal and External $H_2$ Effects

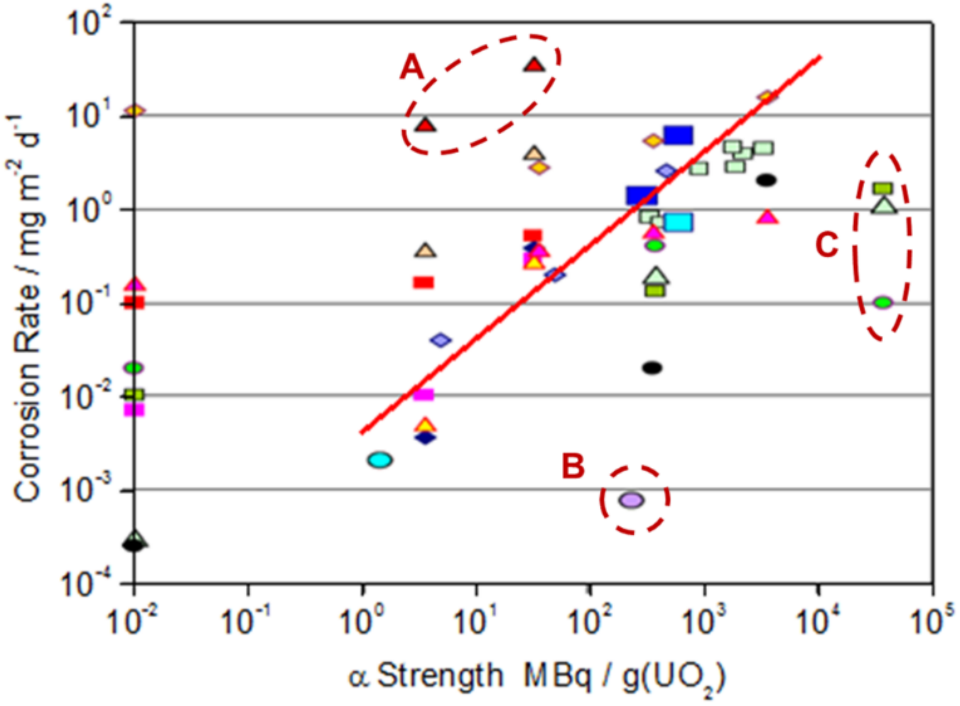
**Crack width**



**As the crack gets narrower with a constant fracture depth, the fraction of internal $H_2$ effect on the suppression of $UO_2$ corrosion increases.**

# Can this Model be Validated by Comparison to Corrosion Rates Measured on Fuel Specimens?

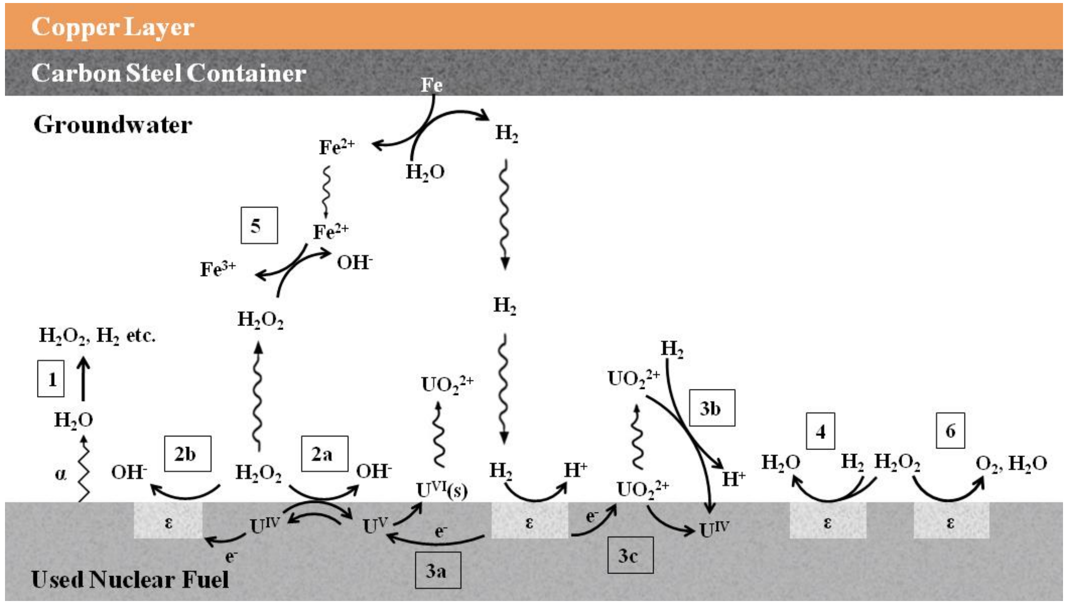
# Corrosion rates of α-doped $UO_2$. non-doped $UO_2$ (0.01 $MBq.g^{-1}(UO_2)$, SIMFUEL and some spent fuels



Linear least squares fit used by the Canadian Nuclear Waste Management Organization in safety assessments (A,B.C data not included)

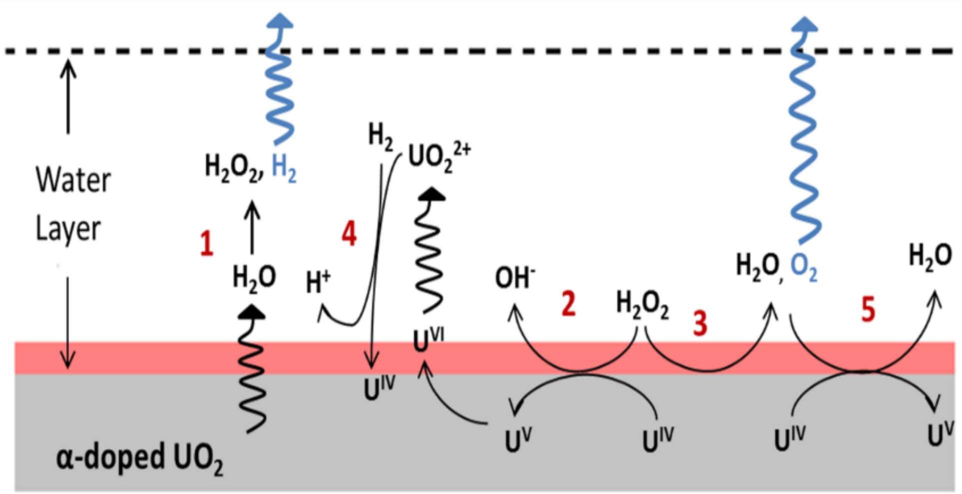
Carbol et al. Swedish Nuclear Fuel and Waste Management Company Report SKB-TR-05-09 (2005)

# Model Reconfigured to Represent the Conditions in the Fuel Experiments

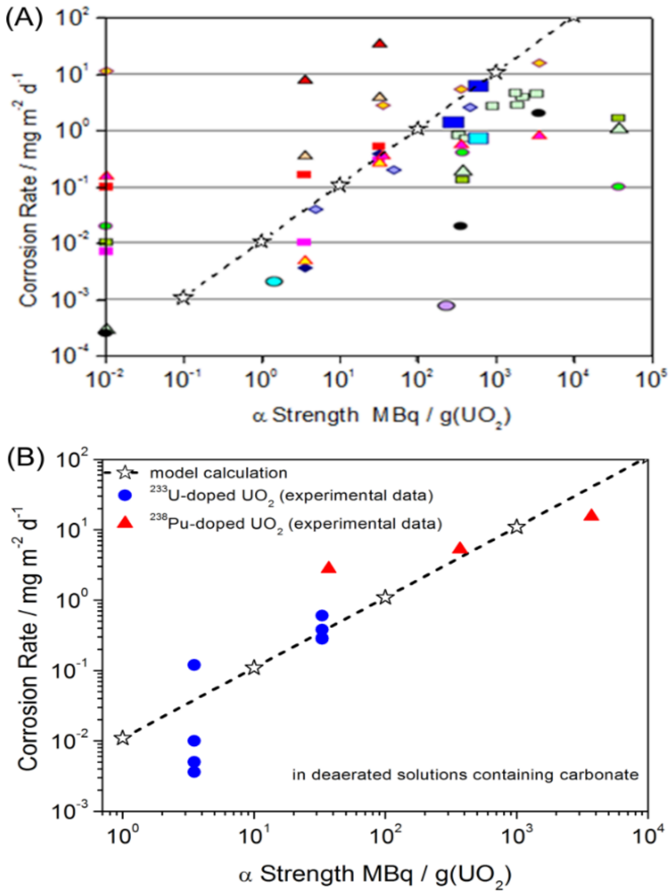


Boundary Conditions: $J_{H_2O_2} = J_{UO_2^{2+}} = 0$

$C_{O_2} = C_{H_2} = 0$



Liu et al. J.Nucl.Mater. 494, 87-94 (2017)



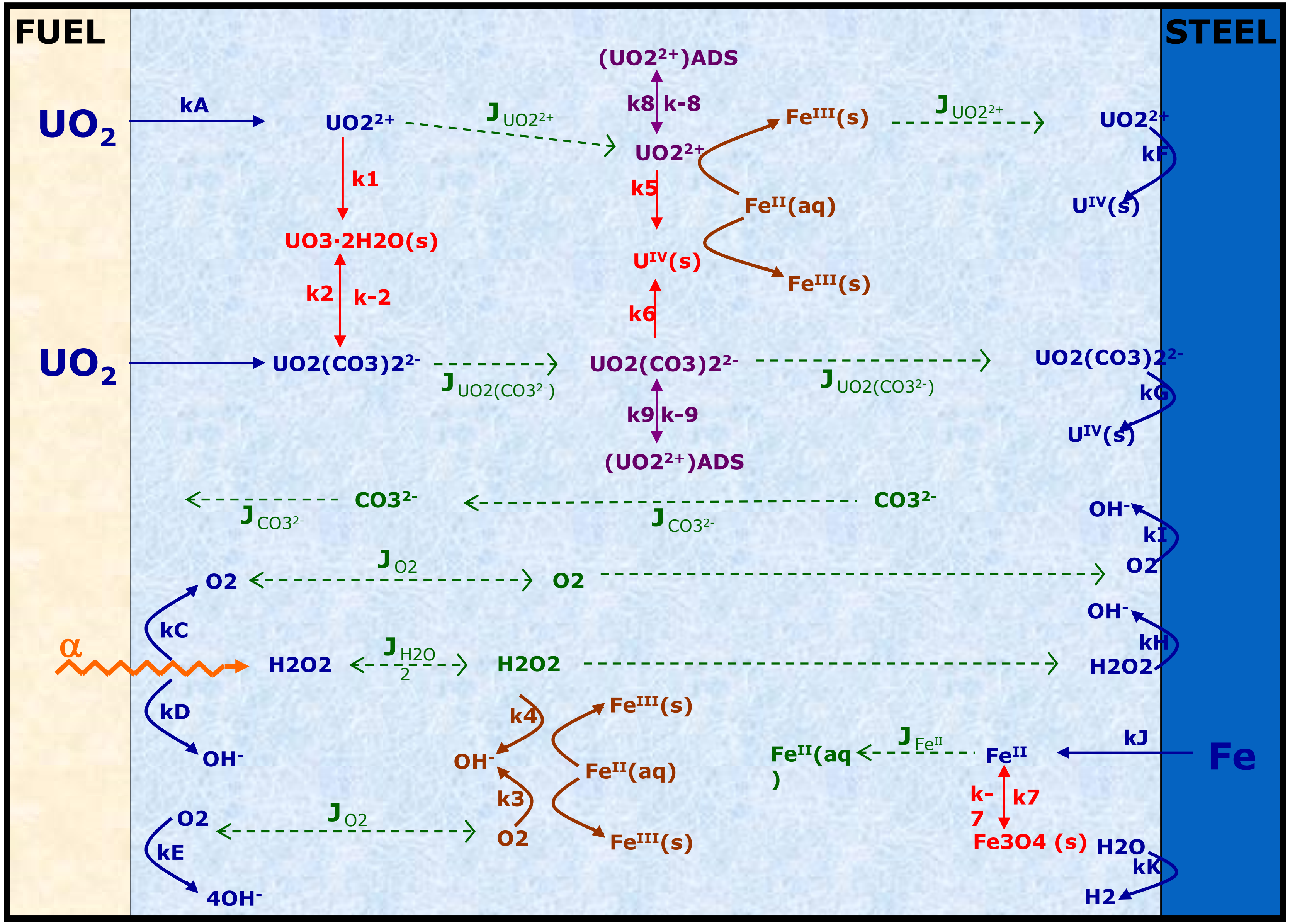
Model calculation compared to the full measurement set

Model calculation compared only to the data measured on specimens similar to those used in compiling the model data base

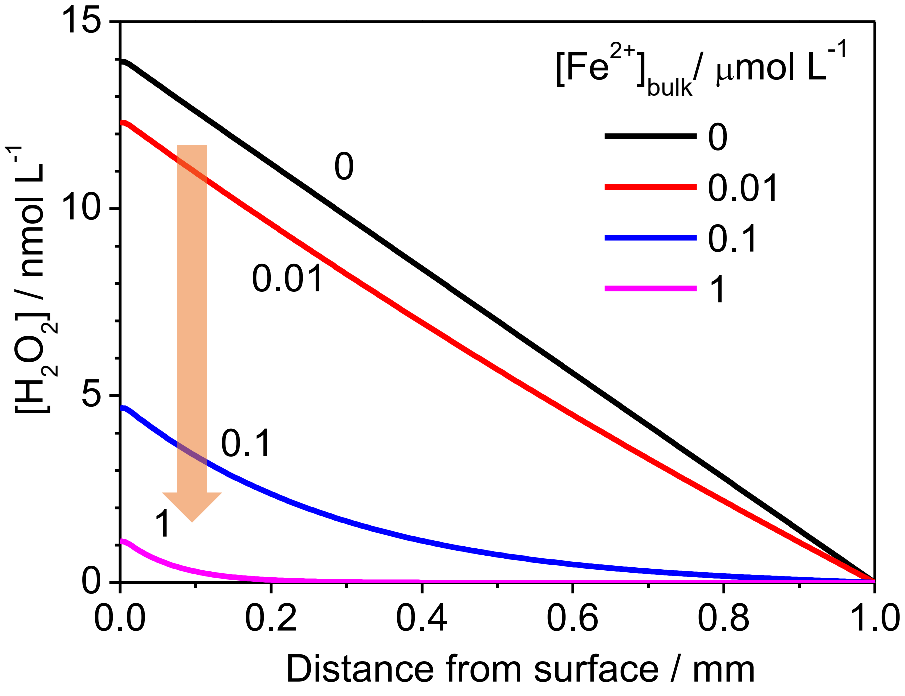
The dominant influence on fuel corrosion is the alpha radiolytic dose rate

# Thank You

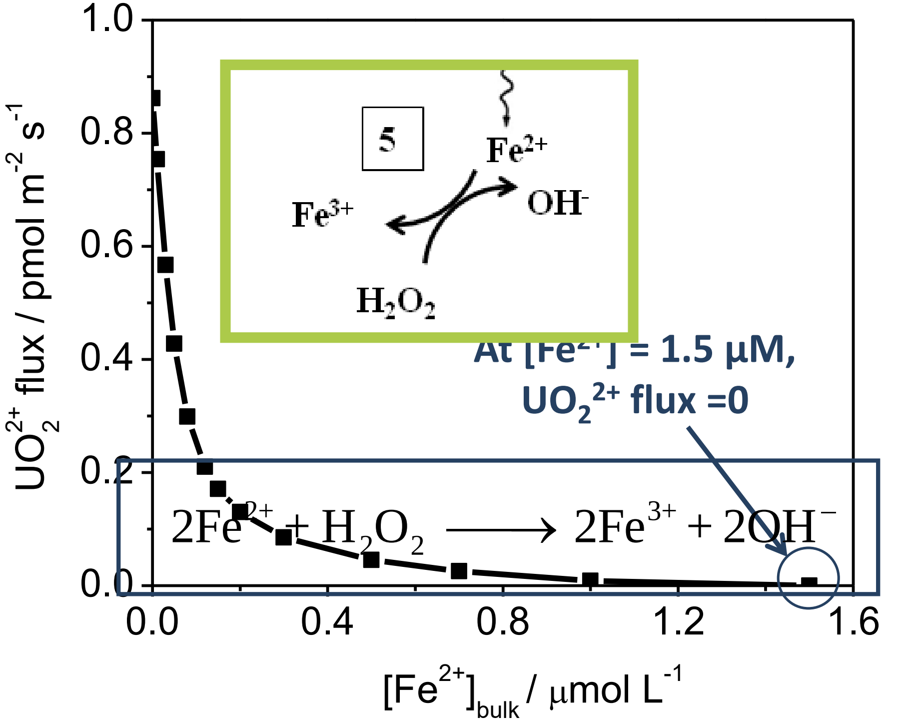
# Mixed-Potential Model (Shoesmith et al. Corrosion 59, 802 (2003))



# THE INFLUENCE OF $Fe^{2+}$ FROM STEEL CORROSION



Steady-state [$H_2O_2$] profiles at various bulk [$Fe^{2+}$]; [$H_2$]$_{bulk}$ = 0.01 µmol $L^{-1}$.



At [$Fe^{2+}$] = 1.5 µM, $UO_2^{2+}$ flux =0

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$

$UO_2^{2+}$ flux (equal to the $UO_2$ corrosion rate) as a function of [$Fe^{2+}$]$_{bulk}$.

**$Fe^{2+}$ consumes radiolytic $H_2O_2$ in the Fenton reaction thus suppressing the fuel corrosion.**

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

# Theme 3 – Spent Fuels

Professor Thomas Scott, University of Bristol

1st Annual Meeting

4 April 2019
Bath

Energy
For a Low Carbon Future

# Technical Challenge

Large & complex inventory (Magnox, AGR, PWR, prototype reactors)

Retrieval operations for legacy fuels imminent

Management options have to consider SNF evolution during:

- long term storage &
- final disposal

# Work Packages

3.1 Properties & Reactivity of Bulk Corrosion Products

- 3 projects: Bristol: PDRA & PhD (RWM), Lancaster: PhD (RWM)

3.2 Pressing Fuel Barrier Corrosion

- 2 projects: Leeds: PhD (NDA), Bristol PhD (SL)

3.3 *In situ* Identification of SNF Materials & Surface Corrosion Products

- 2 projects: Surrey: PDRA & PhD

3.4 Prediction of Long-term SNF Behaviour

- 2 projects: Bristol: PDRA & PhD

# 3.1 Properties & Reactivity of Bulk Corrosion Products

3.1.1 Assessing the properties and release behaviour of products arising from metallic and exotic fuel corrosion (Bristol)

3.1.2 Corrosion and leaching of carbide fuels in a Geological Disposal Facility (GDF) setting (Bristol)

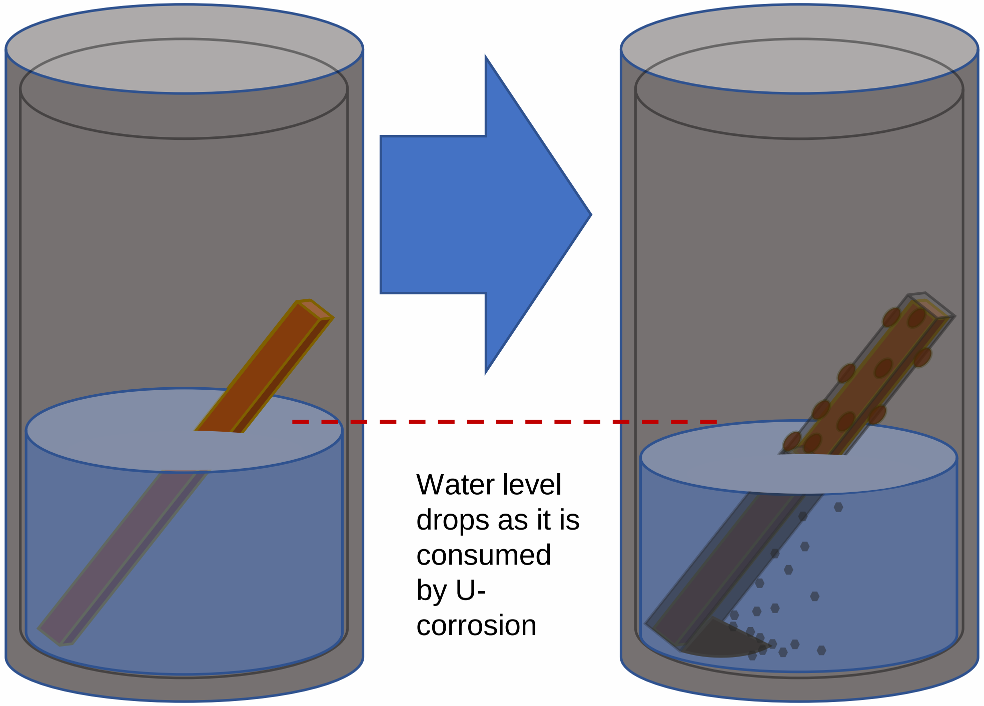
3.1.3 Oxidation of uranium oxide spent fuel at low temperatures (Lancaster)

# Metallic & exotic fuel corrosion - Bristol

**Aims and Objectives:**
To develop a better understanding of the **properties & reactivity** of bulk corrosion products arising from degradation of legacy SNF under reducing conditions

**Methodology:**
Using advanced X-ray imaging, tomography and diffraction methods to understand the corrosion behaviour of spent metallic fuel sealed '**partially wet**' inside metal storage cans. Small-scale simulants will be utilised to understand the relative mass, type and distribution of the arising corrosion products

**Expected Impact:**
Research is directly analogous to challenges on the Sellafield site and will provide better understanding and expectations for canister behaviour (& risk) during retrieval operations



Miniaturised simulant U-containing canister

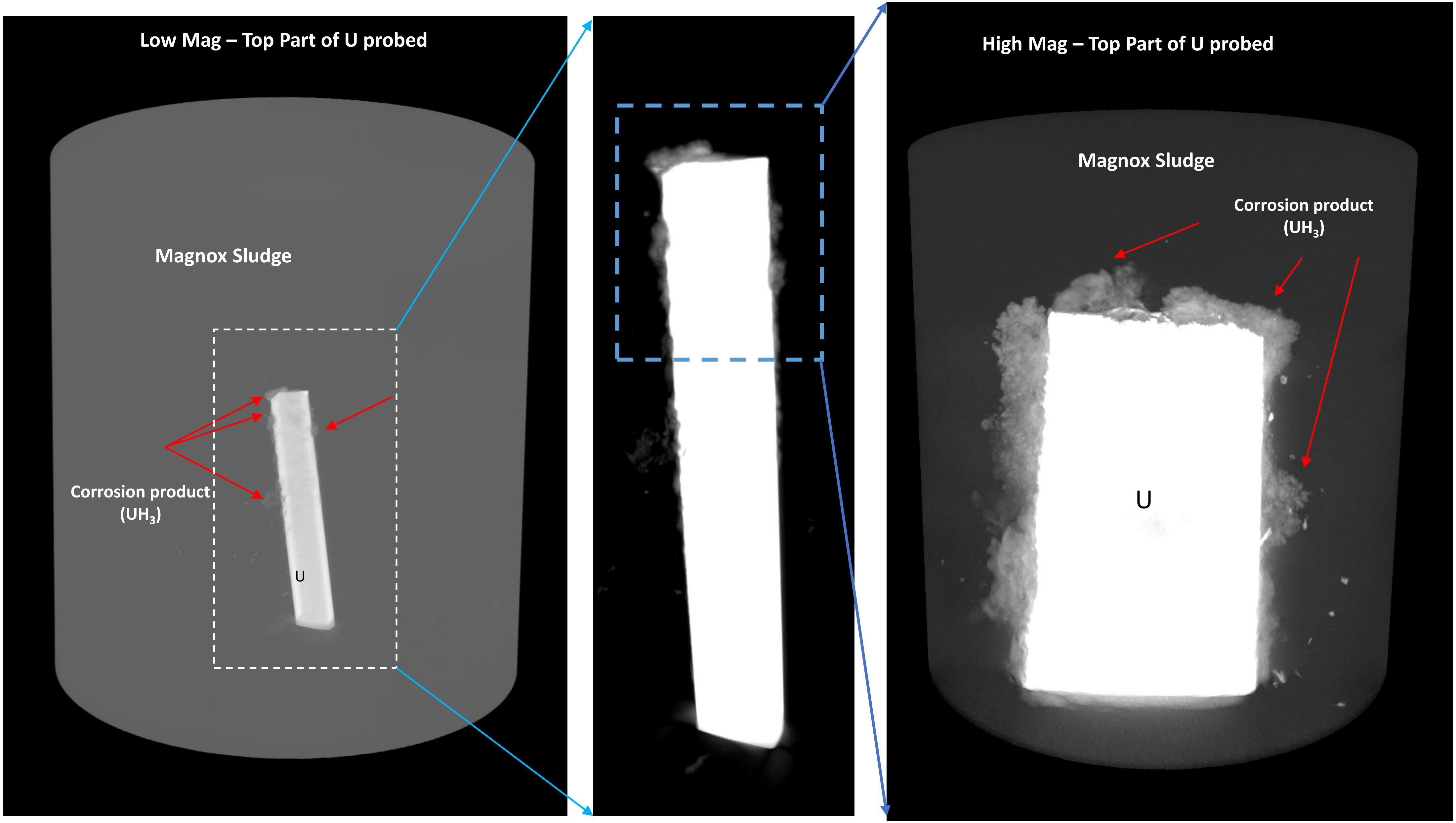
**XRT** used to chart the evolving corrosion state & distribution of material

Water level drops as it is consumed by U-corrosion

Water filling base of the volume with initially no gas in the head space (evacuated)

Analysis will determine the **distribution** of oxide and hydride using lab XRT, synchrotron analysis and neutron imaging at ISIS

# Uranium encapsulated in Magnox CMS sludge for 20 days



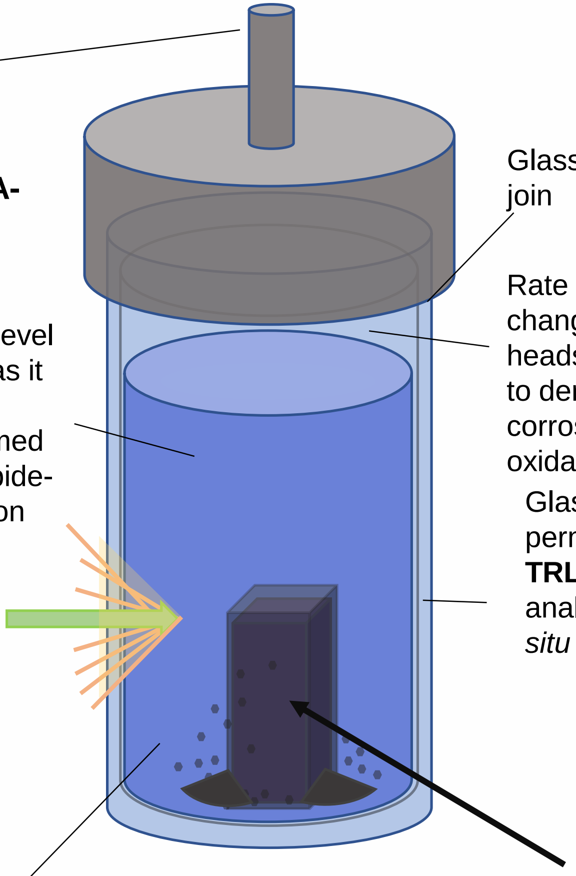
# Corrosion of carbide fuels in GDF setting – Bristol (RWM)

**Aims and Objectives:**
To determine corrosion & leaching behaviour (rates) of UC fuel materials under GDF conditions

**Methodology:**
Combined XRT-XRD and TRLFS study to chart evolving water chemistry & corrosion state *in-situ*. Novel glass cells used to set up a series of long-duration experiments conducted at different temperatures & GDF water chemistries

**Expected Impact:**
Inform modelling predictions for release of U into groundwaters from carbide oxidation & determine off-gases arising; for real spent UC fuels will contain $^{14}C$

Virgin UC fuel material (pellets) to be supplied by NNL Springfields Laboratory



Pressure logging & **Residual Gas Analysis Mass Spectrometry (RGA-MS)** analysis

Glass-metal join

Rate of pressure change in headspace used to derive corrosion-oxidation rates

Water level drops as it is consumed by carbide-oxidation

Glass to permit **XRT & TRLFS** analysis *in situ*

**TRLFS & Raman** (Surrey) utilised to chart evolving U speciation in water

Water chemistry varied to cover range of GDF conditions; high pH, high carbonate versus deionised water

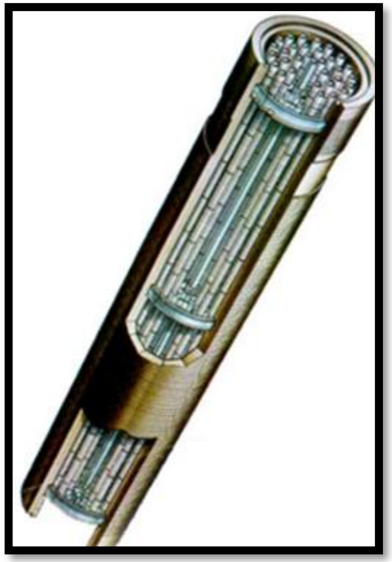
Periodic **XRT** analysis to determine **distribution** of oxide & its surface thickness on the carbide, yielding corrosion rate

**UC (virgin) fuel material**

# Oxidation of uranium oxide spent fuel at low temperatures – Lancaster (RWM)

***Project Background***

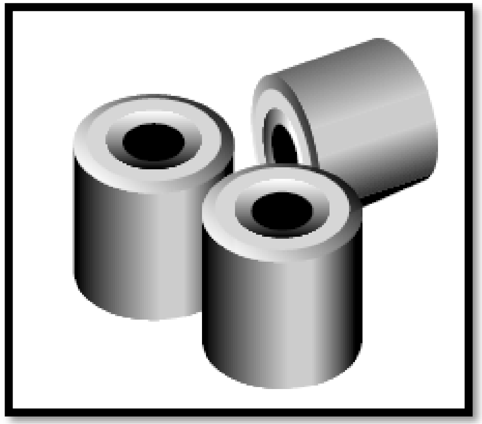
- **UK AGRs**: ~3-4% enriched $UO_2$ ceramic pellets in 20/25/Nb steel cladding, $CO_2$ coolant
- Expected remaining lifetime: ~6600 tonnes of **SNF**
- Fate of UK reprocessing mission:
    - **THORP** reprocessing **END Nov 2018**
    - **Magnox** reprocessing **END 2020**
- Beyond reprocessing: pre-disposal interim storage – ponds at Sellafield

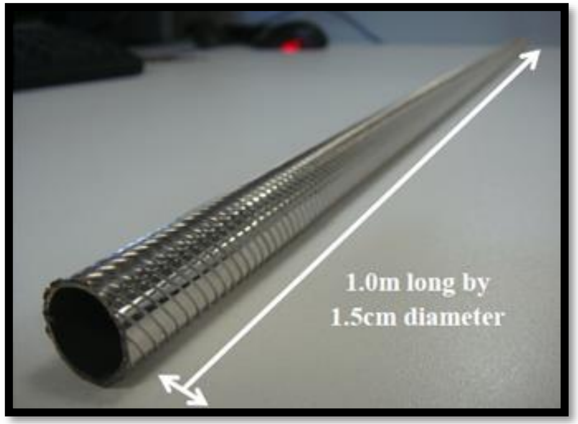


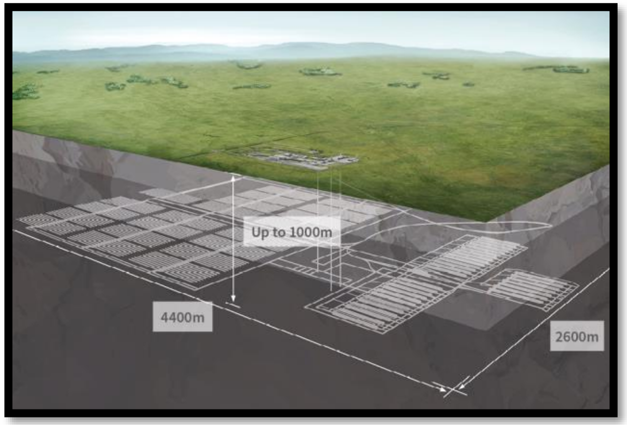
# Oxidation of $UO_2$ SNF at low temperatures

***Importance of Research***

- To underpin options for **pre-disposal storage** of SNF and prediction of behaviour during **final disposal**
- Must satisfy safety case requirements for the UK's **Geological Disposal Facility (GDF)** and for **interim storage** prior to the GDF
- Concerned with the management of **in-reactor** or **in-pond** failed fuels
- $UO_2$ pellets sealed inside steel cladding tubes may be **susceptible to corrosion** & may lead to in-pond **water contamination**







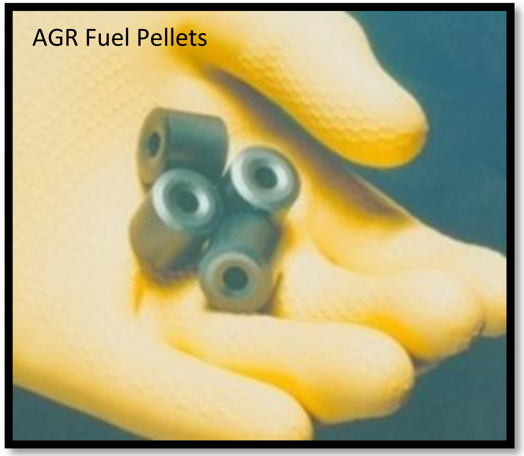
# Oxidation of $UO_2$ SNF at low temperatures

## *Aims*

- Using **AGR SIMFUELS** to understand the oxidation behaviour of the $UO_2$ matrix in **failed AGR spent fuel**, at low temperatures & under conditions relevant to UK interim storage & drying of wet stored SNF

## *Objectives*

- Study $UO_2$ and AGR SIMFUEL oxidation as a function of **simulated burn-up** and **T < 200°C**, in:
  - **simulated interim storage pond-waters** and **repository groundwaters**
  - **dry air** as a function of oxygen partial pressure (***$PO_2$***)
  - **damp air** as a function of relative humidity (**RH**) and ***$PO_2$***
- Hence, determine thresholds for the onset of $UO_2$ oxidation in AGR SIMFUELS and $UO_2$ pellets


AGR Fuel Pellets

# 3.2 Pressing Fuel Barrier Corrosion

2 PhD projects:

3.2.1 Hydraulic behaviour in perforated AGR fuel pins, likely ingress into the fuel & hydraulic behaviour during drying (Leeds)

3.2.2 Stress corrosion cracking in AGR cladding & micromechanical testing of irradiated clad (Bristol)

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

**PhD funded by NNL** (Dr Rob Borrows)
Supervised – Dr M Mostafavi (Bristol University)

## Aims and Objectives:

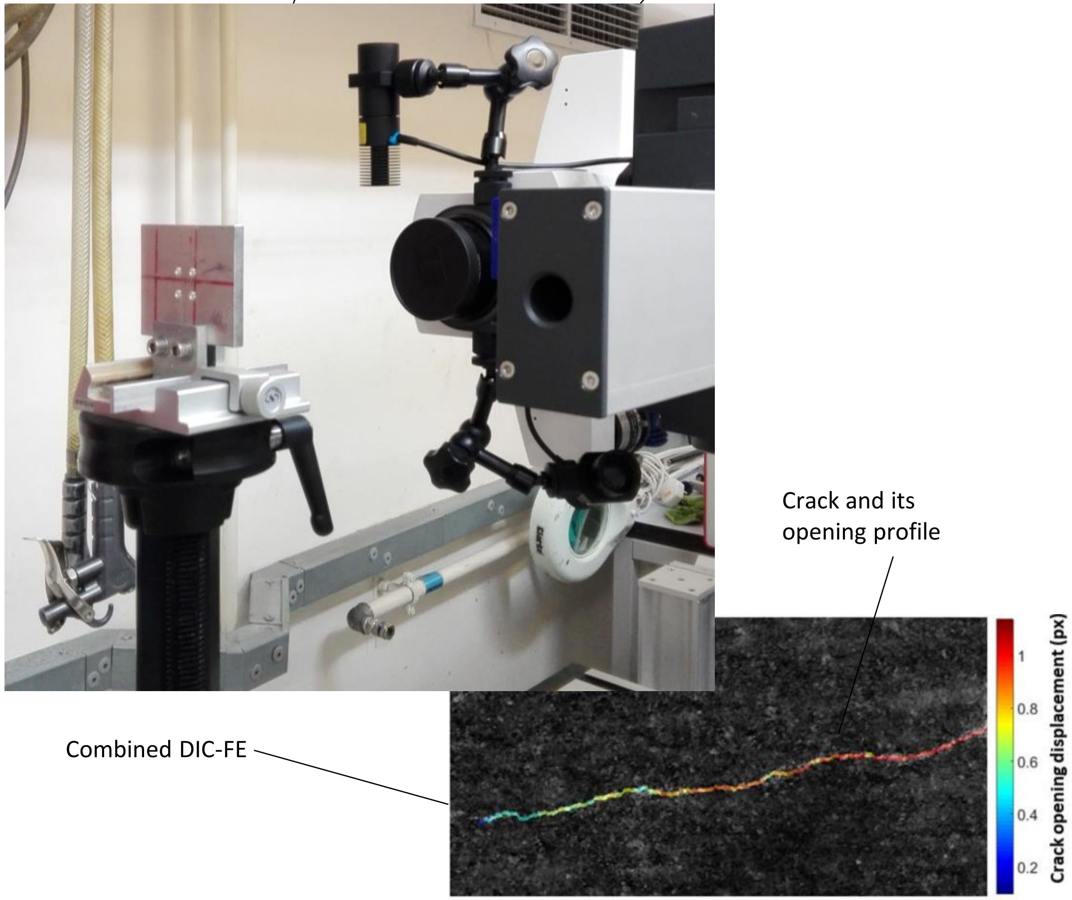
To develop a new methodology to observe and quantify properties and stress corrosion cracking of AGR fuel cladding.

## Methodology:

A combined Digital Image Correlation – finite element simulation method will be developed to quantitatively assess the environmental effects on the rate of stress corrosion cracking of AGR fuel cladding.

## Expected Impact:

The understanding gained in the project on the effects of irradiation accelerated stress corrosion cracking and change in mechanical properties of stainless steel 20-25-Nb AGR cladding will underpin predictions of their structural integrity during transport and in storage and disposal environments.



# 3.3.1 Identification of Corrosion Products on SNF (Surrey)

## *Importance of Research*

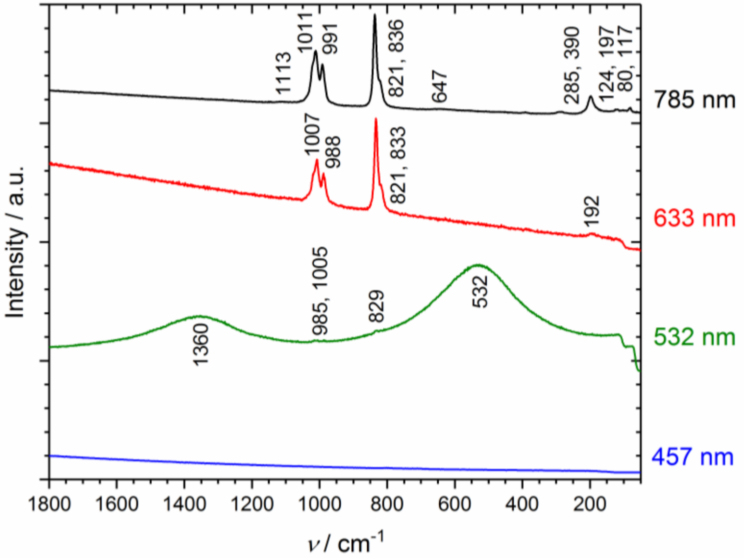
**PDRA funded by EPSRC** (Dr V. Frankland)
Supervisor – Prof D Read (Surrey University & NPL)

Dissolution of $UO_2$ could lead to a very wide range of potential corrosion products during **pre-disposal storage** and **final disposal** in the **GDF**

~250 U mineral species known but many are **poorly characterized** (stability, solubility etc.)

Seeking to develop **laser-based** methods that can be applied remotely (**Raman, TRLFS, LIBS**)

mindat.org



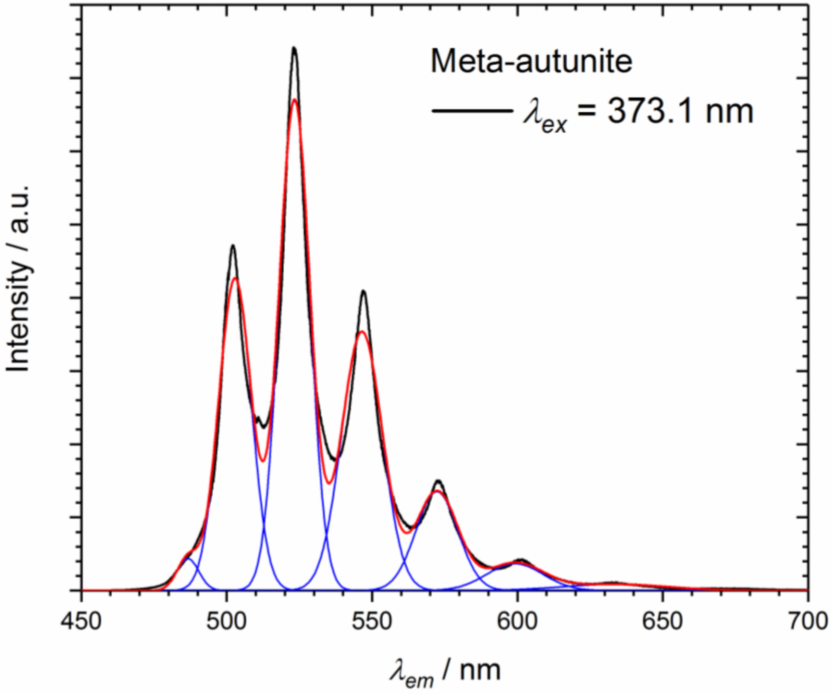
# Identification of SNF Materials & SC Products

## *Aim*

- Construct reference Raman & TRLFS Database for potential corrosion products under conditions relevant to interim storage and final disposal

## *Objectives*

- Use type mineral samples from Reference Collections to obtain pure phase reference spectra
- Interferences from waste matrices ($Mg(OH)_2$, $Ca(OH)_2$)
- Conduct online, real-time corrosion experiments of $UO_2$ oxidation in representative solutions (with Bristol)
- Assess feasibility of field implementation



mindat.org

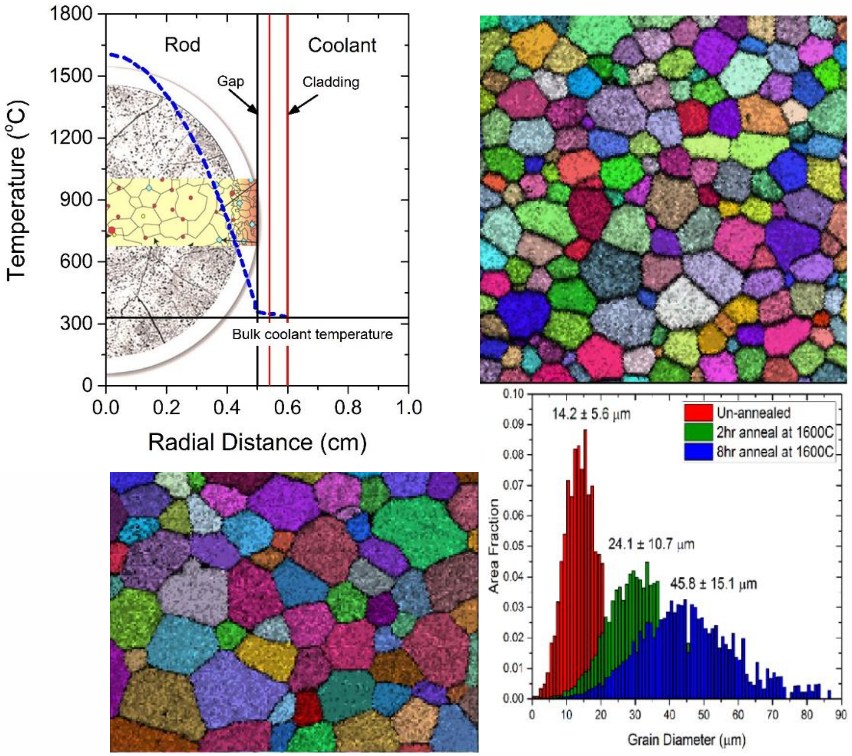
# 3.3.2. Building foundations of a predictive tool for SNF behaviour (Bristol)

**PDRA (12 months) funded by EPSRC**
**PhD UoB DTP**
Supervised - Dr Ross Springell (University of Bristol)

**Aims and Objectives:**
To construct the basis for a predictive tool for spent fuel behaviour, from the microscopic to the macroscopic; closing the loop between experiment and theory, by designing experiments that mimic and test these models.

**Methodology:**
A model will be developed, primarily using FACSIMILE and COMSOL, to develop a model of the aqueous corrosion behaviour of spent fuel. Experiments will be designed to replicate the idealised scenarios in these models in order to test and validate them. This project will make use of the DCF and Surrey Ion Beam facilities as well as a collaboration between the KURRI reactor and UoB.

**Expected Impact:**
The combination of modelling and representative experiments could lead to a reliable and solid foundation on which complexity can be built in terms of a long term predictive tool for spent fuel corrosion.



We are able to engineer samples that represent specific parts of a spent fuel pellet; modifying grain size, fission products, strain, stoichiometry etc.

# 3.4. Simulation of U fuel corrosion by DFT methods (Surrey)

**Aims and Objectives:**

To investigate the corrosion mechanism, including intermediates, products and reaction rates, of SNF in oxidative environments. To predict quantitatively the degree of corrosion and product formation as a function of time by using a combination of experimental (i.e., fluorescence, Raman etc.) & computational techniques (density functional theory).

**Methodology:**

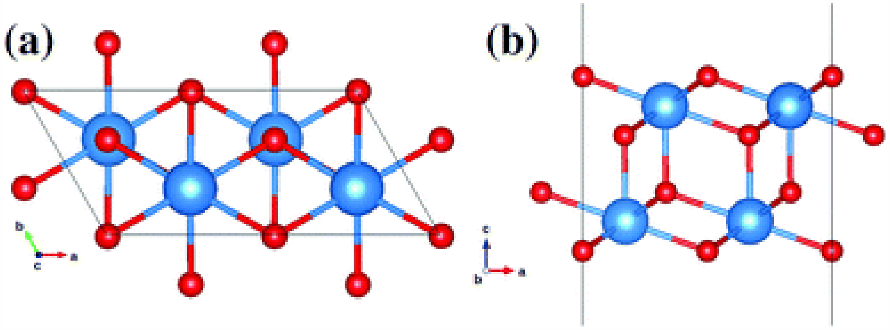
Focus will be on understanding the evolving surface chemistry of surrogate SNF, modelling the formation and dissolution of the surface phases exposed to wet environments via controlled on-line experiments. The project will make use of the Surrey Ion Beam facilities as well as collaboration with UoB.

**Expected Impact:**

The main deliverable will be an analytical, thermodynamic and kinetic description of the corrosion mechanism of U, $UO_2$ and $UO_x$.

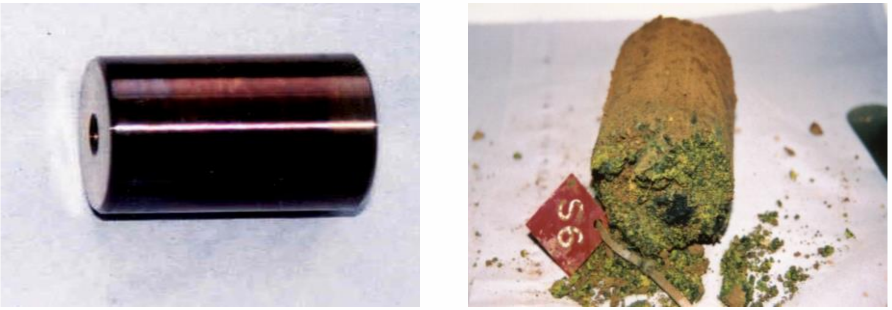
**PhD funded by UoS**

Supervisors – Prof D Read & Dr M. Sacchi (Surrey & NPL)



Ball-and-stick model of the clean (2 × 1) $UO_2$(111) surface

P. F. Weck et al., *Dalton Transactions* **2013,** *42* (13), 4570-4578



# Summary

The spent fuels research activity will deliver new insights and understandings to underpin important decisions on **legacy retrievals**, **waste processing, storage** and **disposal**.

**Cutting-edge** and **complimentary** analysis techniques will be used between the partner Universities, but working also with industry.

We are keen to widen the group of partners we are working with to increase the impact of our research.

**Please get in touch** for further information on the project.

Thank you

Contact Details

# Evaluating the mechanical properties of corium

Dr Haris Paraskevoulakos, University of Bristol

TRANSCEND Annual meeting 2019

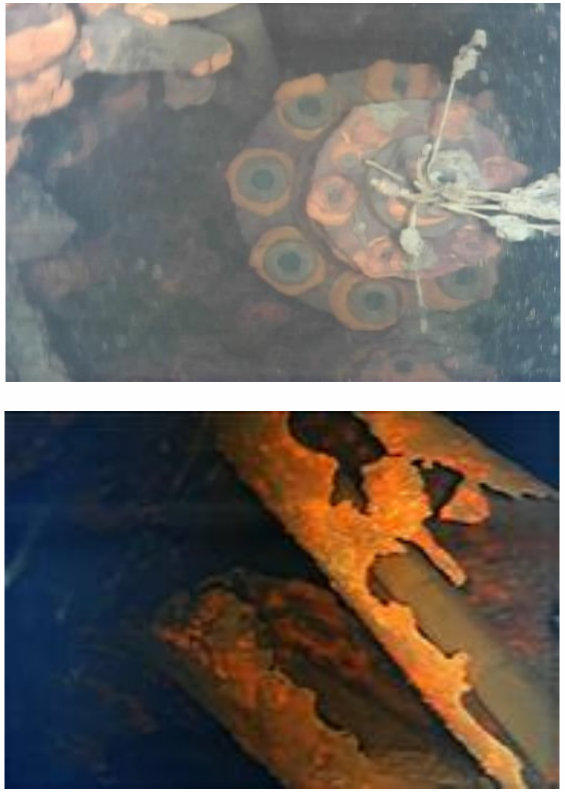
04/04/2019
Bath

- On March 11 2011, the tsunami that engulfed the Fukushima Daiichi NPP resulted in a loss of coolant accident and the partial meltdown of boiling water reactor Units 1 – 3
- Seawater was injected into the reactor cores for emergency cooling
- However this was not sufficient – pellets of $UO_2$ nuclear fuel melted and reacted with steam-oxidised zircaloy fuel cladding
- The resulting materials, known as **fuel debris** and **corium**, are highly hazardous (a mixture of $UO_2$ fuel, zirconium from the cladding and other melted reactor components, such as concrete and steel from the fuel pressure containment vessel).

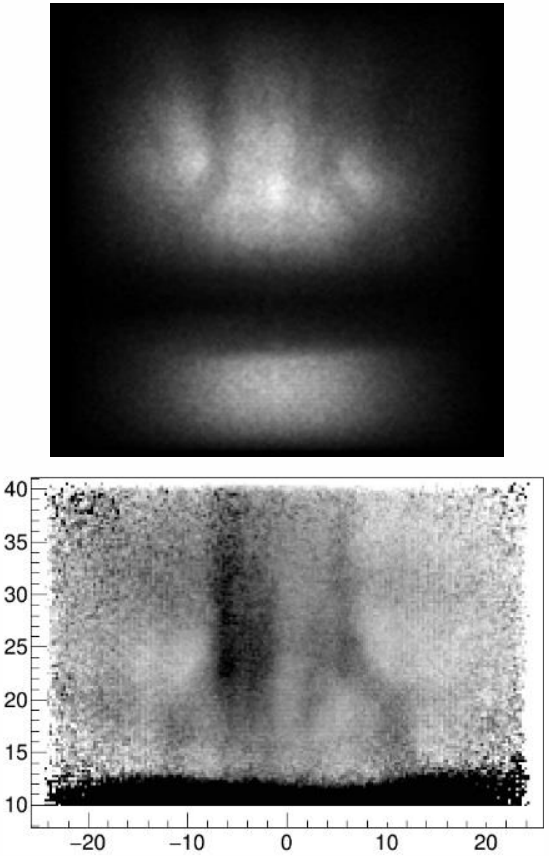
- Since the accident, water has been continuously injected to the reactor
- Coolant water effluent has been shown to contain plutonium (*fuel debris is being dissolved*)

- **Retrieval of the fuel debris and corium** from the reactors is a great challenge
- Before any plans for retrieval can be made it is necessary to understand:
    1. the **chemical and physical properties** of the fuel debris and corium
    2. The **location** where the fuel debris and corium reside within the reactor

- Determining the physical and chemical properties of the fuel debris and corium will support the choice of:
    1. **appropriate decommissioning technology**
    2. **how to handle materials upon retrieval**



*Progress of Unit 3 PCV internal investigation*
*(July 19, 2017 Source: TEPCO)*



*Progress in Fuel Debris Detection Inside the Unit 2 Reactor at FDNPP*
*(May 26, 2016 Source: TEPCO)*

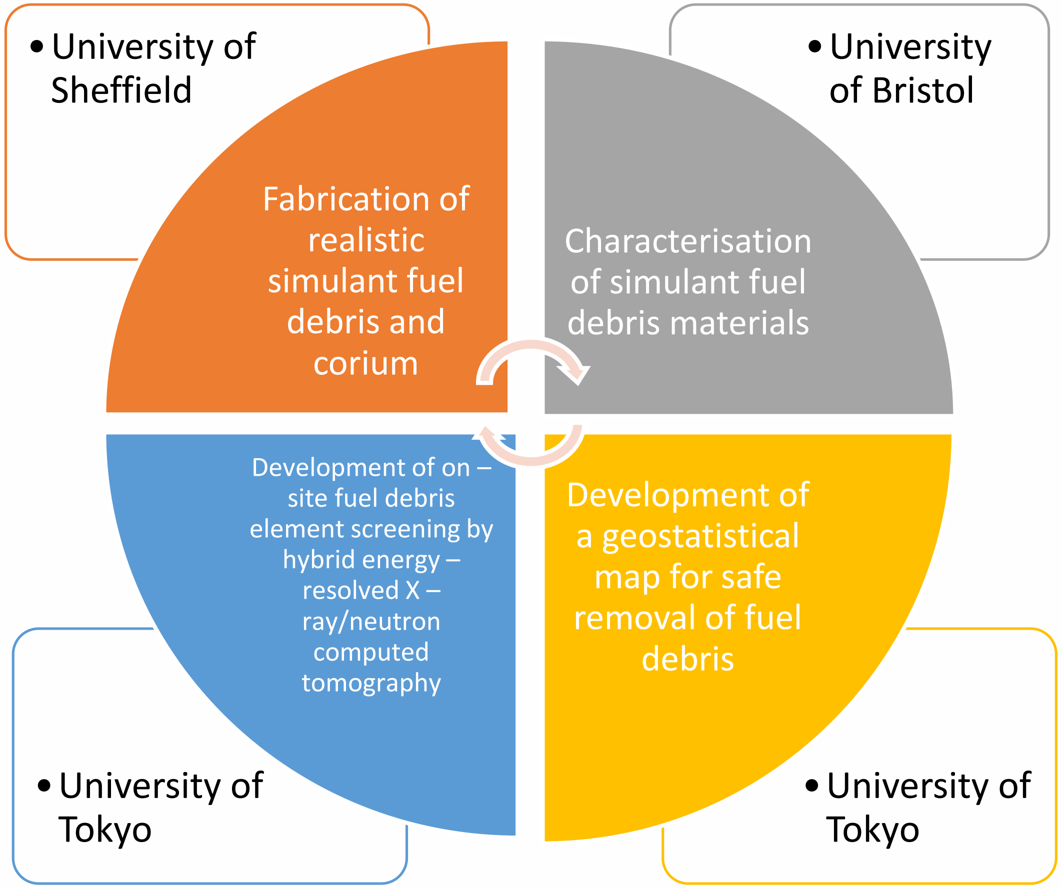
TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

## Partners

- University of Sheffield (UK)
- University of Bristol (UK)
- University of Tokyo (Japan)

## Project Plan



- University of Sheffield

Fabrication of realistic simulant fuel debris and corium

- University of Bristol

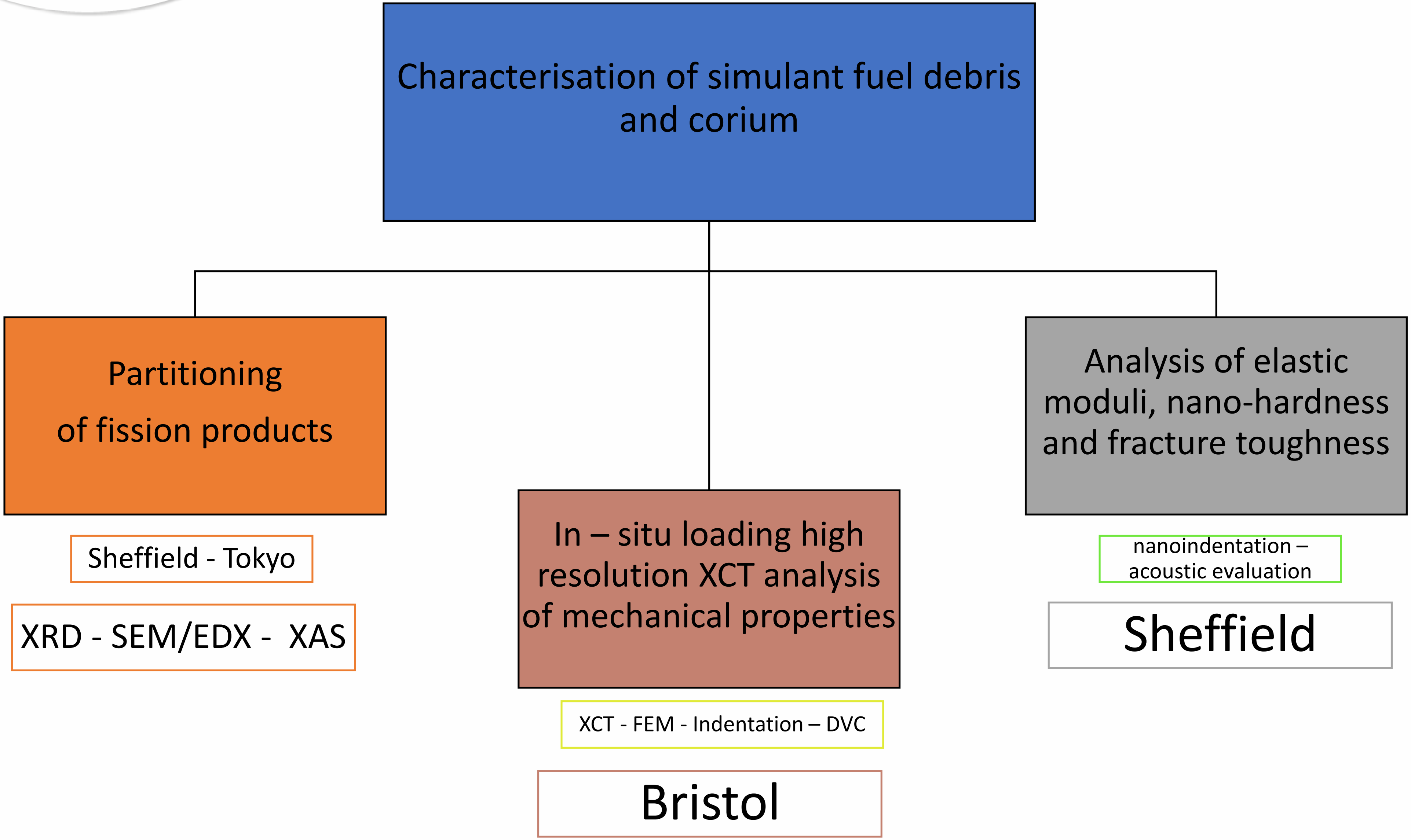
Characterisation of simulant fuel debris materials

- University of Tokyo

Development of on – site fuel debris element screening by hybrid energy – resolved X – ray/neutron computed tomography

- University of Tokyo

Development of a geostatistical map for safe removal of fuel debris



Characterisation of simulant fuel debris and corium

- Partitioning of fission products
  - Sheffield - Tokyo
  - XRD - SEM/EDX - XAS
- In – situ loading high resolution XCT analysis of mechanical properties
  - XCT - FEM - Indentation – DVC
  - Bristol
- Analysis of elastic moduli, nano-hardness and fracture toughness
  - nanoindentation – acoustic evaluation
  - Sheffield

**Goal**

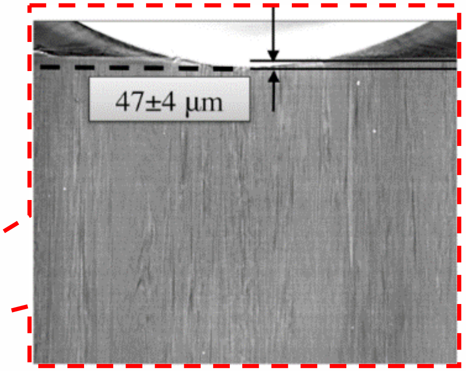
Young’s modulus of the multi-phase material

Fracture toughness of the multi-phase material

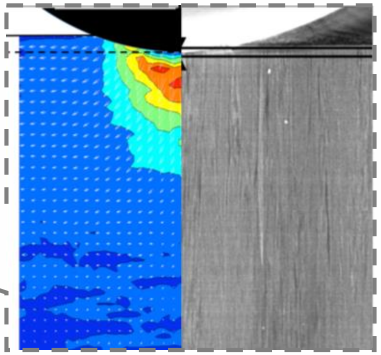
Investigation of the corroded state

Workflow concept to reveal the mechanical properties

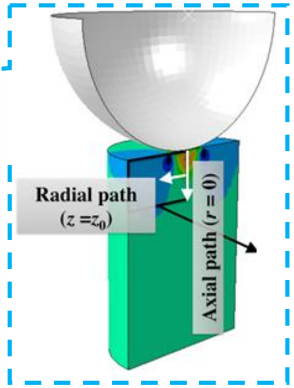
In situ loading tests coupled with x–ray tomography **(XRT)**



**Digital volume correlation (DVC)**
**Displacement field at various loads**



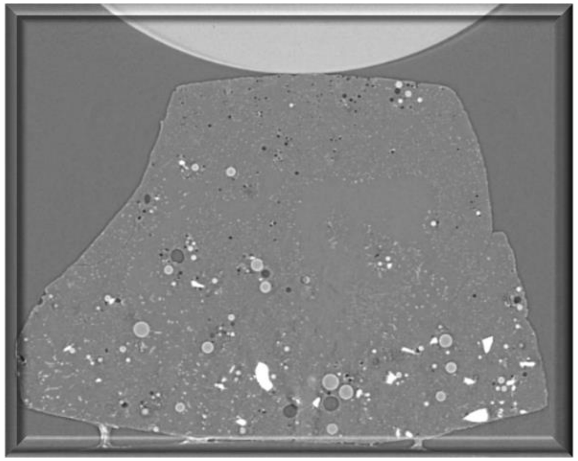
**Finite Element Modelling (FEM)**



**Matching DVC – FEM**

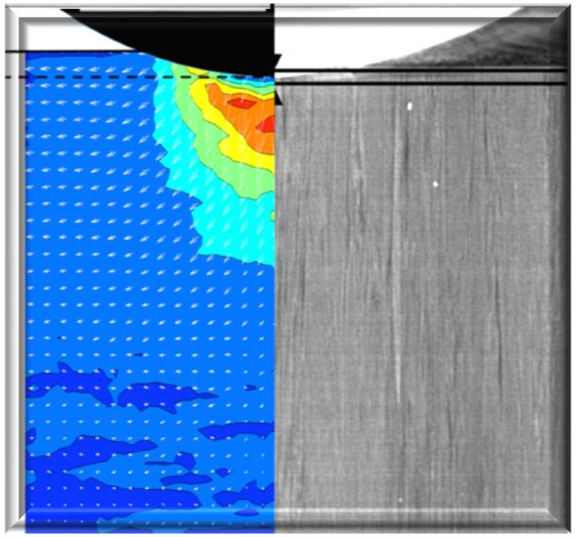
## Materials

- 1 Dry Corium–simulant sample
- 1 Corroded Lava–like fuel containing material sample (**Black LFCM**)
- 1 Dry Lava–like fuel containing material sample (**Brown LFCM**)
- Cuboids 3.0 x 3.0 x 4.0 mm
- Mass: < 0.2 g



## Diamond Light Source I12 Beamline

- Synchrotron X–ray Tomography
- Synchrotron X–ray Powder Diffraction
- Hertzian Indentation loading

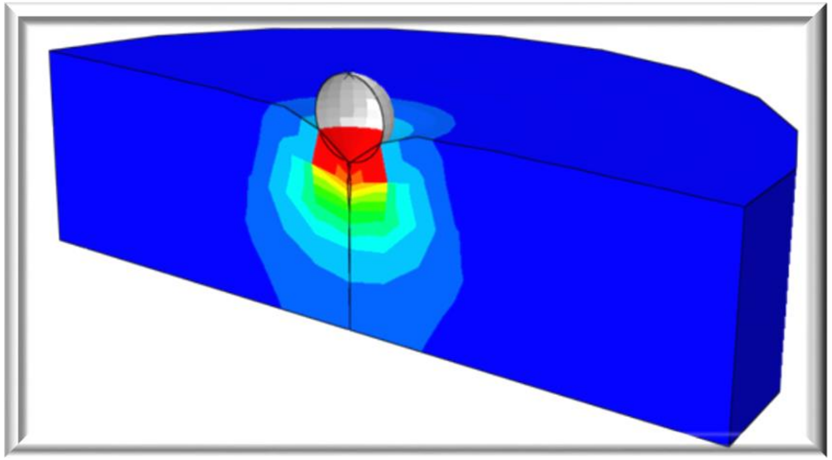


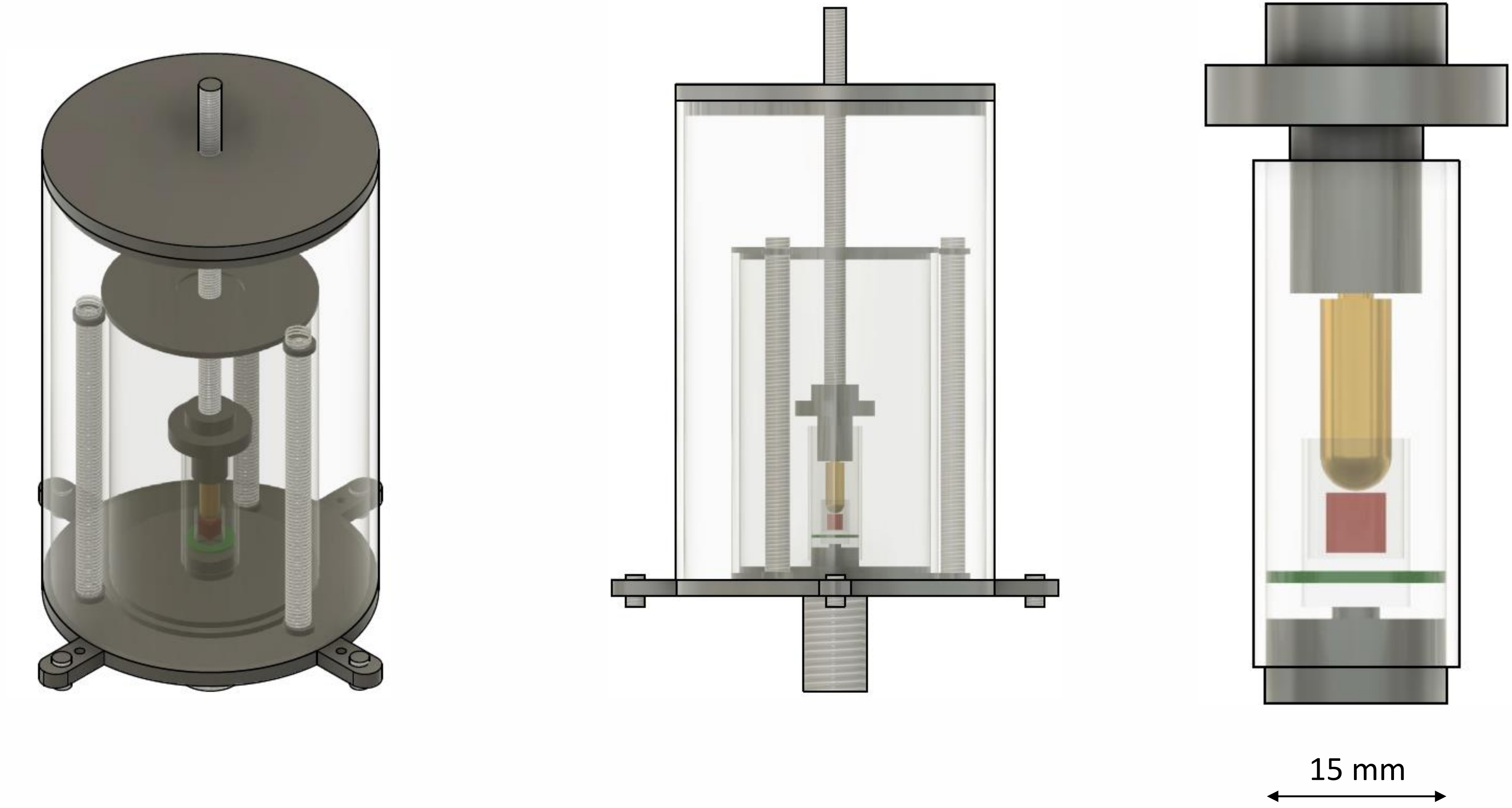
## Post Processing

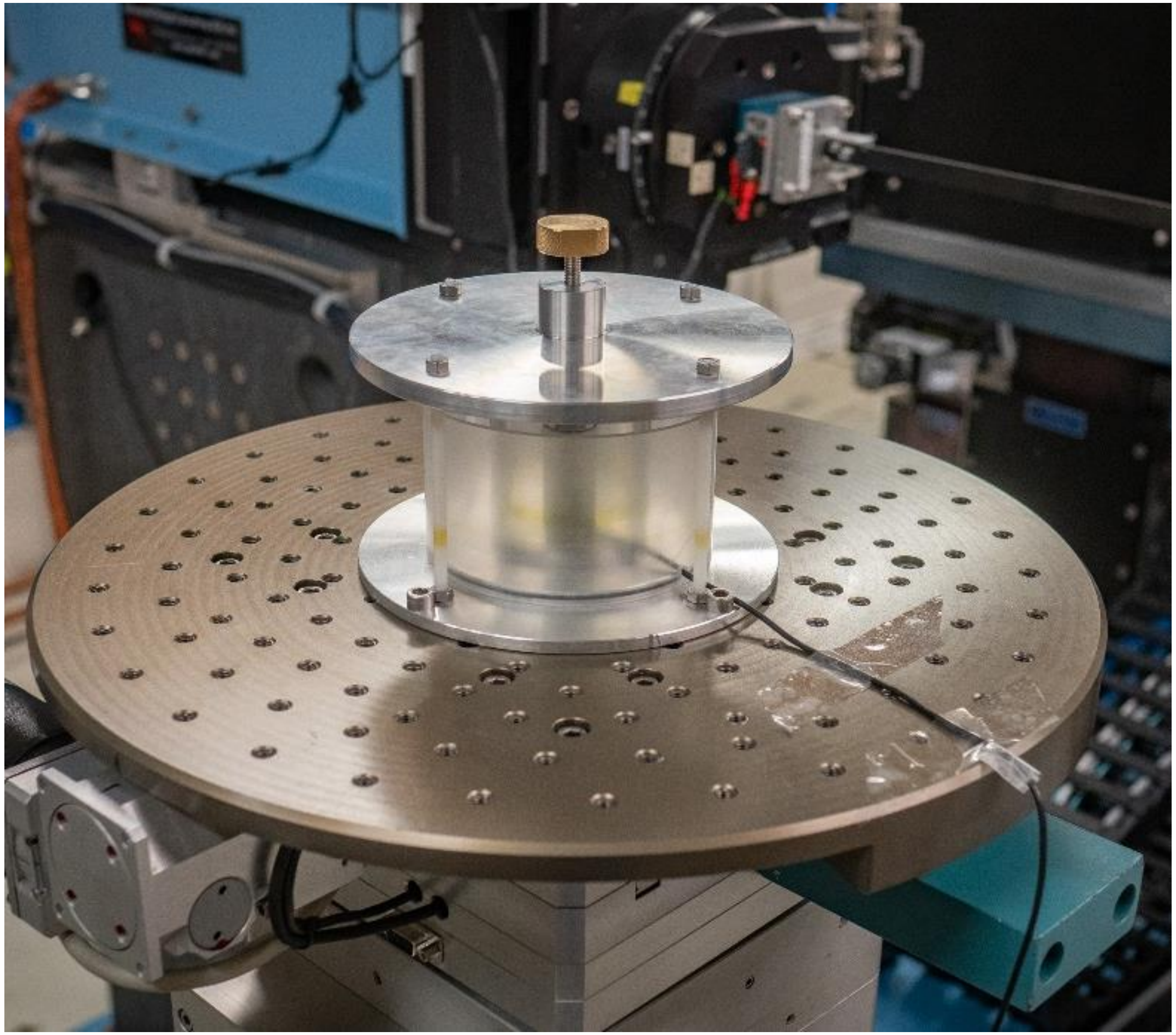
- Digital Volume Correlation
- Determine the displacement maps at different states of loading

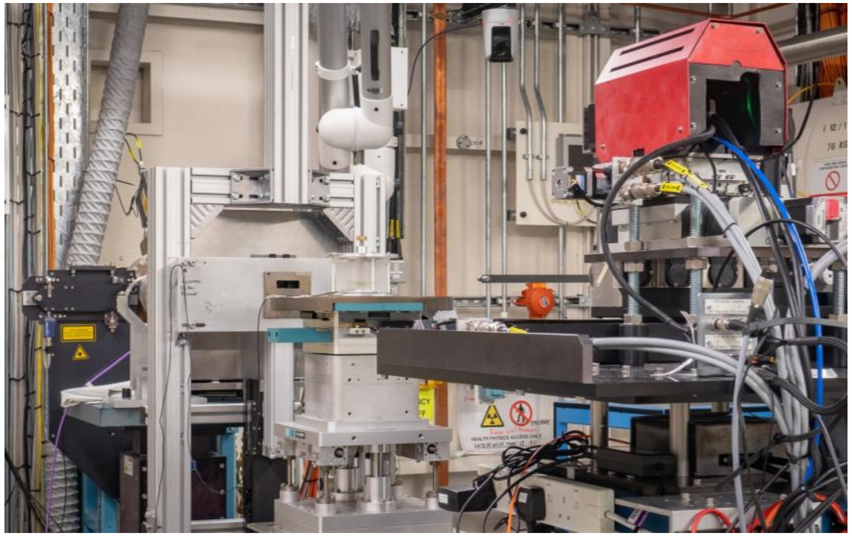
## Experimental Target

- Matching the displacement maps with FEM to determine mechanical properties




15 mm





# Fukushima Corium

Start Load
(10 N)

Failure Load
(159.68 N)

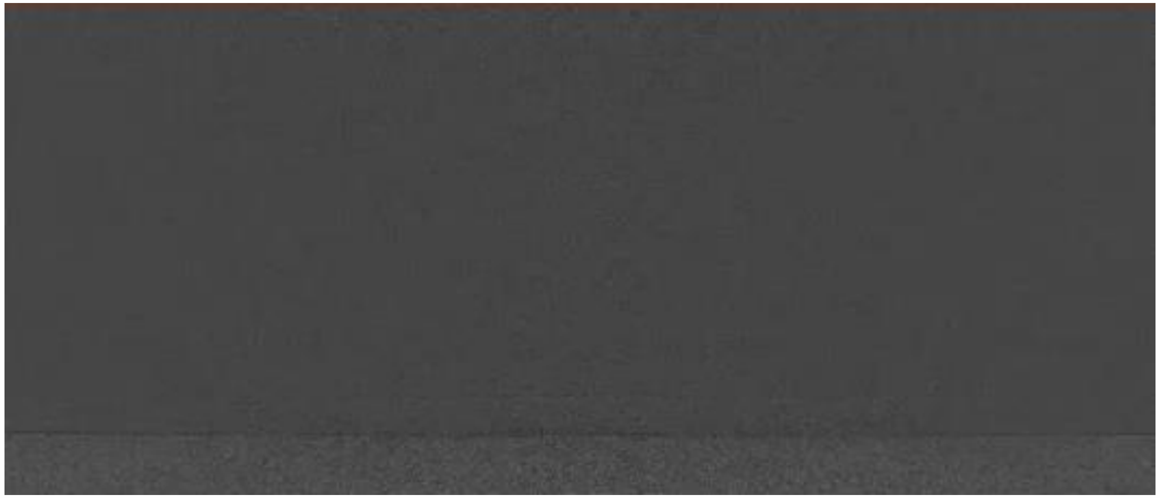
# Chernobyl Black LFCM

Start Load
(10 N)

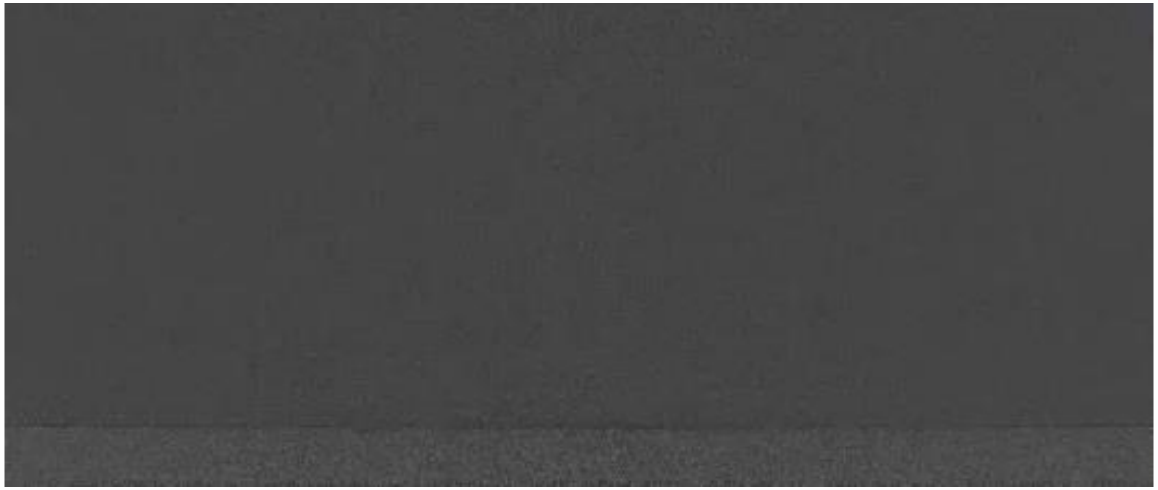
Failure Load
(126.46 N)

# Chernobyl Brown LFCM

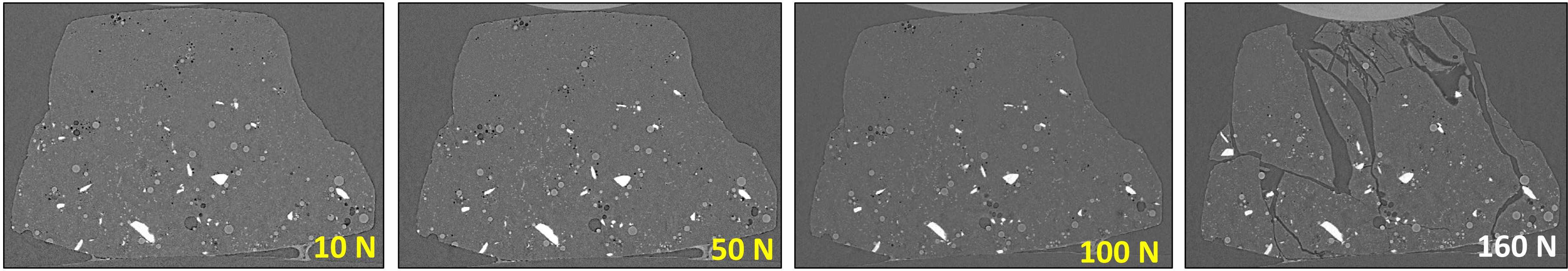
Start Load
(10 N)



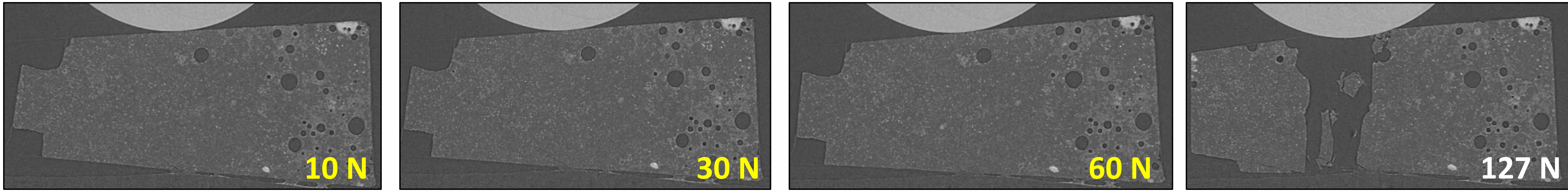
Failure Load
(35.02 N)



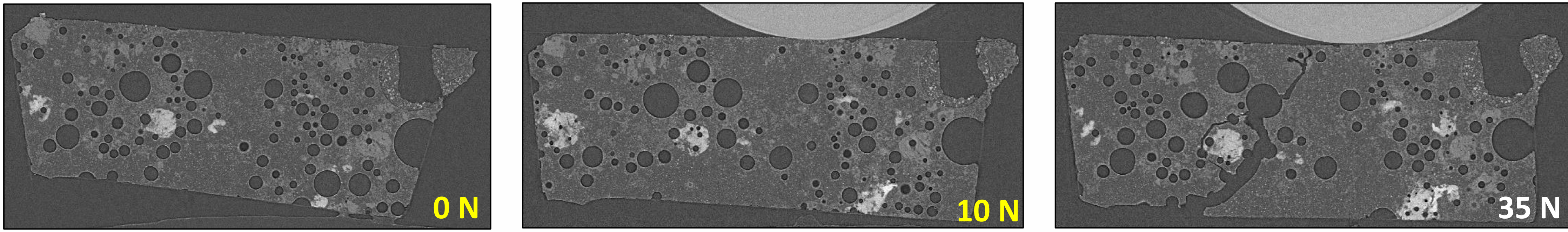
## Fukushima Corium



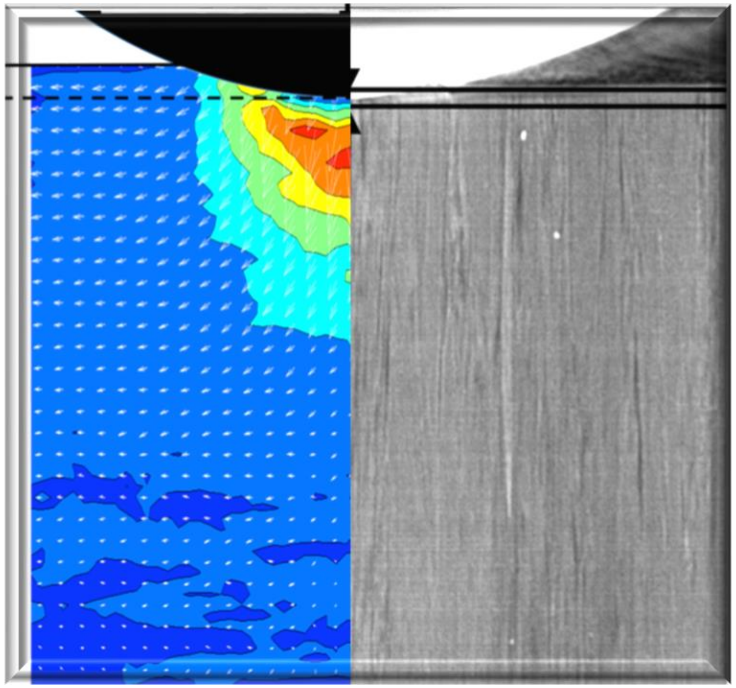
## Chernobyl Black LFCM



## Chernobyl Brown LFCM

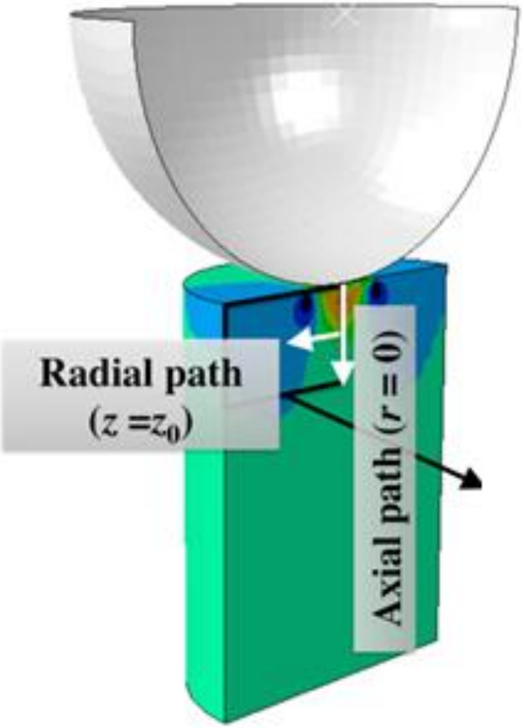


**Digital Volume Correlation**
**Displacement Field**



+

**Finite Element Modelling**
**Displacement Field**



=

**Mechanical Properties**
**E, ν, Yield Stress, Failure mode**

☐ Dr Claire Corkhil
☐ Dr Clemence Gausse

The University Of Sheffield.

☐ Dr Mahmoud Mostafavi
☐ Prof Tom Scott
☐ Dr Keith Hallam
☐ Dr Chris Jones
☐ Dr Chris Simpson

University of BRISTOL

☐ Dr Christina Reinhard
☐ Dr Oxana Magdysyuk

diamond

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Thank you

Haris Paraskevoulakos
cp13846@brsitol.ac.uk

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Transformative Science and Engineering for Nuclear Decommissioning

# Characterisation of Uranium Mineral Phases by Time-Resolved Laser Fluorescence (TRLFS) and Raman Spectroscopy

Victoria L. Frankland [1], Antoni Milodowski [1], Joshua Bright [1] and David Read [1,2]

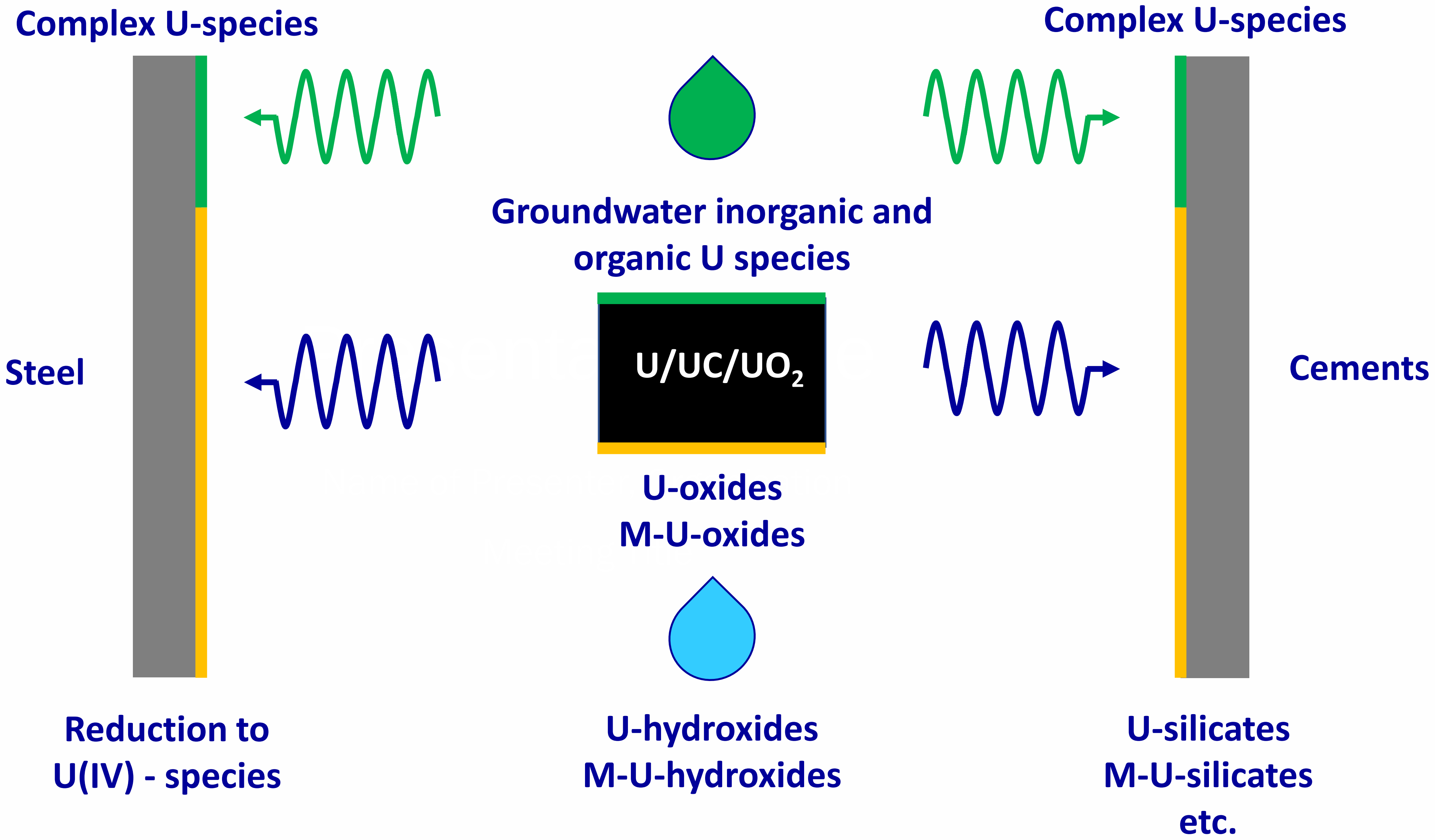
1) University of Surrey, Guildford, UK; 2) National Physical Laboratory, Teddington, UK

TRANSCEND Annual Meeting April 2019

Energy

For a Low Carbon Future

# ~ 250 Natural Uranium Minerals



Complex U-species

Complex U-species

Groundwater inorganic and organic U species

Steel

$U/UC/UO_2$

Cements

U-oxides
M-U-oxides

Reduction to
U(IV) - species

U-hydroxides
M-U-hydroxides

U-silicates
M-U-silicates
etc.

# Aim

- ~ 250 U minerals
  - Few characterised by Raman,
  - Very few characterised by fluorescence, fewer still by TRLFS

- Create a spectral database for non-destructive identification of potential U species arising from spent fuel storage & disposal
  - Reference spectra from high quality type mineral phases
  - Applied to amorphous & ultra-thin surface alteration products
  - Method also capable of characterising aqueous & non-aqueous solutions

- Limitations with conventional techniques for U phase ID:
  - XRD - requires good crystallinity
  - IR spectroscopy - spectra masked by water features
  - Need (trans)portable techniques

- Techniques chosen:
  - Time-Resolved Laser Fluorescence Spectroscopy (TRLFS)
  - Raman Spectroscopy
  - Laser-induced breakdown spectroscopy (LIBS)

# TRLFS and Raman apparatus

- **5 Lasers: 244, 457, 532, 633 and 785 nm**
- **Alternative stage for solutions**

# U Minerals and Analytical Grade Powders

**Oxides:**
- Meta-studtite
- Uranium trioxide

**Metal Oxides**
- Fourmarierite (Pb)
- Vandenbrandite (Cu)
- Vandendriesscheite (Pb)

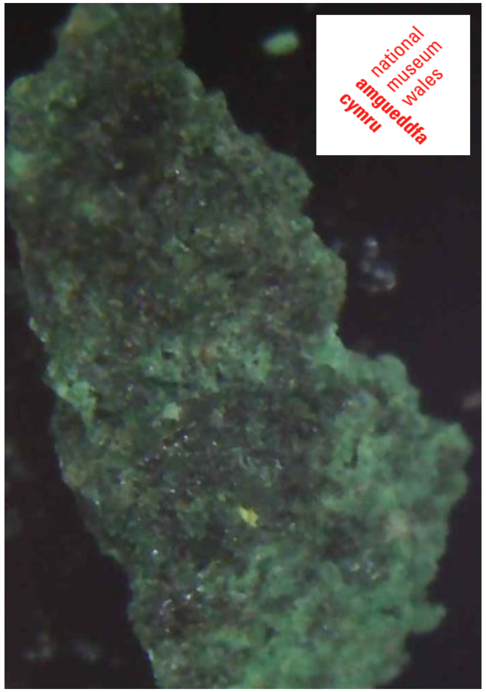
**Carbonates:**
- Andersonite (Na, Ca)

**Phosphates ($PO_4$):**
- Meta-autunite (Ca)
- Meta-torbernite (Cu)
- Saleeite (Mg)

**Silicates ($SiO_4$):**
- Boltwoodite (K)
- Uranophane (Ca)

**Sulfates ($SO_4$):**
- Johannite (Cu)
- Uranyl sulfate

**Vanadate ($VO_4$):**
- Carnotite (K)
- Tyuyamunite (Ca)



# U Oxidation Mechanisms

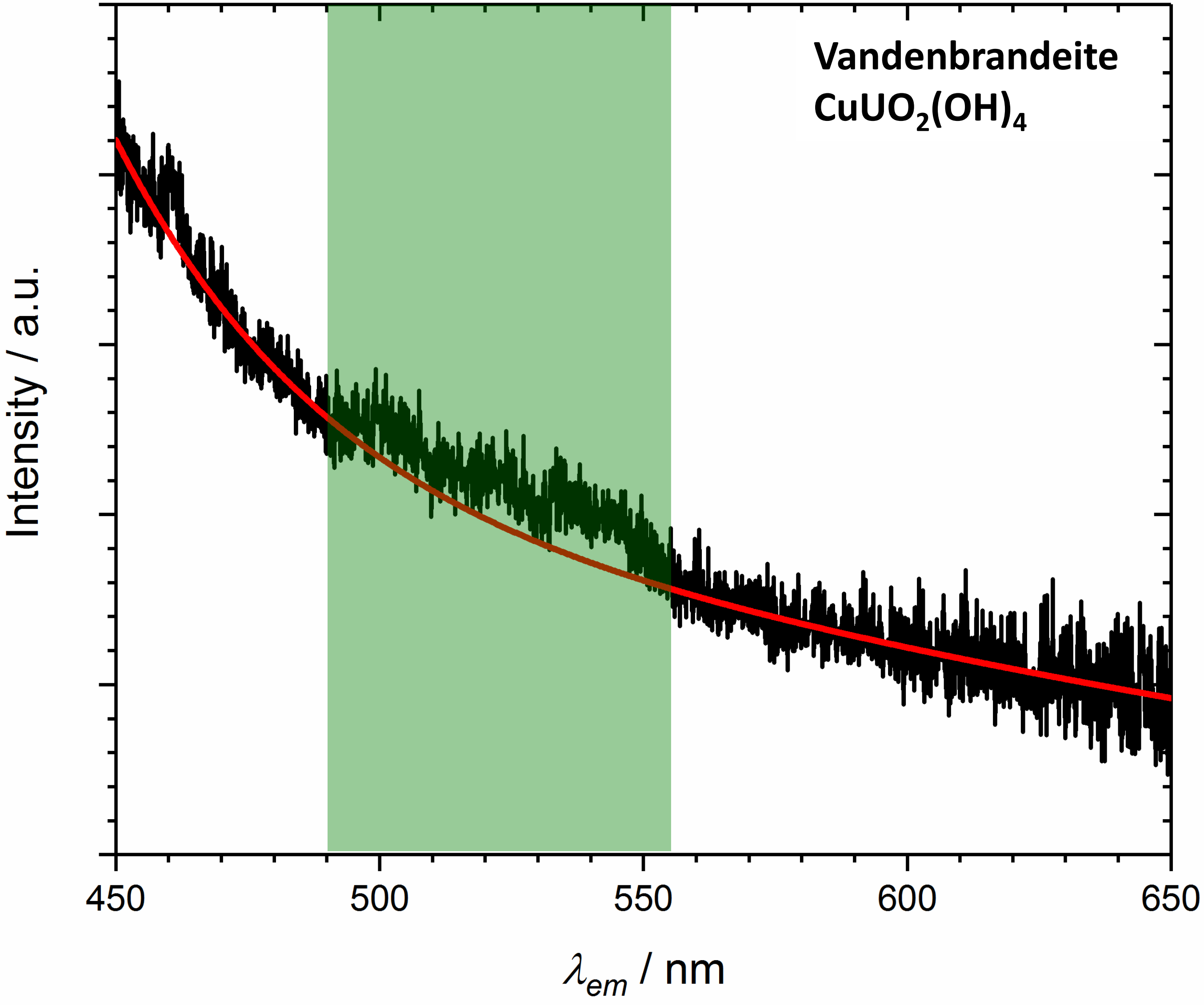
**Reaction path 1 [1]:**
**Uranium metal, U**
$\downarrow$
**Uraninite, $UO_2$**
$\downarrow$
**$U_3O_7/U_4O_9$**
$\downarrow$
**$U_3O_8$**
$\downarrow$
**Uranium trioxide, $UO_3$**

**Reaction path 2 [2]:**
**Uranium metal, U**
$\downarrow$
**Uraninite, $UO_2$**
$\downarrow$
**Ianthinite, $U^{4+}(U^{6+}O_2)_5O_7\cdot 10(H_2O)$**
$\downarrow$
**Schoepite, $(UO_2)_8O_2(OH)_{12}\cdot 12(H_2O)$**
**Studtite, $UO_2O_2(H_2O)_2\cdot H_2O$**
$\downarrow$
**Metal-UOHs**
$\downarrow$
**Metal uranyl complexes (e.g. phosphates)**

**Sweden and Finland plan to disposing of SNF inside a copper canister with steel inserts[3-4]**

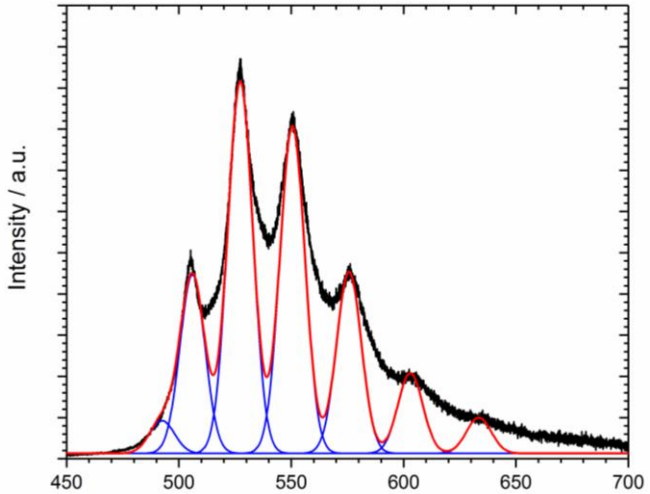
1) McEachern and Taylor, (1998); 2) Baker, (2014); 3) Hedman, *et al.*, (2003); 4) Rosborg and Werme, (2008)

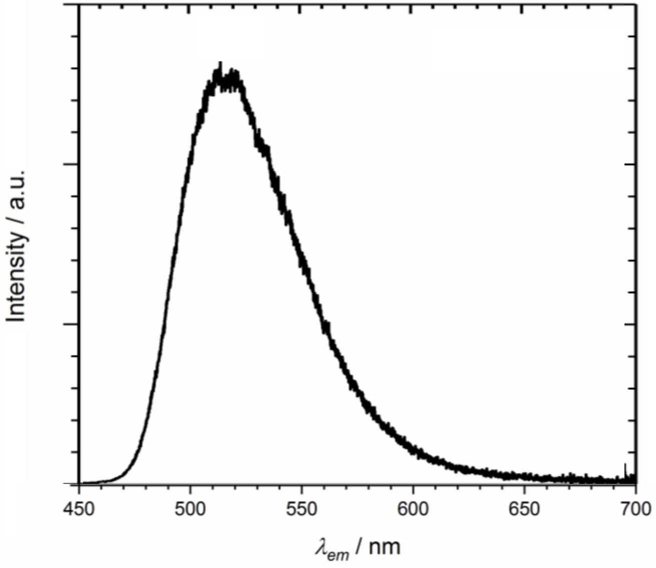
# Fluorescence Emission Spectrum



**Vandenbrandeite**
**$CuUO_2(OH)_4$**

**Vandendriesscheite**
**$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11}\cdot 11(H_2O)$**



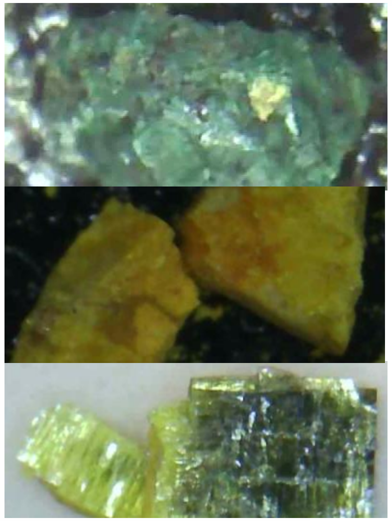


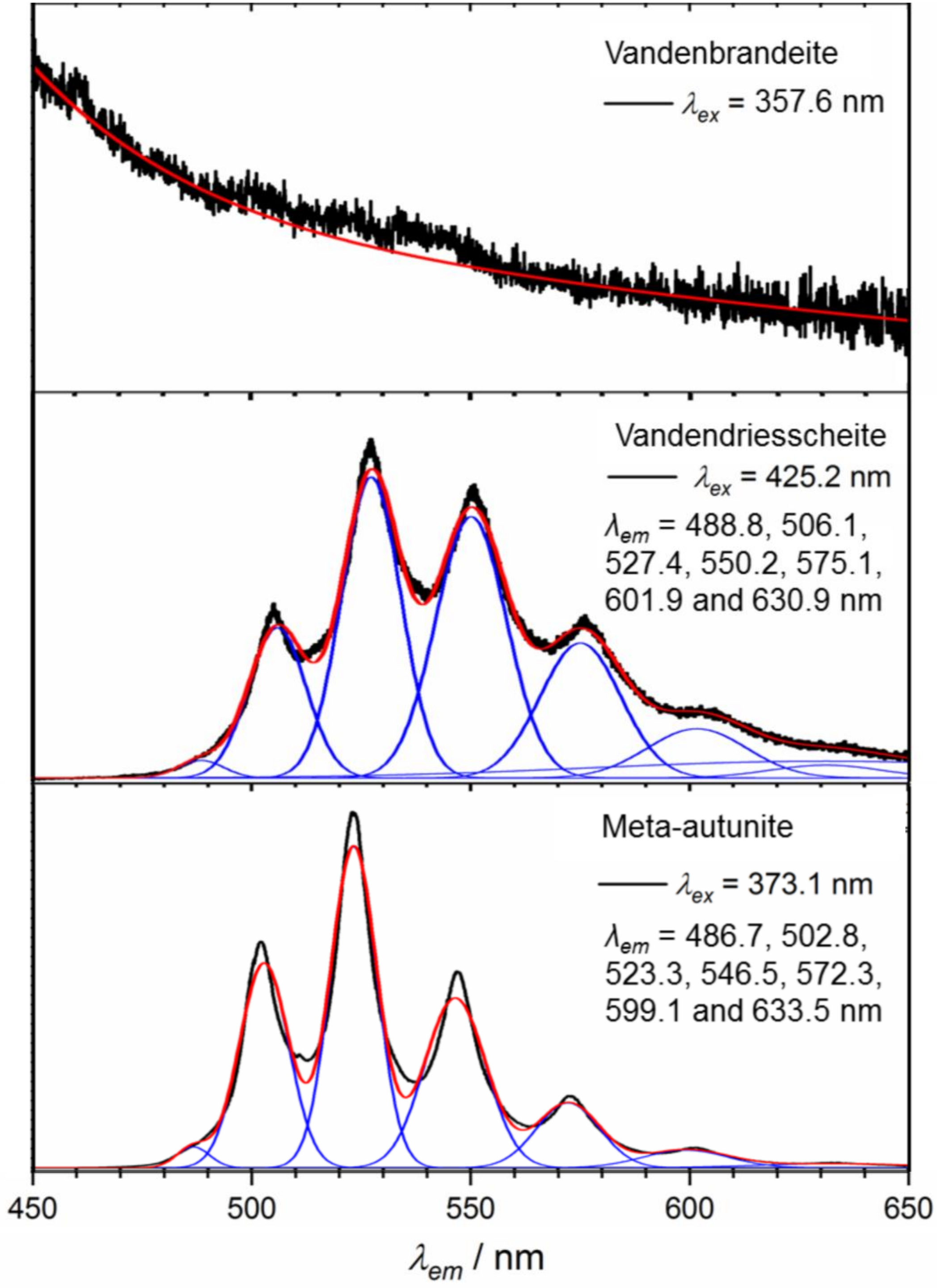
**Uranium trioxide, $UO_3$**

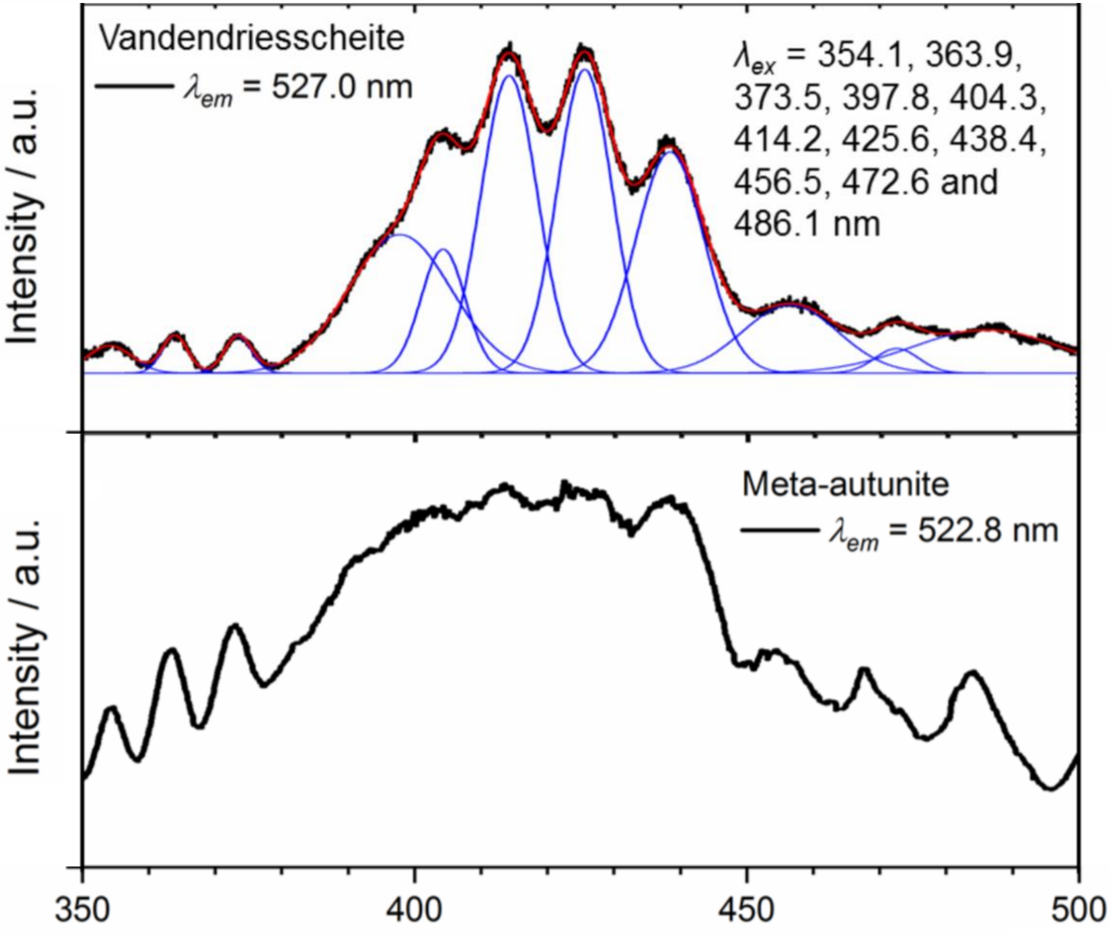
**Vandenbrandeite**
**$CuUO_2(OH)_4$**

**Vandendriesscheite**
**$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11}\cdot 11(H_2O)$**

**Meta-autunite**
**$Ca(UO_2)_2(PO_4)_2\cdot 6\text{-}8(H_2O)$**







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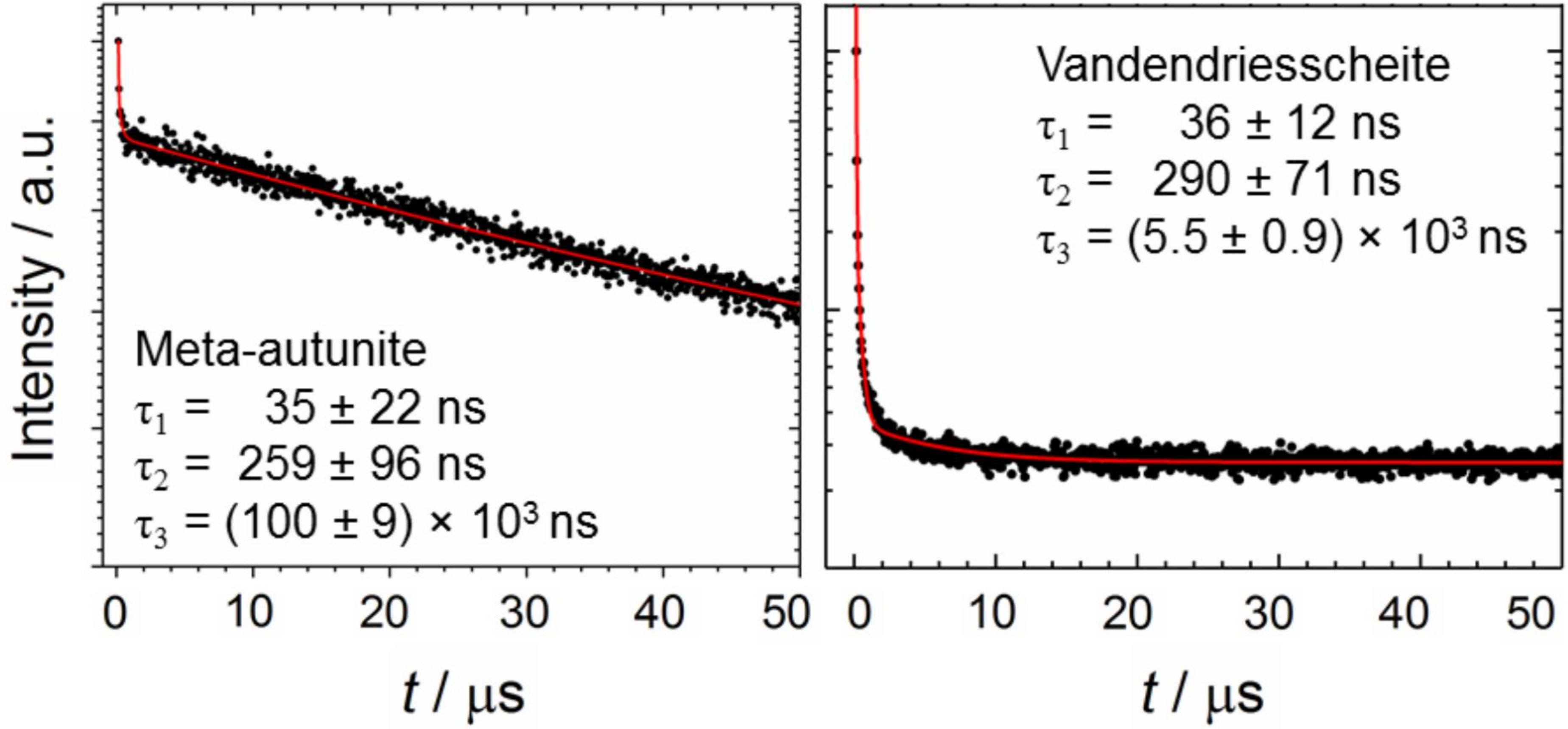
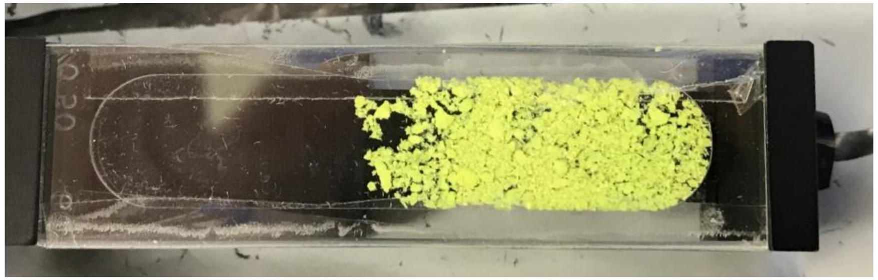
**$Ca(UO_2)_2(PO_4)_2 \cdot 6\text{-}8(H_2O)$**

**Vandendriesscheite**
**$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11} \cdot 11(H_2O)$**



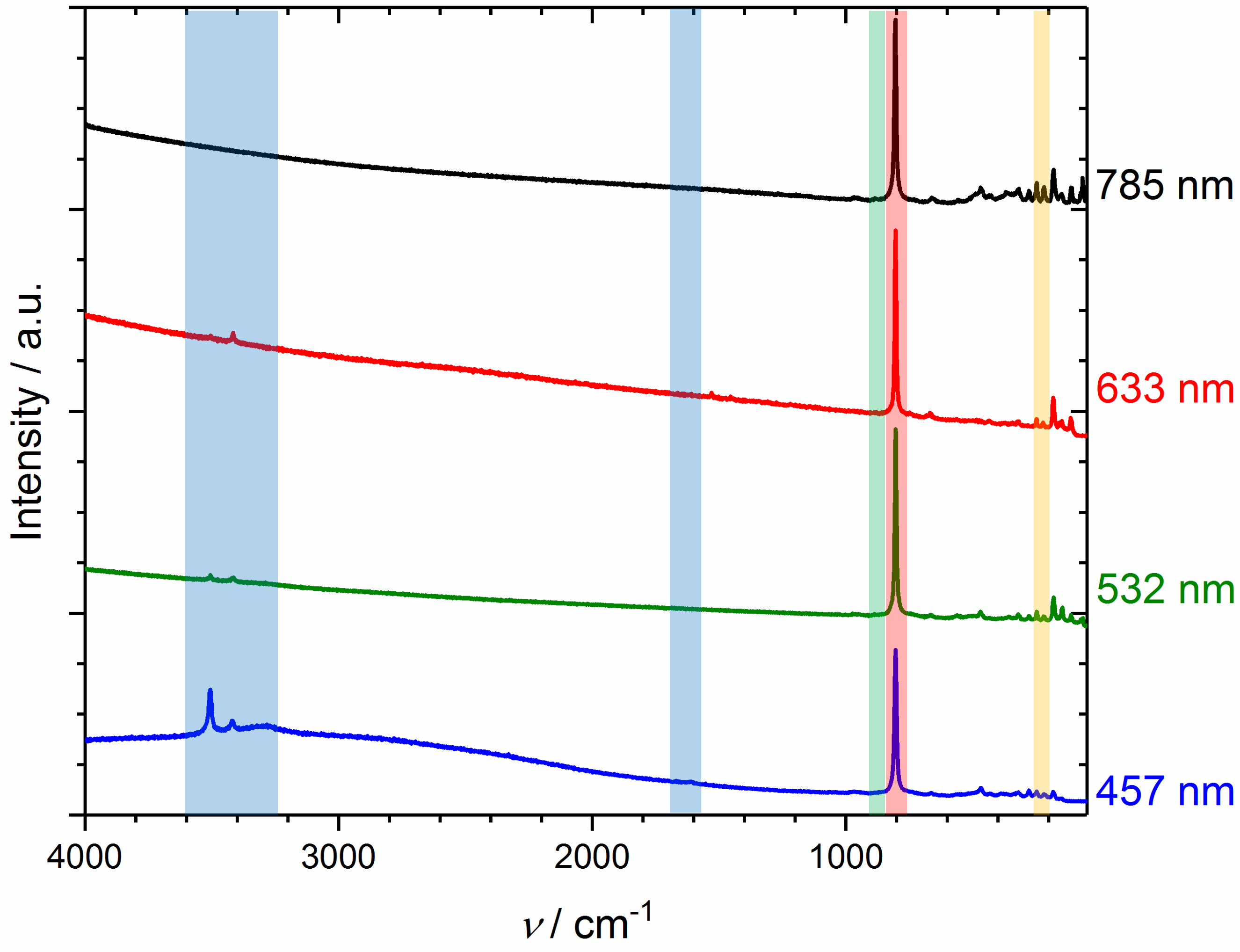
**Uranyl sulfate**
**$UO_2SO_4 \cdot 3.5(H_2O)$**

**$\tau_1 = (122.1 \pm 8.7) \times 10^3$ ns**



# Raman

**Vandenbrandeite**
**$CuUO_2(OH)_4$**



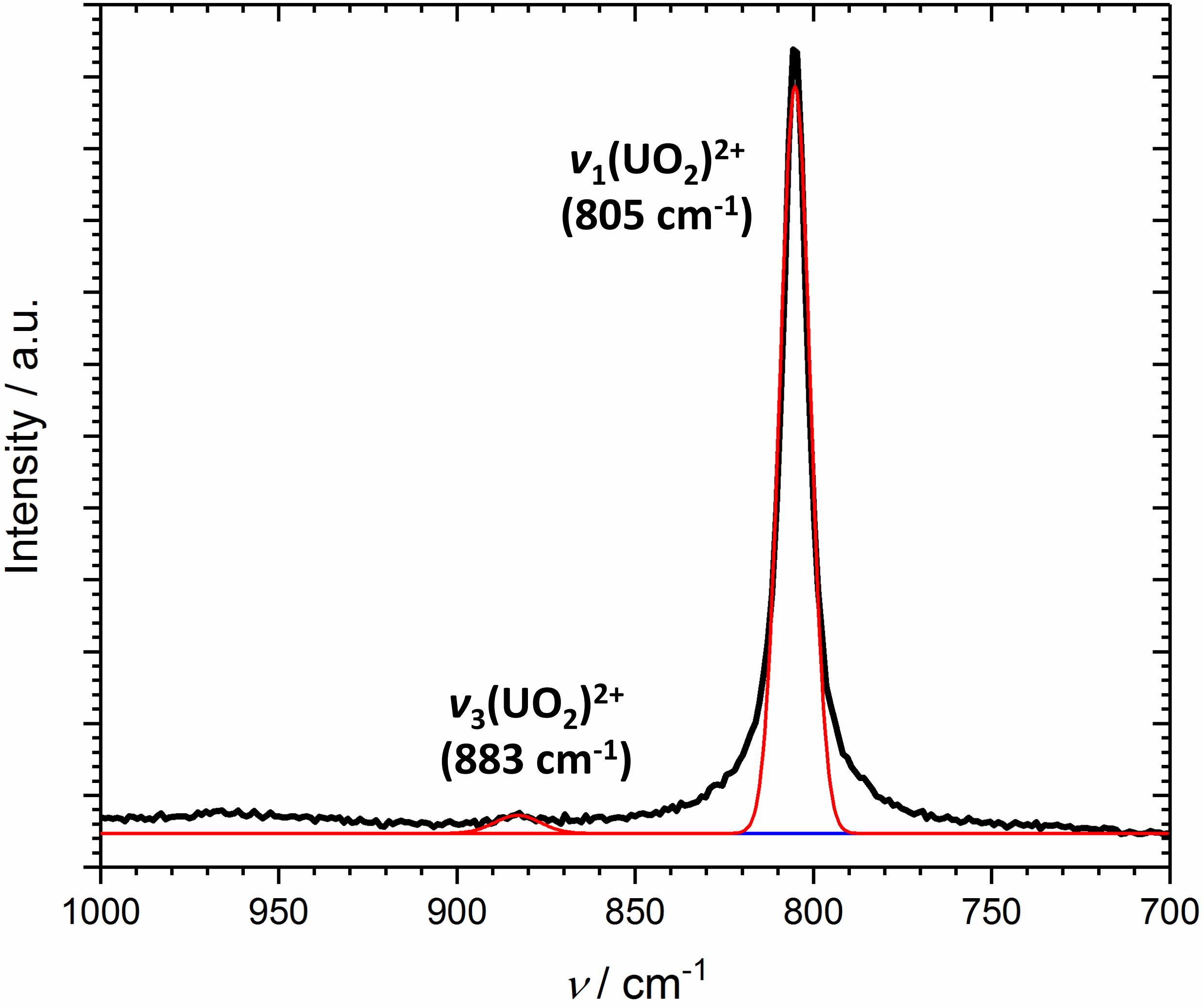
| Assignment | This work | Literature [1] |
|---|---|---|
| $\nu(OH)_{water}$ | 3503 - 3260 | 3508 - 3262 |
| $\delta(H_2O)$ | 1611 | - |
| $\nu_3(UO_2)^{2+}$ | 883 | 862 |
| $\nu_1(UO_2)^{2+}$ | 805 | 805 |
| $\nu_2(UO_2)^{2+}$ | 277 - 248 | 252 |

---

1) Botto *et al.*, (2002);

# Raman

**Vandenbrandeite**
**$CuUO_2(OH)_4$**

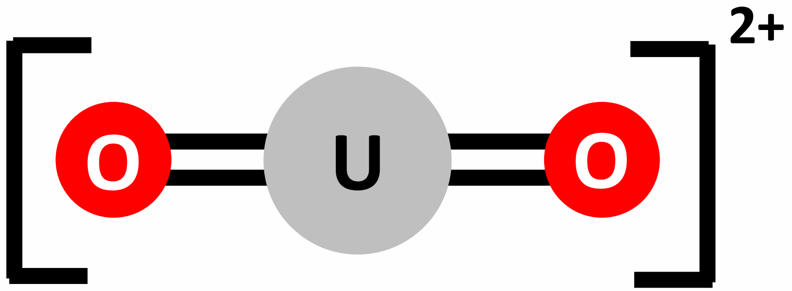


| $\nu_1(UO_2)^{2+}$ / $cm^{-1}$ | 805 ± 3 |
|---|---|
| $d_{U\text{-}O}$ / Å | 1.81 ± 0.01 |
| $k_{U\text{-}O}$ / mdyn $Å^{-1}$ | 4.90 ± 0.07 |
| $\nu_3(UO_2)^{2+}$ / $cm^{-1}$ | 872 ± 4 |

$d_{U\text{-}O}$ (Å) = 106.5 $[\nu_1(UO_2)^{2+}]^{-2/3}$ [1]

$k_{U\text{-}O}$ (mdyn $Å^{-1}$) = $[1.08 / (d_{U\text{-}O} - 1.17)]^3$ [2, 3]

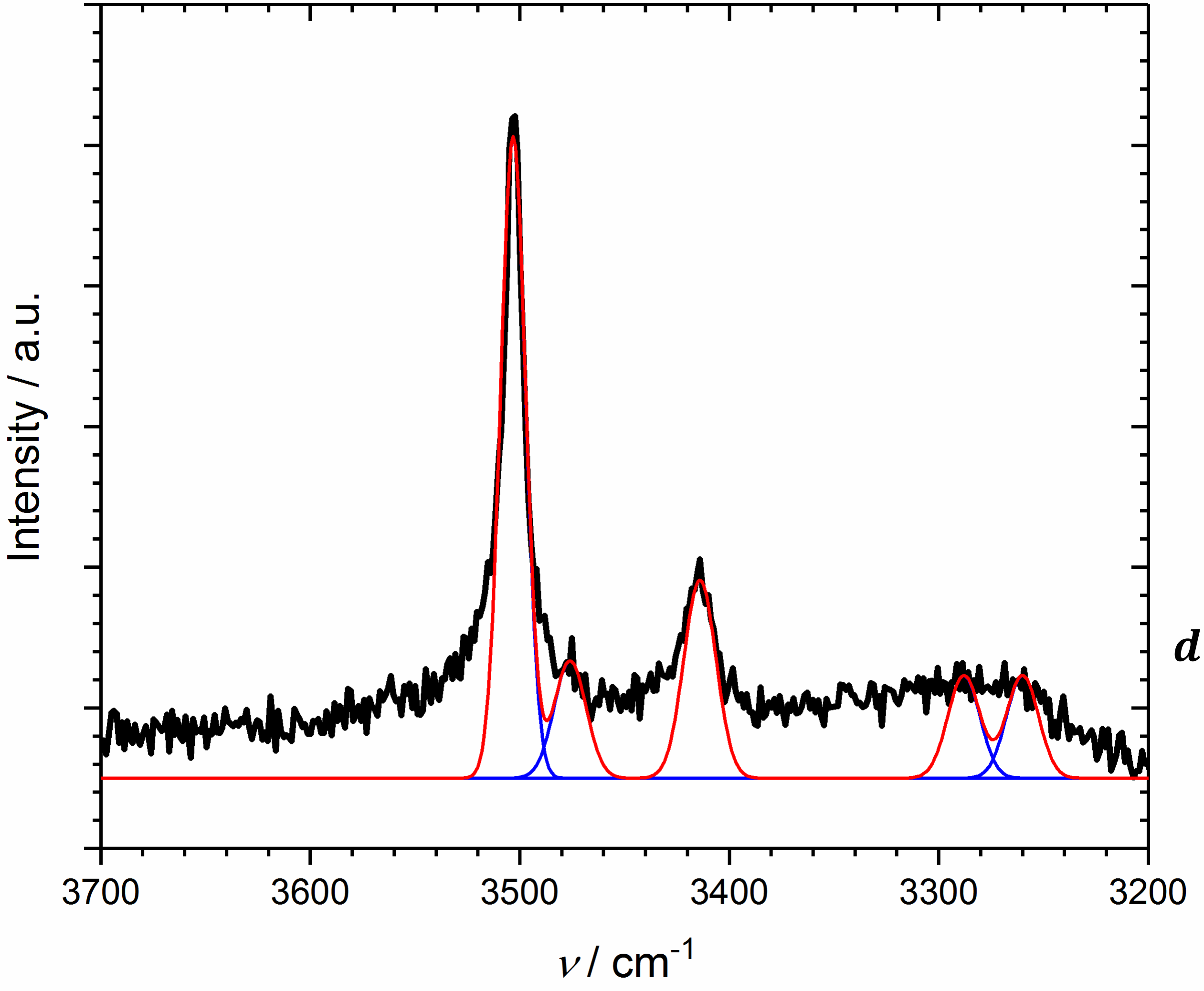
$\nu_3(UO_2)^{2+}$ ($cm^{-1}$) = $[91.41 / (d_{U\text{-}O} - 0.804)]^{3/2}$ [1]



1) Bartlett & Cooney, (1989); 2) Badger, (1935); 3) Jones, (1959)

# Raman

**Vandenbrandeite**
**$CuUO_2(OH)_4$**

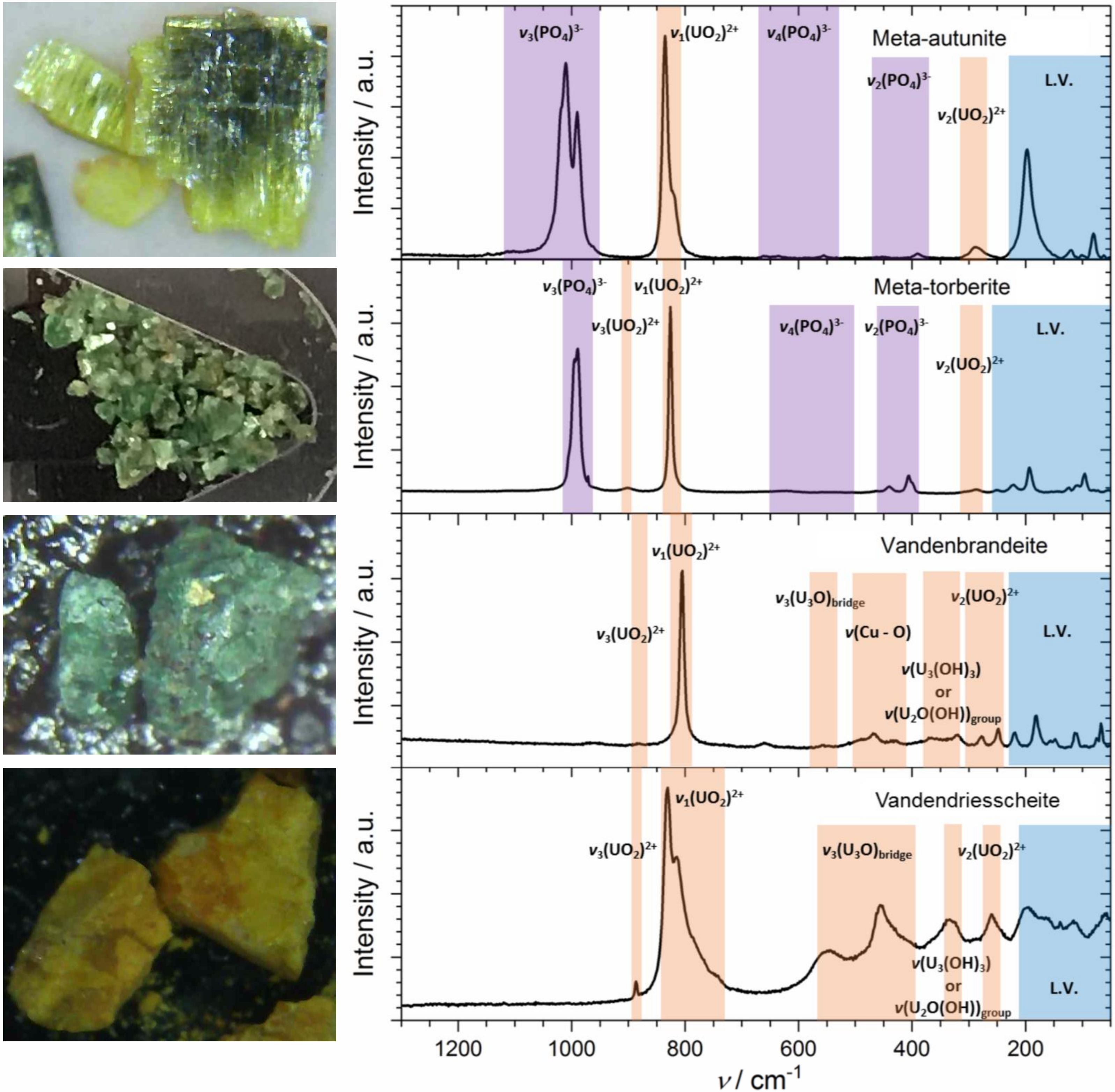


| $\nu$(OH) / cm$^{-1}$ | $d_{O\text{-}H\cdots O}$ |
|---|---|
| 3503 ± 3 | 2.90 ± 0.01 |
| 3476 ± 3 | 2.86 ± 0.01 |
| 3414 ± 3 | 2.81 ± 0.01 |
| 3288 ± 3 | 2.74 ± 0.01 |
| 3260 ± 3 | 2.73 ± 0.01 |

$$d_{O-H\cdots O}(\text{Å}) = -0.1321 \ln\left[\frac{\left(3595 - \nu(OH)\right)}{3.04 \times 10^{11}}\right]$$

[1]

1) Libowitzky (1999)



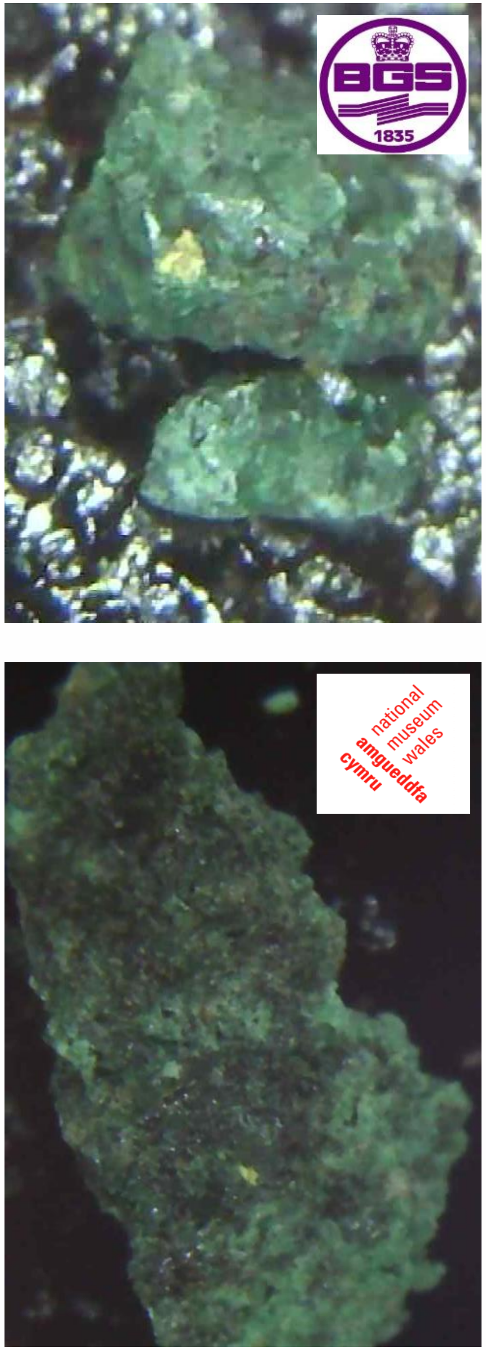
Meta-autunite
$Ca(UO_2)_2(PO_4)_2 \cdot 6\text{-}8(H_2O)$

Meta-torbernite
$Cu(UO_2)_2(PO_4)_2 \cdot 8(H_2O)$

Vandenbrandeite
$CuUO_2(OH)_4$

Vandendriesscheite
$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11} \cdot 11(H_2O)$

# Conclusions



- **Obtained Raman and/or fluorescence spectra for:**

| | |
|---|---|
| - **Uranium trioxide** | $UO_3$ |
| - **Vandenbrandeite** | $CuUO_2(OH)_4$ |
| - **Vandendriesscheite** | $Pb_{1.5}(UO_2)_{10}O_6(OH)_{11}\cdot 11(H_2O)$ |
| - **Uranyl sulfate** | $UO_2SO_4\cdot 3.5(H_2O)$ |
| - **Meta-autunite** | $Ca(UO_2)_2(PO_4)_2\cdot 6\text{-}8(H_2O)$ |
| - **Meta-torbernite** | $Cu(UO_2)_2(PO_4)_2\cdot 8(H_2O)$ |

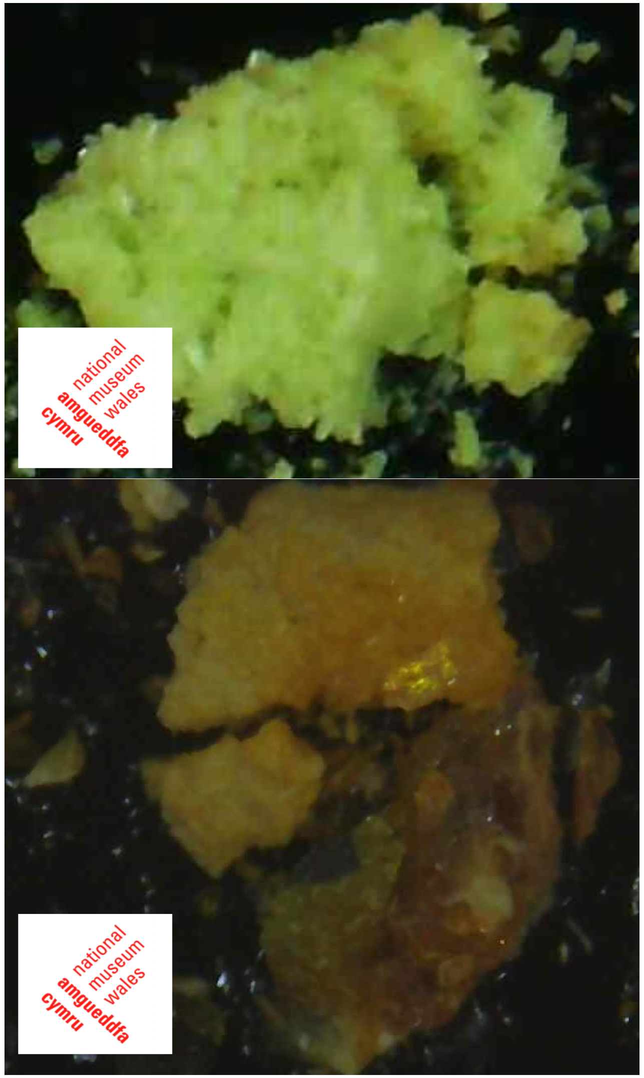
- **Characterisation of far more U minerals and analytical grade samples required to build database**

# Future Work

- TRLFS and Raman spectroscopy
  - Analytical grade U compounds
  - Minerals from: - British Geological Survey
    - National Museum of Wales
    - Natural History Museum
  - U-bearing solutions

⇨ Reference Collection Database

- Guide *in situ*, real time experimental simulations of the corrosion/alteration process
- Assess feasibility of remote environmental measurements



**Radiation Laboratories: John-William Brown & Sarah Heisig**
**TRLFS: Craig Graham (Edinburgh Instruments)**
**Raman: Dr Carol Crean and Dr Rachida Bance-Soualhi**
**SEM-EDX: David Jones**
**XRD: Dr Dan Driscoll**

**Loan of minerals:**
**Kay Green**
**Tom Cotterell**
**Mike Rumsey**

BGS 1835

national museum wales
amgueddfa cymru

NATURAL HISTORY MUSEUM

Thank you

**Funding:**

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Research Councils UK
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DISTINCTIVE

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

# Building the Foundations of a Predictive Tool for Spent Fuel Behaviour

Angus Siberry, University of Bristol

TRANSCEND Annual Meeting, Bath

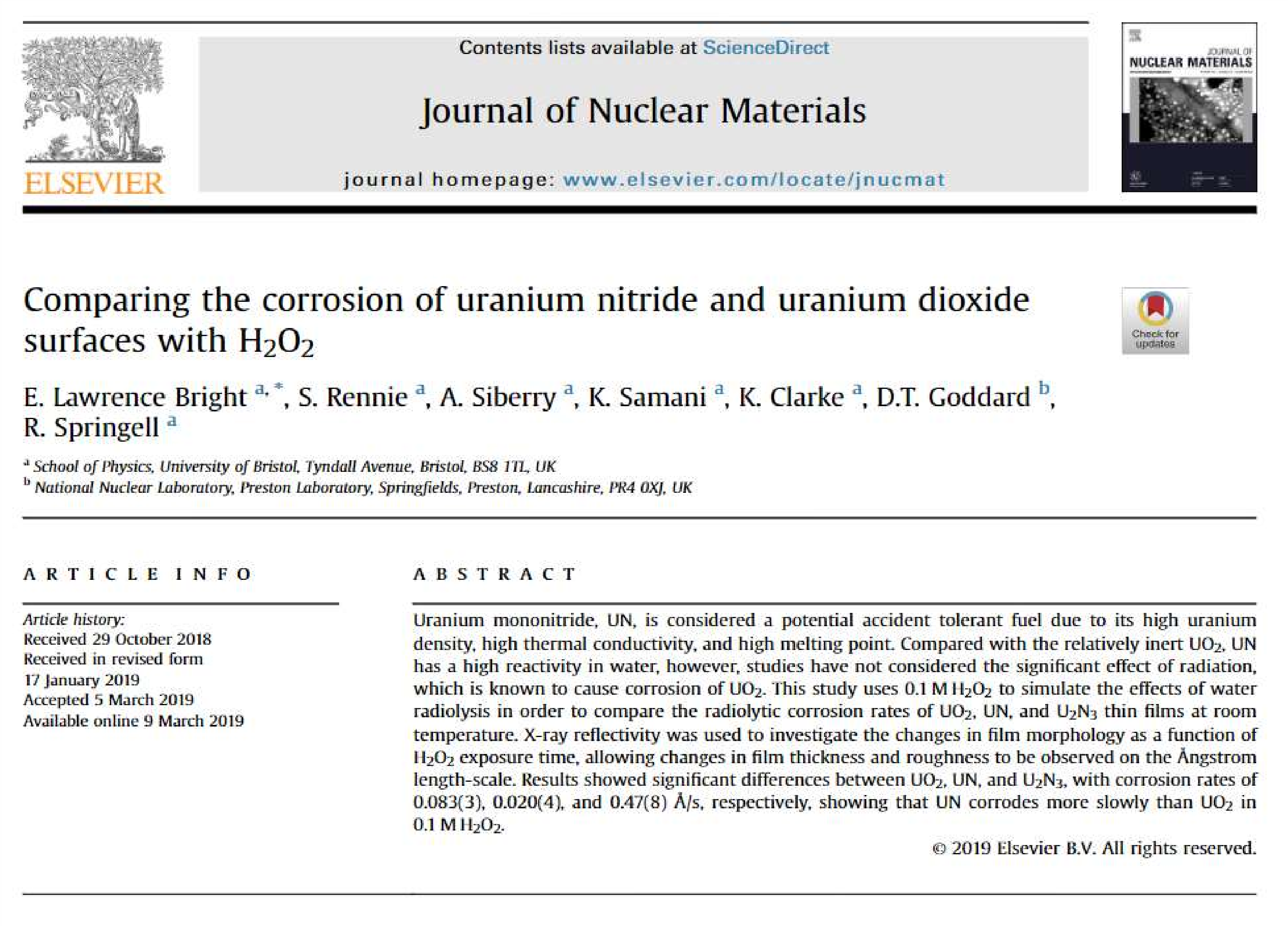
Energy
For a Low Carbon Future

# Who am I?

Physics BSc, University of Bristol 2014-2017

Undergraduate project titled

*‘The Next Generation of Nuclear Fuels: An investigation into the corrosion of Uranium Mononitride’*



Contents lists available at ScienceDirect
Journal of Nuclear Materials
journal homepage: www.elsevier.com/locate/jnucmat

# Comparing the corrosion of uranium nitride and uranium dioxide surfaces with $H_2O_2$

E. Lawrence Bright [a, *], S. Rennie [a], A. Siberry [a], K. Samani [a], K. Clarke [a], D.T. Goddard [b], R. Springell [a]

[a] School of Physics, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, UK
[b] National Nuclear Laboratory, Preston Laboratory, Springfields, Preston, Lancashire, PR4 0XJ, UK

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ABSTRACT

Uranium mononitride, UN, is considered a potential accident tolerant fuel due to its high uranium density, high thermal conductivity, and high melting point. Compared with the relatively inert $UO_2$, UN has a high reactivity in water, however, studies have not considered the significant effect of radiation, which is known to cause corrosion of $UO_2$. This study uses 0.1 M $H_2O_2$ to simulate the effects of water radiolysis in order to compare the radiolytic corrosion rates of $UO_2$, UN, and $U_2N_3$ thin films at room temperature. X-ray reflectivity was used to investigate the changes in film morphology as a function of $H_2O_2$ exposure time, allowing changes in film thickness and roughness to be observed on the Ångstrom length-scale. Results showed significant differences between $UO_2$, UN, and $U_2N_3$, with corrosion rates of 0.083(3), 0.020(4), and 0.47(8) Å/s, respectively, showing that UN corrodes more slowly than $UO_2$ in 0.1 M $H_2O_2$.

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

# Nuclear Science and Engineering MSc, University of Bristol (2018 – 2019)

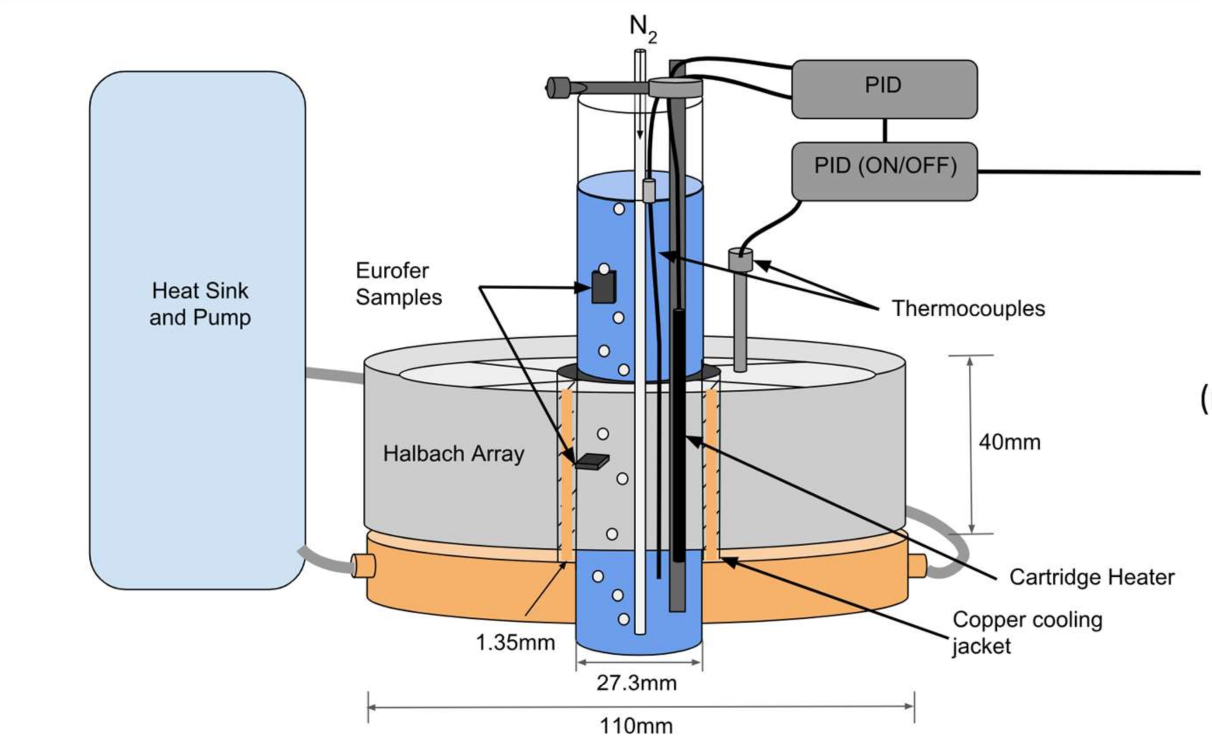
SOUTH WEST
NUCLEAR HUB

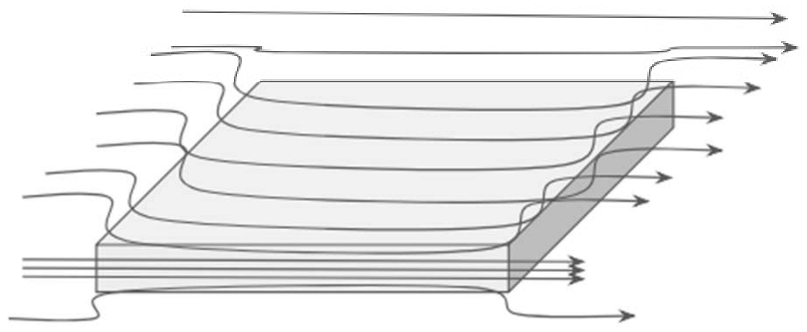
## Research project

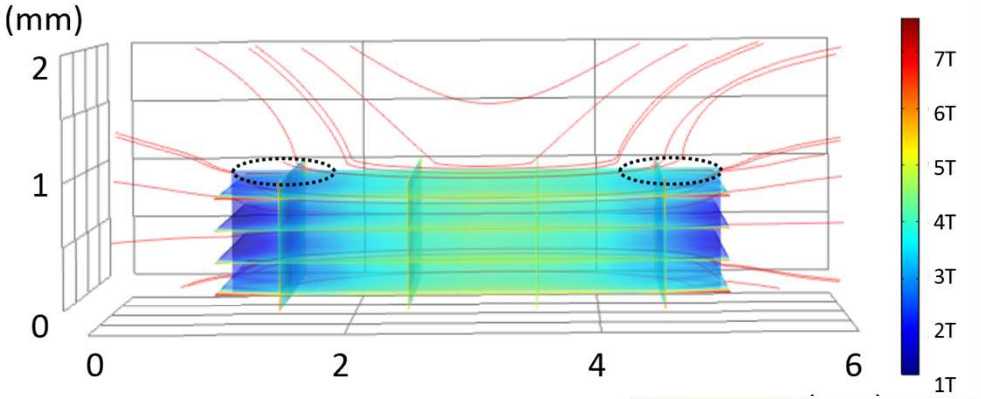
## *‘Magnetic Field Effects on the Corrosion Behaviour of Eurofer-97’*

University of
BRISTOL

IAC
Interface Analysis Centre

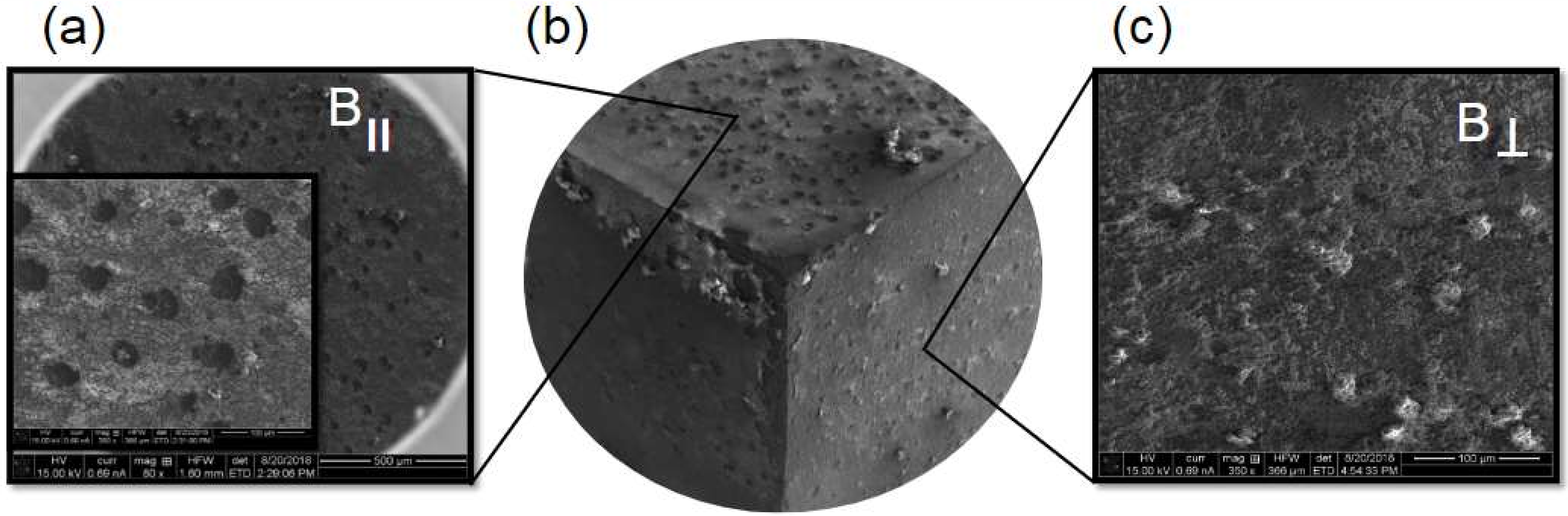






University of BRISTOL

Interface Analysis Centre


(a)
(b)
(c)
B∥
B⊥
HV 15.00 kV curr 0.69 nA mag 80 x HFW 1.60 mm det ETD 8/20/2018 2:29:06 PM
500 µm
HV 15.00 kV curr 0.69 nA mag 350 x HFW 366 µm det ETD 8/20/2018 4:54:33 PM
100 µm

# Physics PhD, University of Bristol

- Micro/meso/macro scale modelling of spent fuel corrosion.

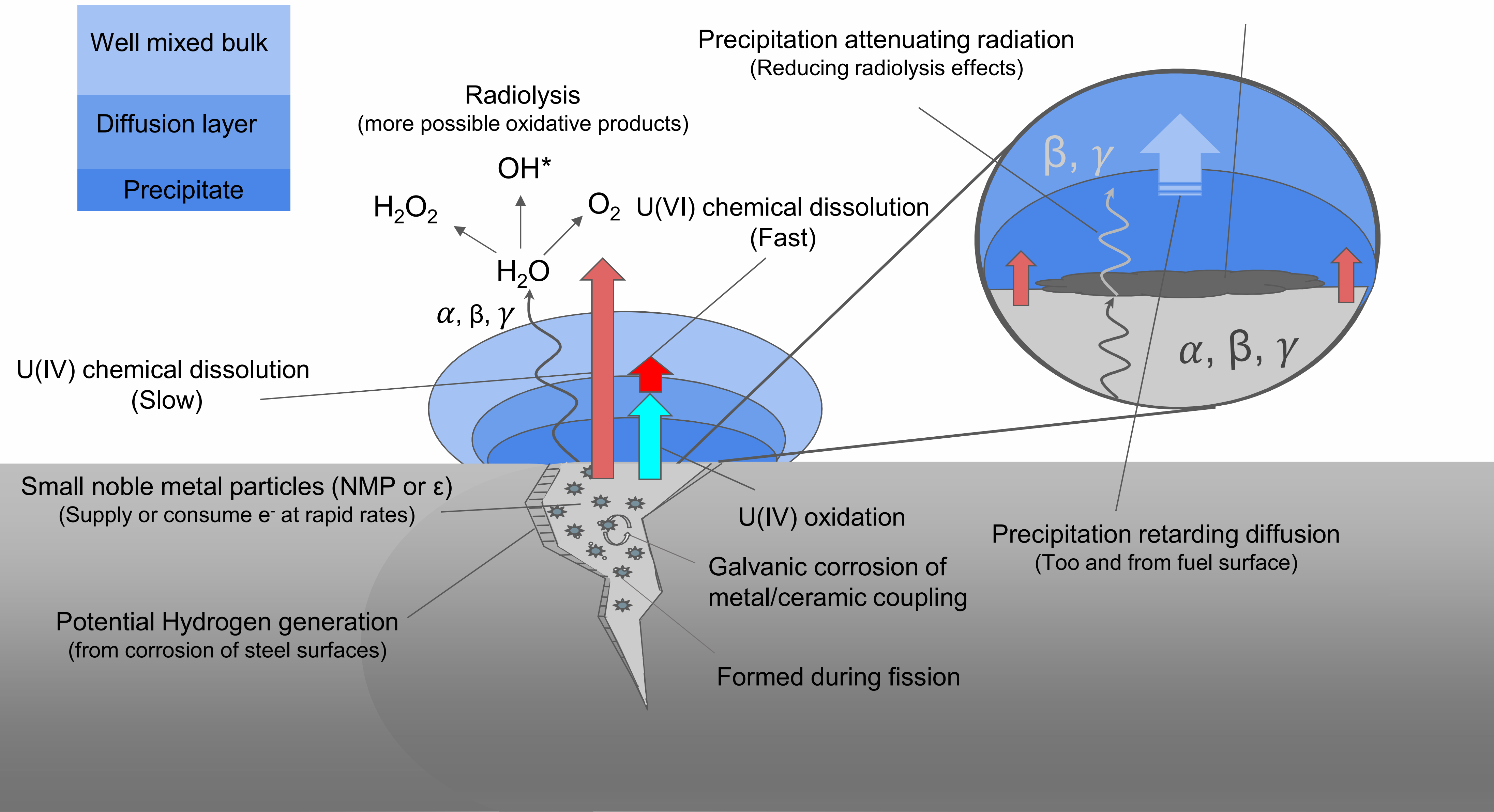
- Experiments on 'engineered' fuel samples to test these models.

- Application of models to scenarios relevant to Sellafield/NNL

- Comparison of FACSIMILE+COMSOL/MOOSE models (mention INL)

# Why is this such a difficult problem?

# Spent fuel dissolution considerations



Well mixed bulk

Diffusion layer

Precipitate

Precipitates limiting dissolution sites
(Reducing the area available)

Precipitation attenuating radiation
(Reducing radiolysis effects)

Radiolysis
(more possible oxidative products)

OH*

$H_2O_2$

$O_2$

$H_2O$

U(VI) chemical dissolution
(Fast)

$\alpha$, β, $\gamma$

β, $\gamma$

$\alpha$, β, $\gamma$

U(IV) chemical dissolution
(Slow)

Small noble metal particles (NMP or ε)
(Supply or consume $e^-$ at rapid rates)

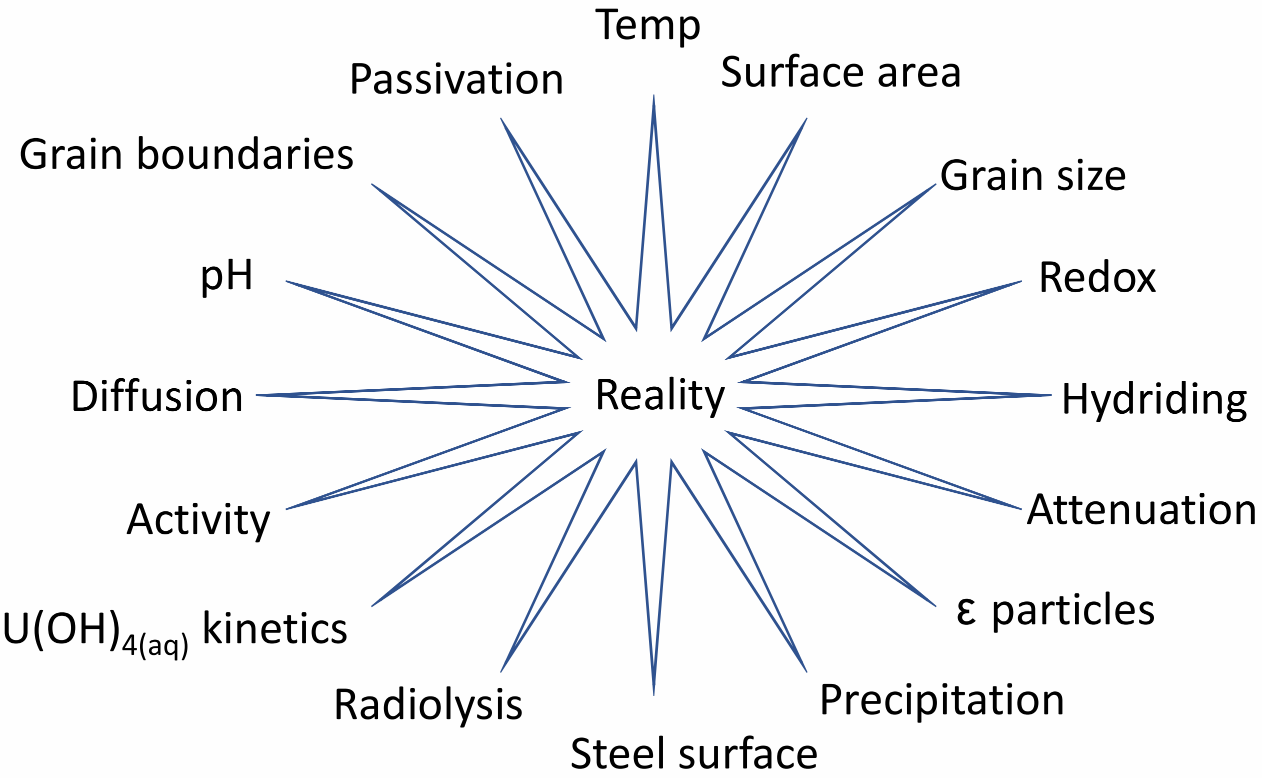
U(IV) oxidation

Precipitation retarding diffusion
(Too and from fuel surface)

Galvanic corrosion of
metal/ceramic coupling

Potential Hydrogen generation
(from corrosion of steel surfaces)

Formed during fission



Temp

Passivation

Surface area

Grain boundaries

Grain size

pH

Redox

Diffusion

Reality

Hydriding

Activity

Attenuation

$U(OH)_{4(aq)}$ kinetics

ε particles

Radiolysis

Precipitation

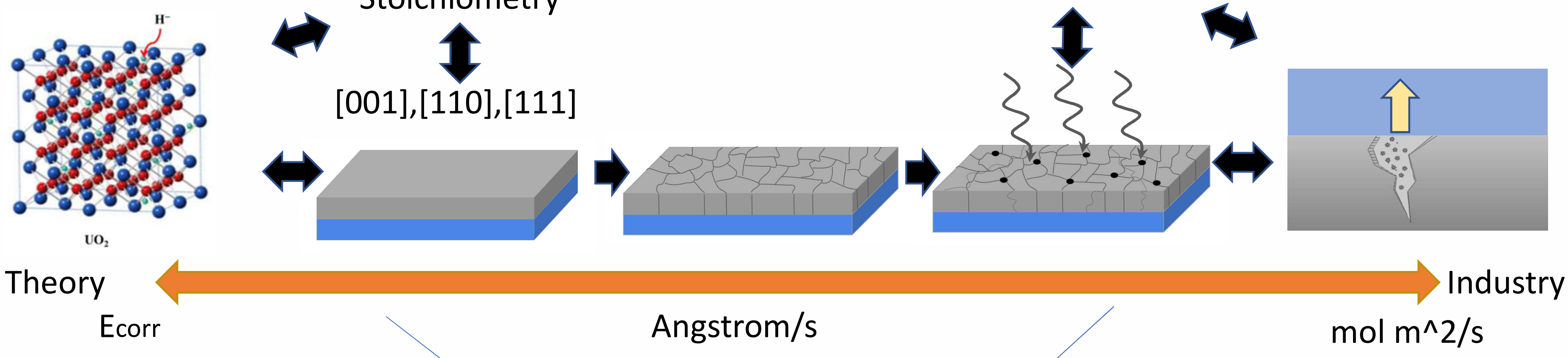
Steel surface

What is our approach?
Simplify sample system - compare with model – add complexity one variable at a time

## DFT

## Thin Films

## Radionuclide release



Reaction kinetics

Stoichiometry

[001],[110],[111]

Microstructural effects

Radiolysis

Chemical reaction and Diffusion

Theory

Industry

Ecorr

Angstrom/s

mol m^2/s

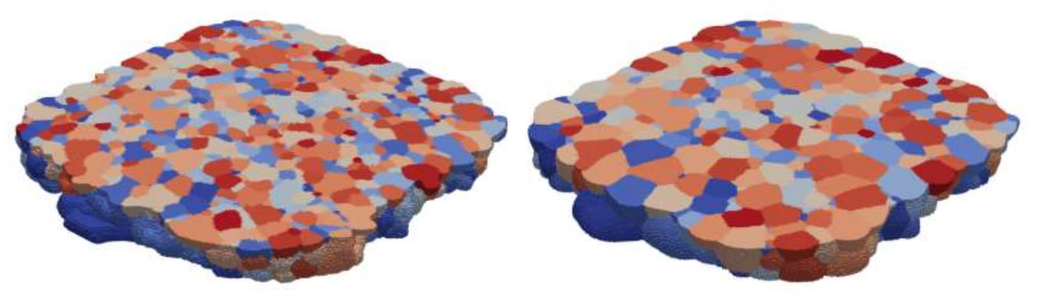
University of BRISTOL

NATIONAL NUCLEAR LABORATORY

How will I model this?

**MOOSE Framework (MARMOT)**
Open source, parallel finite element framework for developing Multiphysics solvers

Use – with the inclusion of mesoscale simulation environment MARMOT modelling of microstructure and material properties under stress, temperature and irradiation damage

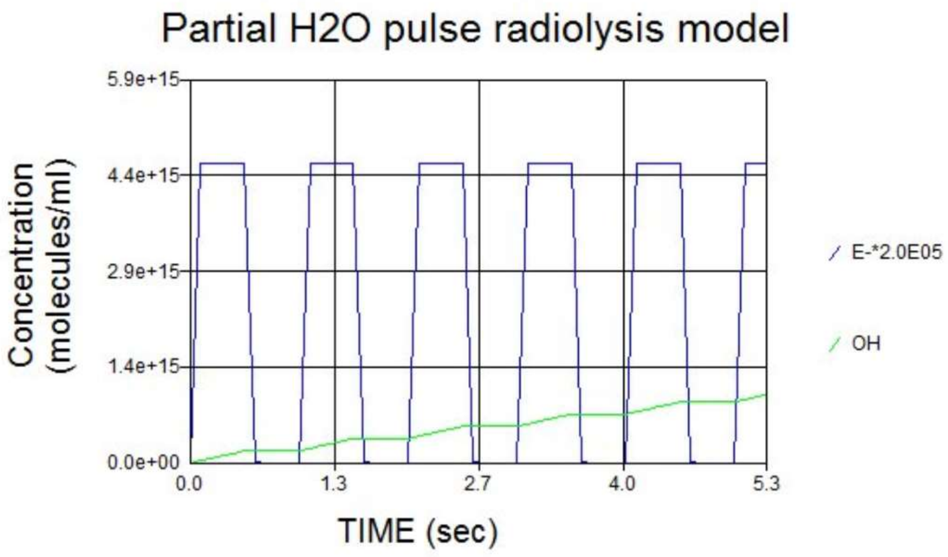


# FACSIMILE

Modelling tool to solve differential equations, specifically for chemical kinetics

Use – Radiolysis and chemical kinetics of dissolution process

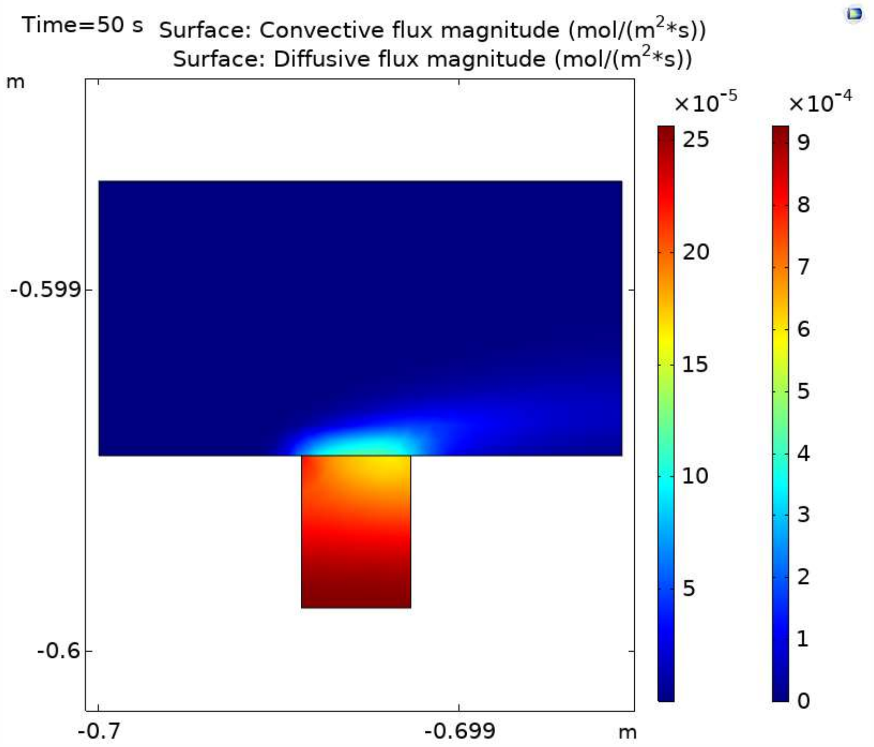
NATIONAL NUCLEAR
LABORATORY

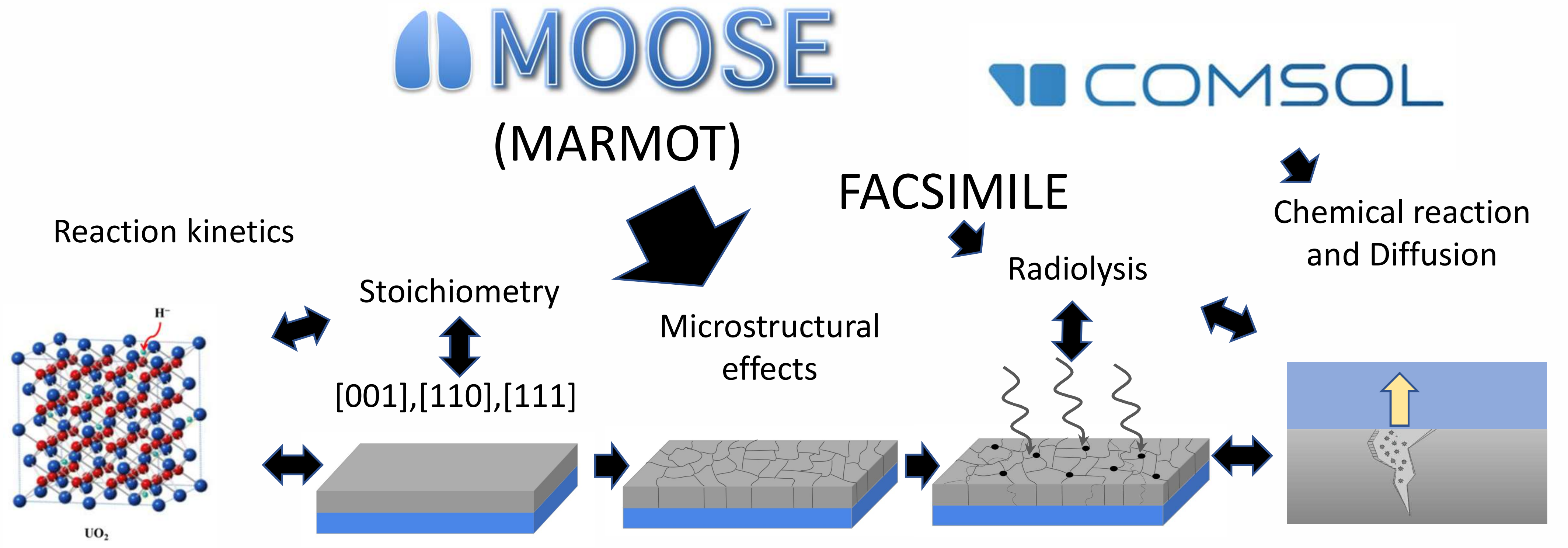


**COMSOL**

Multiphysics simulation software, multiple packages

Use – Multi scale simulation incorporating FACSIMILE and MOOSE





MOOSE

(MARMOT)

COMSOL

FACSIMILE

Reaction kinetics

Stoichiometry

[001],[110],[111]

Microstructural effects

Radiolysis

Chemical reaction and Diffusion

Theory

Ecorr

Angstrom/s

Industry

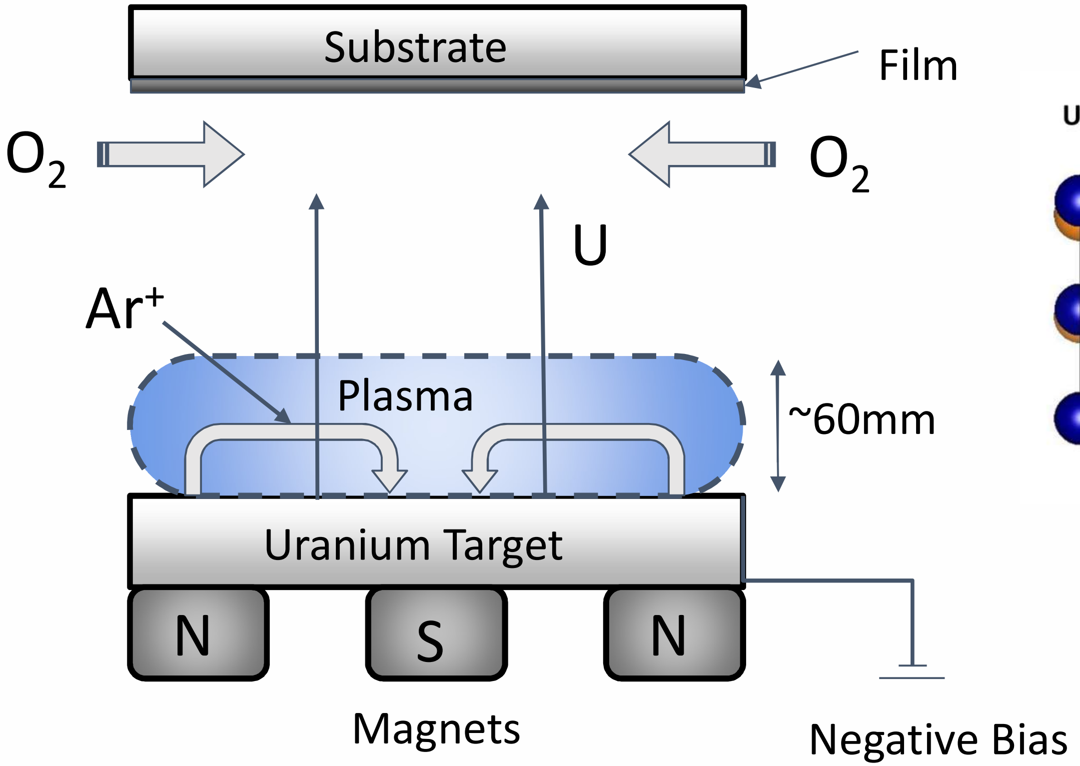
mol m^2/s

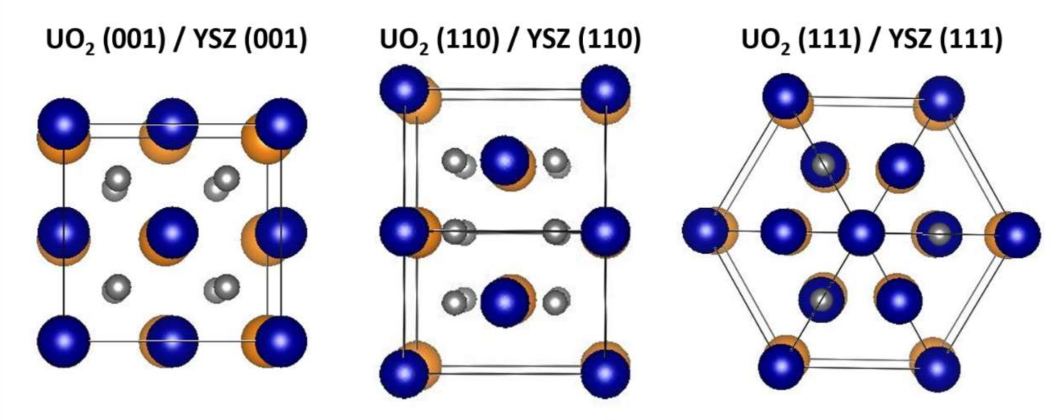
What experiments can be done

University of BRISTOL

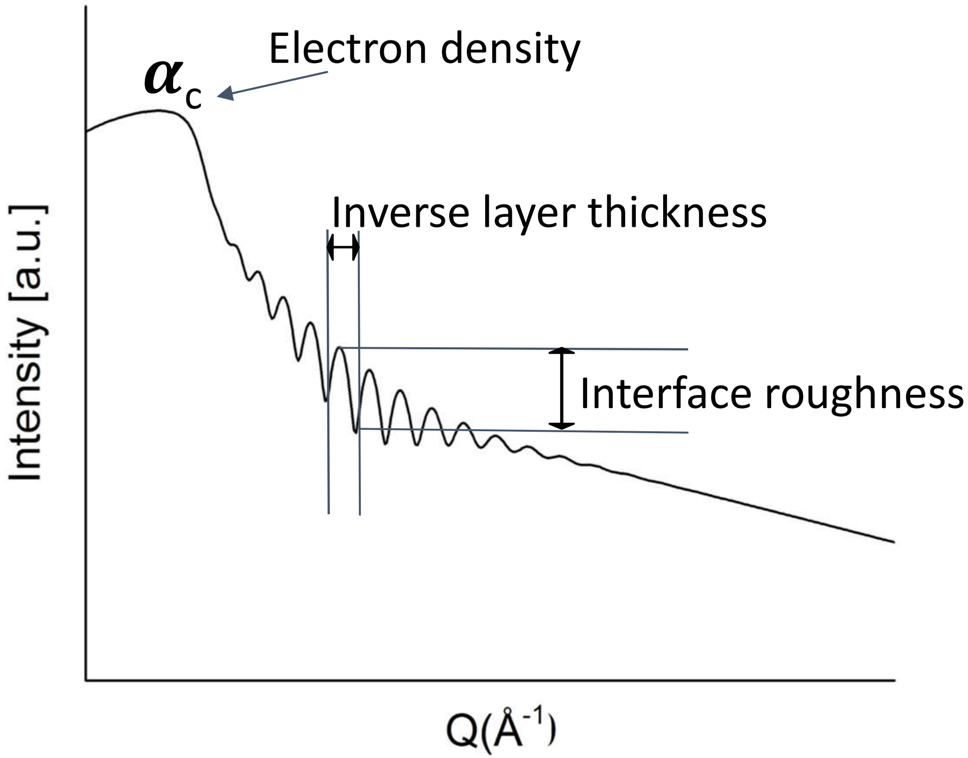
NATIONAL NUCLEAR LABORATORY

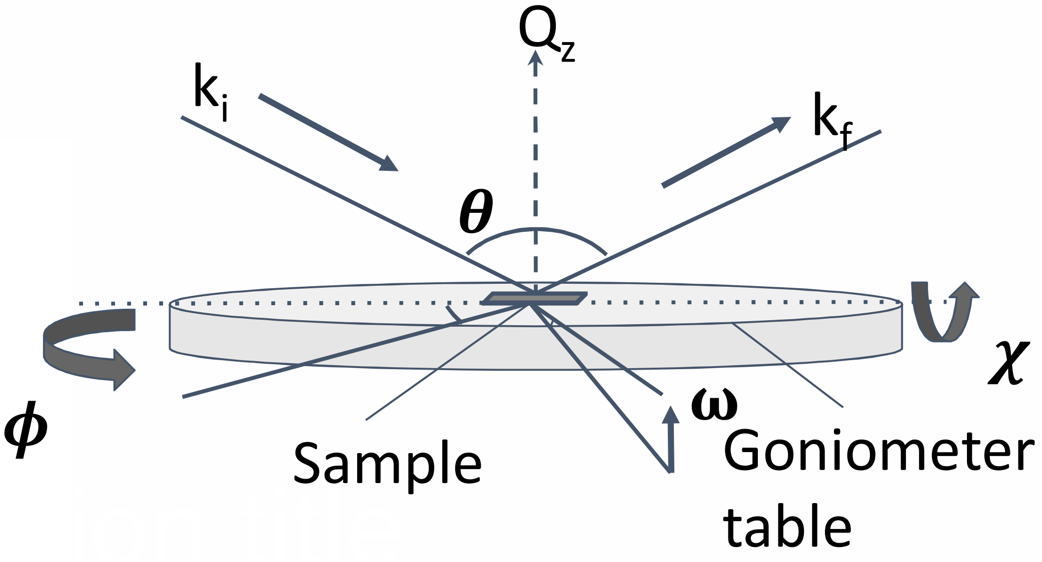
# What are these idealized systems?





Rennie *et al.*, Corrosion Science. **145**, 162-169 (2018).





Reflectivity

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

High angle

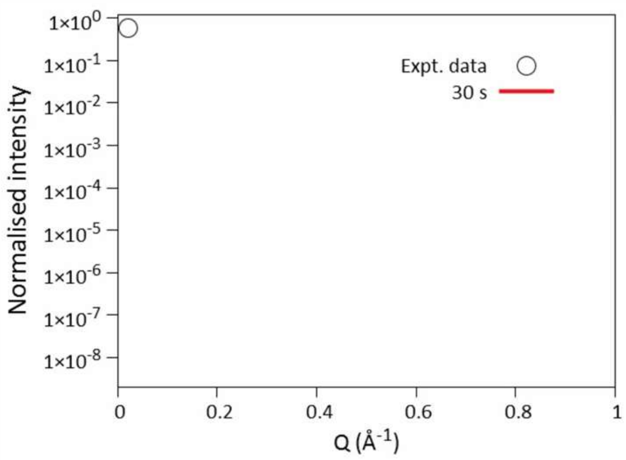
1) number of lattice planes contributing
2) total thickness
3) surface roughness

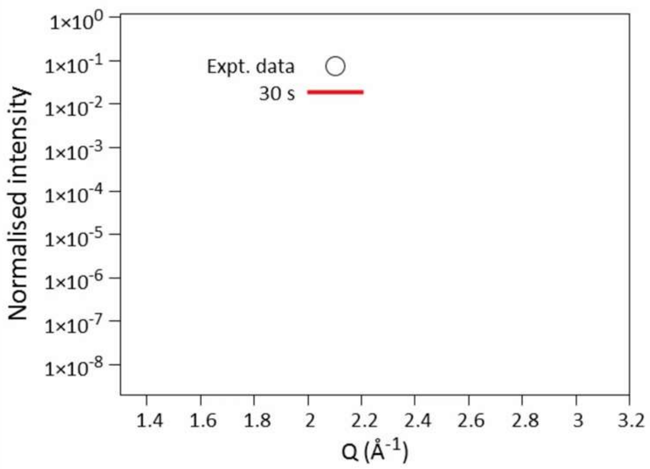
# What can we do with these systems?

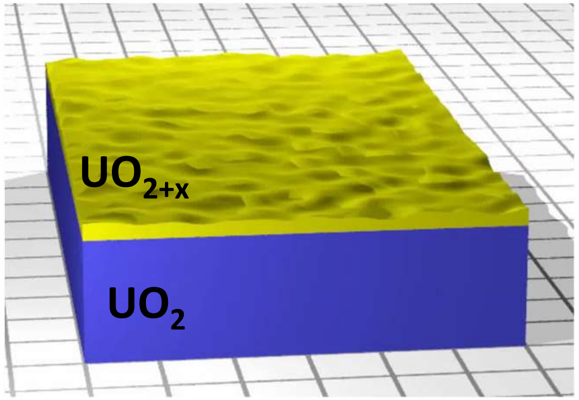
-Radiolysis driven dissolution of $UO_2$

-Radiolytic field from the X-rays themselves (Synchrotron source)

-Could detect changes in oxide composition, roughness and rate of dissolution at the Angstrom level



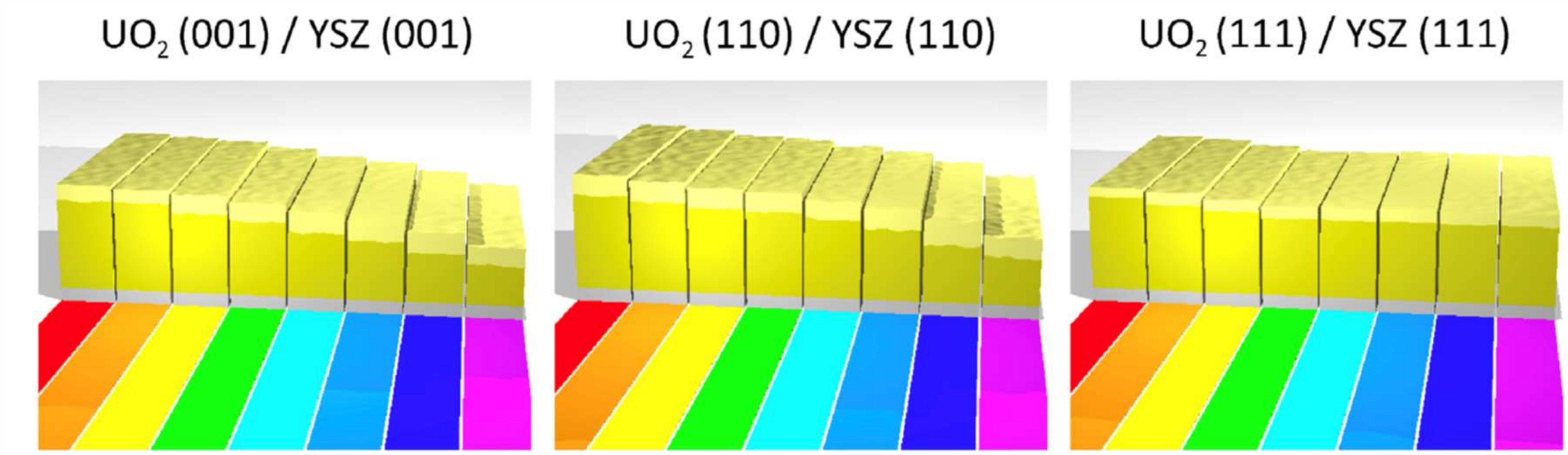




Springell, Rennie *et al.*, Faraday Discuss. **180**, 301 (2015).

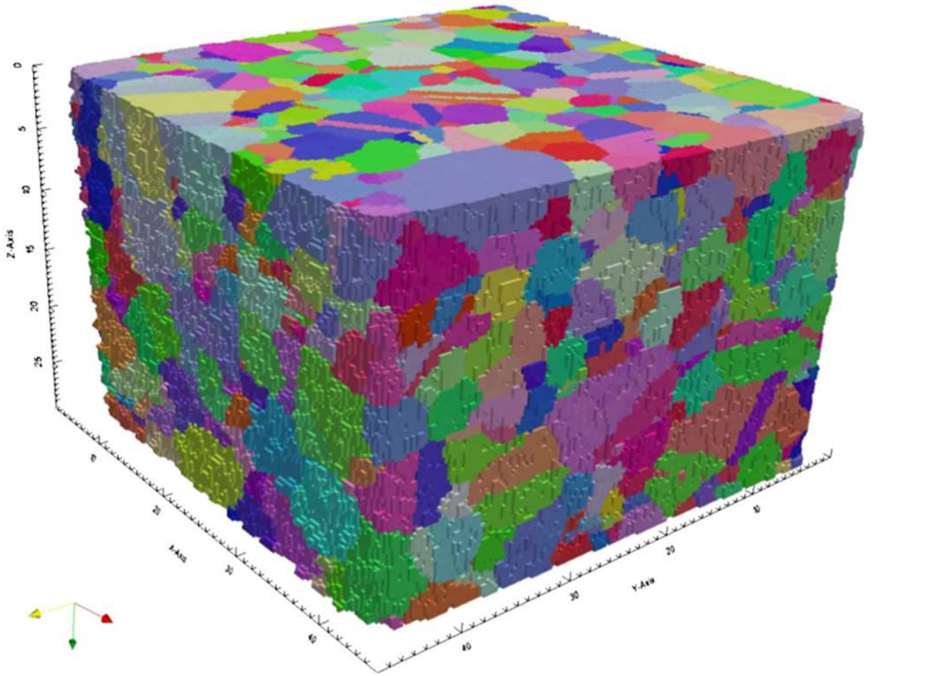
Dependence of dissolution on crystallographic orientation

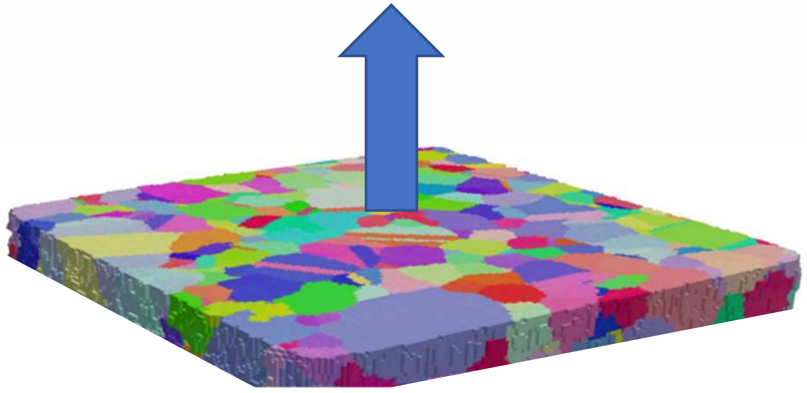
- Repeated previous study with three different high symmetry orientations, [001], [110], and [111] over 270s



Rennie *et al.*, Corrosion Science. **145**, 162-169 (2018).

# Poly-epitaxy: 3D polycrystalline sample of 2D surface

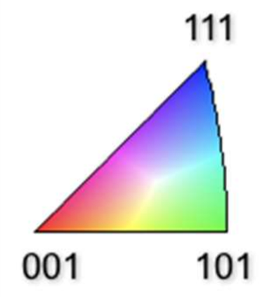


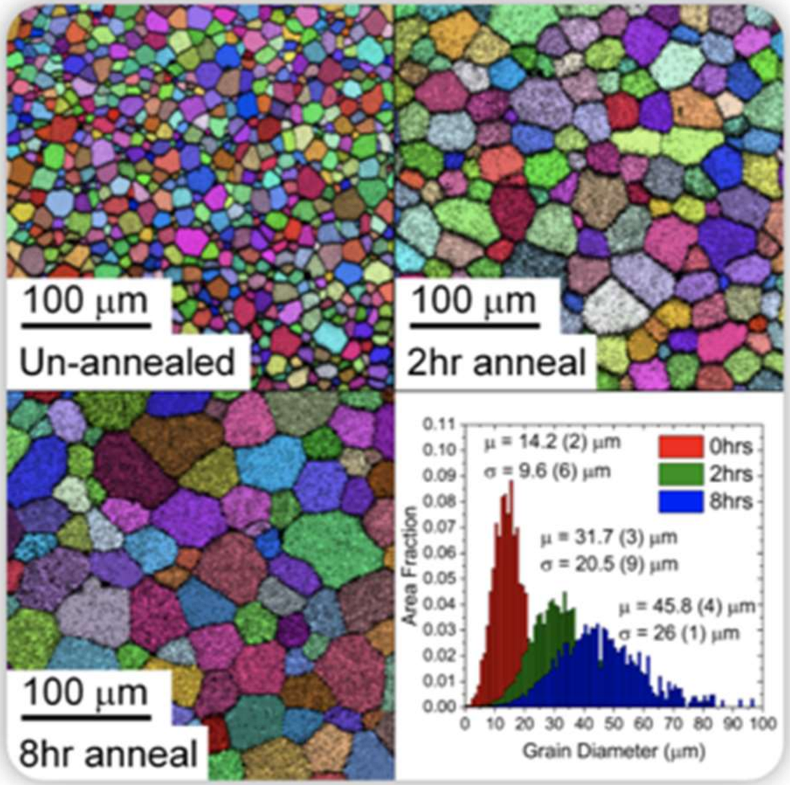


# Grain size and surface area effects

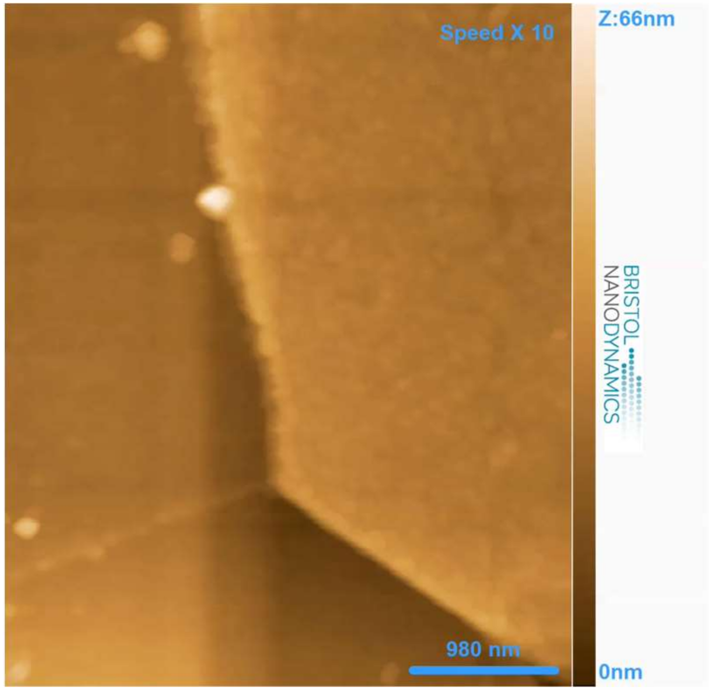
Average fuel grain size is tens of microns

Grain size controllable by annealing

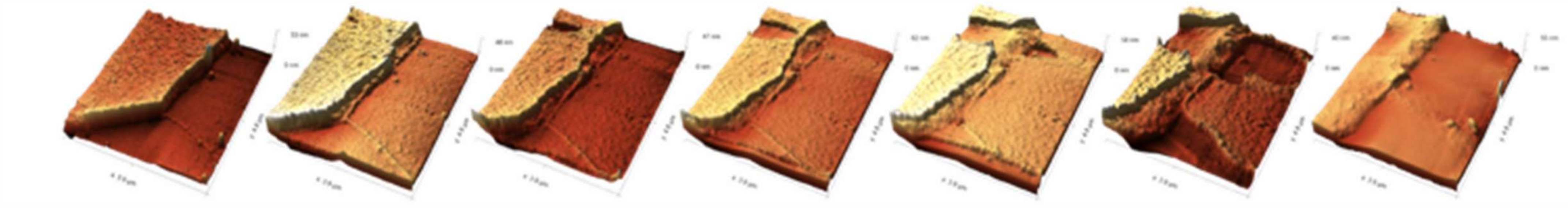




# Poly-epitaxy (in situ High Speed-AFM)



# Poly-epitaxy (in situ High Speed-AFM)

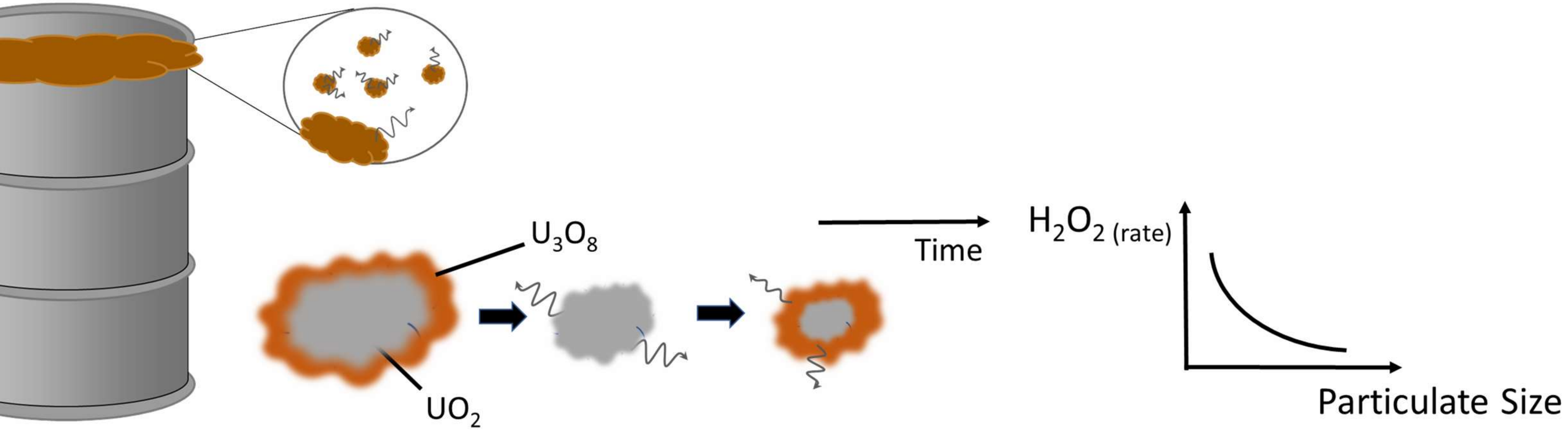


What are the potential applications of this work?

# Surface area effects or suspended particles\sludges from fuel bins in pond storage

Corrosion rates inconsistent

Sellafield Ltd



# Plan for next six months

- Continue developing 1D model in MOOSE, using similar methods to previous literature mostly including work done by NNL

- Incorporate and develop Radiolysis code provided by NNL in FACSIMILE

- Look to model dissolution of $UO_2$ thin films and in line with experimental results

- Begin to consider fuel particle model

# Thank you

as14659@Bristol.ac.uk

# Milli
# Every‸Gram Counts

*Helen Steele*

*Special Nuclear Materials*
*Sellafield Ltd.*

Sellafield Ltd

# Special Nuclear Materials – Plutonium

THORP Reprocessing operations.

MAGNOX Reprocessing Operations.

Mixed Oxide Residues from the MOX manufacturing process.

Historical residues from previous R&D programmes.

Residues recovered from the Decommissioning of redundant Plutonium facilities.

Dounreay un-irradiated material.

# Special Nuclear Materials Sellafield

### Dounreay Exotics Consolidation Programme

*To consolidate all significant stocks of national civil plutonium at Sellafield.*

### Package Integrity Recovery Programme

*Reduce the acute risk presented by degraded packages and maintain long-term safe, secure storage of SNM.*

### First Generation Finishing Line Programme

*Reduce the risk posed by the condition of SNM facilities and infrastructure.*

### Production Operations

*Safe and secure storage of the site's plutonium stocks, whilst continuing to meet the site's Reprocessing programmes.*

### Post Operational Clean Out

*To POCO and decommission SNM Facilities.*

### Alpha Skills

*Retain Alpha Skills capability ahead of a government decision on bulk plutonium disposition.*

# Sellafield Ltd Value Streams

Corporate strategy

Transforming Sellafield

| | |
|---|---|
| Retrievals | The reduction of high hazard from legacy facilities |
| Remediation | The clean up of the Sellafield site |
| Spent Fuel Management | The receipt, reprocessing and storage of spent nuclear fuel |
| Special Nuclear Materials | The safe, secure storage of special nuclear materials |

# THORP Plutonium

Produced since 1994

Oxide material is high burnup

Stainless steel packages

Higher heat output, 60 – 160 watts per package

Most packages 85 watts when aged

# Magnox Plutonium

Produced since 1975

Product placed in a screw top aluminium can

Packaged into stainless steel outer can and welded

Magnox fuel is low burn-up

Low power, 10 – 80 watts per can

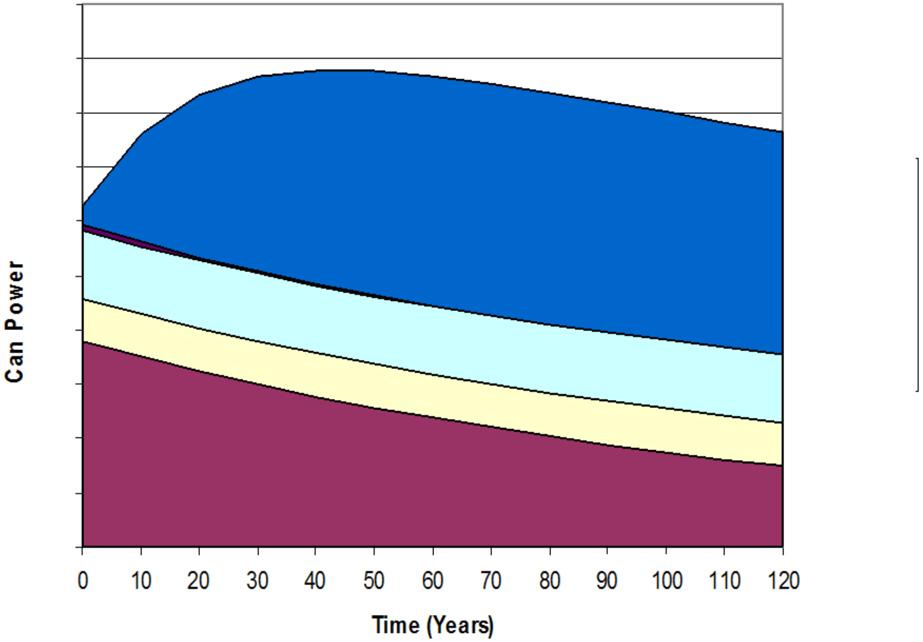
# Potential for Package Pressurisation

Magnox and Thorp material, sealed following calcination under inert atmospheres

Self-heating

Main concerns:

1. Water desorption
2. Water radiolysis (head gas)
3. Helium gas production (alpha)



# Behaviour of Water on Fresh $PuO_2$ – Sealed System

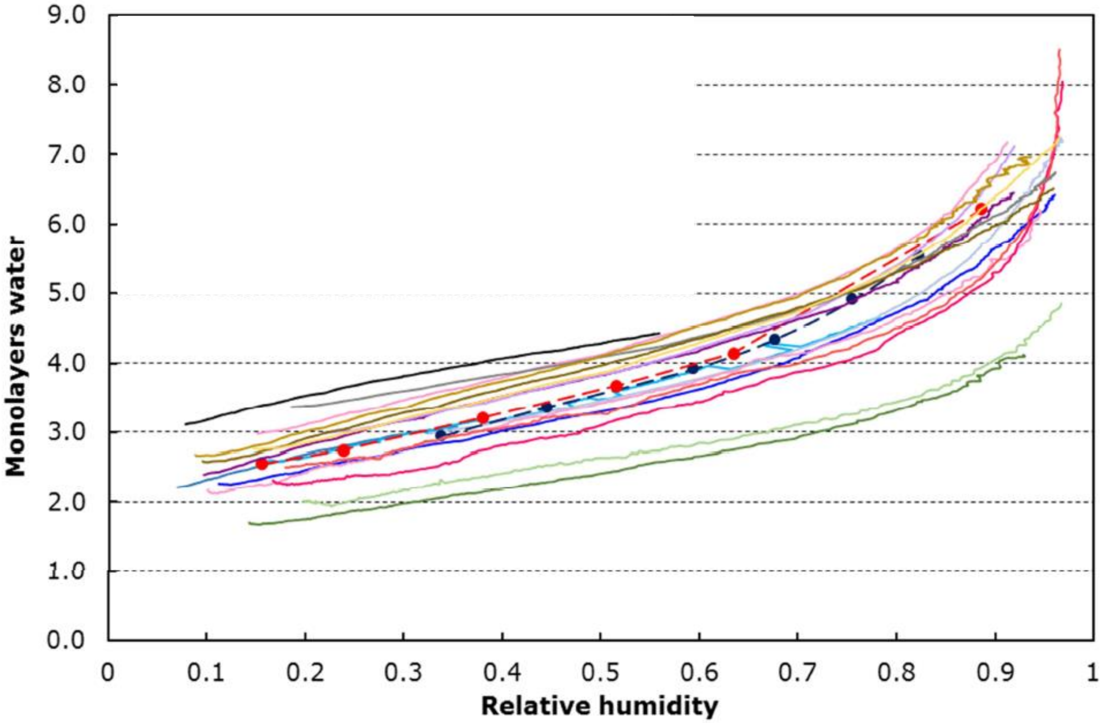
$PuO_2$ is hygroscopic.

Measured
LOH or Pu:H ~0.2-0.5 wt%

Two modes of interaction:
- Physisorbed
- Chemisorbed

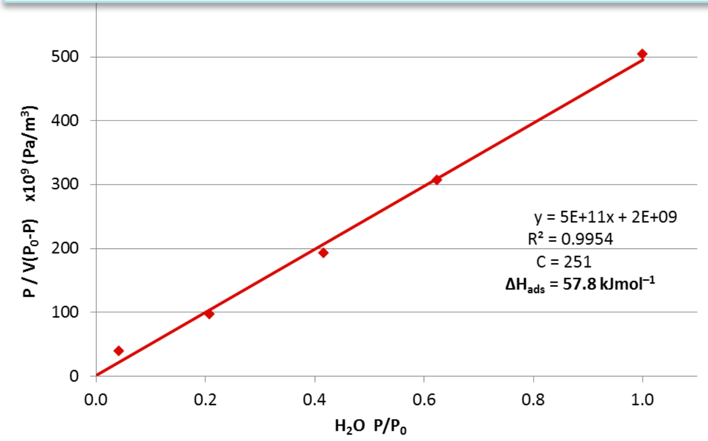
Questions

How much can be adsorbed?
How is it partitioned?



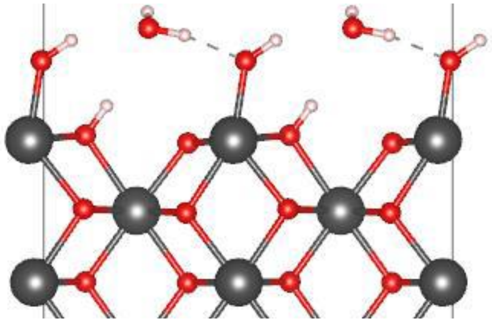
Monolayers of water on the $PuO_2$ surface as a function of relative humidity for a range of $PuO_2$ sources (NNL)

## Dominic Laventine (University of Lancaster)

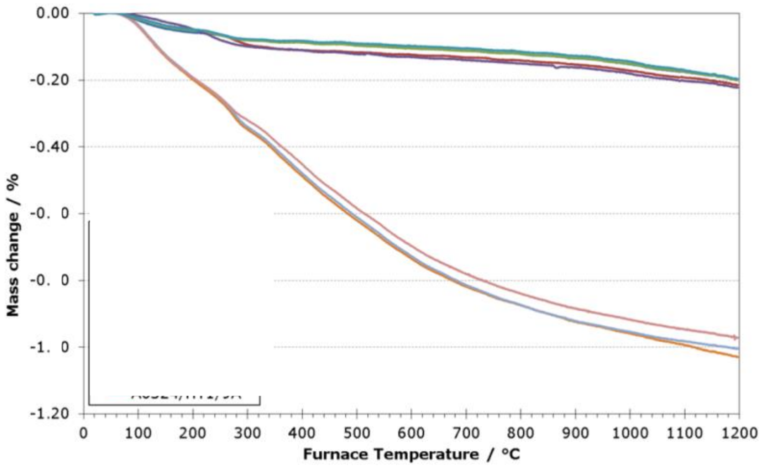


Adsorption of water on $CeO_2$ measured using Ceria films on $GaPO_4$ crystals.

Energy of adsorption of water molecule in the 2nd layer ~-50kJ mol



## Bengt Tegner (University of Manchester)



## Greater understanding of partitioning of water

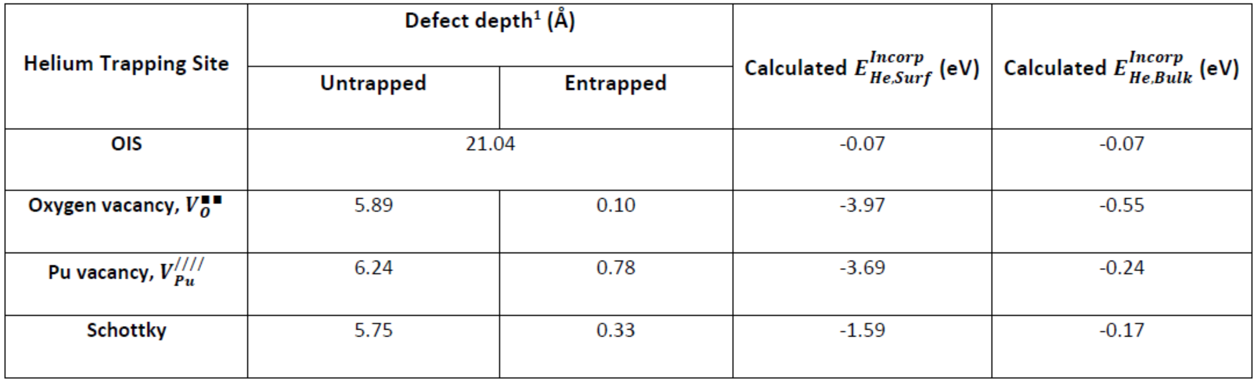
- Radiolysis,
- Predicting potential pressurisation behaviour more accurately
- Fine tune criteria for safe acceptance

Sellafield Ltd

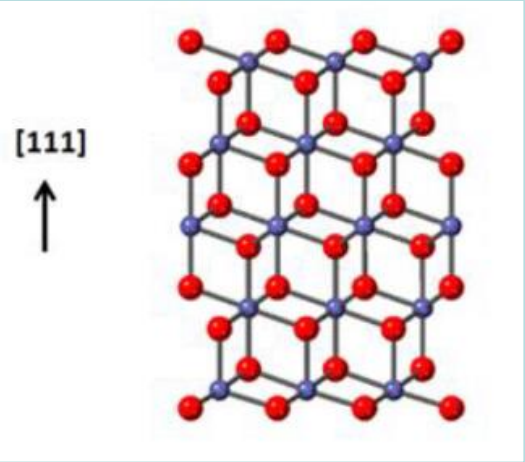
# Helium

| Storage duration / years | He mole fraction / ppm | Helium release fraction / % |
|---|---|---|
| 2.81 | 711 | 25.3 |
| 0.42 | 21.9 | 5.2 |
| 2.81 | 581 | 21.9 |
| 0.42 | 22.2 | 5.3 |

Measurements from stored small samples (NNL)



| Helium Trapping Site | Defect depth[1] (Å) |  | Calculated $E^{Incorp}_{He,Surf}$ (eV) | Calculated $E^{Incorp}_{He,Bulk}$ (eV) |
|---|---|---|---|---|
|  | Untrapped | Entrapped |  |  |
| OIS | 21.04 |  | -0.07 | -0.07 |
| Oxygen vacancy, $V_O^{\bullet\bullet}$ | 5.89 | 0.10 | -3.97 | -0.55 |
| Pu vacancy, $V_{Pu}^{''''}$ | 6.24 | 0.78 | -3.69 | -0.24 |
| Schottky | 5.75 | 0.33 | -1.59 | -0.17 |



Calculated surface segregation energies Nathan Palmer University of Birmingham

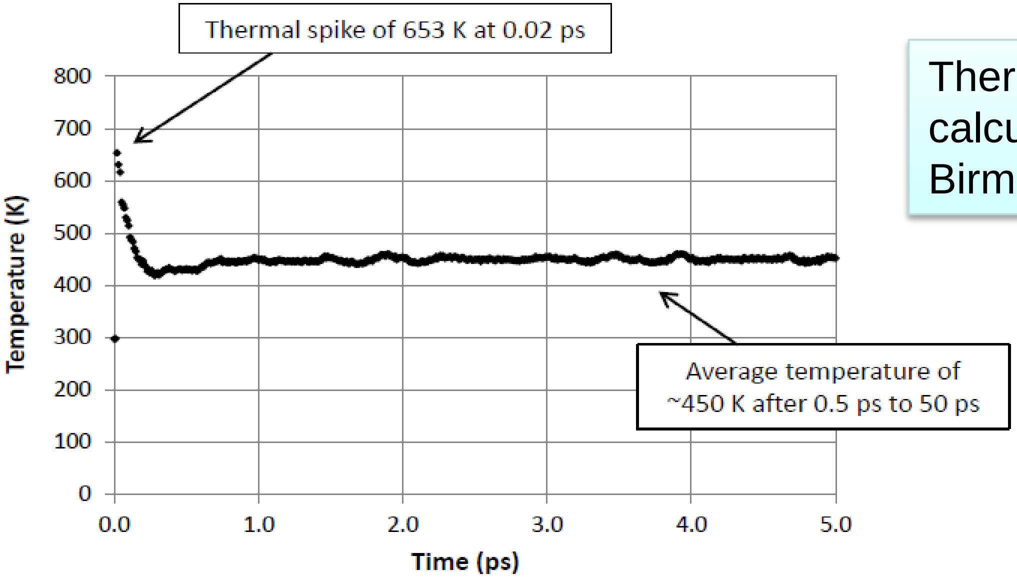
# Gas analysis following can puncturing of gas-tight Magnox packages (NNL)

| **Separation date** | | | | | | **SSA of recovered powder ($m^2/g$)** | **He release fraction (%)** | **Crystallite size (nm)** |
|---|---|---|---|---|---|---|---|---|
| | | **He** | **$N_2$** | **Ar** | **$N_2O$** | | | |
| **1975** | Air | 61.2 | 28.8 | 10.0 | 0.037 | 2.24 | 79 | 15 |
| **1979** | Air/Argon | 52.3 | 1.25 | 46.3 | ND | 2.56 | 68 | 17 |
| **1982** | Air/Argon | 14.8 | 47.5 | 37.8 | 0.032 | 2.51 | 26 | 53 |
| **2002** | Air/Argon | 29.4 | 61.6 | 9.05 | 0.027 | 4.70 | 68 | 18 |
| **2002** | Air/Argon | 28.3 | 57.6 | 14.1 | 0.005 | 5.50 | 57 | 19 |

Packages not pressurised at the time of opening

Mathematically there should be more evidence of package pressurisation. What might change that?

# Ongoing work: PhD at University of Lancaster Samantha O'Sullivan

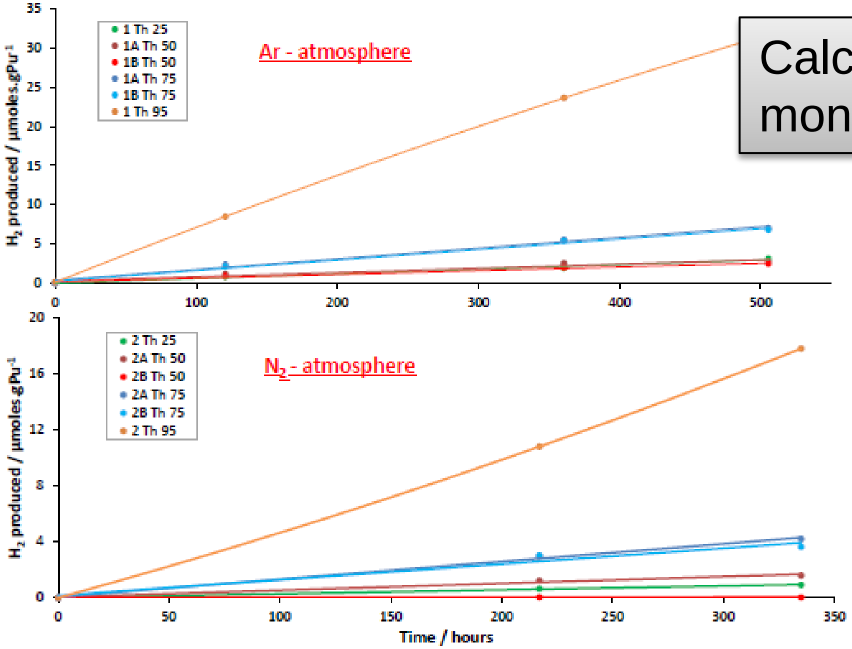


Thermal spike as a result of the recoil atom calculated by Nathan Palmer University of Birmingham

Pursuing He desorption from $PuO_2$ samples at ITU!

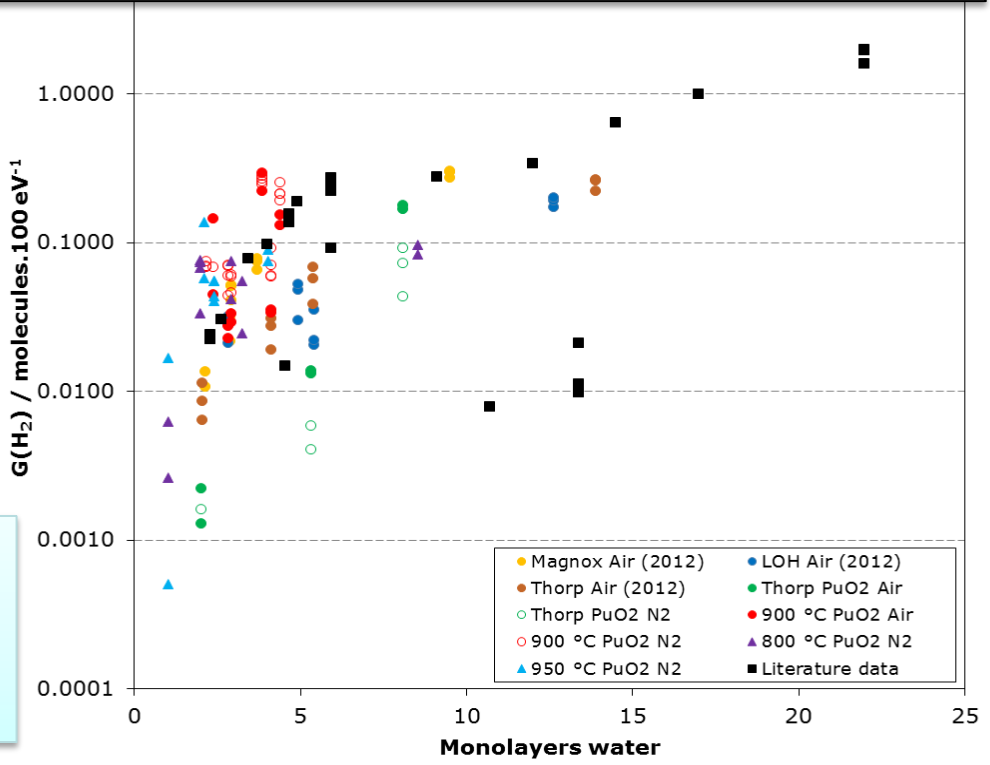
# Radiolysis of Adsorbed Waters

- Need to understand potential maximum rates and dependencies
- Wide spread pressurisation from radiolysis not observed



Measured $H_2$ production for a range of relative humidities
Luke Jones University of Manchester DCF / NNL

Calculated G-values as a function of water monolayer coverage (NNL)



# Summary – so far

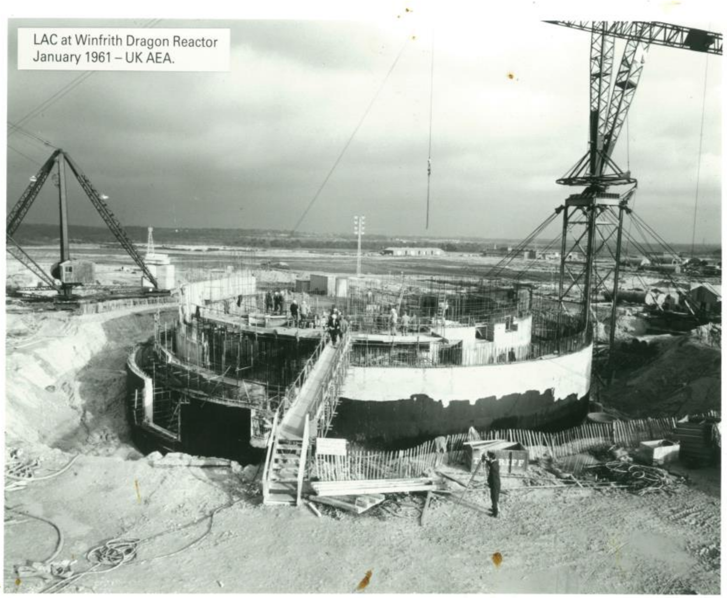
- Good progress in characterising water on production $PuO_2$
- More questions than answers with respect to head gas evolution and helium (more to come)
- Improved understanding of radiolysis

# Residues

- Historical residues from previous R&D programmes.
- Residues recovered from the Decommissioning of redundant Plutonium facilities.
- Dounreay un-irradiated material
- In terms of mass ~1% of total inventory
- In terms of number of packages ~10%
- In terms of technical difficulties XX%
- In terms of unknowns YYY%

# Consolidation

- Large degree of uncertainty in material chemical and physical form and power



LAC at Winfrith Dragon Reactor
January 1961 – UK AEA.

# Residues

Cermets

Spheres

Powders

$PuO_2$ /$UO_2$ /SiC

Pu metal/swarf

Pellets

Plates

Pu alloys

$UO_2$

$PuO_2$

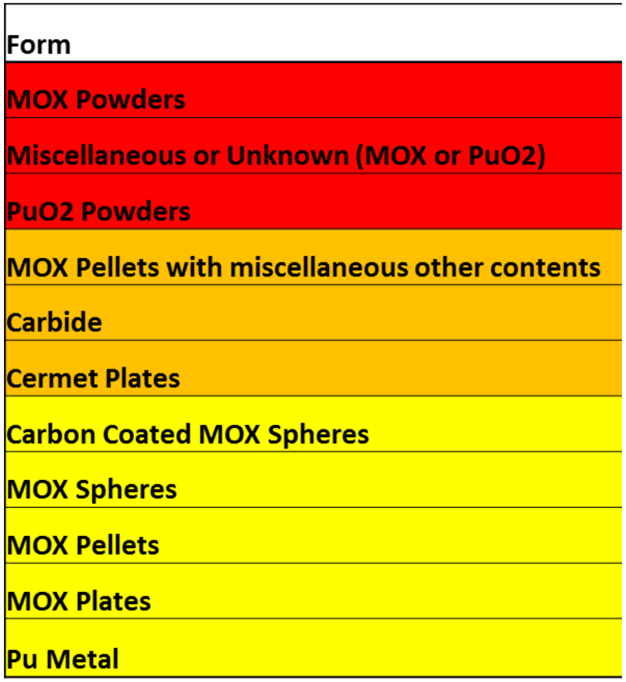
PuU$O_2$

PuUC

PuUN

$Pu_xC_y$

$PuO_2$ /SiC



| Form |
|---|
| MOX Powders |
| Miscellaneous or Unknown (MOX or PuO2) |
| PuO2 Powders |
| MOX Pellets with miscellaneous other contents |
| Carbide |
| Cermet Plates |
| Carbon Coated MOX Spheres |
| MOX Spheres |
| MOX Pellets |
| MOX Plates |
| Pu Metal |

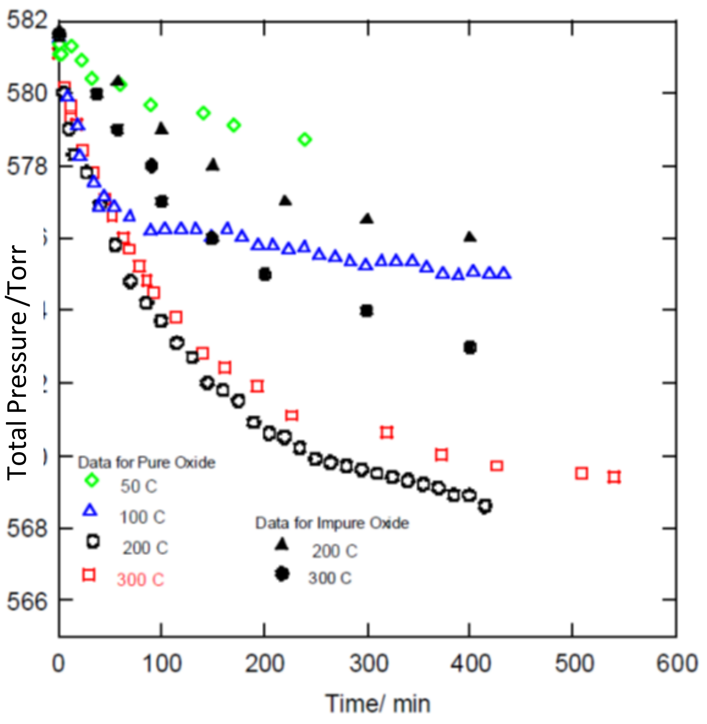
- Require a bounding and generic safety case
- A case of the unknown unknown acknowledging uncertainty

# MOX (*pellets and powders)*

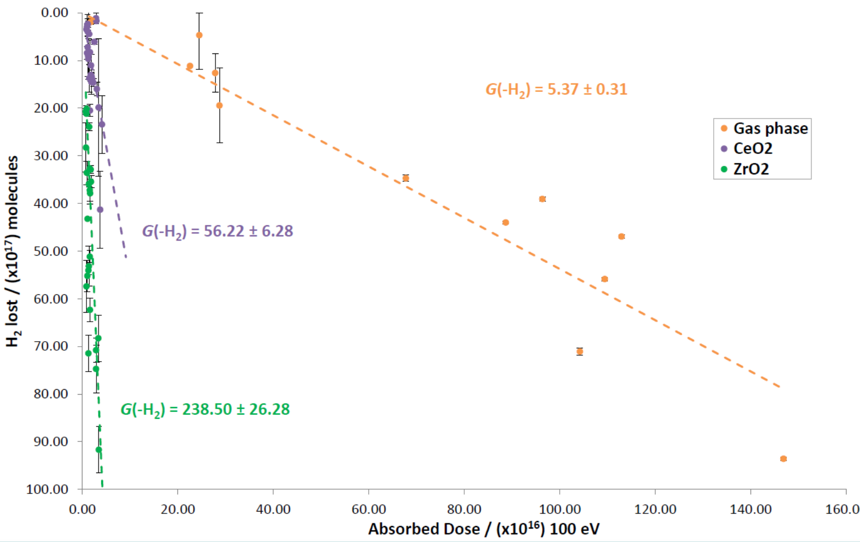
- Primarily sintered low surface area pelleted material
- “filling in the gaps”
- Always some uncertainty
- Historical knowledge
- Known not to generate $H_2$

# Recombination ($H_2$ & $O_2$) - Flammable Atmosphere

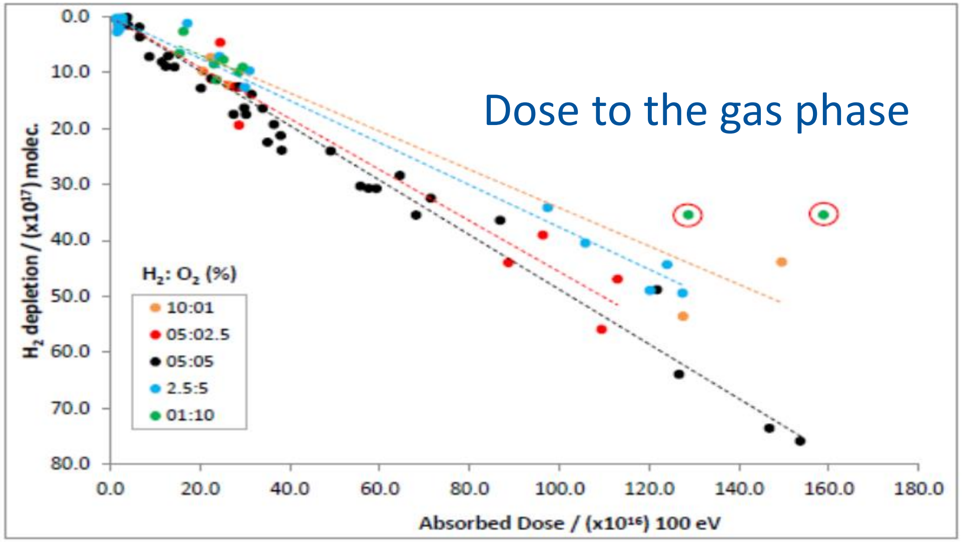
## Surface and radiation Catalysed



Pressure-Time curves for 2% $H_2$/air mixture in the presence of both pure and impure plutonium oxide surfaces, for each temperature studied (US-DOE)



Radiation and surface catalysed recombination of $H_2$ and $O_2$ Luke Jones University of Manchester (DCF)

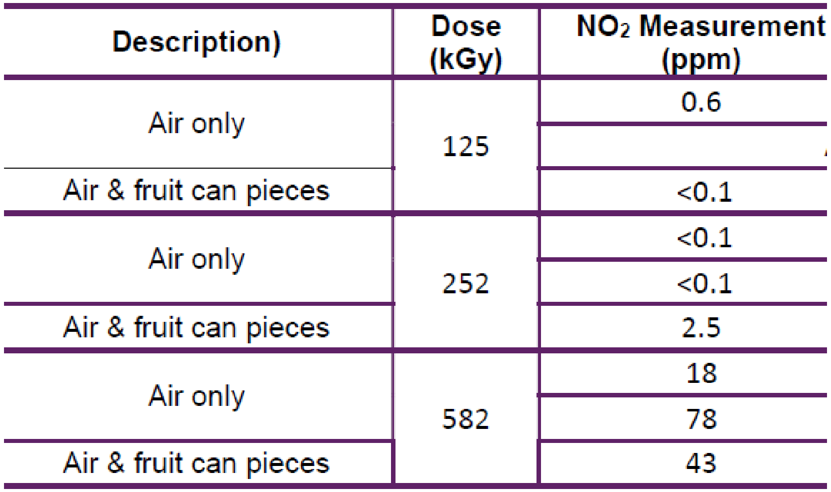


Dose to the gas phase

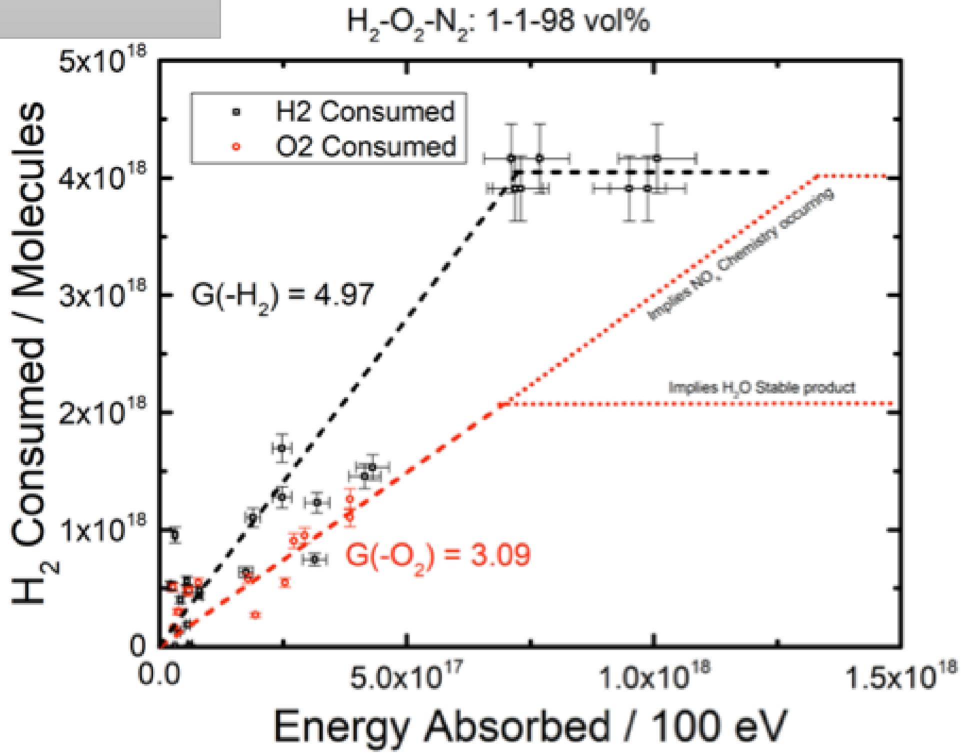
# Potential for a flammable atmosphere

- Some packages with $H_2$ enriched atmospheres
- In the process of understanding recombination in air
- R&D significant portion sealed in air

Measurement of NOx species preliminary results by Wood



| Description) | Dose (kGy) | $NO_2$ Measurement (ppm) |
|---|---|---|
| Air only | 125 | 0.6 |
| | | |
| Air & fruit can pieces | | <0.1 |
| Air only | 252 | <0.1 |
| | | <0.1 |
| Air & fruit can pieces | | 2.5 |
| Air only | 582 | 18 |
| | | 78 |
| Air & fruit can pieces | | 43 |

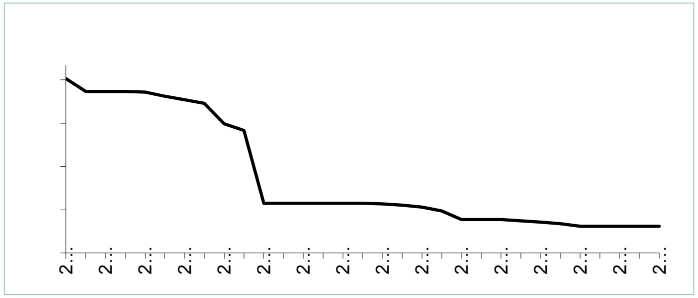


Dose catalysed recombination of $O_2$ and $N_2$
Darryl Messer University of Manchester (DCF)

# Science in support of risk reduction

Gas tight packages cannot maintain a flammable atmosphere ($O_2$ and $H_2$ >LFL)

- $H_2$ and $O_2$ will not have been generated.
  - During storage water susceptible to radiolysis will decrease.
- Any $H_2$ and $O_2$ present will re-combine rapidly
  - Recombination of $H_2$ and $O_2$ over hot $PuO_2$ is very fast.
  - $PuO_2$ powder centerline temperatures high enough to drive off water rapidly.
  - $PuO_2$ surfaces at 24°C have been shown to prevent the net co-production of $O_2$ and $H_2$
  - Recombination of $H_2$ and $O_2$ over hot stainless steel is rapid.
  - Depletion of $H_2$ and $O_2$ has been demonstrated to be catalysed by stainless steel surfaces
  - Recombination of $N_2$ and $O_2$ maybe catalysed by Sn surfaces
  - Recombination of $H_2$ and $O_2$ catalysed by adsorbed alpha dose to the gas phase
  - Recombination of $N_2$ and $O_2$ catalysed by adsorbed alpha dose
- $O_2$ gas is preferentially adsorbed on $PuO_2$ surfaces.
- No SL or DOE sealed packages (~130) have opened have contained flammable atmospheres.



# Residues (a few more)

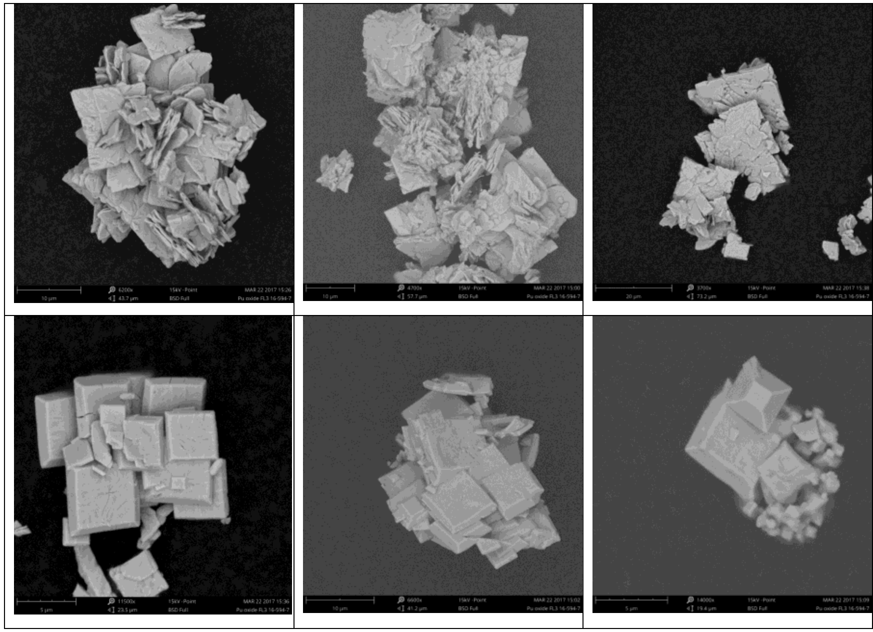
- MOX and $UO_2$ powders
- Oxidation of Fruit tin
- Radiolysis of air and subsequent adsorption ($N_2O$ and $NO_3$-) ?
- $O_2$ sequestering bagging material
- Organics …..

# Summary (Today)

- Case made for **No flammable atmospheres** within sealed SNM packages
- Significant cost savings
- Feed into the safety case for the emptying of legacy stores
- Risk reduction
- Demonstrable use of data from Distinctive

# Corrosion and Pu Ageing – Future

Notable fraction of the total $PuO_2$ inventory is contaminated with Cl from PVC bagging material

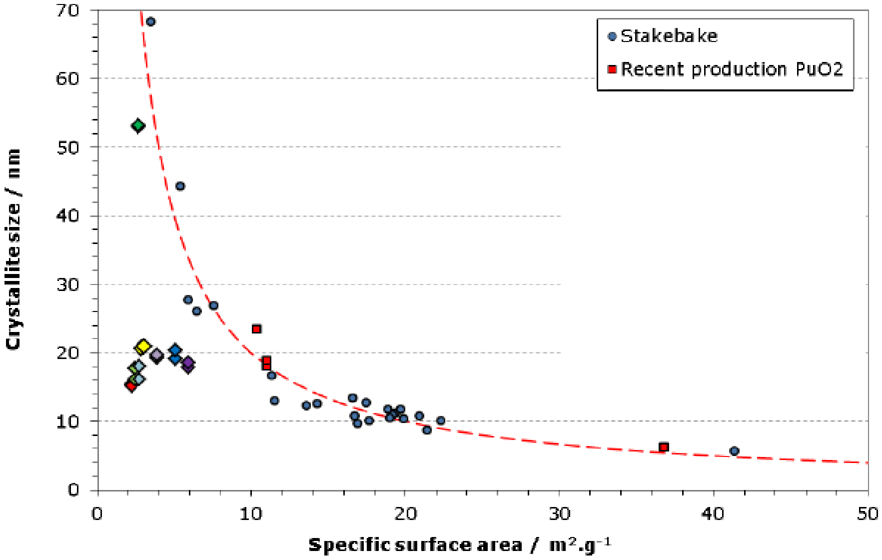


Thermal desorption of Cl from Cl contaminated $PuO_2$ Sophie Sutherland-Harper University of Manchester and NNL

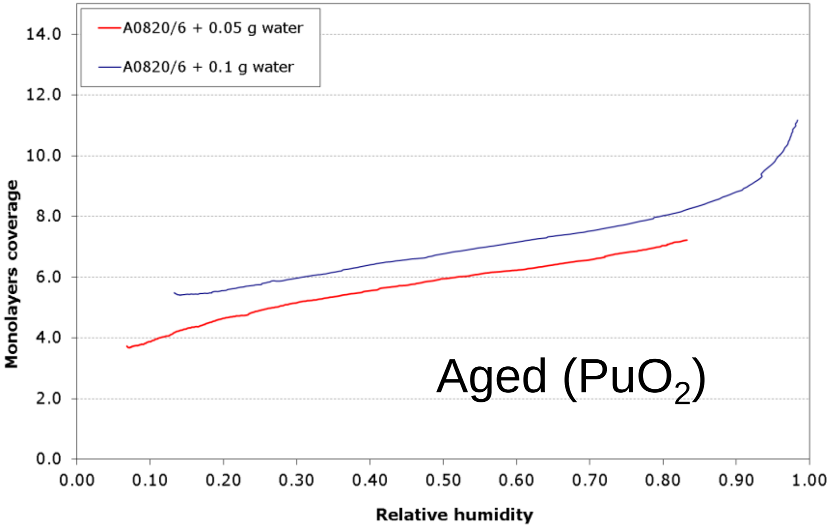
Sellafield Ltd

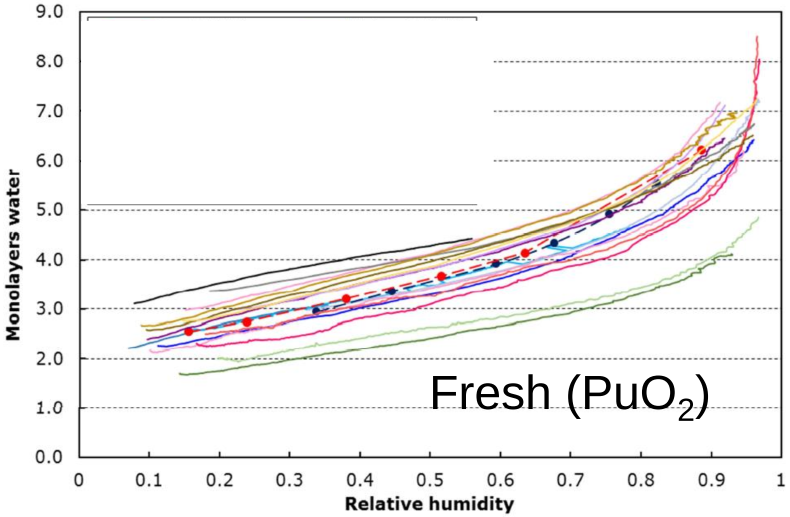
# Pu Ageing – Future

Opening of 30-40 yr old sealed Magnox packages at NNL



Comparison between recent production PuO$_2$, literature values and long stored material (NNL)





# The Future - SPRS Retreatment Plant (SRP)

SRP to repackage all material and heat treat (if required) to allow long term storage in SPRS

Into new pressure tolerant package (100 yr package)

Major new build project

Forecast to be actively commissioned in 2025

# Alpha Skills

To maintain UK alpha skills capability

Retain Alpha skills where appropriate to maintain future options

To support development of UK civil Pu disposition strategy

# Summary - Future

Great alignment in DISTINCTIVE resulting in demonstrable progress….. still plenty of questions to answer:

Susceptibility pressurisation from He

Understanding $PuO_2$ ageing during storage

Consequences of aged $PuO_2$ (1) Onward Storage (2) Future Disposition

Sellafield Ltd

# Special Nuclear Materials

***Vision:***

***To be the UK Centre of Excellence for the Management of Special Nuclear Materials.***

***Mission:***

***Safely and Securely – Reducing the Risk, Managing the Hazard, Creating Future Solutions.***

To reduce the acute risk presented by degraded packages.

To maintain sufficient space in modern standard stores to support reprocessing and risk reduction .

To reduce the risk by consolidating Pu and Pu residues held at Sellafield in modern stores .

To support the development of the UK civil Pu disposition strategy.

To reduce the risk posed by the condition of SNM facilities and infrastructure.

To consolidate all significant stocks of national civil Pu at Sellafield.

To operate the finishing lines to enable completion of reprocessing.

To POCO and decommission SNM facilities.

To maintain long term safe, secure storage of packages.

To maintain UK alpha skills capability.

# Acknowledgements

- DISTINCTIVE
- University of Manchester
- University of Lancaster
- University of Birmingham
- NNL (Robin Orr and Robin Taylor)
- Wood
- Sellafield Ltd (Jeff Hobbs)

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

# Projects in Theme 4: Nuclear Materials

Professor Colin Boxall, Lancaster University

2nd Industry Roadshow

14th January 2019
Mercure Holland House Hotel & Spa, Bristol

Energy
For a Low Carbon Future

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

# Projects in Theme 4: Nuclear Materials

## Theme Leads: Colin Boxall and Nik Kaltsoyannis

Lancaster University

MANCHESTER 1824
The University of Manchester

UNIVERSITY OF BIRMINGHAM

The University Of Sheffield.

EPSRC
Engineering and Physical Sciences Research Council

Sellafield Ltd

NATIONAL NUCLEAR LABORATORY

Radioactive Waste Management

NDA
Nuclear Decommissioning Authority

# Introduction, Aims & Objectives, Work Packages

The UK's civil inventory of nuclear materials contains significant stocks of separated Pu, from the reprocessing of Magnox and AGR spent fuels.

Options for the eventual 138.4 tonnes of separated Pu include: (i) re-use as heterogeneous Mixed Oxide (MOX) fuel; (ii) long term interim storage; (iii) direct disposal to a GDF. Whilst (i) is currently the NDA's favoured option, 5% of the stockpile is not suitable for re-use and is recommended for direct disposal.

The UK does not currently have a GDF, and it will take at least 15 years to implement re-use, so the UK's Pu must be kept in its current state for a significant period; *i.e.* as $PuO_2$ powder in interim storage canisters at Sellafield.

**Aim**. To provide scientific and technical underpinning to the ongoing development of options for the UK's stockpile of separated Pu.

**Objectives**.

- **Interim Storage:** To understand how the surface structure and properties of pristine and radiation damaged $PuO_2$ change with time in the absence and presence of water contaminant.
- **Disposition:** To understand the mechanisms of incorporation of Pu into ceramic and glass-ceramic wasteforms, and to understand the effect of self-induced radiation damage on such wasteforms

**WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage**

⇒

**WP4.2: Plutonium Immobilisation in Advanced Ceramic Wasteforms**

# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

Interim storage of $PuO_2$ involves sealing in inert, multi-layer steel canisters. Inside some of these canisters gas has been accumulating, potentially leading to the build-up of pressure.

Several routes to gas production have been suggested, including:

(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 to produce $H_2$;

(v) $H_2$ generation by chemical reaction of $PuO_2$ with $H_2O$, producing a postulated $PuO_{2+x}$ phase – essentially a corrosion reaction.

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

Approximately 5% of the $PuO_2$ is contaminated with chloride, as a result of thermal degradation of intermediate PVC liners, releasing HCl gas. Adsorption of HCl on to the $PuO_2$ powder surface has consequently occurred.

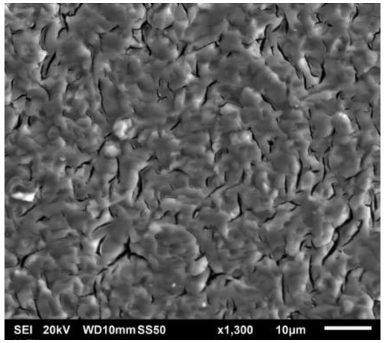
# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

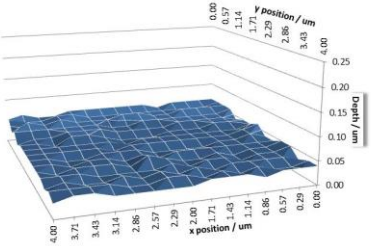
**PDRA project (EPSRC): “Fundamental Surface Chemistry of $PuO_2$” Dom Laventine**

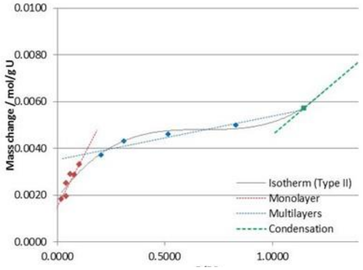
State & amount of water sorbed at the surface (**surface wettability**) is determined by crystal faces and radiation damage at the surface. The latter will also affect $PuO_2$ **corrosion susceptibility** and so mechanism (v) – as will the bulk defect structure.

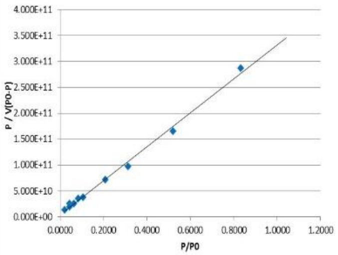
- Pre-DISTINCTIVE, we developed a contact angle technique for measuring metal oxide surface wettability and thus OH group concentration.[1]
- Work in DISTINCTIVE focussed on nanogravimetric measurement of total $H_2O$ sorption on **pristine single element** $CeO_2$, $UO_2$ and $ThO_2$ [2] and**, imminently, $PuO_2$ in Central Lab**.
- Preliminary studies of $PuO_2$ electrochemistry at JRC Karlsruhe indicates that $PuO_2$ may be oxidised as predicted by calculations conducted by NiK Kaltsoyannis. Work at CEA indicates similar in aqueous using $PuO_2$ loaded carbon paste electrodes, forming Pu(V).

However, these studies have **effectively eliminated mechanism (v)** as a source of hydrogen – although have provided strong indications that $PuO_2$ surfaces may be oxidised/corroded/aged by radiogenic oxidants









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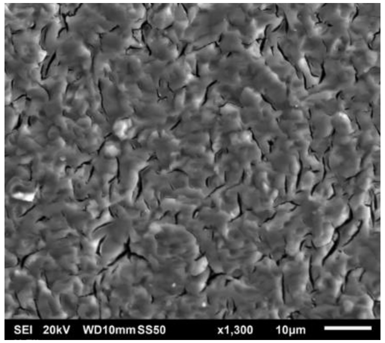
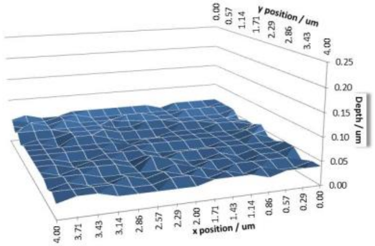
1. *Langmuir*, **23**, 4358 (2007) & **28**, 17647 (2012)
2. *MRS Advances*, (2017) DOI: 10.1557/adv.2016.671 *Prog.Nucl.Sci.Tech*, **5**, (2018). DOI: 10.15669/pnst.5.136

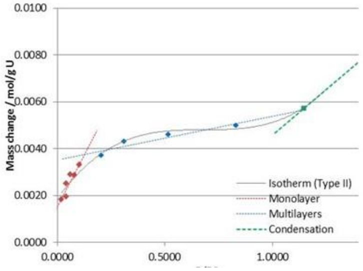
# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

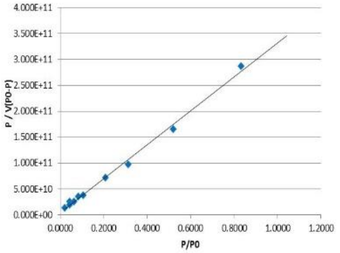
Thus, in TRANSCEND, **we will seek to understand how bulk defects & surface radiation damage affect mechanisms (iii)-(v)** and so can pressurisation.

1. Using $ThO_2$ as a surrogate we will build on the techniques described above to determine the extent, nature and speciation of surface-sorbed water and the effect of heat treatment on same.
2. Surrogate samples will then be irradiated to study the effect of rad damage-derived surface defects on water sorption – focussing on consequences for wettability, balance between non- & dissociative sorption and surface oxyhydroxide, $MO_2OH$, formation as a route to $H_2$.
3. Subsequent active work (at NNL), will use thin $PuO_2$ films to study
   - (i) Water adsorption on $PuO_2$ using nanogravimetry (again**, imminent**!) & contact angle measurements
   - (ii) effects of self irradiation and Am in-growth on surface chemistry, matrix conductivity and so peroxide / hydroxyl radical driven $PuO_2$ corrosion – the latter investigated by corrosion studies analogous to those commonly conducted on $UO_2$ SIMFUELs in Lancaster's UTGARD Lab; this will also be assessed in the presence of added radiolysis simulants $H_2O_2$, $HO_2$● and OH● (produced via Fenton Chemistry).
   - (iii) $PuO_{2+x}$ formation by electro-nanogravimetry









# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

**PDRA project (EPSRC): "Quantum chemical modelling of $PuO_2$ surface chemistry" Nik Kaltsoyannis**

Two complementary approaches: density functional theory within

(i) periodic boundary condition framework and

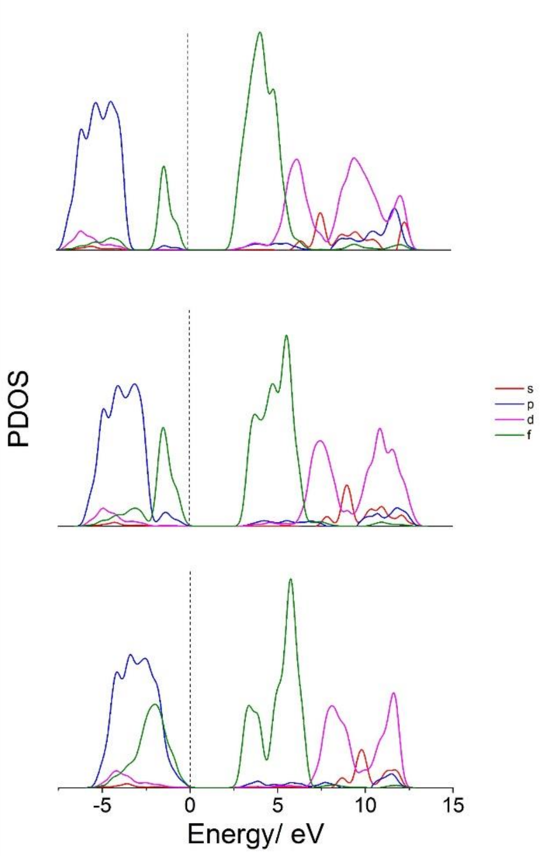
(ii) periodic electrostatic embedded cluster method (PEECM). Both techniques were used by the Kaltsoyannis group during Distinctive.[1]

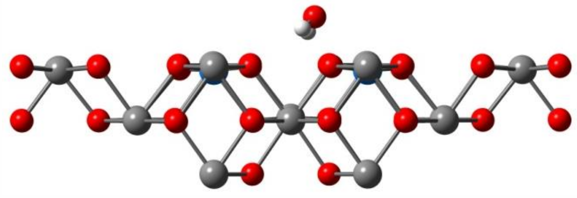
Work in DISTINCTIVE focused on $UO_2$ and $PuO_2$ bulk electronic structure, and the geometric structure and energetics of non- & dissociative water adsorption (monolayers and multiple layers) on stoichiometric {111}, {110}, {100} surfaces, including predictions of water desorption temperatures.

In TRANSCEND, we will study:

- Surface defect formation (substoichiometric and superstoichiometric) and chemistry of water and chloride around those defects
- Mechanism(s) of $H_2$ formation
- Effects of Am ingrowth on surface chemistry
- $ThO_2$

Align with and support experimental studies at Lancaster





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1. *J. Phys. Chem. C* **121** (2017) 1675, *J. Nuc. Mat.* **482** (2016) 124

# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

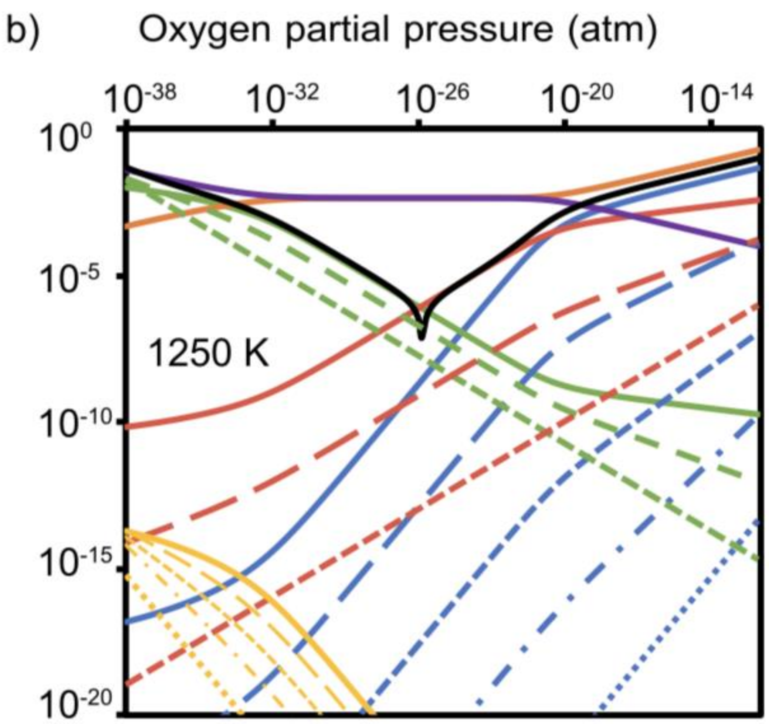
**PhD project (Lancaster): "Quantum chemical simulation of Am incorporation in $PuO_2$" Sam Murphy.**

This project will use Density Functional Theory (DFT) to understand how the incorporation of Am into $PuO_2$ may contribute to gas production.

Broken down into three steps:

1. Determination of intrinsic defect chemistry of $PuO_2$
2. Determination of mode of Am accommodation in $PuO_2$
3. Examination of the properties of $(Am_x,Pu_{1-x})O_2$ oxides for $x < 0.1$

Enables determination of the charge state of the Am as a function of its concentration, ultimately revealing whether $PuO_2$ becomes electrically active during storage and informs us as to whether this contributes to gas production.



Intrinsic defect chemistry of $UO_2$ as a function of oxygen partial pressure (Cooper *et al*. JNM 504 (2018) 251).

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# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

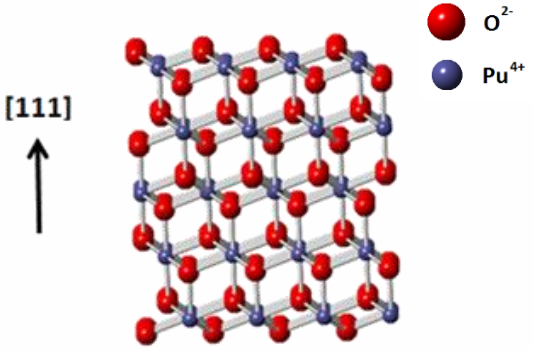
**PhD project (NDA): "Atomistic simulation of He incorporation within $PuO_2$, and the effect of ageing" Mark Read**

Static, free energy and molecular dynamics simulation techniques employing pair potentials, refined and developed in the Read group during DISTINCTIVE, were used to investigate $PuO_2$ bulk and surfaces, especially properties and behaviour relevant to storage scenarios.

More specifically, using a classical potential approach, a variety of purpose-built codes have been used to model properties of the bulk material, surfaces and defects including helium.

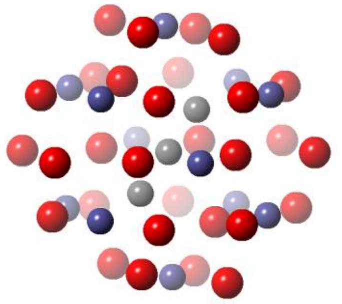
In TRANSCEND, we will study:

- Investigation of He trapping sites and accumulation in Schottky voids/grain boundaries
- Predict He behaviour and effects on $PuO_2$ lattice and surfaces
- Effect of radiation damage on mobility of defects and ageing mechanisms
- Ageing defect chemistry under a variety of stoichiometries (*e.g.* Am ingrowth)
- Effects of extrinsic defects on surface chemistry



$E_{Surf}^{Relaxed} = 1.32\ Jm^{-2}$

**Structure of (111) surface**



**Entrapment of He in a Schottky void**

# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

**PhD project (Sellafield/UoM, Aligned Resource): "PEECM modelling of $PuO_2$ surface chemistry" Nik Kaltsoyannis.**

Focuses on modelling the interactions of HCl and $H_2O$ on the surfaces of $PuO_2$

**PhD project (Sellafield/NNL): "Radiolysis of Water on Uranium Oxides and $ThO_2$" Fred Currell (DCF).**

Will investigate the radiolysis of water on oxides including uranium and thorium oxides as surrogate materials for $PuO_2$ and MOX powders

- radiation chemistry at low water coverage, typical of stored materials
- if/how radiation damage influences the radiation chemistry
- influence of impurities within the adsorbed water on the oxide surface, *e.g.* HCl (from PVC degradation) and $NO_x$ (from air radiolysis).

# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

**PhD project (Sellafield/NNL/NDA): "Hydrogen / Oxygen Recombination at Metal Oxide Surfaces" Colin Boxall, Robin Orr, Helen Steele**

Storage can atmospheres can potentially be $H_2$ rich but rarely flammable (i.e. $H_2$ + $O_2$), raising the question as to whether this is due to

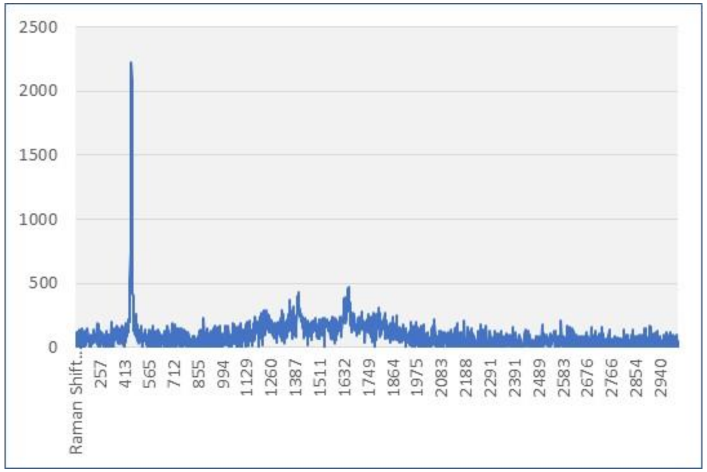
- $PuO_{2+x}$ formation or
- Thermally or radiolytically driven gas phase recombination
- Thermally or radiolytically driven recombination with $PuO_2$ acting as a catalyst
  – the latter two routes preventing the coincident observation of the two gases.

Such recombination may limit the extent of packages pressurisation. Preliminary studies conducted at DCF indicate that He ion / gamma irradiation of gas phase mixtures of hydrogen and oxygen can lead to loss of hydrogen, presumably through radiation-induced reaction with oxygen to form water. This loss of hydrogen is found to be accelerated by the presence of Zr and Ce oxides. Questions arise as to whether this catalysis exists on $PuO_2$ and whether it can be challenged by surface saturation (moisture, gases) or aging.

This PhD, which with a significant period of placement at NNL Central Lab, will work to address these questions. The student will work to further the understanding of the efficacy of PuO2 as a catalyst, and understand dependencies of the composition of the gas-phase on the surface activity of the metal oxide.

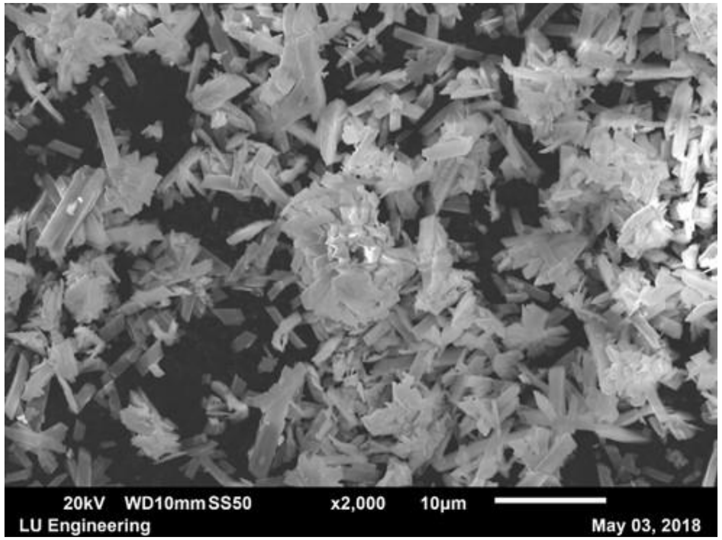
Parallel/preliminary work at LU will focus on method development for the on-line sampling of both hydrogen and oxygen and potentially other species as a function of T, P, water content, dose rate, specific surface area, co-adsorbed species etc. during recombination / catalytic reaction studies.

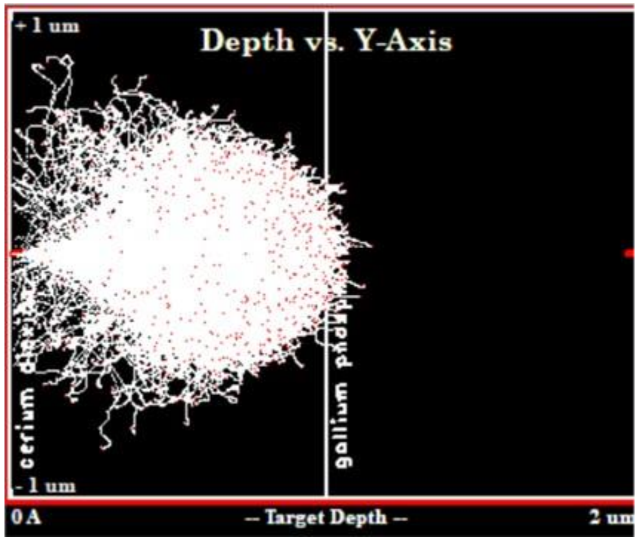
# WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage

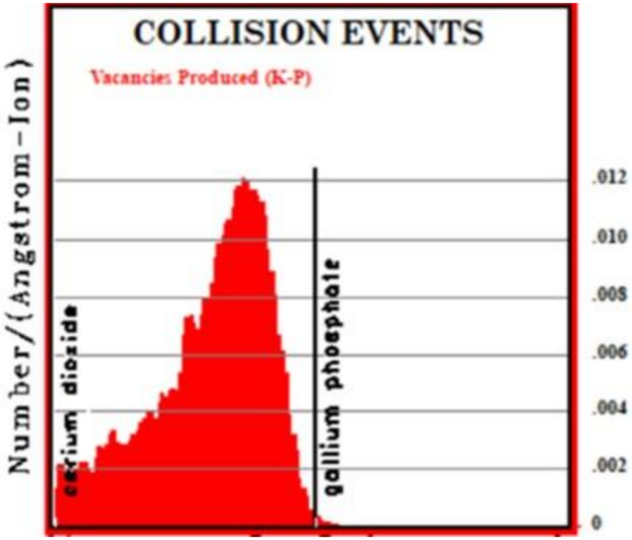


**PhD project (Sellafield/EPSRC, Aligned Resource): "Helium Retention & Release in $PuO_2$ Powders" Colin Boxall.**

Employing the nanogravimetric technique described earlier, this will initially focus on determining the temperature profile of the release of He that has been implanted into metal oxide matrices using the ion beam at DCF.







## TRANSCEND Theme 4: Nuclear Materials

Transformative Science and Engineering for Nuclear Decommissioning

# WP4.2: Plutonium Immobilisation in Advanced Ceramic Wasteforms

**PDRA project (EPSRC): "Plutonium immobilisation" Neil Hyatt.**

<u>**Aim**</u>: this project aims to build on our work within DISTINCTIVE and resolve a key uncertainty regarding the impact of radiation damage on the dissolution kinetics of ceramic wasteforms. Current evidence is conflicting and sample preparation likely obscures a marginal impact; nevertheless, this may be significant over a $10^4$ yr service lifetime.

**1. High quality ceramic substrates will be fabricated** from candidate ceramic wasteforms (*e.g.* $CaZrTi_2O_7$ and $Nd_2Zr_2O_7$), exploiting our novel reactive spark plasma sintering process to rapidly optimise ceramic density and microstructure (*J. Nucl. Mat.*, **500**, 11-14, 2018).

**2. Impact of radiation damage on dissolution** behaviour will be investigated by

- Masking the ceramic surface and inducing radiation damage by ion beam implantation, to achieve a crystalline to amorphous phase transition (Fig. 1-2), to achieve damaged / undamaged areas on the *same specimen* (Fig 3).
- Ceramics will be dissolved as a function of pH and temperature and the surface retreat quantified by high resolution AFM and VSI, with solution chemistry determined by ICP-MS.
- Quantification of the retreat rate with spatial resolution, with respect to masking, on the same specimen, will enable the effect of radiation damage on dissolution rate to be established in isolation of surface preparation effects.

**3. Pu solid solution mechanisms in $CaZrTi_2O_7$** will be explored in the dilute limit using Pu-242 in the TransMat (Transuranic Materials) Facility of the Henry Royce Institute, exploiting m-XAS/XRD at DLS, coupled with defect energy calculations.

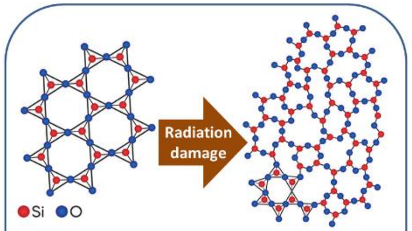


**Figure 1:** Example of crystalline to amorphous phase transition induced by radiation damage in $SiO_2$, transforming quartz (left) into silica glass (right) with a disordered atomic structure.

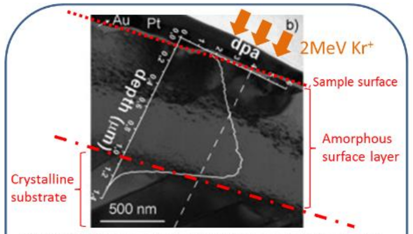


**Figure 2:** Cross sectional TEM image showing result of 2MeV $Kr^+$ ion beam implantation of $CaTiO_3$ and formation of surface amorphised layer, from our research group (Davoisne et al., J. Nucl. Mater., 415 (2011) 67-73.

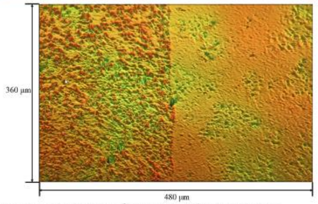


**Figure 3:** VSI image of titanate glass-ceramic implanted by 2 MeV $Au^+$, right side of sample masked, height range ca. 100 nm. Note the increased surface surface area of sample induced by ion beam irradiation and crystalline to amorphous phase transition on left side (unmasked).

# WP4.2: Plutonium Immobilisation in Advanced Ceramic Wasteforms

**PDRA project (RWM): "Disposability of wasteforms for plutonium immobilisation and efficacy of surrogates" Claire Corkhill**.

**Aim and scope**: to understand and contrast the behaviour of surrogates in the dissolution behaviour of ceramic/glass-ceramic wasteforms for plutonium disposition.

The project will utilise state of the art dissolution methods (e.g. single pass flow through; surface retreat rate analysis), to determine the mechanism of ceramic/glass-ceramic wasteform dissolution as a function of thermodynamic parameters (pH, Eh, T) and model ground water compositions, supported by geochemical modelling. A focus will be placed on the efficacy of surrogates in guiding understanding of plutonium behaviour, in particular the different redox behaviour of Ce, U and Th. Pu glass ceramic durability will be tested at ANSTO.

The project will integrate with project S2 below, which will provide a suite of high quality simulant wasteforms, and the Sheffield EPSRC PDRA project which will develop the surface retreat rate methodology.

**Sheffield Aligned PhD projects**

It is proposed to associate current NDA supported PhDs (scope unchanged, subject to agreement);

- **S1: "Efficacy of surrogates for plutonium immobilisation"** (Blackburn; fr. 11/18, 3.5y, NDA)
- **S2: "Brannerite glass-ceramics for plutonium immobilisation"** (Dixon-Edwards; fr. 10/18, 3.5y, NDA)
- **S3: "Treatment of degraded fuel residues"** (TBC; fr. 10/19, 3.5y, NDA).

# TRANSCEND
# Theme 4: Nuclear Materials
# Summary of Projects

**WP4.1: The Surface Chemistry of $PuO_2$ under Conditions Relevant to Interim Storage**
Lancaster (Boxall, Murphy), Manchester (Kaltsoyannis, Currell), Birmingham (Read)

2 x PDRA (EPSRC)
1 x university PhD (Lancaster)
3 x industry PhD (Sellafield, NNL, NDA)
2 x aligned PhD (Sellafield, EPSRC, Manchester)

**WP4.2: Plutonium Immobilisation in Advanced Ceramic Wasteforms**
Sheffield (Hyatt, Corkhill, Blackburn, Dixon-Edwards)

1 x PDRA (EPSRC)
1 x industry PDRA (RWM)
3 x aligned PhD (NDA)

N.B. Manchester and Sheffield are also contributing PhD positions in Themes 1 and 3

# Thank you

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# Investigating the interaction of water with plutonium oxide and analogues

Dominic Laventine, University of Lancaster

Transcend Annual Meeting 2019

4th April 2019
Bath Spa

*Ca*. 250 tonnes of separated Pu currently stockpiled worldwide.
Approx. 50% in stored in UK whilst the Government
"develops its options".

Interim storage of $PuO_2$ involves sealing in nested steel containers,
under a partial argon atmosphere with (PVC) packing material.

During storage the radioactivity of the plutonium results in heating of the canisters ntral line temperature of 600°C

Ina small number of cases, cans may pressurise;
this makes storage and efficient heat transfer more difficult

Need to understand how the structure and properties of $PuO_2$ change with time under storage condition .

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.

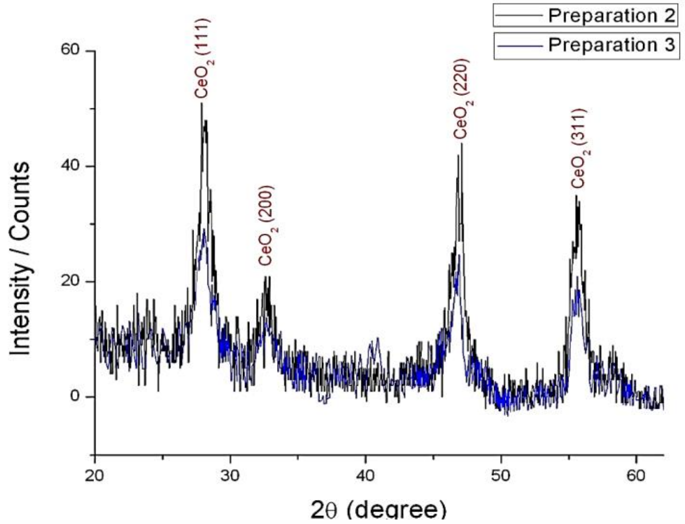
The last 3 processes all involve $PuO_2/H_2O$ interactions and are complex, inter-connected & poorly understood.

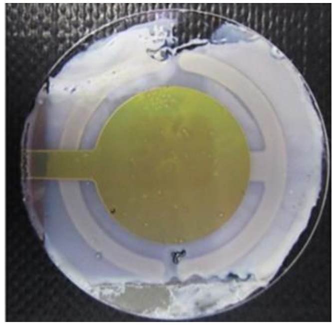
- Experimental methods have been employed to determine extent of $H_2O$ adsorption, typically through measurement of pressure changes and use of the ideal gas equation to indirectly determine water adsorption at the plutonium oxide surface.

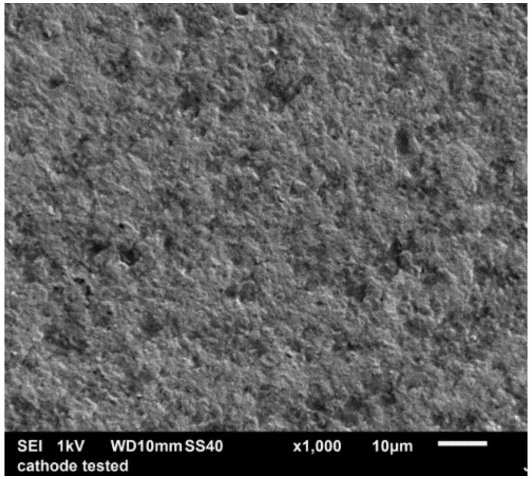
- Current models suggest water is initially absorbed onto metal oxides as a chemi-absorbed monolayer followed by multiple, physi-sorbed layers (with possible intermediate layers of differing binding energies).

At Lancaster we have used thin (10-100s nm thick) layers of metal oxides to allow surface characteristics to be investigated while using only small amounts of radioactive material.

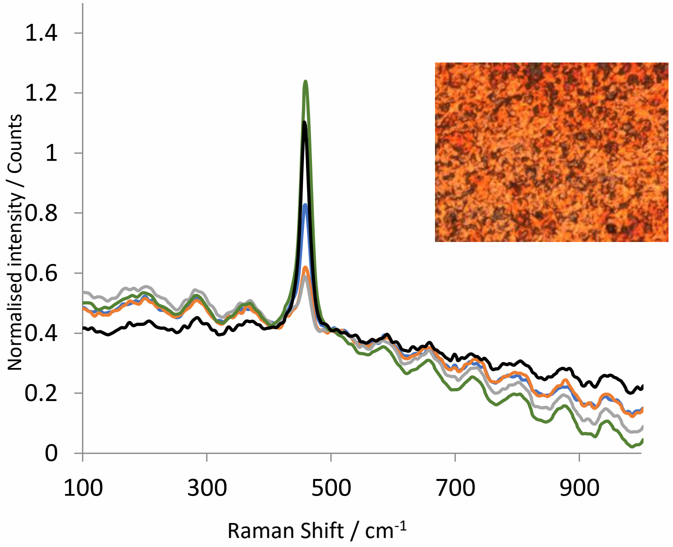
Cerium, Thorium, and Uranium oxides used as analogues of plutonium oxide due to their similar structures and atomic radii.



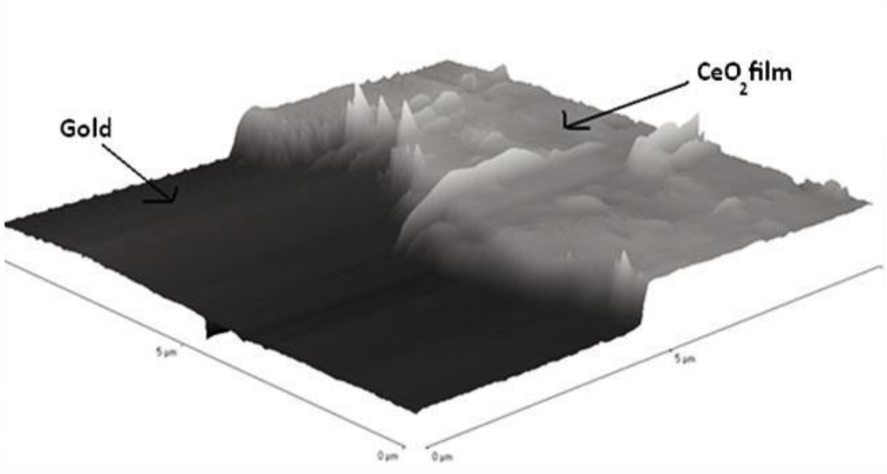




50 ug $Ce(NO_3)_3$
10 uL $H_2O$
10 uL MeOH
5% Triton-X
Calc.: 350°C

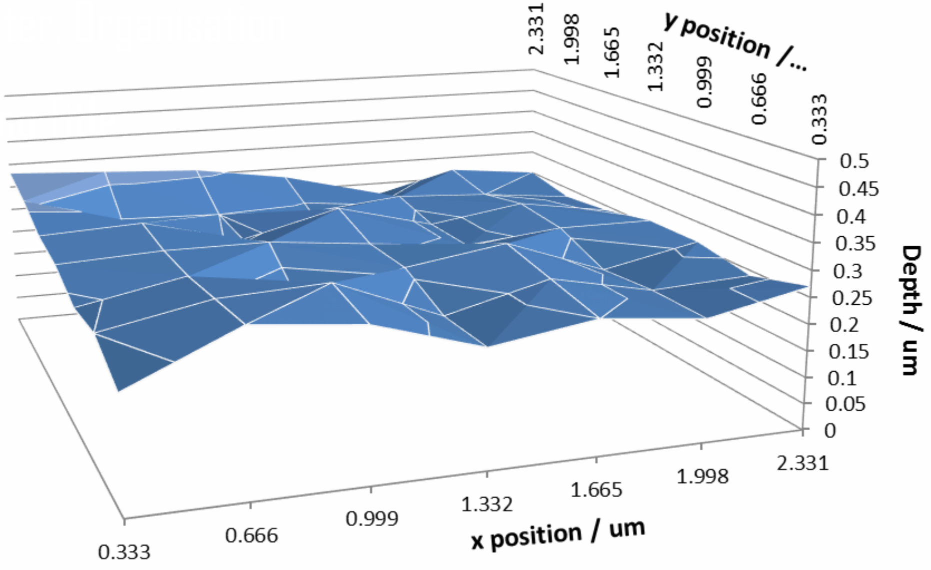


Uncoated crystal $F_{25ºC}$ = 5833918 Hz
Coated crystal $F_{25ºC}$ = 5826468 Hz
D $F_{25ºC}$ = –7450 Hz
D m = 42 ug
vol = $5.5 \times 10^{-6}$ cm$^3$
Thickness = 125 nm



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

$\rho_q$ = 3.570 g.cm$^{-1}$ n = 1
$\mu_q$ = $2.147 \times 10^{11}$ g.cm$^{-1}$s$^{-2}$
Coated area = 1.33 cm$^2$
Active area = 0.46 cm$^2$
$d_{CeO_2}$ = 7.65 g.cm$^{-3}$

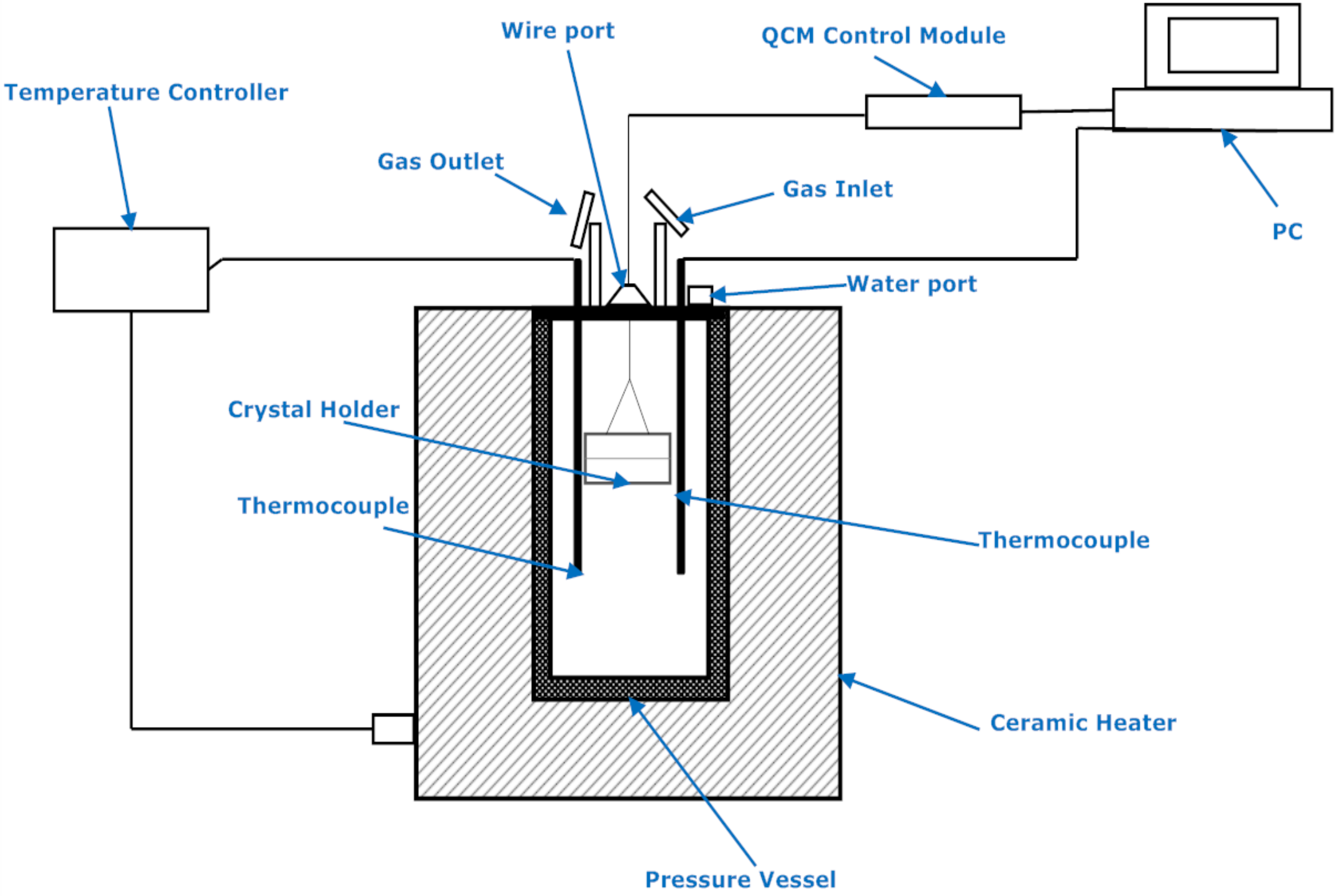


Nano crystal microbalance

Electrochemistry (voltammetry and impedance)

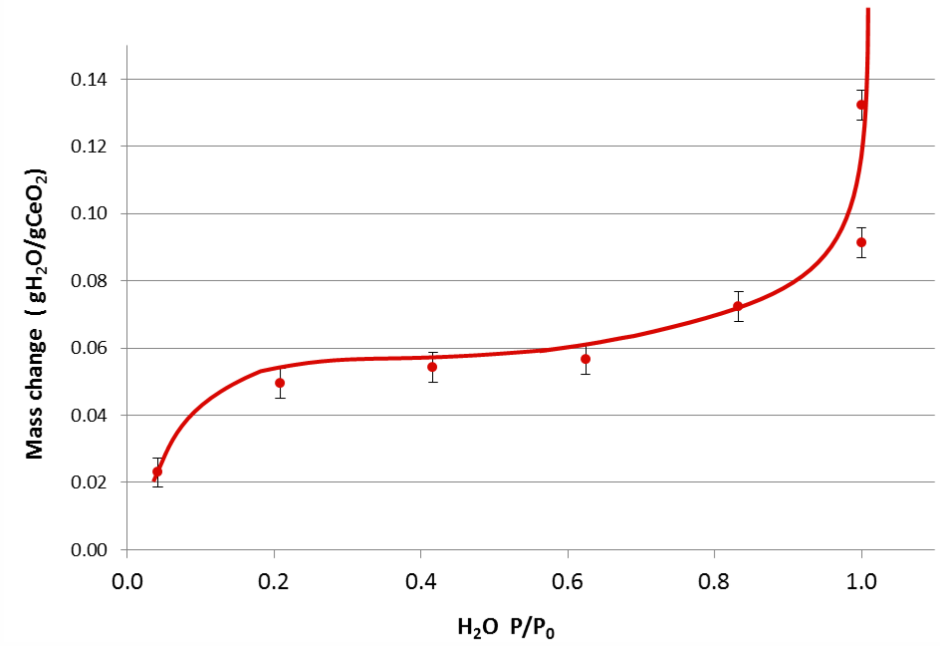
Contact angle measurement

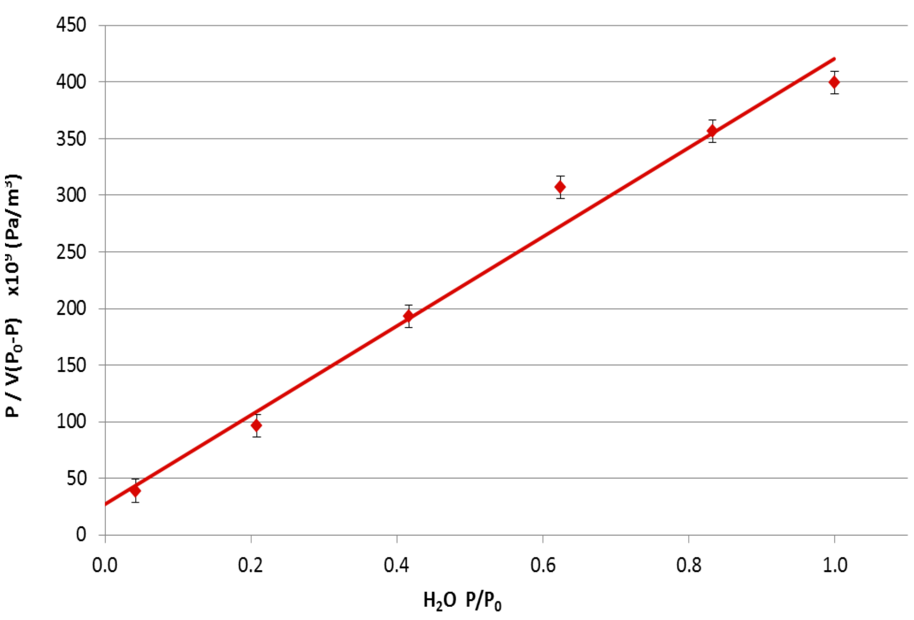
# Nano crystal microbalance



The BET equation allows the volume of a monolayer and the enthalpy of absorption to be calculated:

$$1/\left[Va\left(\frac{P0}{P}-1\right)\right] = \left(\frac{C-1}{V_M C}\right)\left(\frac{P}{P_0}\right) + \frac{1}{VmC} \qquad C = e^{(\Delta H_{ads} - \Delta H_{liq}/RT).}$$



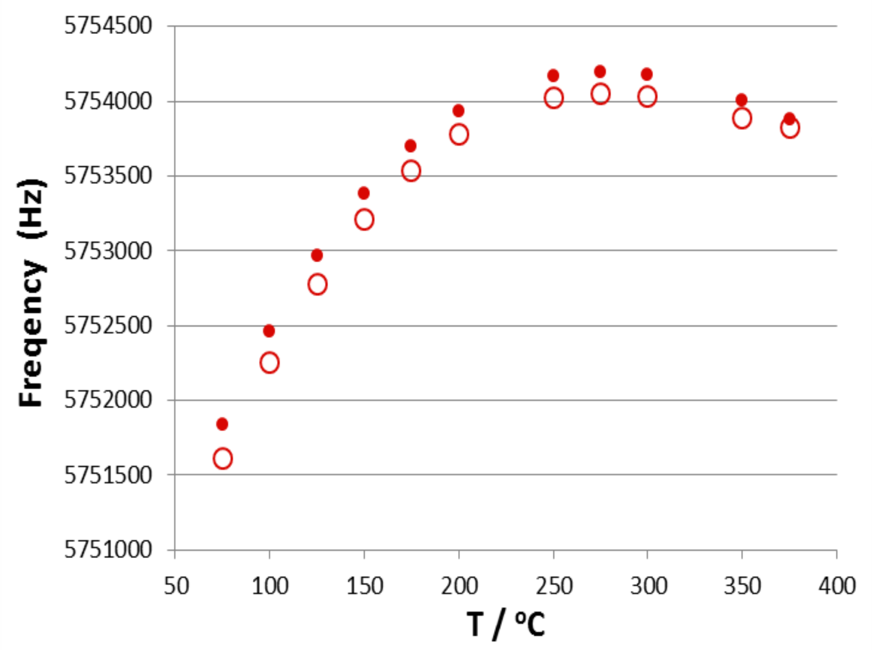


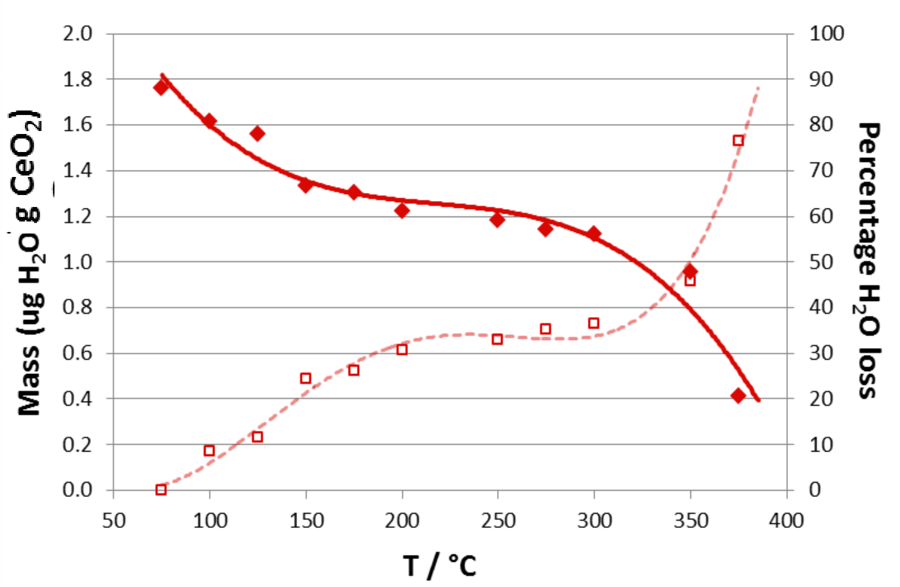
A plot of $P/V(P_0\text{-}P)$ against $P/P_0$ gives an intercept of 1/VmC and a gradient of $(C-1)/(V_M C)$, therefore we can calculate:

$V_m$ = 2.43 x $10^{-12}$ $m^3$ SA = 28 $m^2g^{-1}$

$\Delta H_{abs}$ = 44.3 $kJmol^{-1}$ $\Delta H_{bind}$ = 2.5 $kJmol^{-1}$

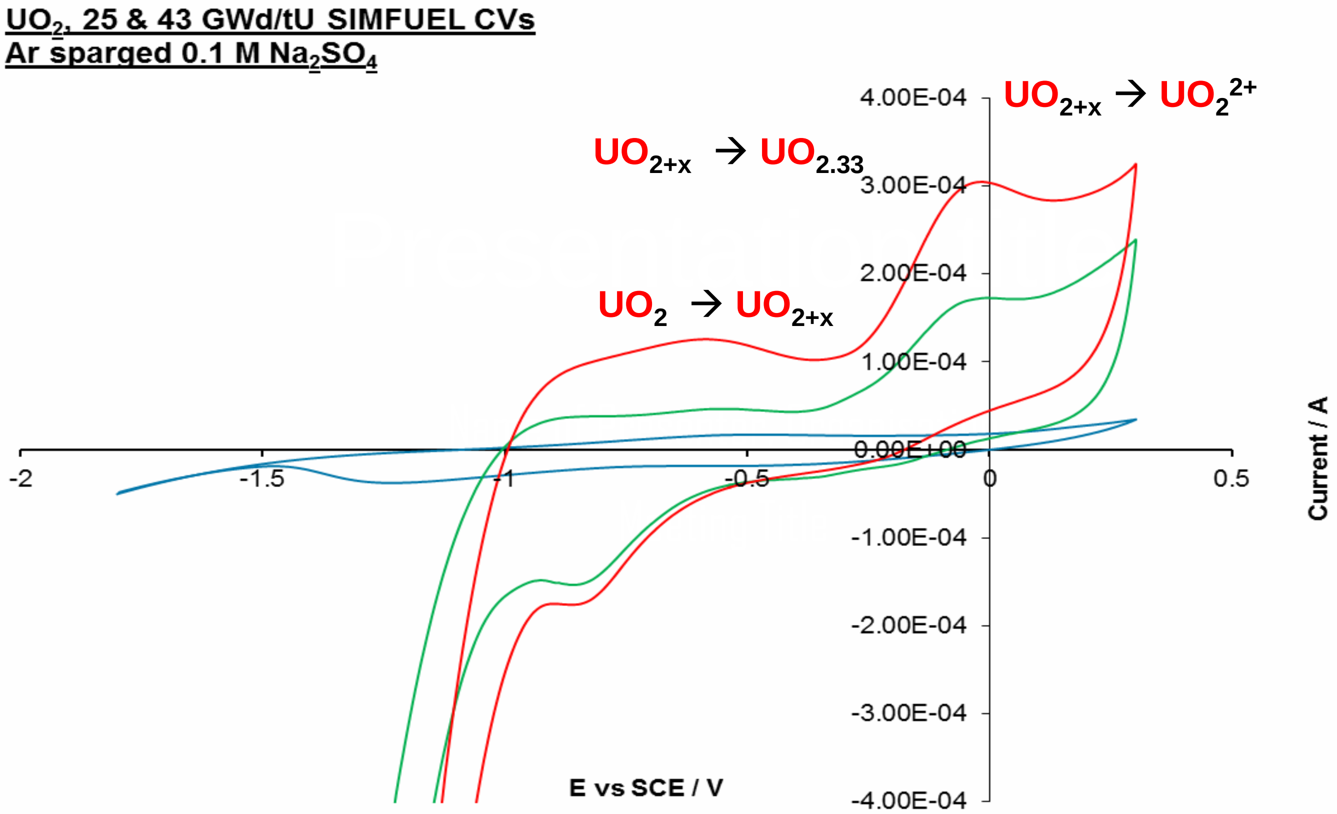
The water saturated system (75°C, 100% rel. humidity) was then heated to approx. 400°C, causing the bound water to desorb as the relative humidity drops.





Approximately 20% of the water remains bound to the surface at 375°C.

# Electrochemistry (voltammetry and impedance)



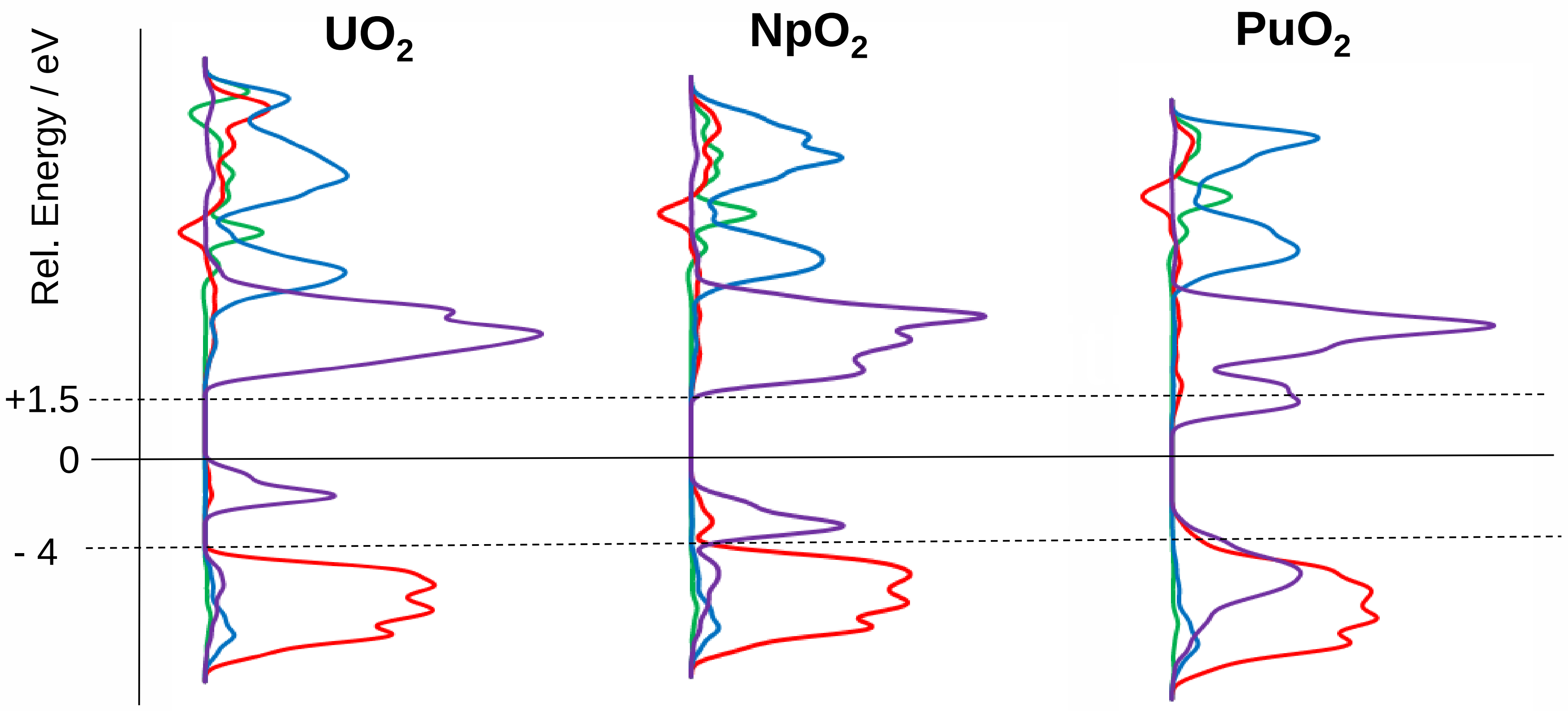
**$UO_2$, 25 & 43 GWd/tU SIMFUEL CVs**
**Ar sparged 0.1 M $Na_2SO_4$**

$UO_{2+x} \rightarrow UO_2^{2+}$

$UO_{2+x} \rightarrow UO_{2.33}$

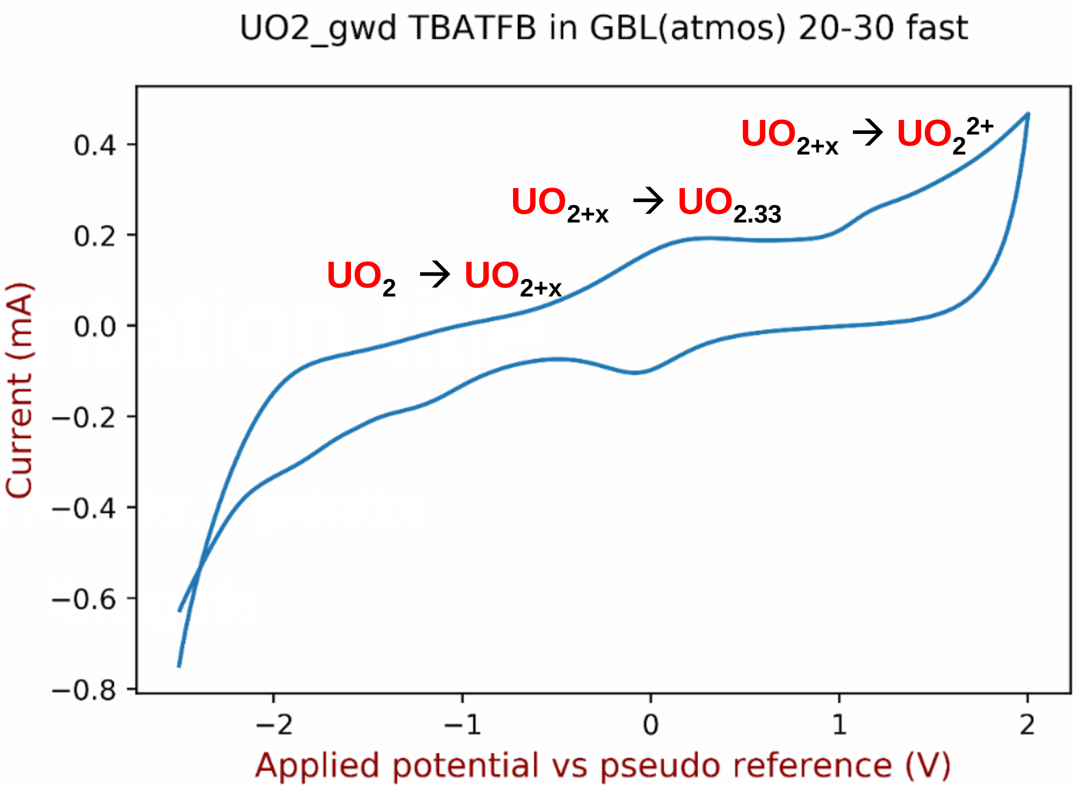
$UO_2 \rightarrow UO_{2+x}$

- Voltammetry of AGR SIMFUELs in aqueous systems show them to be susceptible to electrochemical oxidation
- Aqueous electrochemical limited to approx. max 1.23 V

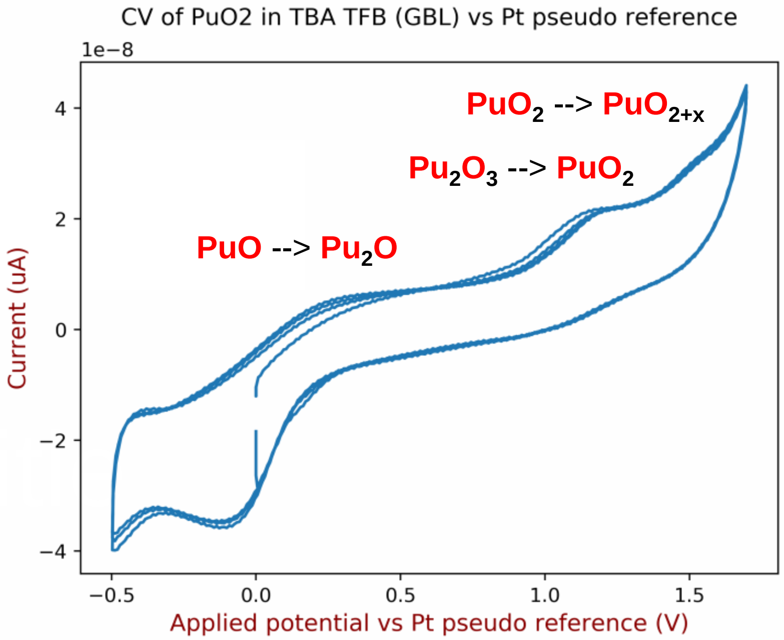


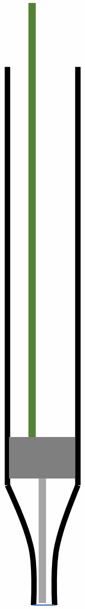
- Electronic structure of bulk AnO$_2$ clusters calculated with PBE0 function (Joseph Wllington, Uni. Manchester)
- UO$_2$ and NpO$_2$ predicted to be Mott-Hubbard insulators, PuO$_2$ predicted to be a charge transfer insulator.
- MO$_2$ IV -> V oxidation required entry into 5f. This overlaps the valence band in PuO$_2$.

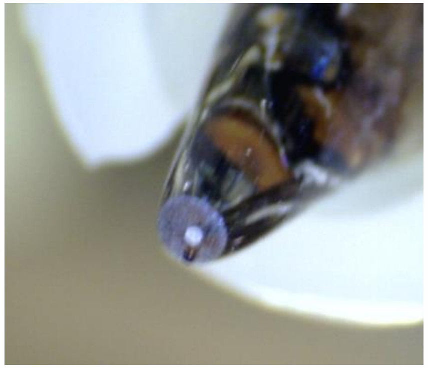
- 43 gwd/tU SIMFUEL
- Pt pseudo reference electrode
- 1M TBA-TFB in GBL

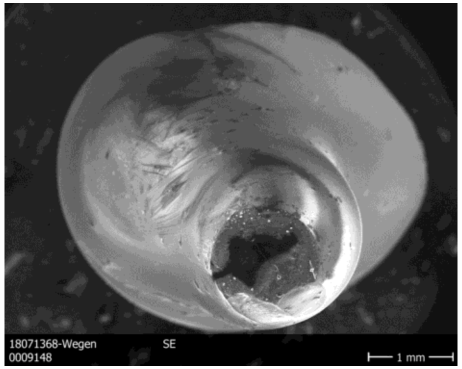


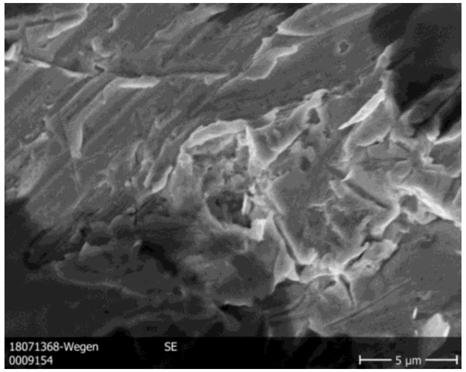
- Dip-coat electrode in $M(NO_3)_x$ solution, calcine at 400ºC
- Use microelectrodes to minimise metal required for coating
- Vary $M(NO_3)_x$ solution 8 – 40 mM to give
  ~ 200 nm – 1 um layers
- Dope with Eu to increase p-type semiconductor behaviour

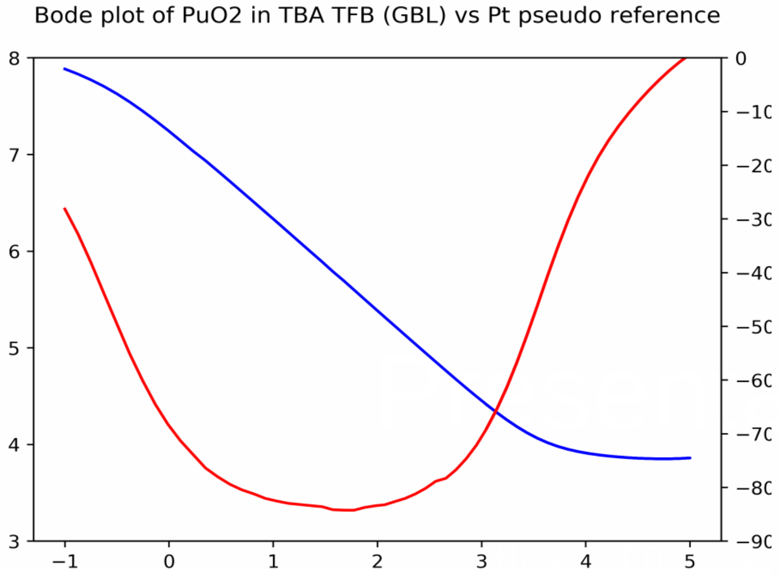


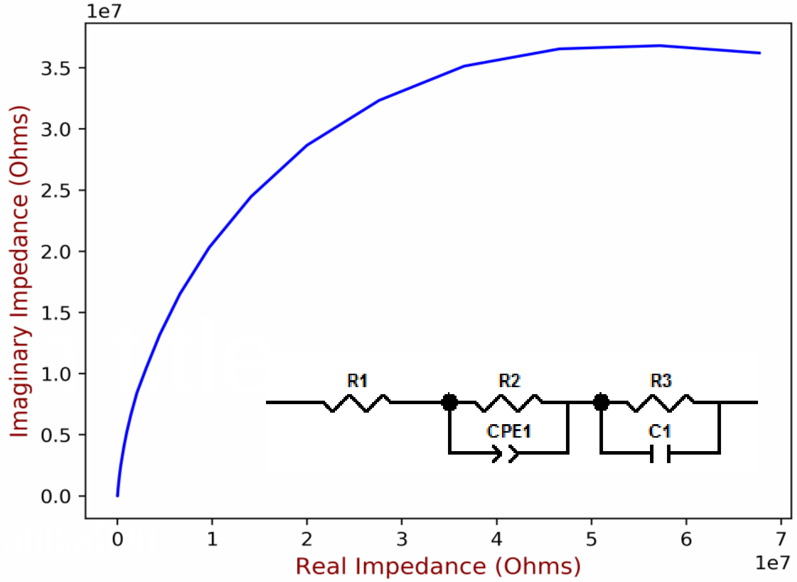




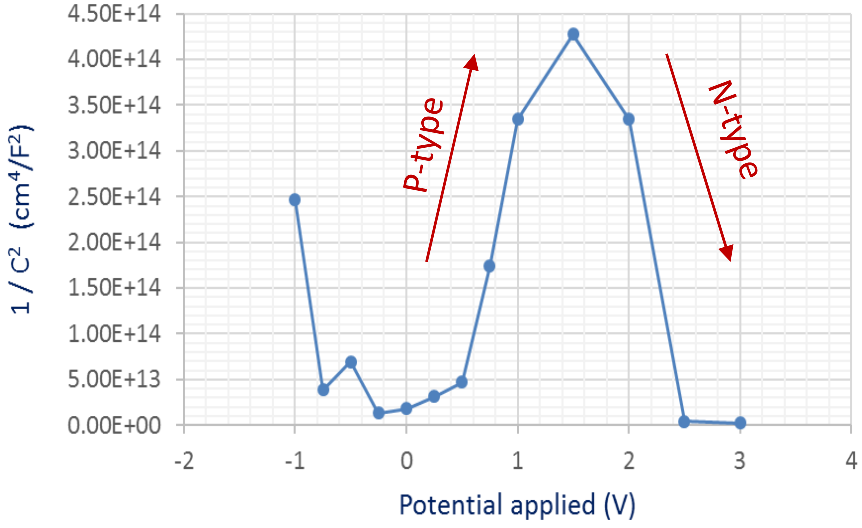








- Bode and Nyquist plots obtained and fitted to Randall circuits.
- Capacitance of $PuO_2$ coating calculated.
- Mott-Shottky plot shows reflex point at 1.4 V, indicating change in semi-conductor type.



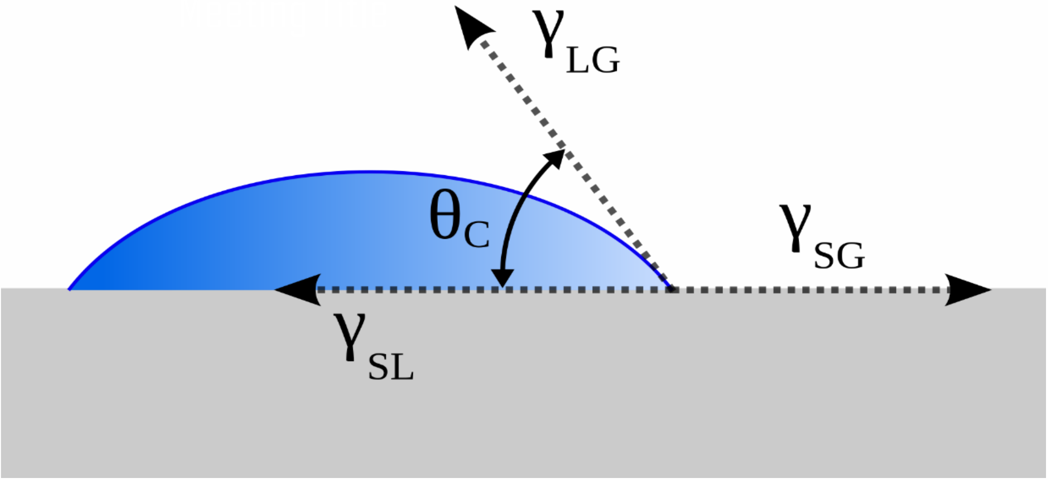
## Contact angle measurement

- Contact angle measurements of liquids on surfaces give an indication of the wettability of the surface.
- Surface irregularities disrupt droplet cohesion, increasing the wettability of a surface. Chemical characteristics also effect wettability.
- Therefore the surface finish resulting from different processing methods will alter the wettability.
- Plutonium’s intrinsic radioactivity and high levels of decay heat causes surface damage during storage to an unknown extent.

$$r.\cos\Theta_c = \cos\Theta_m$$

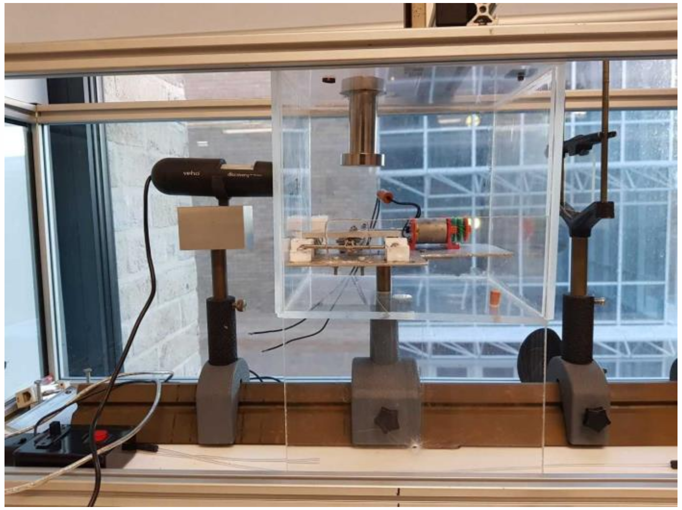
$$\gamma_{LG}.\cos\Theta_c = \gamma_{SL} - \gamma_{SG}$$

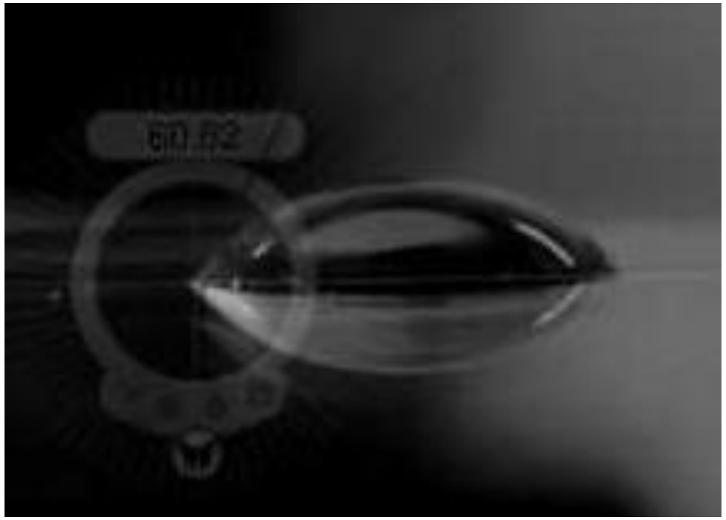
$\Theta_{c}$ = *contact angle*
r: roughness factor
$\gamma_{LG}$: surface tension
$\gamma_{SL}$: solid-liq IE
$\gamma_{SG}$: solid-gas IE



Water droplet on oxide nano-thick layer at 100% humidity, before and after UV irradiation.

- Measure contact angles of plutonium oxide analogues ($CeO_2$, $ThO_2$, $UO_2$, $Ce_{1-x}Eu_xO_2$) produced at a range of calcination temperatures.
- Vary humidity, pH, salt content of droplet
- Measure contact angles before and after irradiation with α-particle beam at DCF, to simulate sample aging.
- Automate droplet measurements using image recognition / machine learning.





# Conclusions

- Investigate surface effects of $PuO_2$ analogues, particularly interaction with water.
- Produce nano-thick layers of $PuO_2$ analogues by drop coating.
- Microbalance measurements on plutonium oxide and analogues can determine the extent of water ab/desorption under storage conditions.
- Electrochemical measurements in organic solvents to allow investigation of possible oxidations at higher potentials.
- Contact angle measurements of plutonium analogues and radiation damaged surfaces can indicate surface wettability under storage condition and changes over time.

# Thank you

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Transformative Science and Engineering for Nuclear Decommissioning

# Atomistic Simulation of the ageing of $PuO_2$

Elanor Murray

University of Birmingham

TRANSCEND Annual Meeting

4th April 2019
Apex City of Bath Hotel

# Contents

# Stockpile

The UK does not currently have a GDF, and it will take at least 15 years to implement re-use, so the UK's Pu must be kept in its current state for a significant period; *i.e.* as $PuO_2$ powder in interim storage canisters at Sellafield.

HOUSES OF PARLIAMENT
PARLIAMENTARY OFFICE OF SCIENCE & TECHNOLOGY

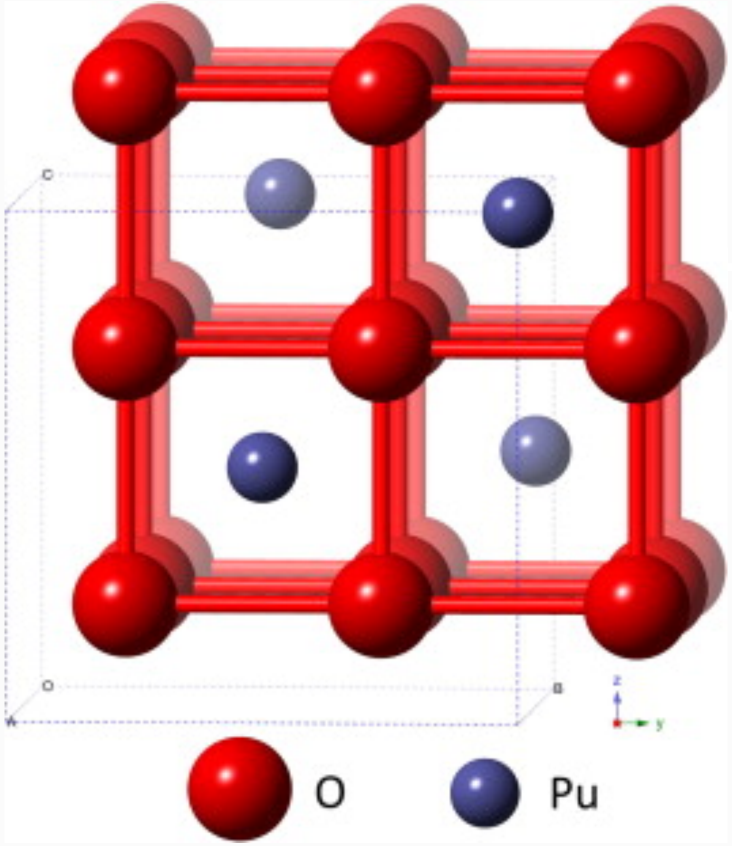
POSTNOTE
Number 531 September 2016

Managing the UK Plutonium Stockpile

**Overview**

- The UK is storing the largest 'separated' civil plutonium stockpile in the world. This poses safety, security and cost challenges.
- The Nuclear Decommissioning Authority is assessing long term options for managing the stockpile with industry pushing for a timetable for the selection and delivery of an

# Plutonium Dioxide

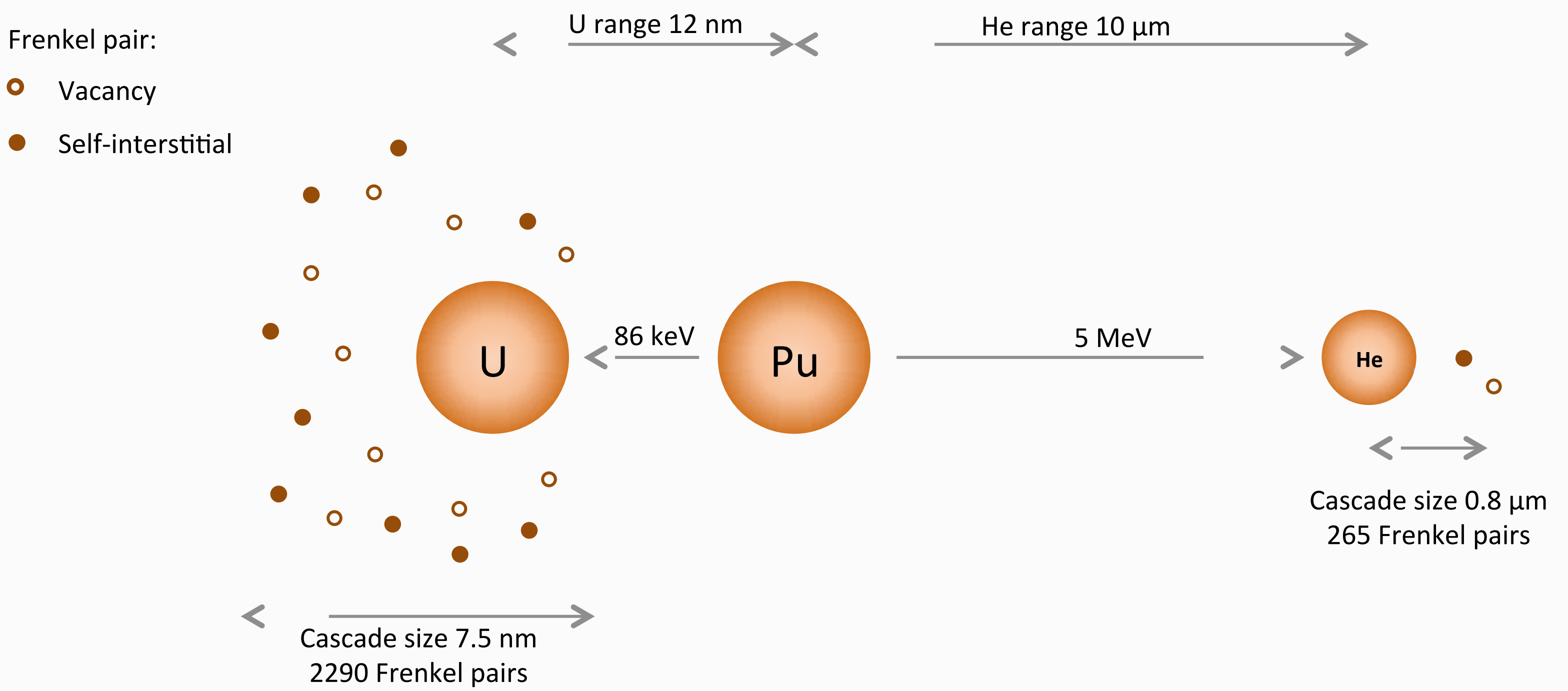


***Ref:*** *Read MSD, Jackson RA. Journal of Nuclear Materials. 2010;**406(3)**:293*

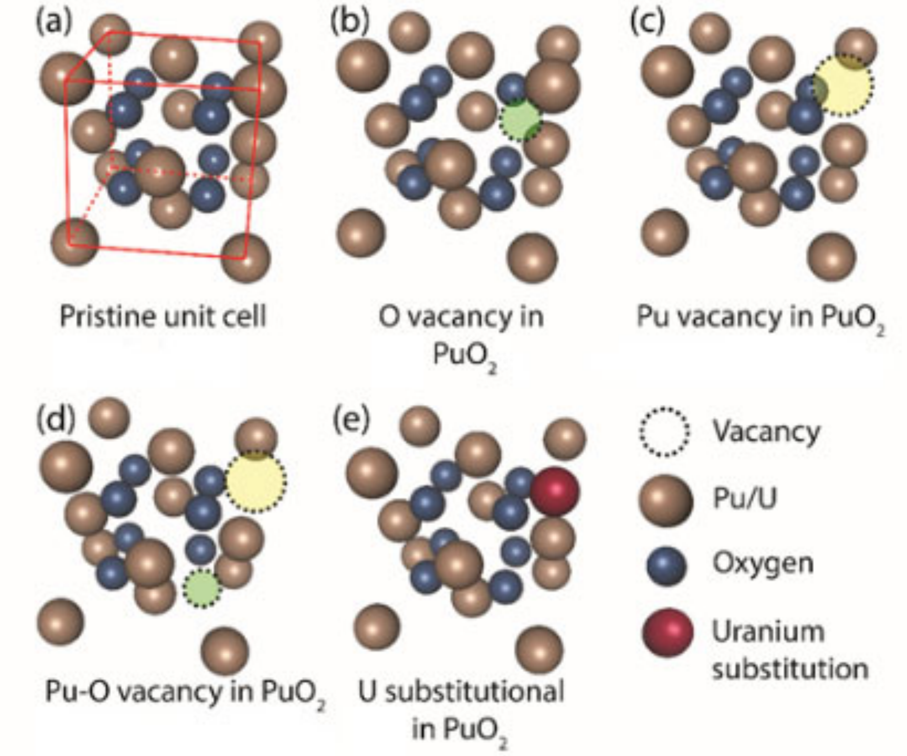
# Ageing Effects in Plutonium

- Lattice damage
- Helium bubble in-growth
- Potential void swelling

# Ageing Effects in Plutonium

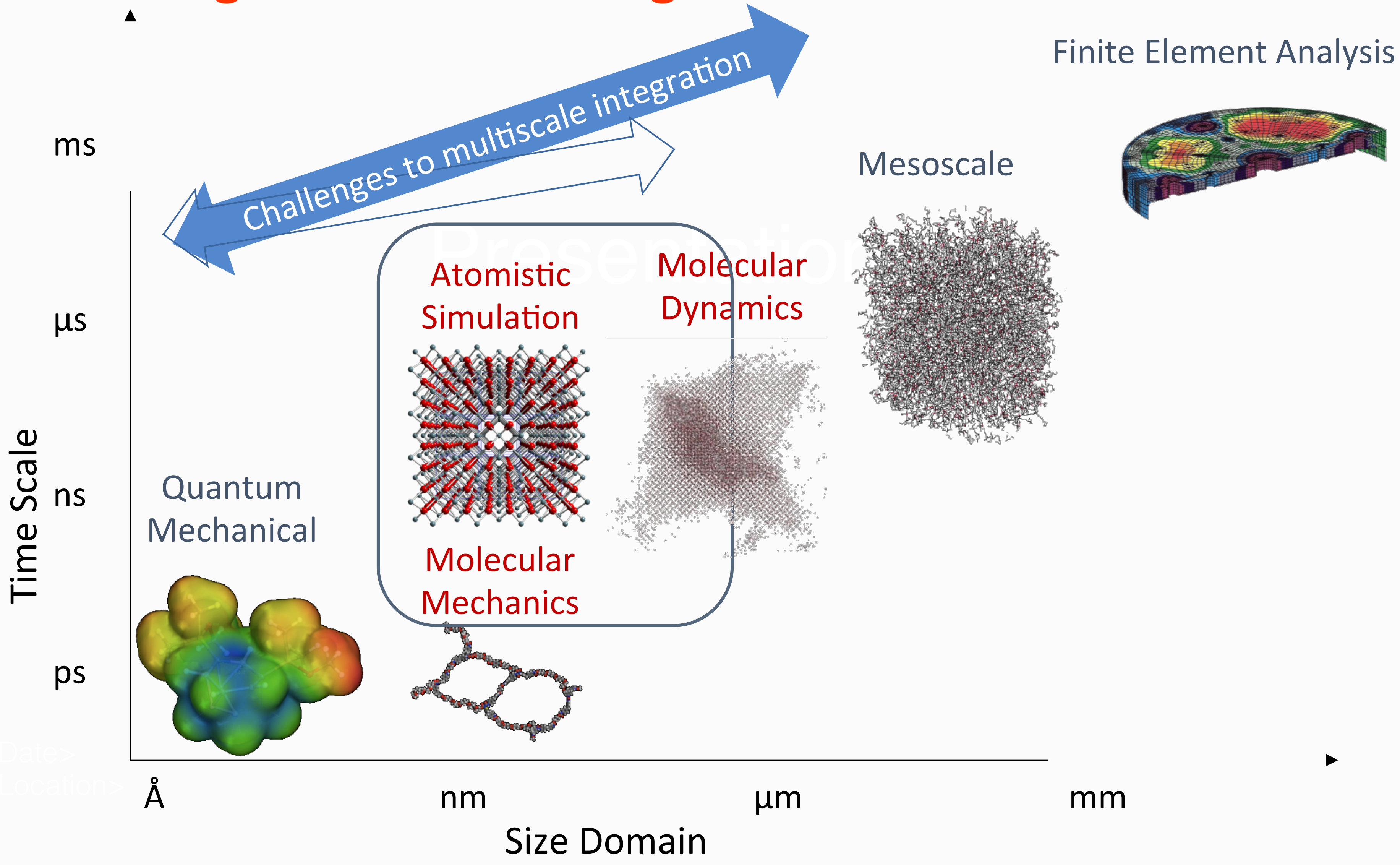


# Ageing Effects in Plutonium



***Ref:*** *A. Resnick, Nuclear energy science and engineering laboratory, 2018.*

# Modelling scales and regimes



Challenges to multiscale integration

Finite Element Analysis

Mesoscale

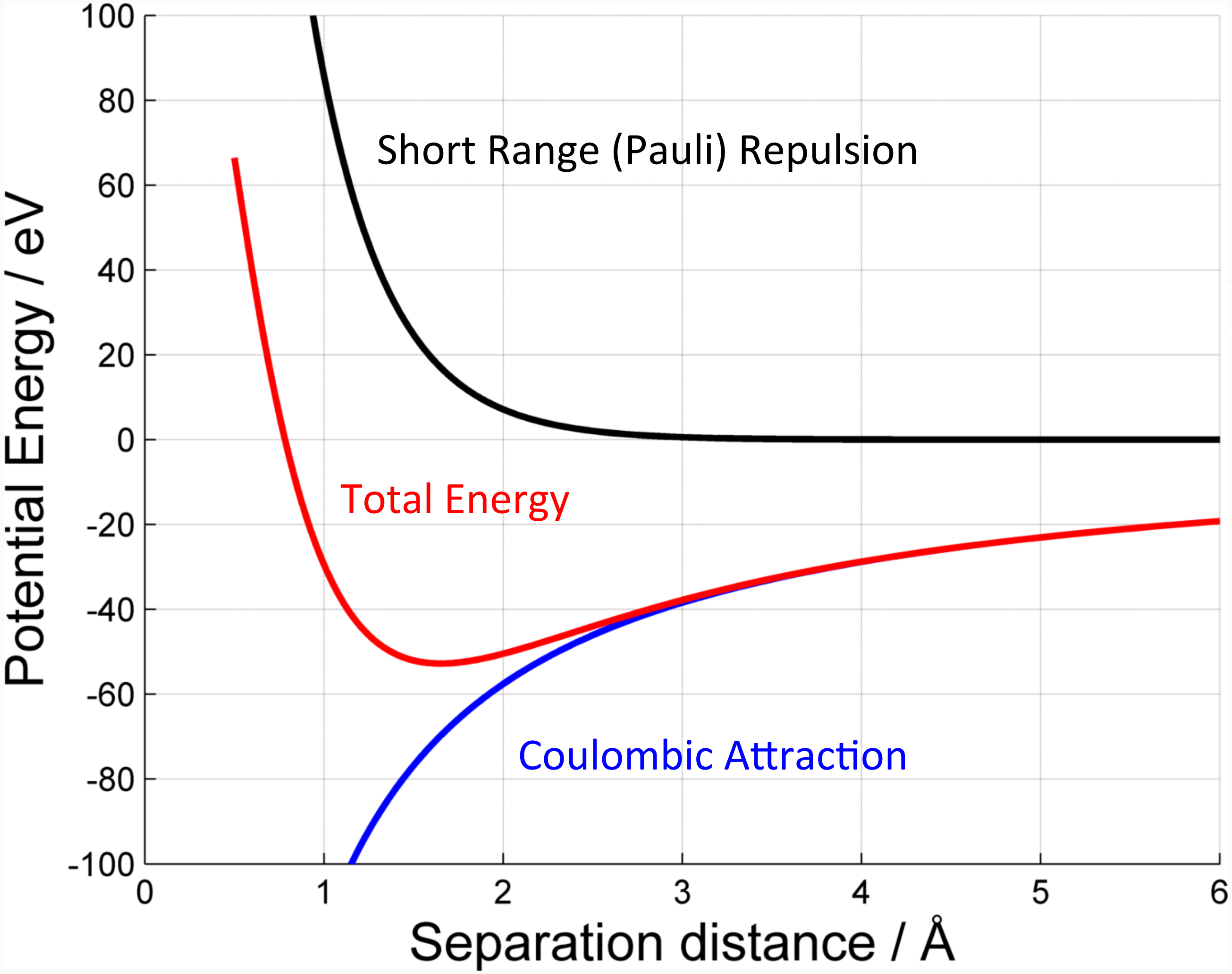
Atomistic Simulation

Molecular Dynamics

Molecular Mechanics

Quantum Mechanical

# The Potential Model



$$U_\mathrm{L} = \underbrace{\sum_{ij} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}}_{\text{Coulombic Energy}} + \underbrace{\sum_{ij} \Phi_{ij}(r_{ij})}_{\text{Short-Range}}$$

# The Potential Model

## - The short range potential

**The Lennard-Jones Potential:**

$$\phi_{ij}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

**The Morse Potential:**

$$\phi_{ij}(r_{ij}) = D_e\left[e^{(-2\gamma(r-r_0))} - 2e^{(-\gamma(r-r_0))}\right]$$

**Buckingham potential:**
Suitable for ionic solids

$$\phi(r_{ij})_{Buck} = \underbrace{A_{ij}\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right)}_{\text{Electron repulsion}} - \underbrace{\frac{C_{ij}}{r_{ij}^{6}}}_{\text{Transient dipole attraction}}$$

# Potential Evaluation for $PuO_2$

| **Property** | | **Calculated** | **Experimental** | **Δ%** |
|---|---|---|---|---|
| **Lattice Constant** | **$a_0$ (Å)** | 5.398117 | 5.39819[a] | -0.001 |
| **Ionic Distances** | **$Pu^{4+}$ - $Pu^{4+}$ (Å)** | 3.817 | 3.816[b] | 0.026 |
| | **$Pu^{4+}$ - $O^{2-}$ (Å)** | 2.3375 | 2.337[b] | 0.021 |
| | **$O^{2-}$ - $O^{2-}$ (Å)** | 2.6991 | 2.698[b] | 0.041 |
| **Elastic Constant Matrices** | **$C_{11}$ (GPa)** | 408.557 | 430.6[b] | -5.119 |
| | **$C_{12}$ (GPa)** | 130.2112 | 128.4[b] | 1.411 |
| | **$C_{44}$ (GPa)** | 67.3014 | 67.3[b] | 0.002 |
| **Bulk Modulus** | **B (GPa)** | 222.99314 | - | - |
| **Shear Modulus** | **K (GPa)** | 84.8231 | - | - |
| **Youngs Moduli** | **Y (GPa)** | 345.6173 | - | - |
| **Static dielectric constant tensor** | **$\varepsilon_0$** | 15.91823 | - | - |
| **High frequency dielectric constant tensor** | **$\varepsilon_\infty$** | 3.22557 | - | - |

**Ref a** *R. Belin, P. Valenza, M. Reynaud, P. Raison J. Appl. Crystallogr., 37 (6) (2004), pp. 1034-1037*
**Ref b** *Meis et al. Materials Science and Engineering: B. 1998; 57(1):52:61*

The potentials used for $PuO_2$ provide agreement with elastic constants and crystallographic data.

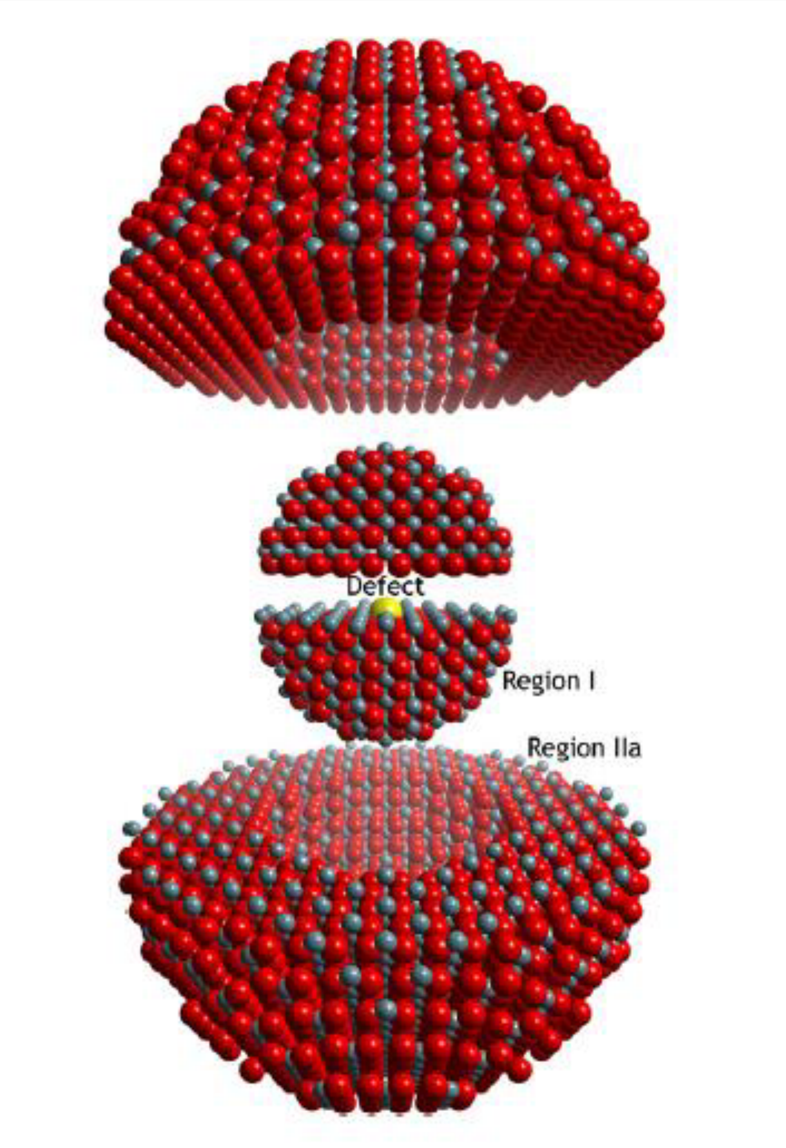
# Mott - Littleton

Divide the defective lattice into two regions:

**Region I:** containing the defect and a certain number of immediate neighbours

**Region IIa:** containing the rest of the crystal lattice, described by a continuum approximation

| | Size (Å) | Number of Ions |
|---|---|---|
| **Region I** | 14 | 1888 |
| **Region IIa** | 28 | 12344 |



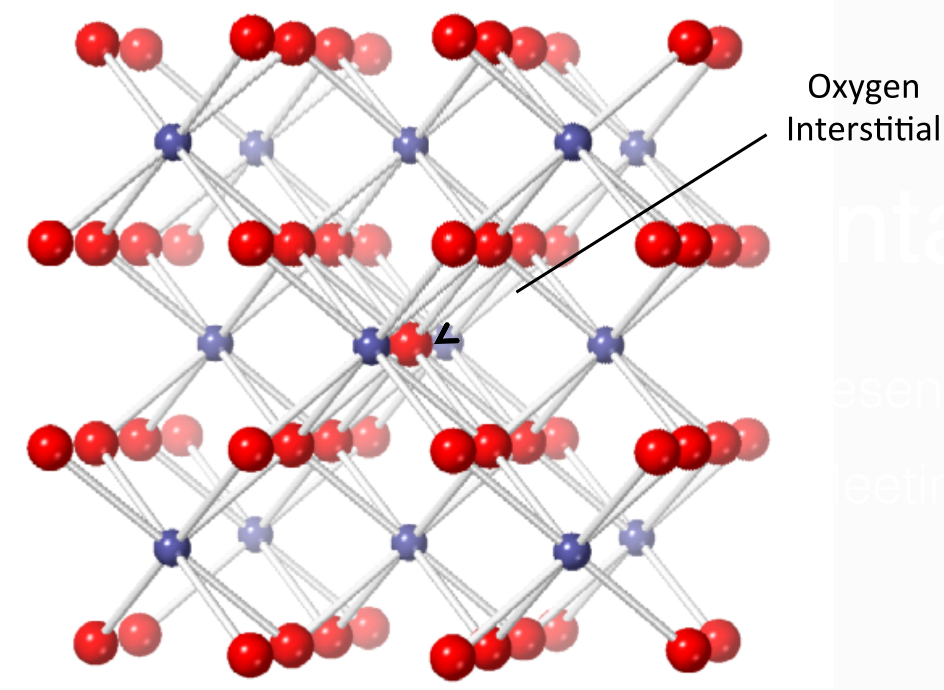
***Ref:*** *Read MSD, Jackson RA. Journal of Nuclear Materials. 2010;**406(3)**:293*

# Defect Formation Energies for Isolated Defects

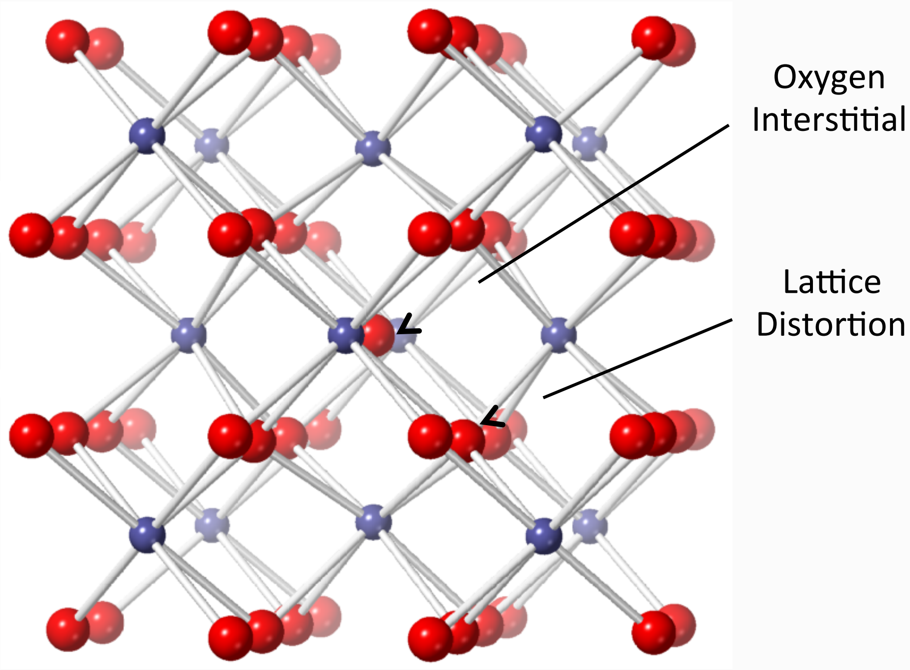
| Point Defect | | Position | Formation energy (eV) |
|---|---|---|---|
| **Plutonium vacancy** | $V_{Pu}^{''''}$ | (0, 0, 0) | 80.03 |
| **Oxygen vacancy** | $V_{O}^{\bullet\bullet}$ | (1/4, 1/4, 1/4) | 17.09 |
| **Plutonium interstitial** | $Pu_{i}^{\bullet\bullet\bullet\bullet}$ | (1/2, 1/2, 1/2) | -59.97 |
| **Oxygen interstitial** | $O_{i}^{''}$ | (1/2, 1/2, 1/2) | -11.75 |

Plutonium and Oxygen interstitials were placed in octahedral holes.

# Oxygen Interstitial Visualisation



Unrelaxed structure



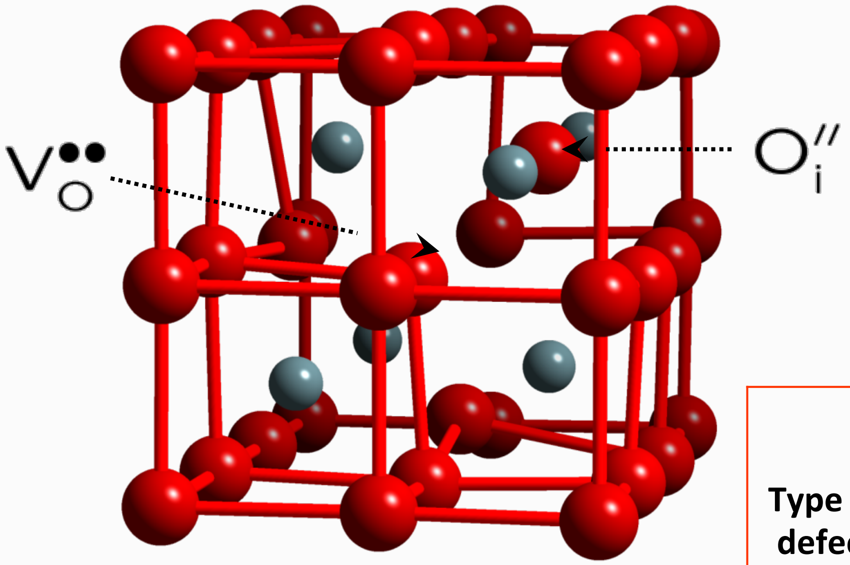
Relaxed structure

# Unbound Defect Formation Energies

| Defect | Formation reaction | Formation Energy (eV/Defect) |
|---|---|---|
| **Schottky Trio** | $Pu_{Pu}^{x} + 2O_{o}^{x} \rightleftharpoons V_{Pu}^{''''} + 2V_{o}^{\bullet\bullet} + PuO_{2\,(surface)}$ | 3.545 |
| **Oxygen Frenkel Pair** | $O_{o}^{x} \rightleftharpoons V_{o}^{\bullet\bullet} + O_{i}^{''}$ | 2.668 |
| **Plutonium Frenkel Pair** | $Pu_{Pu}^{x} \rightleftharpoons V_{Pu}^{''''} + Pu_{i}^{\bullet\bullet\bullet\bullet}$ | 10.029 |

The oxygen Frenkel pair is calculated to be the most energetically favourable.

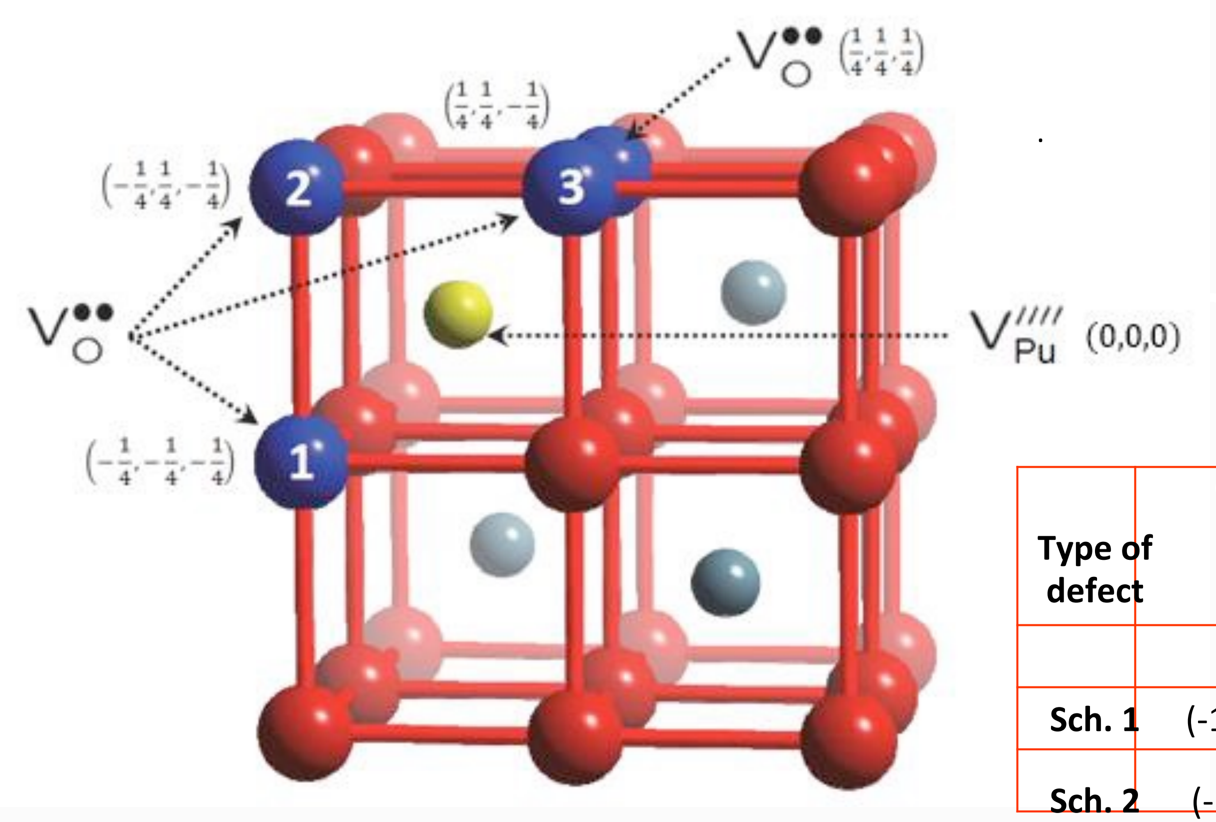
# Oxygen Frenkel Pair Configurations



To prevent recombination, oxygen defects are separated by a plutonium ion.

| Type of defect | $V^{\cdot\cdot}_O$ position | $O_i''$ position | Formation energy (eV) | Formation energy (eV/ Defect) | Binding energy (eV/ Defect) |
|---|---|---|---|---|---|
| **OFP 1** | (-1/4, -1/4, -1/4) | (1/2, 1/2, 1/2) | 4.138 | 2.069 | -0.599 |
| **OFP 2** | (-1/4, -1/4, 1/4) | (1/2, 1/2, 1/2) | 4.2321 | 2.116 | -0.552 |

# Schottky Defect Configurations



Compared the three different Schottky configurations.

| Type of defect | Second $V_O^{\cdot\cdot}$ position | Formation energy (eV) | Formation energy (eV/ Defect) | Binding energy (eV/ Defect) |
|---|---|---|---|---|
| | | | | |
| **Sch. 1** | (-1/4, -1/4, -1/4) | 109.363 | 1.929 | -1.616 |
| **Sch. 2** | (-1/4, 1/4, -1/4) | 109.369 | 1.931 | -1.614 |
| **Sch. 3** | (-1/4, 1/4, 1/4) | 109.916 | 2.114 | -1.432 |

***Ref:*** *Read MSD, Jackson RA. Journal of Nuclear Materials. 2010;**406(3)**:293*

# Intrinsic Defect Energies

| **Defect** | **Formation reaction** | **Defect Formation Energy** | | **Binding Energy (eV/Defect)** |
|---|---|---|---|---|
| | | **Unbound (eV/Defect)** | **Bound (eV/Defect)** | |
| **Schottky Trio** | $Pu_{Pu}^{x} + 2O_{o}^{x} \rightleftharpoons \{V_{Pu}^{''''} : 2V_{o}^{\bullet\bullet}\}^{x} + PuO_{2\,(surface)}$ | 3.545 | 1.929 | -1.616 |
| **Oxygen Frenkel Pair** | $O_{o}^{x} \rightleftharpoons \{V_{o}^{\bullet\bullet} : O_{i}^{''}\}^{x}$ | 2.668 | 2.069 | -0.599 |
| **Plutonium Frenkel Pair** | $Pu_{Pu}^{x} \rightleftharpoons \{V_{Pu}^{''''} : Pu_{i}^{\bullet\bullet\bullet\bullet}\}^{x}$ | 10.029 | 7.868 | -2.161 |

The Schottky trio and oxygen Frenkel pair are the most energetically favourable defects.

# Future work

- ○ Investigate helium migration pathways.
- ○ Simulation of pure surface structures.
- ○ Simulation of defective surface structures.

Presentation title

Name of Presenter, Organisation

Meeting Title

<Date>
<Location>

# Thank you

exm350@student.bham.ac.uk

# Am incorporation into $PuO_2$

Transcend Annual Meeting – April 2019

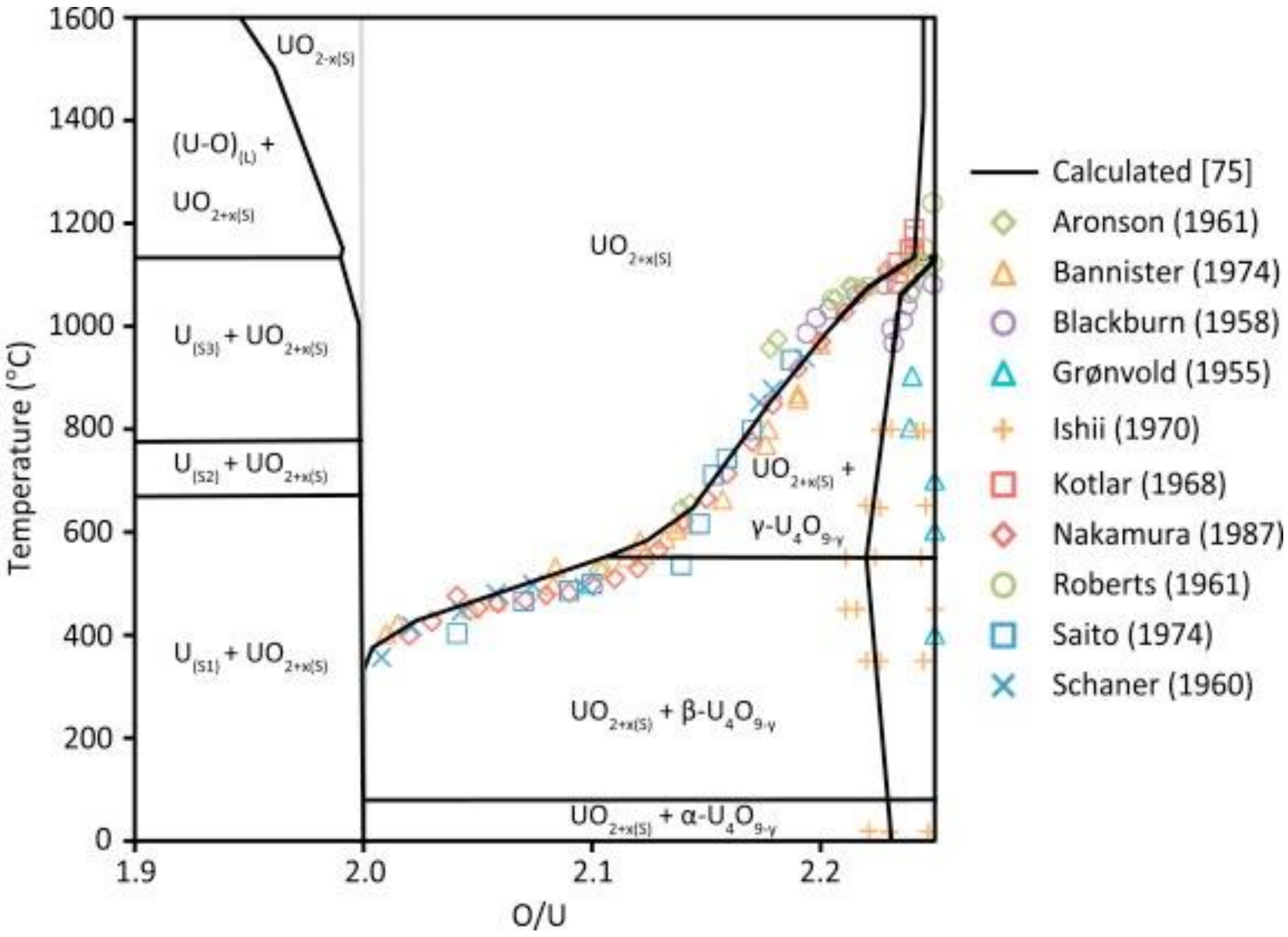
samuel.murphy@lancaster.ac.uk

# Atomistic simulation of Am incorporation into $PuO_2$ (TRANSCEND)

- This project will use Density Functional Theory (DFT) to understand how the incorporation of Am into $PuO_2$ may contribute to can pressurization.
- Broken down into three steps:
    - Determination of intrinsic defect chemistry of $PuO_2$
    - Determination of mode of Am accommodation in $PuO_2$
    - Examination of the properties of $(Am_x,Pu_{1-x})O_2$ oxides for $x < 0.1$
- Enables determination of the charge state of the Am as a function of its concentration, ultimately, revealing whether $PuO_2$ becomes electrically active during storage and informs us as to whether this contributes to pressurization.

# Non-stoichiometry in $UO_2$

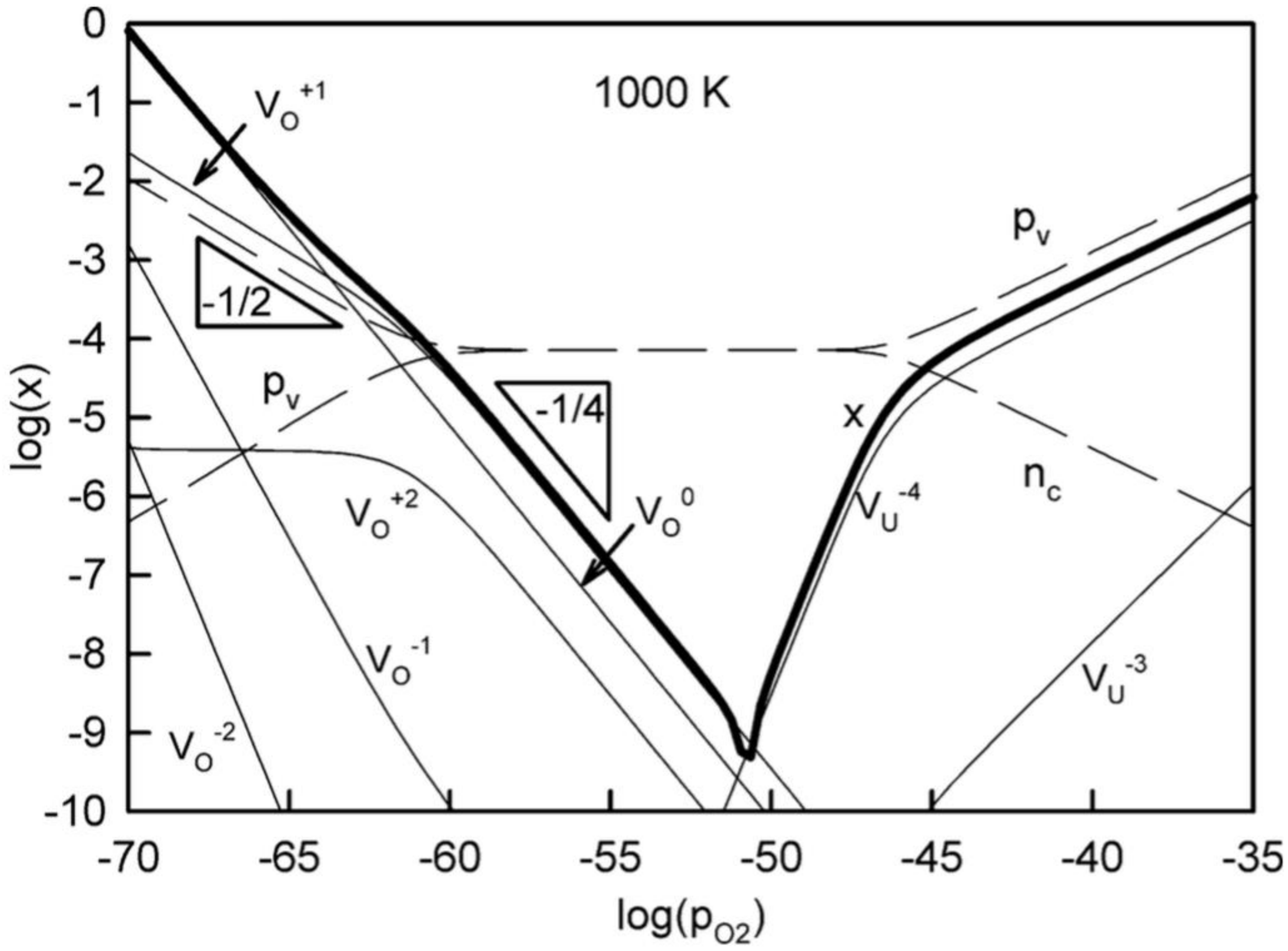
- Fission product solubility and mobility in the fuel depends on the availability of point defects, such as vacancies and interstitials.
- As the uranium is burnt up the fuel moves from being $UO_2$ to $UO_{2+x}$.



Uranium-oxygen phase diagram

# Non-stoichiometry in $UO_2$

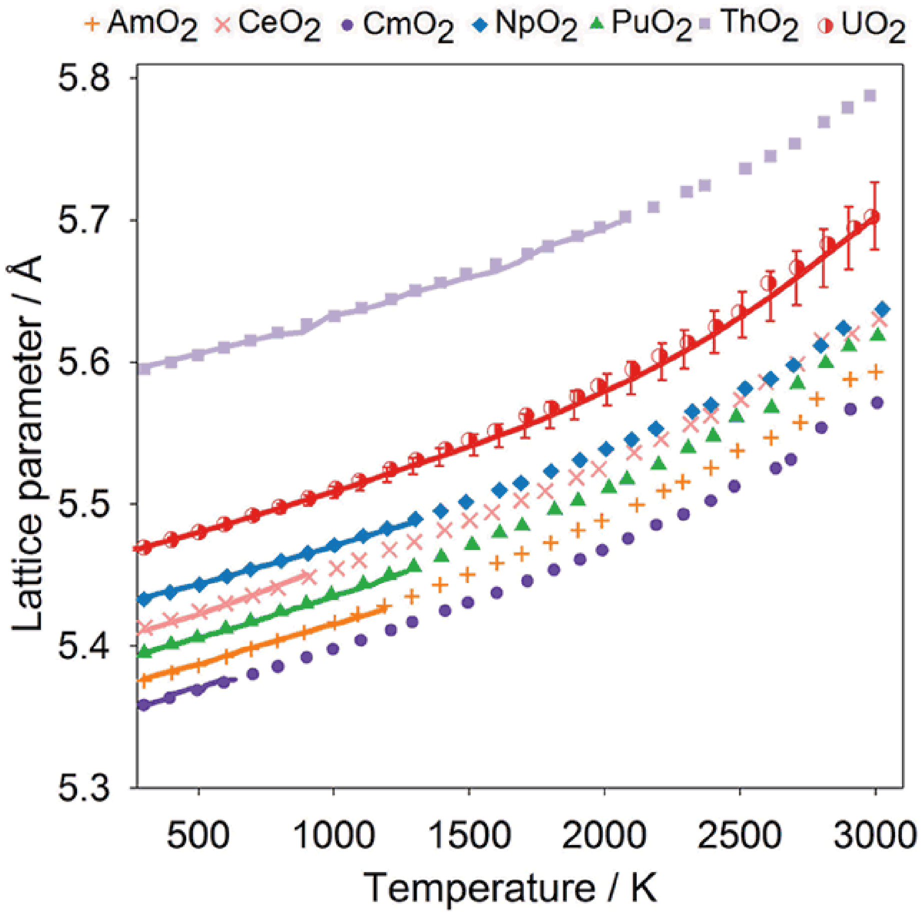
- Experimental observations predict that in the hyperstochiometric regime ($UO_{2+x}$), oxygen interstitial defects are dominant, however, Brouwer diagrams generated from DFT data consistently predict the uranium vacancy to be dominant.



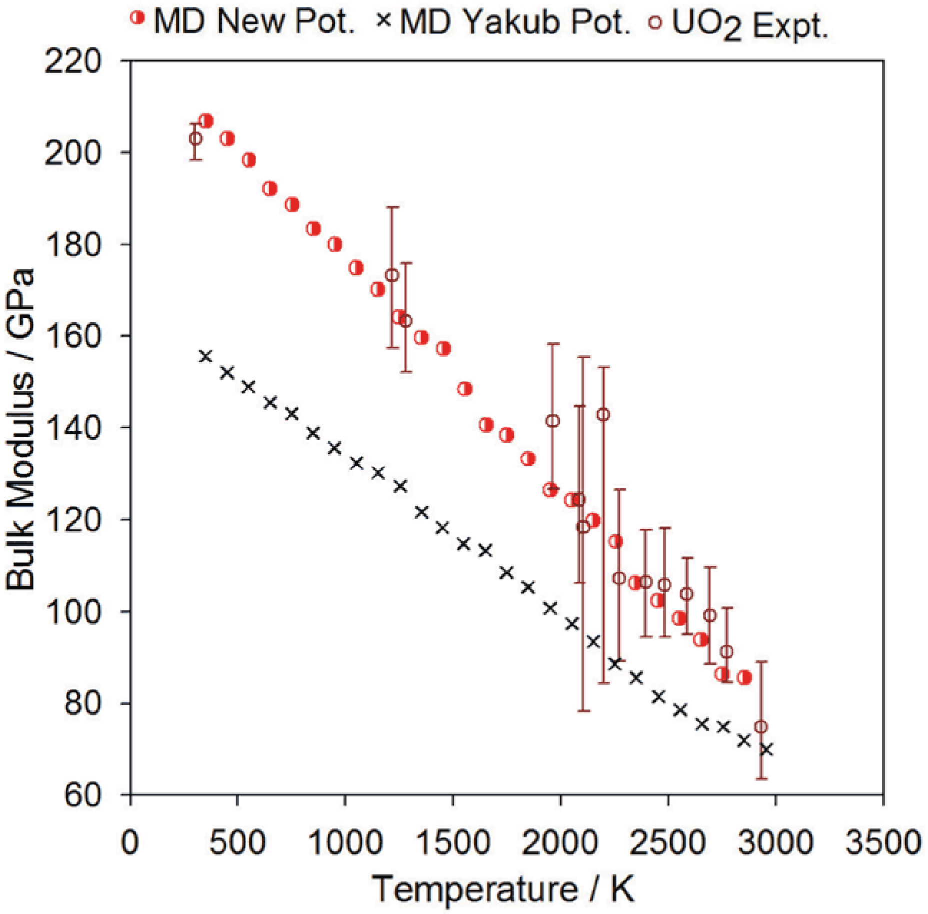
Brouwer diagram for $UO_2$ constructed from defect energies calculated using PBE0 hybrid functionals (PRB 83 (2011) 184107).

# What are we missing?

- In the point defect model temperature only enters the calculation via the chemical potentials, and so vibrational contributions to the free energy are ignored.
- Can we have a go at incorporating these effects?
- Phonon calculations for defect containing supercells using DFT are computationally prohibitive, but perhaps we can use an empirical pair potential?



Lattice parameters of the actinide oxides using the CRG potential (Cooper *et al*. J. Phys. Condens. Matter 26 (2014) 105401.



Bulk modulus for $UO_2$ using the CRG potential (Cooper *et al*. J. Phys. Condens. Matter 26 (2014) 105401.

# Some simulation details

- Simulations employed the DFT+U functional in VASP/Abinit.
- U-ramping method of Meredig is applied to ensure we don’t get stuck in metastable state during optimisation.
- Supercells constructed from 2x2x2 unitcells (96 atoms).
- Electrostatic and potential alignment corrections applied to ensure this represents the dilute limit.
- Defect concentrations can be related to the formation energy via:

$$[c] = me^{\left(\frac{-\triangle G_f}{k_B T}\right)}$$

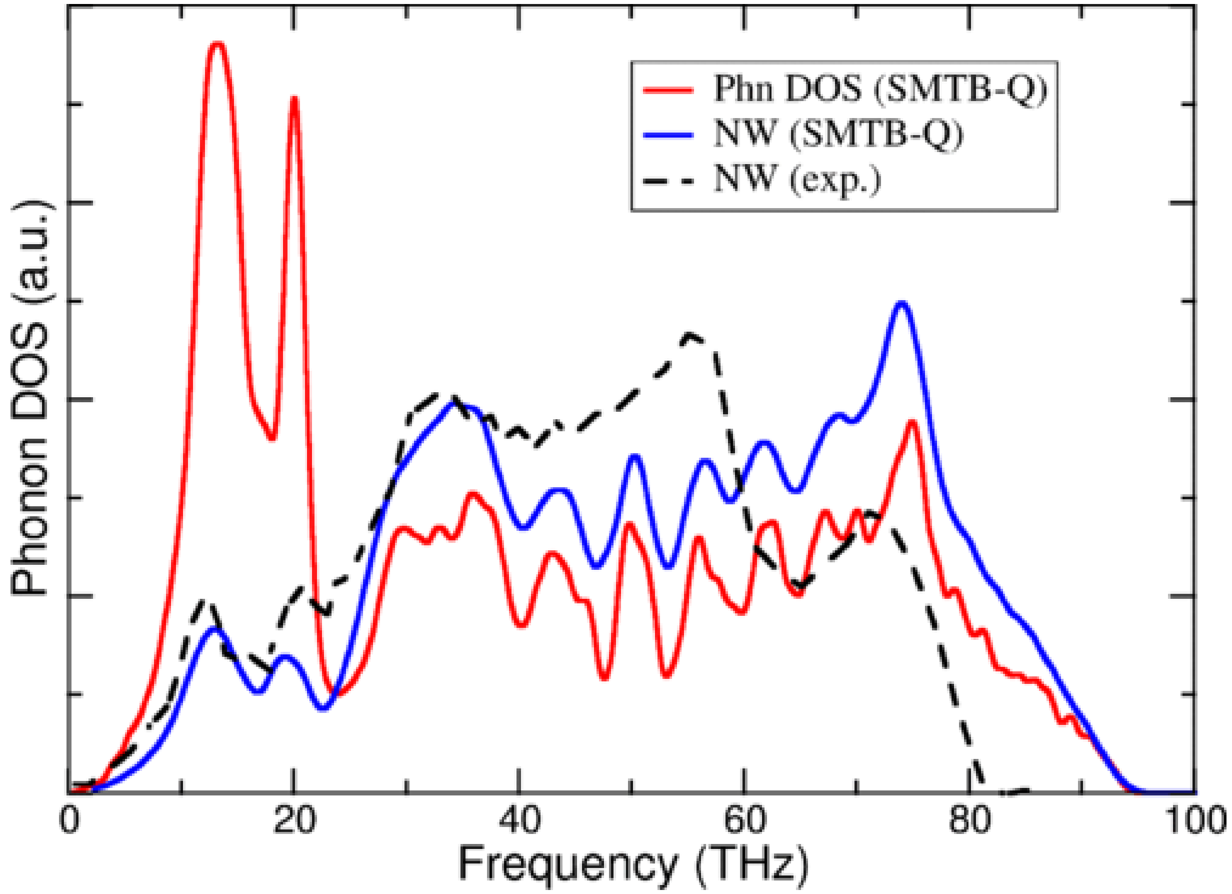
- Where:

$$\triangle G = E^{def} - E^{per} \pm \sum_i n_i \mu_i + q\mu_e - T \triangle S$$

- The vibrational entropy comes from the empirical potential within the harmonic approximation.

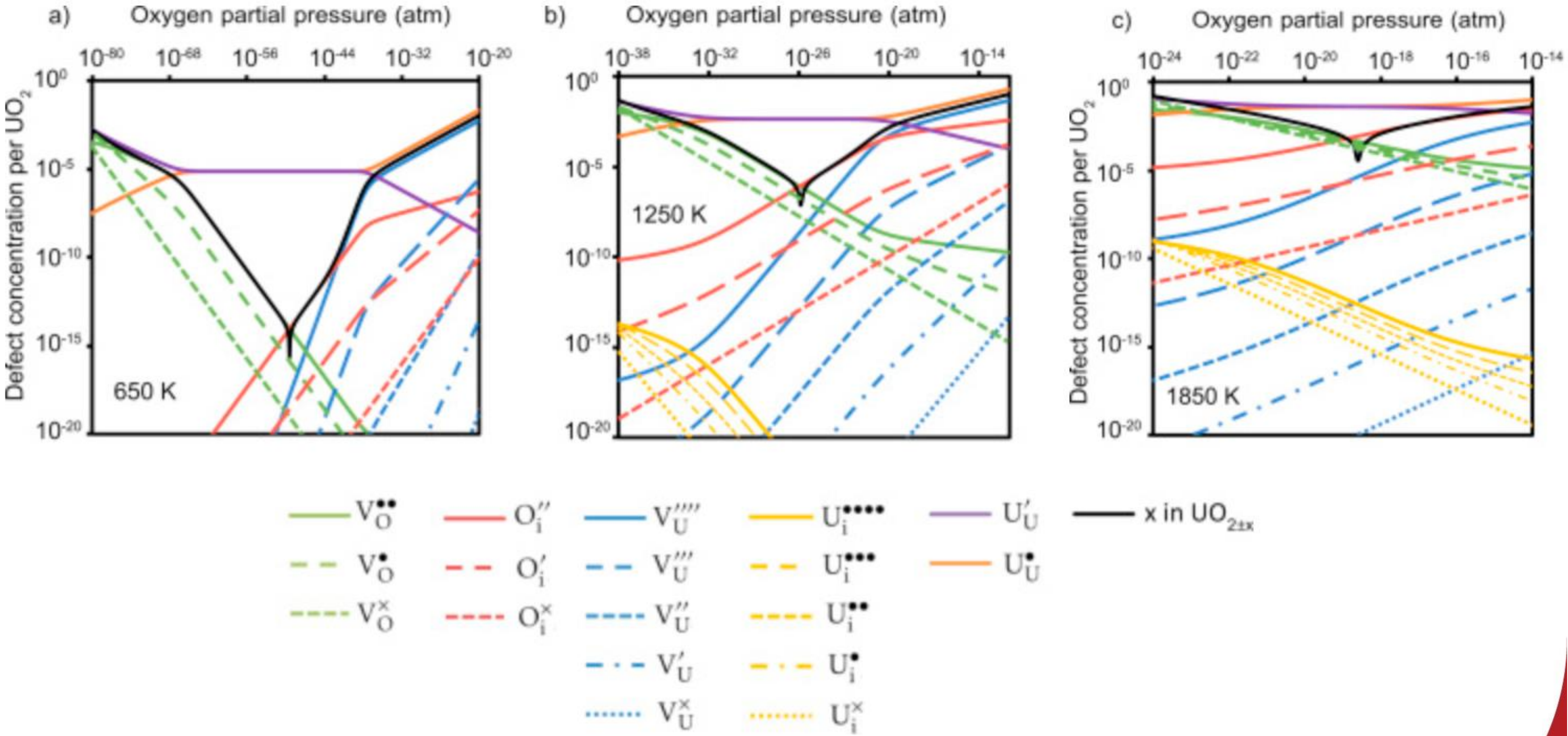
# Phonon density of states for $UO_2$

- In the point defect model temperature only enters the calculation via the chemical potentials, and so vibrational contributions to the free energy are ignored.
- Can we have a go at incorporating these effects?
- Phonon calculations for defect containing supercells using DFT are computationally prohibitive, but perhaps we can use an empirical pair potential?



Phonon density of states using the SMTBQ potential.

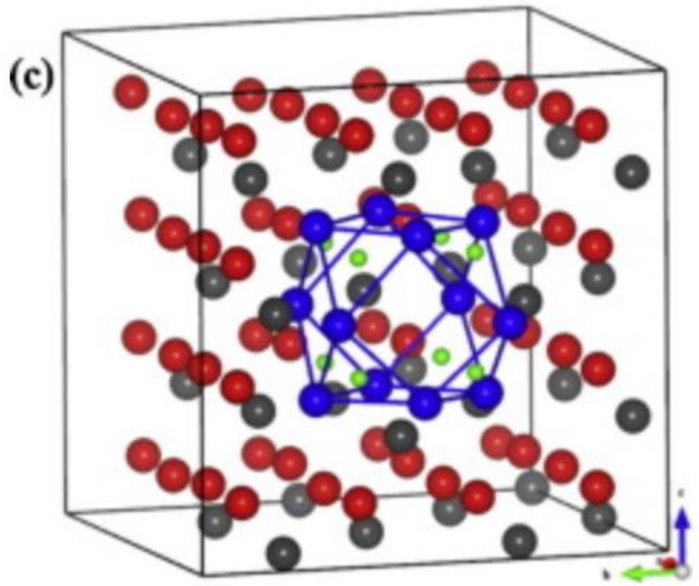
# Including vibrational entropy into Brouwer diagrams



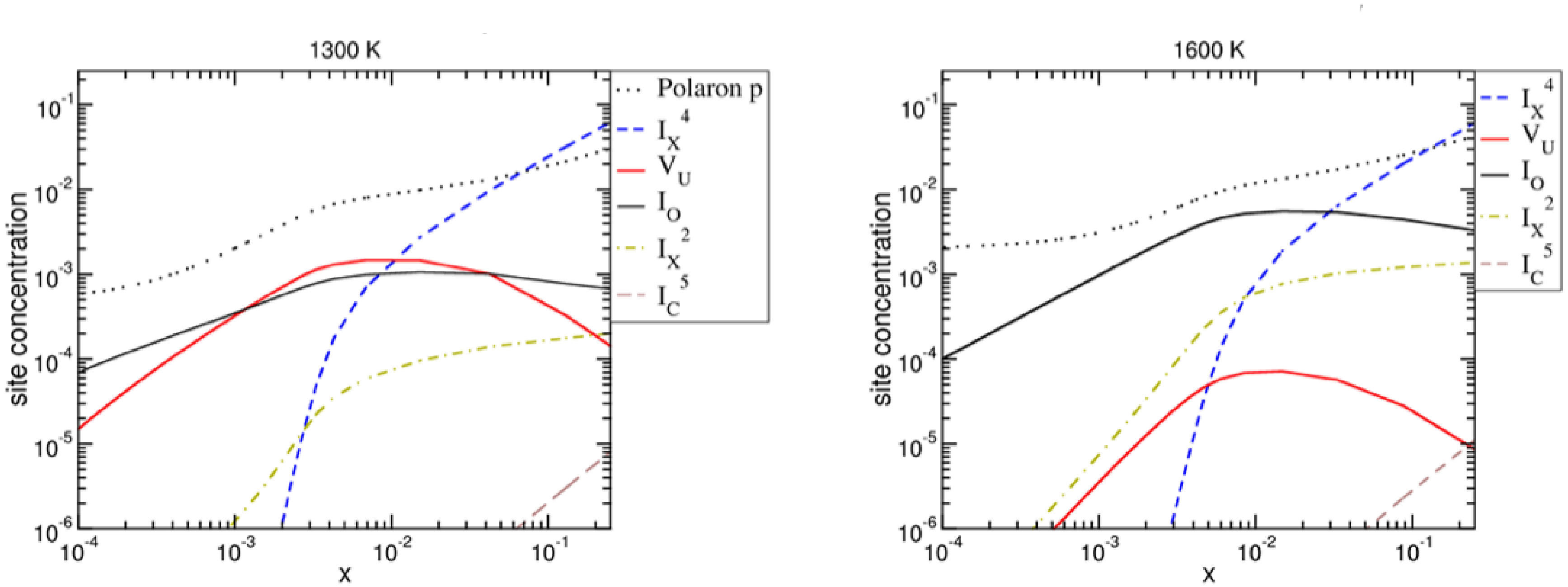
Brouwer diagrams showing the defect concentrations in $UO_2$, including vibrational entropy into the calculation of defect concentrations (Cooper *et al*. JNM 504 (2018) 251).

# Still something missing…….

- At higher deviations from stoichiometry oxygen interstitial defects are expected to cluster together to form clusters.



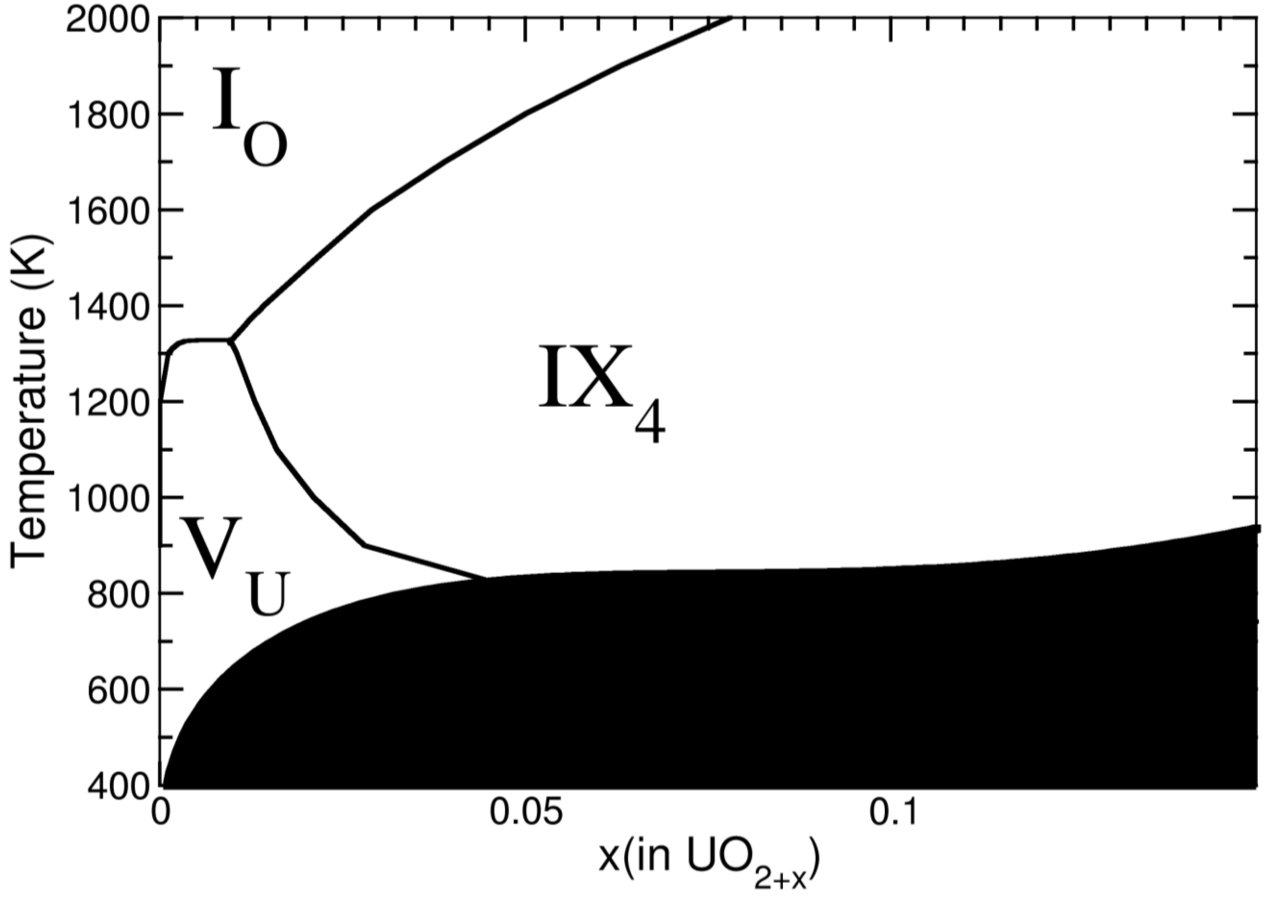
Complex interstitial oxygen interstitial defects in $UO_2$.



Brouwer diagrams showing the hyperstoichiometric $UO_2$ (Soulie PRM 2 (2018) 083607).

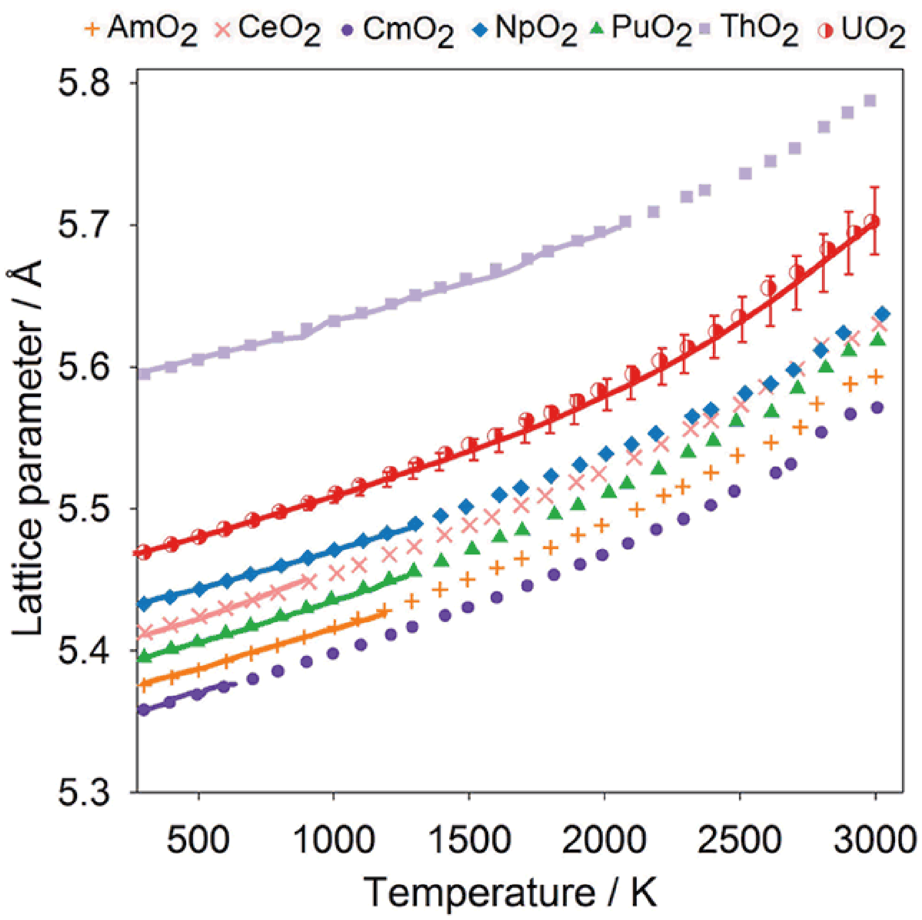
# Summary of $UO_2$ simulations

- The inclusion of vibrational entropy into the calculation of defect concentrations is essential at high temperatures.
- Now DFT data is in much better agreement with experimental observations showing that excess oxygen is indeed accommodated predominantly by oxygen interstitial defects.
- The data also allows us to explain why the uranium diffusivity decreases as the hyper-stoichiometry increases.

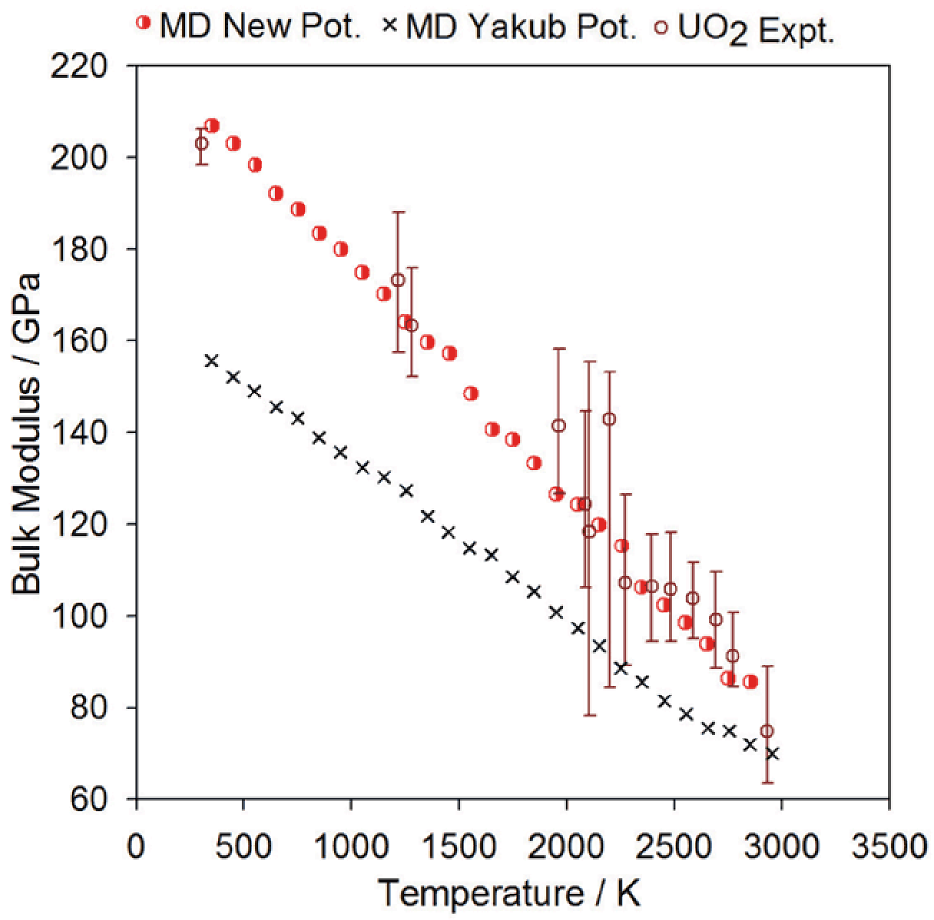


# Am incorporation into $PuO_2$

- If we assume that the Am maintains the 4+ charge state then we can perform molecular dynamics simulations using empirical pair potentials.
- Here we use the Cooper-Rushton-Grimes potential that was developed for the study of mixed oxides.

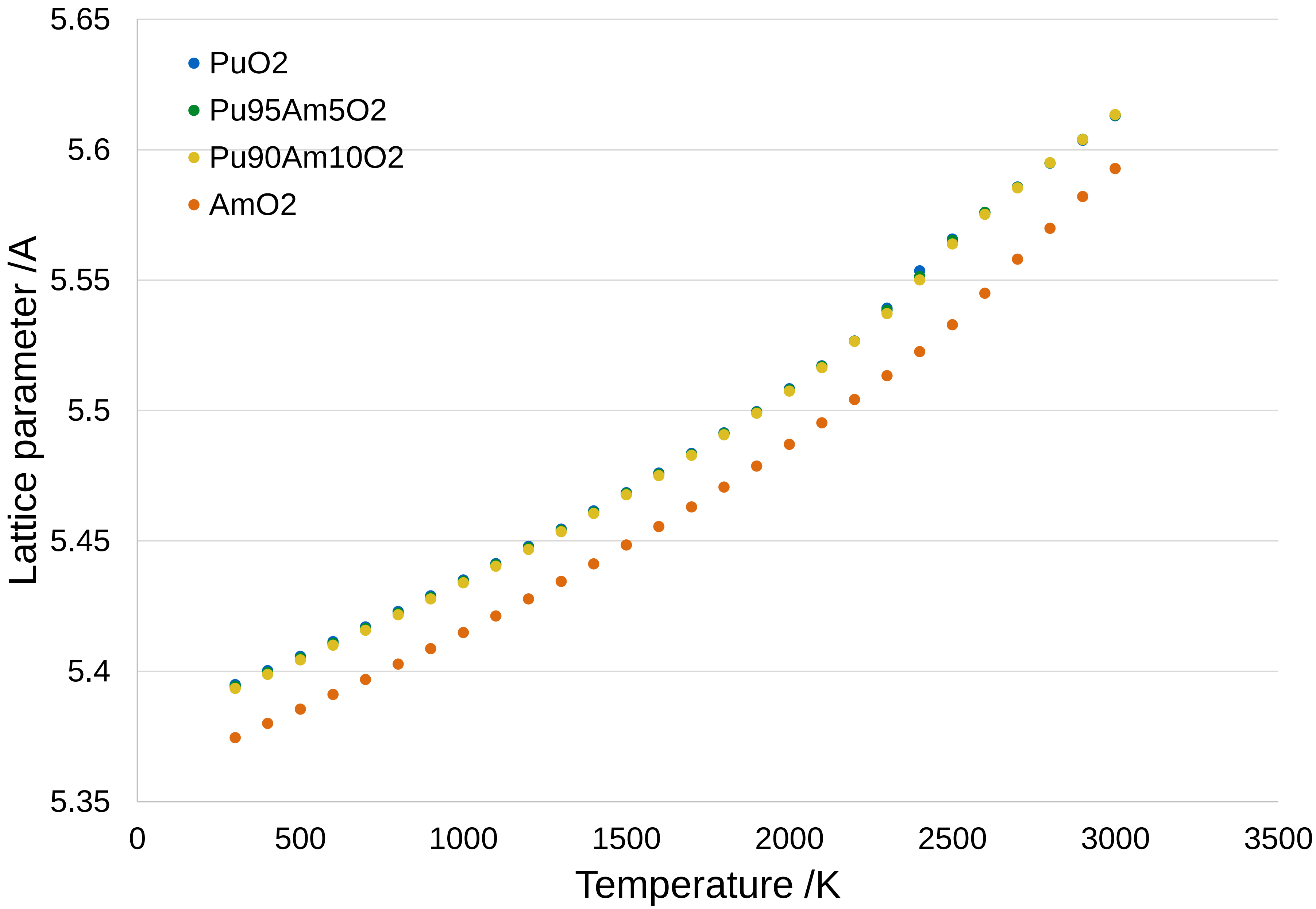


Lattice parameters of the actinide oxides using the CRG potential (Cooper *et al*. J. Phys. Condens. Matter 26 (2014) 105401.



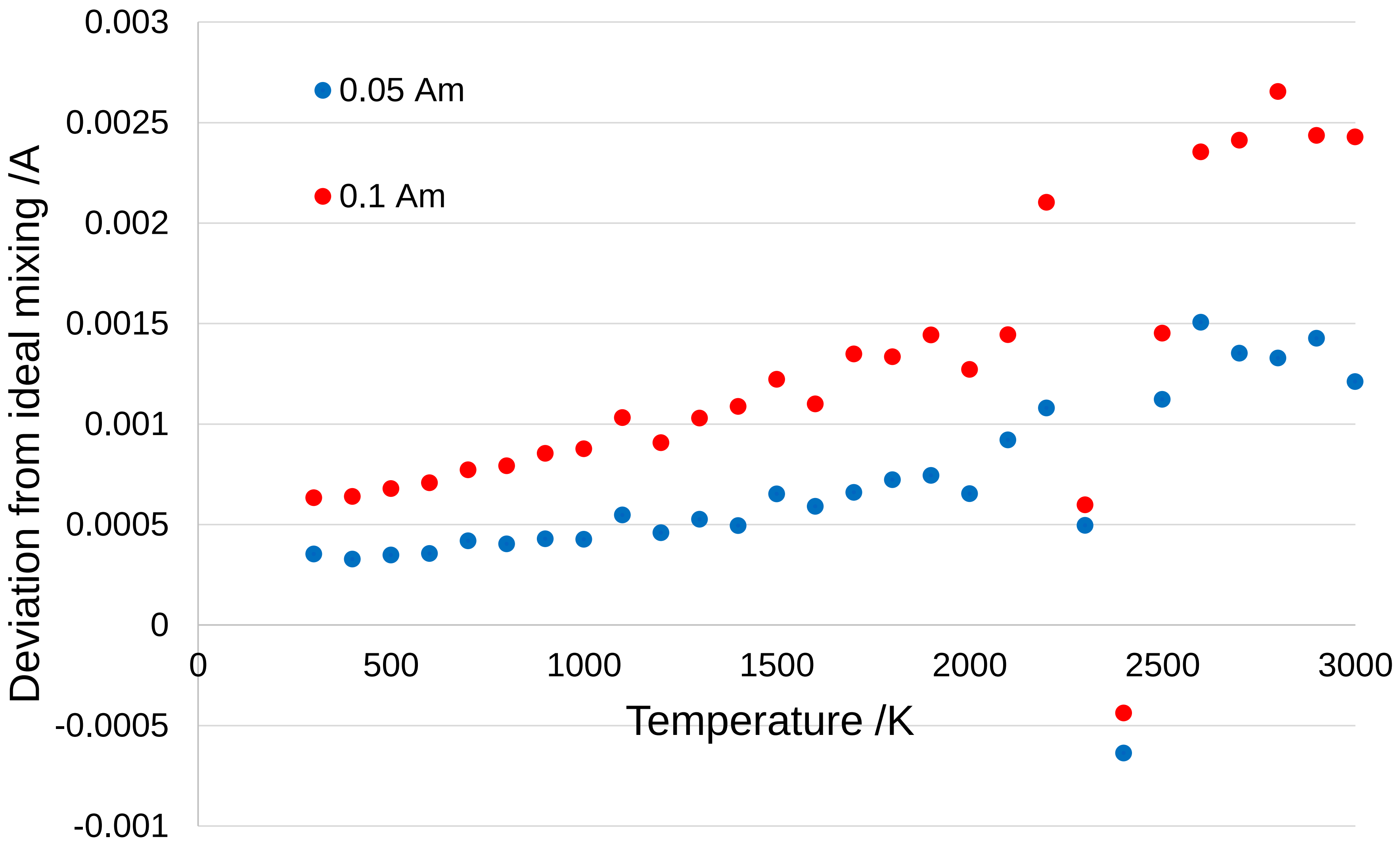
Bulk modulus for $UO_2$ using the CRG potential (Cooper *et al*. J. Phys. Condens. Matter 26 (2014) 105401.

# Am incorporation into $PuO_2$



Lattice parameter of (Pu,Am)O2 as a function of temperature.

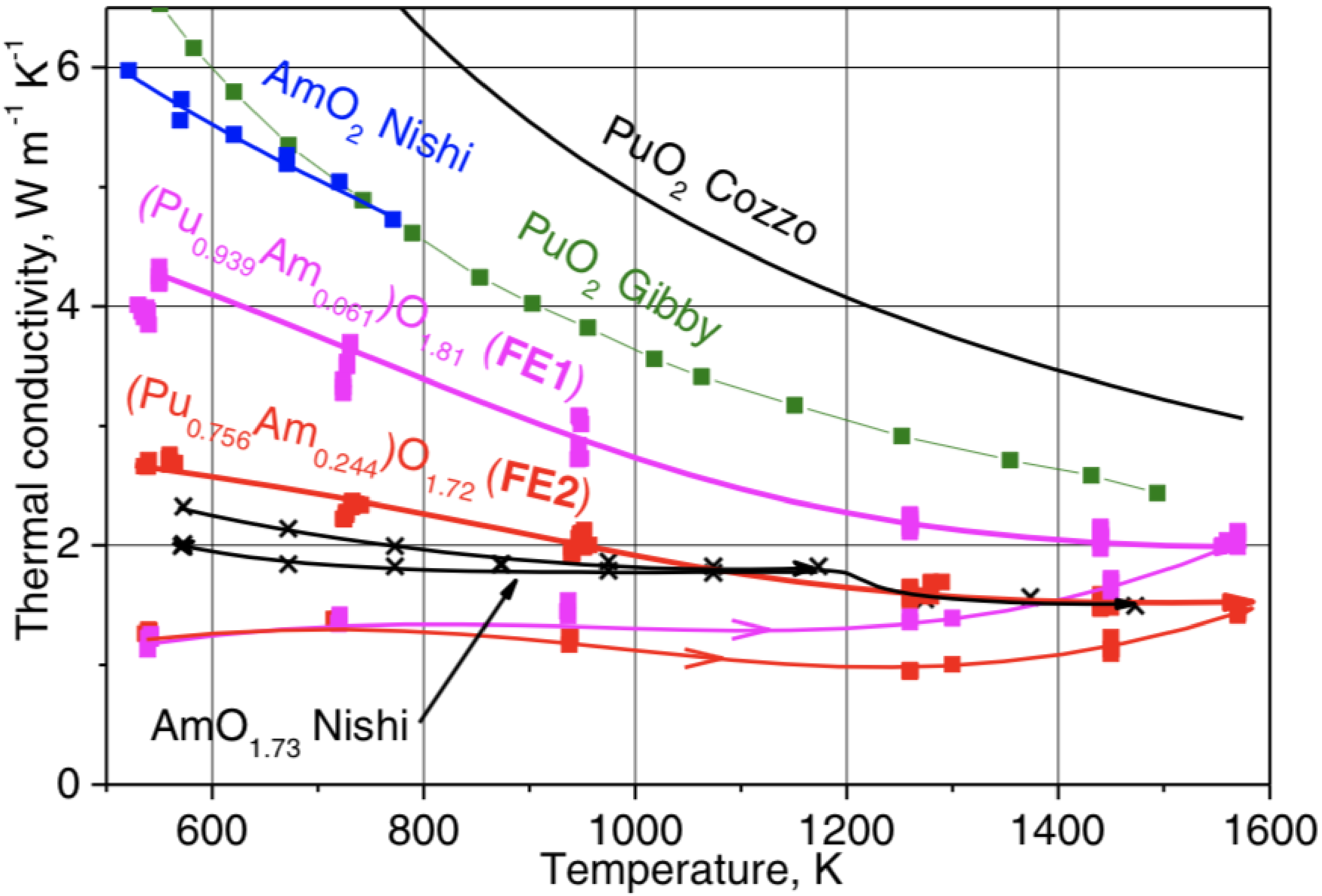
# Am incorporation into $PuO_2$



Deviation from ideal lattice parameter as a function of temperature.

# Thermal conductivity in $(Pu,Am)O_2$

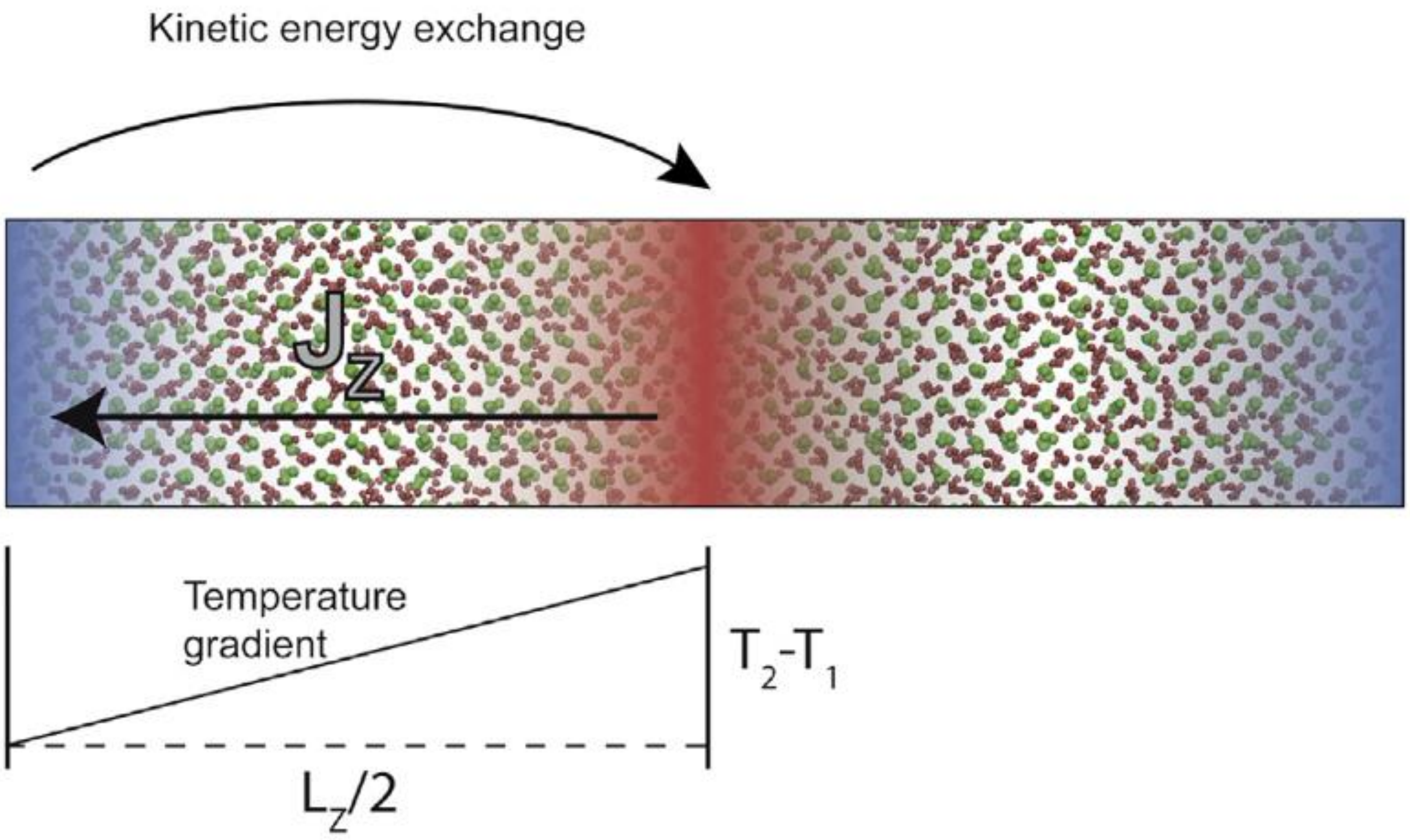
- The experimental picture of thermal conductivity in $(Pu,Am)O_2$ is complex:



Experimental data for thermal conductivity in $(Pu,Am)O_2$ as a function of temperature.

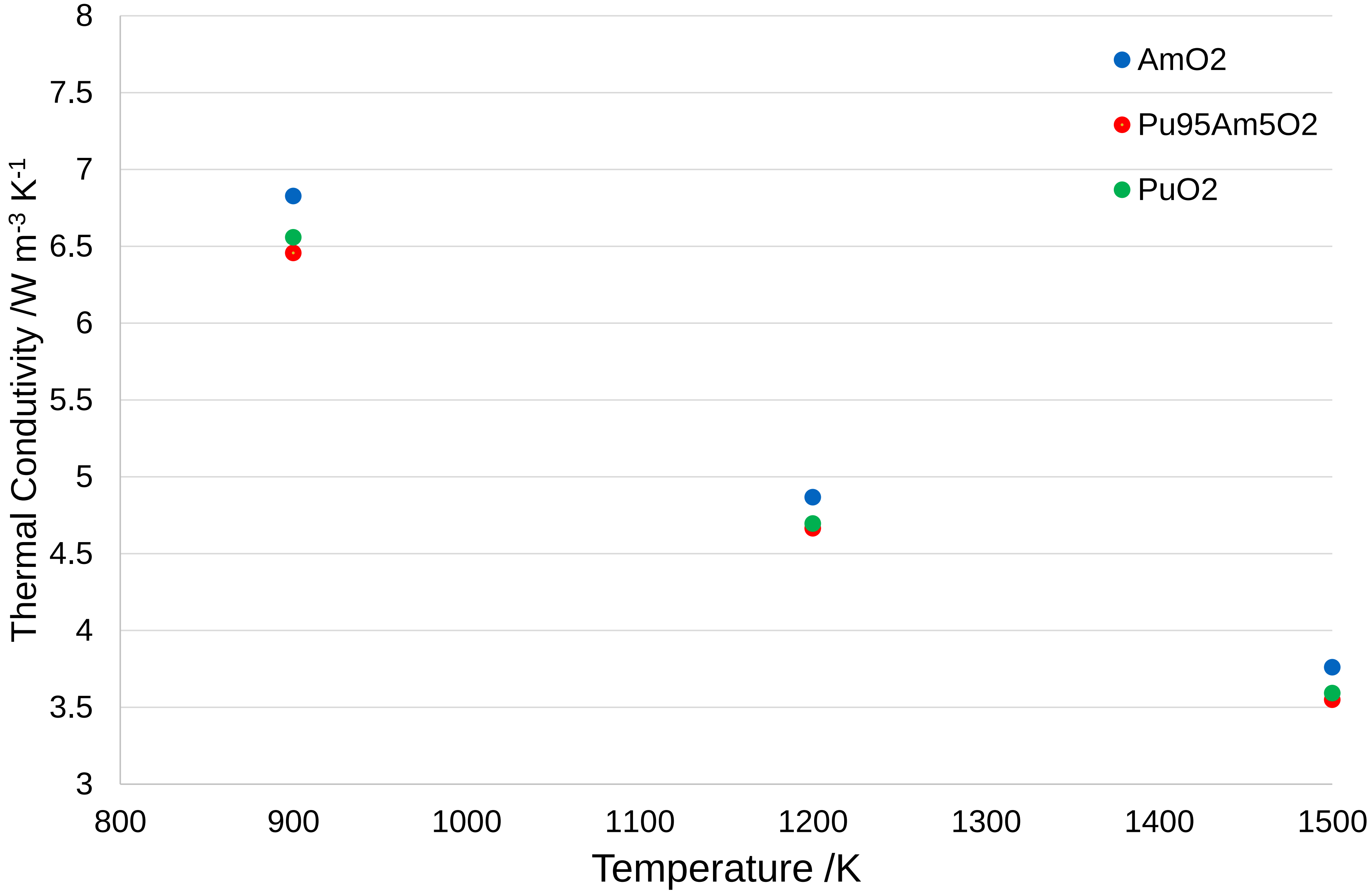
# Thermal conductivity in (Pu,Am)$O_2$

- Thermal conductivity can be calculated using the Non-Equilibrium Molecular Dynamics.



$$\kappa = \frac{J_Z L_Z}{2(T_2 - T_1)}$$

# Thermal conductivity in $(Pu,Am)O_2$



Calculated thermal conductivity in (Pu,Am)O2.

# Summary of $(Pu,Am)O_2$ simulations

- A very small positive deviation in the lattice parameter from ideal mixing.
- The thermal conductivity of stoichiometric $AmO_2$ is predicted to be higher than for $PuO_2$.
- Introduction of Am into $PuO_2$ leads to a small decrease in the thermal conductivity due to phonon scattering.

# Acknowledgments

- Michael Cooper (Los Alamos, US)
- John-Paul Crocombette (CEA Saclay)

# Robotics and TRANSCEND

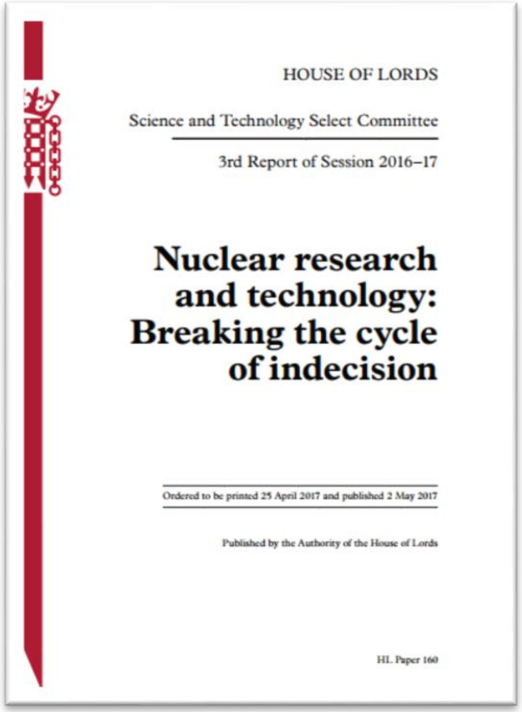
Professor Thomas Scott, University of Bristol

1st Annual Meeting

4 April 2019
Bath

# Reducing costs for nuclear

## An Innovation imperative…



HOUSE OF LORDS

Science and Technology Select Committee

3rd Report of Session 2016–17

**Nuclear research and technology: Breaking the cycle of indecision**

Ordered to be printed 25 April 2017 and published 2 May 2017

Published by the Authority of the House of Lords

HL Paper 160

***"If nuclear is safer it will be more expensive"***

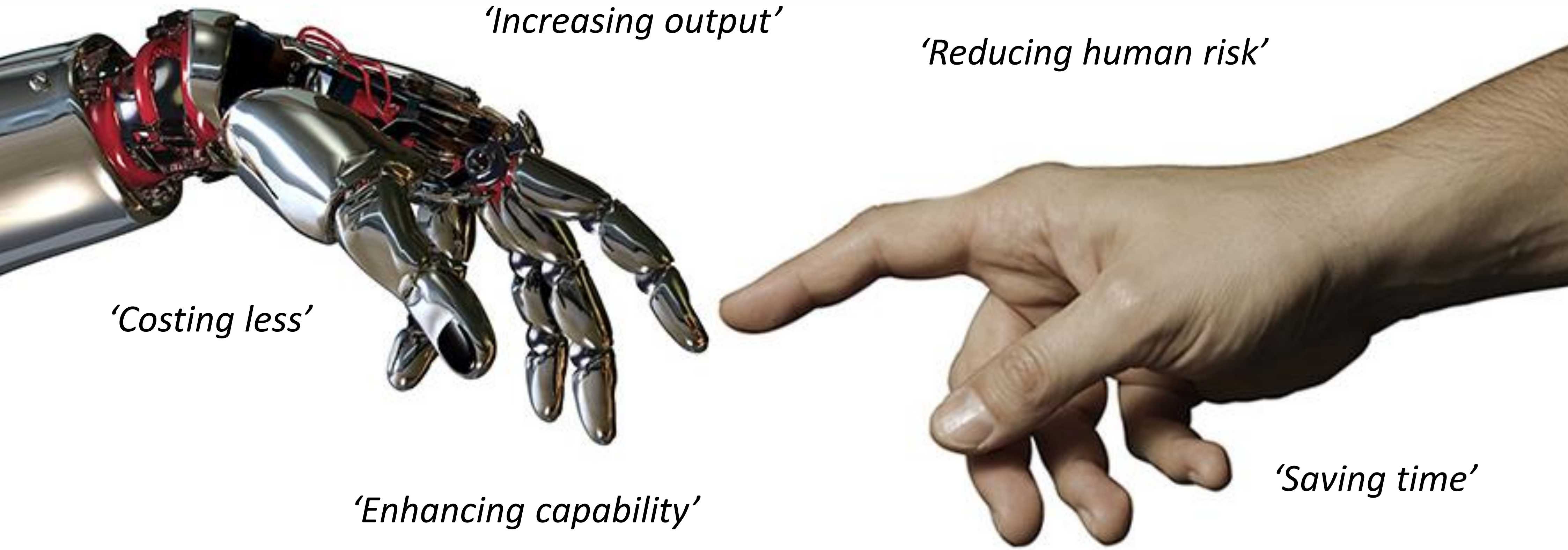
***"Nuclear is either a problem or needs more money"***

***"Nuclear needs to reduce costs to remain competitive"***

Something **MUST** change

# RAI – part of the solution

- Realising the value for robotics in nuclear



*'Increasing output'*

*'Reducing human risk'*

*'Costing less'*

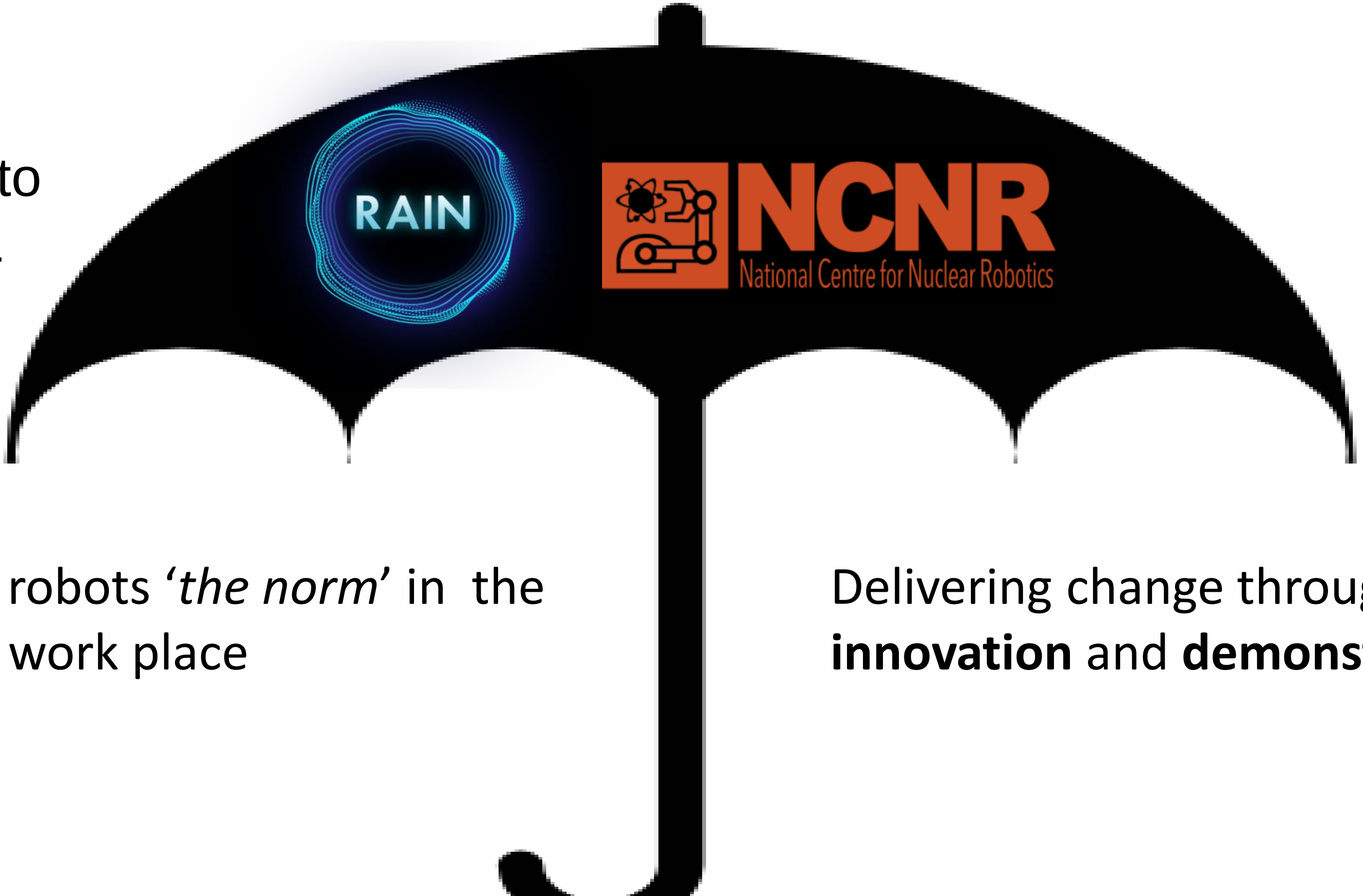
*'Saving time'*

*'Enhancing capability'*

# UK Hubs for Nuclear Robotics

## EPSRC Extreme Environment Robotics Hubs Initiative

Phase 1
Oct 2017 to
April 2021



£100M investment (ISCF, institutions and industry)

Making robots '*the norm*' in the nuclear work place

Delivering change through **innovation** and **demonstration**

# An opportunity for Collaboration

EPSRC
Engineering and Physical Sciences
Research Council

## With TRANSCEND and others!

RAIN

NCNR
National Centre for Nuclear Robotics

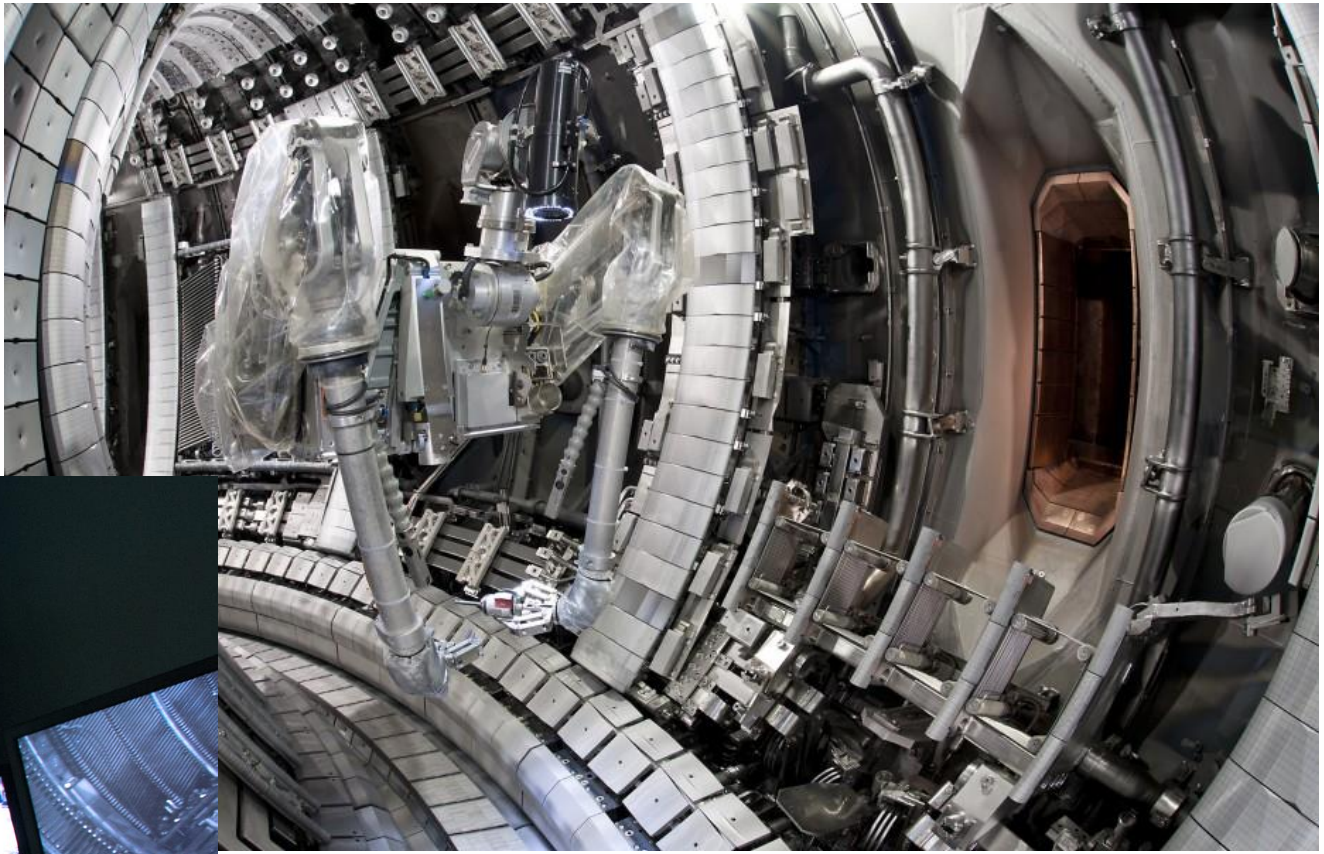
- Substantially supported by industry
- Flexi-funds to facilitate collaboration
- Developing a programme of demonstrators
  (from augmented reality operations to sort-n-seg robots)

Sellafield Ltd
EDF ENERGY
JACOBS
National Nuclear Laboratory
AWE
ROLLS ROYCE
UK Atomic Energy Authority
NUCLEAR AMRC
bp
And many more…

# Teleoperation

Major expertise for CCFE (RACE) in relation to the JET programme – MASCOT and TARM.

Next generation remote handling of nuclear materials



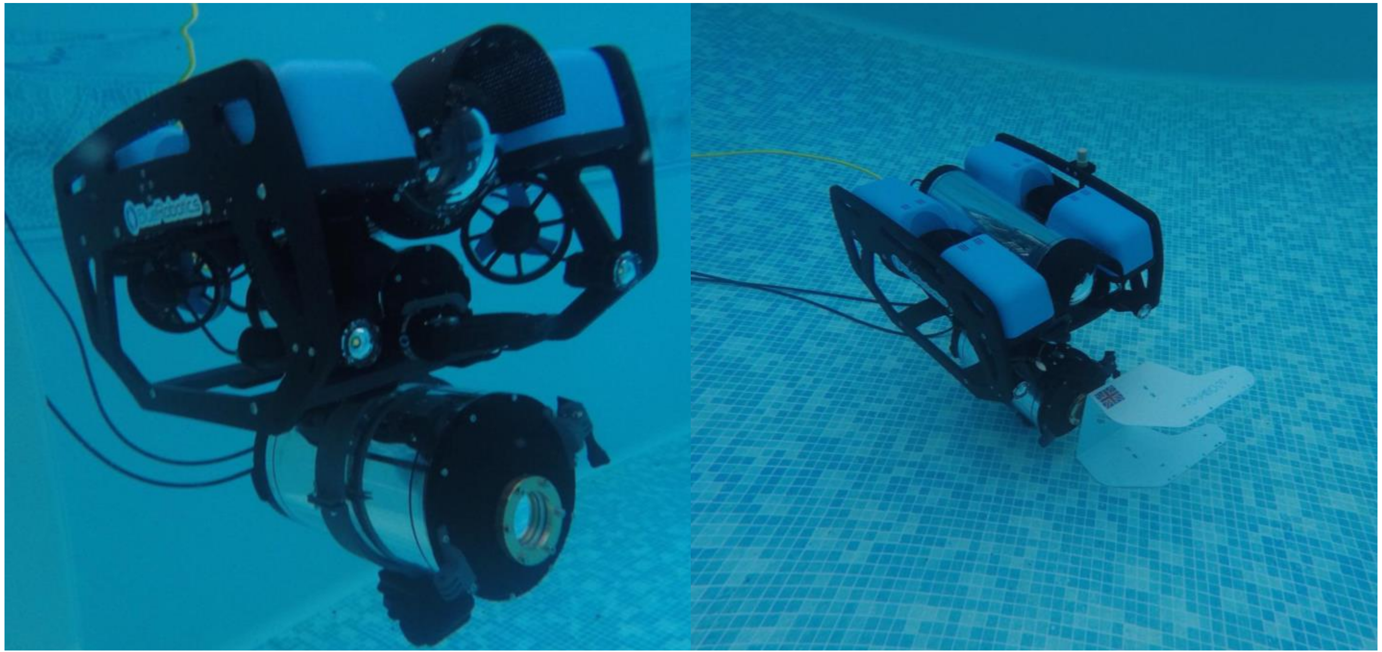
- Virtual and Augmented Reality
- Haptics and Force Feedback
- Human-Robot interactions
- Sensing and Gripping
- AI and robot learning

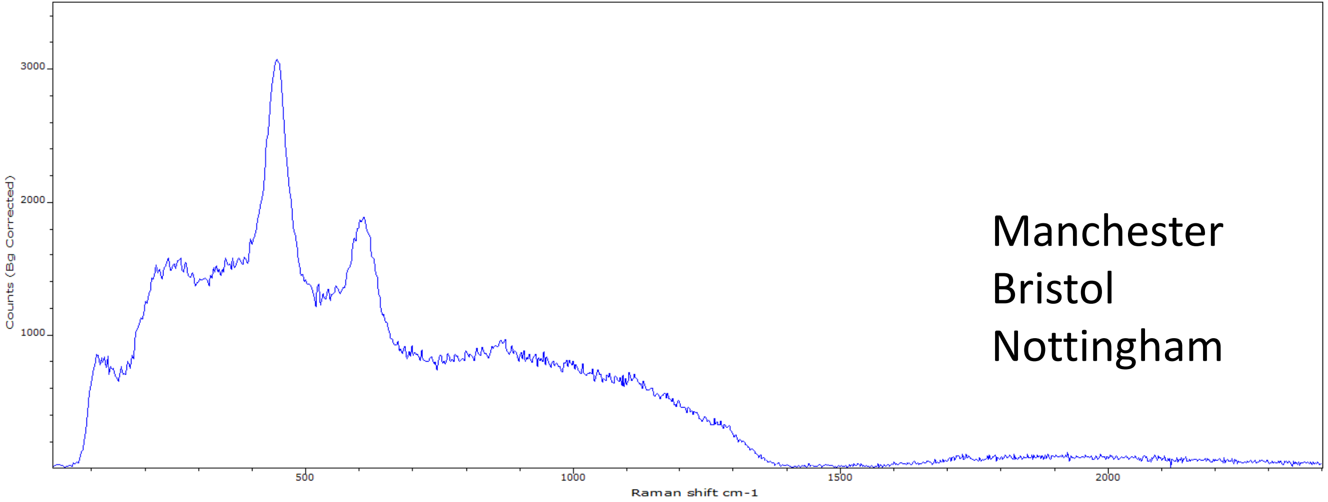
# In-situ Raman and Hyperspectral imaging

Linking with TRANSCEND theme 3 activity on Raman and TRLFS.

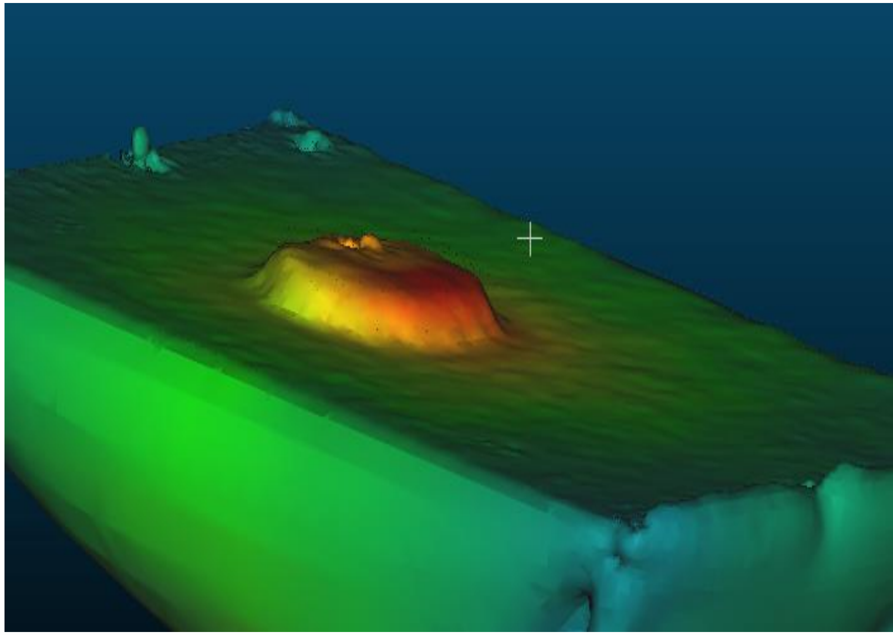
Bristol have developed an underwater Raman and Hyperspectral imaging system (2 different units).

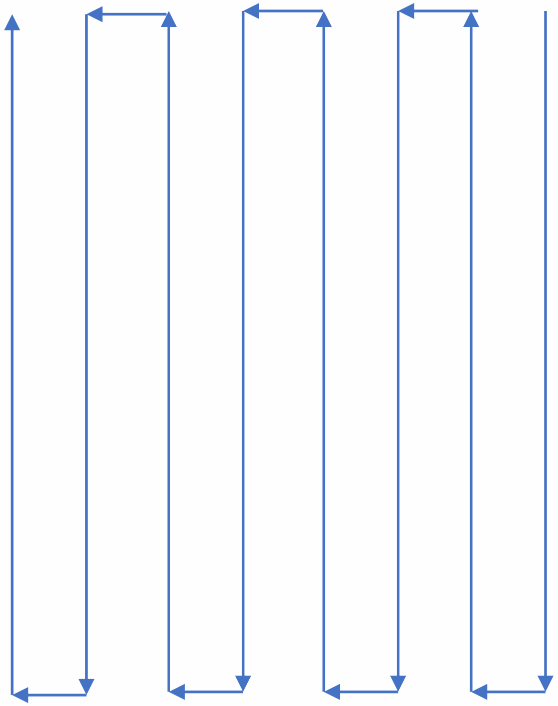
Units work underwater but

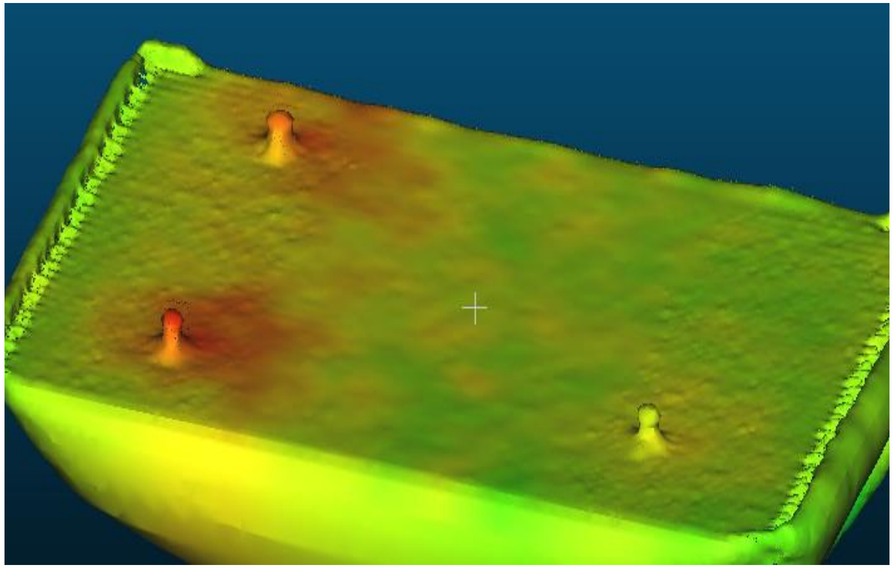




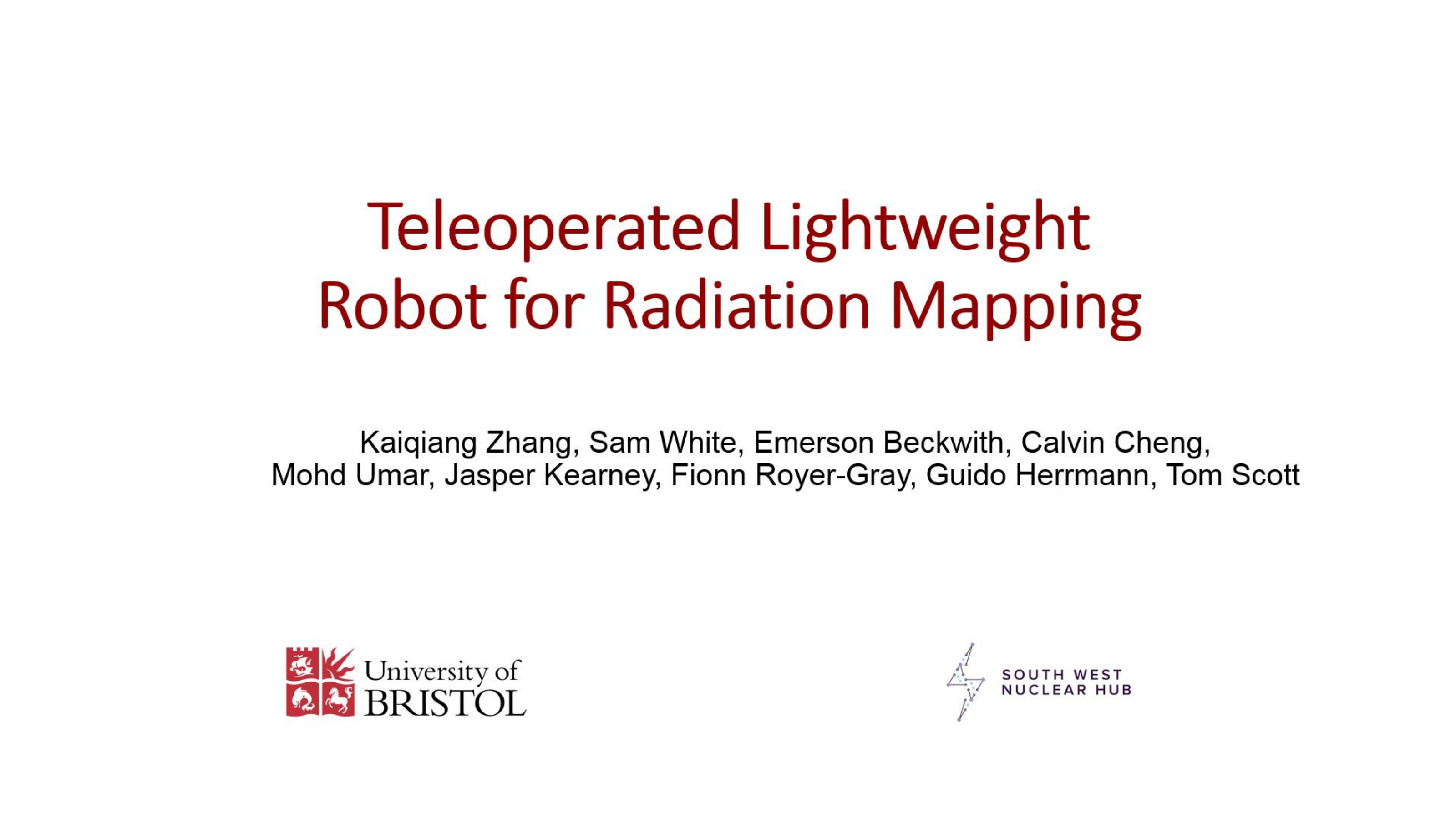
Manchester
Bristol
Nottingham







- Case study: Remote inspection (via teleoperation module + sensor module)



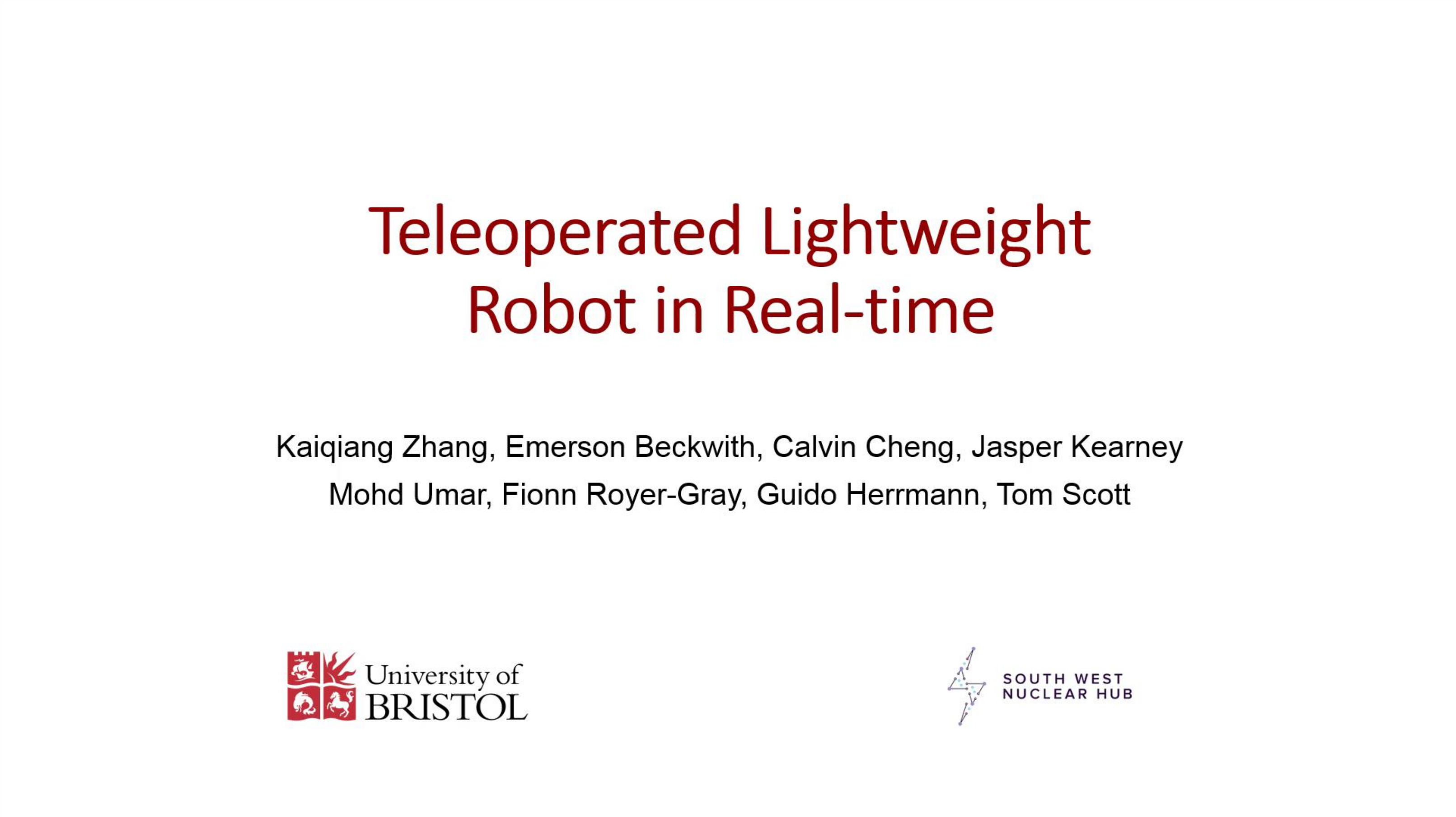
# Teleoperated Lightweight Robot for Radiation Mapping

Kaiqiang Zhang, Sam White, Emerson Beckwith, Calvin Cheng,
Mohd Umar, Jasper Kearney, Fionn Royer-Gray, Guido Herrmann, Tom Scott

University of BRISTOL

SOUTH WEST NUCLEAR HUB

- Current achievement: 100 Hz real-time control aiming for 1kHz real-time control



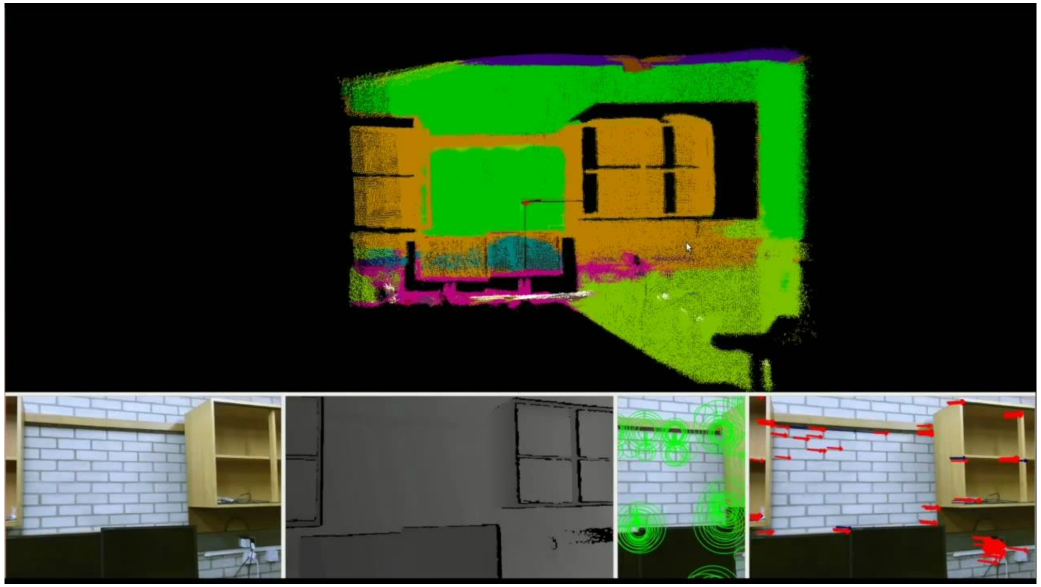
## Teleoperated Lightweight Robot in Real-time

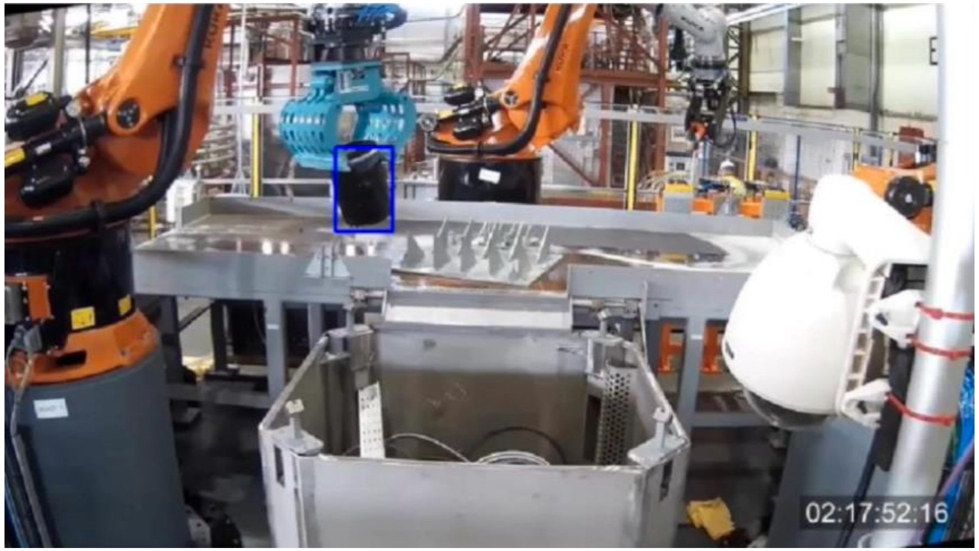
Kaiqiang Zhang, Emerson Beckwith, Calvin Cheng, Jasper Kearney
Mohd Umar, Fionn Royer-Gray, Guido Herrmann, Tom Scott

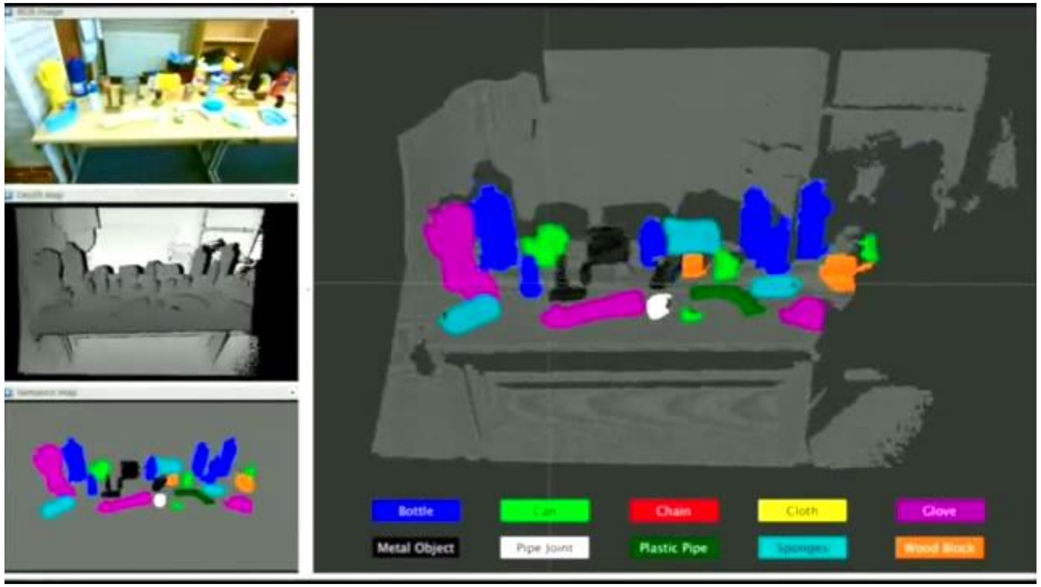
University of BRISTOL

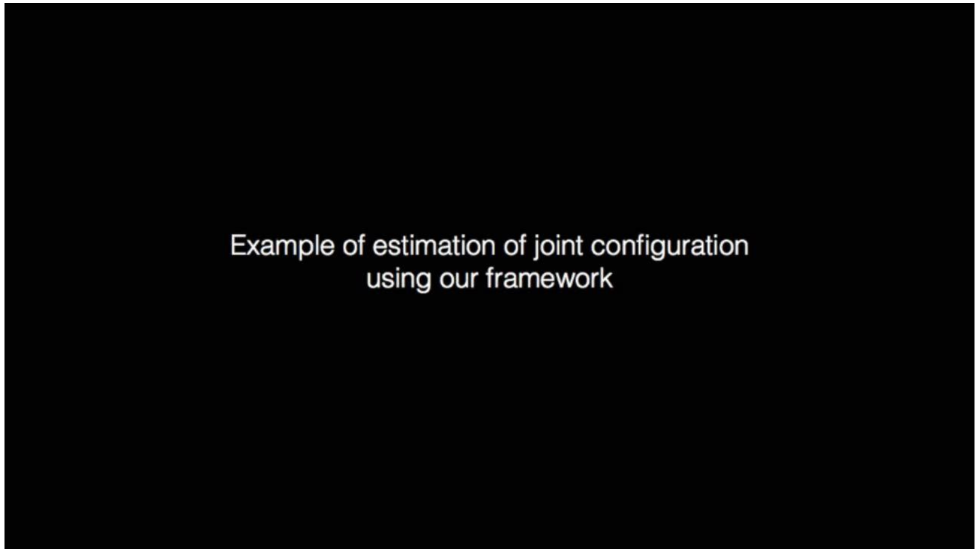
SOUTH WEST NUCLEAR HUB

# Robotic perception and learning (Bham, QML, Lincoln, Essex)







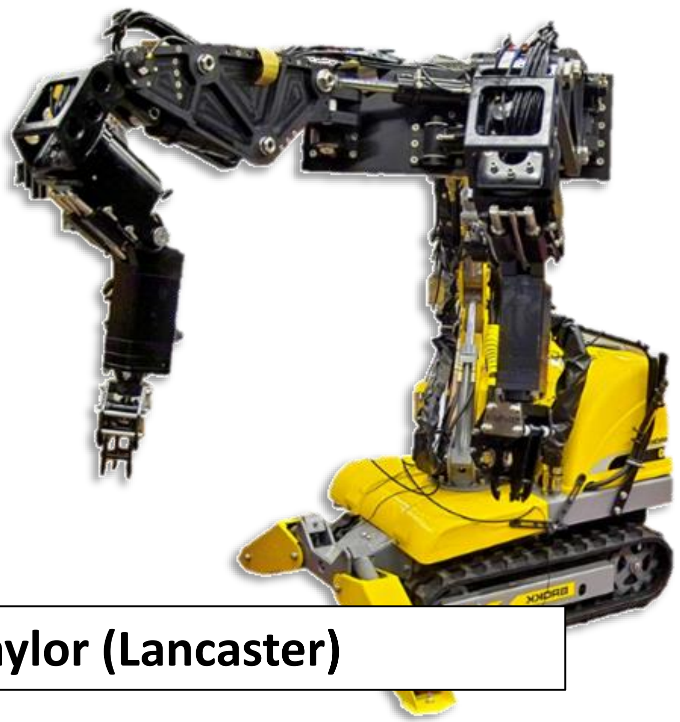


Example of estimation of joint configuration
using our framework

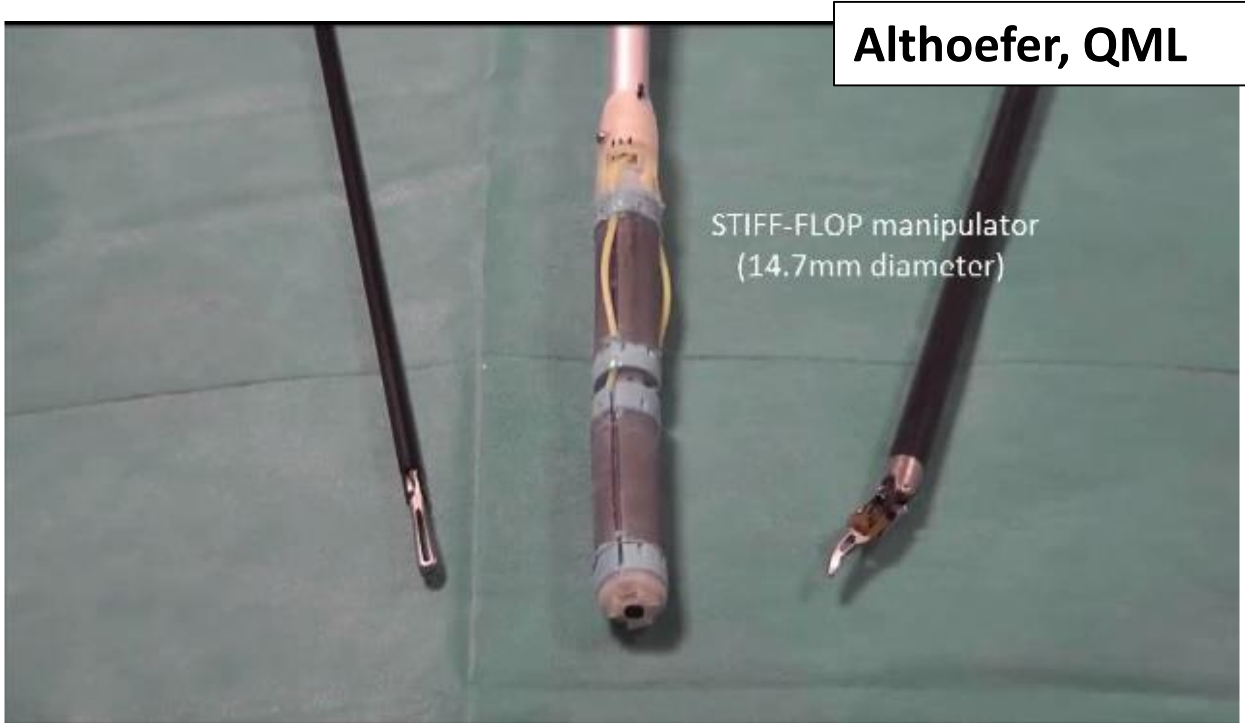
**Demo videos Stolkin, Birmingham**

NCNR
NATIONAL CENTRE FOR NUCLEAR ROBOTICS

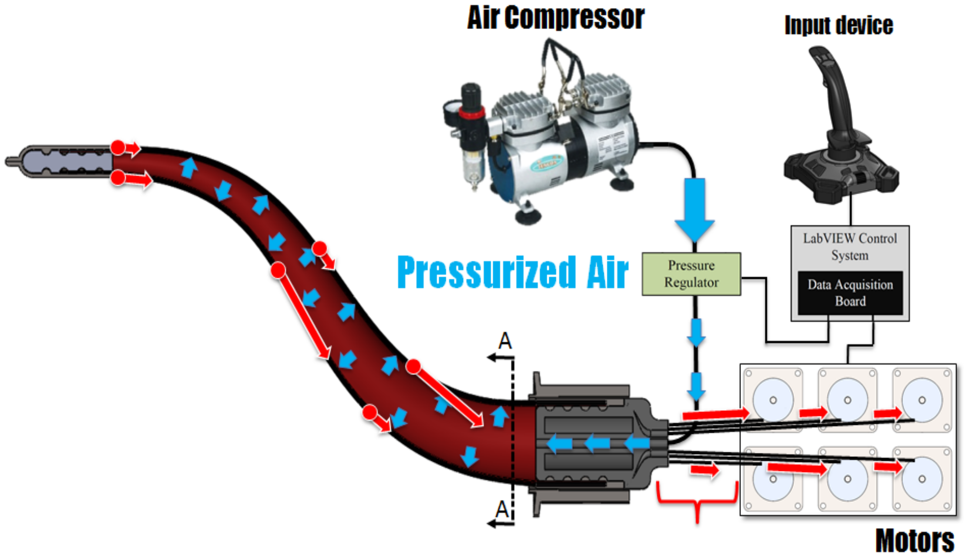
# Hard versus soft manipulators



Taylor (Lancaster)



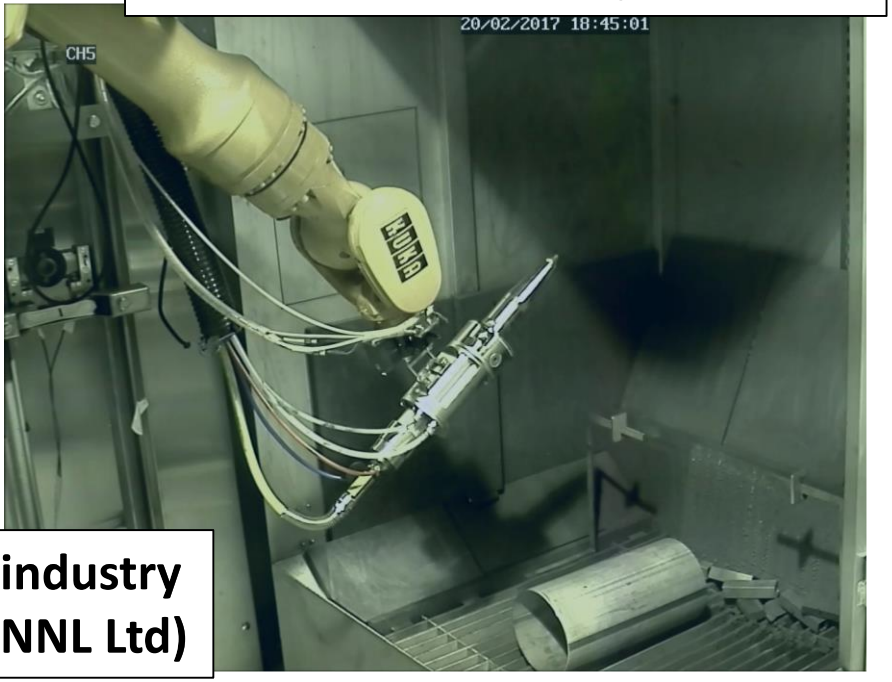
Althoefer, QML



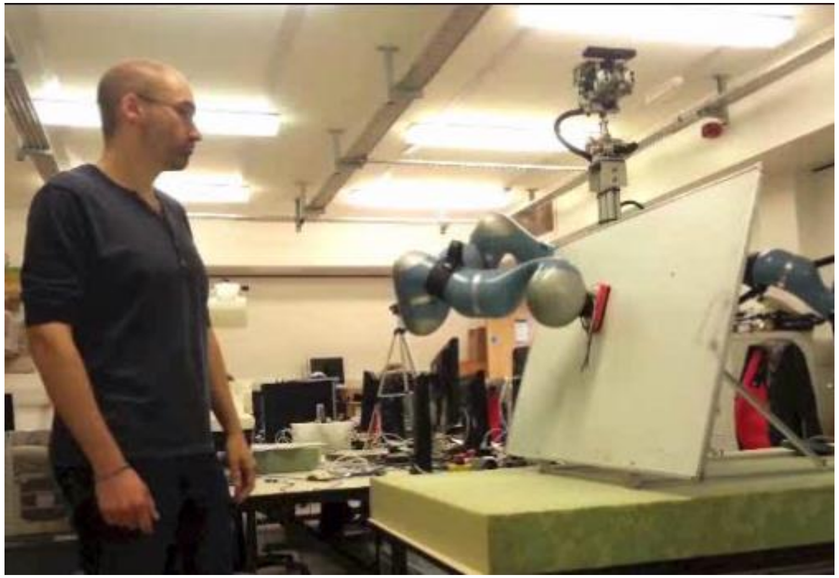
Althoefer, QML

# Robotic cutting:

(world-first: autonomous robot in radioactive hot cell)



Academia => industry
(Birmingham) (NNL Ltd)



U Birmingham + BRL-UWE

# Multimodal, augmented human-robot interfaces – VR/AR/Telepresence (BRL, Bham, Lincoln)

**Bham, NNL (RoMaNS)**

cea tech

6 dof CEA slave arm

>Low-inertia

>Low-friction

>Back-drivable actuation technology

>No extensive use of force sensors

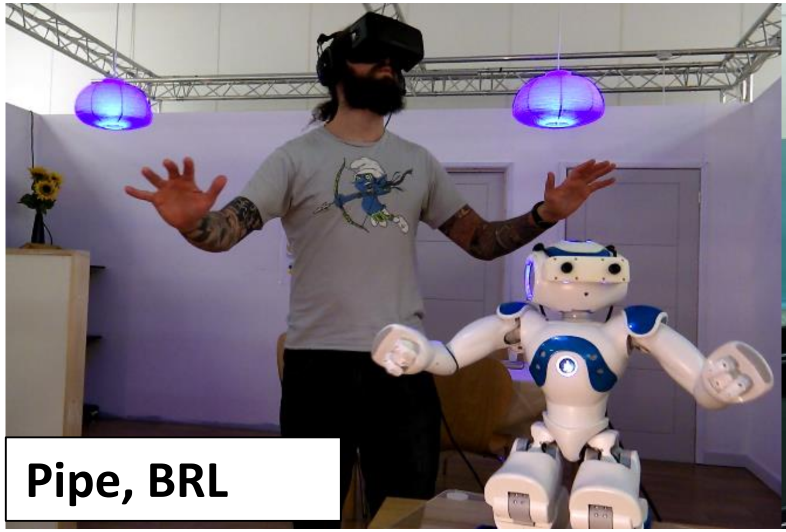
Haptic Device
(Virtuose 6D interface
from Haption)

RoMaNS

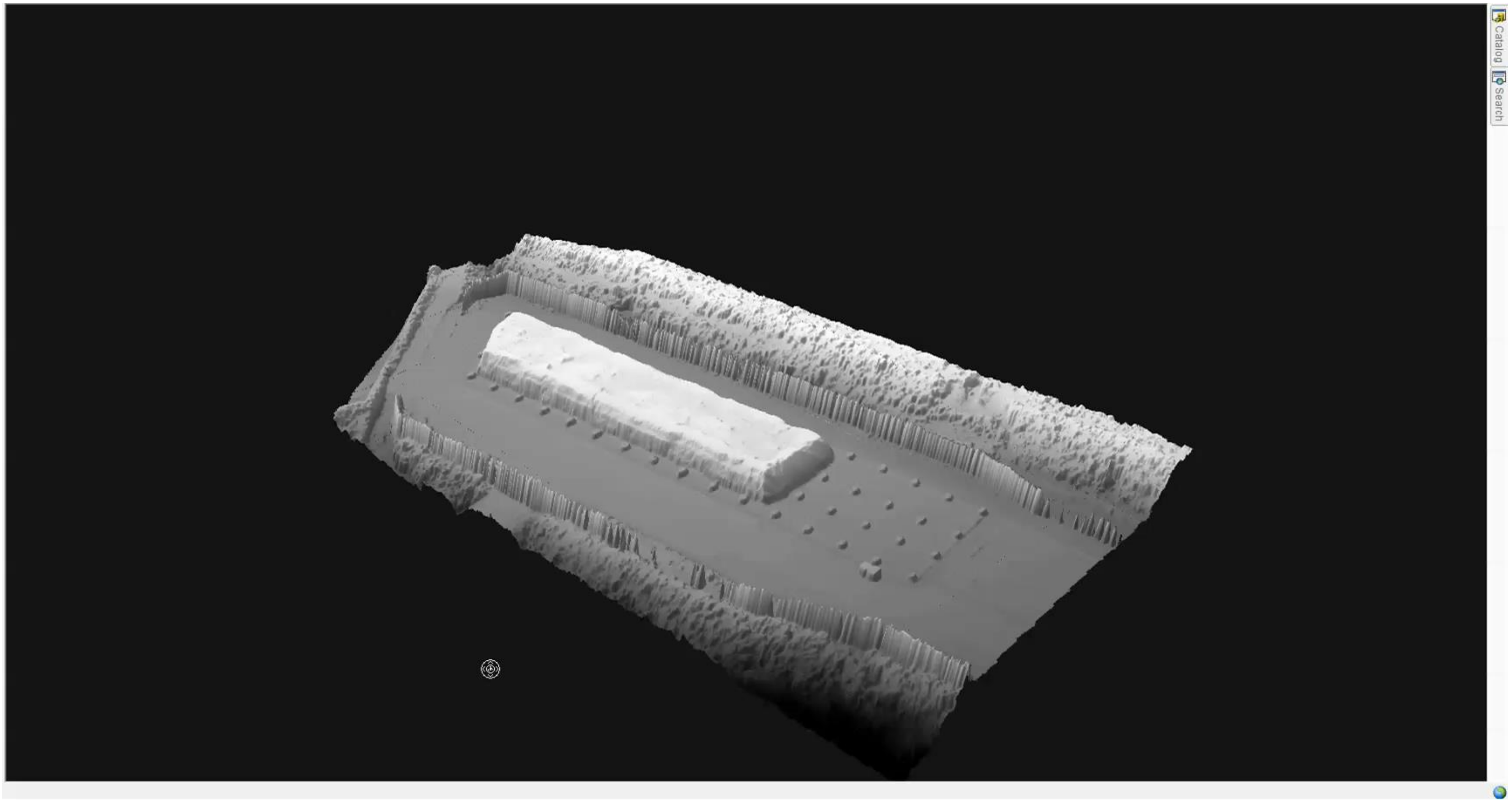
**CEA (RoMaNS) => Bham => NNL**

Simulated nuclear waste - such as contaminated construction materials

EPSRC
Engineering and Physical Sciences
Research Council

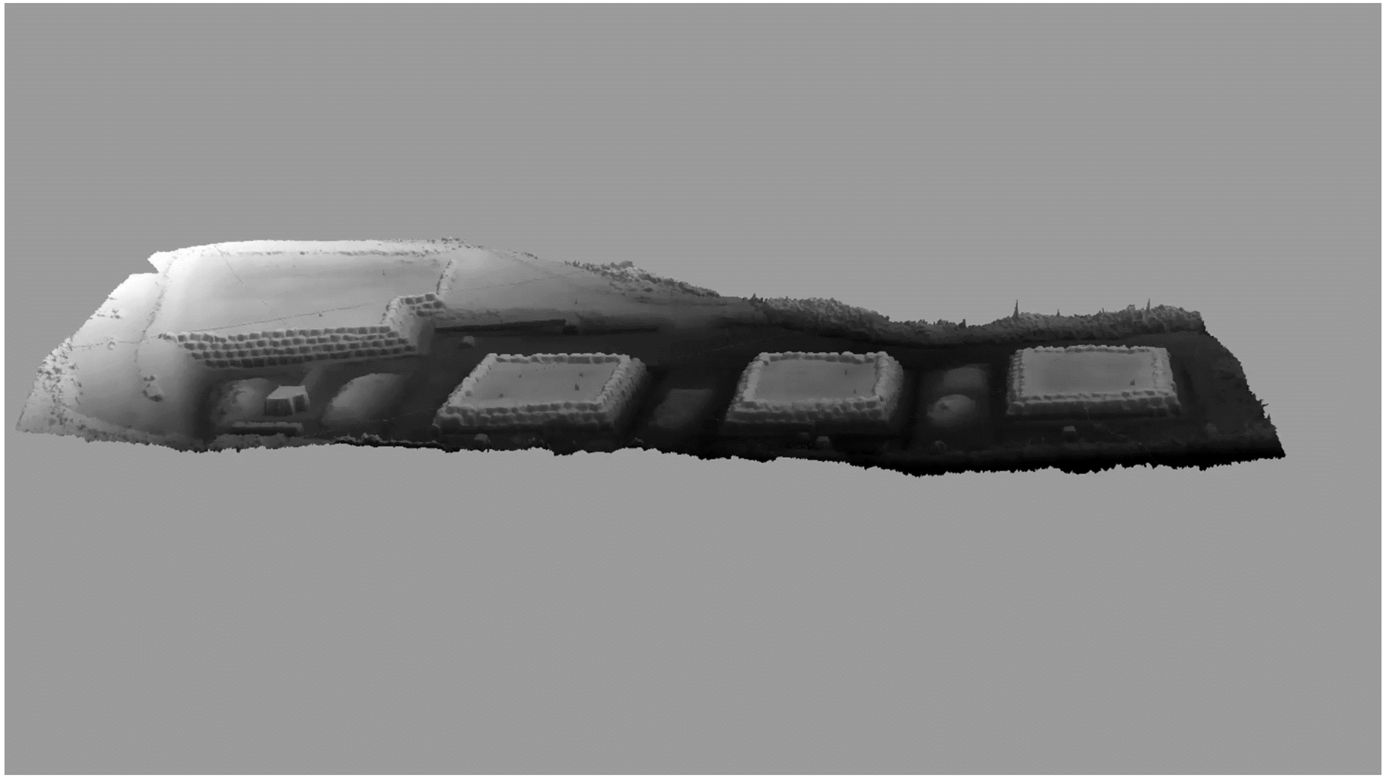


**Pipe, BRL**

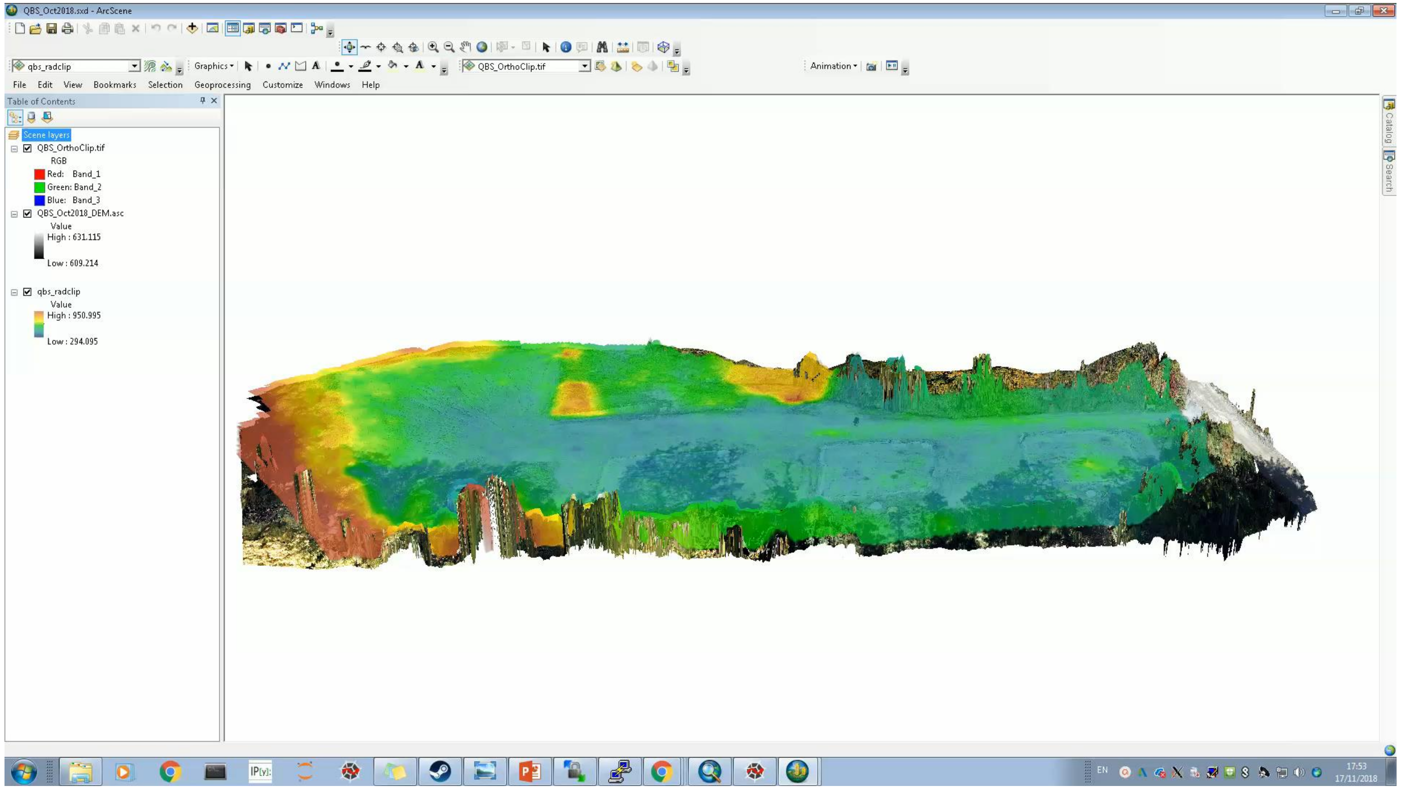


Dean Connor
Interface Analysis Centre, School of Physics

# Before….



# After…



Scene layers

☑ QBS_OrthoClip.tif
RGB
🟥 Red: Band_1
🟩 Green: Band_2
🟦 Blue: Band_3

☑ QBS_Oct2018_DEM.asc
Value
High : 631.115
Low : 609.214

☑ qbs_radclip
Value
High : 950.995
Low : 294.095

# Summary

**RAIN** and **NCNR** are conducting novel robotics and sensor development work which is truly complimentary to TRANSCEND

Regular '**grand challenge**' thematic meetings organised by RAIN and open to all on '**Remote Handling**' and '**Remote Inspection**' – PLEASE do come and get involved.

John Jukes - john.jukes@ukaea.uk RAIN
Peter Brewer - P.A.Brewer@bham.ac.uk NCNR

https://rainhub.org.uk/ https://www.ncnr.org.uk/

Thank you

Contact Details

School of Chemical and Process Engineering
FACULTY OF ENGINEERING

UNIVERSITY OF LEEDS

# ATLANTIC: Accident ToLerANT fuels In recycling

TRANSCEND Annual Meeting – 4th April 2019
Bath

# ATLANTIC: Accident ToLerANT fuels In recycling

***ATLANTIC will aim to provide a clear view on the ATFC technology of choice for implementation in a UK reactor and the effects of its implementation on the whole fuel UK.***

## Objectives

- to development manufacturing and treatment routes for new fuels and claddings;
- to take a multi-disciplined approach on the effectiveness of ATFC in UK reactors.
- to take an interlinked approach to research, combining modelling with experiments and using results across different areas of experimentation.
- to consider wider applications of ATFC technology.

# ATLANTIC: The Team

- *Joint leadership: Prof. Bruce Hanson and Prof. Tim Abram*
- *20 named Co-Investigators*
- *12 leading research-focussed universities in partnership with NNL*
- *Blend of established, newly established, and Early Career Researchers*

Imperial College London
Lancaster University
UCL
University of Bristol
University of Leeds
The University of Edinburgh
University of Cambridge
University of Oxford
Manchester 1824 The University of Manchester
The University Of Sheffield.
University of Reading
University of Liverpool

National Nuclear Laboratory

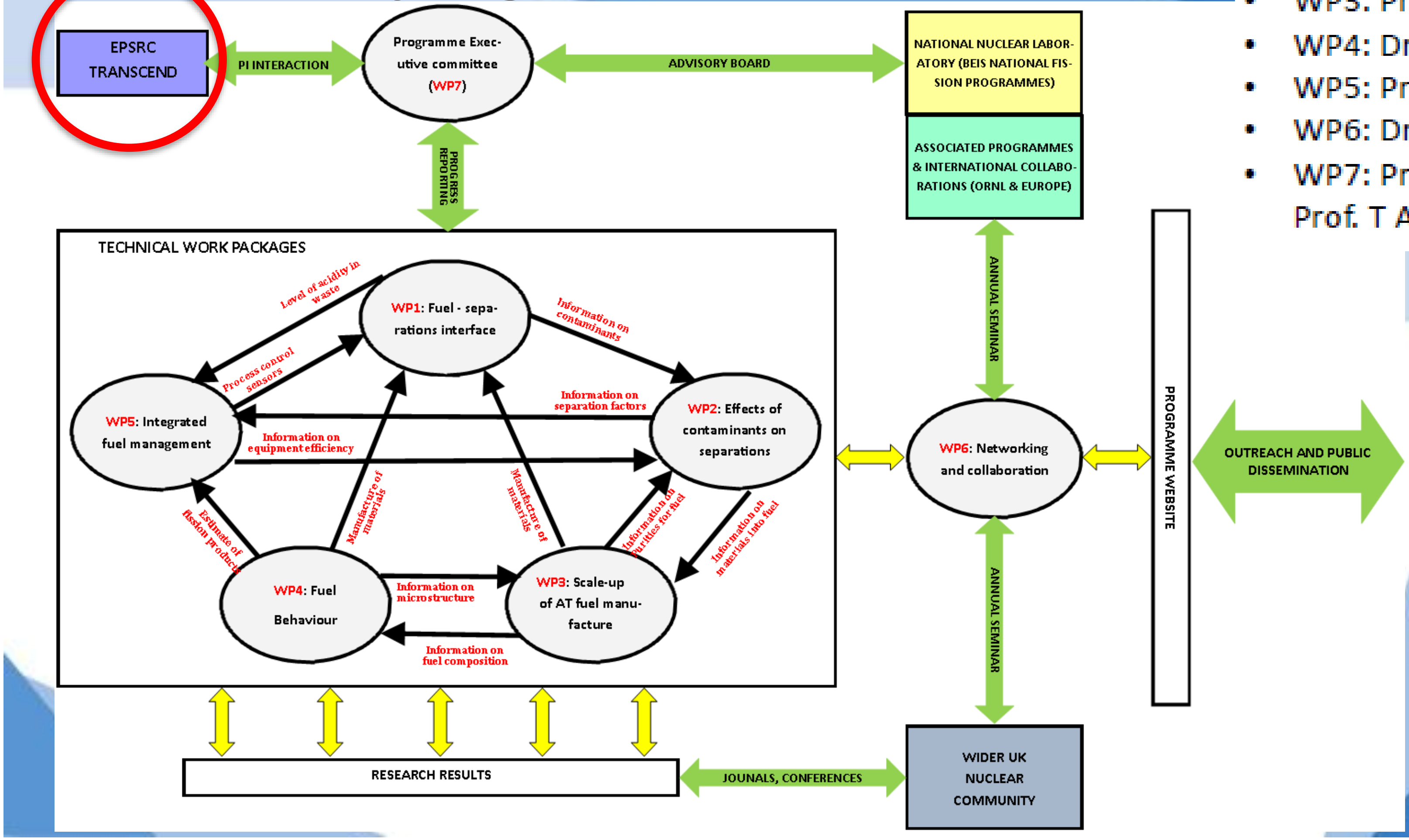
expert to links to WP

Oak Ridge National Laboratory
Horizon 2020 GENIORS

Knowledge exchange

# ATLANTIC: programme structure

structure
- WP1: Prof. C Boxall
- WP2: Prof. L Harwood
- WP3: Prof. K Whittle
- WP4: Dr I Farnan
- WP5: Prof. P Angeli
- WP6: Dr C Sharrad
- WP7: Prof. B Hanson, Prof. T Abram



EPSRC TRANSCEND

PI INTERACTION

Programme Executive committee (WP7)

ADVISORY BOARD

NATIONAL NUCLEAR LABORATORY (BEIS NATIONAL FISSION PROGRAMMES)

ASSOCIATED PROGRAMMES & INTERNATIONAL COLLABORATIONS (ORNL & EUROPE)

PROGRESS REPORTING

TECHNICAL WORK PACKAGES

WP1: Fuel - separations interface

WP2: Effects of contaminants on separations

WP3: Scale-up of AT fuel manufacture

WP4: Fuel Behaviour

WP5: Integrated fuel management

Level of acidity in waste

Process control sensors

Information on contaminants

Information on separation factors

Information on equipment efficiency

Manufacture of materials

Manufacture of materials

Estimate of fission products

Information on purities for fuel

Information on materials into fuel

Information on microstructure

Information on fuel composition

ANNUAL SEMINAR

WP6: Networking and collaboration

ANNUAL SEMINAR

PROGRAMME WEBSITE

OUTREACH AND PUBLIC DISSEMINATION

RESEARCH RESULTS

JOUNALS, CONFERENCES

WIDER UK NUCLEAR COMMUNITY

# ATLANTIC: The Programme

**WP1: Fuel - Separations interface**
**(WP leader: Prof. Colin Boxall, Lancaster University)**

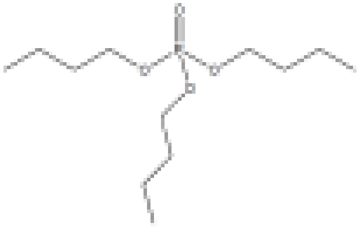
- Current knowledge on U metal and $UO_2$ fuels
- UN dissolves rapidly in nitric acid; silicides are known to be more difficult to dissolve

Two parts:

- Small scale using Electrochemical Quartz Crystal Nanobalance (EQCN) @ Lancaster
- Pellet scale @ Leeds
- WP3 & 4 provide information and fuel simulant
- WP5 provides a sensor to test/use in pellet dissolution
- Link to WP2 with results

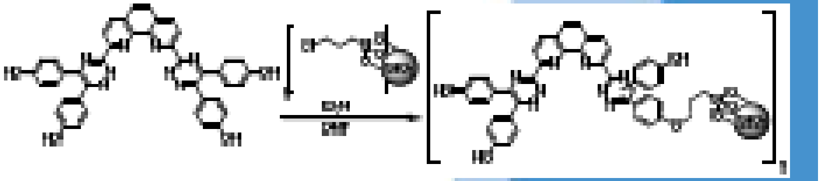
# ATLANTIC: The Programme

**WP2: Effects of Contaminants on Separations**
**(WP leader: Prof. Laurence Harwood, University of Reading)**



- Current generation of reprocessing = PUREX
- Next generation of reprocessing = SANEX/GANEX
- Developed for Minor Actinide recovery
- Main process chemistry proven for reference conditions
- Assumes oxide, metal, carbide fuels

*What is the effect of impurities from head end (Cr, Al, Fe, Si and Zr)?*
*Focus on a candidate ligand and its performance at edge of knowledge*



# ATLANTIC: The Programme

**WP 3 – Investigation and Optimisation of Accident Tolerant Fuel Materials**
**(WP leader: Prof. Karl Whittle, University of Liverpool)**

*WP3 focuses on the optimisation and manufacture of ATF materials:*

- *fabrication of ceramic fuel pellets ($U_3Si_2$ and UN): UoM & UoS*
- *materials characterisation and performance: UoM & UoS*
- *modelling the effects of radiation damage on their properties and how this may modify in-reactor behaviour: UoL*

*Partners have U-active facilities to manufacture, characterise, and test kg-scale quantities of fuels*

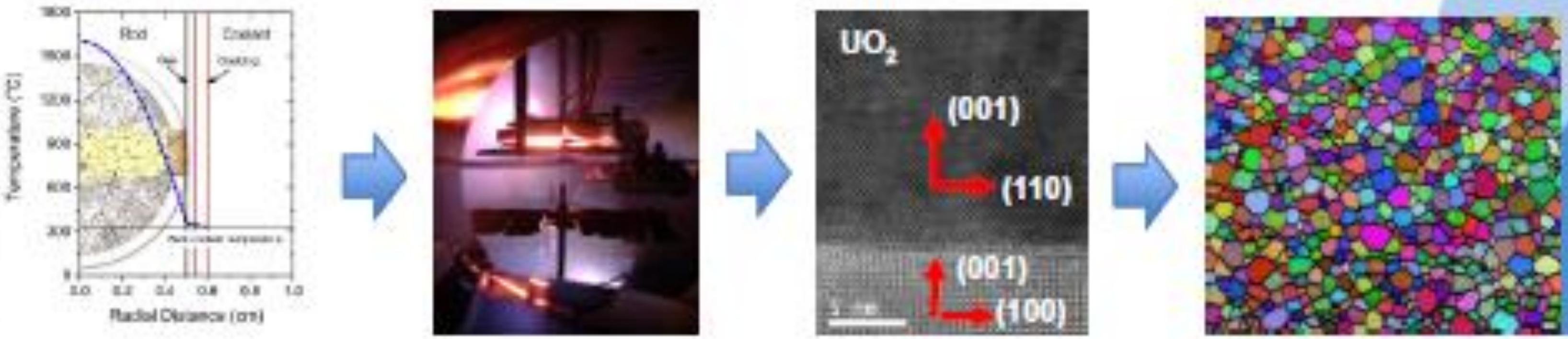
# ATLANTIC: The Programme

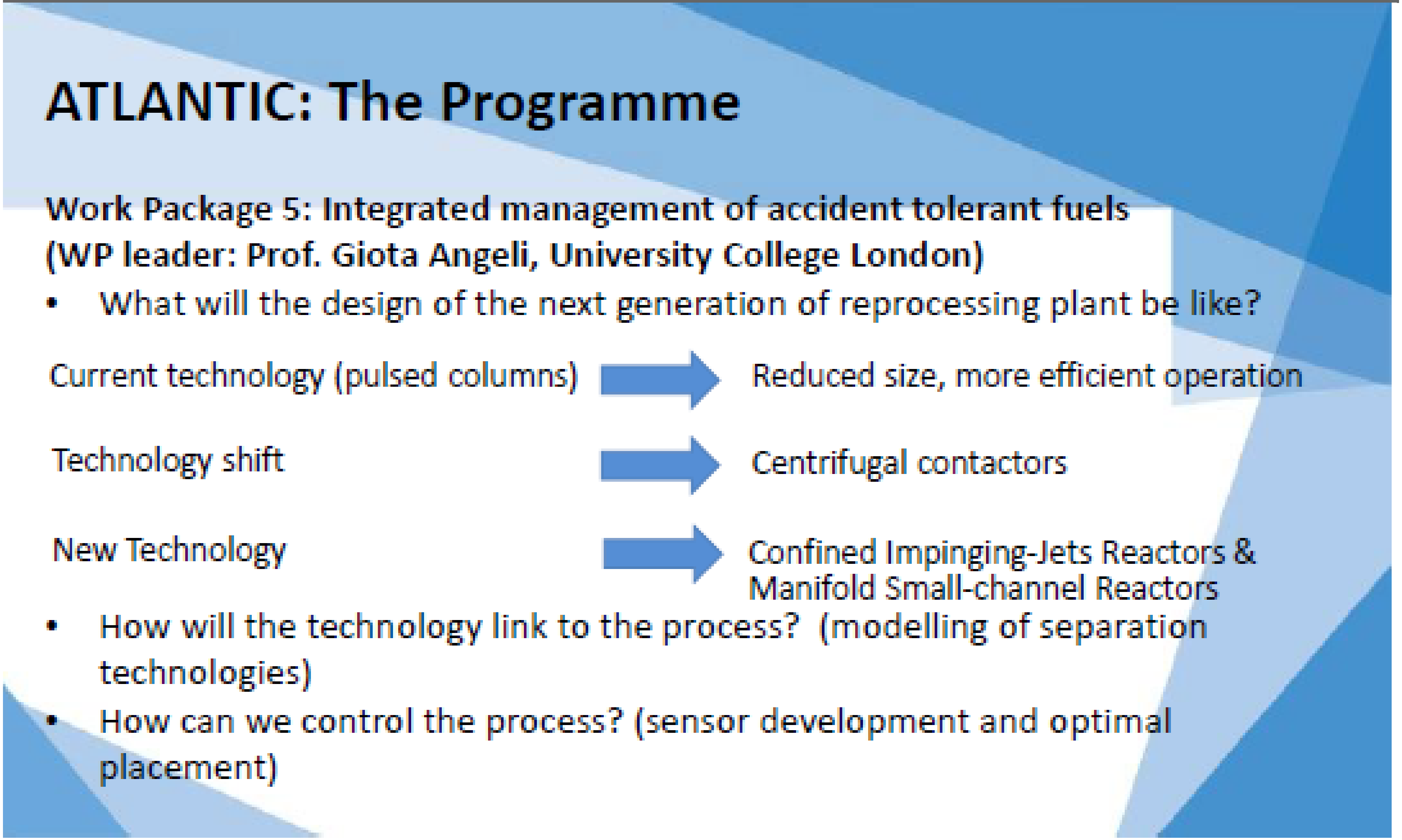
**Work Package 4 – Fuel Behaviour: non-stoichiometry and the fuel-water interface (WP leader: Dr Ian Farnan, University of Cambridge)**

*WP4 focuses addresses two crucial physical behaviours of ATFs, using novel experimental approaches, and addresses the historical chasm between modelling and experiment in this field.*

- *Non-stoichiometry of ATFs, U-Si and U-N systems*
- *Investigation of ATF behaviour in aqueous environments*
- *Cooperation of theoretical modelling and experimental design*

*Unique UK deposition facility will be employed to engineer samples targeted at each of the three WP4 strands*





# ATLANTIC: The Programme

**Work Package 5: Integrated management of accident tolerant fuels**
**(WP leader: Prof. Giota Angeli, University College London)**

- What will the design of the next generation of reprocessing plant be like?

Current technology (pulsed columns) → Reduced size, more efficient operation

Technology shift → Centrifugal contactors

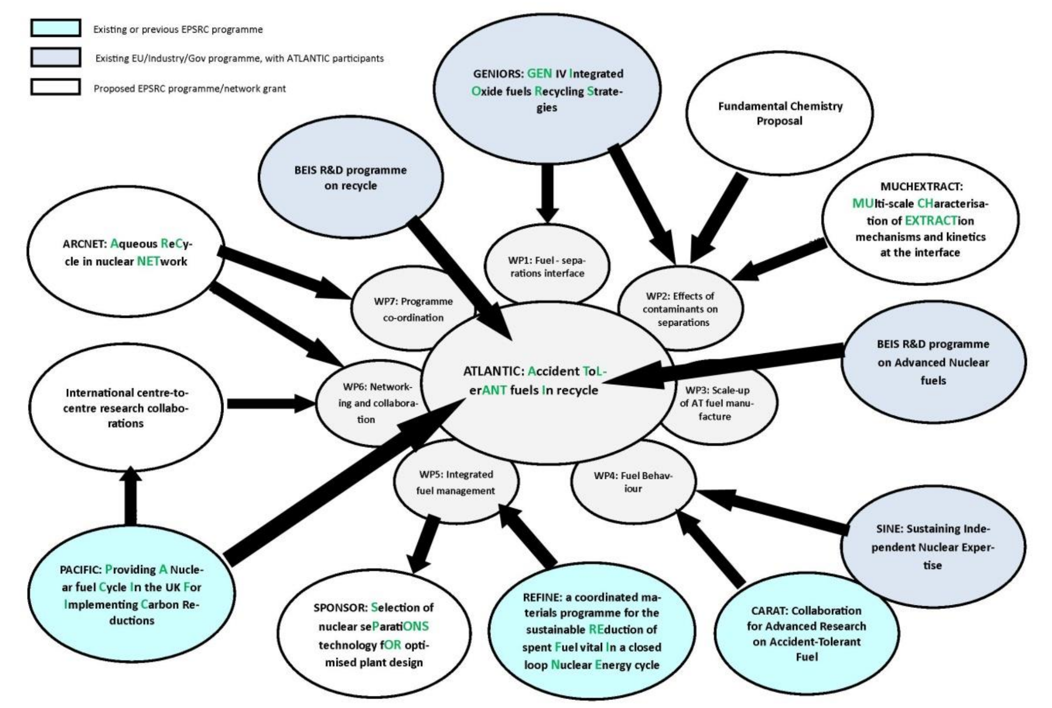
New Technology → Confined Impinging-Jets Reactors & Manifold Small-channel Reactors

- How will the technology link to the process? (modelling of separation technologies)
- How can we control the process? (sensor development and optimal placement)

# ATLANTIC: Building and connecting on other research

**Links to *future* programmes**

- *TRANSCEND*
- *BEIS recycling*
- *Next H2020 call*
- *EPSRC proposals*



)

# Acknowledgements

- EPSRC
- NNL
- ORNL
- EU – GENIORS

EPSRC
Engineering and Physical Sciences
Research Council

National Nuclear Laboratory

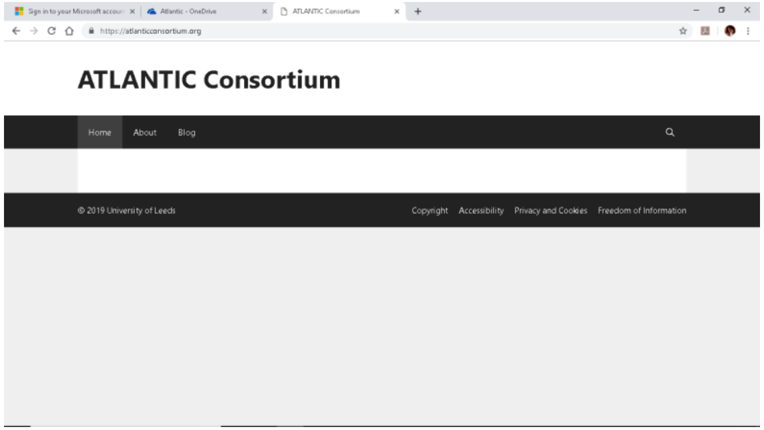
OAK RIDGE
National Laboratory

European Commission
HORIZON 2020

GENIORS
GEN IV integrated oxide fuels recycling strategies

# Thank you for your attention

www.atlanticconsortium.org



ATLANTIC Consortium

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# ASPIRE – Links to TRANSCEND

## Prof Tom Scott

*Interface Analysis Centre, School of Physics, University of Bristol, United Kingdom

EPSRC Pioneering research and skills

ROYAL ACADEMY OF ENGINEERING

AWE

UK Research and Innovation

In partnership with

NRC

The **South West Nuclear Hub** incorporates the **Bristol-Oxford Nuclear Research Centre** (NRC)
www.southwestnuclearhub.ac.uk
sw-nuclearhub@bristol.ac.uk

# EPSRC call funding 3 nuclear-related projects

Requirement to develop sensors able to operate in extreme environments to provide important operational information.

- Environmental extremes include radiation, chemical, physical, thermal.
- Remote measurements: either stand-off or in-situ measurements.

- Bristol + Oxford
- Birmingham
- Manchester + NNL

# Diamond energy technology

## “The diamond battery”

A long life **power cell** made from diamond which incorporates radioactive C-14 harvested from nuclear graphite waste (fission and fusion)

# Nuclear Graphite – waste or resource?

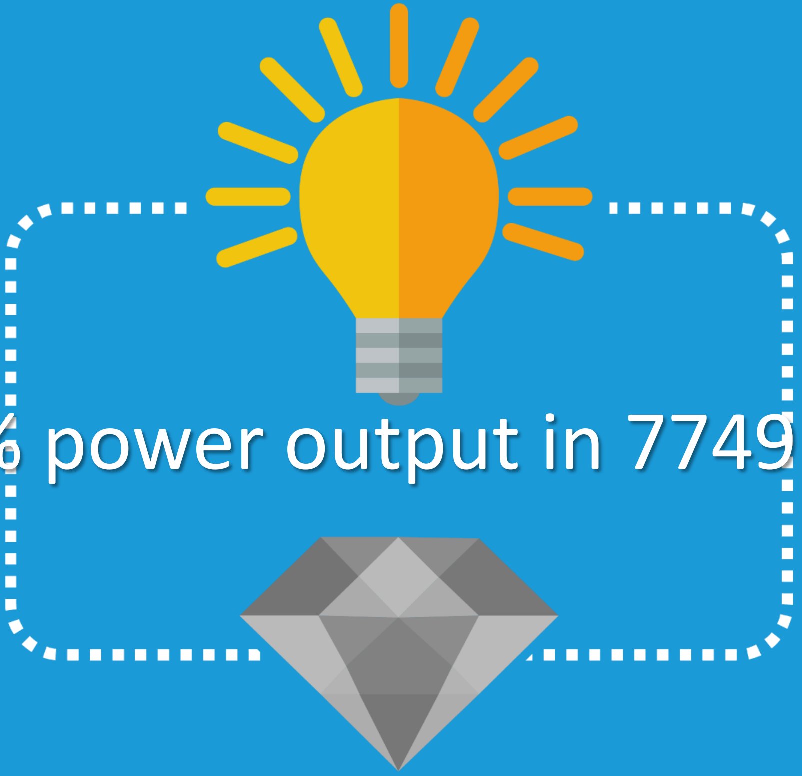
90,000 tonnes of UK irradiated graphite waste; about 1/3 of the world's total

~1% is C-14 ($T_{1/2}$ = 5730 years), equates to ~900 tonnes

University of BRISTOL

# The never ending battery

SOUTH WEST NUCLEAR HUB



50% power output in 7749 AD!

# A Double-sided Business Case

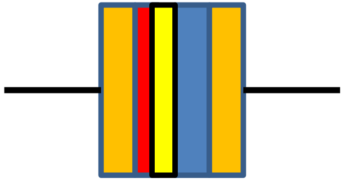
## Capturing the opportunity

- **Waste reduction**
  - By processing the graphite to extract C-14 we reduce the residual activity and convert ILW to LLW (with an associated cost saving)
- **A new energy technology**
  - A multi £Bn market exists for micro-batteries that don’t run out, spanning many sectors


C-12
C-14

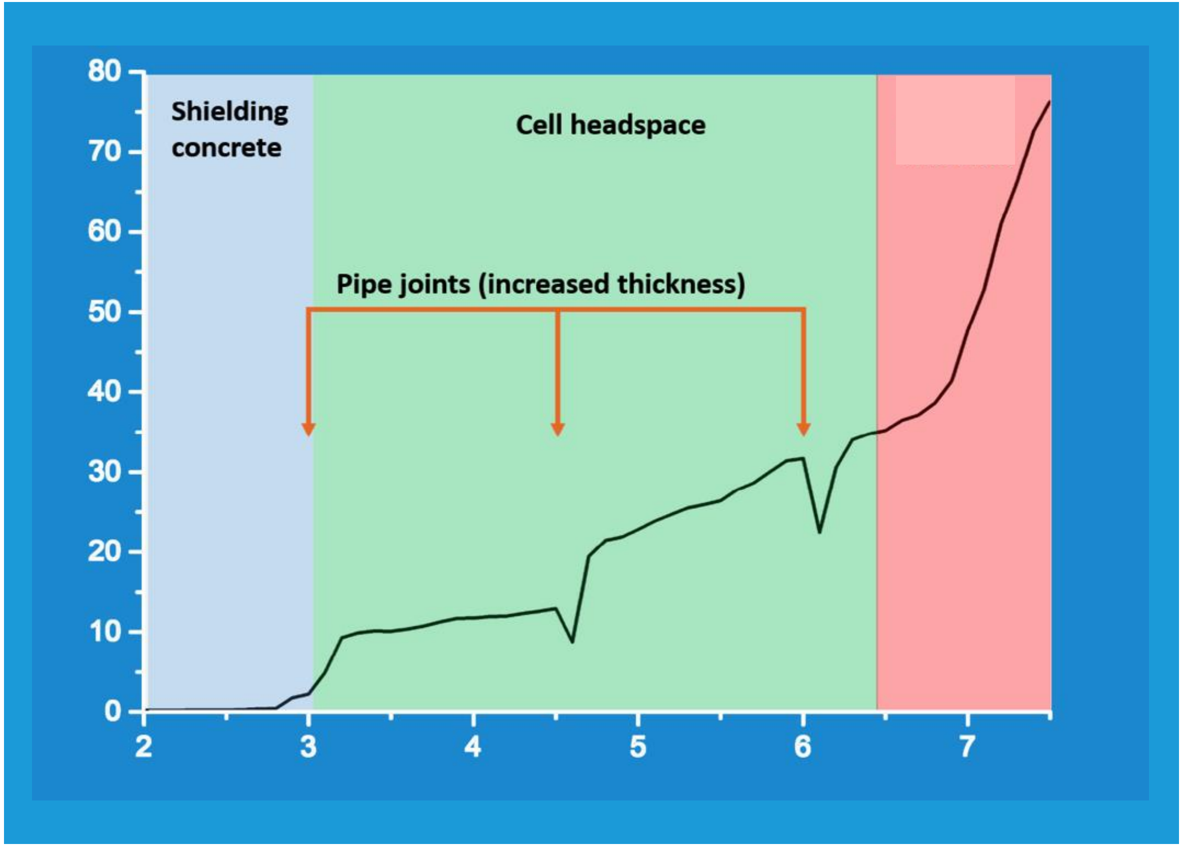
# ASPIRE is a voltaics project!

- Diamond Beta Battery (DBB)
  - Synthesis and incorporation of $^{14}$C diamond layer into DBB structure composed of insulating and semiconducting diamond
    - Transmutation of nitrogen-doped diamond
    - CVD diamond growth



- Diamond Gamma Battery (DGB)
  - Fabrication of Schottky metal-insulator-metal diodes many millimetres thick.

# Translated from detector technology



- Device testing and deployments on site!
- Extending the detection level downwards
- Sellafield and STFC funding

# Why go extreme with Diamond?

## Advantages as a detector material

- Intrinsically simple device (no p-n junction required)
- Robust, compact devices
- No need for cooling
- Close to 100% Charge-Collection efficiency for MIP
- **Extreme resilience to harsh environments i.e. corrosive and radioactive**

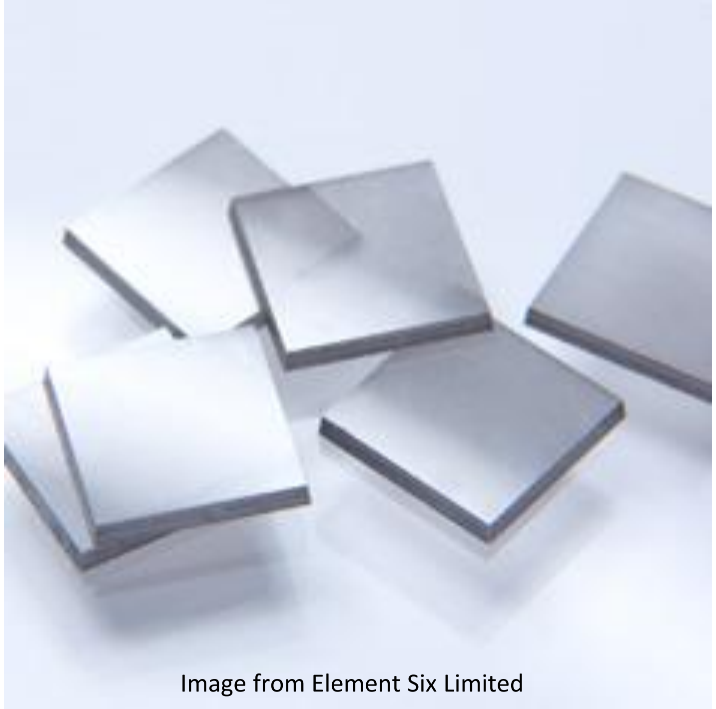


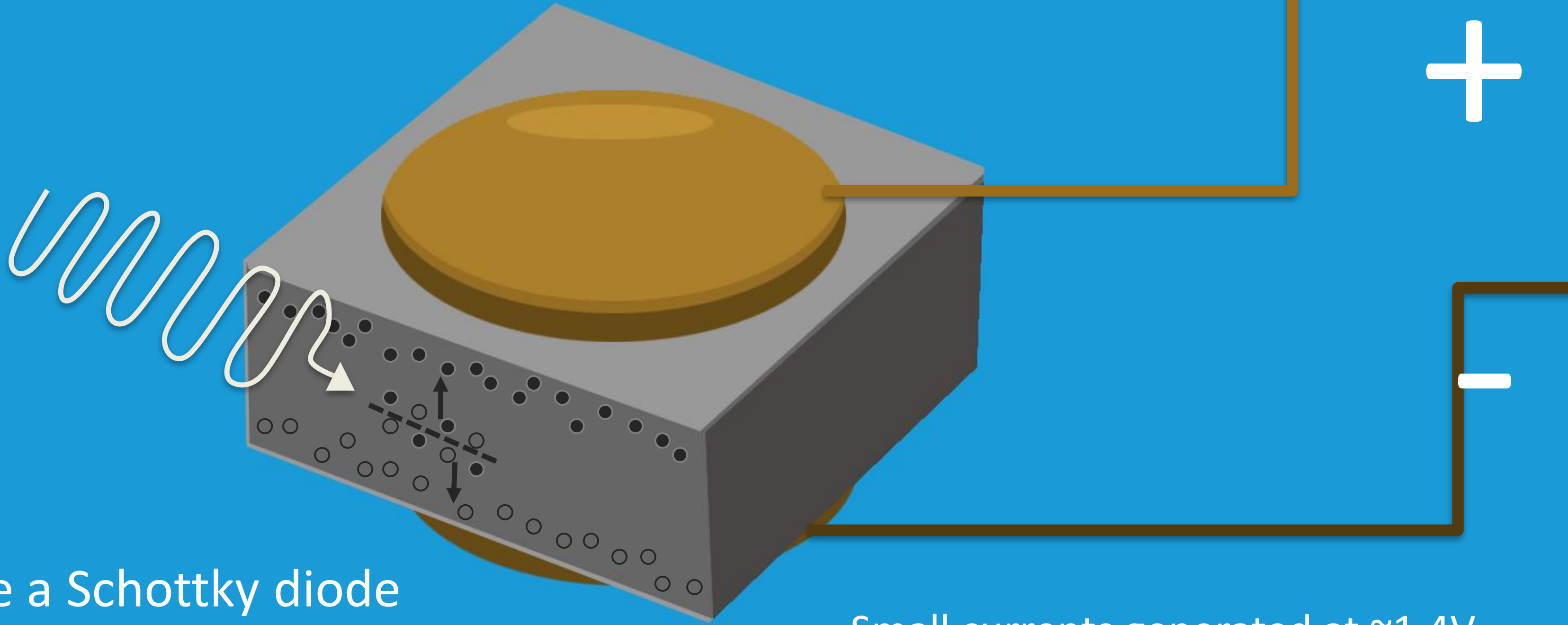
Image from Element Six Limited

## Further capability still being developed

# Prototype devices
# (Gamma voltaics)

# A Gamma-voltaic device

With the bias switched off the device STILL generates current

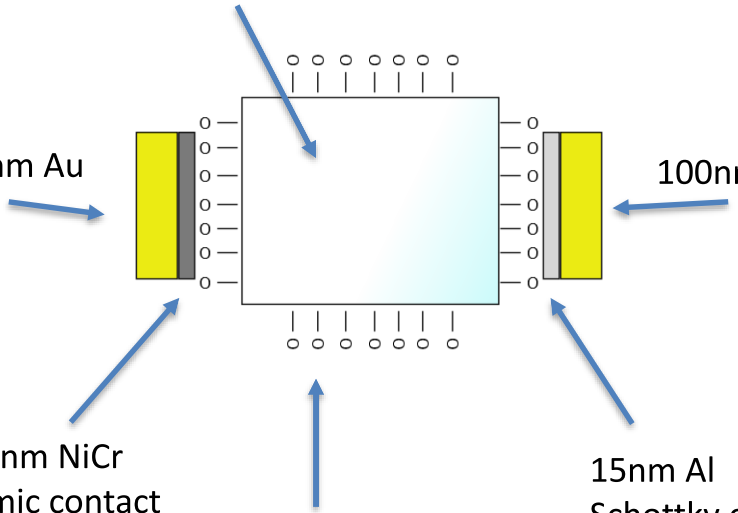


Acting like a Schottky diode
But not yet optimised

Small currents generated at ~1.4V

# The gamma-voltaic device

## A (relatively) low cost design



500µm undoped diamond

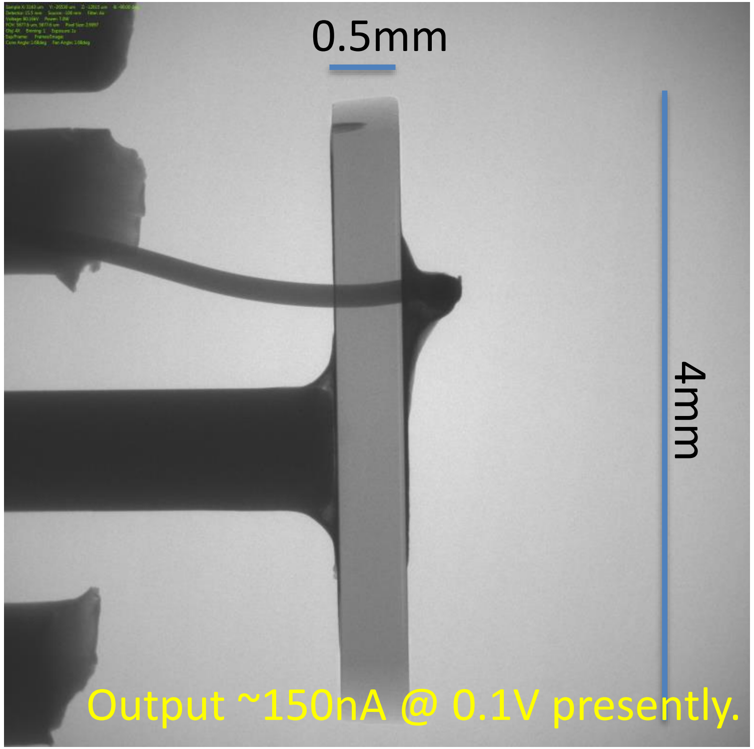
100nm Au

100nm Au

5nm NiCr
Ohmic contact

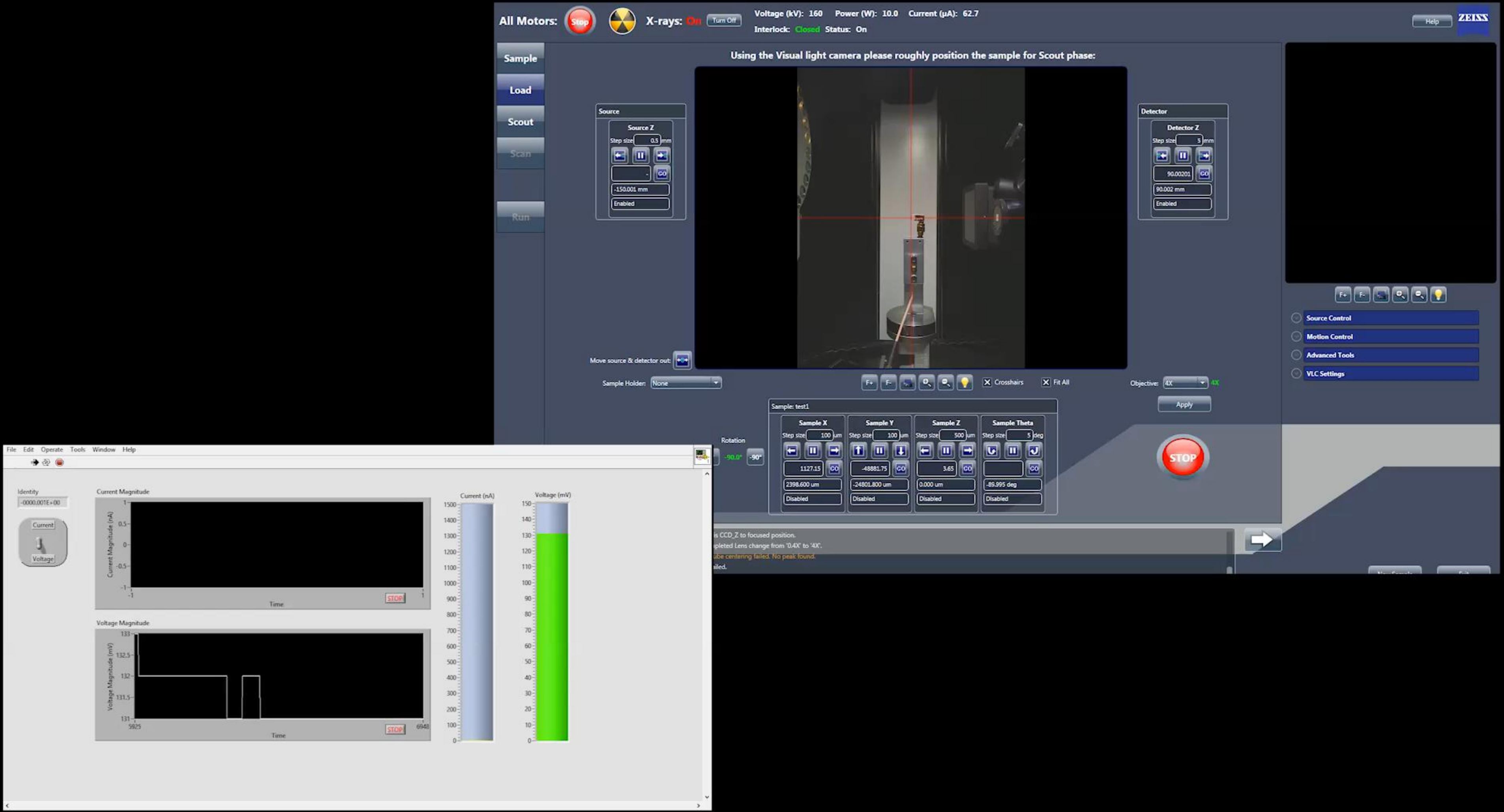
Oxygen termination

15nm Al
Schottky contact



Output ~150nA @ 0.1V presently.

# Testing in the lab



All Motors: Stop
X-rays: On
Voltage (kV): 160 Power (W): 10.0 Current (µA): 62.7
Interlock: Closed Status: On

Using the Visual light camera please roughly position the sample for Scout phase:

**Source**
Source Z
Step size 0.5 mm
-150.001 mm
Enabled

**Detector**
Detector Z
Step size 5 mm
90.00201
90.002 mm
Enabled

Sample Holder: None
☒ Crosshairs ☒ Fit All
Objective: 4X 4X
Rotation -90.0°

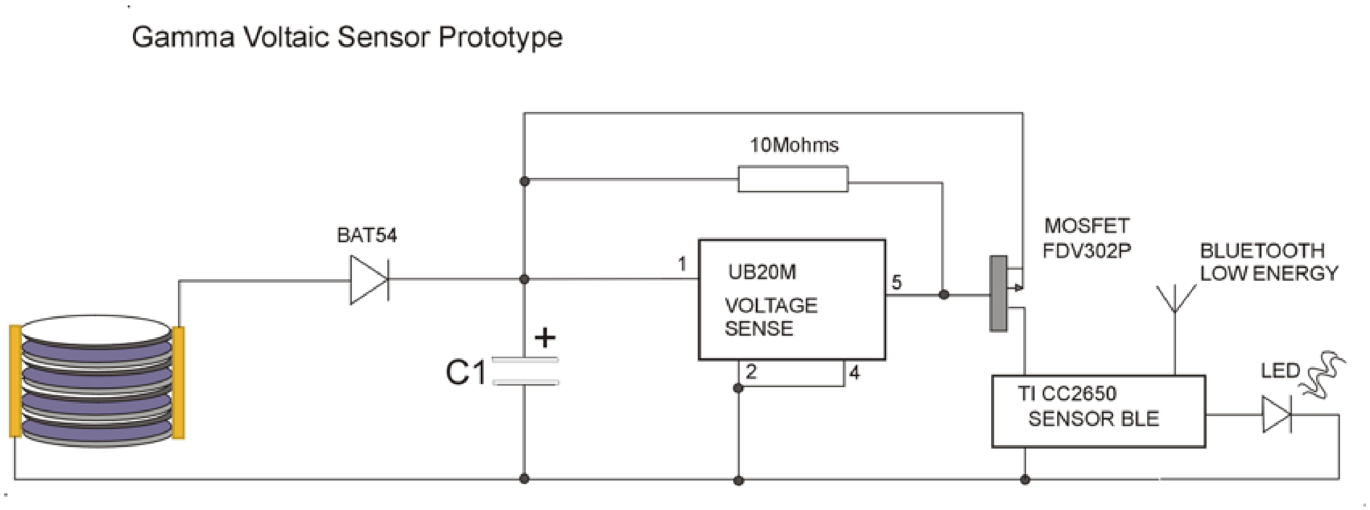
Sample: test1

| Sample X | Sample Y | Sample Z | Sample Theta |
|---|---|---|---|
| Step size 100 um | Step size 100 um | Step size 500 um | Step size 5 deg |
| 1127.15 | -48881.75 | 3.65 | |
| 2398.600 um | -24801.800 um | 0.000 um | -89.995 deg |
| Disabled | Disabled | Disabled | Disabled |

```
is CCD_Z to focused position.
pleted Lens change from '0.4X' to '4X'.
ube centering failed. No peak found.
iled.
```

Identity -0000.001E+00

# Gamma voltaic sensor prototype



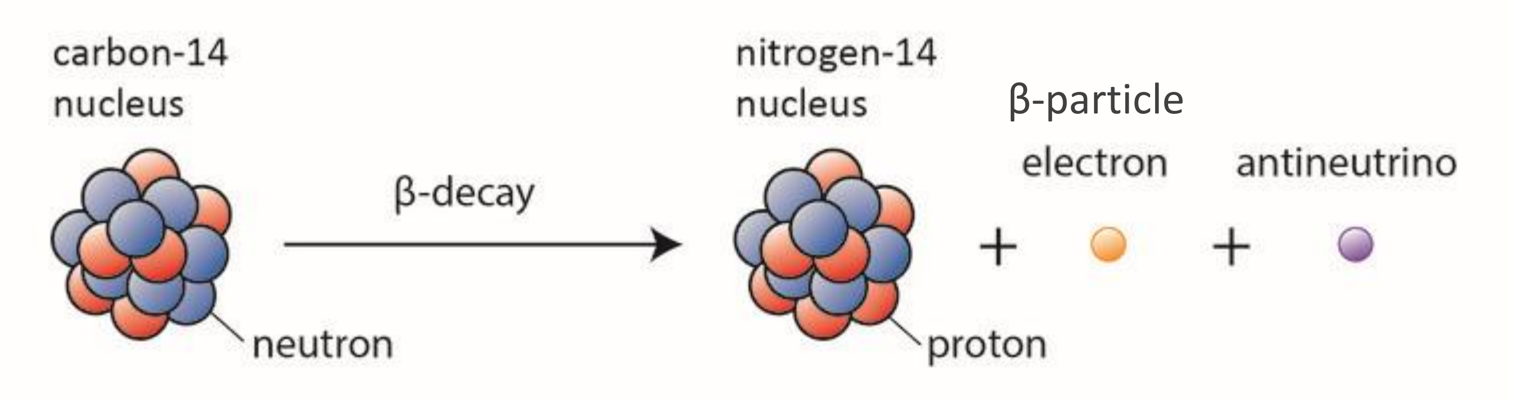
- Power Budget, even in short burst or chirp mode on minimal data represents a challenge at 65uW.
- Use of commercial low power chipsets is the preferred design, ultra low power Bluetooth LE 2.4GHz ISM band(BLE), BT Smart, iBeacon (Texas CC2650 provides a ARM Cortex M3 microprocessor (16 bit @ 48MHz, 128k Flash, 8kb SRAM, 12bit ADC, tx 0 to -30dBm, 2.1-3.6V @ tx -12dBm, with ultra low power down modes.
- Bluetooth low energy is ideal for applications requiring episodic or periodic transfer of small amounts of data, this can be combined with redundancy in transmission data, optimised for sensor environment and antenna tuning.

# Prototype devices (beta voltaics)

# C-14 – a useful isotope….

## Why is C-14 useful in a nuclear battery?

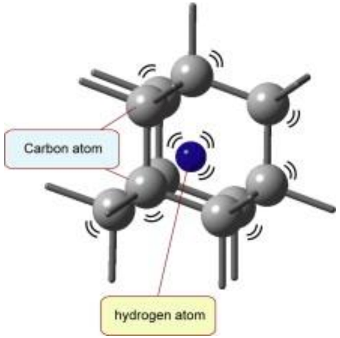
- C-14 is a β-emitting radioisotope
- Energy of C-14 β-particle
  Max = 156 keV, Mean = 49 keV
  (Tritium β-particle Mean = 6 keV)
- When C-14 decays it forms N-14 (compatible in diamond)
- Produced in nuclear reactors by both N-14 & C-13 transmutation



# H-3 (Tritium) – another isotope….

## Why is H-3 useful in a nuclear battery?

- H-3 is another β-emitting radioisotope
- Energy of β-particle
  Max = 18.6 KeV, Mean = 6 keV,
  Generally low energy
- $T_{1/2}$ = 12.3 y (relatively short)
- When H-3 decays it forms He-3
- Produced in various routes including from D, Li and B neutron reactions



Hydrogen has a remarkably good solubility in the diamond lattice.
**Ubiquitous in CVD diamond films**

# Three routes to production

**Direct CVD growth from C-14 methane**

Will produce the highest power output utilising C-14 and H-3 in the diamond structure

**Neutron activation of C-13 diamond**

Will produce the lowest power output utilising C-14, H-3 and Be-10 as emitters.

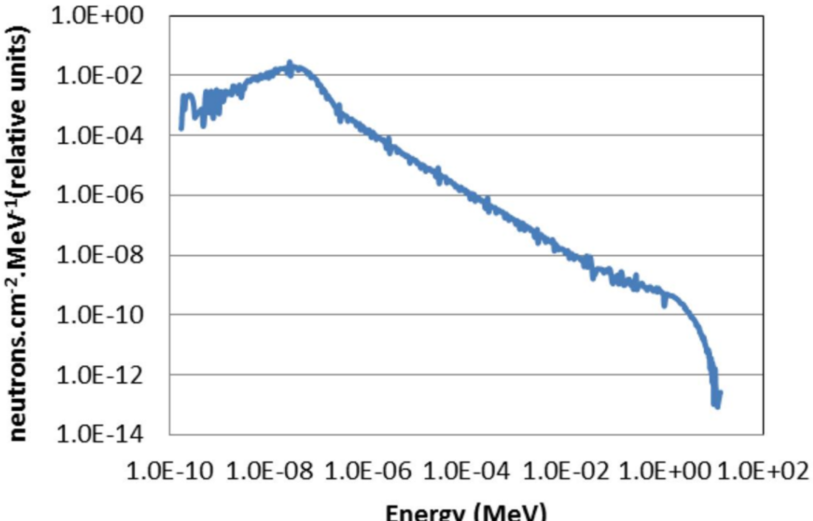
**Tritium infusion of CVD diamond**

Will produce high power for a reduced period due to utilising H-3 only ($T^{1/2}$ = 12.3 years)

# Utilising ‘friendly’ test reactors

## Collaborative research

- Device testing in mixed gamma/neutron fields (KUR, Japan)
- First and second trials in KUR now completed (13 diamond samples in total)
- Reactor exposure of C-13 diamonds for C-14 activation in June/July 2019



SOUTH WEST NUCLEAR HUB

# A working nuclear battery

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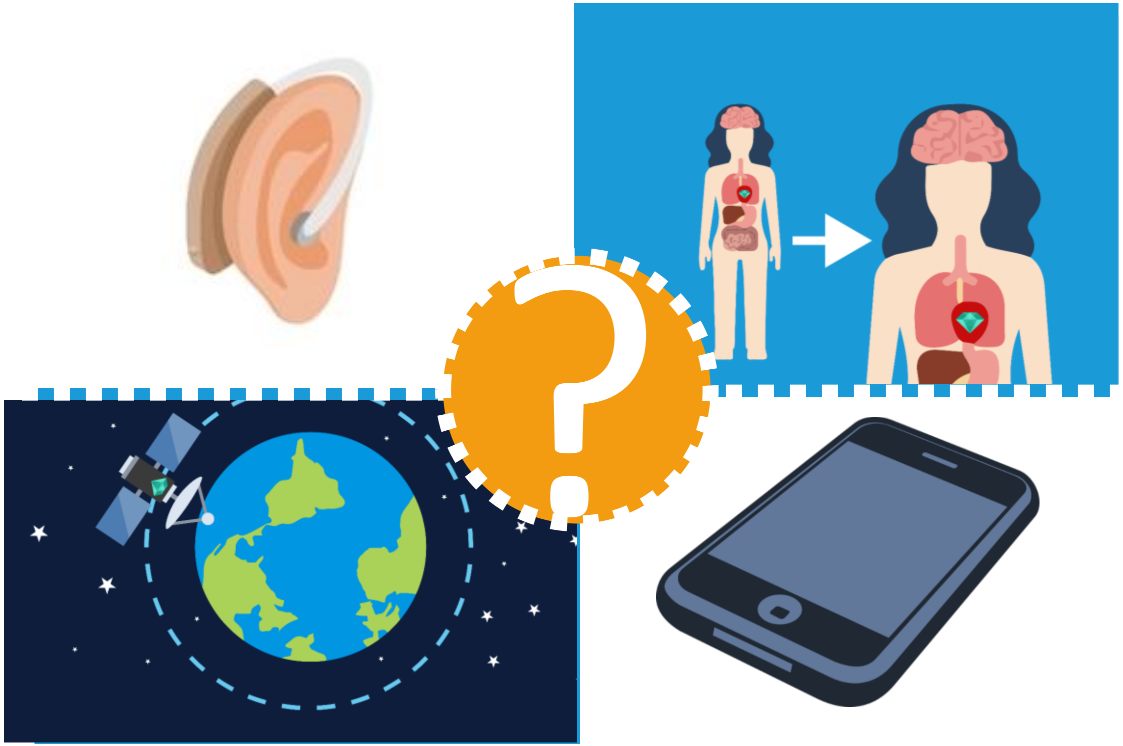
UK Research and Innovation

Sellafield Ltd

# Value from waste opportunities



## Applications….

- Medical implants
- Space/Satellite technology
- Security/Surveillance
- Automotive
- IoT devices
- Nuclear monitoring
- Ecology/environmental
- Sporting goods!

# Many thanks!

*Interface Analysis Centre, School of Physics, University of Bristol, United Kingdom

EPSRC
Pioneering research and skills

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In partnership with NRC

The **South West Nuclear Hub** incorporates the **Bristol-Oxford Nuclear Research Centre** (NRC)
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sw-nuclearhub@bristol.ac.uk

# Product features!

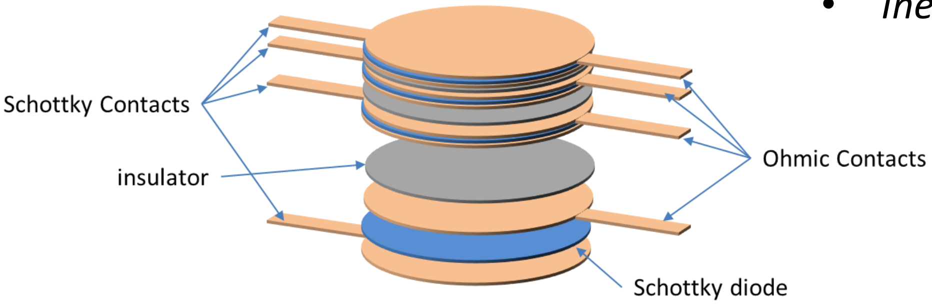
- Long Life
- Low Power
  High Energy Density
- Reliability
- Low E.M. Signature
- Low Maintenance

- Robust
- Bio-Compatible
- Remote Use
- Chemically Resistant

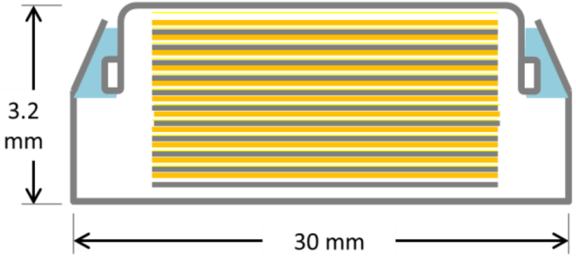
- Expensive
- High Specific Activity

# Diamond Coin Cells

- *A well established battery manufacturing technique*
- *Inexpensive equipment*

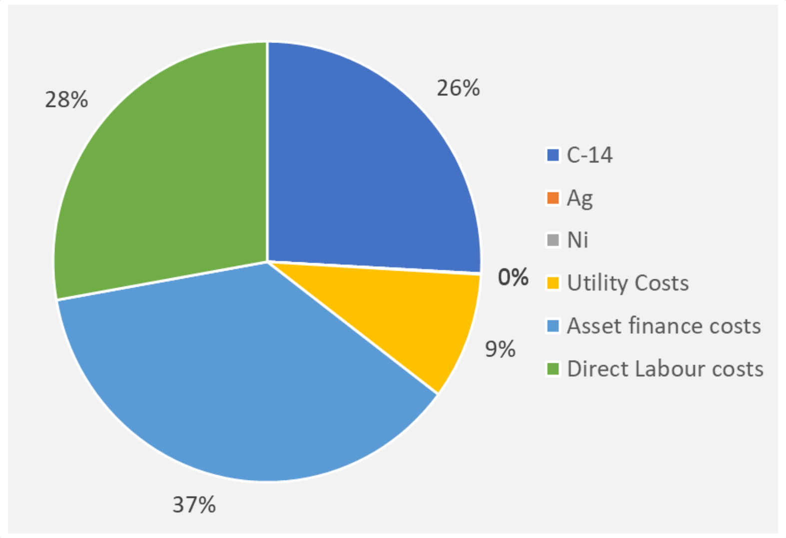


- 30 mm diameter / 3.2 mm thick



| **DI3032 10 µW Battery** | |
|---|---|
| Number of layers | 5 |
| Battery weight | 1.8 g |
| Total Battery power | 10.5 µW |
| Voltage | 1.8 V |
| Specific power | 5.8 µW/g |
| **DI3032 50 µW Battery** | |
| Number of layers | 24 |
| Battery weight | 5.2 g |
| Total Battery power | 50.5 µW |
| Voltage | 1.8 V |
| Specific power | 9.8 µW/g[1,2] |

# The production methods were financially modelled and looks okay!



| Battery Costs | |
|---|---:|
| DI3032 10 µW | £34 |
| DI3032 50 µW | £173 |

*This is for production volumes in the order of 30,000 per year*

- The production depends on modified CVD reactors that can use $^{14}$C methane and $^{3}$H (tritium) to make the plasma
- It is a capital intensive process

# Market Analysis - Medical

## Pacemaker and defibrillators

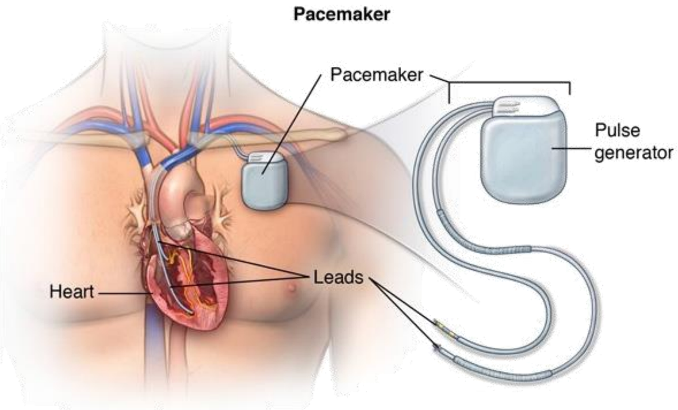
- *Premium, high-margin market*
- *Would last a patients' lifetime*

- Ultra-reliable
- Long operational lifetime, longer than the patient's lifetime
- Safe: bio-compatible, no-radiation leakage, no-sharp edges
- Compact and lightweight
- Power draw of 10 µW
- Little or no voltage drop

Market Size
$7.5 billion
7.5% CAGR

## Implantable medical sensors

- *Portable medical sensors for therapeutic and diagnostic purposes*
- *Glucose monitors are estimated to surpass 366 million by 2030*



# Market analysis – Internet of Things

- *Applications typically contain*
  - *a sensor*
  - *some processing capability*
  - *perhaps a transmitter*
- *Many applications are possible with a 50 µW*

Reliable

Long operational lifetime 10 – 20 years

Safe: no radiation leakage

Power draw of 50 µW

Conform to emerging standards

Market Size
$1.7 trillion