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Transformative Science and Engineering for Nuclear Decommissioning

A Geometrical Model of Alpha Radiation Dosimetry (redacted for publication purposes)

By Angus Siberry,

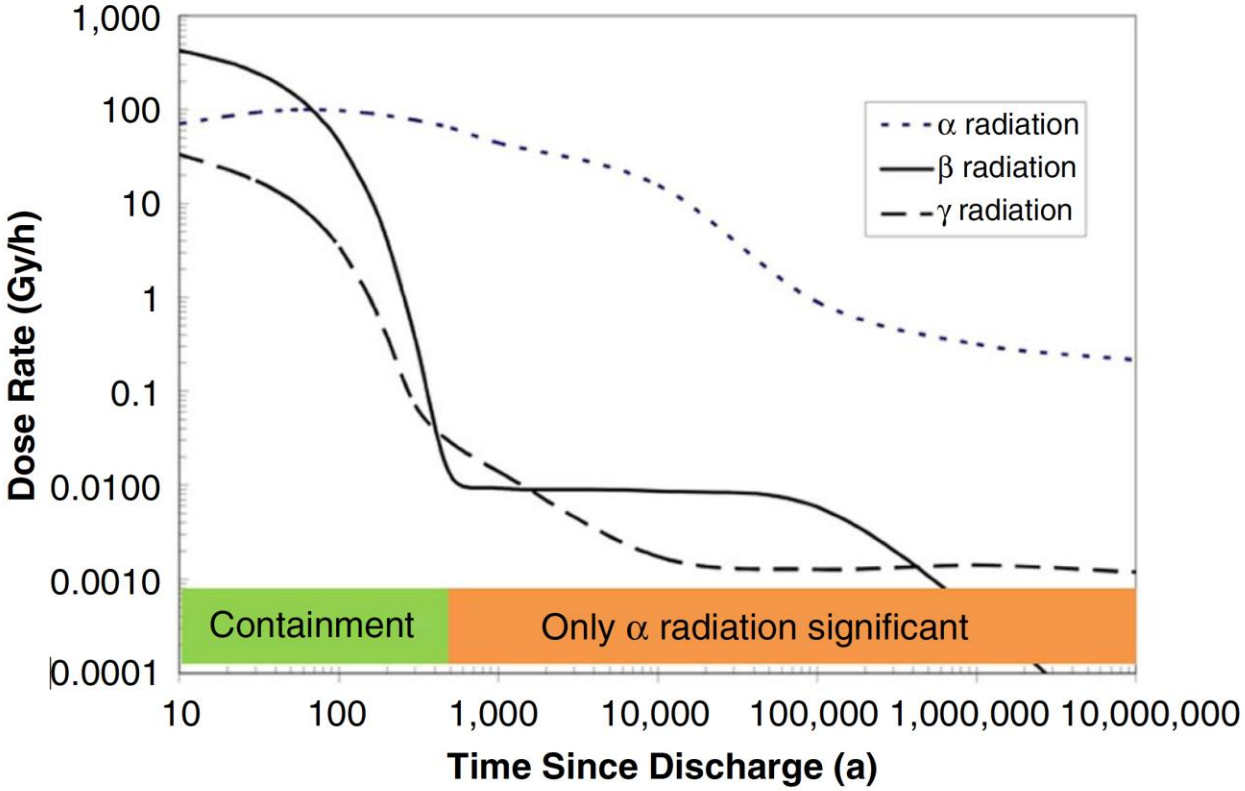
University of Bristol

Energy For a Low Carbon Future

Alpha Radiation

Alpha radiation: Commonly occurs from heavy elements, low penetration depth in materials in micron range. Activity **prevalent in spent fuel** throughout long-term storage.

Alpha Dose: the energy received by **per unit mass** of a medium through exposure to alpha radiation **Unit:** Gray or JKg^{-1}



[1] Liu, Nazhen, et al. *Corrosion* 75.3 (2019): 302-308.

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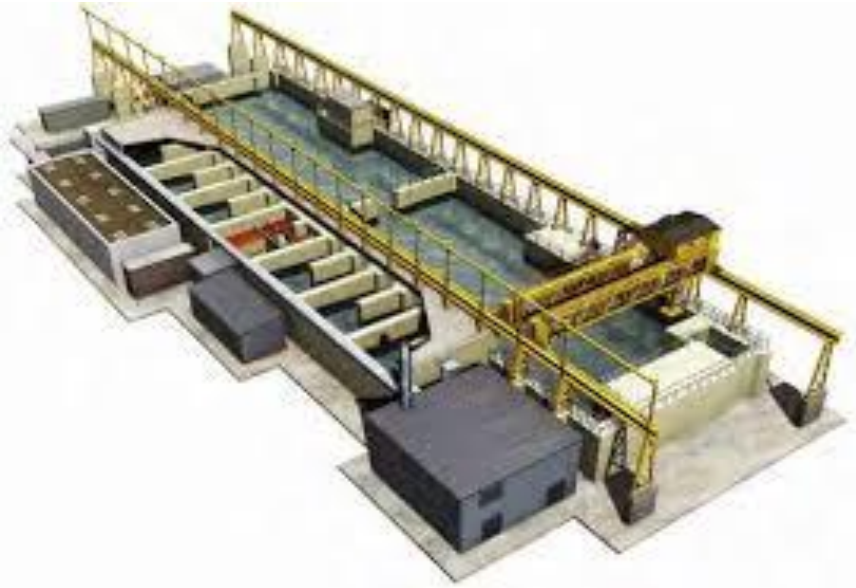
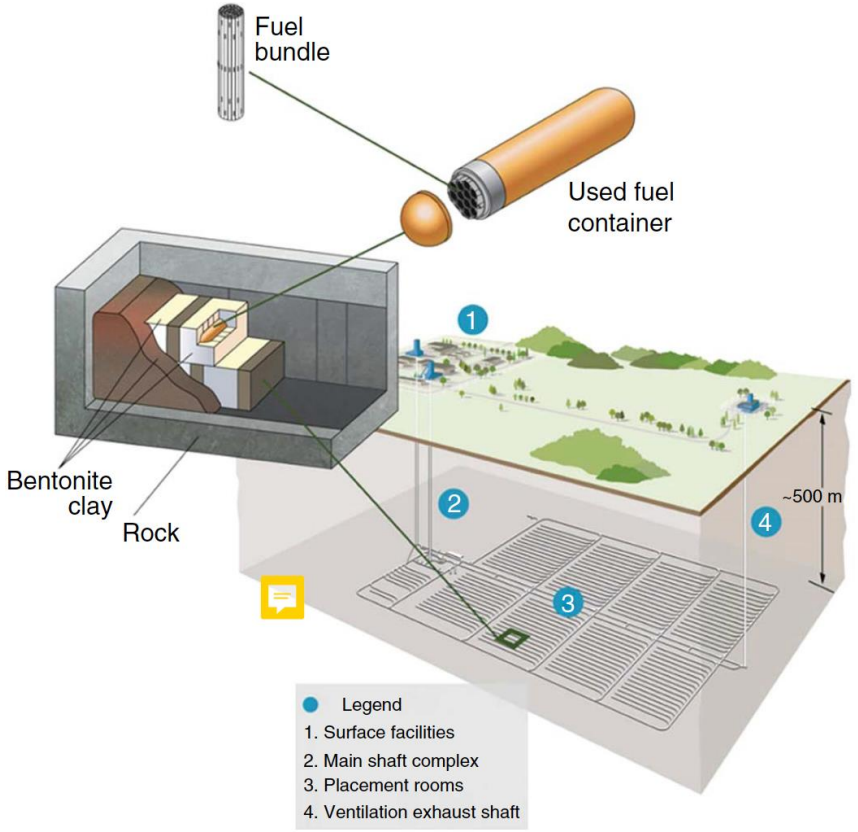
Interaction with water

Interim Wet storage (Spent fuel Pond)



Geological Disposal Facility (GDF)



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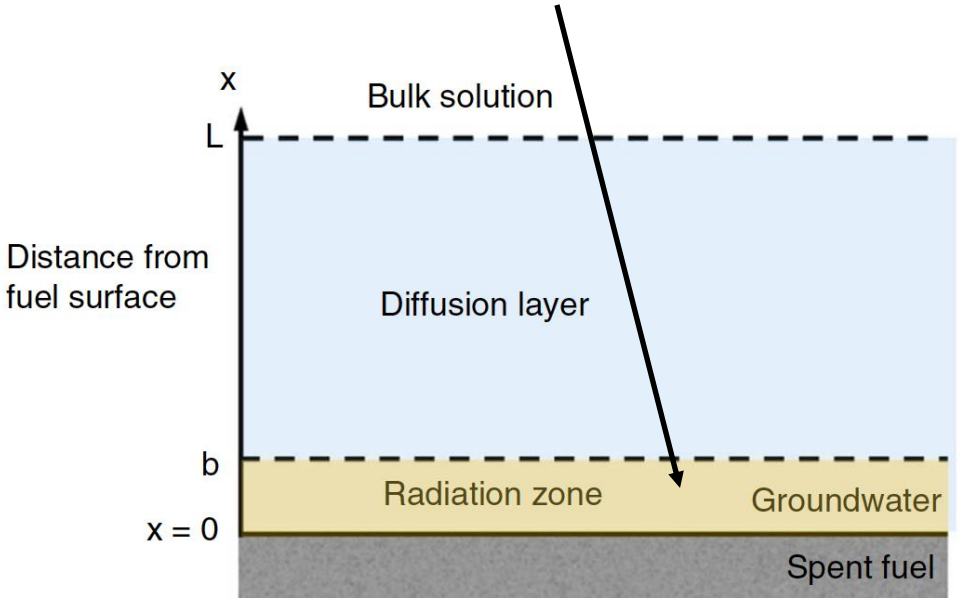
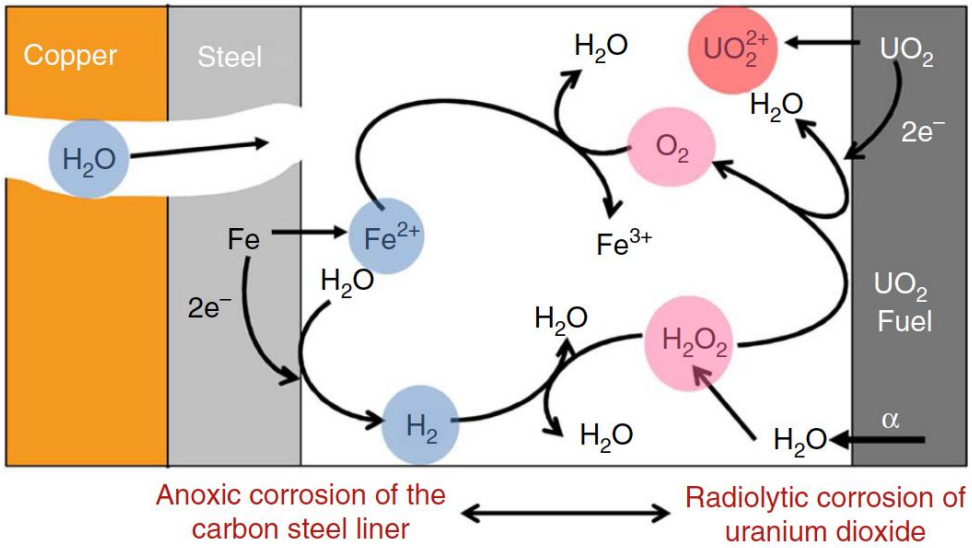
Radiolysis and induced fuel dissolution

Source term for radiolytic species



Used in multitude of spent fuel dissolution models



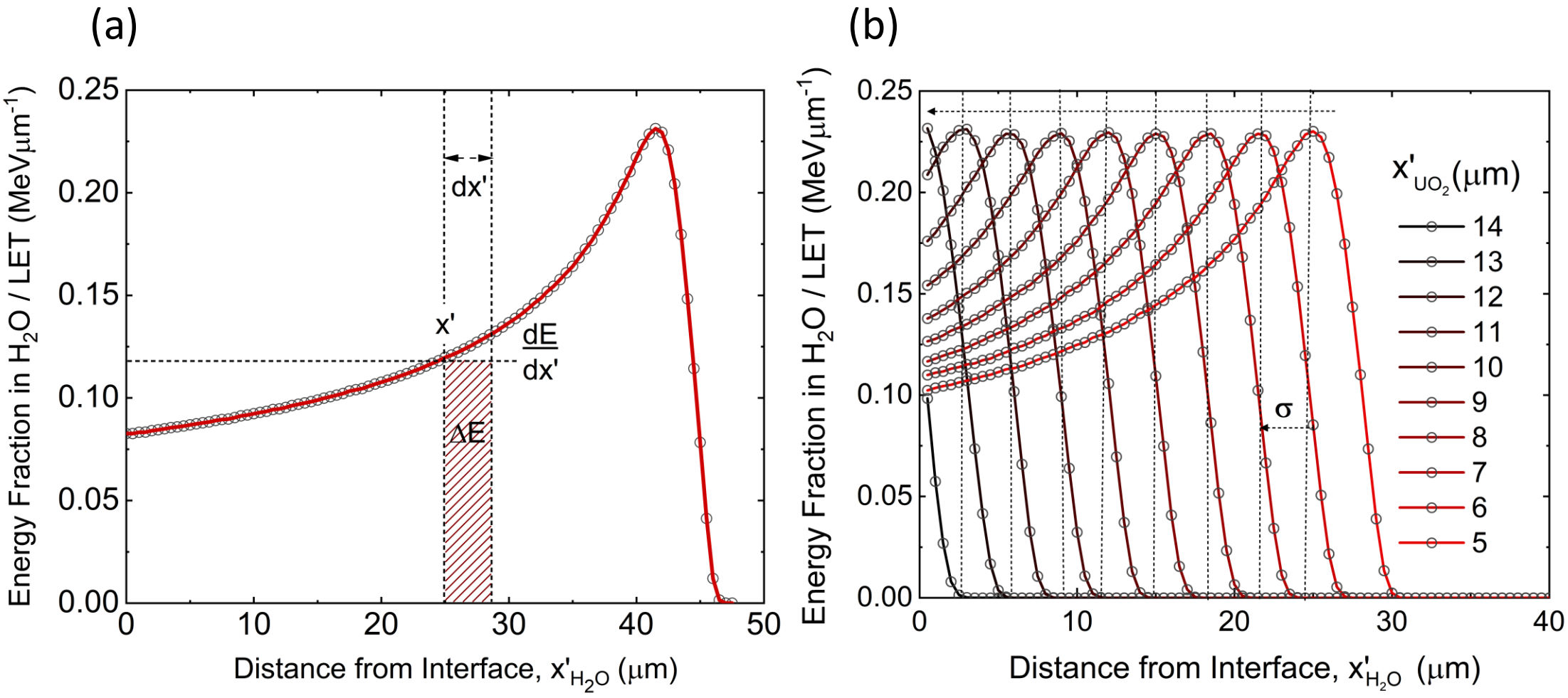
[1] Liu, Nazhen, et al. *Corrosion* 75.3 (2019): 302-308.

Problem Statement

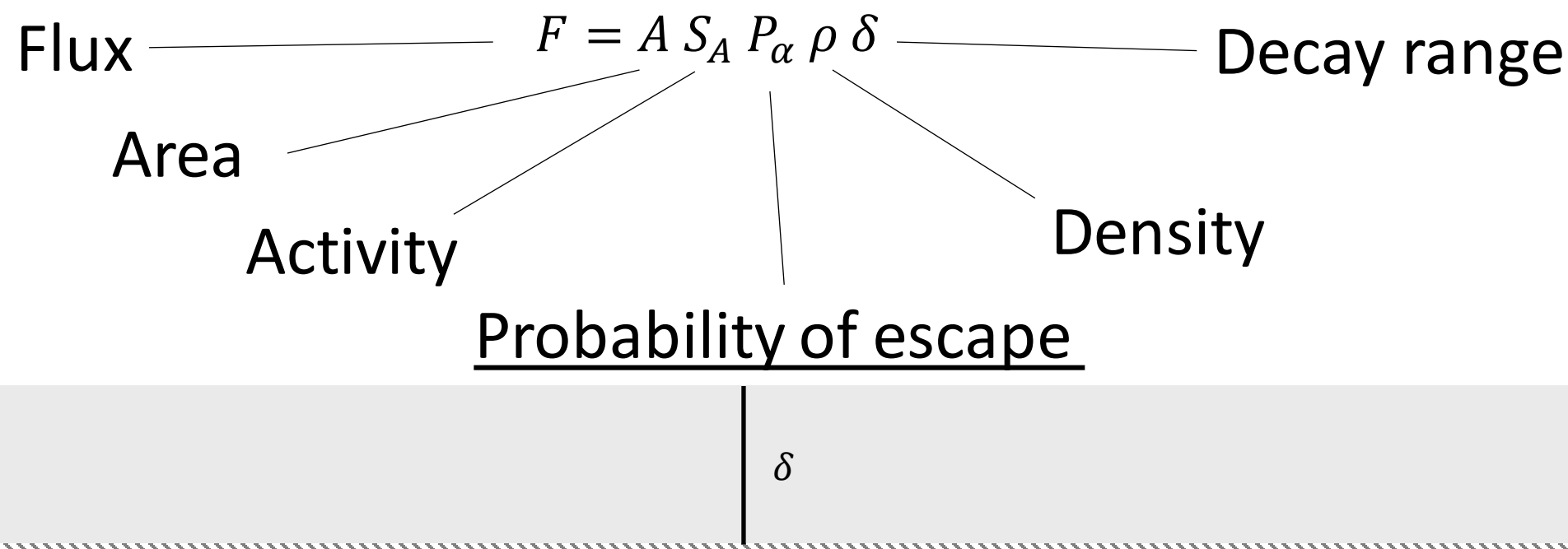
Legacy Ponds are open ponds with spent fuel of predominantly UO_2

No known models able to predict rate of alpha dose as a function of particle size **< 50 µm in fuel pond storage.** Hence determine radiolytic generation of H_2, H_2O_2, OH-,… in the event of fuel exposure to water

Linear Energy Transfer (SRIM)



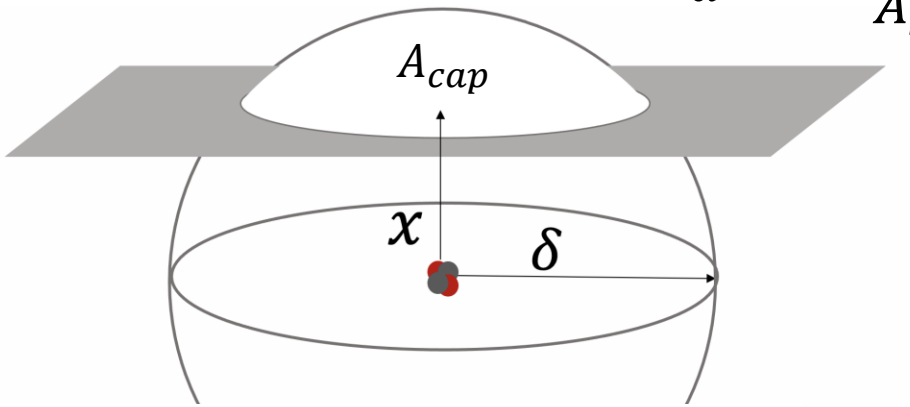
Flux

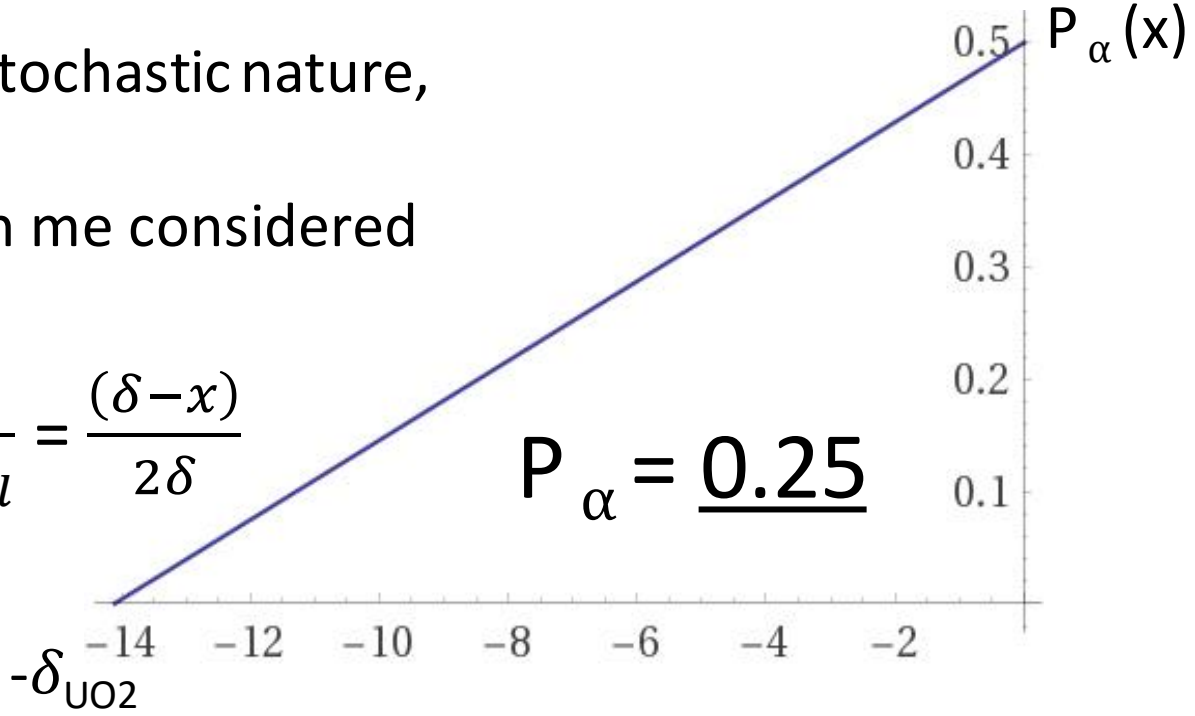

Flux
$F = A\ S_A\ P_\alpha\ \rho\ \delta$
Decay range
Area
Activity
Density
Probability of escape
δ

Probability of alpha particle escape (planar)

- Assuming all decays travel in a stochastic nature,
- The possible decay positions can me considered a spherical shell [2-4]

$$P_\alpha(x) = \frac{A_{cap}}{A_{shell}} = \frac{(\delta - x)}{2\delta}$$





$P_\alpha = \underline{0.25}$

[2] Hosoe, M., et al. *Nuclear Instruments and Methods in Physics Research* (1984): 377-381.
[3] Nielsen, Fredrik, and Mats Jonsson. *Journal of nuclear materials* 359.1-2 (2006): 1-7.
[4] Dzaugis, Mary E., *Radiation Physics and Chemistry* 115 (2015): 127-134.

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Derivation and results due to be published in Radiation Physics and Chemistry May 2021

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What about…

- α-particles starting with a different decay energy than 5.8MeV or 5.3MeV?
- A mix of isotopes in the fuel possessing different E_0 and Activity values?
- Different densities or fuel type?
- What about dose rates inside cracks in the fuel matrix?
- The results from this model Radii > 50 µm?

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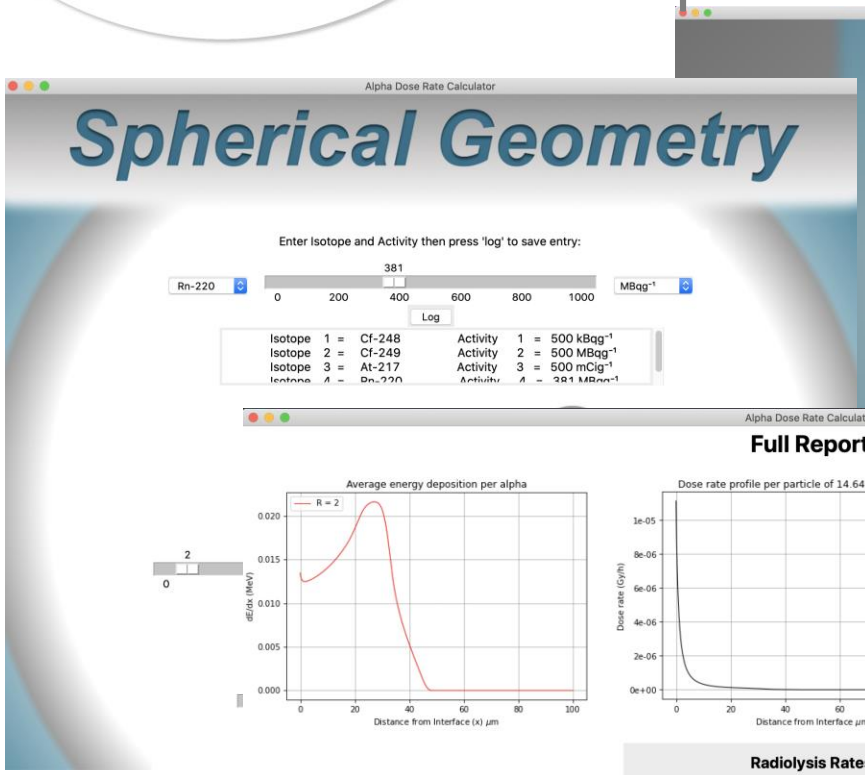
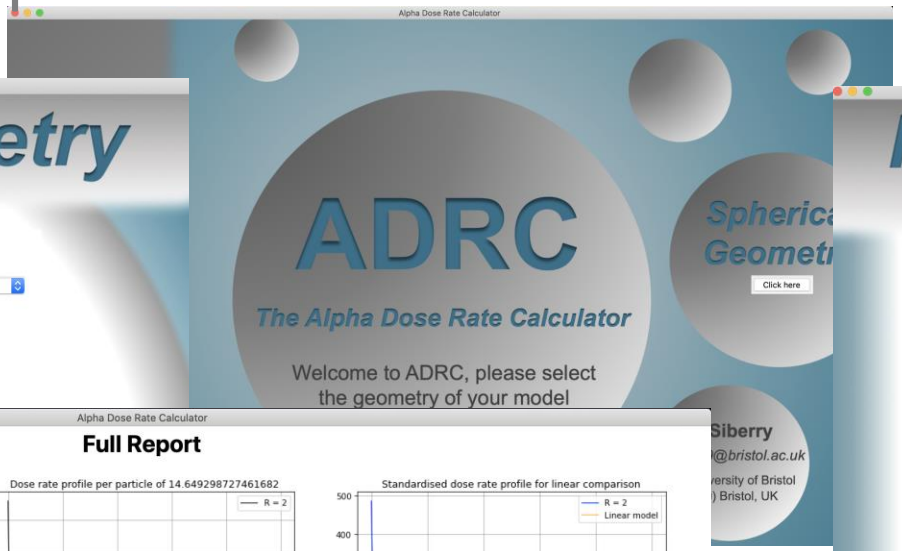
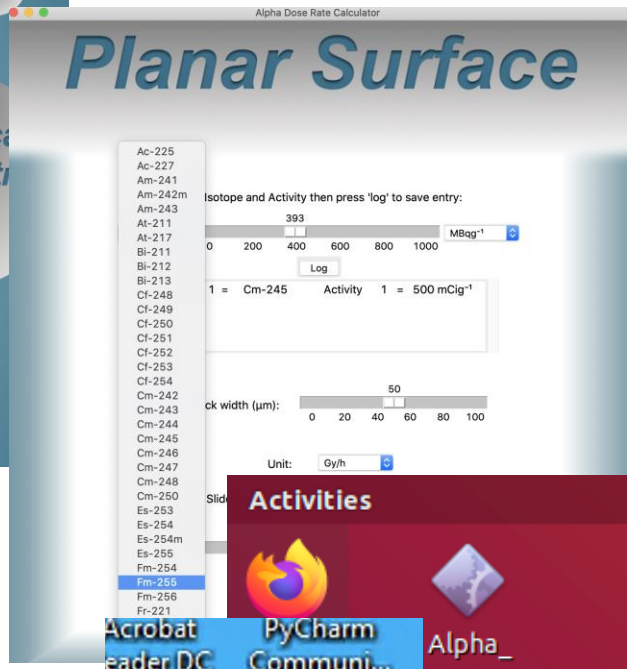
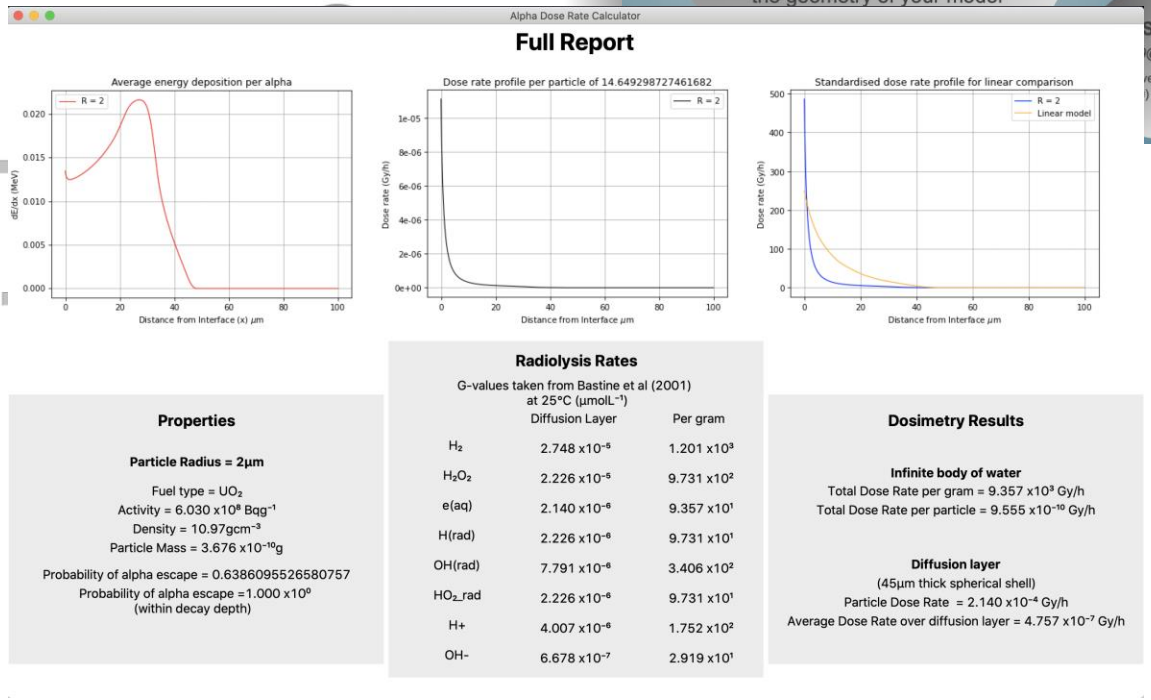
Alpha Dose Rate Calculator









Properties

Particle Radius = 2μm

Fuel type = UO_2
Activity = 6.030×10^8 Bqg^{-1}
Density = 10.97gcm^{-3}
Particle Mass = 3.676×10^{-10}g

Probability of alpha escape = 0.6386095526580757
Probability of alpha escape =1.000×10^0
(within decay depth)

Radiolysis Rates

G-values taken from Bastine et al (2001)
at 25°C (μmolL^{-1})

	Diffusion Layer	Per gram
H_2	2.748×10^{-5}	1.201×10^3
H_2O_2	2.226×10^{-5}	9.731×10^2
e(aq)	2.140×10^{-6}	9.357×10^1
H(rad)	2.226×10^{-6}	9.731×10^1
OH(rad)	7.791×10^{-6}	3.406×10^2
HO_2_rad	2.226×10^{-6}	9.731×10^1
H+	4.007×10^{-6}	1.752×10^2
OH-	6.678×10^{-7}	2.919×10^1

Dosimetry Results

Infinite body of water
Total Dose Rate per gram = 9.357×10^3 Gy/h
Total Dose Rate per particle = 9.555×10^{-10} Gy/h

Diffusion layer
(45μm thick spherical shell)
Particle Dose Rate = 2.140×10^{-4} Gy/h
Average Dose Rate over diffusion layer = 4.757×10^{-7} Gy/h

Available in Ubuntu, Windows and Mac OS

[Click here to download]

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Acknowledgements:

Supervisor: Ross Springell

Industry Supervisors:

NNL – David Hambley
Sellafield – Anna Adamska

Thank you

as14659@Bristol.ac.uk

Conclusion

Planar model:

- Good performance over current models
- Highlighted issues with 2D models and model by Hansson et al. (2020)
- Emphasises the importance of deriving probability of alpha escape analytically

Spherical model:

- Derivation for probability of alpha escape $P_{\alpha}(R,r,\delta)$ dramatically reduces calculations required before convergence. (Never been done before)
- Model agrees with MCNP modelling approach done by Tribet (2017) yet can be implemented in Python,C,C++ with fast computation time

Future work:

- Link radiolysis results to dissolution model in COMSOL (inc Beta radiation)

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Investigating Uranium Corrosion in different environments Using X-ray Tomography

Dr Haris Paraskevoulakos, University of Bristol

TRANSCEND/NDA/NWDRF Virtual Conference

2nd December 2012

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For a Low Carbon Future

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INDUSTRIAL CASE

- As of March 2015, the FGMSP has processed 27,000 tonnes of nuclear fuel (14,000 m^3 of contaminated water)
- Content: **Magnox** (Mg-Al alloy) cladding and **uranium** swarf
- Over the storage period Corrosion of Magnox cladding
- Formation of sludge (CMS)

NOWADAYS

- Pond decommissioning (Uranium and CMS)
- *What is the uranium state ?*
- *Has it corroded in the CMS environment ?*
- *What are the corrosion products ?*

- ***Sellafield Ltd**: (FGMSP) The storage pond has processed 27,000 tonnes of nuclear fuel*

THEORY

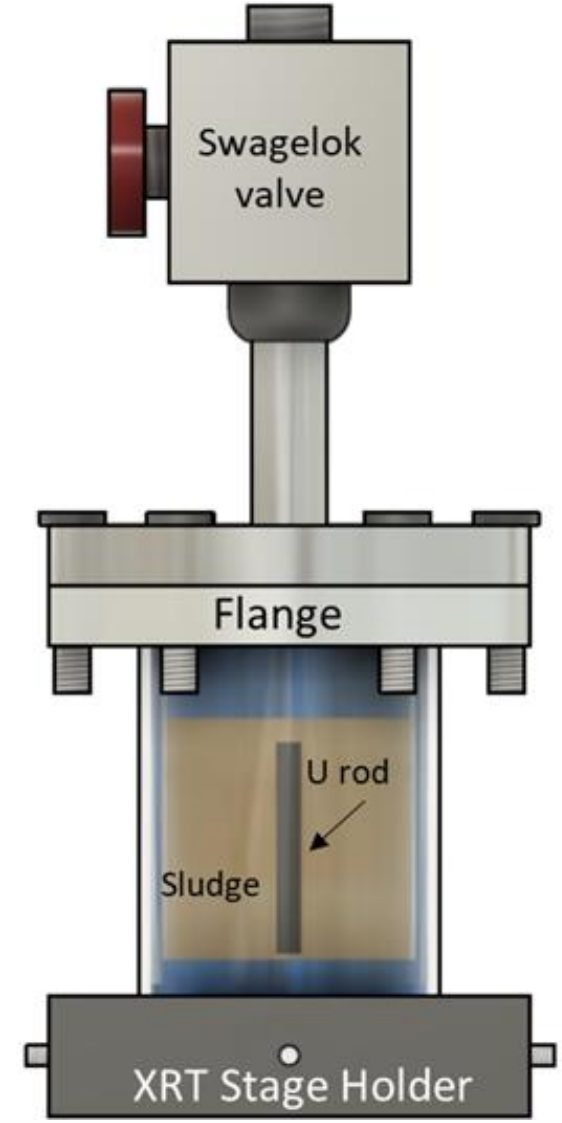
$$Mg + 2H_2O \rightarrow \boldsymbol{Mg(OH)_2} + H_2$$

$$U + 2H_2O \rightarrow \boldsymbol{UO_2} + H_2$$

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

HAZARDS

- *Radioactivity/Toxicity*
- *Hydrogen Flammability*
- *UH_3 Pyrophoricity*



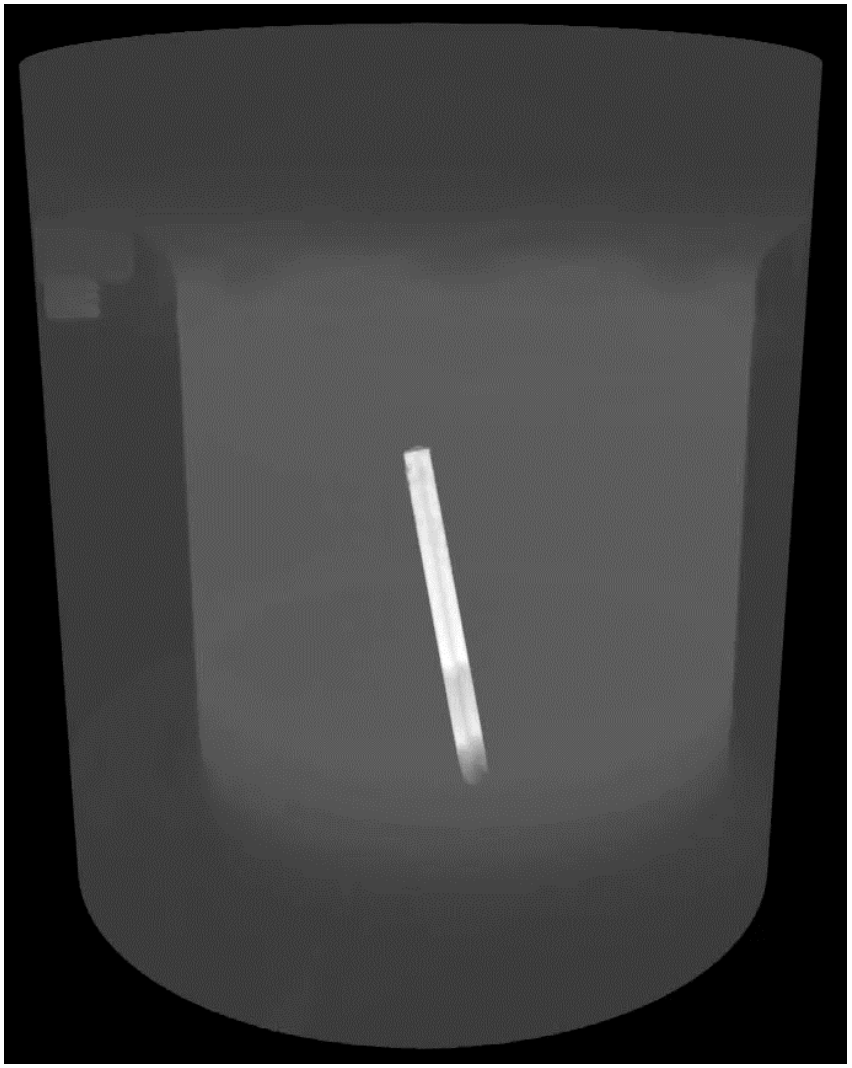
Scans

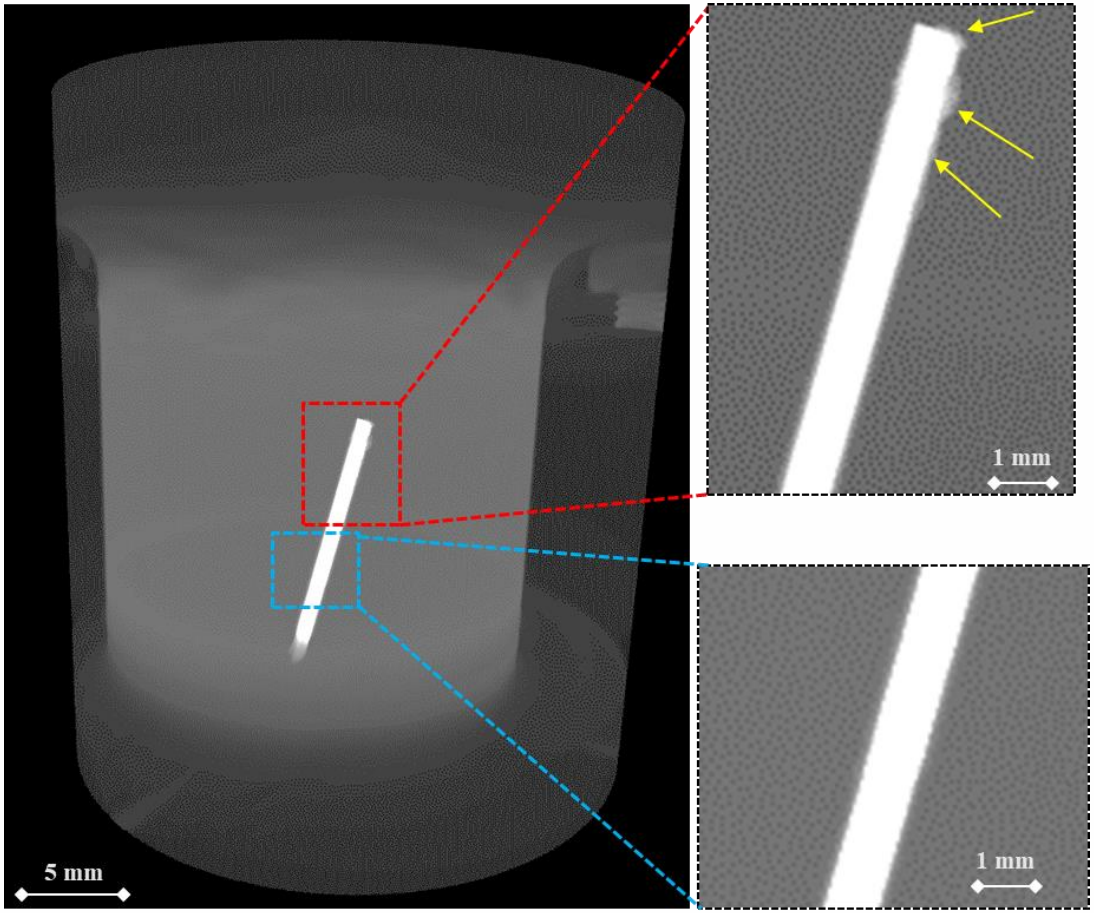
- Low-resolution, high FOV
  (~30µm/pixel, ~1 h 30 mins per scan)
- High-resolution, low FOV
  (~2.8µm/pixel, ~20 hours per scan)

Data Collection

- 20 days after preparation
- 50 days after preparation
- 360 days after preparation
- 540 days after preparation

20 Days Post Preparation





Key findings

- *First signs of corrosion*
- *Crater/blister type of morphology – No Layer*
- *No signs of corrosion across lower uranium*

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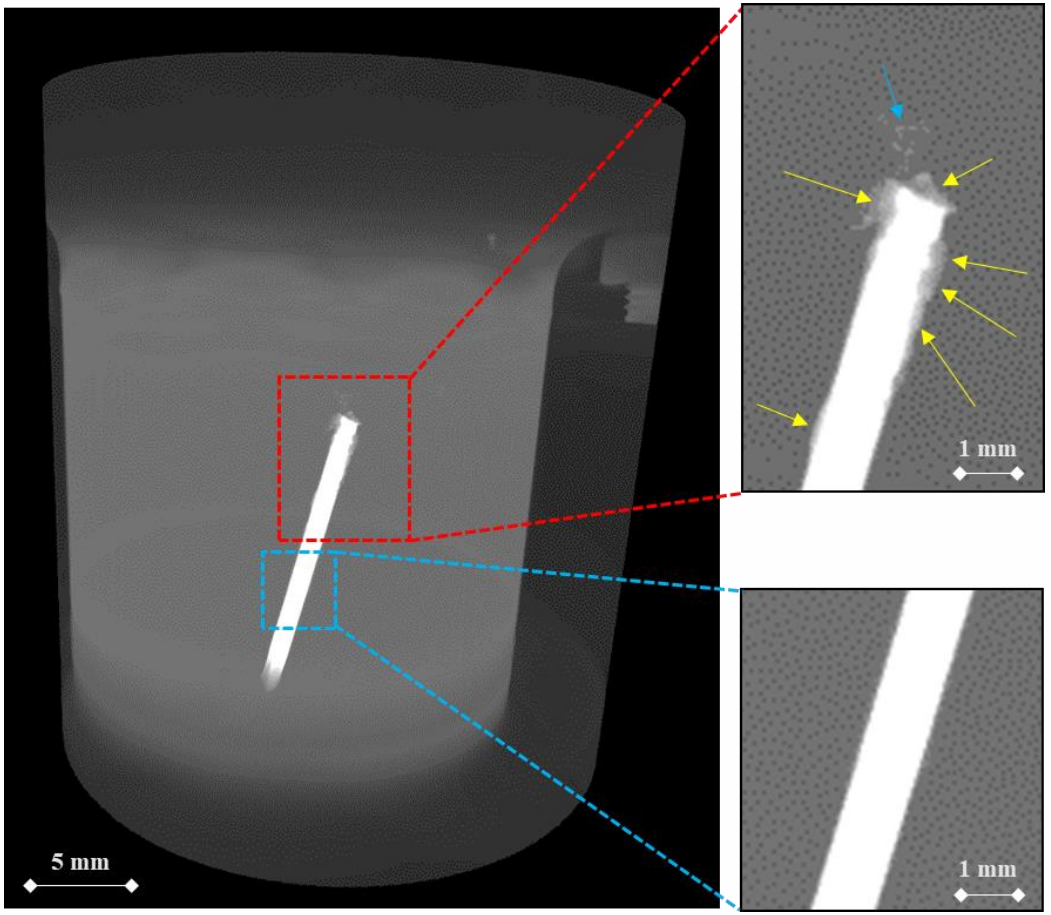
50 Days Post Preparation



Key findings

- *Corrosion Product Volume Growth*
- *Signs of Coalescence*
- *Migration away from the Corroding Front*
- *Intact Low Surfaces*

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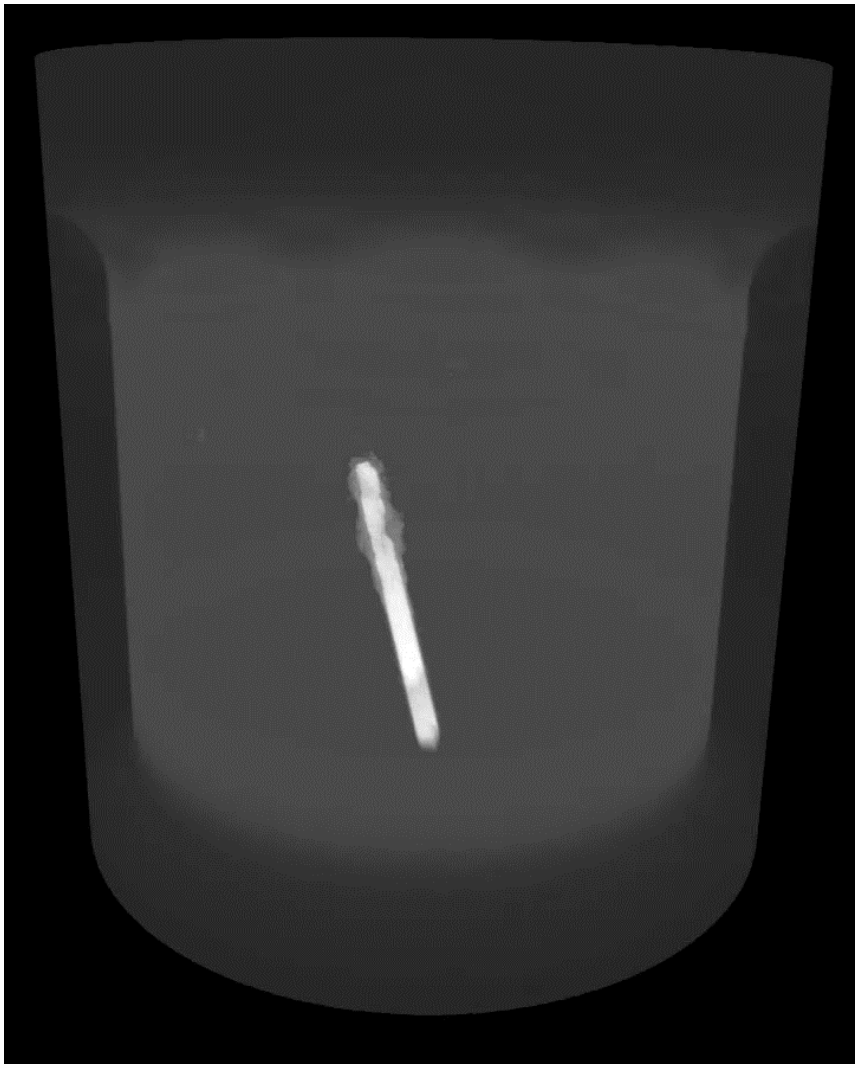
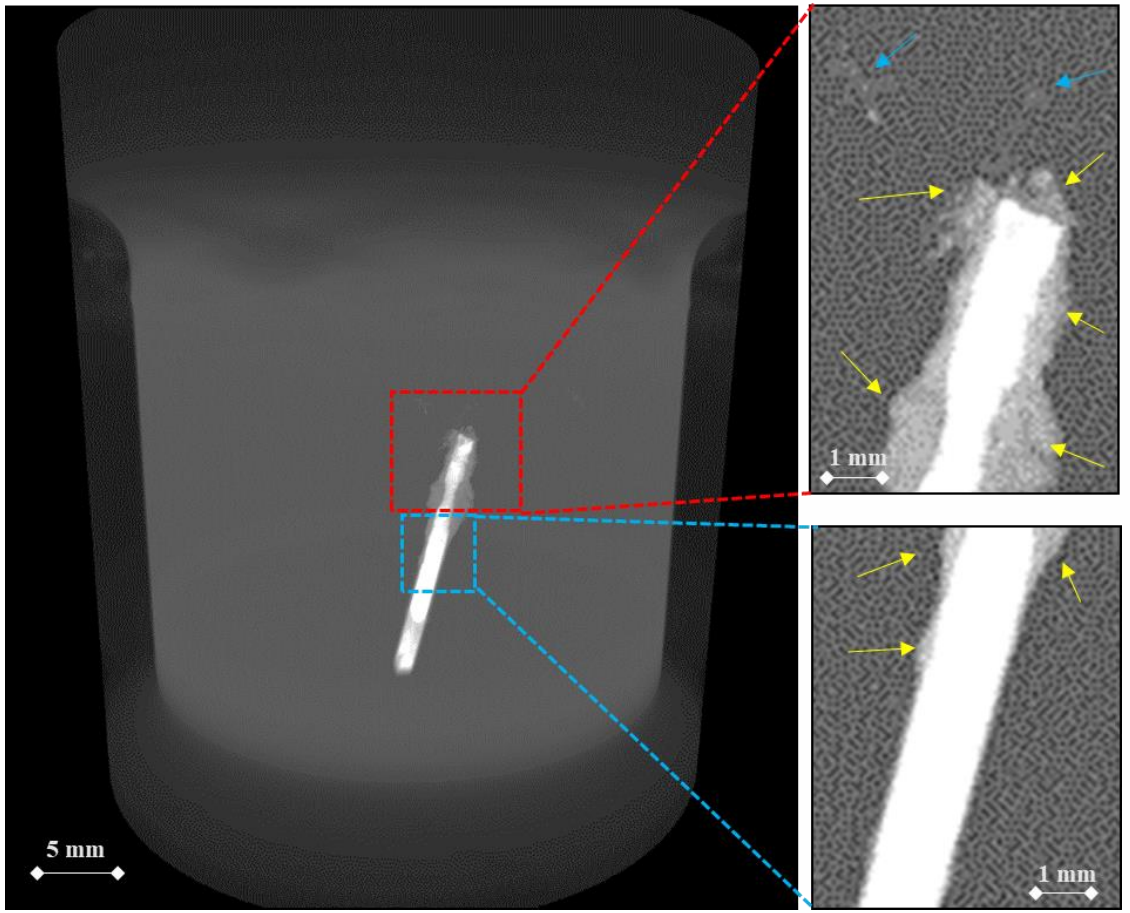
360 Days Post Preparation





Key findings

- *Significant growth of Corrosion Product Volume*
- *Coalescence at the Top Part of the Specimen*
- *Signs of Corrosion across the Middle Height*
- *Intact Low Surfaces*

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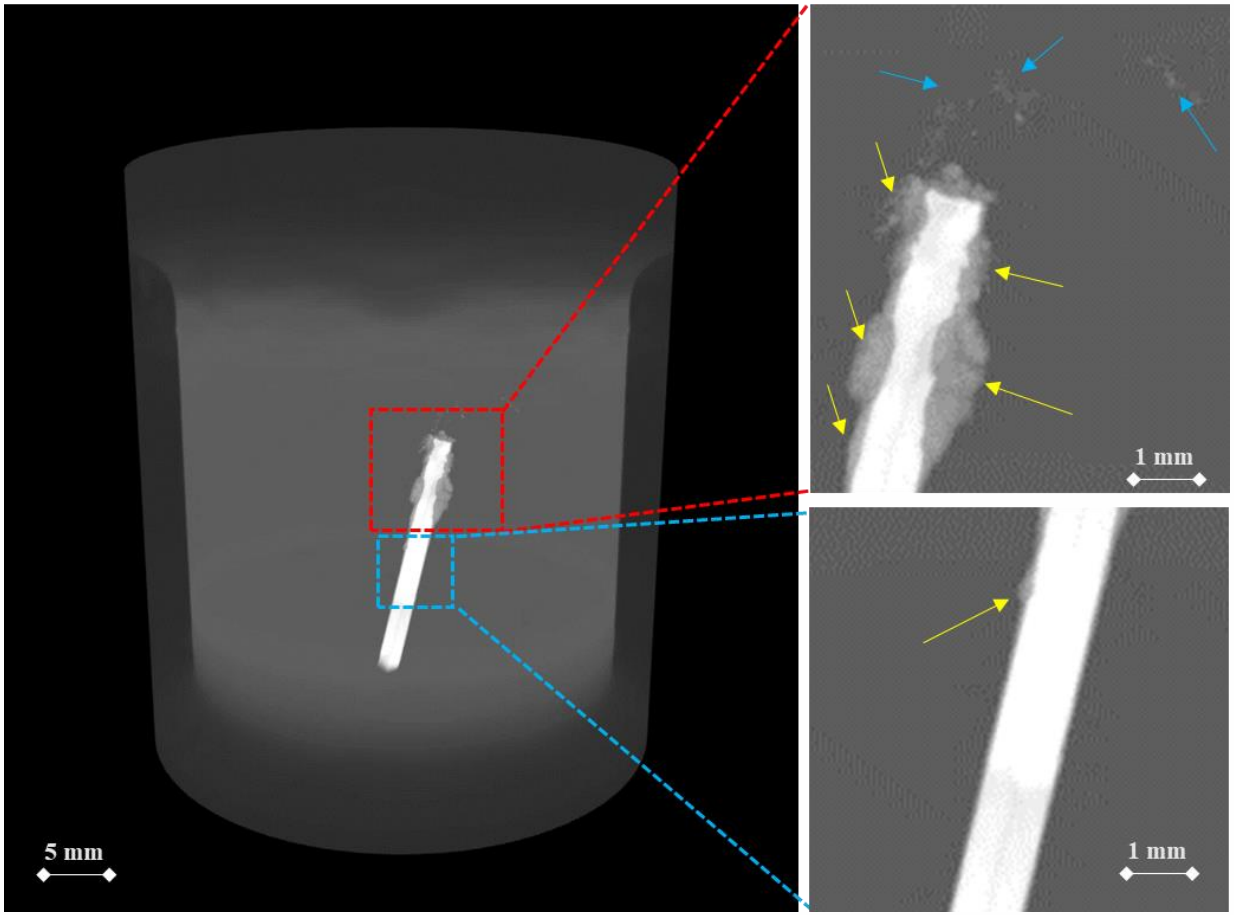
540 Days Post Preparation

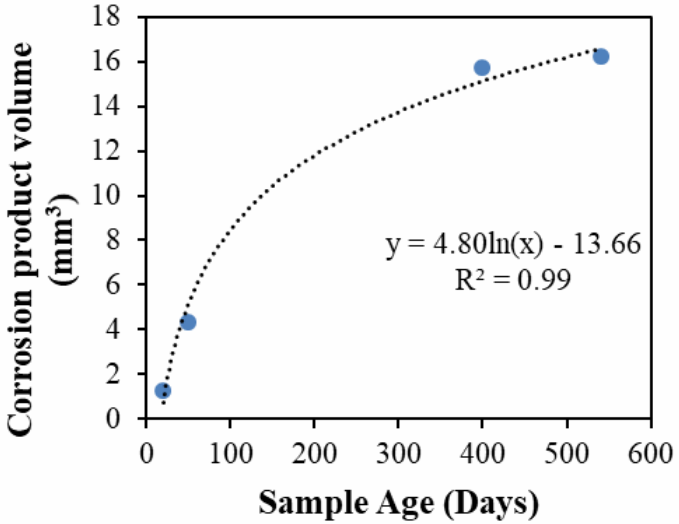


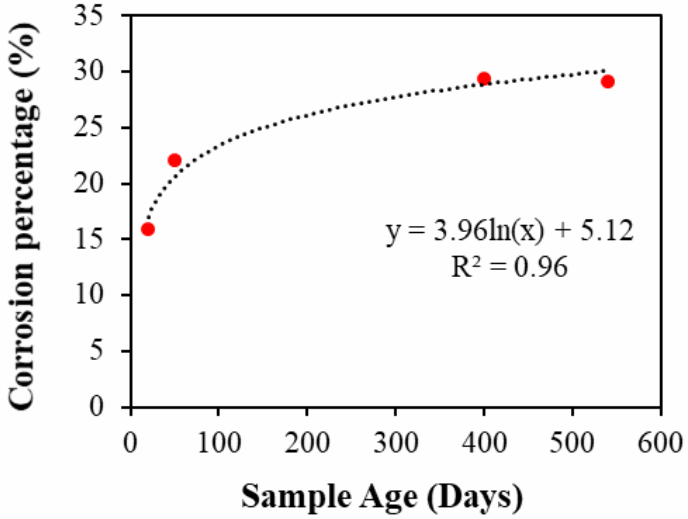
Key findings

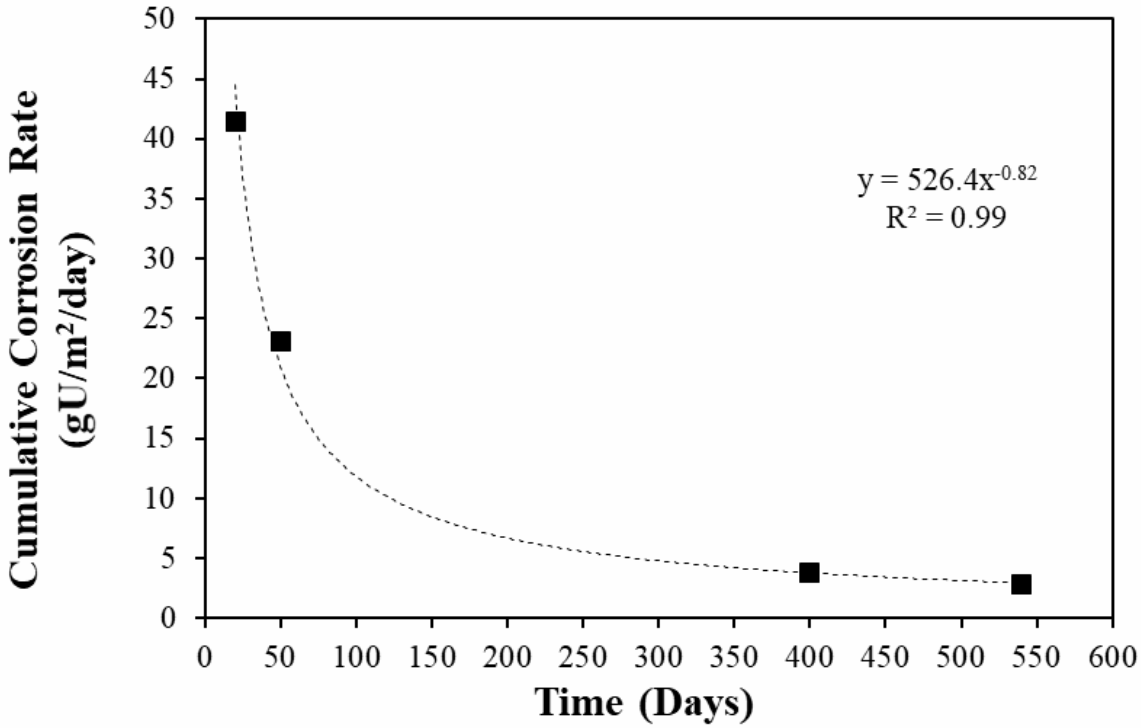
- *Corrosion product volume remained constant*
- *Intact low surfaces*
- *Further migration of particles away from the uranium*

Quantitative Analysis

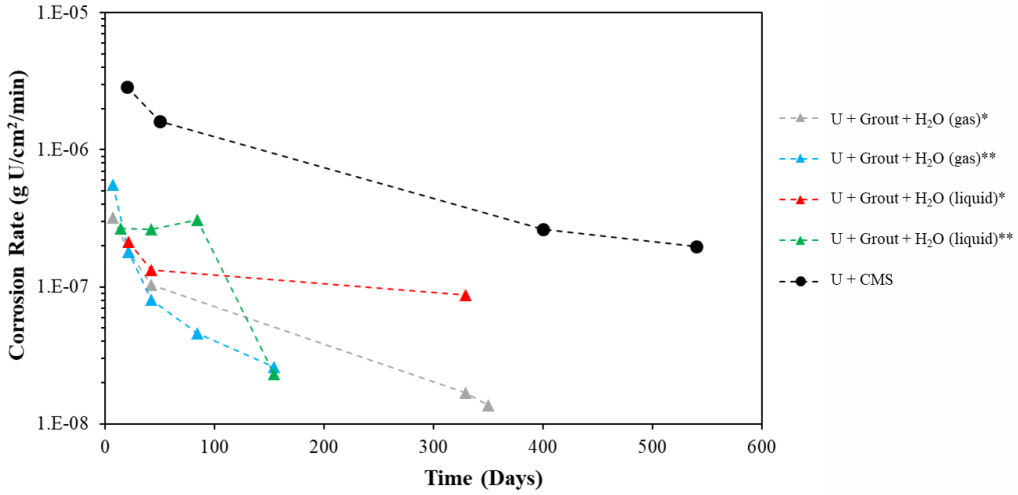
- Image processing software Avizo®
- Material segmentation (Uranium, Corrosion products)
- Determination of relevant volumes
- ***Calculation of corrosion percentage***
- ***Calculation of corrosion rate***





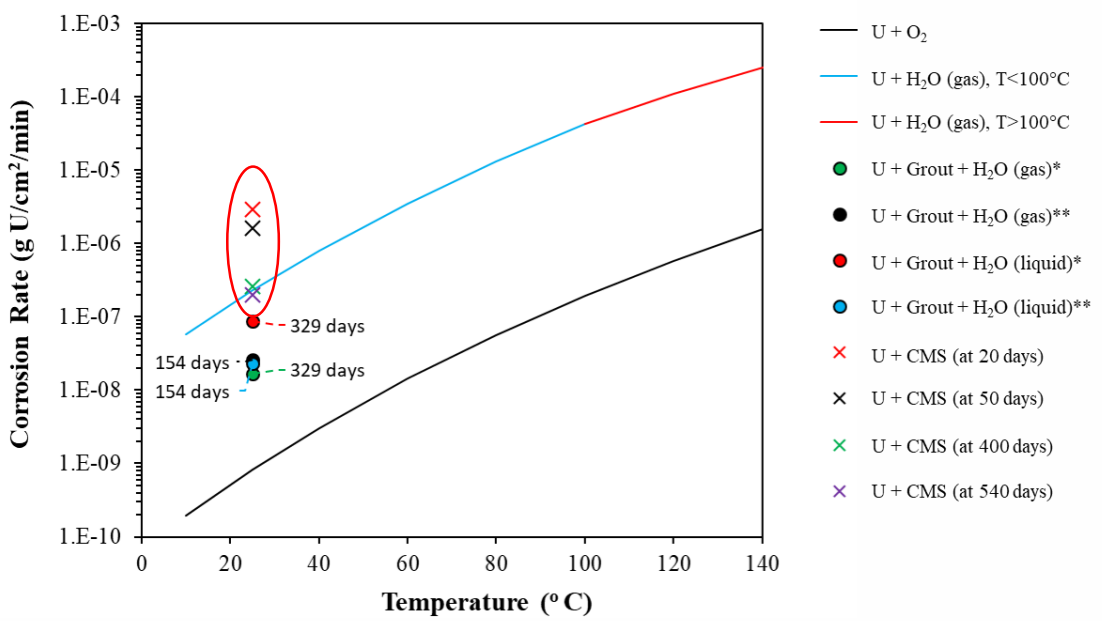


Corrosion Rate vs Time (Against Literature)



*Uranium was used in as-received state
**Uranium was pickled in nitric acid prior to encapsulation

Corrosion Rate vs Temperature (Against Literature)



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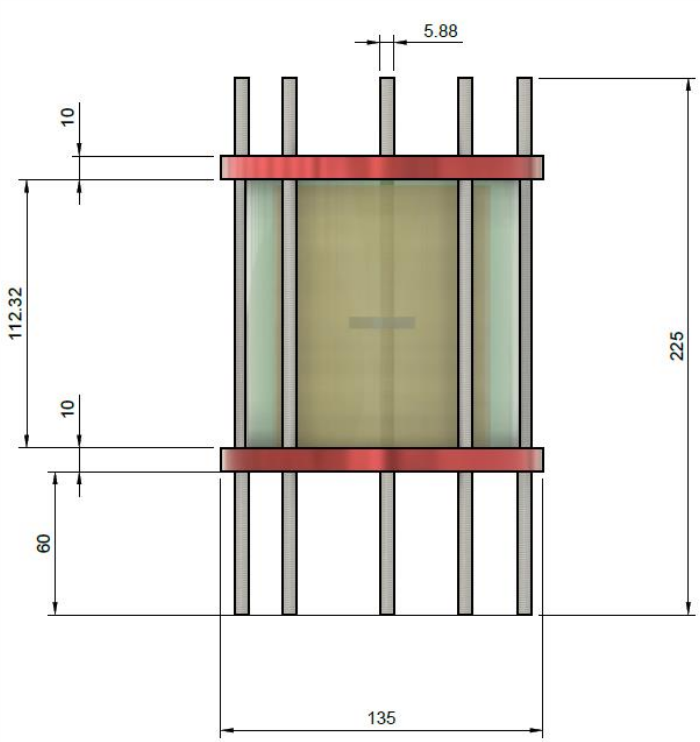
**Uranium was pickled in nitric acid prior to encapsulation

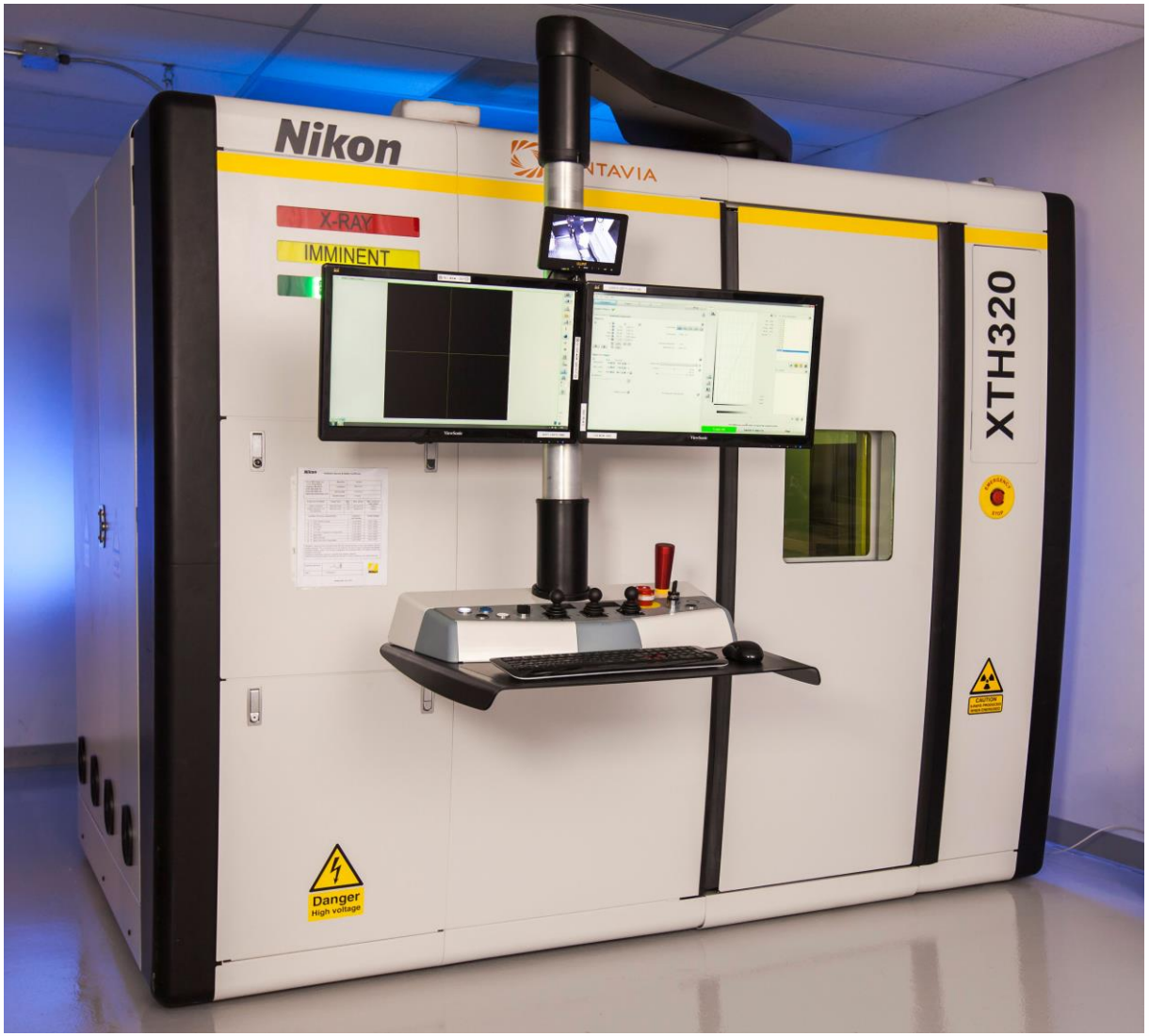
C. Paraskevoulakos et al. Monitoring uranium corrosion in Magnox sludge using X-ray computed tomography: A direct analogue to "legacy" fuel storage ponds. Corros. Sci., vol. 168 (2020)

Uranium Corrosion in Mixed Grout Systems

- Custodians of 14 samples originally produced by NNL
- Uranium long term (~15 years) metallic corrosion in mixed grout (and/or sludge) formulations
- Corrosion under ambient conditions
- Calculation of corrosion rate using gas monitoring (H_2 pressure)

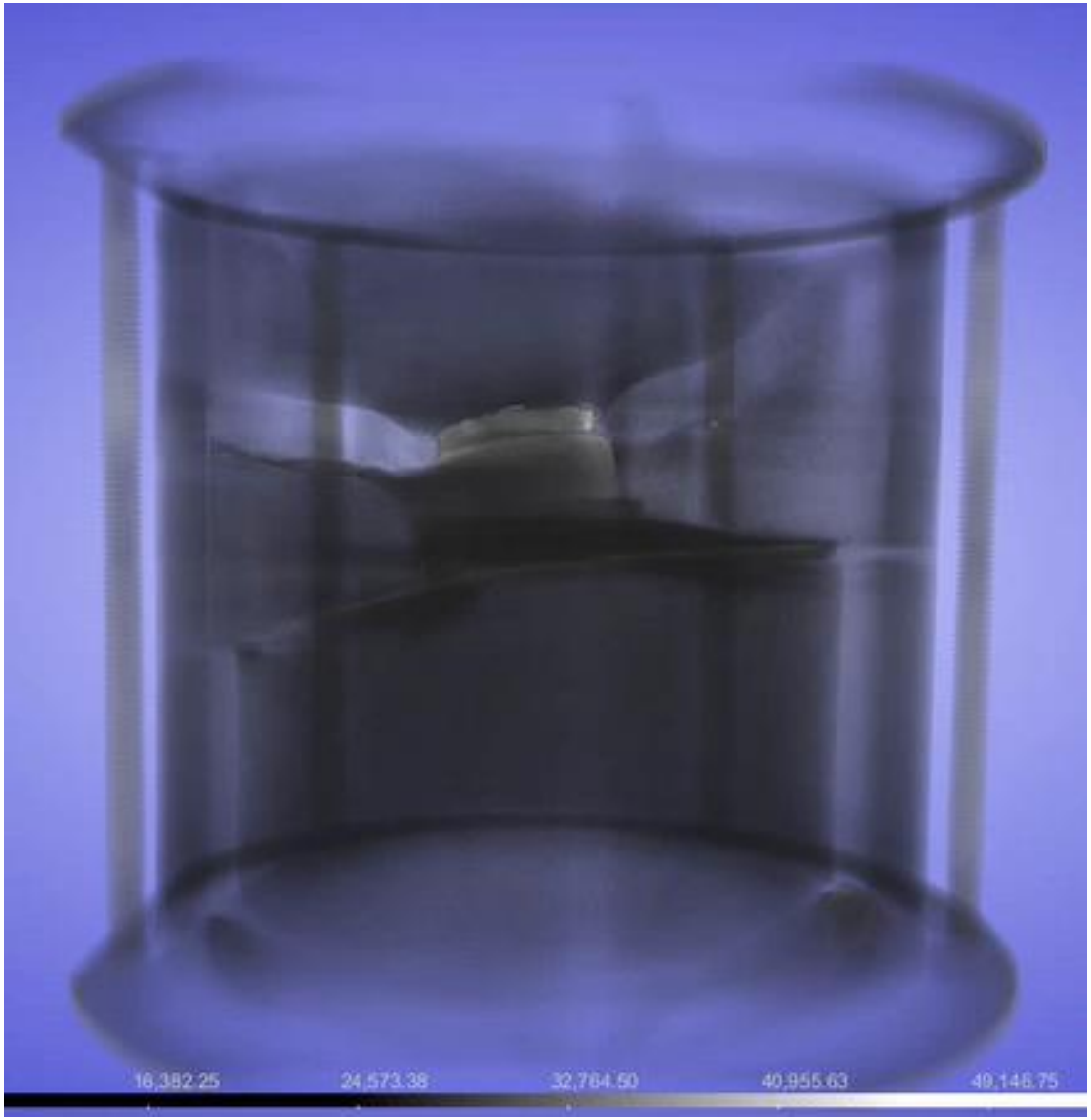
- What is the state of uranium?
- What is the state of corrosion products?
- What is the identity of corrosion products?
- What is the state of the encapsulants?





Primary Research Activities

- X – Ray Tomography
- National Composite Centre (NCC)
- High Energy X-Ray beam (<320 kV – Limited Energy)
- 7 samples scanned
- Voxel resolution 83.5 µm
- FOV: Entire Sample

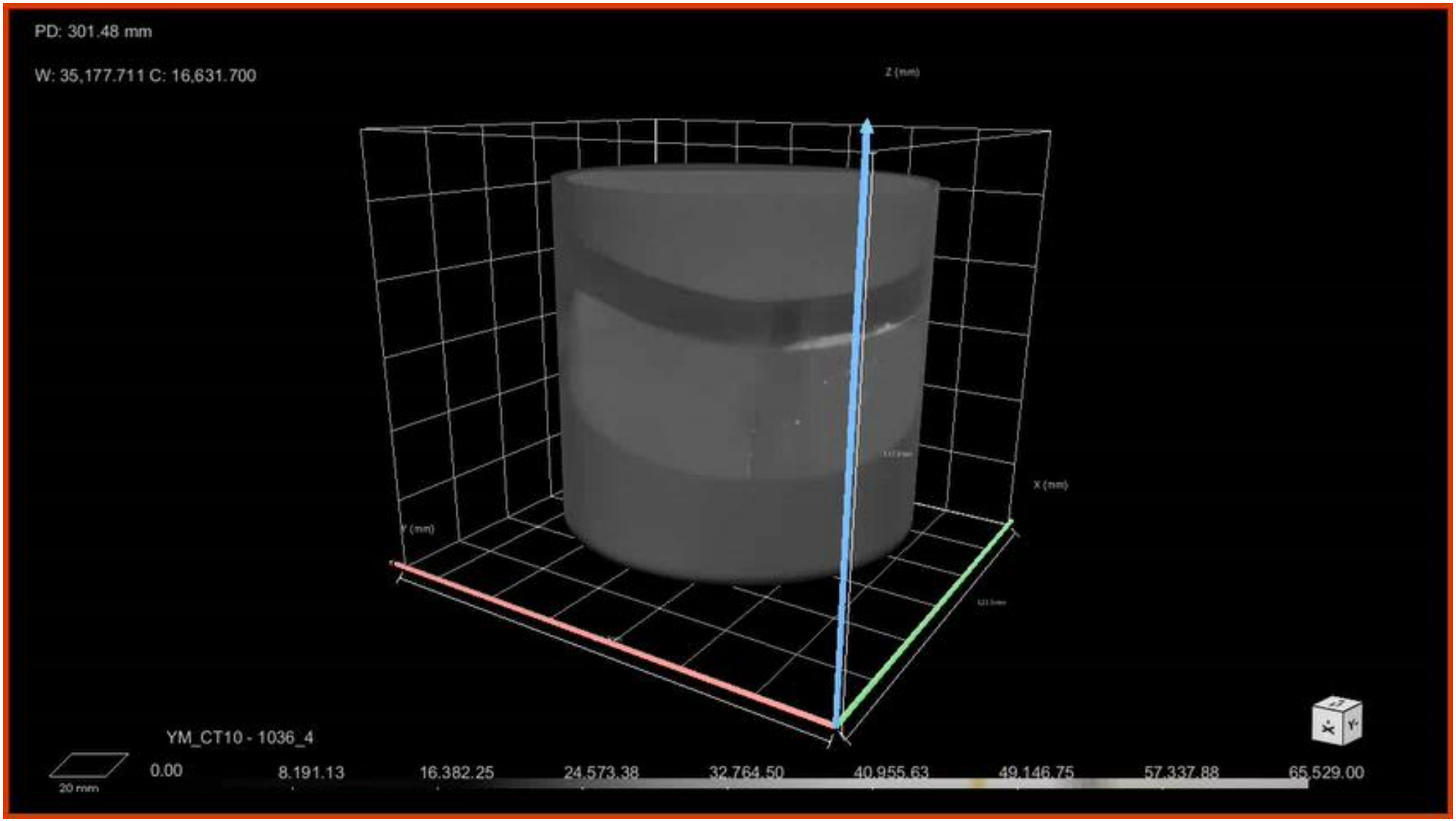


Targets

- *Uranium corrosion magnitude*
- *Uranium corrosion product identity*
- *3D mapping of uranium corrosion products diffusion/migration*
- *Grout damage magnitude (crack volume)*
- *Corrosion-Degradation quantitative correlation*

Primary Results-Visualisation

- *Natural Uranium disc (137.35 g)*
- *Grout (5:1 GGBS/CEM I)*
- *No Sludge*



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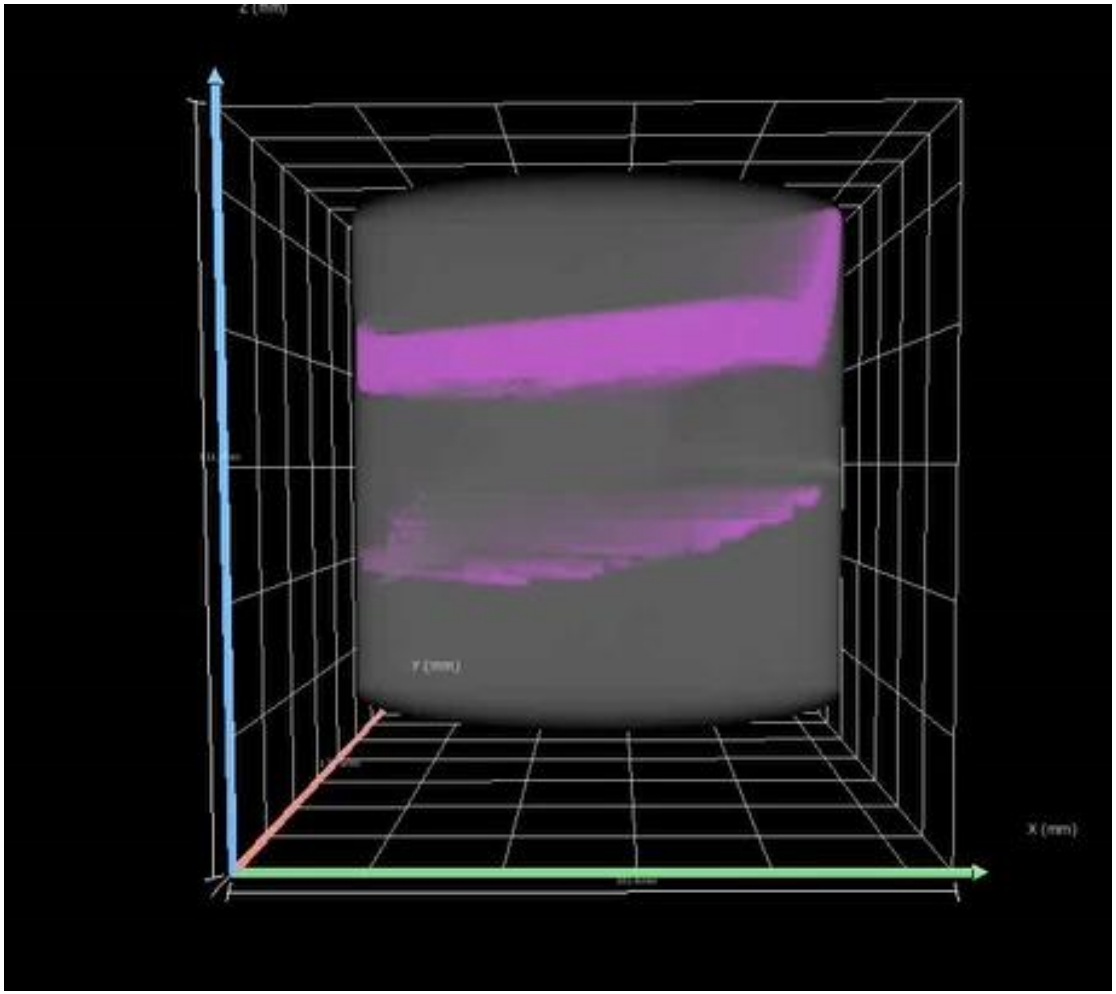
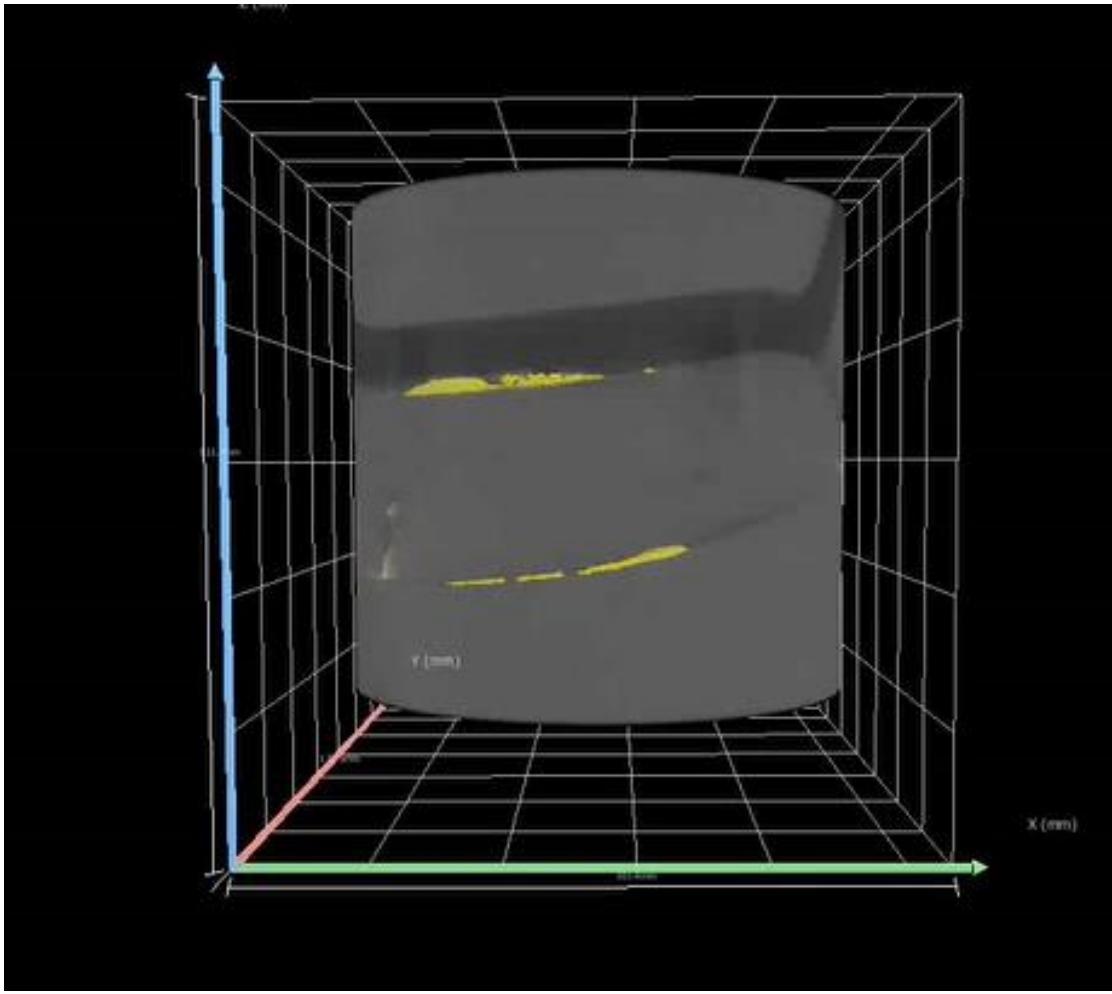
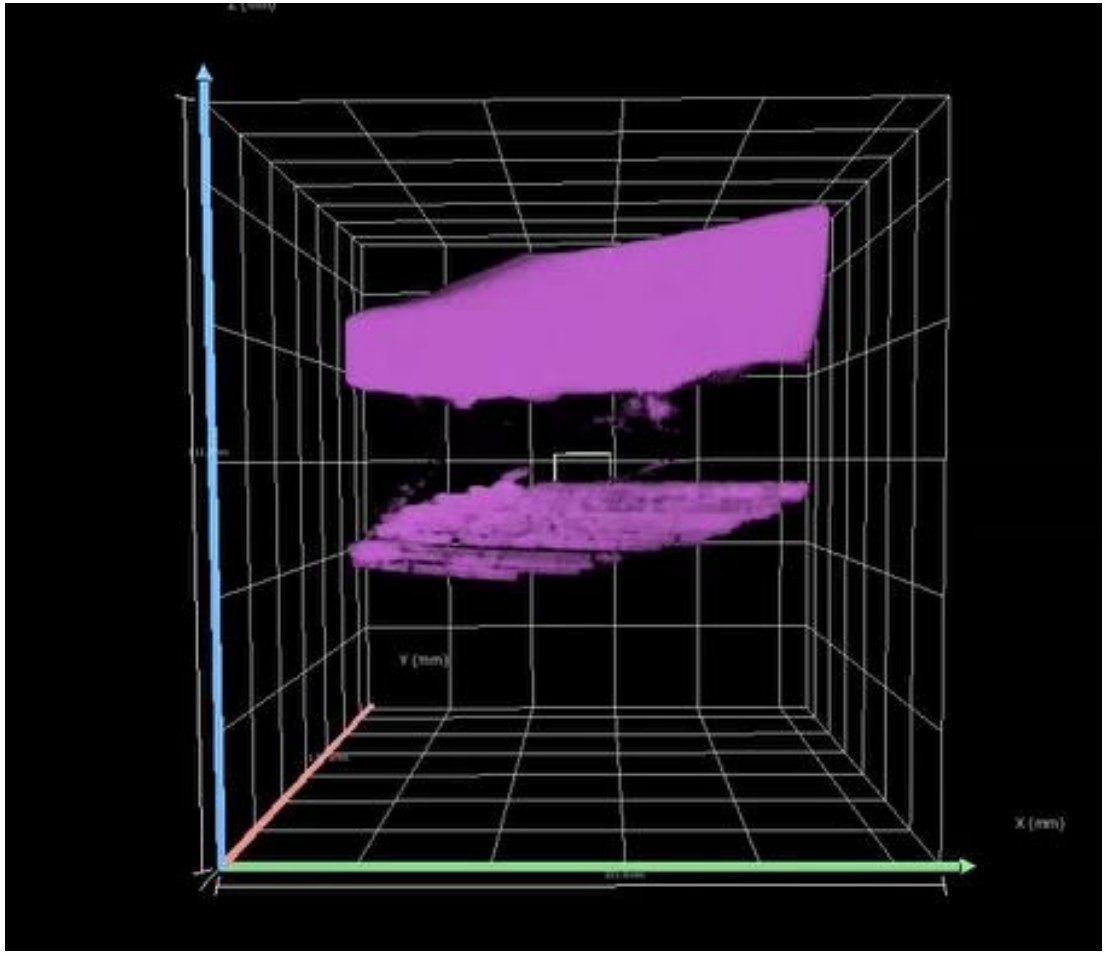
Primary Results-Material Segmentation



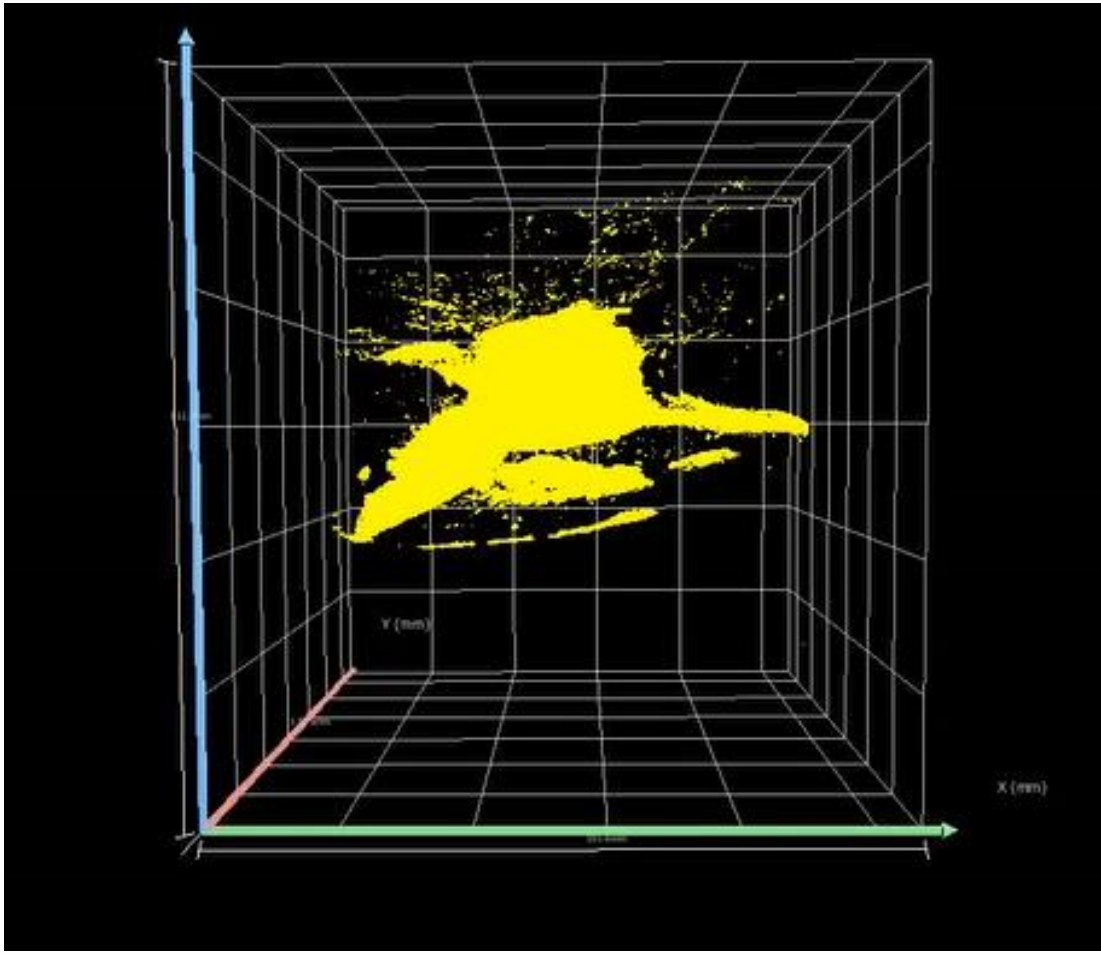


Primary Results-Material Segmentation

- 3D Crack Volume Rendering



- 3D Uranium Volume Rendering



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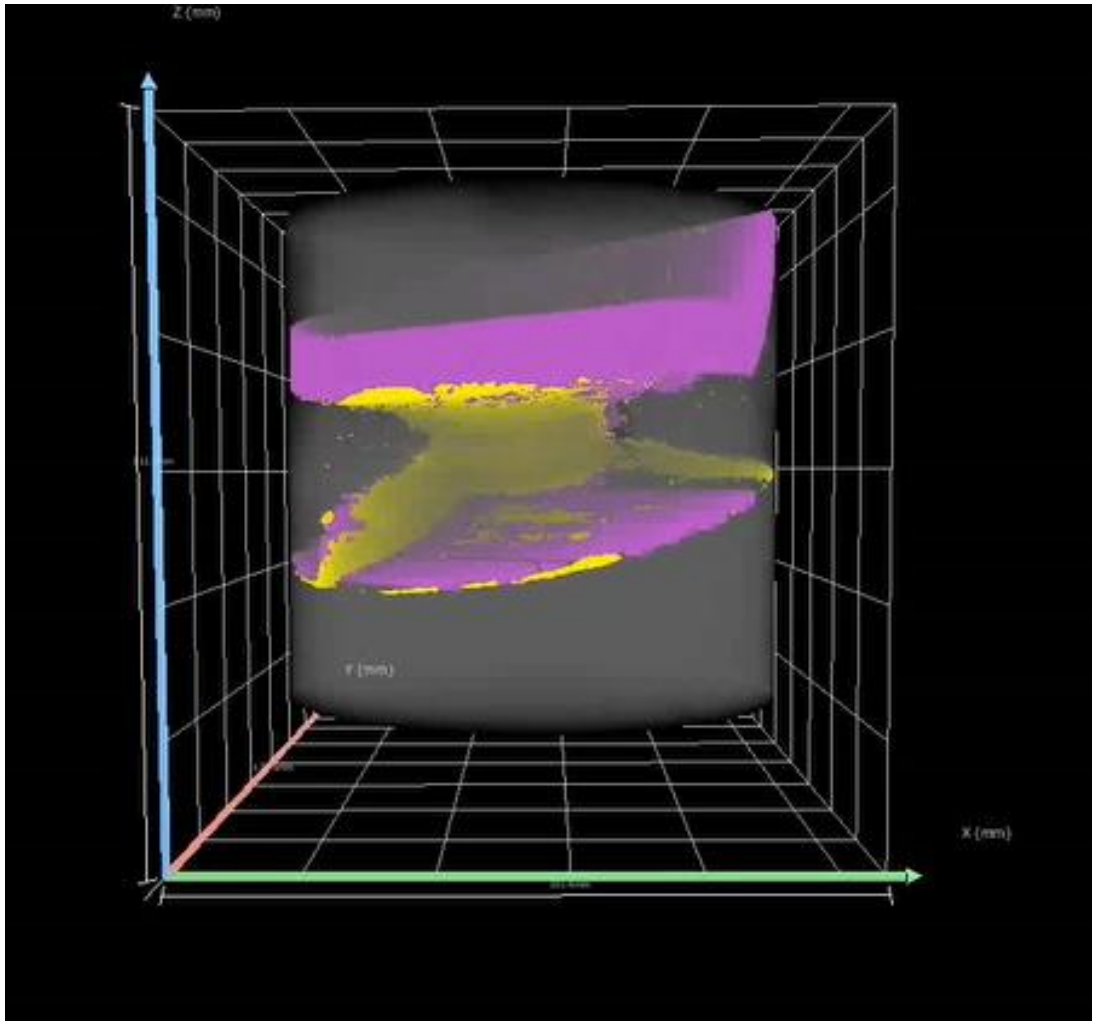
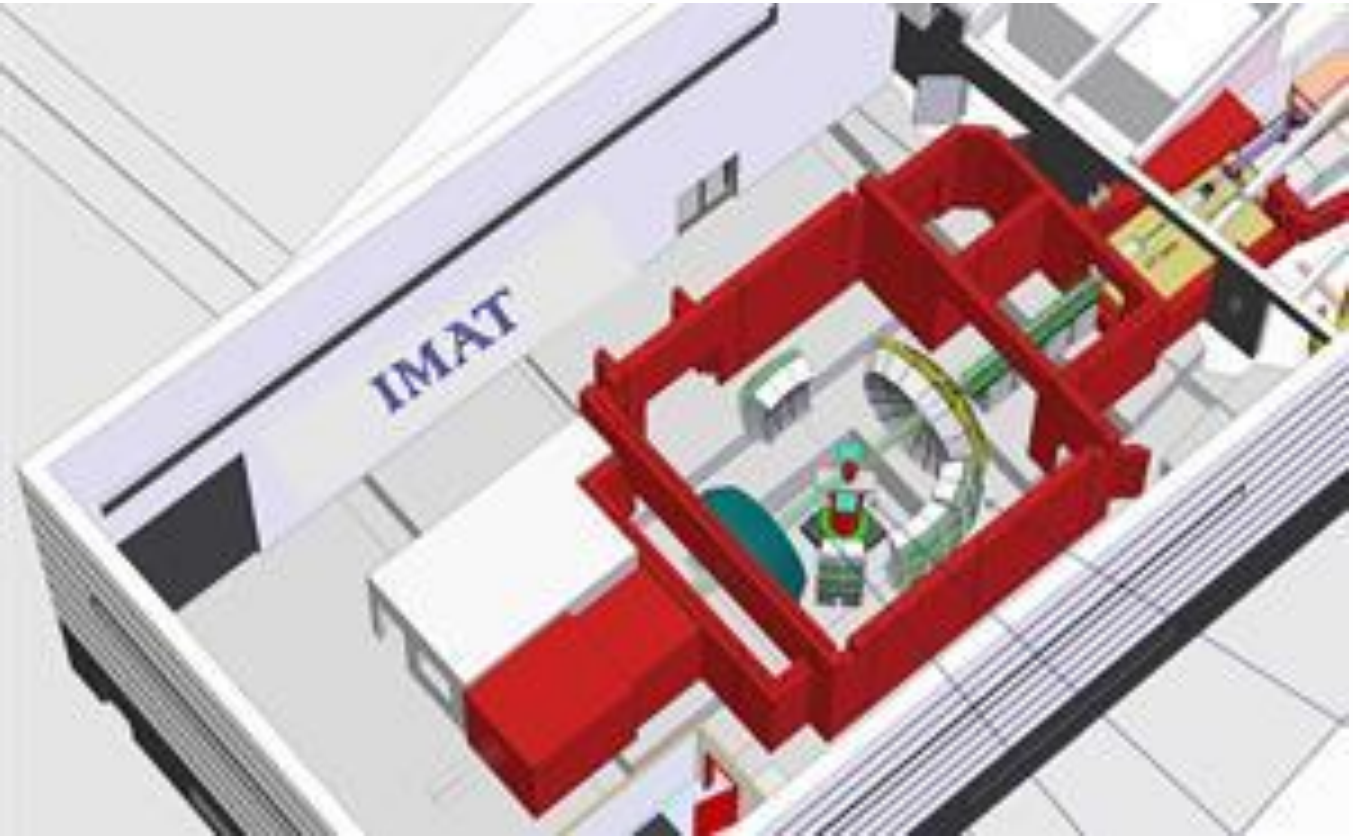


Quantitative Analysis

- Volume of uranium plus corrosion products (3.57 % of entire volume)
- Volume of cracks (10.15 % of entire volume)

Quantitative Analysis Pros

- Comparison between samples (Crack volumes – Grout Degradation)
- Grout Porosity
- Corrosion Percentage



Future Research Activities

- XRT at higher energy (Full Power at 320 kV
- Higher geometric magnification
- Scanning of all samples
- ISIS Neutron Imaging
- ISIS Neutron Diffraction

Acknowledgments

- Dr Chris Jones
- Dr Yusuf Mahadik
- Prof Tom Scott
- Dr Genoveva Burca

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Contact Details

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In-situ Small Punch Test for Stress Corrosion Cracking

Kuo Yuan University of Bristol

Transcend theme meetings 2020

2nd December 2020

Energy For a Low Carbon Future

My Research

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

- Use surrogate materials such as thermally sensitised 304 stainless steel to develop the micromechanical testing methods
- Digital Image Correlation will be used to track the development

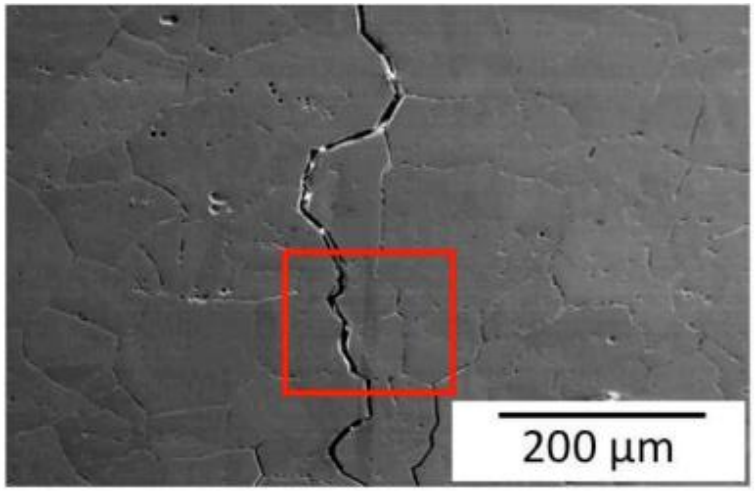

Fig. 1. SEM image of a stress corrosion crack; the crack initiation site is highlighted[1]

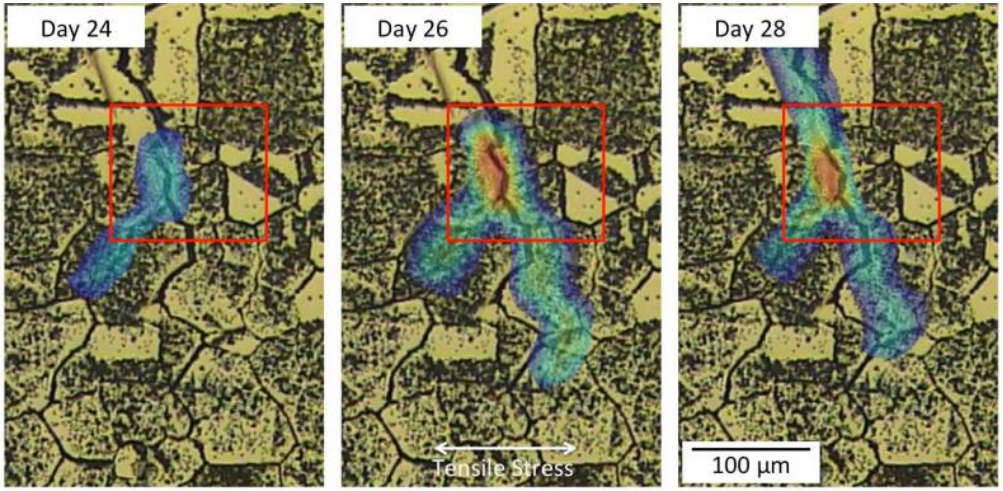

Fig. 2. DIC strain mapping of the development of a crack [1]

[1] Stratulat, A., Duff, J., Marrow, J. (2014), Grain boundary structure and intergranular stress corrosion crack initiation in high temperature water of a thermally sensitised austenitic stainless steel, observed in situ, Corrosion Science, 85, 428-435

Why Small Punch Test?

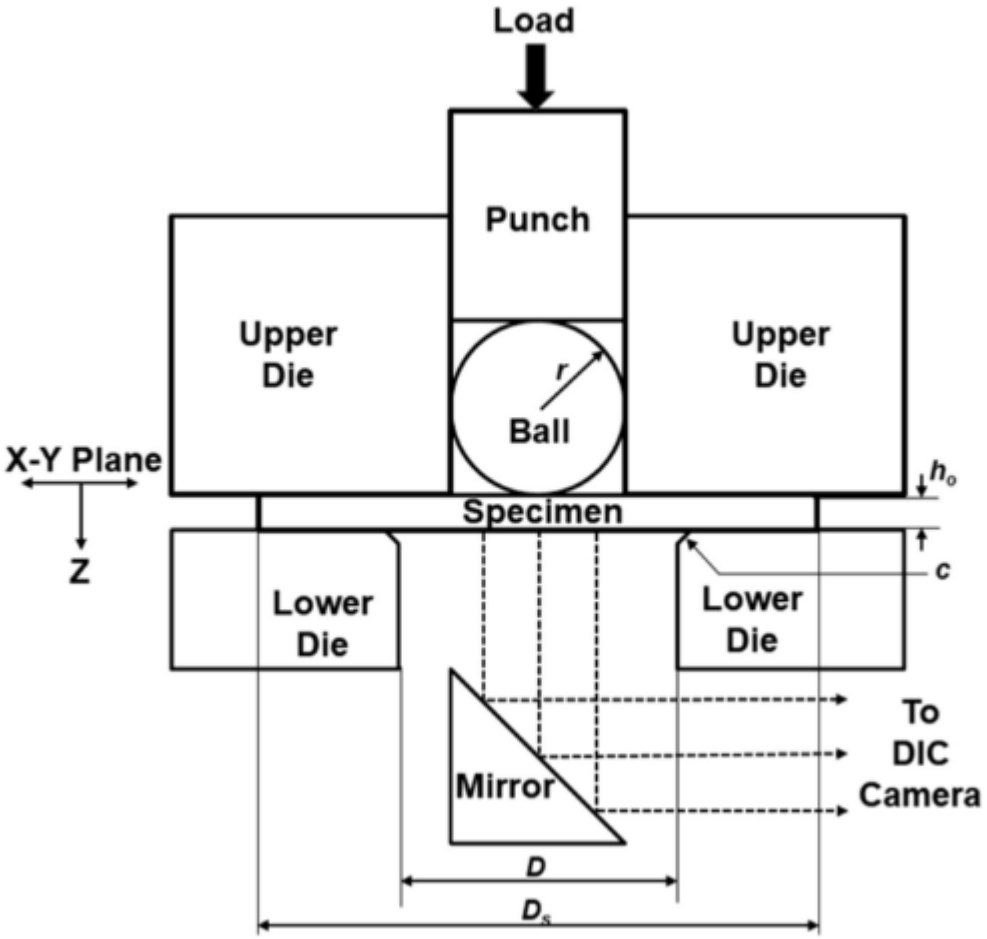

Fig. 3. a small punch test rig with a mirror to accommodate DIC[2]

- SPTs are used to determine the mechanical properties
- Only a small sized sample is required, ideal for ex-serviced AGR cladding materials
- The service condition of the material can be introduced, e.g. LWR conditions and storage pond condition
- DIC can also be introduced to monitor the cark propagation

[2]V. D. Vijayanand *et al.*, "A novel methodology for estimating tensile properties in a small punch test employing in-situ DIC based deflection mapping," *J. Nucl. Mater.*, p. 152260, 2020, doi: 10.1016/j.jnucmat.2020.152260.

My Design

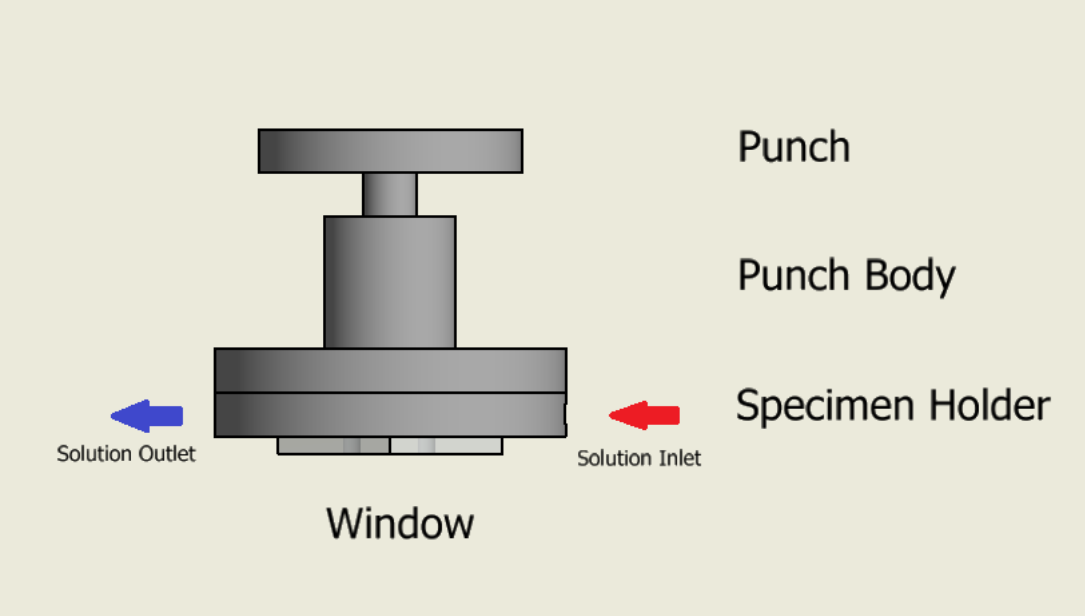

Fig. 4. modified small punch test rig with a loop system

- Previous tests either applied the solution on the specimen [3] or submerged the whole rig into the solution [4]
- A loop will be used in the system to introduce the corrosive solution
- A window is used to seal the specimen hold and also allows DIC observation with the mirror

[3] J. Isselin, A. Kai, K. Sakaguchi, and T. Shoji, "Assessment of the effects of cold work on crack initiation in a light water environment using the small-punch test," *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.*, vol. 39 A, no. 5, pp. 1099–1108, 2008, doi: 10.1007/s11661-008-9492-7.

[4] T. Bai and K. Guan, "Evaluation of stress corrosion cracking susceptibility of nanocrystallized stainless steel 304L welded joint by small punch test," *Mater. Des.*, vol. 52, pp. 849–860, 2013, doi: 10.1016/j.matdes.2013.06.019.

In-situ Synchrotron test for SCC

- Cracks can propagate in 3D
- In-situ synchrotron tests are proposed to observe the cracks with Digital Volume Correlation by reconstructing the tomography
- A tensile load is applied on the specimen and a similar circulation of corrosive solution is introduced
- The results of DIC and DVC will be compared

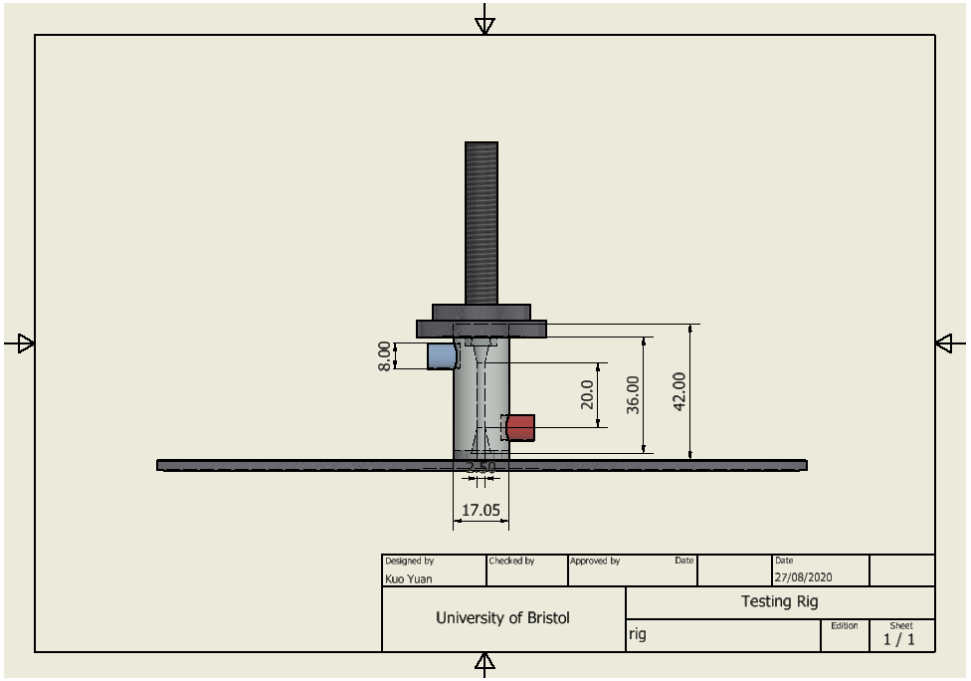

Fig. 5 testing rig for in-situ synchrotron test with inlet and outlet for the solution

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Transformative Science and Engineering for Nuclear Decommissioning

Acknowledgement

This project is funded by TRANCEND and NNL

Supervised by Mahmoud Mostafavi (UoB) and Ronald Clark (NNL)

Thank you

k.yuan@bristol.ac.uk

University of BRISTOL

NATIONAL NUCLEAR LABORATORY

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

Drying of Spent AGR Fuel

Thomas Bainbridge, University of Leeds

Theme Meeting 3

2/12/2020
Online

Energy
For a Low Carbon Future

Motivation

- To support NDA strategy / decision making on the long term storage and disposal of SNF.
- In dry storage / disposal any water remaining can cause additional corrosion.
- Also potential for the water to undergo radiolysis producing H_2 and H_2O_2
- Do not want these products formed – H_2 is flammable and explosive while H_2O_2 will accelerate any corrosion occurring.
- SNF must therefore be dried before storage / disposal to reduce this risk.

AGR Fuel element [1]

[1] https://collection.sciencemuseumgroup.org.uk/objects/co5473/agr-fuel-element-c-1982-nuclear-fuel-fuel-rods

Aim

- To create a process model for drying spent fuel through radiation induced stress corrosion cracks in AGR fuel cladding.

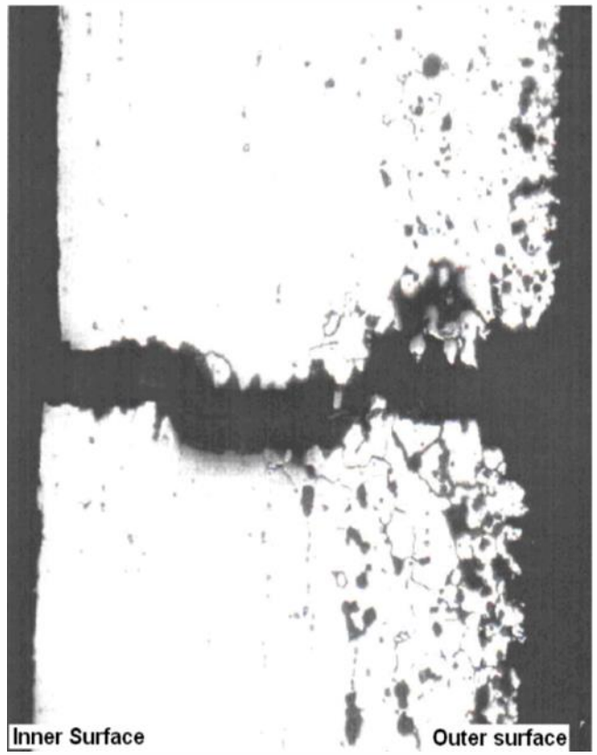
Sections

Computational

- Model drying through a complex crack.
  - Obtain geometrical parameters of the crack.
  - Apply fluid dynamics calculations to find the flow through the crack.

Experimental

- Produce representative cracks in stainless steel.
- Generate test pieces of cracked stainless steel for use in the drying rig.
- Use the drying rig to validate the process model.



Failed AGR cladding [2]

[2] John Kyffin. Technological Development to Support a Change in the United Kingdom's Strategy for Management of Spent AGR Oxide Fuel. In Proceedings of the International Conference on Management of Spent Fuel from Nuclear Power Reactors, Vienna, June 2015. IAEA

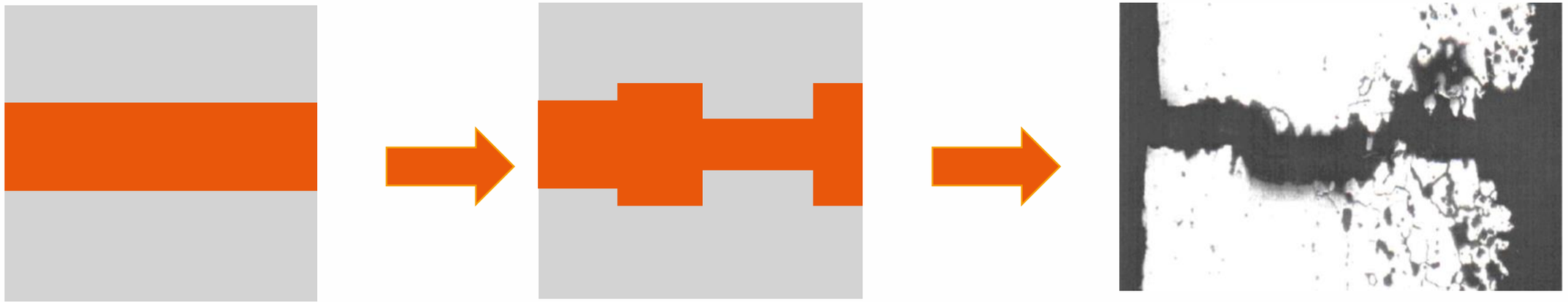
Modelling of Cracks and Pinholes

- Start on a pinhole to be able to compare to experimental data from currently available samples.
- If computation matches experimentation progress to multiple connected pinholes/sharp edged orifices.
- Finally move to complex, tortuous cracks.

Pinhole

Multiple connected pinholes

Complex crack

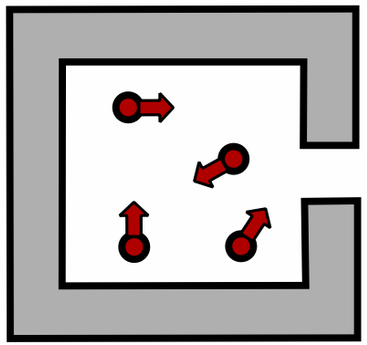


Bomelburg [3]

- Mainly used for determining flow rate through a sharp edged orifice.

$$Q = \alpha a \psi_{max} \sqrt{2 g P_0 \rho_0}$$

$$\psi_{max} = \left(\frac{2}{\gamma + 1}\right)^{\frac{1}{(\gamma - 1)}}$$



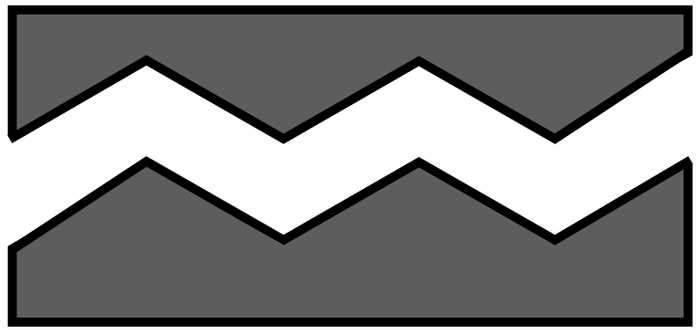
Sharp edged orifice

Beck [4]

- For idealised cracks.

$$Q = u \cdot d_{eff}$$

$$0 = \frac{2\,u}{\rho}\left[\frac{12\,\mu\,l_{eff}}{{d_{eff}}^2}\right]$$



Idealised crack

[3] Bomelburg, H.J. *Estimation of gas leak rates through very small orifices and channels.* Battelle Pacific Northwest Labs., 1977
[4] Beck, S.B.M., Bagshaw, N.M. and Yates, J.R. Explicit equations for leak rates through narrow cracks. *International Journal of Pressure Vessels and Piping.* 2005, **82**, pp.565-570.

Gill

L-b-B [5]

- Single phase leakage through narrow orifice.

$$m = 2\rho(z)awu(z)$$

$$m = C_D(p_0\rho_0)^{\frac{1}{2}}wl$$

- Can be adapted for turbulent flow.

ODE [6]

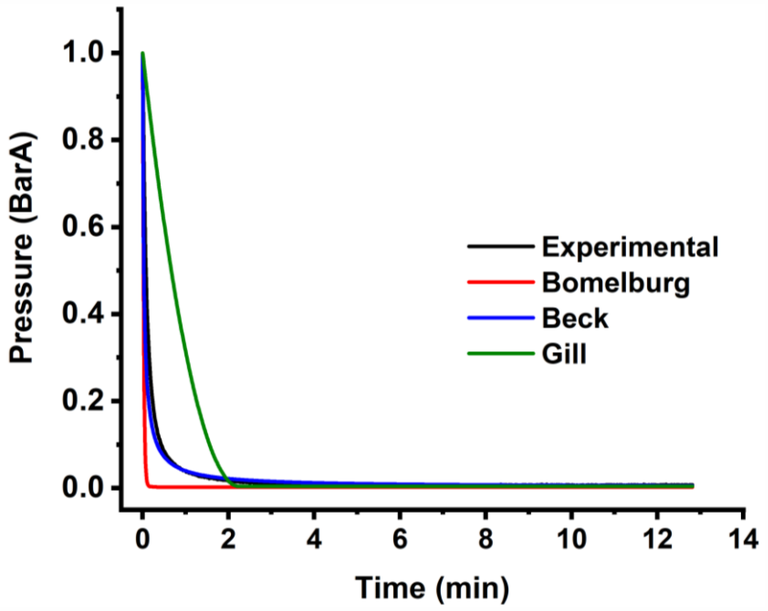
- ODE system for idealised crack.

$$\begin{pmatrix} \frac{\partial u}{\partial T} & \frac{\partial u}{\partial P} & -\frac{u}{v} \\ 0 & 1 & \frac{v}{u} \\ \frac{\partial h}{\partial T} & \frac{\partial h}{\partial P} & v \end{pmatrix} \begin{pmatrix} \frac{dT}{dz} \\ \frac{dp}{dz} \\ \frac{dv}{dz} \end{pmatrix} = \begin{pmatrix} \frac{u}{A}\frac{dA}{dz} \\ -\frac{P_f}{A}\tau - \frac{1}{u}\frac{dF}{dz}\frac{v^2}{2} \\ \frac{P_f q u}{Av} \end{pmatrix}$$

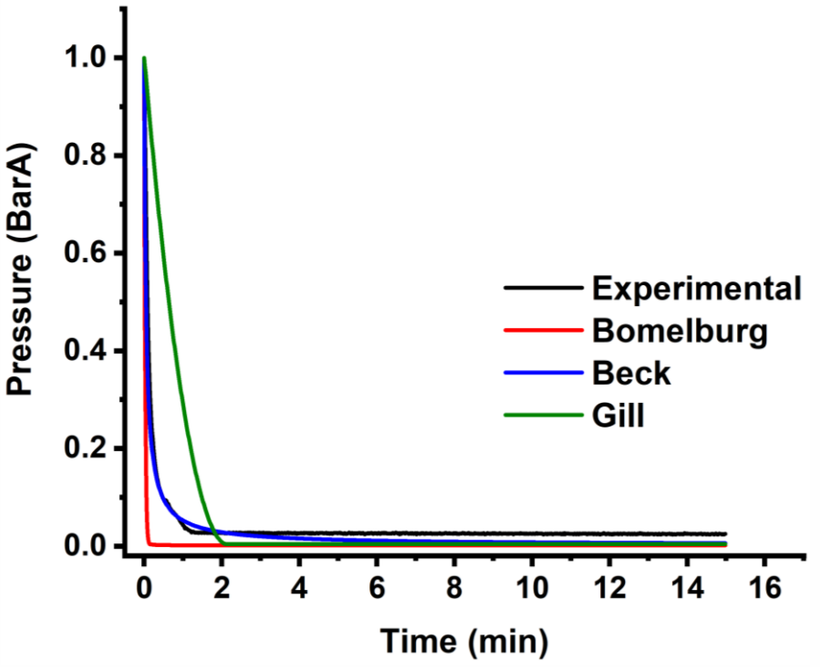
- Solution procedure assumes isentropic flow.
- Iterative until max and min flow within user chosen tolerance.

[5] P. Gill, Investigating Leak Rates for “Leak-Before-Break” Assessments, Thesis, 2013
[6] P. Gill, J. Sharples and P. Budden, Leakage Rates Through Complex Crack Paths Using An ODE Method, Proceeding of the ASME 2015 Pressure Vessels and Piping Conference, 2015

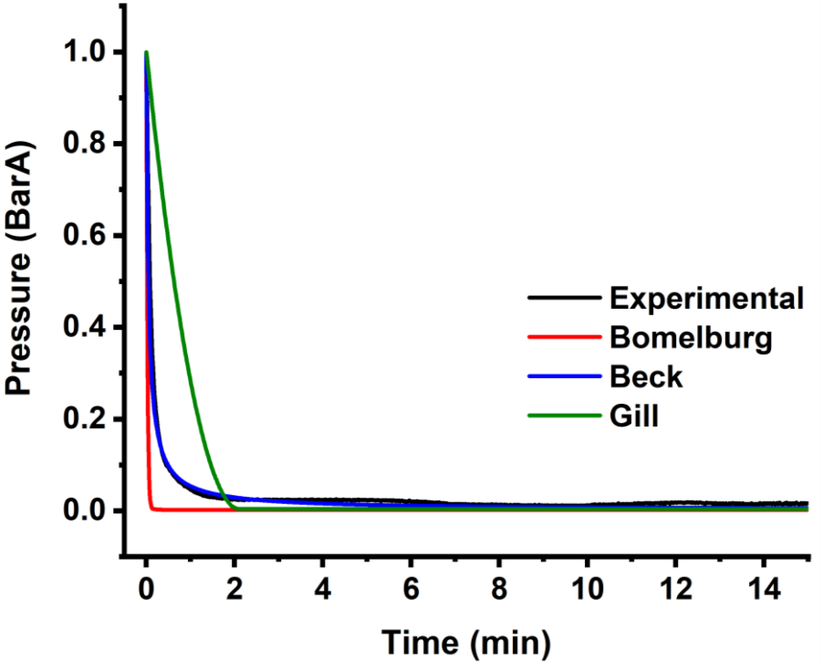
Method Comparison



40°C Evacuation



50°C Evacuation



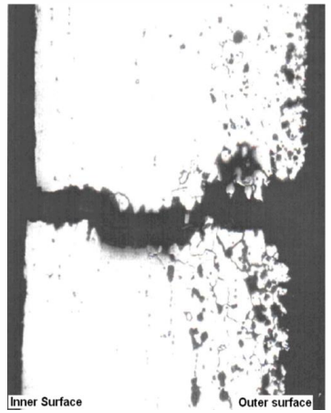
60°C Evacuation

Image Analysis

- Need a way to analyse cracks once produced.
- Find path length through the crack and the average width of the crack.

Steps:

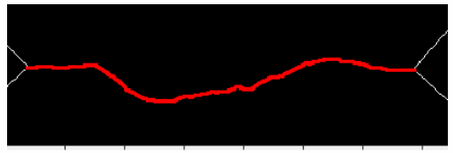
1) Manually “tidy” the image.
2) Convert the image to a binary image.
3) Skeletonise and remove spurs.
4) User selects the start and end of the “main” part of the crack.
5) User inputs coordinates of a edge pixel from the “triangle section”.



Tidy image

Convert to binary image

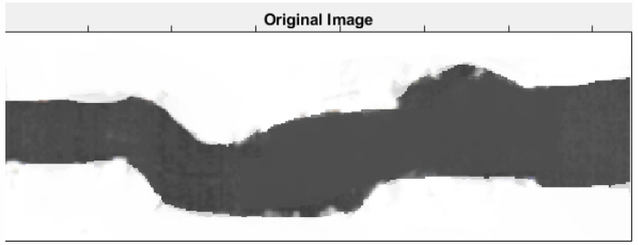
Find path

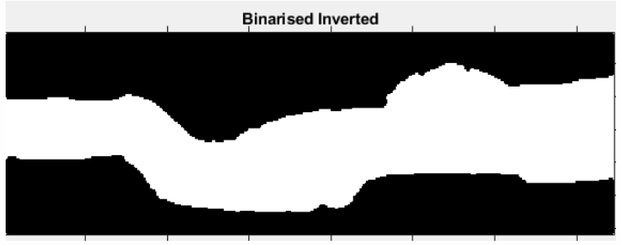


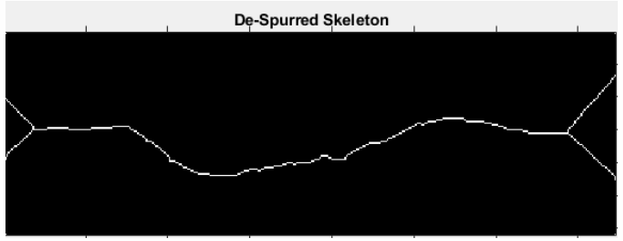
Output length and width of crack

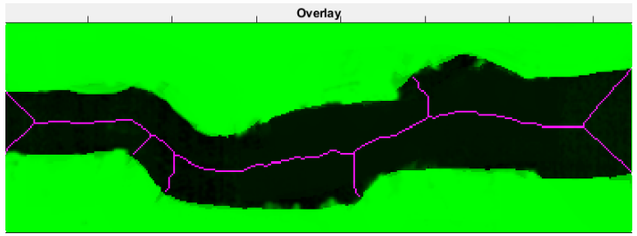
Width
Path Length

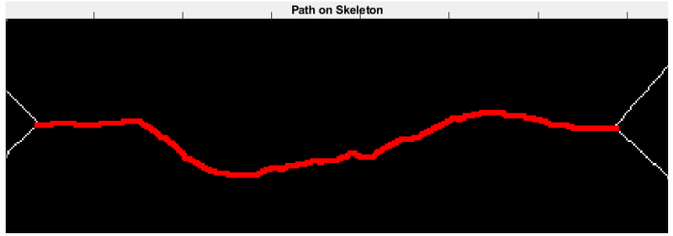
Failed Cladding Crack



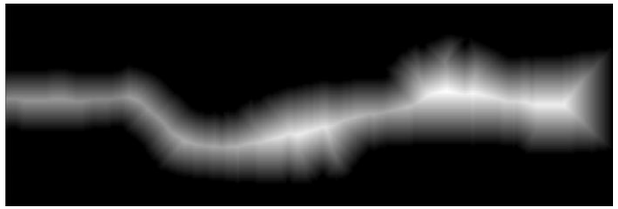






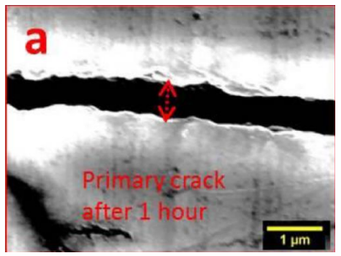


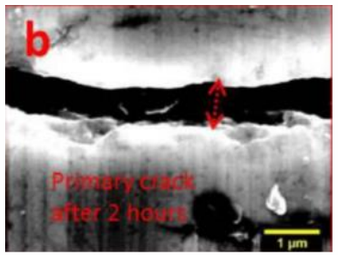
Distance Transform

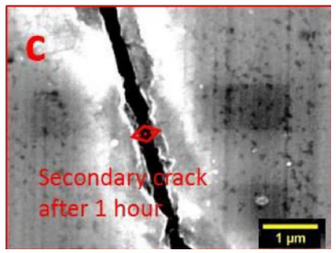


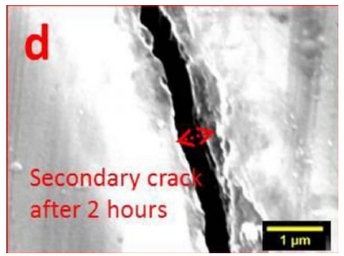
Sample	Measured		Calculated		% Variation	
	Length	Width	Length	Width	Length	Width
Failed Cladding	412.5	50	442.1	49.7	10.5	0.7

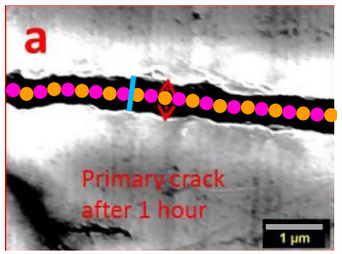
Corrosion Cracks

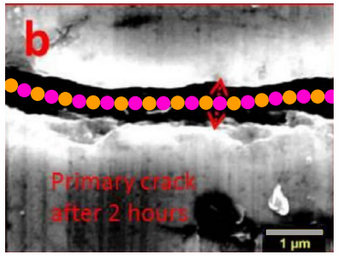


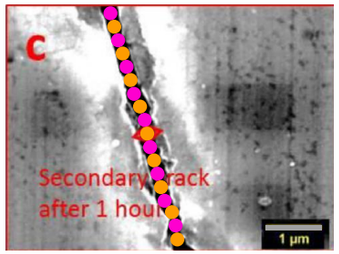


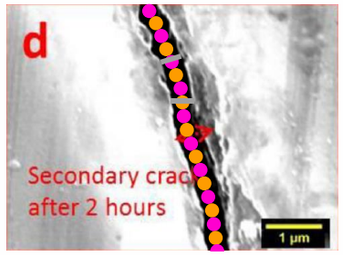












Sample	Measured		Calculated		% Variation	
	Length	Width	Length	Width	Length	Width
a	5.94	0.64	6.27	0.54	5.68	15.67
b	5.94	0.66	6.75	0.66	13.77	0.22
c	4.50	0.25	5.10	0.27	13.38	9.52
d	4.63	0.38	4.93	0.38	6.57	0.71

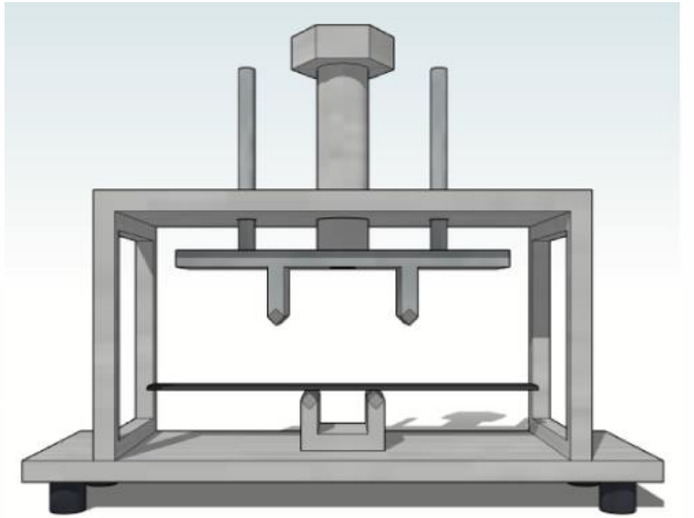
Variation on pinhole tests:
Length < 1%
Width <5%

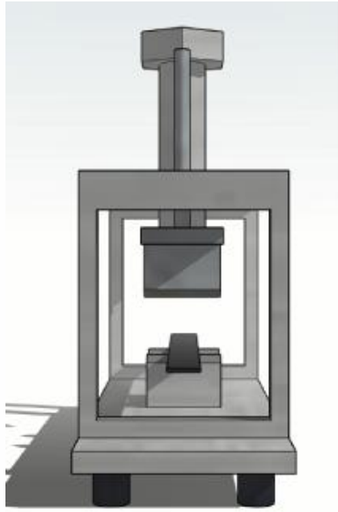
Variation on geometric tests:
Length < 5%
Width < 5%

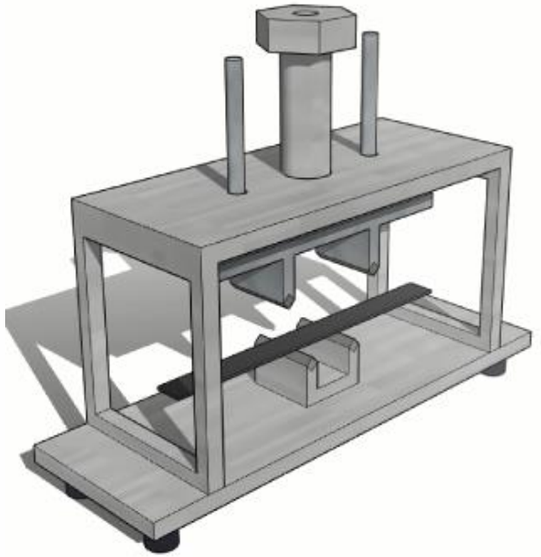
[7] J.R. Rajaguru, Arunchalam Nara, *Investigation on Machining Induced Surface and Subsurface Modifications on the Stress Corrosion Crack Growth Behaviour of Super Duplex Stainless Steel,* Corrosion Science, 2018

DET Rig Design

- Lower jaw fixed to base.
- Upper jaw allowed to move and rests on sample.
- Deflection applied using central screw.
- Trace heating wire and thermocouple wires brought to sample through holes on the side.
- Hole in screw to allow for deflection measurement as well as solution delivery.
- Dowels to guide top jaw onto sample with minimal rotation.







Future Work

Experimental

- Begin experimental work to crack plate samples.
- Analyse cracked samples.
- Conduct permeability tests.
- Crack stainless steel tube.
- Conduct drying experiments using the drying rig.

Computational

- Refine crack analysis code.
- Finalise code from Gill ODE method and validate.
- Adapt most suited code to include effects of vacuum pump and water in the pin.
- Validate final code.

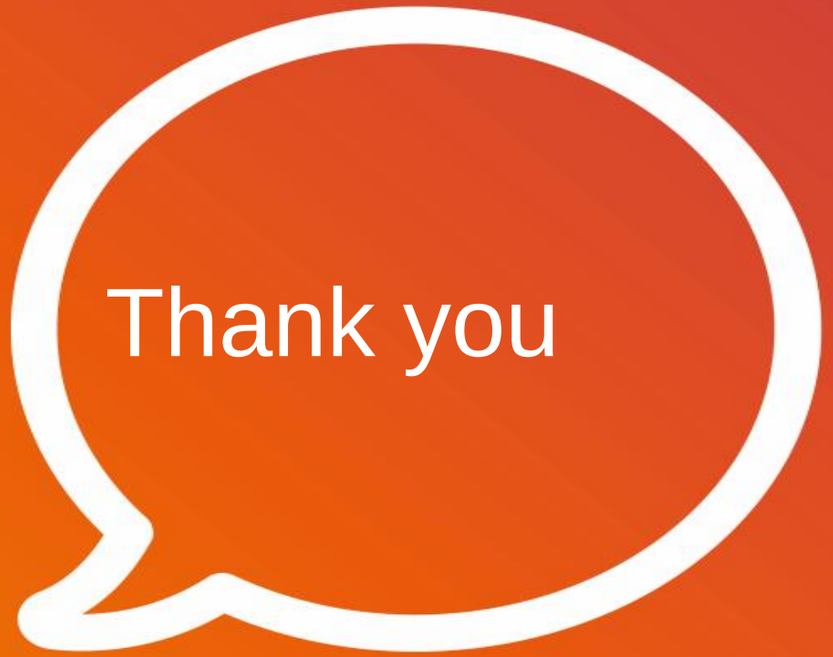
Acknowledgements

Academic Supervisor: Prof. Bruce Hanson

Industrial Supervisor: Dr Carlos de la Fontaine

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning



pmtoba@leeds.ac.uk

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

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

Victoria L. Frankland, Antoni Milodowski, Joshua Bright, Sam Rickman and David Read

University of Surrey, Guildford, UK

2nd December 2020
TRANSCEND Theme Meeting

Energy
For a Low Carbon Future

Alteration of Spent Nuclear Fuel

Alteration of U metal and UO_2 can follow several pathways

Environment	Potential SNF Species
Oxidising/fresh	*Uranyl (per)oxides* ((meta)schoepite, (meta)studtite, ianthinite)
Cementitious	*Ca uranyl oxides* (becquerelite, calcium uranates, clarkeite) *Ca uranyl silicates* (uranophane, haiweeite)
Groundwater	*Uranyl carbonates* (rutherfordine, liebigite, zellerite) *Uranyl silicates* (boltwoodite, uranophane, soddyite, weeksite) *Uranyl phosphates* (autunites), *arsenates, vanadates, etc…*
Seawater	*Uranyl oxides* (schoepite) *Metal uranyl oxides* (becquerelite, compreignacite)

Aims and Objectives:

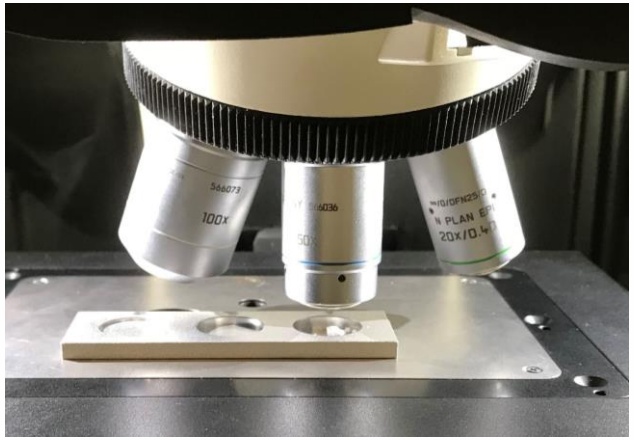
- **Characterise all the potential alteration products using remotely operated techniques.**

Possible Remote Operation Characterisation Techniques

Laser-induced breakdown spectroscopy (LIBS)

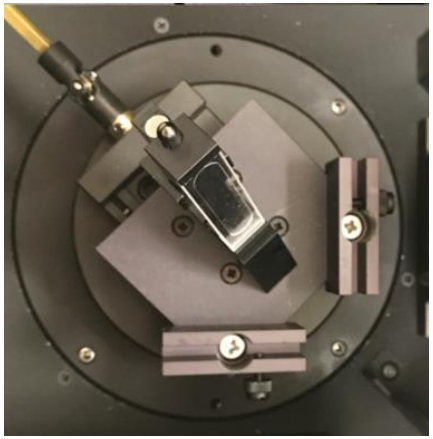
- Elemental abundance
- Surface mapping
- Depth mapping

Multiple-laser Raman



- Structural information

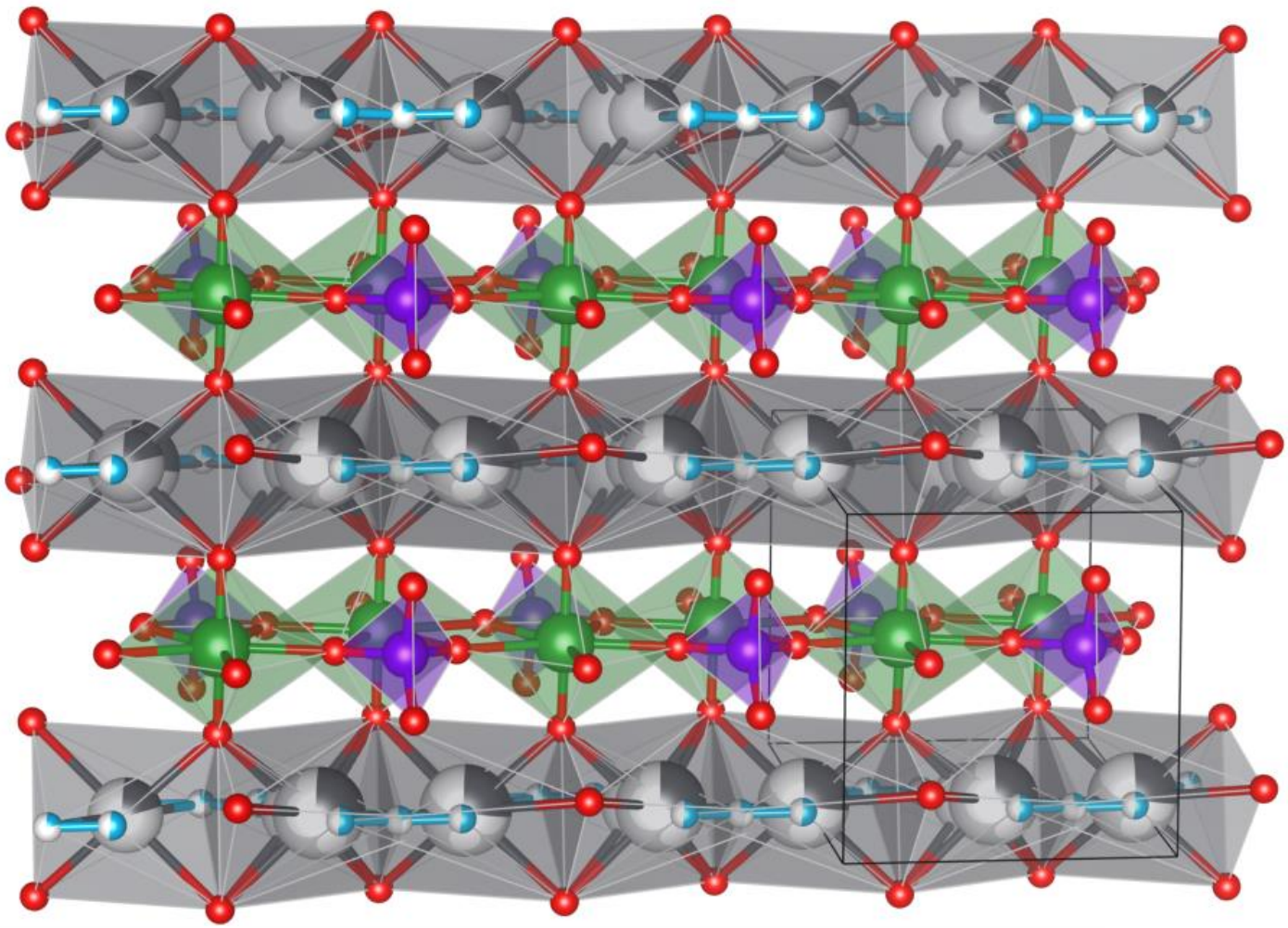
Time-resolved laser fluorescence spectroscopy (TRLFS)



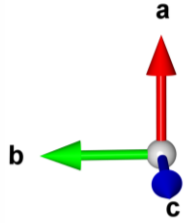
- Phase identification

Uranophane-type Samples

- Uranyl silicates
  - Boltwoodite
  - Uranophane
- Form in cementitious and groundwater environments.
- Can incorporate other radionuclei into their crystal structure matrix



Boltwoodite; $K,Na(UO_2)(SiO_3OH)\cdot 1.5(H_2O)$



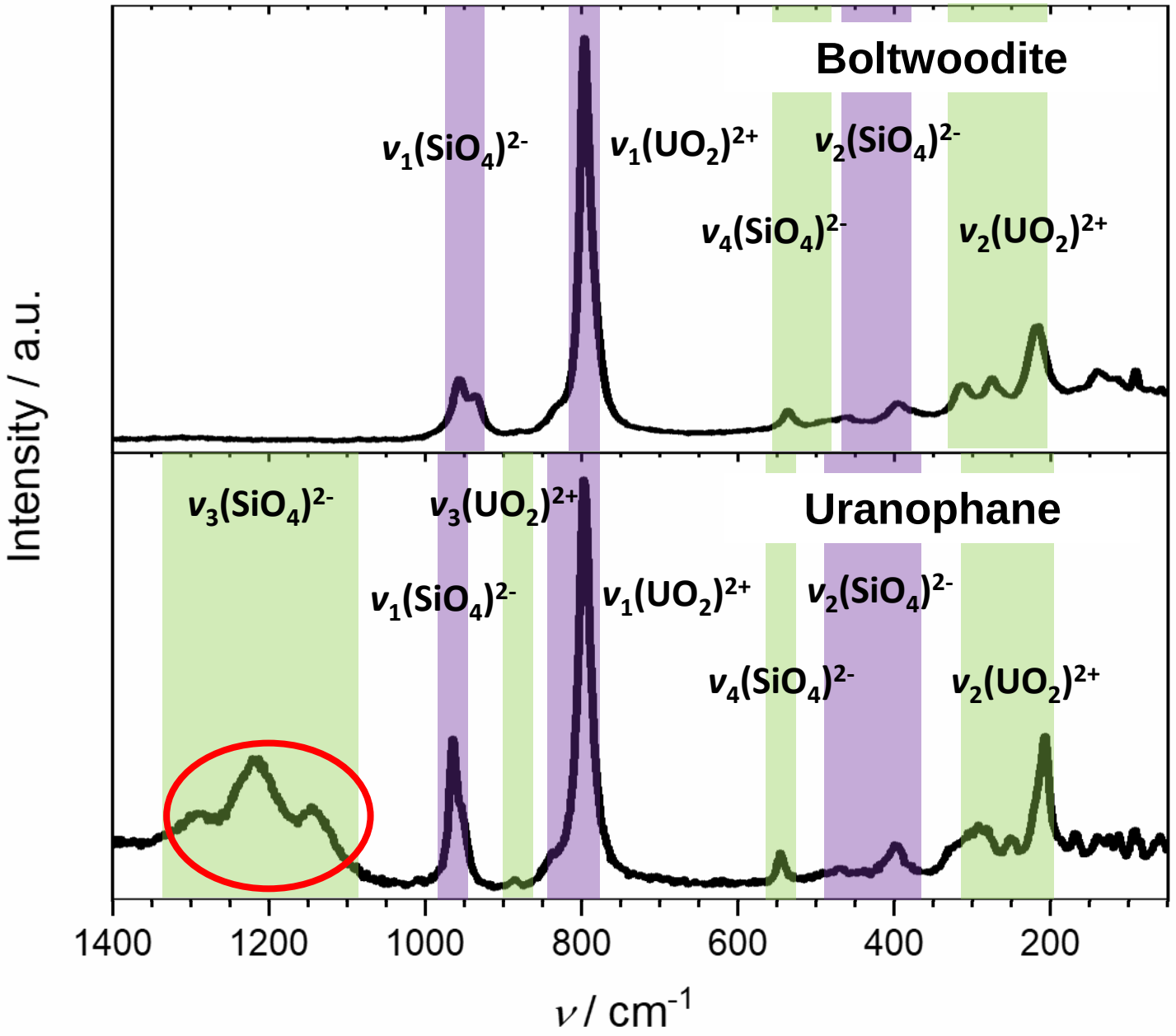
Raman Spectra

Uranophane phase sensitive $\nu_3(SiO_4)^{2-}$ mode:

Our mixed sample 1290, 1218 and 1144 cm^{-1}

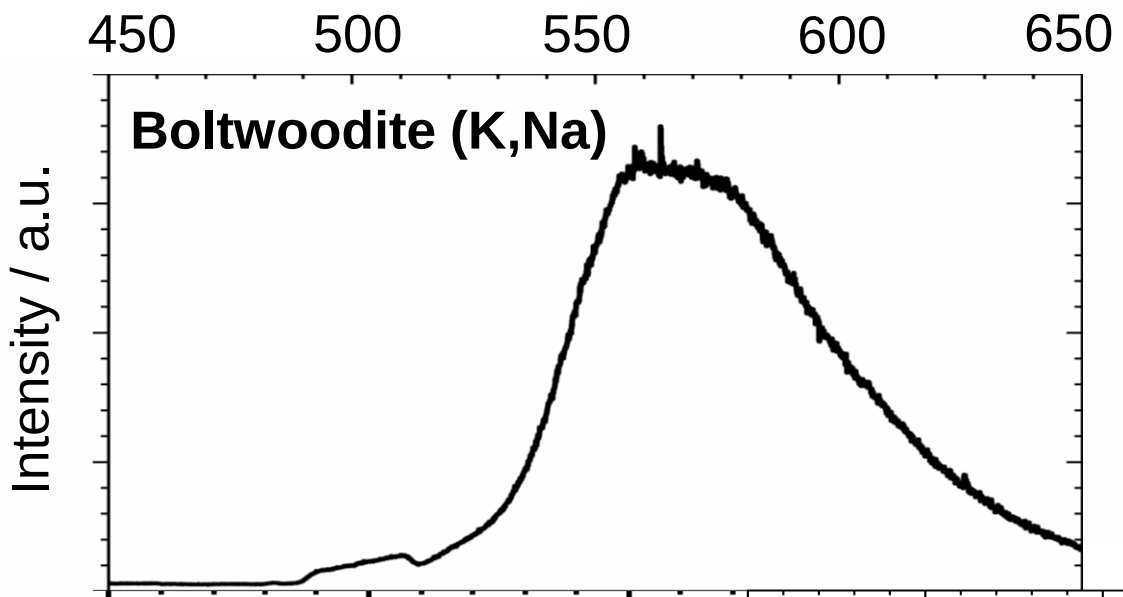
-α = 1272 and 1169 cm^{-1} (Frost et al., 2006)

-β = 1210 and 1042 cm^{-1} (Colmenero et al., 2019)



Boltwoodite: Frost et al. (2006a)
Uranophane: Biwer et al. (1990); Frost et al. (2006a, b); Wall et al. (2010); Driscoll et al., (2014); Bonales et al. (2015, 2016); Colmenero et al. (2019)

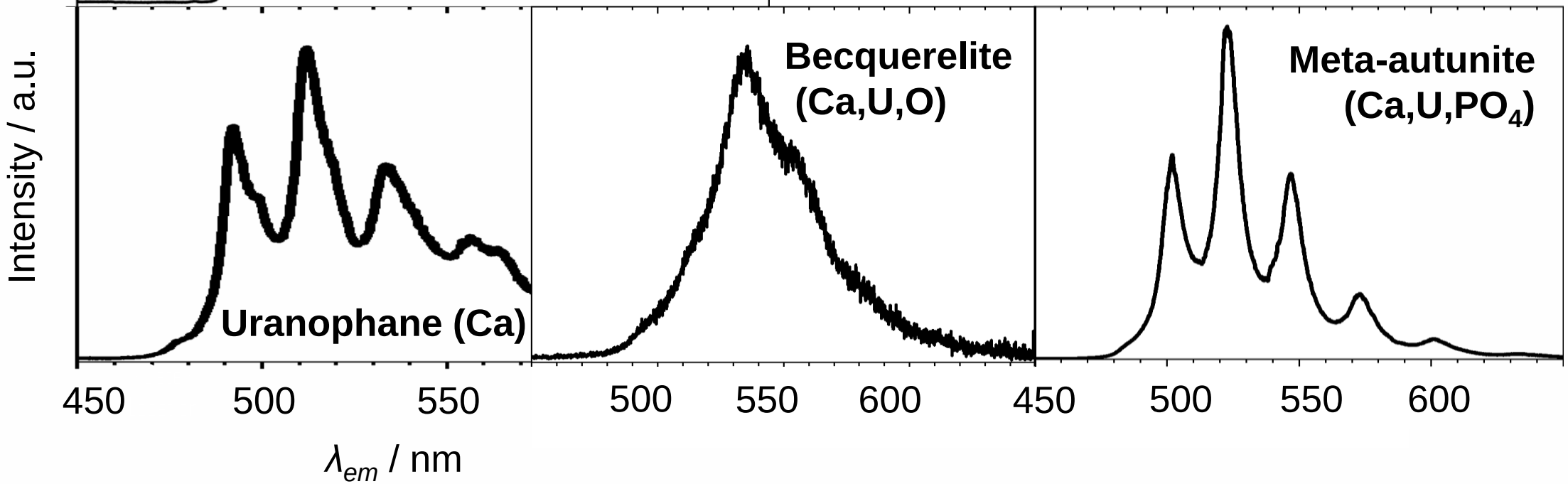
Luminescence Emission Spectra



Cation luminescence quenching:

K,Na > Ca

Anion luminescence quenching:
oxide > silicate (SiO_4) > phosphate (PO_4)

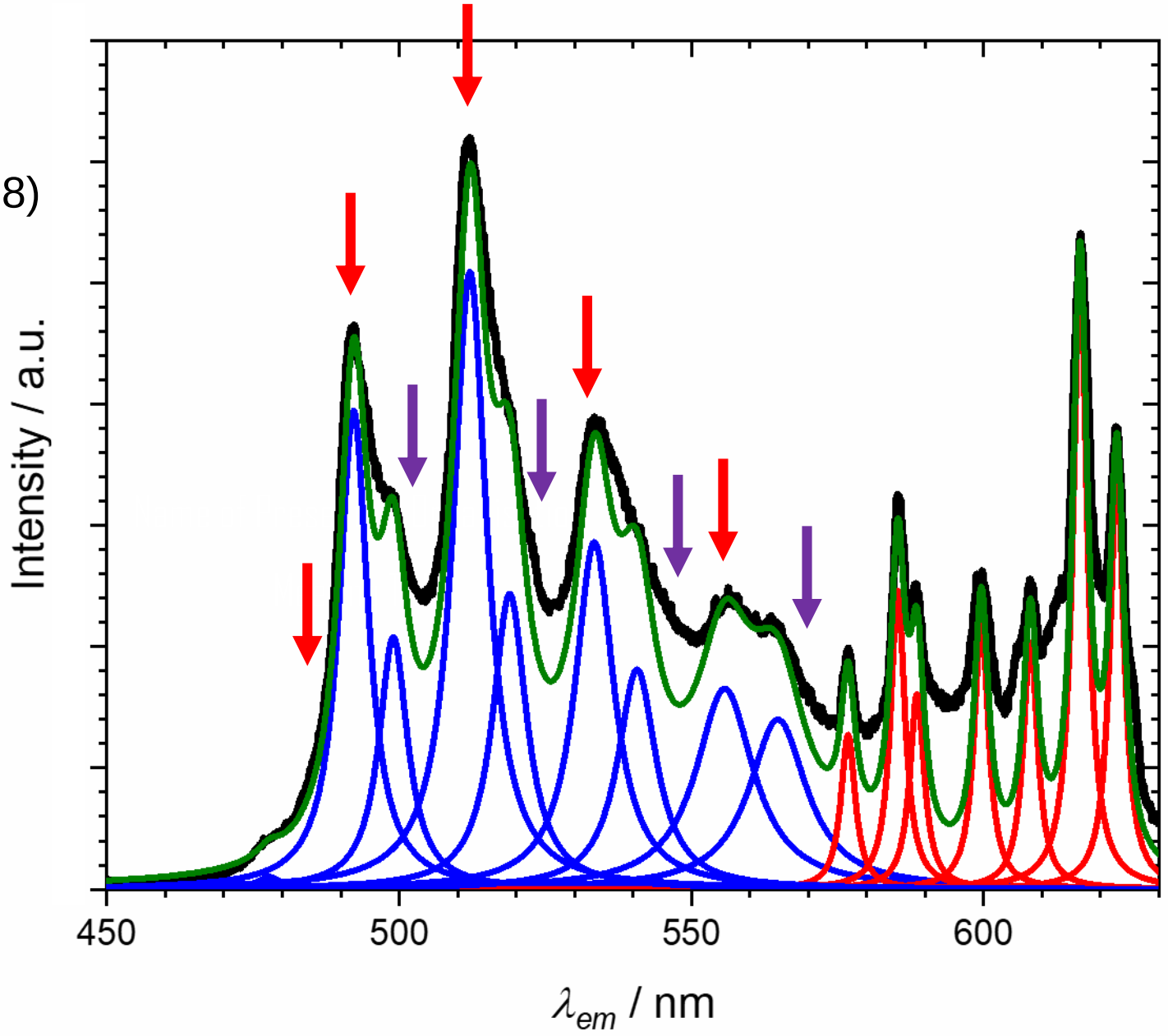


Uranophane Emission Spectrum

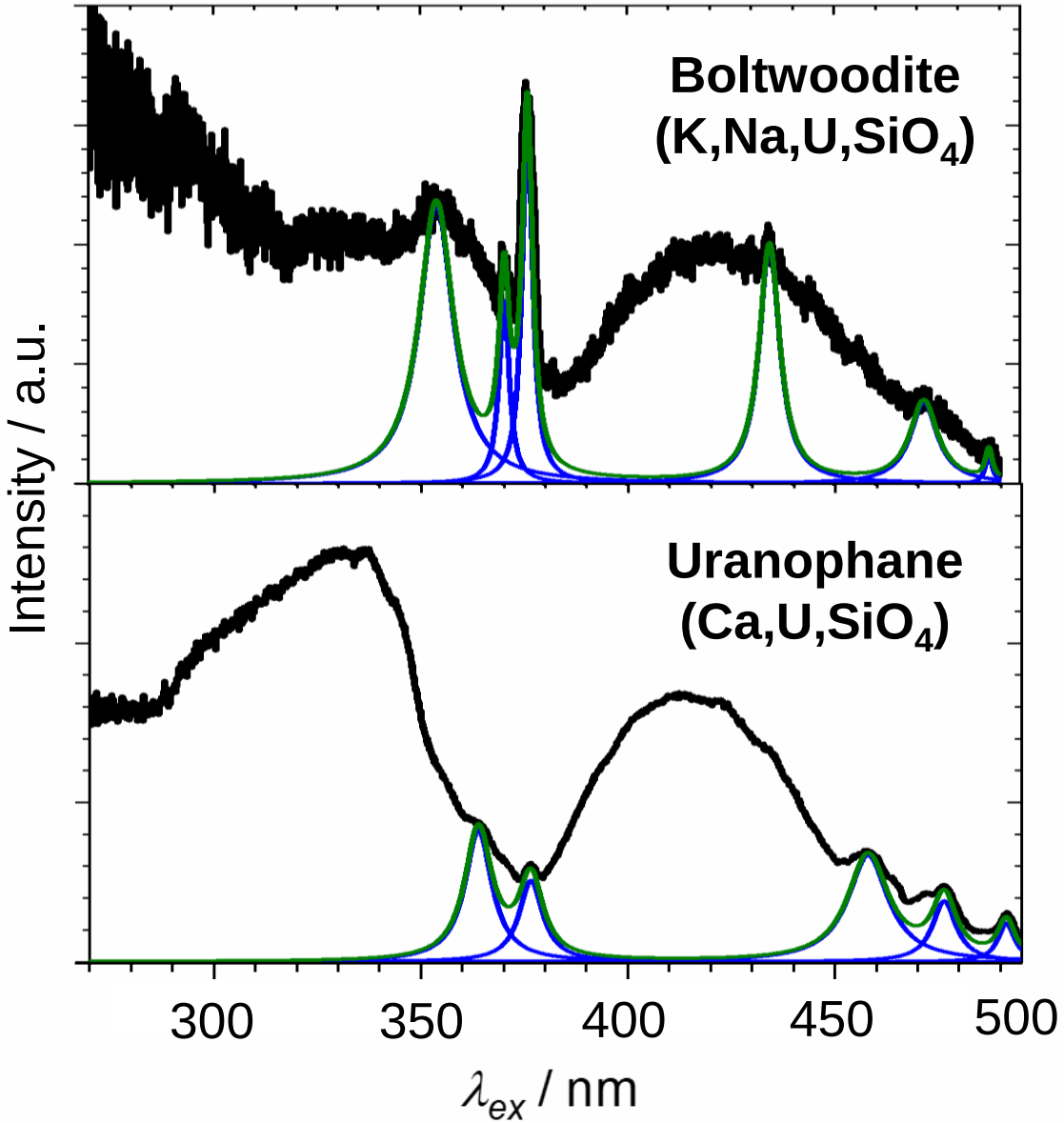
Literature Comparisons

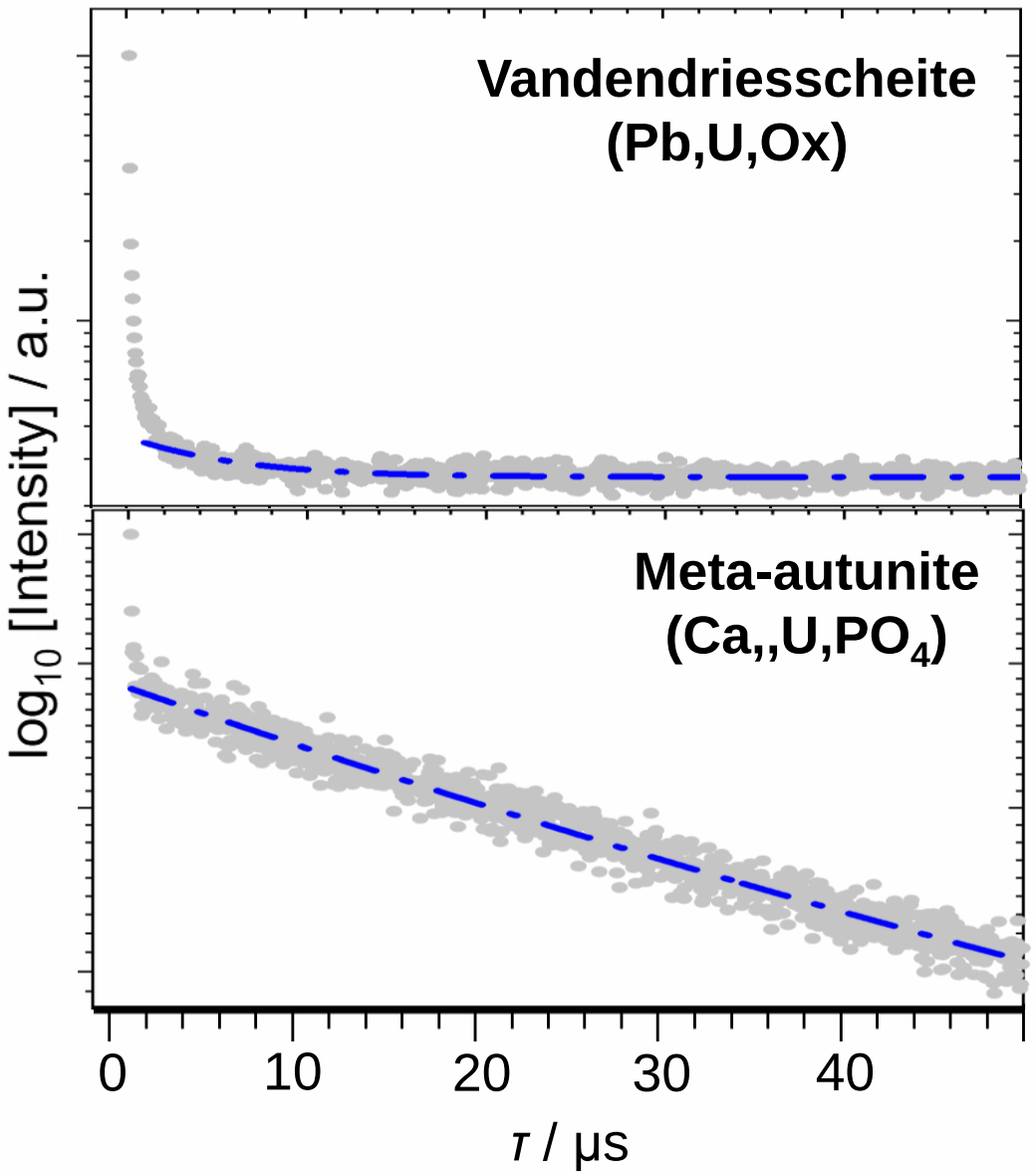
- Lehmann et al. (2008)
- Wang et al. (2005)

Uranophane-α and -β phase sensitivity



Luminescence Excitation Spectra and Decay



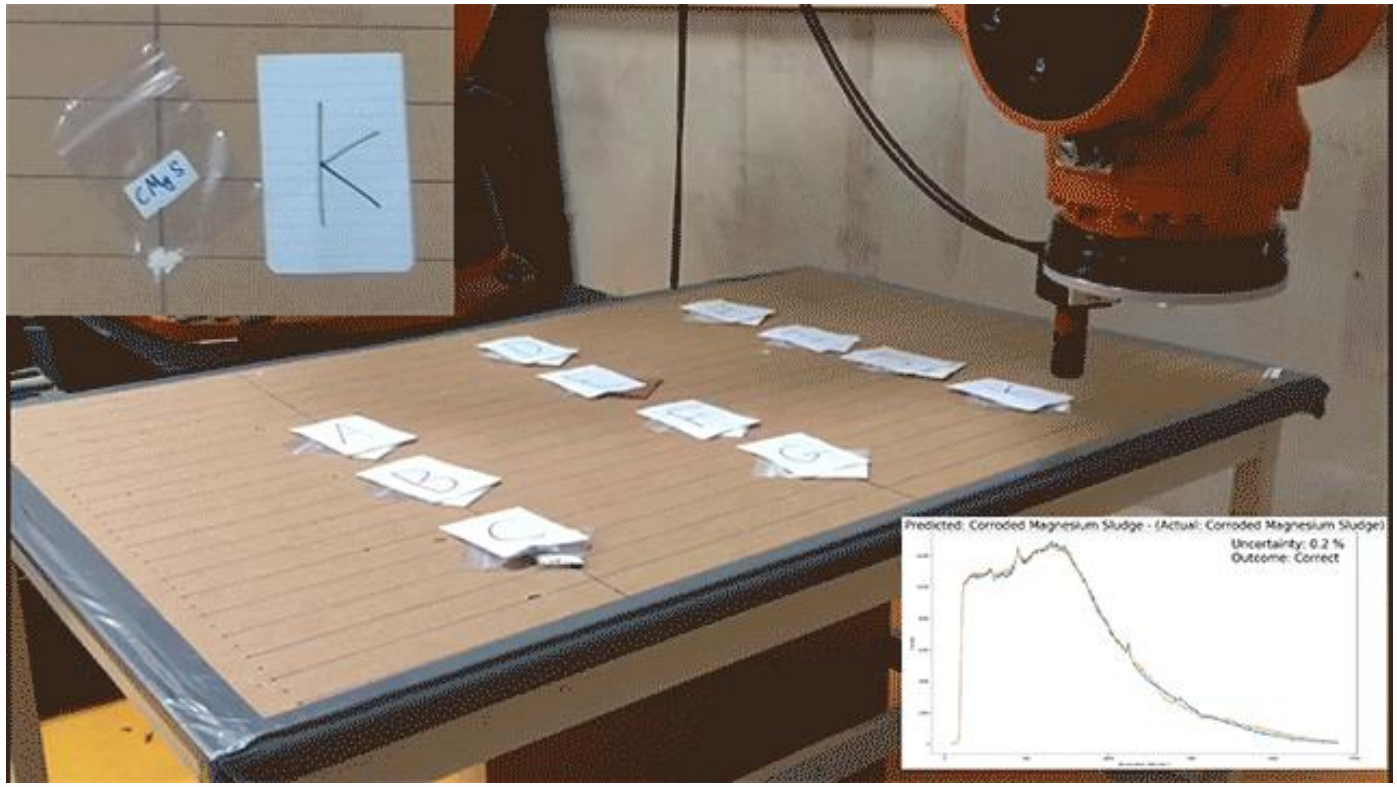


Conclusions

- **Raman spectroscopy is very effective for identifying main phases (e.g. autunites)**
- **Time-resolved laser fluorescence spectroscopy can potentially differentiate hydration states (e.g. autunite vs meta-autunite)**
- **Luminescence quenching dependent on:**
  - **Associated metal cation**
  - **Ligand in the uranyl sheet**

Future Work

- Expand the range of uranyl-bearing minerals and synthetic compounds. Incorporate new LIBS characterisation
- Construct spectral database for nuclear specific compounds.
- Perform “blind testing exercise” on a selection of our characterised U phases using apparatus at the University of Bristol



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Loan of minerals:

Kay Green (BGS)
Tom Cotterell (NMW)
Mike Rumsey (NHM)

Instruments:

LIBS - Dr Monica Felipe-Sotelo
Raman - Dr Carol Crean
- Dr Rachida Bance-Soualhi
SEM-EDX - David Jones
XRD - Dr Dan Driscoll

Funding:

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Have a great winter break!

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Transformative Science and Engineering for Nuclear Decommissioning

Density Functional Theory Modelling of UO_2 Crystal surfaces in the Context of Spent Nuclear Fuel Alteration

Joshua W. G. Bright[1], Victoria L. Frankland[1], Marco Sacchi[1] and David Read[1]

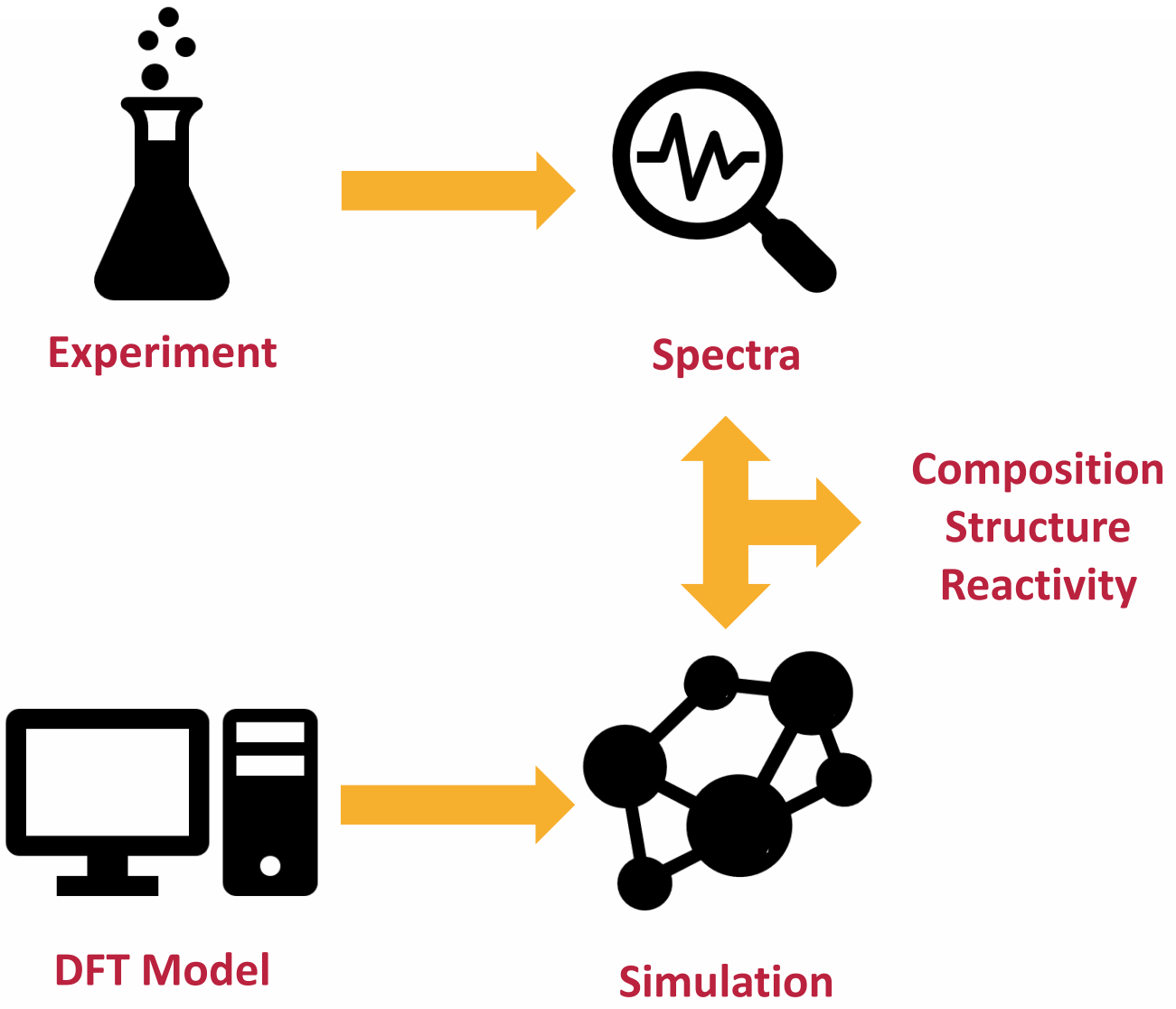
2 Dec 2020

[1] Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

Energy
For a Low Carbon Future

PhD project focus, Year 2

- Experiment and computational modelling together to determine alteration mechanism of UO_2 fuels.
- Use of thin films and laser based techniques to study surface reactions in real time in tandem with surface alteration reaction simulations.
- Full characterisation of reactants and products.



Predicting the Alteration of Spent Nuclear Fuels

- Alteration of uranium fuels is expected to lead to the formation of any of the 250+ naturally occurring uranium minerals.

Suggested mechanisms of alteration

Uranium Metal, U

↓

Uraninite, UO_2

↙ ↘

U_3O_7 / U_3O_9

↓

U_3O_8

↓

Uranium Trioxide, UO_3

McEachern and Taylor, 1998

Ianthinite, $U(UO_2)_5O_7 \cdot 10H_2O$

↓

Schoepite, $(UO_2)_8O_2(OH)_{12} \cdot 12H_2O$

Studtite, $(UO_2)\,O_2(H_2O) \cdot H_2O$

↓

Metal Uranyl Oxyhydroxides

↓

Metal Uranyl complexes i.e. phosphates, silicates

Baker, 2014

Experimental Techniques

- Laser Ablation / Laser Induced Breakdown Spectroscopy
  - Sample introduction method for ICP-MS
  - Atomic spectroscopy technique probing atomic and ionic electronic structure.
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
  - Mass spectroscopy technique suited for total elemental analysis.
- Raman Spectroscopy
  - Vibrations characteristic to bonding environments.
- Fluorescence Spectroscopy
  - Electronic transitions probing of solid state band structures.

Initial characterisation by Fluorescence, Raman, SEM, AFM, XRD, UV-vis and IR

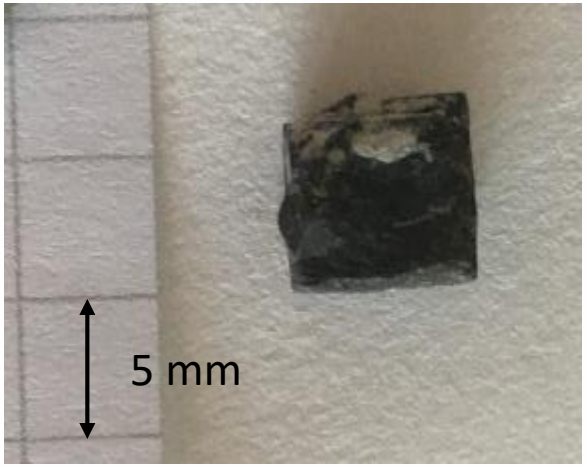
Deliberate alteration with known solution in closed system, real time Raman analysis of alteration

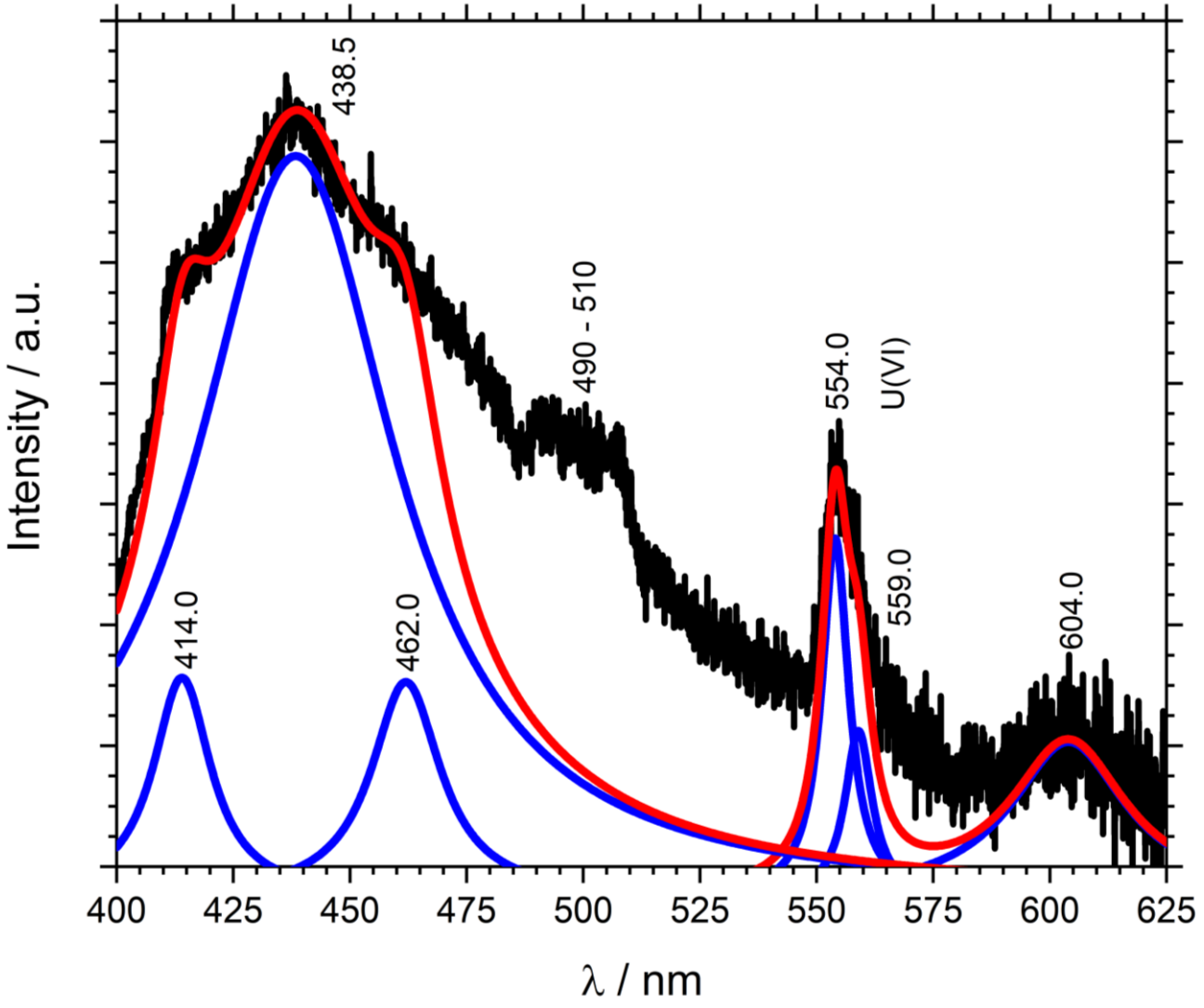
Resulting solution analysed by Fluorescence and ICP-MS to determine dissolved species

Altered surface characterised by Fluorescence, Raman, SEM, AFM, XRD,UV-vis and IR

Fluorescence Spectrum from UO_2 Mineral Sample

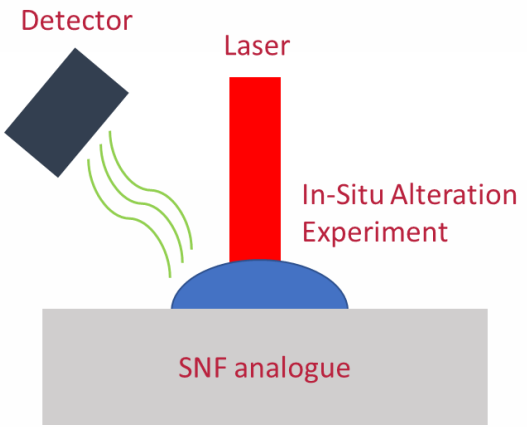
- Natural UO_2 mineral sample
- Evidence for surface alteration with U(VI) peak at 554.0 nm.





Future Experimental Work:

Thin Film Alteration



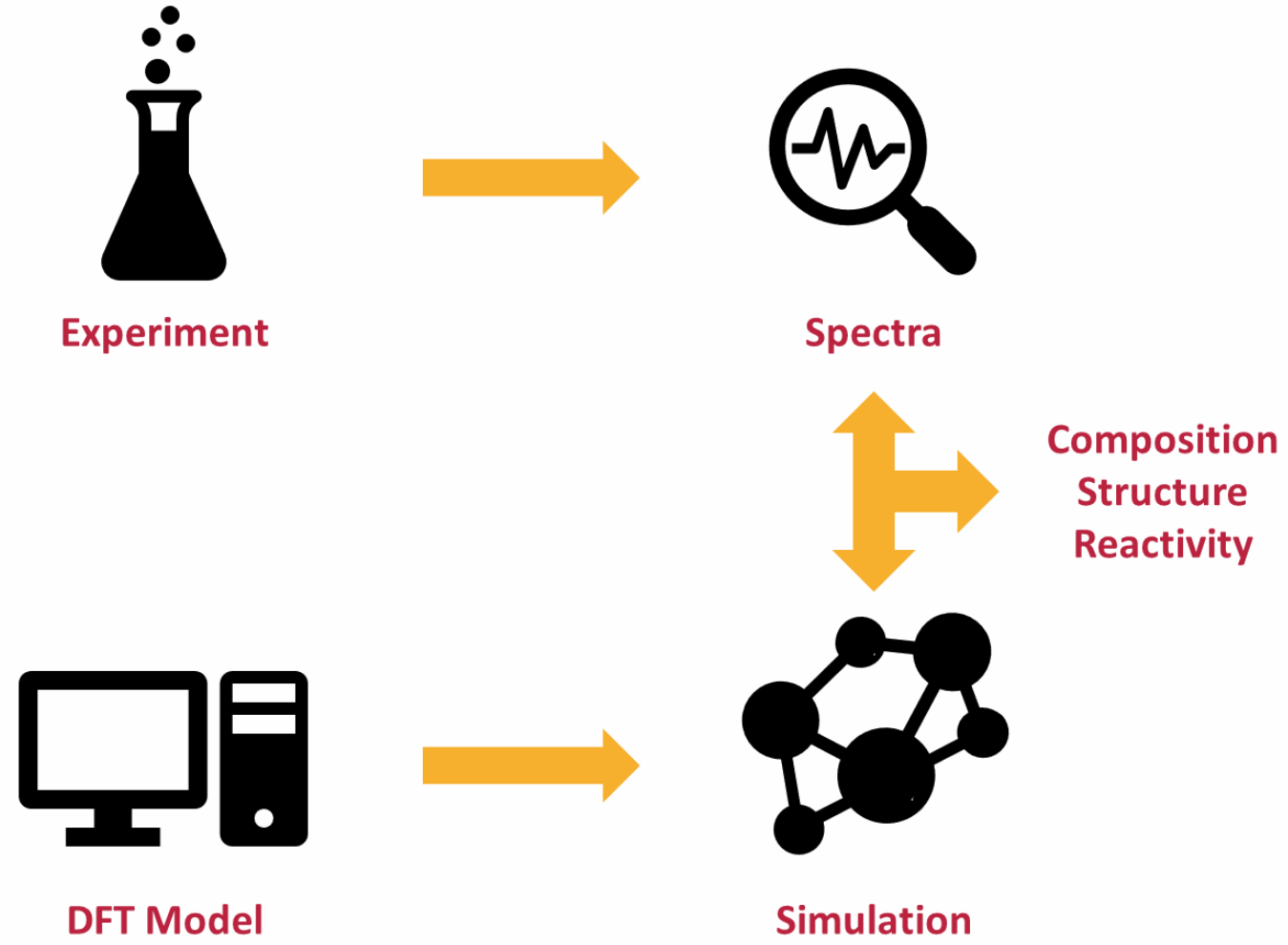
- Alteration of epitaxial UO_2 thin films with deionised water.
- Monitor real time alteration with Raman spectroscopy.
- Identify dissolved species with Fluorescence spectroscopy and ICP-MS of remaining solution.
- Elemental map of reactants and products with SEM-EDX, Raman and LA/LIBS-ICP-MS.
- Surface morphology with AFM.

Analogue	Deionised Water	Simulated storage pond water	Simulated deep groundwater
Epitaxial thin films			
Crystalline UO_2			
Sintered UO_2 pellets			
(AGR UO_2 Pellets)			

Experimental matrix

The Bridge Between Simulation and Experiment

- Combining techniques creates a more complete understanding of reactivity, composition and structure.
- Alteration of epitaxial UO_2 thin films in tandem with simulating these reactions on selected surface orientations.
- Simulations of reactant and product spectra.

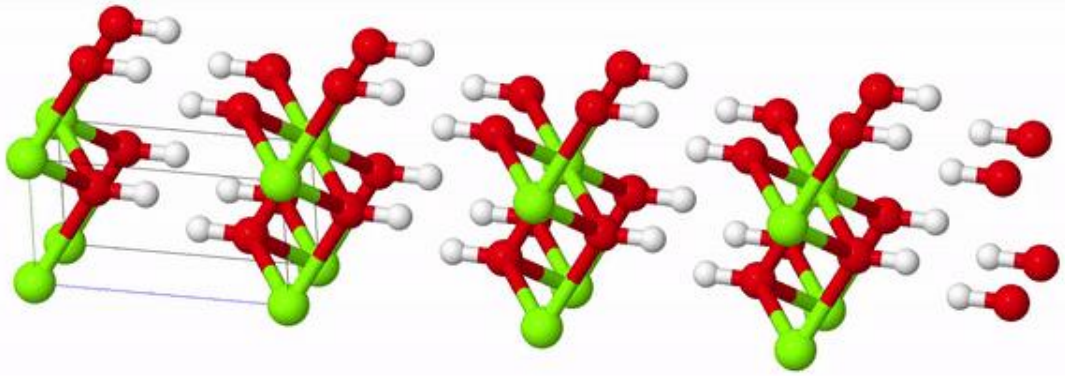


Why Simulate Spectra?

Example of Simulated Raman for $Mg(OH)_2$

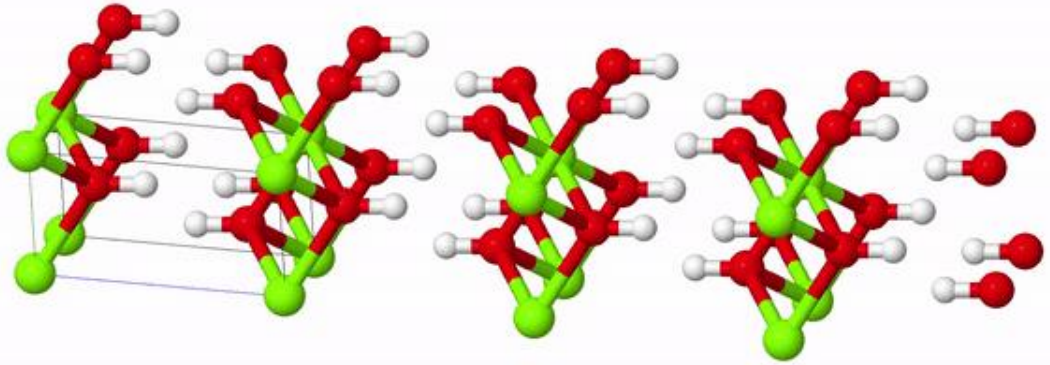
- Certainty that spectrum produced represent the sample modelled.
- Visualisation of phonon/vibrational modes responsible, aiding in identification of Raman/IR shifts.

Raman active 290 cm^{-1} ν_2(MgO)

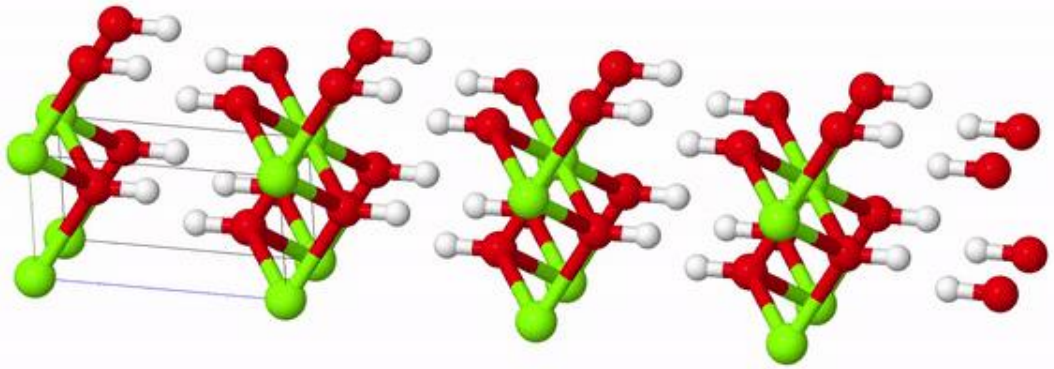


Raman active 434 cm^{-1} ν_1(MgO)

Raman active 775 cm^{-1} ν_2(OH)

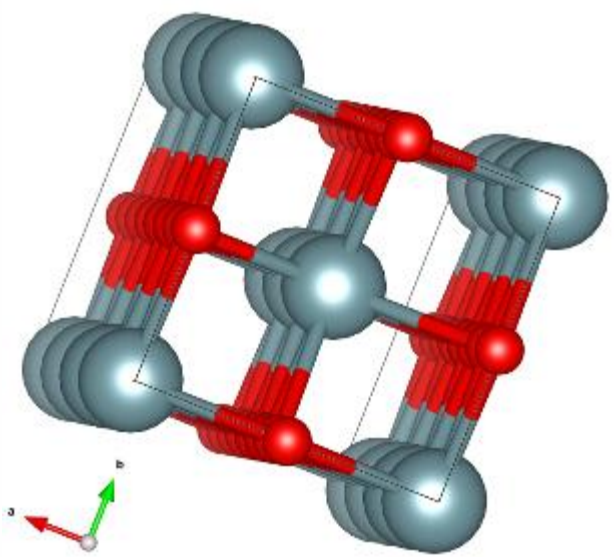


Raman active 3686 cm^{-1} ν_1(OH)



Preparation of UO_2 Surfaces for Simulation

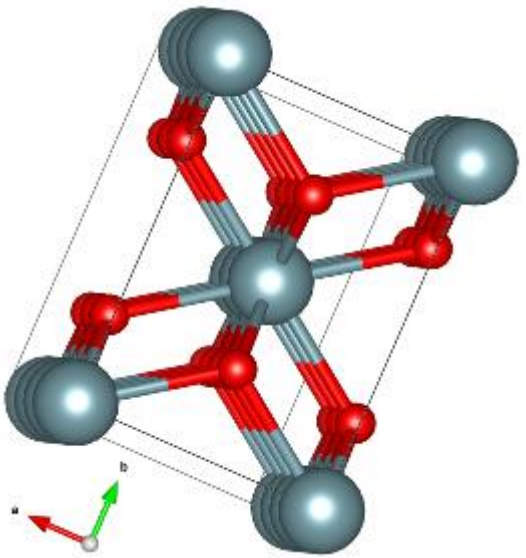
- The UO_2 [001] and [110] surface orientations have been prepared for reaction modelling with DFT.
- For this work, CASTEP 19.11 and the Perdew-Burke-Ernzerhof (PBE) functional were used.



0 0 1

Polar surface
Higher surface energy

More reactive



1 1 0

Non-polar surface
Lower surface energy

More stable

Clark et.al., ***Z. Kristall***., 2005, **220**, 567-570
Perdew et.al., ***Physical Review Letters***, 1996, **77**, 3865-3868
Springell *et. al.*, ***Faraday Discussions***, 2015, **180**, 301-311
Skomurski *et. al.*, ***American Mineralogist,*** 2006, **91 (11-12)**, 1761–1772

Future Computational Work:

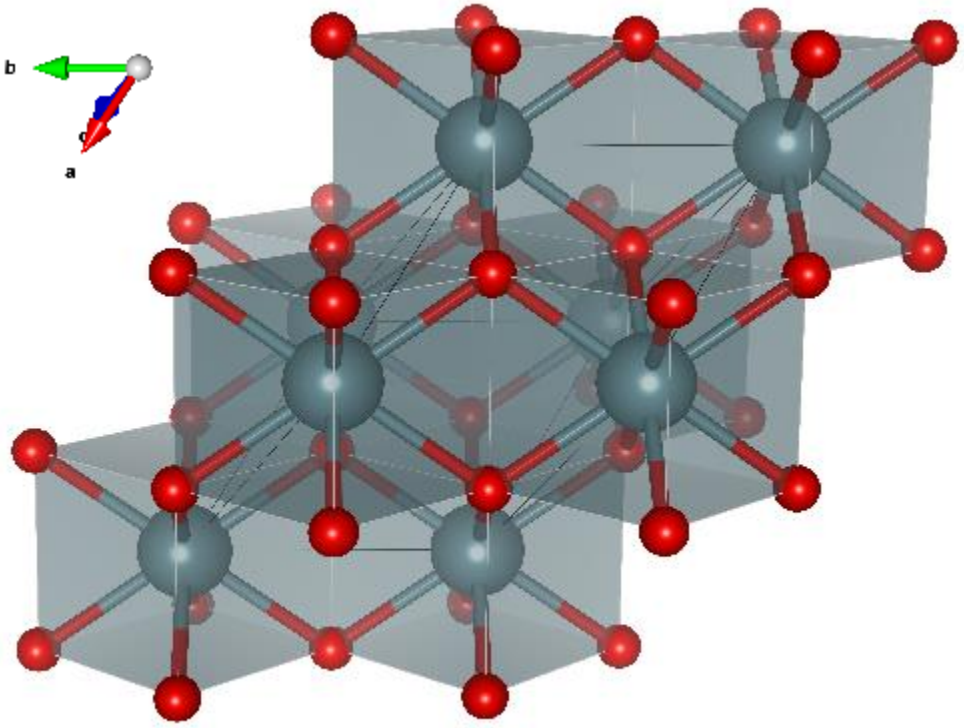
Simulating thin film alteration

- Match surface reaction modelling to experimental reactions on epitaxial thin films, specifically with oxidising components produced by water radiolysis in pond water.

- Model Raman and IR spectra of reactants and alteration products. Allows for direct comparisons to experimentally obtained Raman and IR.

- Determination of the mechanism for UO_2 SNF alteration.

	Control	Simulated Pond Water			
UO_2 Surface	H_2O	H_2O_2	$OH^{\cdot}$	$HO_2^{\cdot}$	OH^-
0 0 1					
1 1 0					



In Conclusion…

- Initial experiments show promising results for identifying partially altered UO_2 phases.
- Experimental techniques selected and workflow designed to investigate alteration of selected analogues in simulated pond water and groundwater environments.
- UO_2 surfaces prepared for computational simulations of surface reactions.
- Computational techniques selected and workflow designed to investigate alteration of selected surface orientations in simulated pond water environment.

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Transformative Science and Engineering for Nuclear Decommissioning

Acknowledgements

LIBS - Dr Monica Felipe-Sotelo

Raman - Dr Carol Crean

- Dr Rachida Bance-Soualhi

SEM-EDX - David Jones

XRD - Dr Dan Driscoll

Thank you

Funding

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j.bright@surrey.ac.uk

linkedin.com/in/joshbri