TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

Theme 3 – Spent Fuels

Professor Tom Scott/David Read

University of Bristol/Surrey

1st Thematic Meeting

Lancaster 12 November 2019

Energy For a Low Carbon Future

Technical Challenge

>250,000t SNF worldwide, mostly in cooling ponds

UK has complex inventory (U metal, oxides, UC, UF_6, UO_2F_2).

Fuel storage ponds @ Sellafield - major cost component

Retrieval operations for legacy fuels

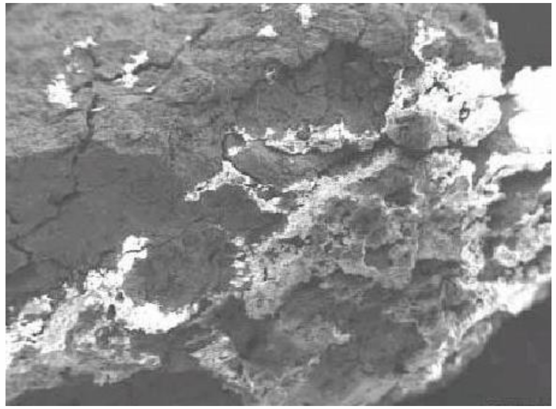
Management options have to consider SNF evolution during:

- long term storage & final disposal

~200 U minerals. Many other minerals can incorporate U

Lessons can be applied to DNLEU inventory

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

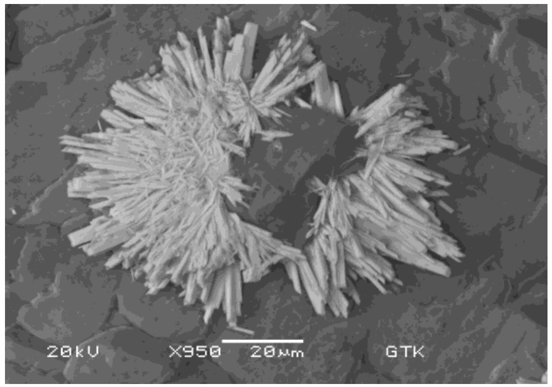
- 2 projects: Leeds: PhD (NDA), Bristol PhD (SL)

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

- 2 projects: Surrey: PDRA & PhD

3.4 Prediction of Long-term SNF Behaviour

- 2 projects: Bristol: PDRA & PhD

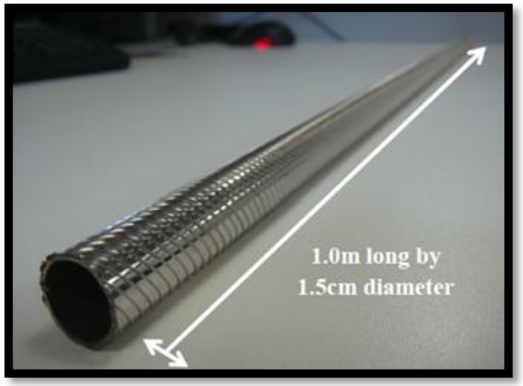


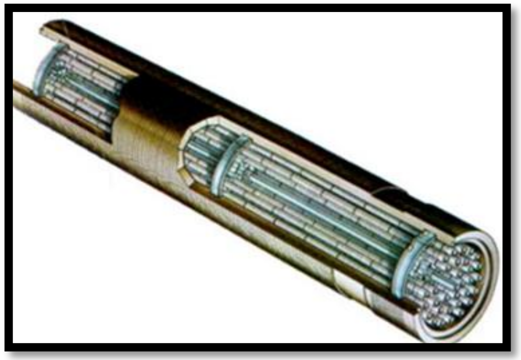
3.1 Properties & Reactivity of Bulk Corrosion Products

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

3.1.2 Corrosion and leaching of carbide fuels in a GDF setting (Dimitris Samaras)

3.1.3 MOX SIMFUEL - development of simulants (Sam Murphy)





3.2 Pressing Fuel Barrier Corrosion

3.2.1 Characterisation of perforated AGR fuel & its behaviour during drying (Bruce Hanson)

Drying wet stored & corroded Magnox fuel for interim dry storage (Matt Jackson)

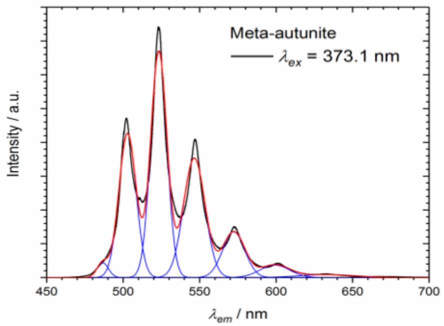
3.2.2 Development of micromechanical testing methods for spent AGR cladding to examine effects of sensitisation and stress corrosion cracking (Mohammed Mostafavi)

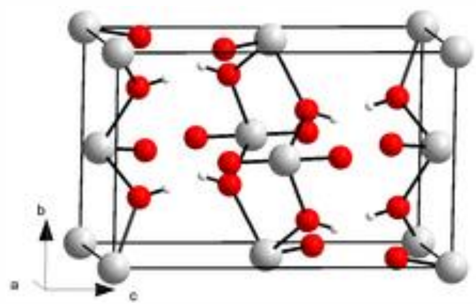
3.3/3.4 Identification of Corrosion Products on SNF & Predictive Modelling

3.3.1 *In situ* Identification of Corrosion Products on SNF (Victoria Frankland)

3.3.2 Predicting alteration of SNF (Joshua Bright)

3.4.1 & 2 Building a predictive tool of SNF behaviour (Angus Siberry)





Thank you

NNUF

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Investigating uranium corrosion in sludge using X-ray Computed Tomography – A feasibility study

Dr Haris Paraskevoulakos, University of Bristol

TRANSCEND Annual meeting 2019

Energy

For a Low Carbon Future

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)

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

NOWADAYS

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

Theoretical background – Reactive Metals

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

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

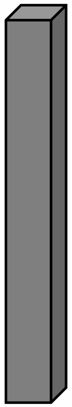
$$2U + 3H_2 \rightarrow 2UH_3$$

Hazards

- Radioactivity/Toxicity/Powdery
- Generation of H_2: flammable
- UH_3: Pyrophoricity

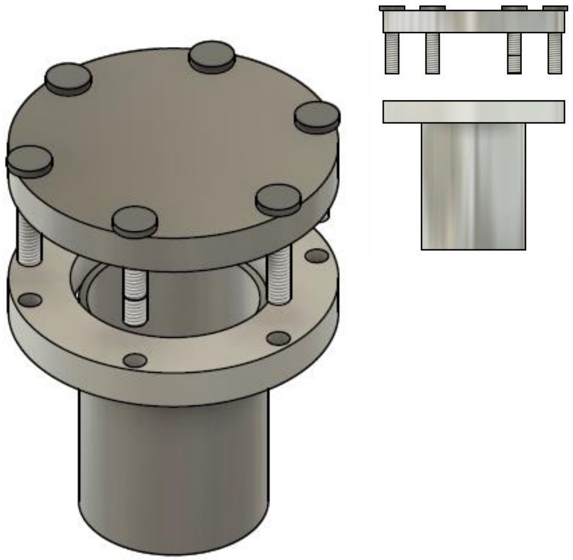
Project: Investigation of uranium corrosion in sludge environment

Materials



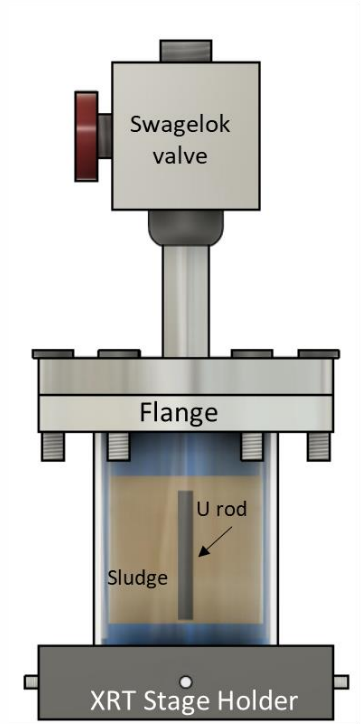
Natural Uranium

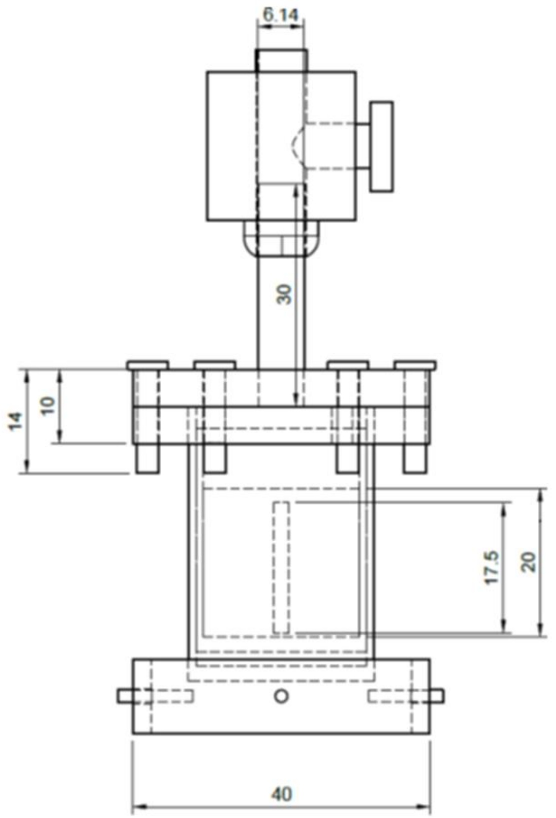
CMS

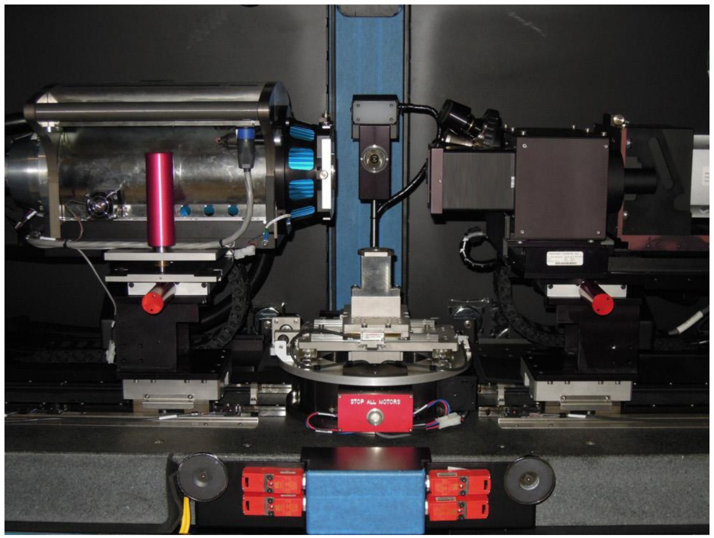


Stainless steel

Time-resolved X-ray Computed Tomography (XCT)



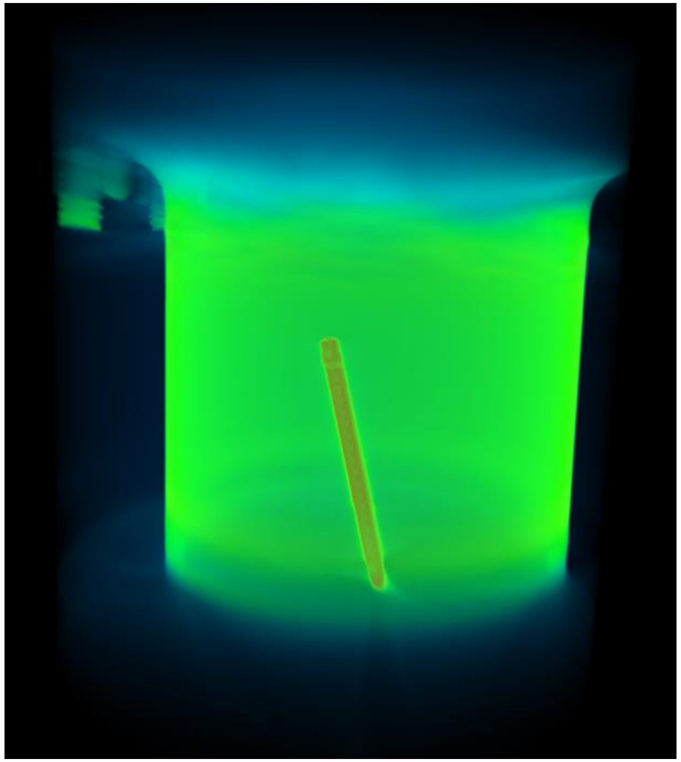




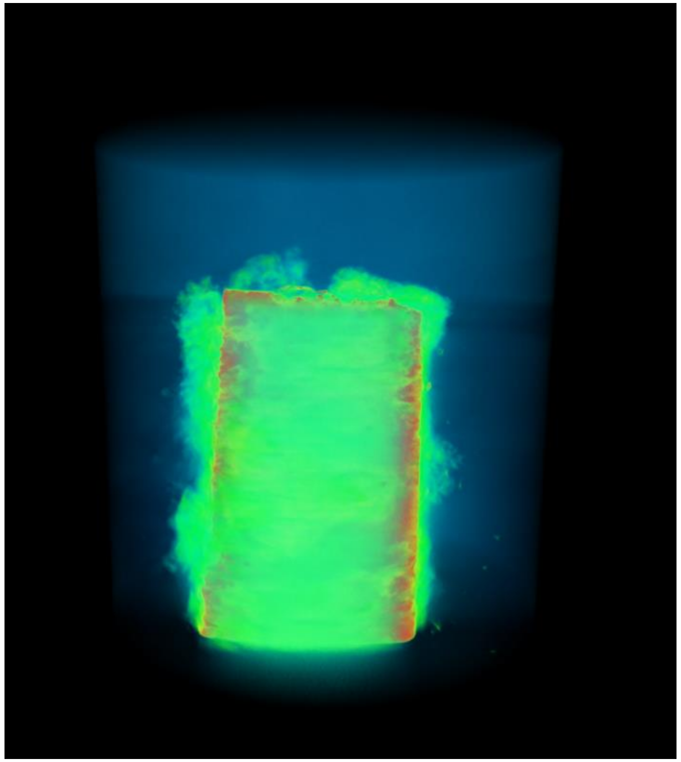
Scans

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

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

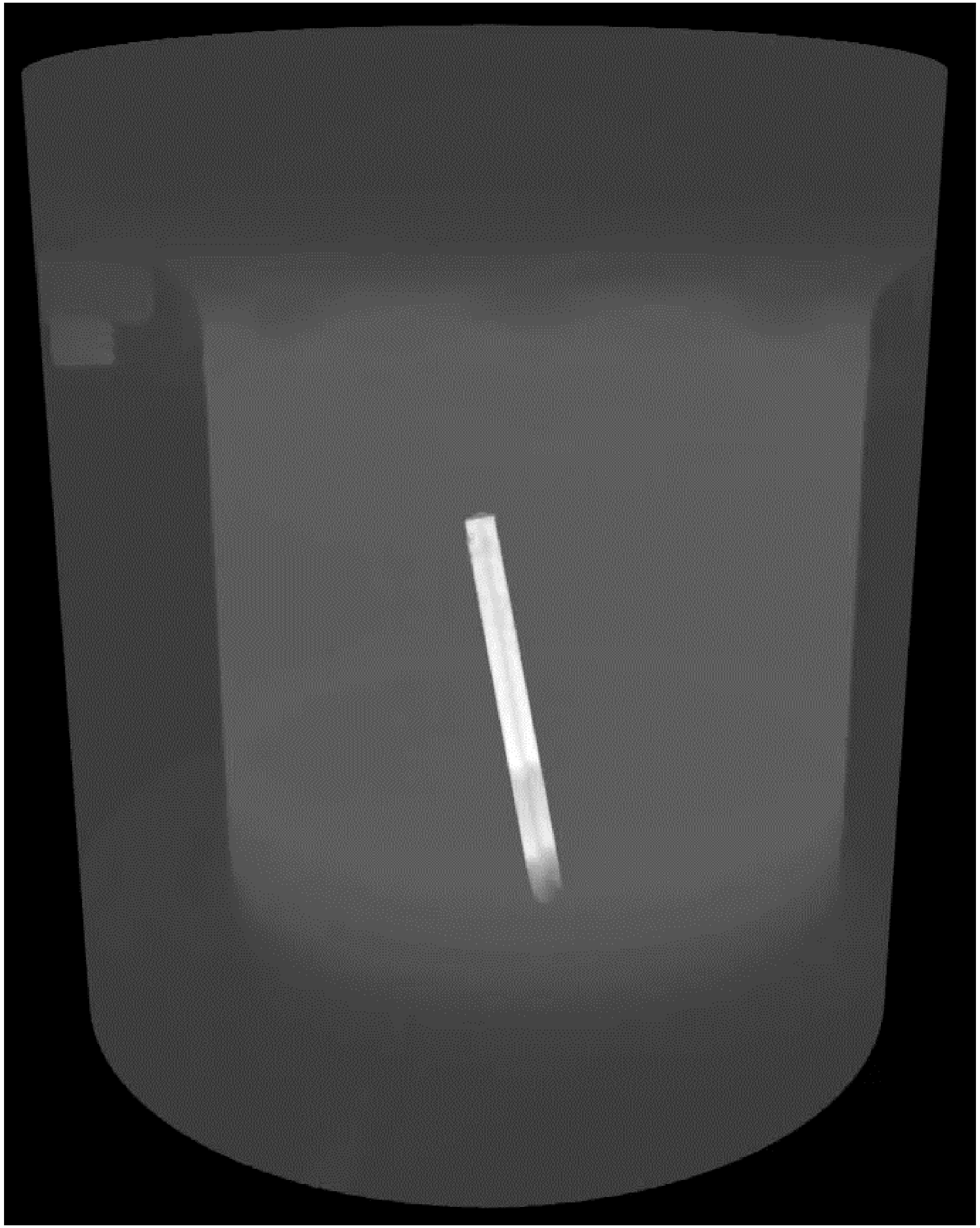


Example of low-resolution scan

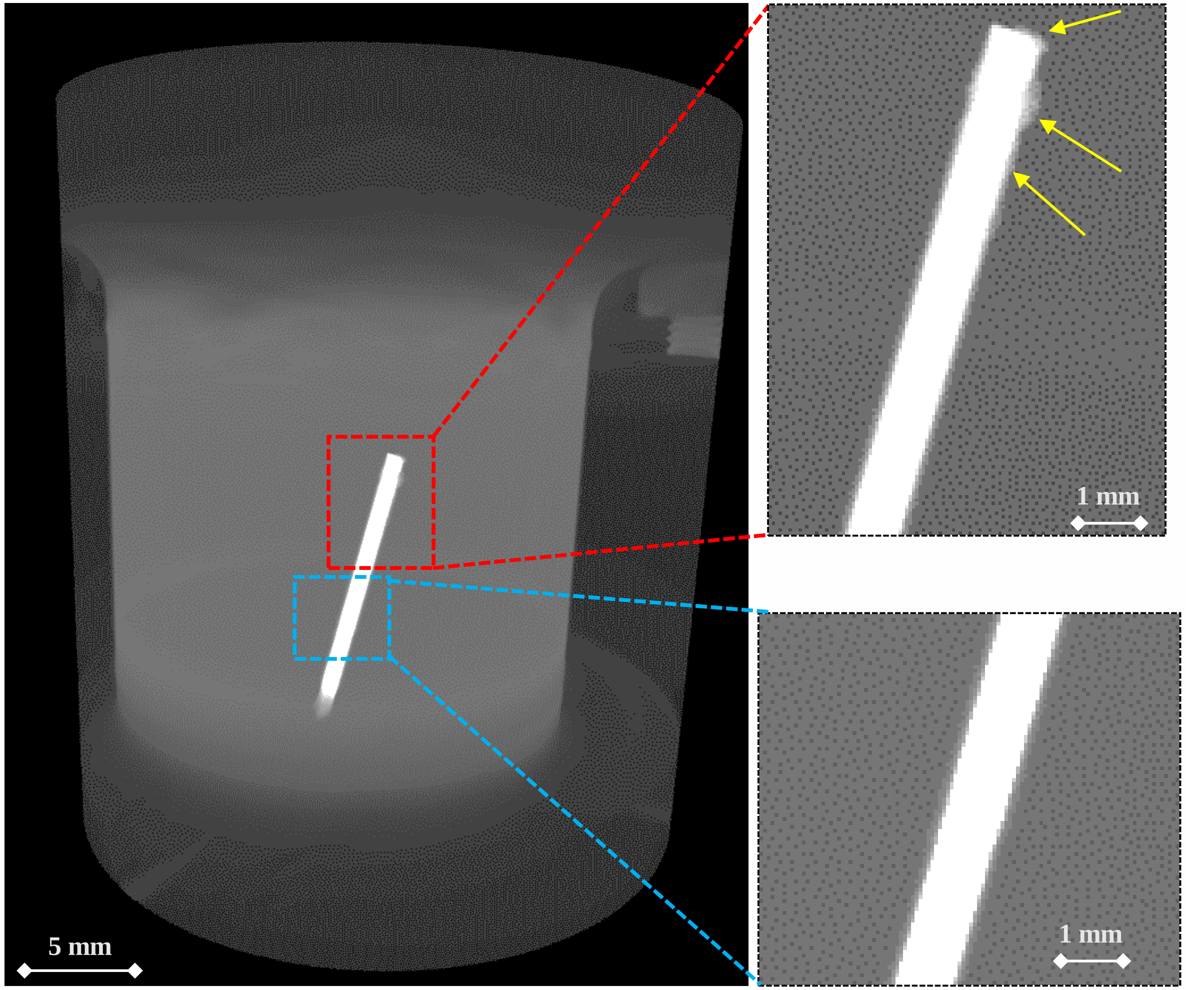


Example of high-resolution scan

Results 20 days after preparation



Results 20 days after preparation



Key findings

- First signs of corrosion
- Upper uranium surface
- Crater/blister type of morphology
- No signs of corrosion across the lower uranium part

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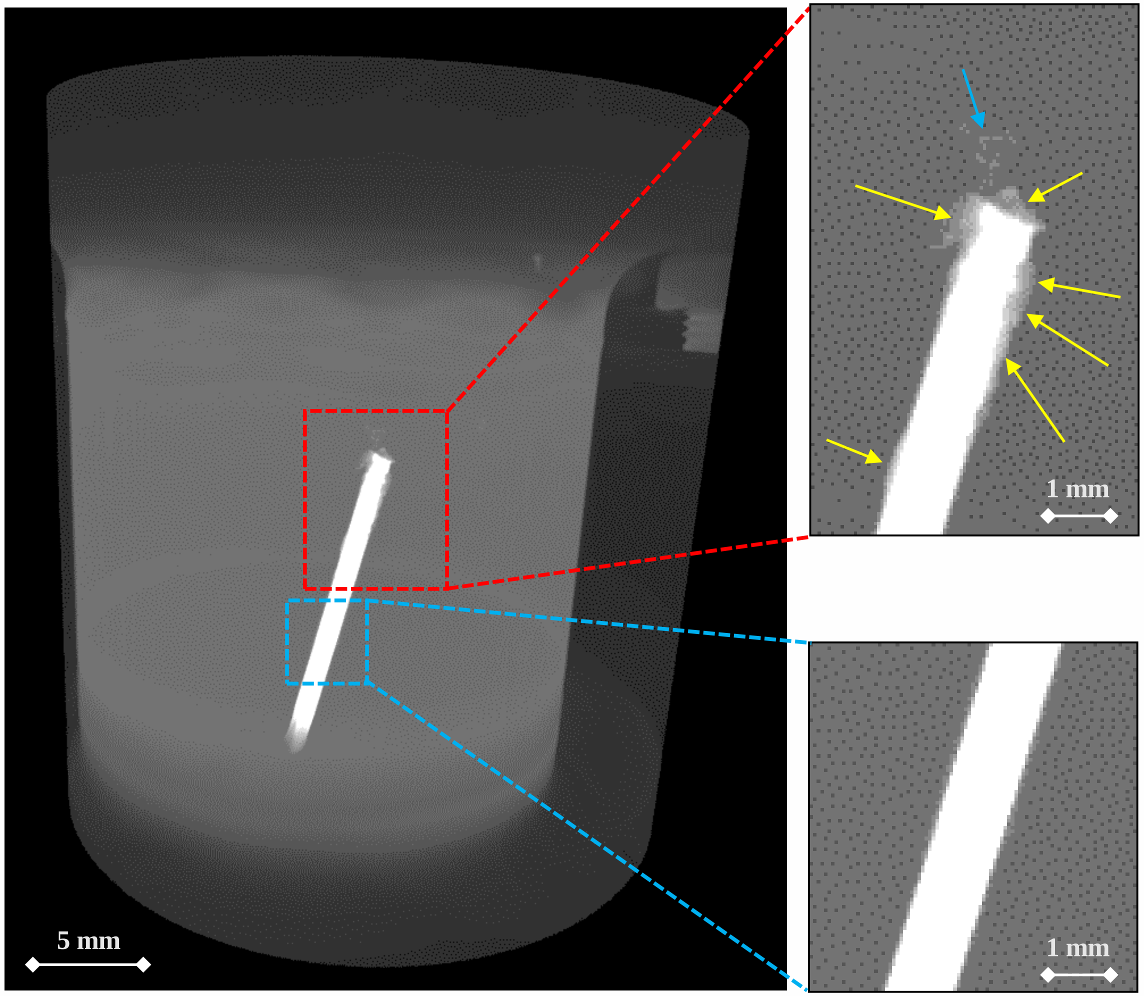
Results 50 days after preparation

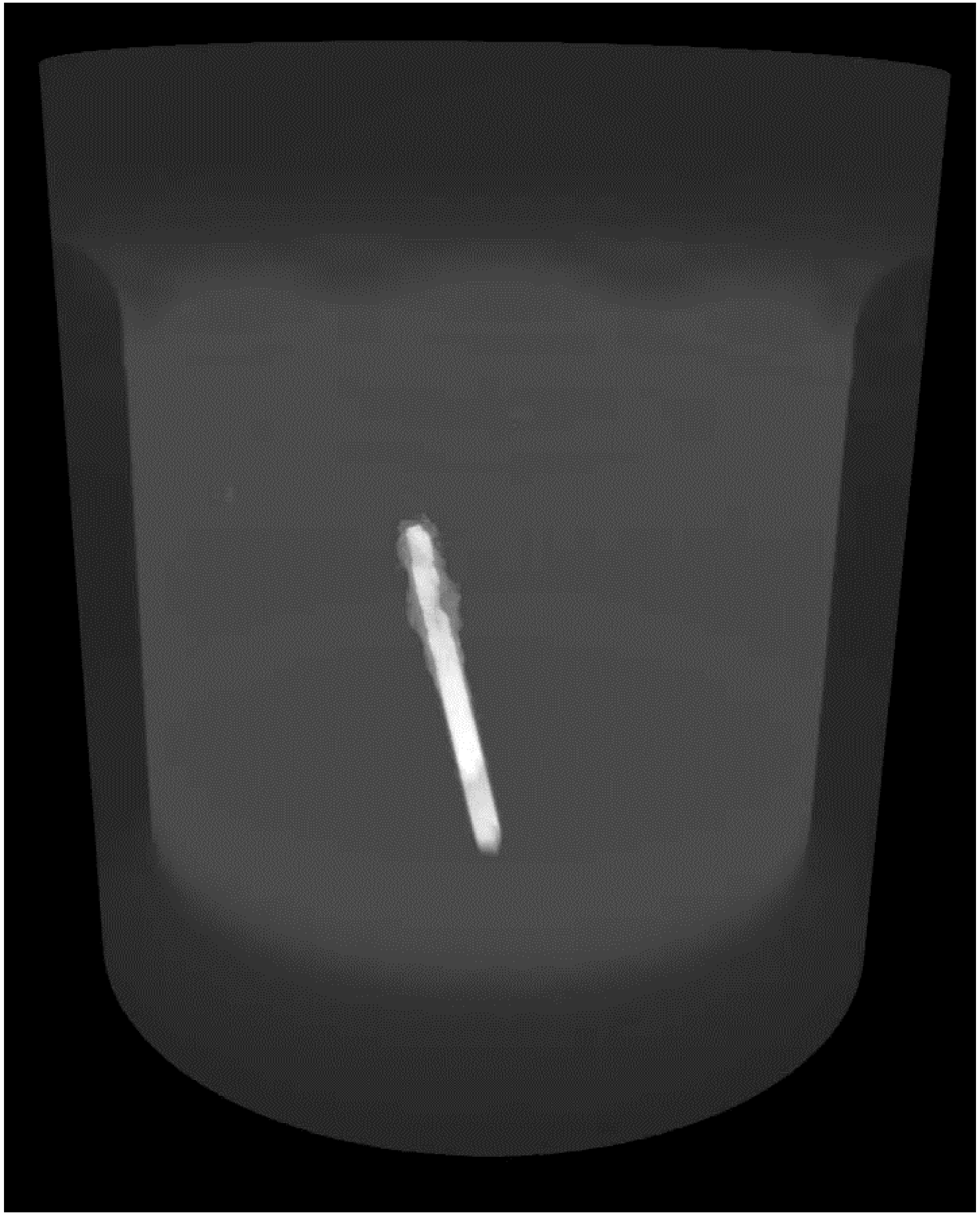
Results 50 days after preparation



Key findings

- Growth of corrosion product volume
- Signs of coalescence
- Migration away from the corroding front
- Intact lower surfaces

Results 360 days after preparation



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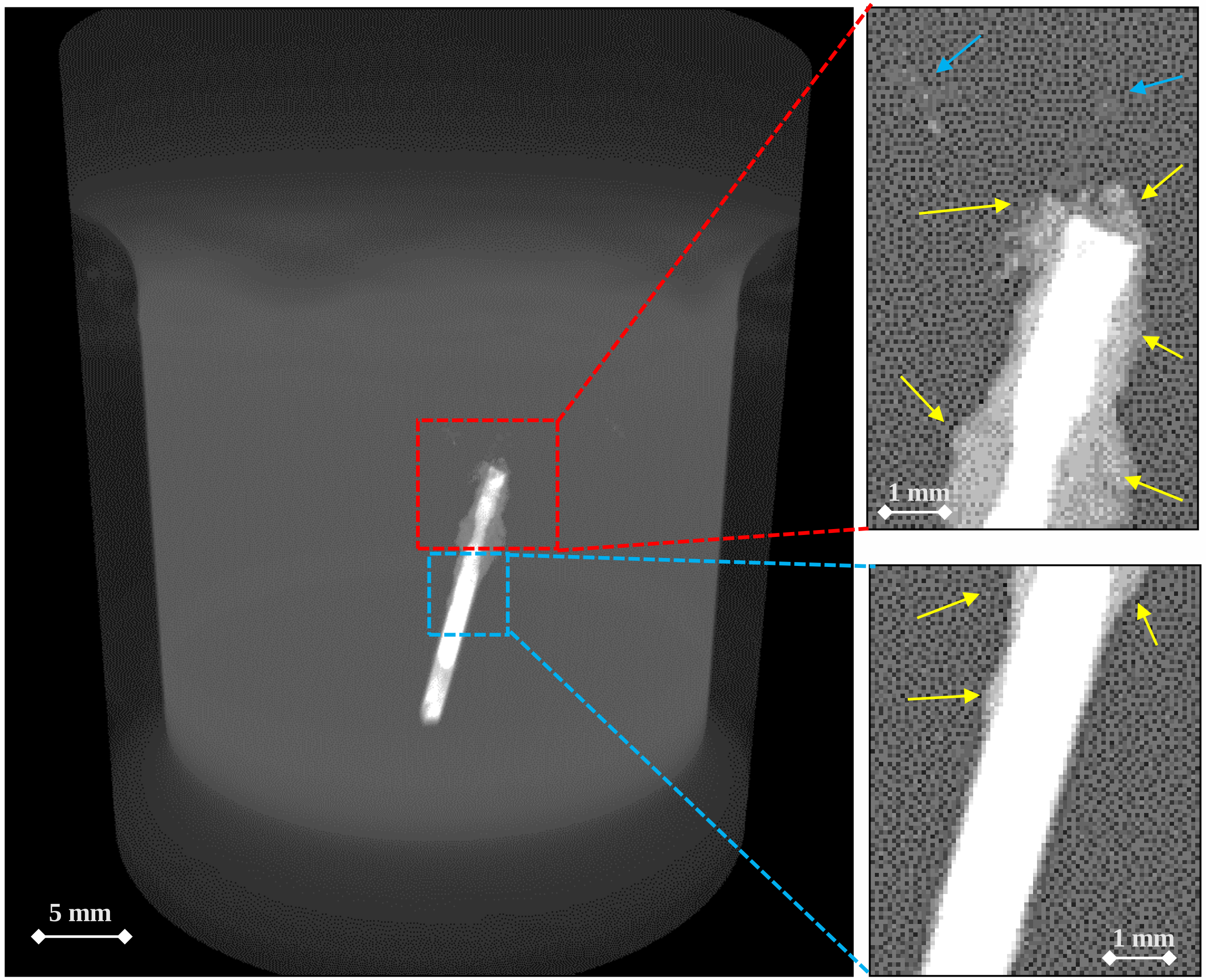
Results 360 days after preparation

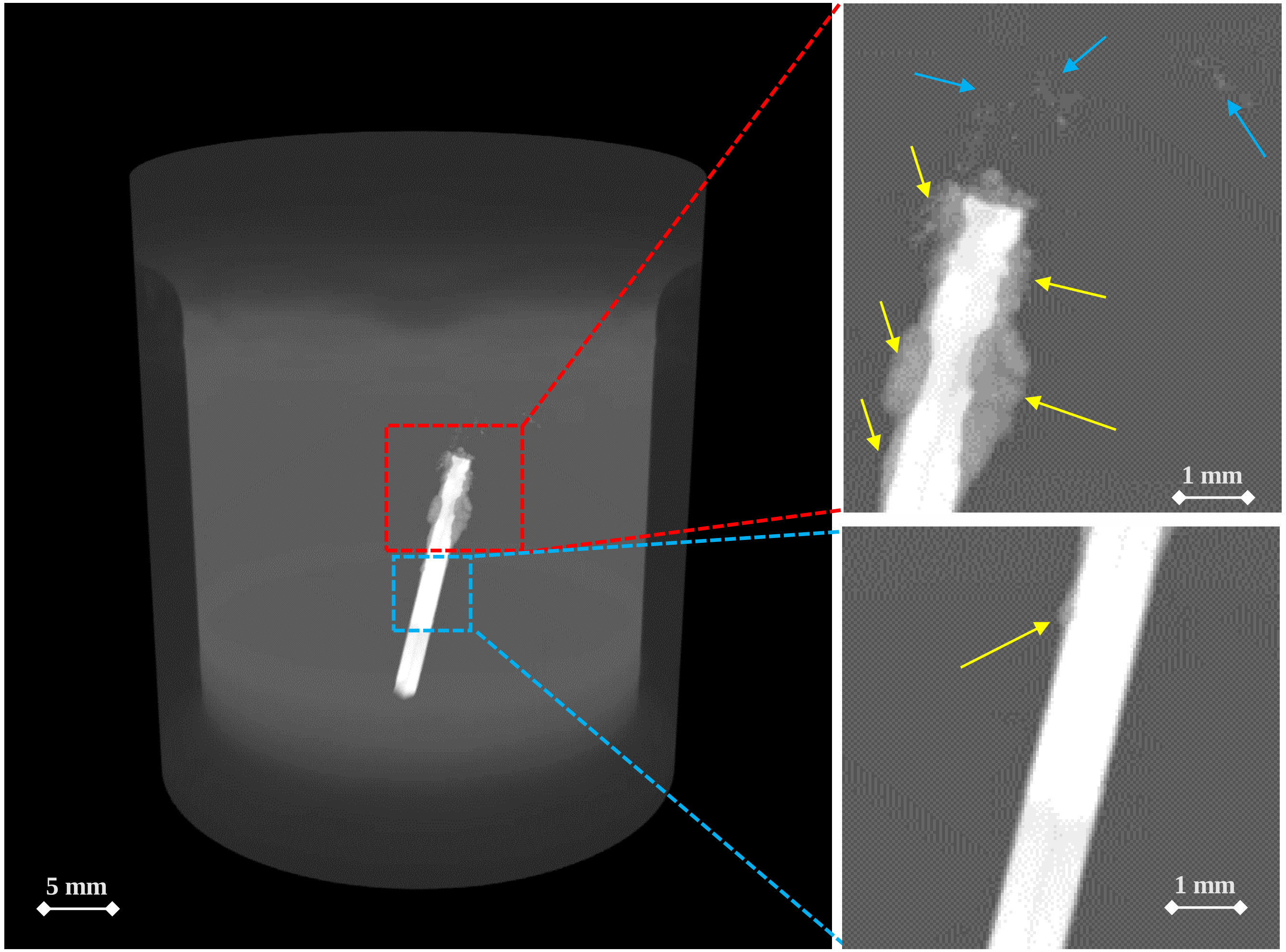


Key findings

- Significant growth of corrosion product volume
- Coalescence across the top part of the specimen
- Signs of corrosion across the middle height
- Intact low surfaces

Results 540 days after preparation

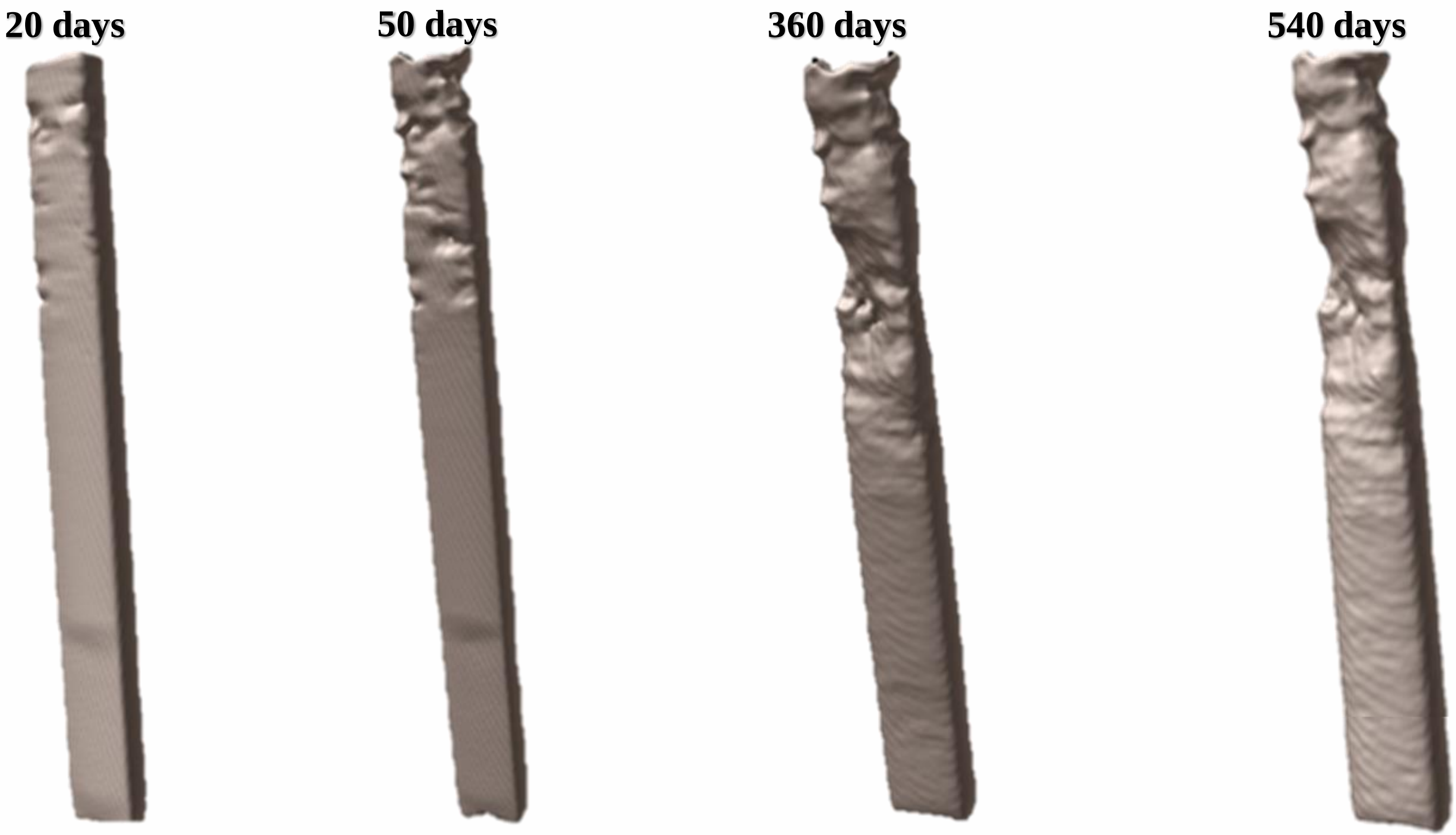
Results 540 days after preparation



Key findings

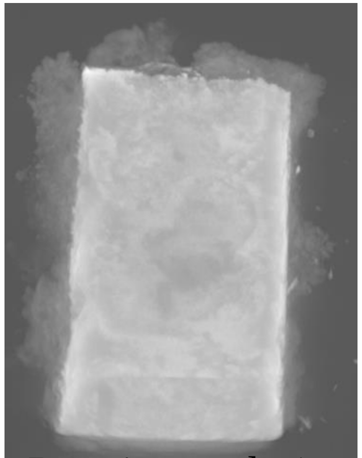
- Corrosion product volume remained constant
- Intact low surfaces
- Further migration of particles away from the uranium

Comparison: from 20 days to 540 days

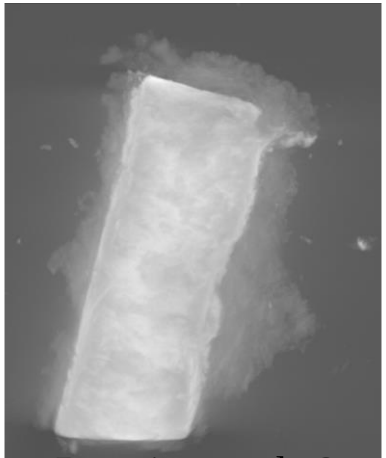


High-magnification scans

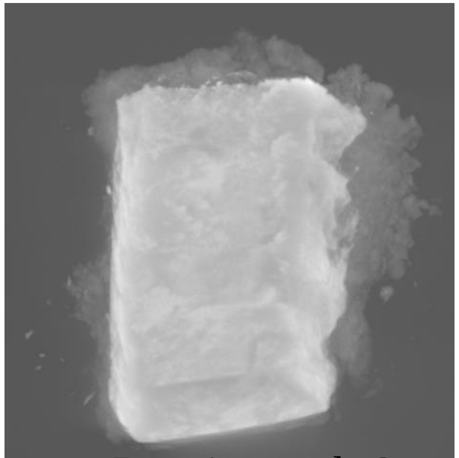
20 days



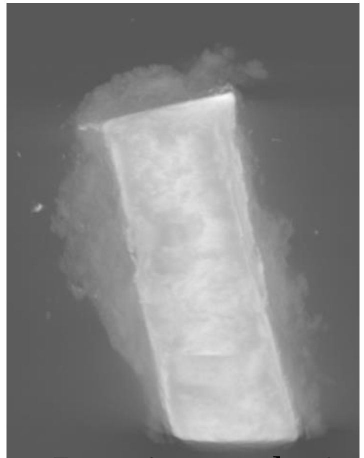
Rotation angle 1



Rotation angle 2

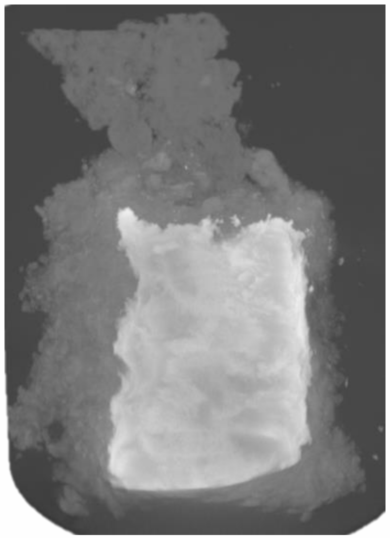


Rotation angle 3

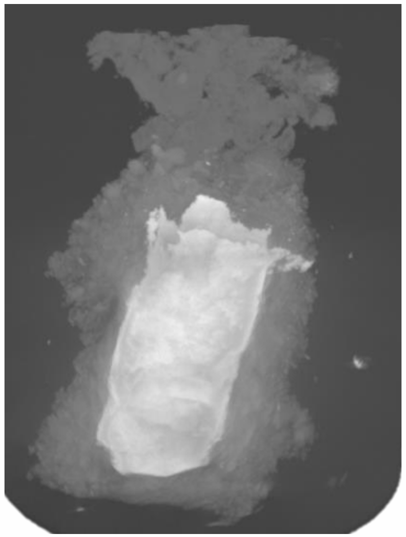


Rotation angle 4

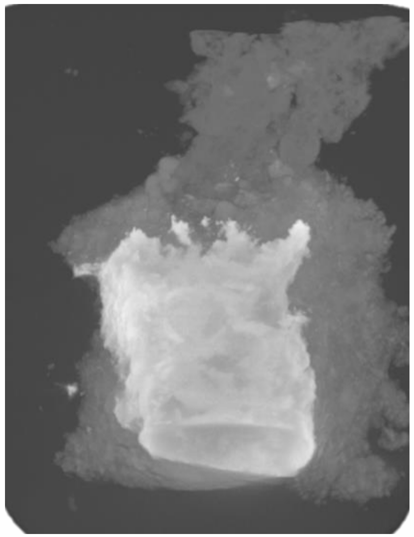
50 days



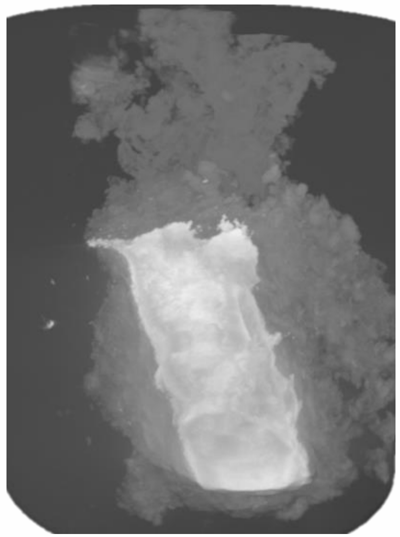
Rotation angle 1



Rotation angle 2



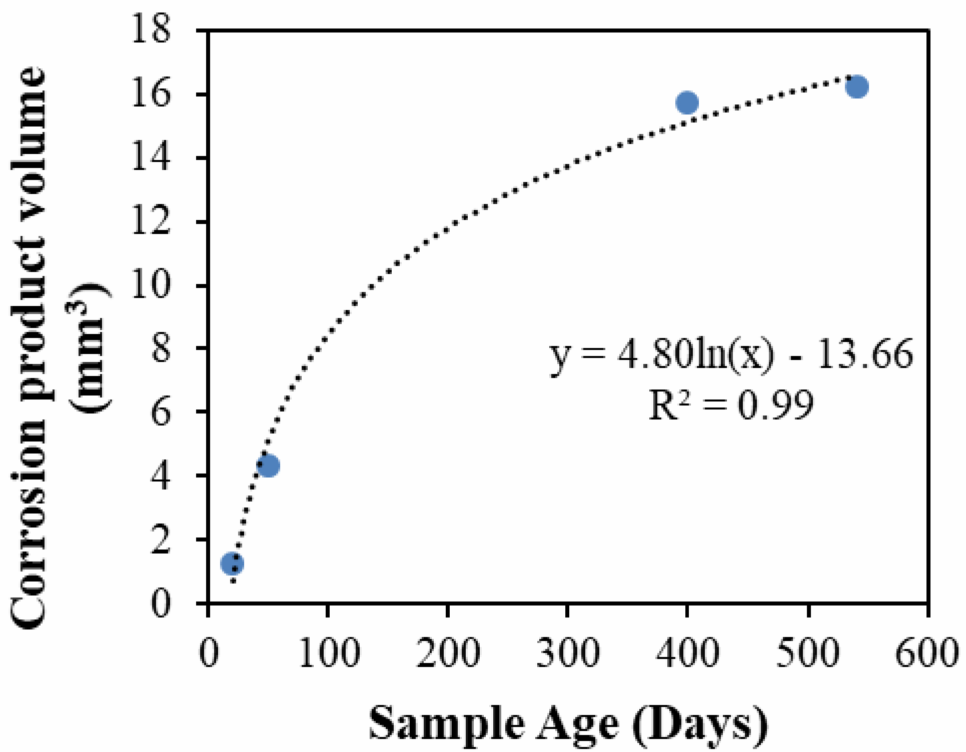
Rotation angle 3

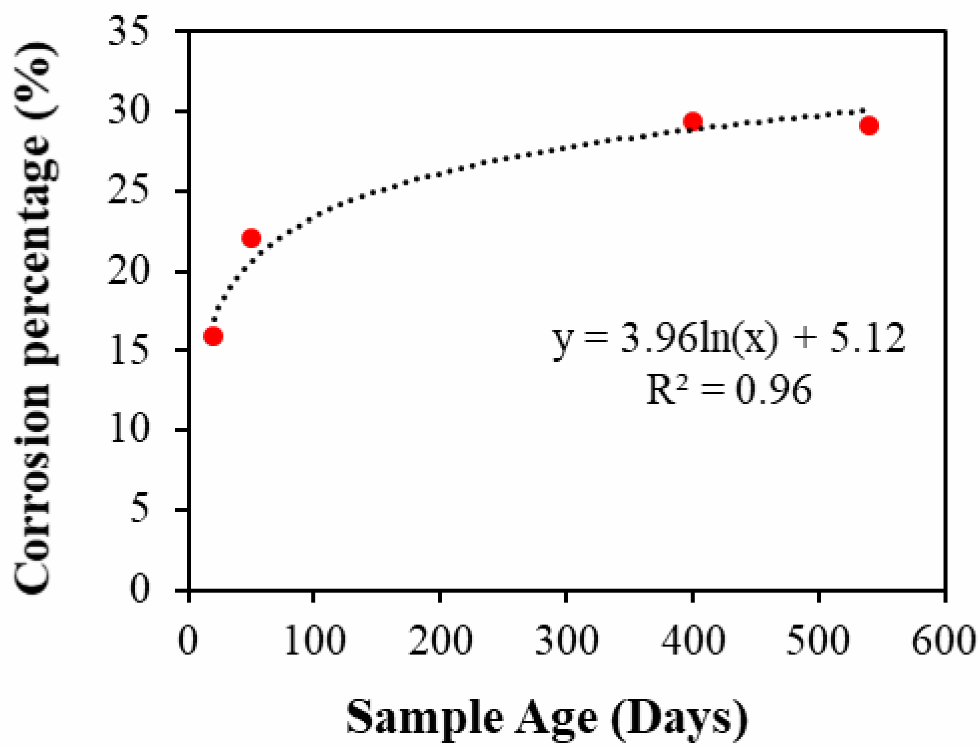


Rotation angle 4

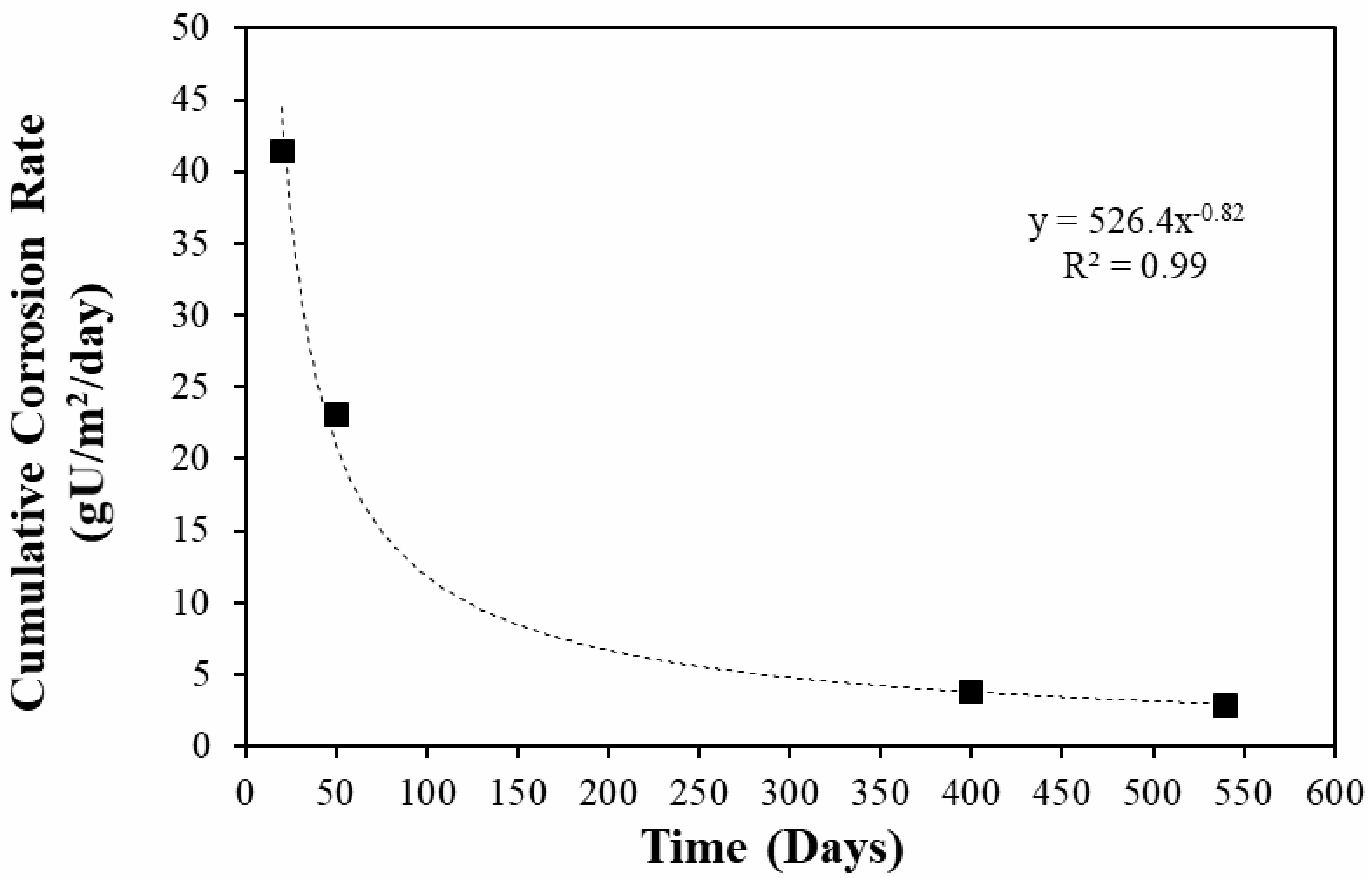
Quantitative Analysis

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

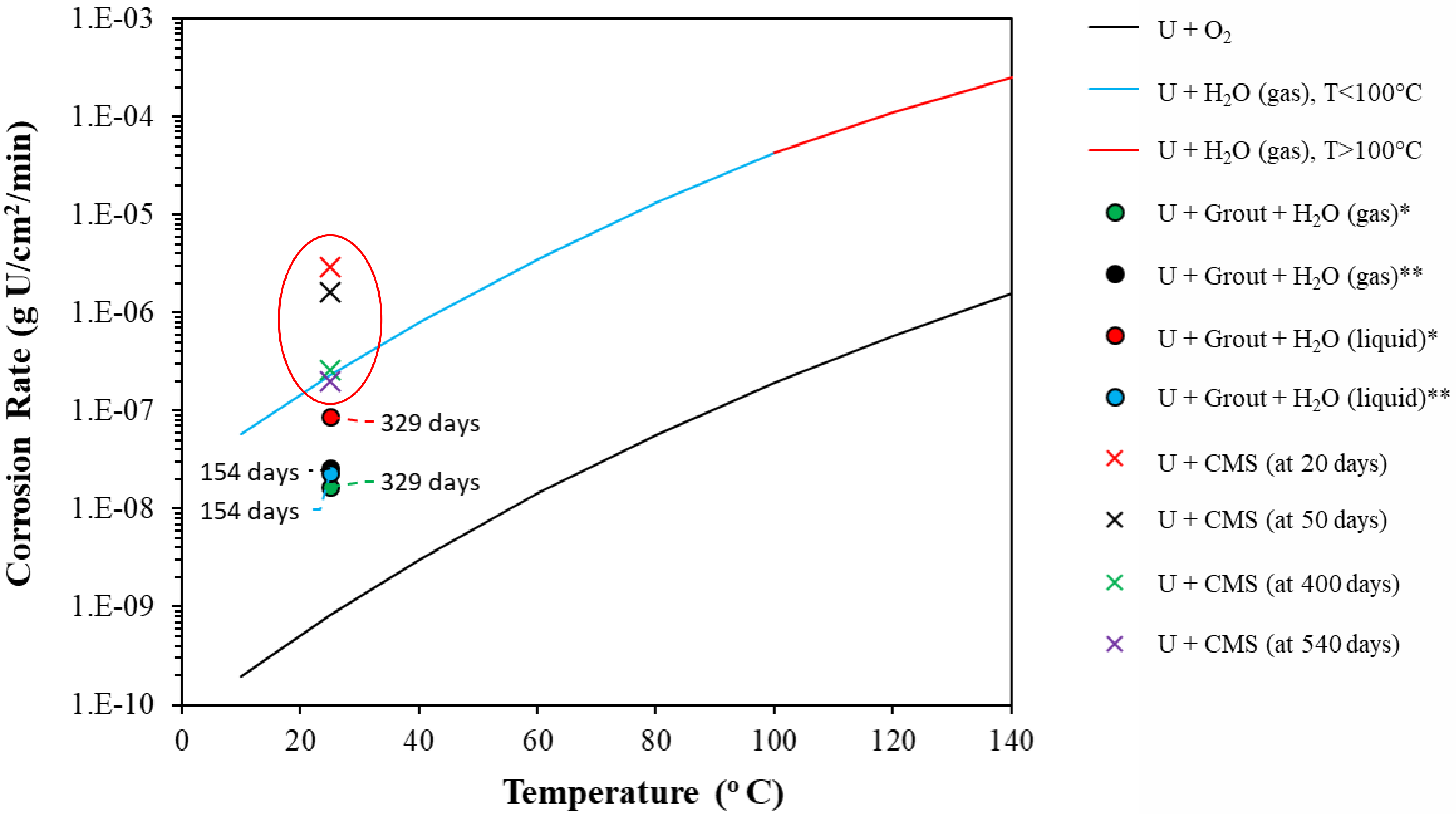




Corrosion rate vs Time



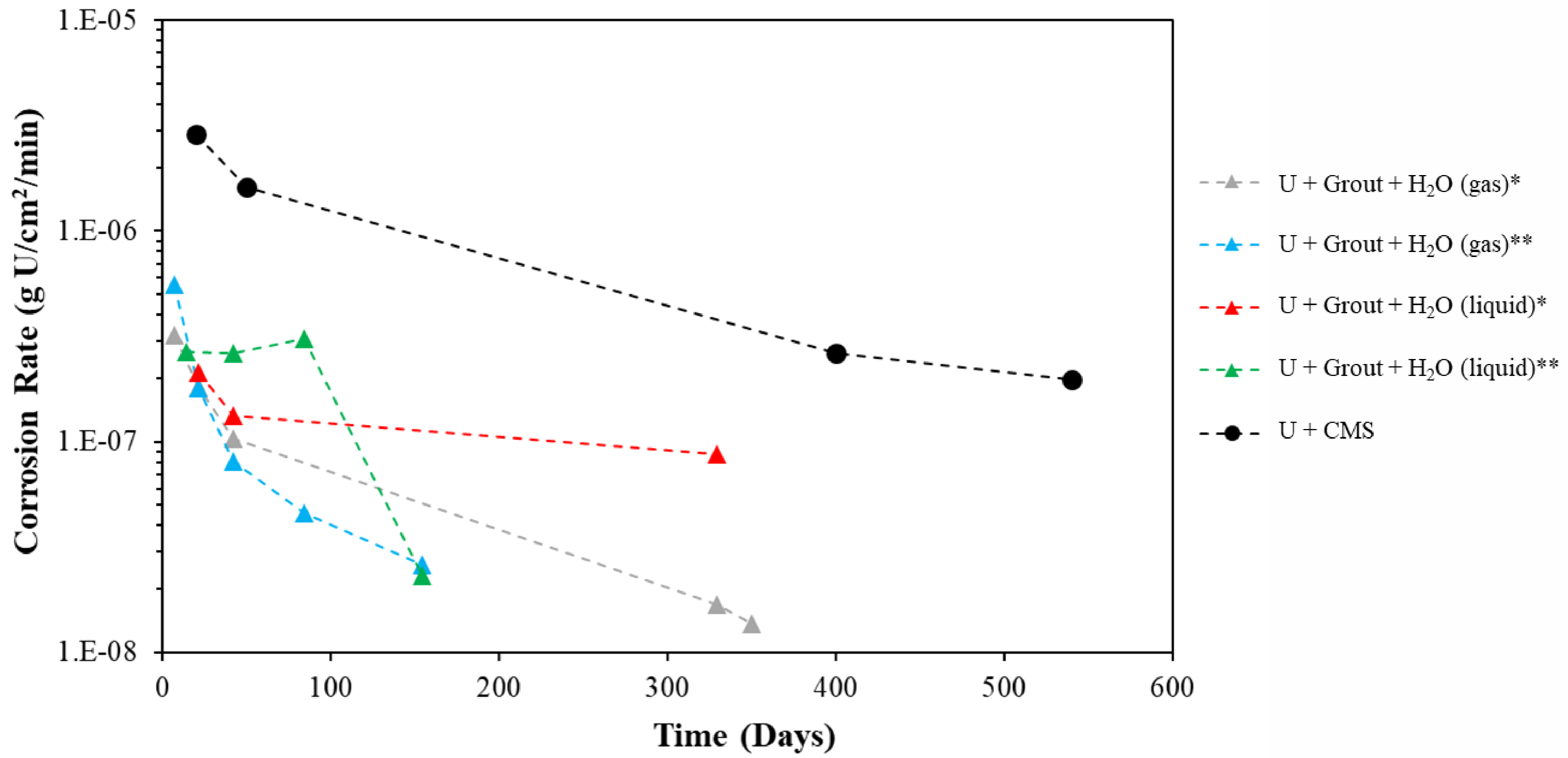
Corrosion rate vs Temperature – Against the literature



**Uranium was used in as-received state*

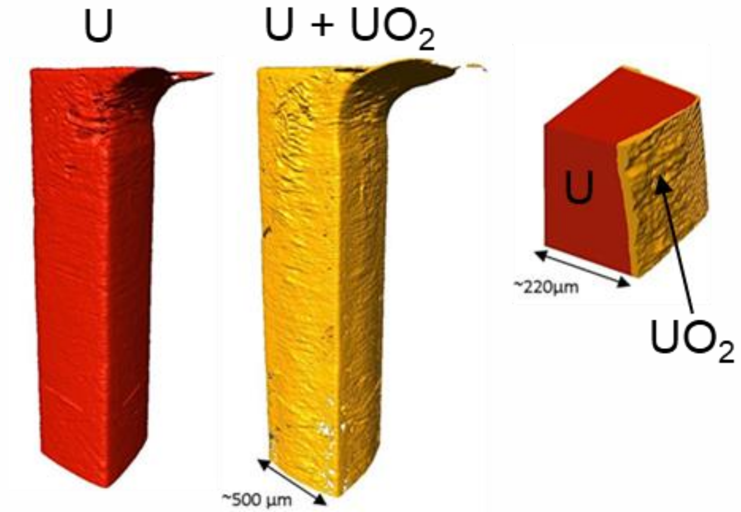
***Uranium was pickled in nitric acid prior to encapsulation*

Corrosion rate vs Time – Against the literature

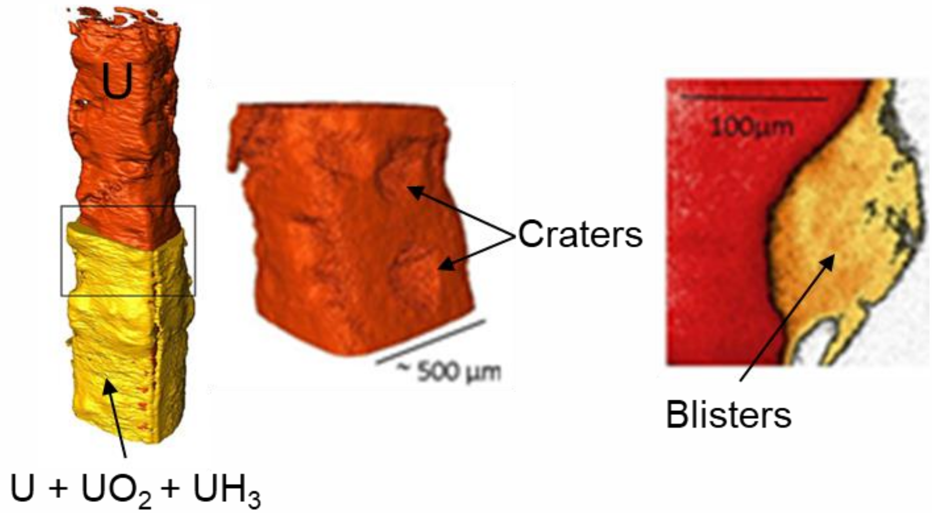


**Uranium was used in as-received state*
***Uranium was pickled in nitric acid prior to encapsulation*

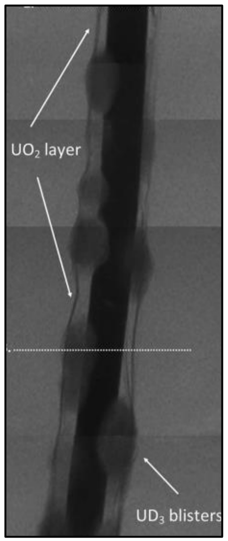
Phase Identification:
UO_2 or UH_3?



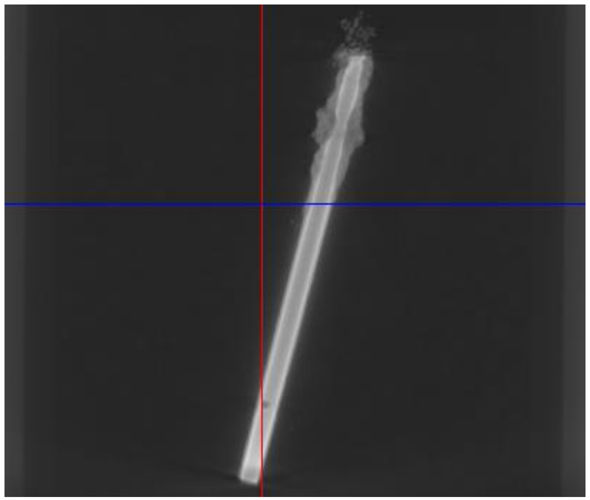
a) 3D model-UO_2 layer at uranium-grout interface



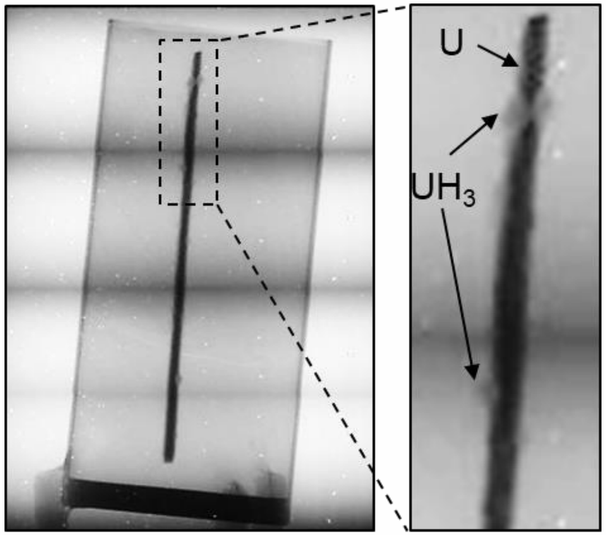
b) 3D model-UH_3 blisters at uranium-grout interface



c) 2D radiograph, UO_2 layer and UH_3 blisters at uranium-grout interface



e) 2D projection, UH_3-like blisters at uranium-CMS interface



d) 2D radiograph, UH_3 blisters at uranium-grout interface

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Thank you

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An Investigation of Corrosion and Leaching of Carbide Fuels in a Geological Disposal Facility (GDF) Setting

Dimitris Samaras, University of Bristol

Theme 3: Spent Fuel

Tuesday 12th November 2019
Lancaster

Energy
For a Low Carbon Future

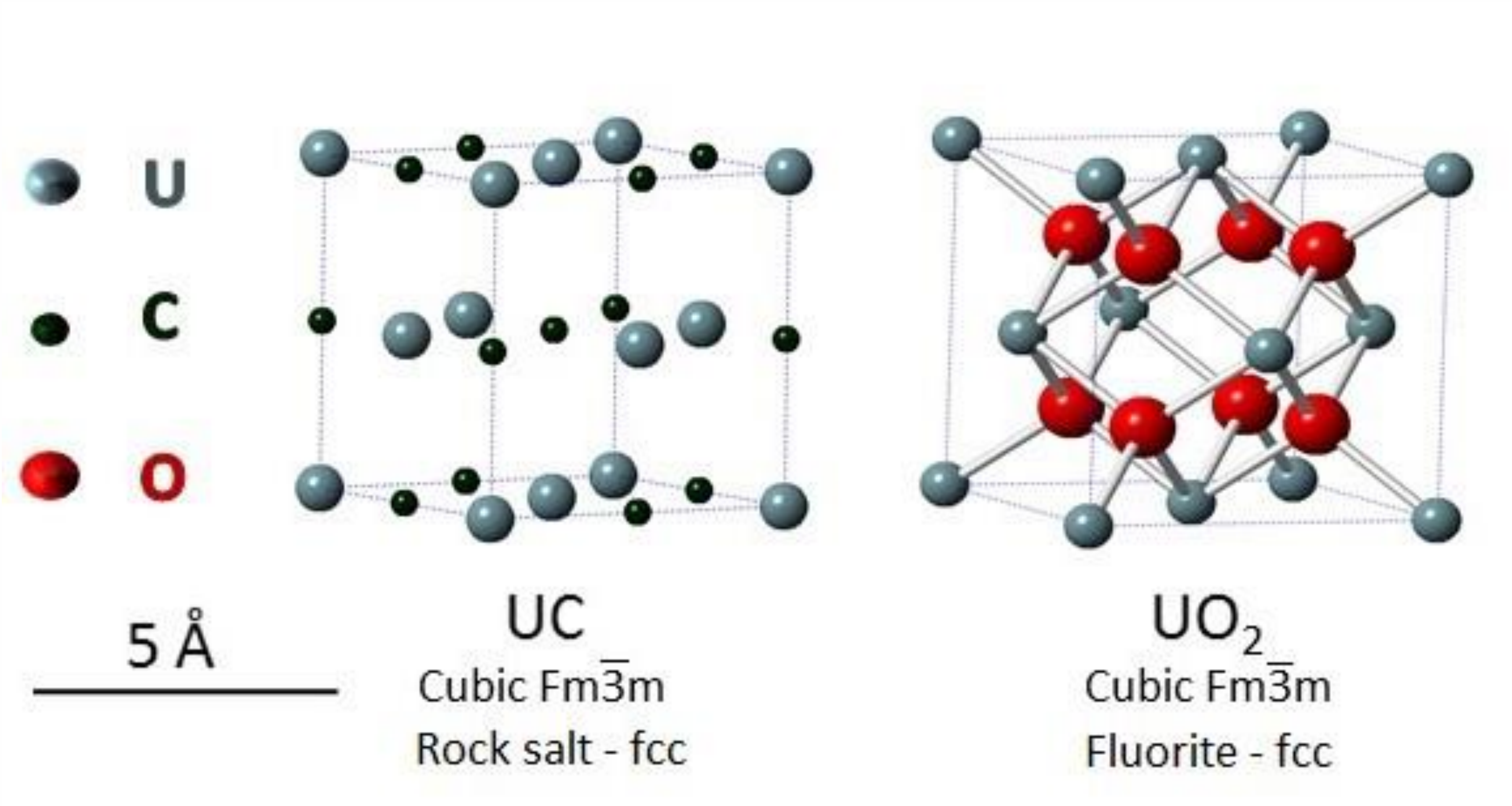
Briefing

- UC: Exotic Fuel from UK Nuclear Test Program
  - Experimental Reactor Fuel (Dounreay, Scotland)
  - Fission target in research facilities (e.g. CERN)
- NDA Inventory
- Potentially Pyrophoric in Water and Oxygen
  - Reactivity compared to U metal
- GDF: Ultimate Fate
  - Interaction with Groundwater?

Why UC fuel research?

Jones, R.W. (1972). Uranium Carbide as a Nuclear Fuel. pp 13-16

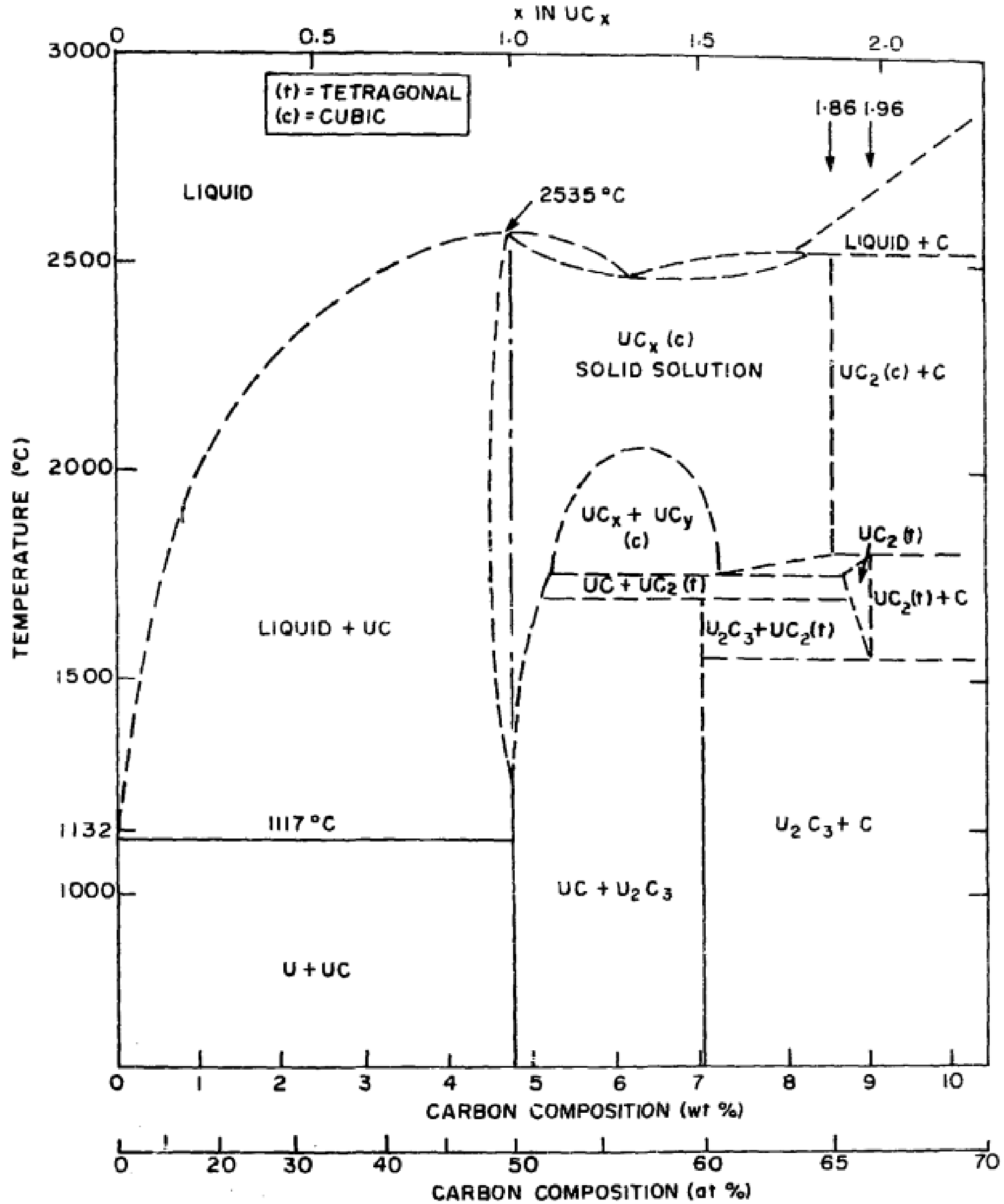
- 30% higher density over UO_2 - 6x Thermal Conductivity
- M.P. 2500 °C
- Good dimensional stability - Fission Gas Retention
- But
  - Impossible to use in water reactors
  - Reason: rapid reaction with water



Uranium Monocarbide and Dioxide Molecular Structures
Image: C. Gasparrini, Oxidation of Zirconium and Uranium Carbides, Doctoral Thesis, 2018

Stoichiometries

- Strictly, Carbide -> UC
- 3 stoichiometries – U_xC_y
  - Monocarbide - UC
  - Sesquicarbide – U_2C_3
  - Dicarbide – UC_2
- Phase Diagram
  - Potential coexistence
  - 4.8 % w/o threshold



Uranium-Carbon Phase Diagram
Image: Jones, R. W. (1972). *Uranium Carbide as a Nuclear Fuel*.

Reaction with Water

- Hydrolysis rate dependant on temperature
  - Vigorously at around and above 40 °C

    K.M. Taylor and C.H. McMurtry. Synthesis and Fabrication of Refractory Uranium Compounds, *U.S. Atomic Energy Commission,* 1960
- Compound formulas dependant on the stoichiometry

  M.J Bradley and L.M. Ferris , Hydrolysis of Uranium Carbides between 25 and 100 °C : I and II (1962 & 1964)
  - UC -> CH_4
  - UC_2 & mixtures -> C_2H_6, C_3H_8, and heavier.

Reaction with Oxygen

- Oxygen: another degrading agent
- Diluted in groundwater
- Dry oxidation: linear rate law,
  K.A. Peakall and J.E. Antill, Oxidation of Uranium Monocarbide, *Journal of the Less-Common Materials,* 1962
- N.B. Min temp: 230°C

First Actions - Precautions

- First Inspection (in inert environment: Ar glovebox)
  - Dimension Measuring
  - Weighing – Activity Validation (163 gr / 6 MBq) (in total)
- Initial Techniques
  - Electron Microscopy (SEM) (Surface Examination – Composition)
  - X-Ray Diffraction (XRD) (Crystallography – Composition)
  - High Speed Atomic Force Microscopy (HSAFM) (Surface Topography)
  - X-Ray Fluorescence (Composition)
- Minimal exposure to oxygen and water vapour.

Further Steps

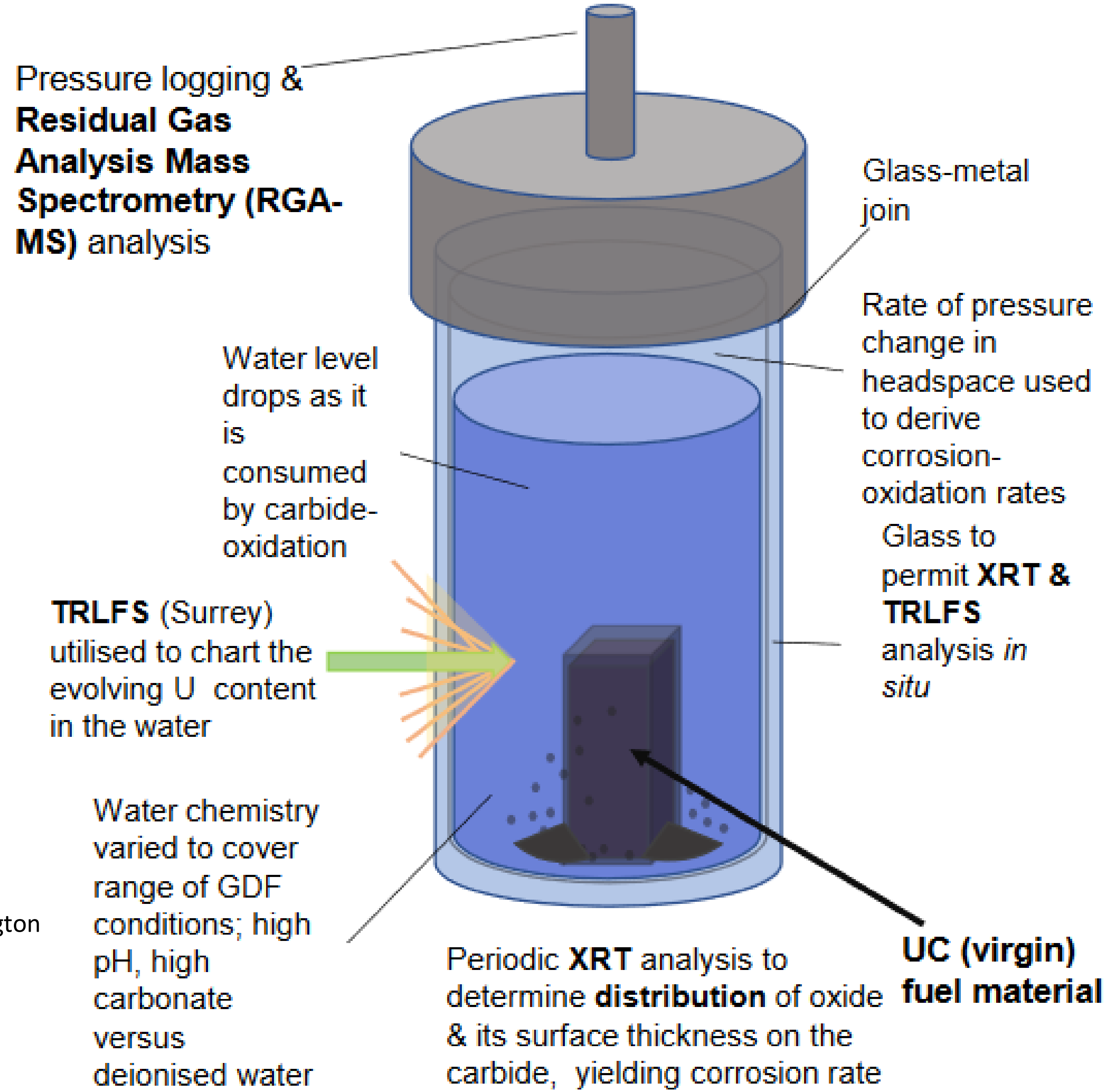
- Two modes
  - Initial material evaluation
  - Corrosion simulation & monitoring
- 2nd mode: sample fully immersed in water
  - Sealed Vessel
- Two groups of techniques
  - Material Analysis
  - Chemical Solution Analysis

Further Techniques - Materials

- X-Ray Tomography (XRT)
  3D Structure and Corrosion Progression
- Secondary Ion Mass Spectrometry (SIMS)
  Depth Composition -> Oxide Thickness
- Electron Microscopy Affiliated Techniques
  - Energy Dispersive X-Ray Spectroscopy (EDX)
    Elemental Composition
  - Electron Backscatter Diffraction (EBSD)
    Crystallographic Orientation

Further Techniques – Chemical

- Inductively Couple Plasma…
  Plasma Torch -> Sample Composition
  - …Mass Spectrometry (ICP-MS)
  - …Optical Emission Spectrometry (ICP-OES)
- Time Resolved Light Fluorescence Spectroscopy (TRLFS)
  Measure of water chemistry alteration
- Residual Gas Analysis (RGA) for hydrocarbon detecting



UC Corrosion Experimental Cell Concept
Image: Prof. David Reed, TRANSCEND 1st Industry Roadshow, Warrington

Acknowledgements

- Professor Tom Scott
- Dr. Ross Springell

Also

- Dr. Keith Hallam
- Dr. Oliver Payton
- Dr. Xander Warren
- Dr. Peter Heard
- Dr. Christopher Jones
- Dr. Tomas Martin

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Thank you

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Sustainable Management of Spent Fuel – Context for Research

David Hambley

TRANSCEND Meeting, 12 November 2019

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International perspectives

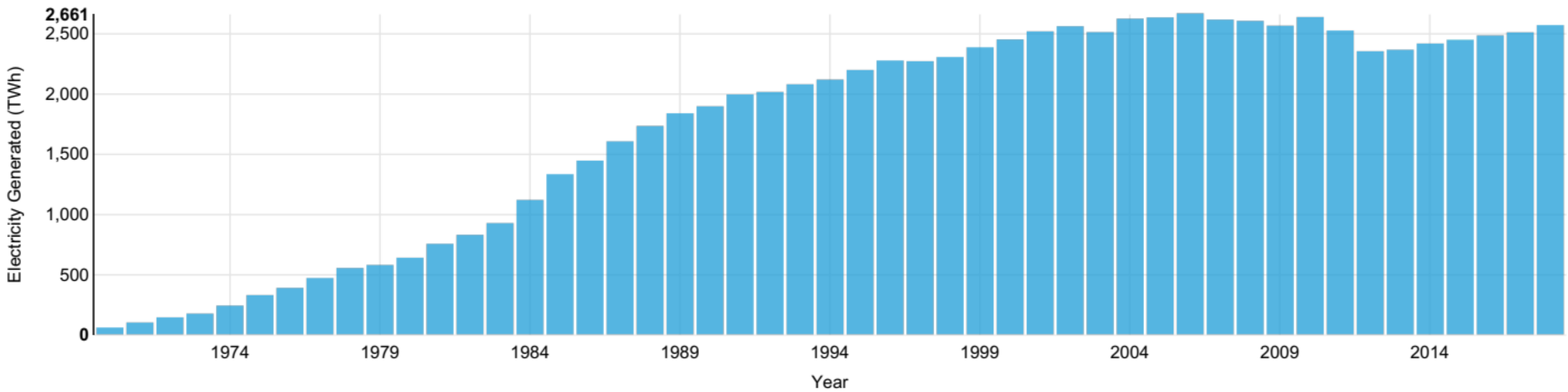
UK spent fuel management – context & strategy

Trends and emerging challenges

Worldwide Nuclear Generation

Current status:	World	UK
• operating reactors	444	15
• power production	394 GWe	8.9 GWe
• fract. of electricity consumption	10.5%	17.7%
• reactors under construction	52 GWe	1.6 GWe

2,563 TWh: global electricity generation from nuclear energy in 2018

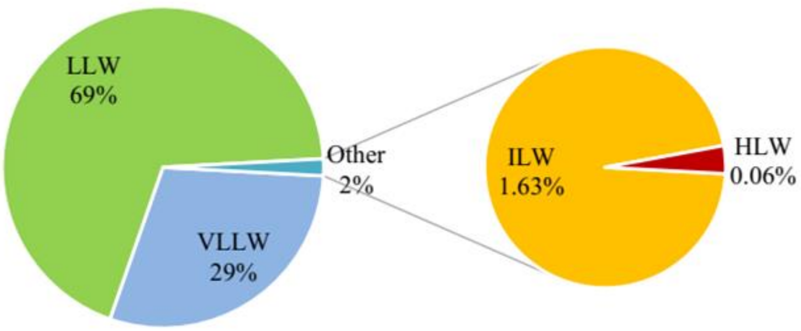


85,000 TWh electricity generated since 1970, equivalent to 7.5 bn tonnes of oil or 255 bn tonnes of coal

Accumulation of Fuel

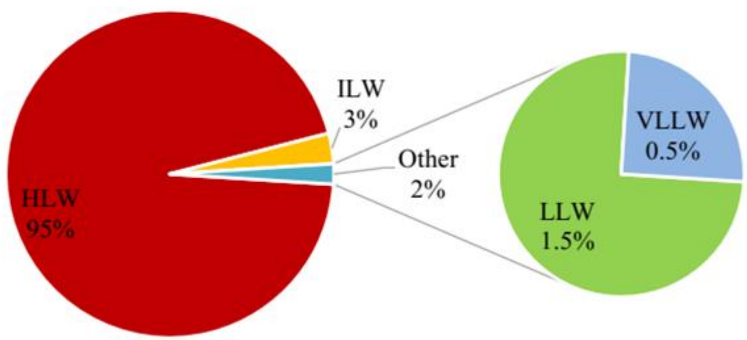
Fuel storage

- Cooling to transport
- Cooling to reprocess
- Cooling for disposal



Source: National Profiles and NEWMDB.

FIG. 24. Share of total waste volumes in storage and disposal.



Source: National Profiles and NEWMDB.

Region	W			
Africa				
Eastern Europe				
Western Europe				
Far East				
North America				
Latin America				
Middle East and South Asia				
South East Asia and Pacific				
Global total	180,800	56,900	120,300	367,600
Research Reactor total	362	2,831		3,193

IAEA. Status and trends in spent fuel and radioactive waste management. NW-T-1.14, 12018.

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Storage Systems

Principal Functions

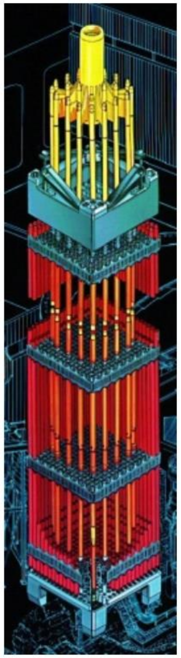
- Shielding
- Containment
- Cooling
- Preservation

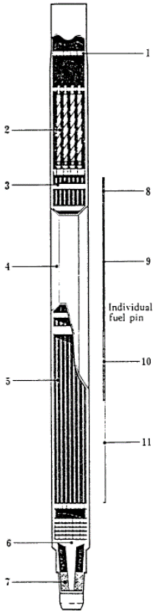
Options depend on nature of fuel

- CANDU/PHWR/Magnox – low heat output
- PWR/BWR – high heat output
- MOX/ FRBR – very high heat output

Time horizons

- <10 years reprocessing
- 20 years initial storage assumption
- 100 year typical for storage systems
- 200 years to disposal facility closure





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Storage Systems

Options depend on

- Technical factors
- History
- Politics

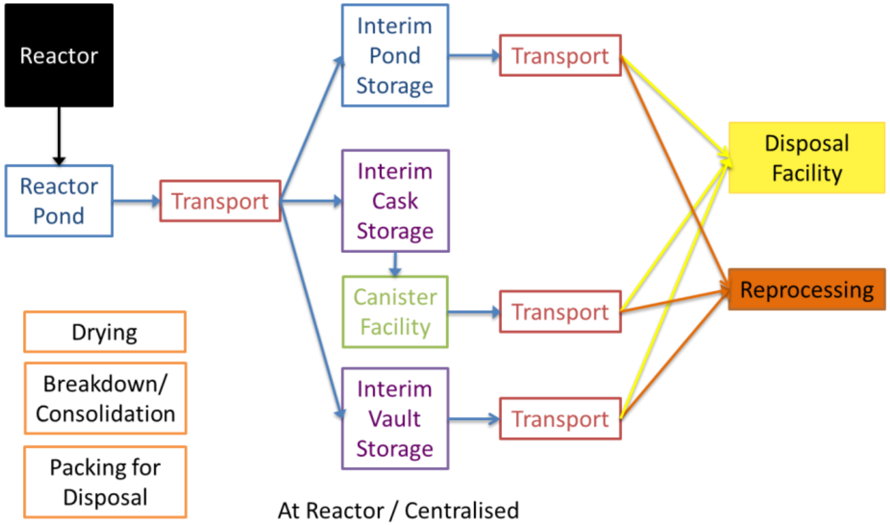
Principal Types

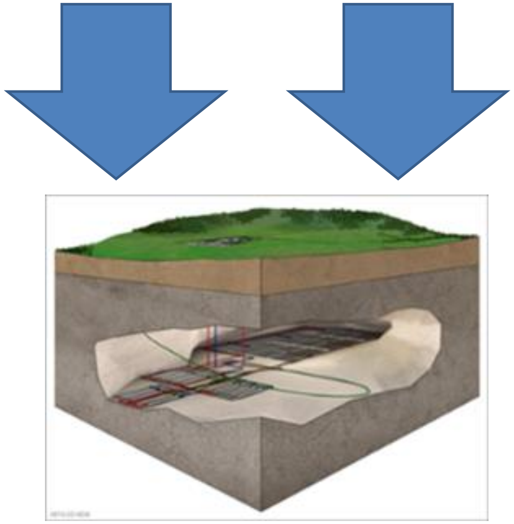
- Wet - Dry
- Fixed capacity – modular
- Store till disposal – move and re-store

Disposition

Repositories are necessary part of fuel cycle. Their design is affected by fuel properties, e.g.

- Geometry
- Heat load
- Criticality
- Evolution

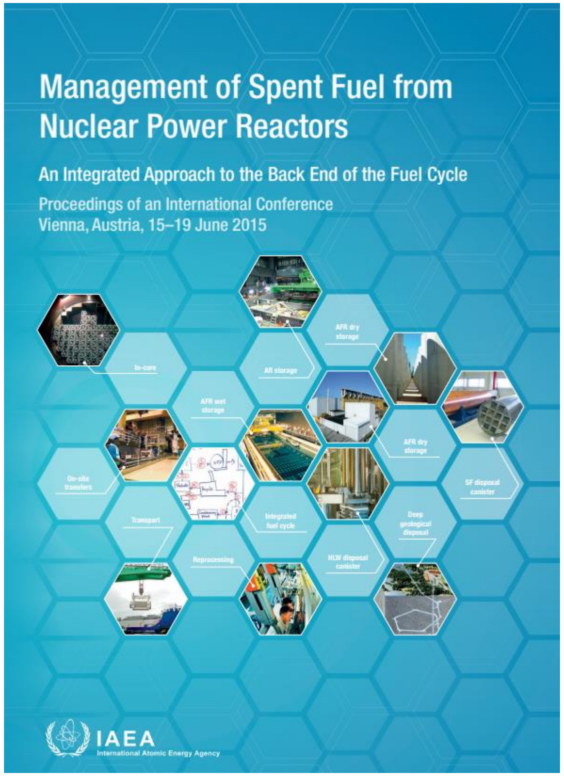




Trends from SFM’19

Trends in spent fuel management

- Limited take-up of reprocessing continues
- Long term dry storage uptake increasing for capacity expansion
- Diverse storage systems in use
- Some important progress in repository deployment
- Increase focus on
    - **Closing back-end**
    - **Failed fuel**
    - **Ageing management and monitoring**
- Skills and knowledge management



International perspectives

UK spent fuel management – **context** & strategy

Trends and emerging challenges

Magnox Reactors

26 reactors built between 1956 and 1971

Total nominal output 4.4 GWe

Design life 20 years

Most operated > 40 years, max 47 years

Last station closed 2015

Magnesium clad, natural Uranium fuel

> 50,000 tU fuel reprocessed

< 500 tU fuel to be reprocessed

~300 tU of legacy Magnox fuel and residues

Operating Power Reactors

AGR

7 stations, 880 – 1,230 MWe

total output 8.2 GWe

started operation 1976-1989

scheduled closure 2023-2030

Stainless steel clad, UO_2 fuel

Fuel discharges 150-200 tU/y

PWR

1 station, 1,198 MWe

started operation 1995

scheduled closure 2035

expect 20 years extension

Zircalloy clad, UO_2 fuel

Fuel discharges ~25 tU/y

New Build: EDF & CGN

Hinkley Point C

3.2 GWe capacity (2 EPR)

under construction

earliest operation 2026

Sizewell C

3.2 GWe capacity (2 EPR)

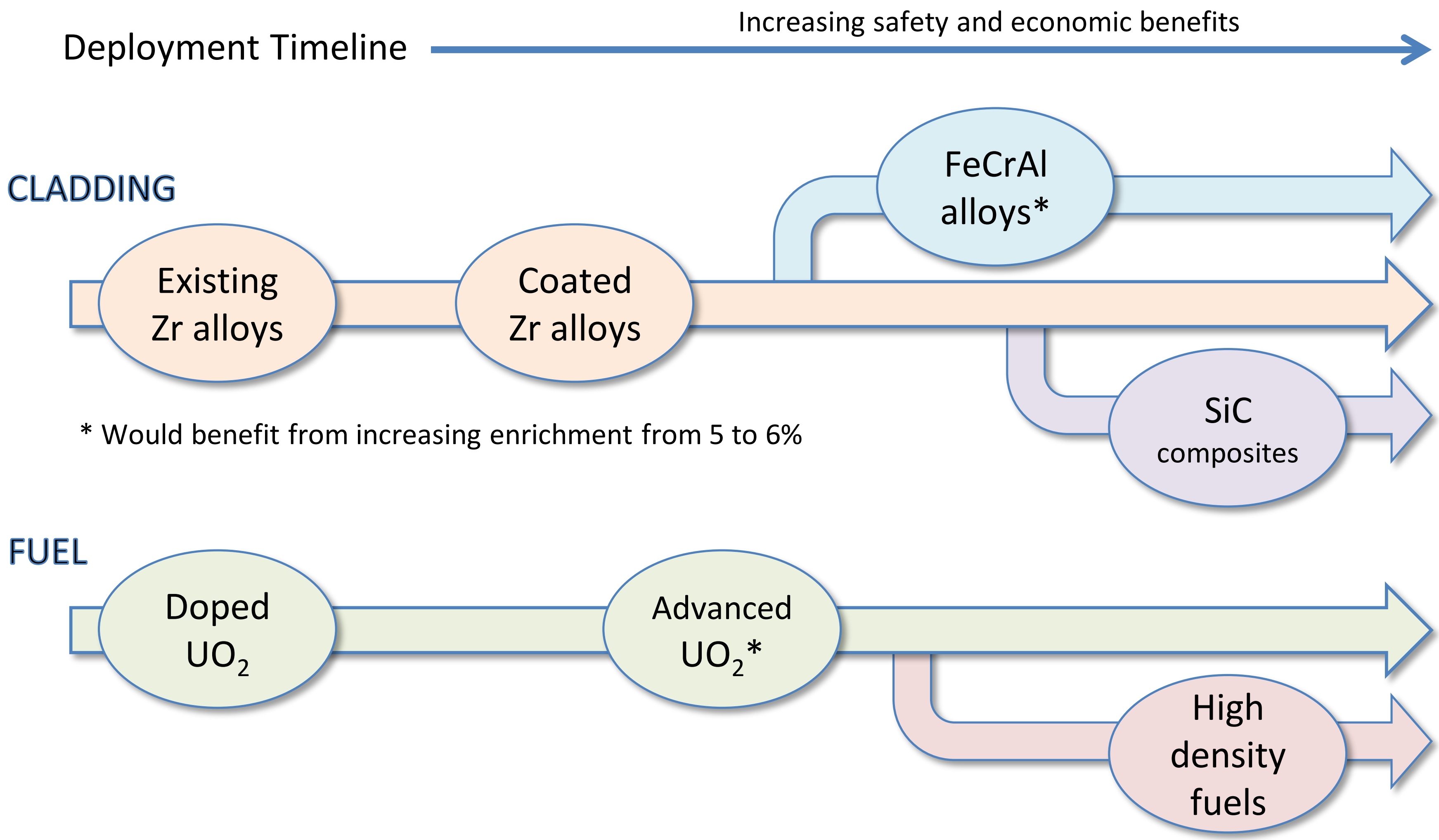
Stage 4 consultation

Bradwell B

3.2 GWe capacity (2 HPR1000)

Site investigation and Generic Design Assessment

LEADING ATF CONCEPTS



* Would benefit from increasing enrichment from 5 to 6%

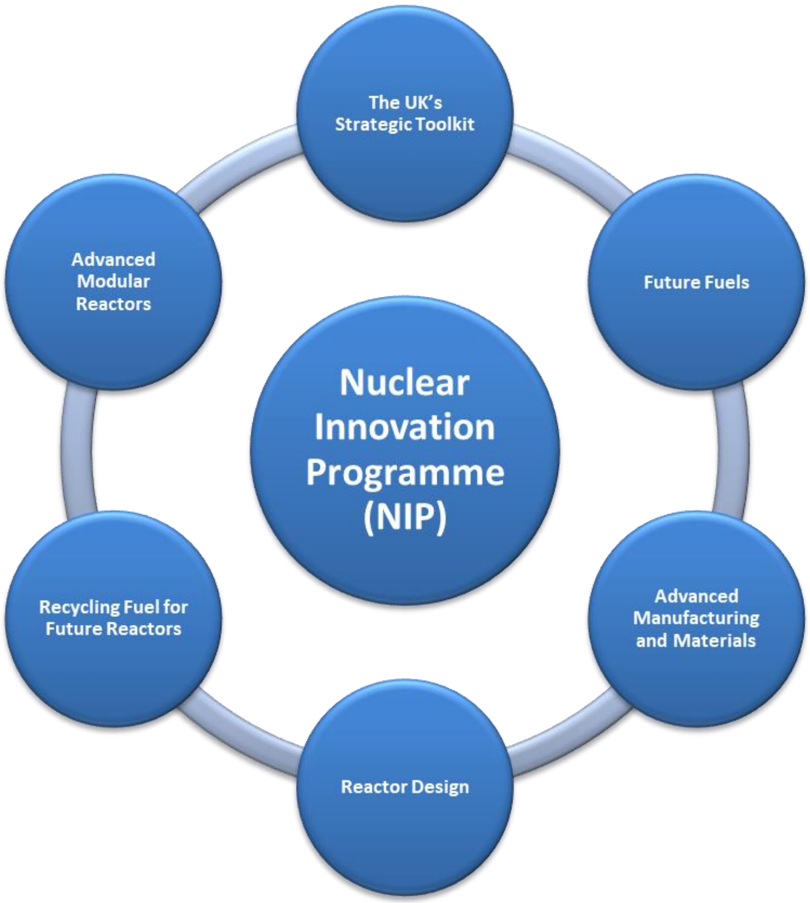
Vision 2050+

Scenarios for decarbonisation of electricity production and transport envisage:

- >> 16 GWe new reactors
- Closed fuel cycles to minimise repository

To support future closed cycles, ongoing national programme for:

- Aqueous recycle:
- Advanced Reactor fuel recycle
- Molten salts recycle
- Waste management



Research and Development Legacy

Legacy fuels from

- research reactors
- prototype reactors

<500 tHM

Fuel being consolidated at Sellafield

Long term storage pending disposal

- Wet storage
- Dry storage

Some fuels

- Reprocessed
- Packaged in ILW concepts

International perspectives

UK spent fuel management – context & **strategy**

Trends and emerging challenges

"Spent fuel management is a matter for the commercial judgement of its owners, subject to meeting the necessary regulatory requirements."

NATIONAL NUCLEAR LABORATORY

National Strategy (1)

UK is pursuing an Open Fuel Cycle

UK is committed to the clean-up and decommissioning of historical Civil nuclear legacy and progressing radioactive waste management and disposal

UK Government recognises nuclear power as a low carbon energy source and are considering pathways that could deliver up to 75GW installed nuclear capacity by ~2050 in the context of its carbon reduction strategy….

The option for a future transition to a Closed Fuel Cycle remains

https://www.gov.uk/government/publications/the-carbon-plan-reducing-greenhouse-gas-emissions--2

https://www.gov.uk/government/publications/nuclear-energy-research-and-development-roadmap-future-pathways

National Strategy (2)

Geological disposal of higher activity radioactive waste is UK Government policy.

- Fuel
- High and Intermediate level waste

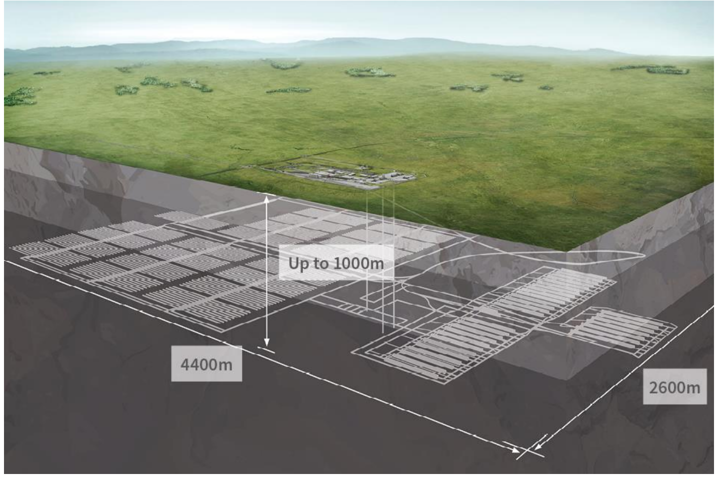
Radioactive Waste Management Ltd will be the developer of the disposal facility.

Approach for GDF site selection based on voluntarism and partnership - starting with local communities expressing an interest, with no commitment.

- Siting process to restart 2017,
- Expressions of interest period started December 2018.

Earliest spent fuel disposal ~2075

(Ref: Nuclear Decommissioning Authority. Geological Disposal - Steps towards implementation, Executive Summary March 2010, ISBN 978 1 84029 402 6)



Current Fuel Management Strategies

AGR

Reactor pond storage capacity < 1 year

Routine transport of fuel (to mid 2030s)

Centralised pond storage

Dry storage being evaluated as contingency

Repackage

Transport

Disposal ~2075-2090

LWR

Pond storage capacity 10-20 years

Storage in reactor pond

AR dry storage (2016 – 2100??)

Repackage

Transport

Disposal > 2090

Fuel Storage Requirement Evaluation

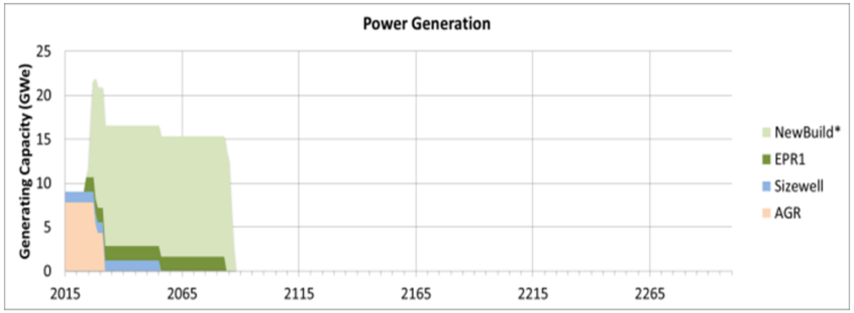
Illustration of key characteristics of fuel storage requirements for

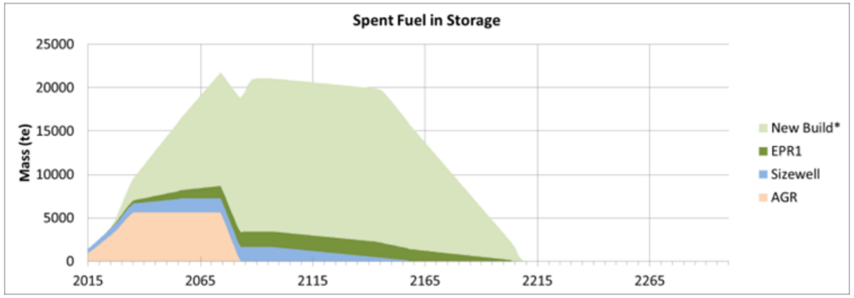
- Legacy fuels
- Current AGR & PWR
- New Build of 16 GWe

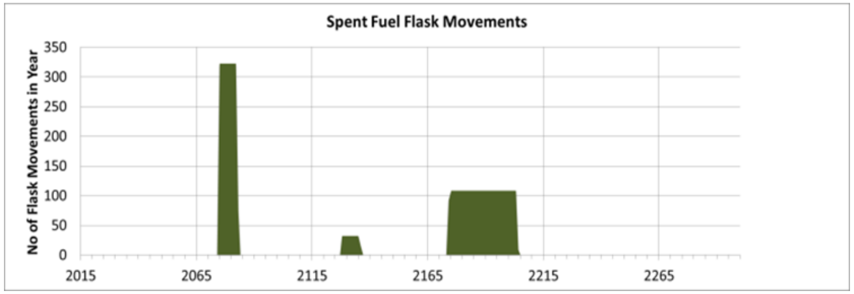
Assumptions

- New LWR stations operate for 60 years
- Fuel discharged a max design burn-up
- Granitic GDF

Interim Storage of Thermal Reactor Fuels Implications for the Back End of the Fuel Cycle in the UK. EPJ Nuclear Sci. Technol. 2, 21 (2016).







Current Focus

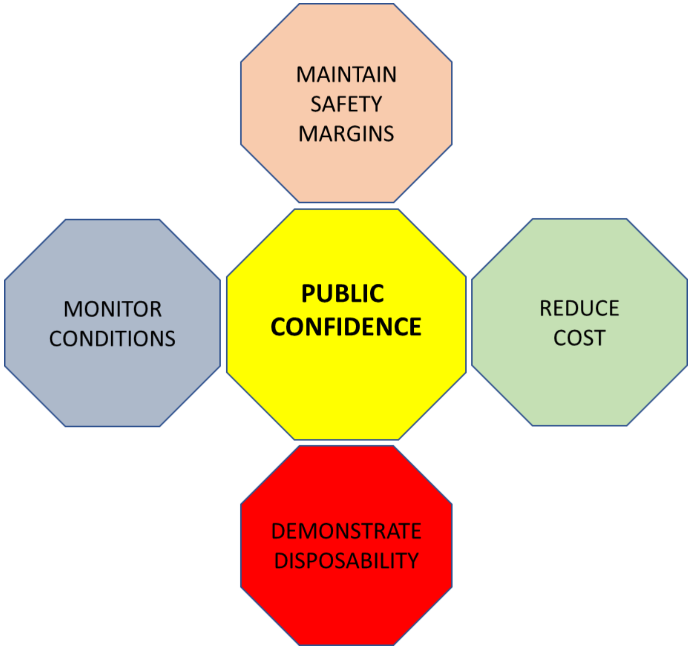
AGR fuel	change from reprocessing to long term storage
LWR fuel	longer term storage of higher burn-up fuel
Exotic fuels	managing a variety of fuels many in degraded condition
PuO_2	decision on re-use as MOX fuel or disposal

Accident Tolerant Fuels

Small Modular Reactors

Advanced Reactors

Challenges for Long Term Storage



Understanding fuel and system behaviour

Designing out likely failure modes

Keeping defence in depth approach

Utilising passive safety as far as possible

Demonstrating system performance

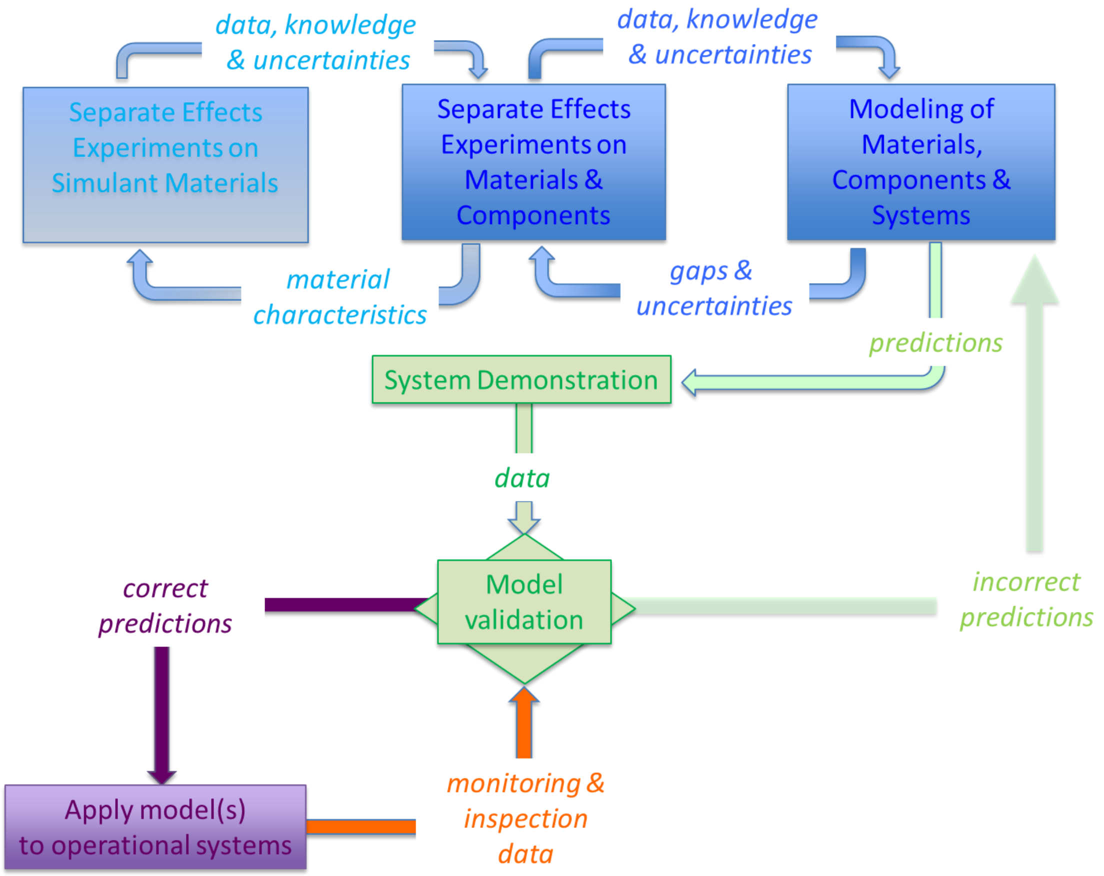
Reducing total cost: discharge to disposition

Managing knowledge, skills and capability across long periods of minimal activity

Underpinning the Long Term

Approach to underpinning long term behaviour needs to be based on

- Good science
- Good record keeping
- Continued activity to keep skills and knowledge alive
- Watchfulness



UK power reactors

Spent fuel management strategy

Current focus in spent fuel management

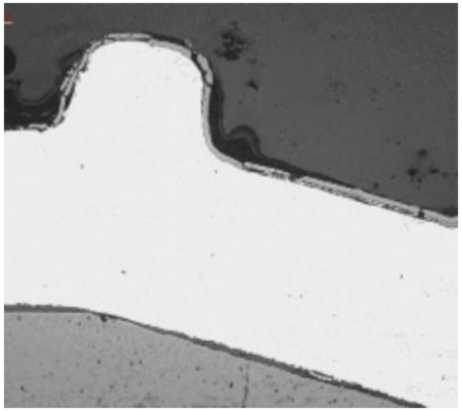
Status of Current Spent Fuel Storage

AGR fuel

Experience > 25 years pond storage

Existing high capacity, modern pond

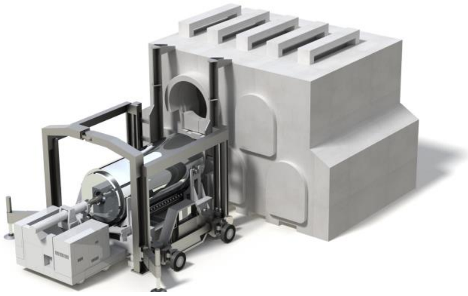
Hambley, DI. Technical Basis for Extending Storage of the UK's Advanced Gas-Cooled Reactor Fuel. Paper 7722. Global 2013, Salt Lake City, USA.



LWR fuel

international experience with wet & dry storage

New build storage in mid-late 2030s



Sound technical basis for current strategy backed by ongoing R&D commitment

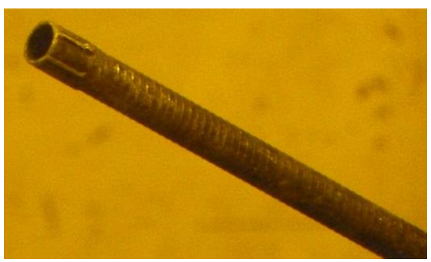
Current R&D for long term storage

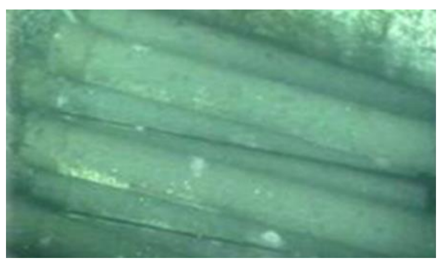
Understanding

- Evolving fuel characteristics
- Post storage examination
- Resilience of stored fuel
- Fuel drying

Managing degraded oxide fuel

Managing degraded uranium metal fuel





Characterisation of fuel for disposal

Monitoring & mitigation technologies

MOX Reuse

- Government position on plutonium from 2011 “Consultation”
  - On the grounds of nuclear security, pursue reuse as MOX fuel for the vast majority of the UK civil separated Pu for use in civil nuclear reactors, with any remaining Pu immobilised and treated as waste for disposal
- Reuse options considered include
  - MOX in light water reactors as proposed by Areva,
  - MOX in a CANMOX reactor as proposed by Candu
  - Reuse in a PRISM fast reactor as proposed by GE Hitachi Nuclear Energy
- Option of immobilisation also developed as an alternative reuse
  - Hot isostatic pressing technique to produce a ceramic waste form suitable for disposal to a repository
  - A proportion of the plutonium will have to be disposed of as it will be unsuitable for use as a fuel.
- NDA view, as managers of the liability
  - insufficient understanding to move to implementation
  - continue our work to bring options to maturity to support a government decision
  - next few years will include trials to show that all UK plutonium can be reused as either MOX and that material can be immobilised or as a ceramic wasteform.

Summary

Sustainability of nuclear power relies on responsible fuel management

Spent fuel management covers a broad range of topics:

- Policy, strategy, fuel cycle selection
- Storage and disposal system design
- Operations, maintenance and ageing management
- Research and knowledge management
- Development

We have a good foundation BUT there is much still to do

- **to support innovation in nuclear generation**
- **to deliver on our commitment to society**

Thank you for your attention

Any questions ?

David Hambley
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National Nuclear Laboratory
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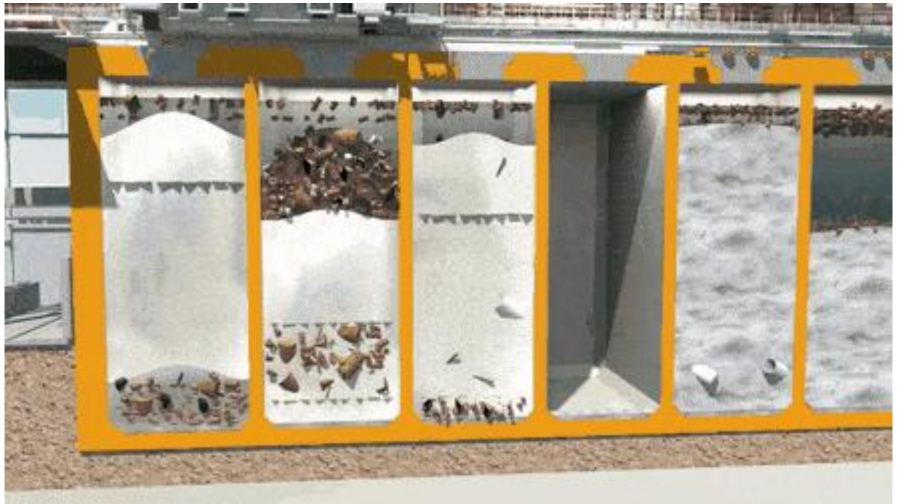
Enhancing Corrosion as a Treatment for Magnox Swarf Wastes

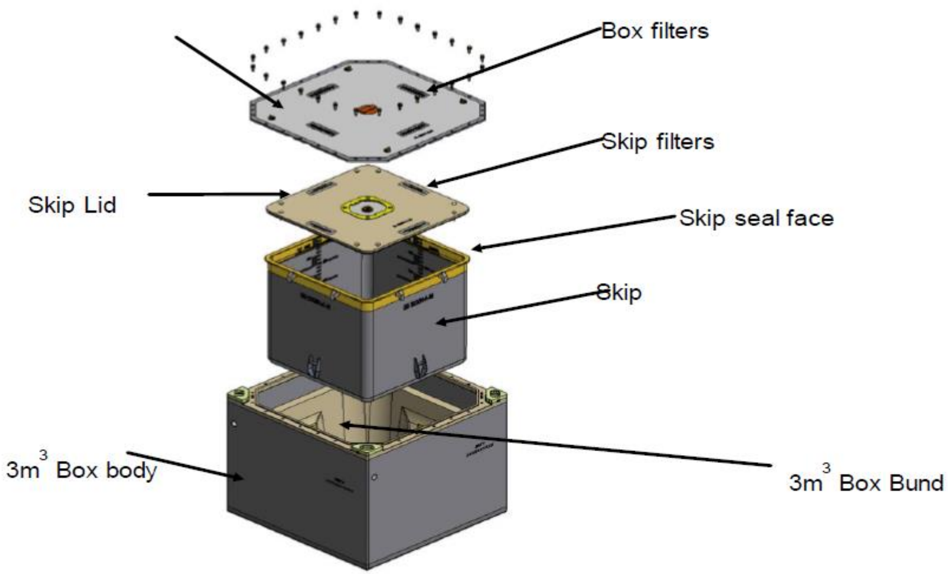
Joe Vickers, University of Leeds

Theme 3: Spent Fuels

12/11/19
Lancaster University

Magnox Swarf Storage Silo (MSSS)





- Currently preparing for emptying as part of risk reduction programme
- $3m^3$ boxes to be used as interim storage pending disposal
- Chronic corrosion of magnesium-based wastes presenting 2 major issues:
  - Volume Expansion ($Mg \rightarrow Mg(OH)_2$
  - Pressurisation (H_2 evolution)
- Restrictions on loading as low as 60%
- Procurement cost anticipated to be >£250m for MSSS boxes alone

Aqueous Corrosion of Mg

$$Mg + H_2O \rightarrow MgO + H_2$$

$$MgO + H_2O \leftrightarrow Mg(OH)_2$$

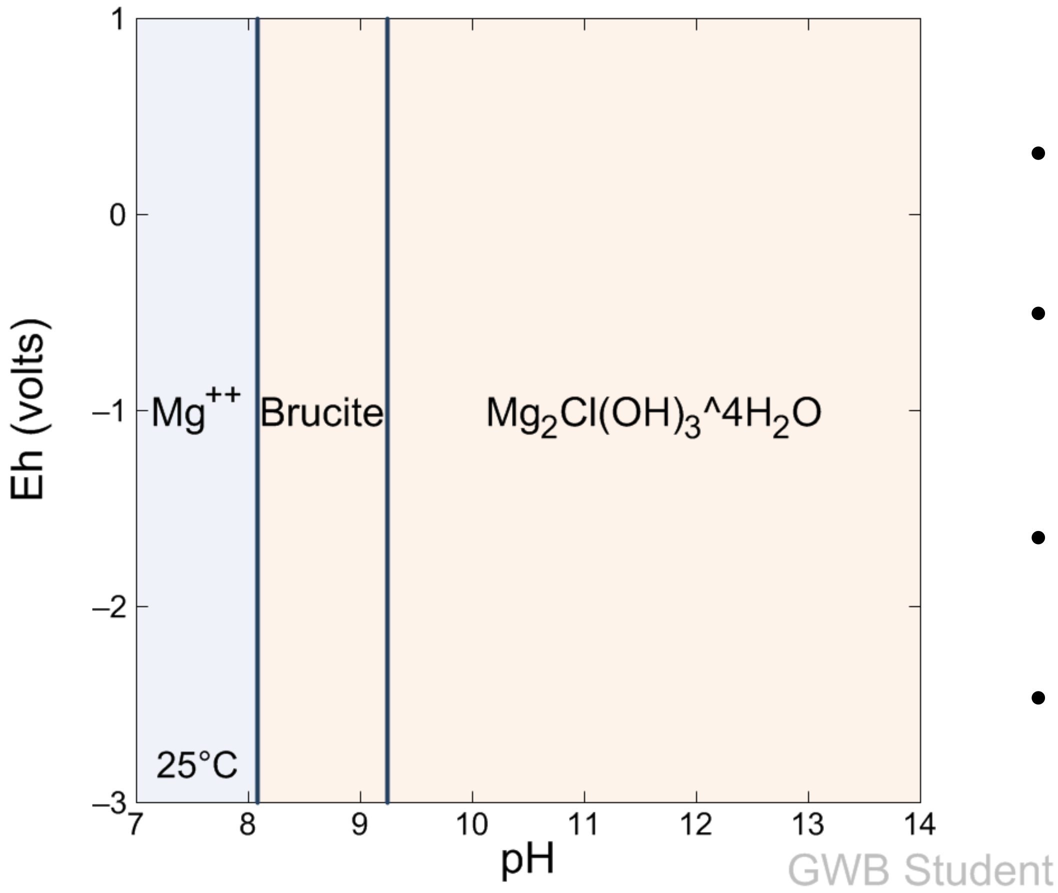
Magnesium Oxychloride (Cement) Formulation

$$5MgO + MgCl_2 + 13H_2O \rightarrow 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$$

$$Mg + H_2O \rightarrow \boxed{MgO} + H_2$$

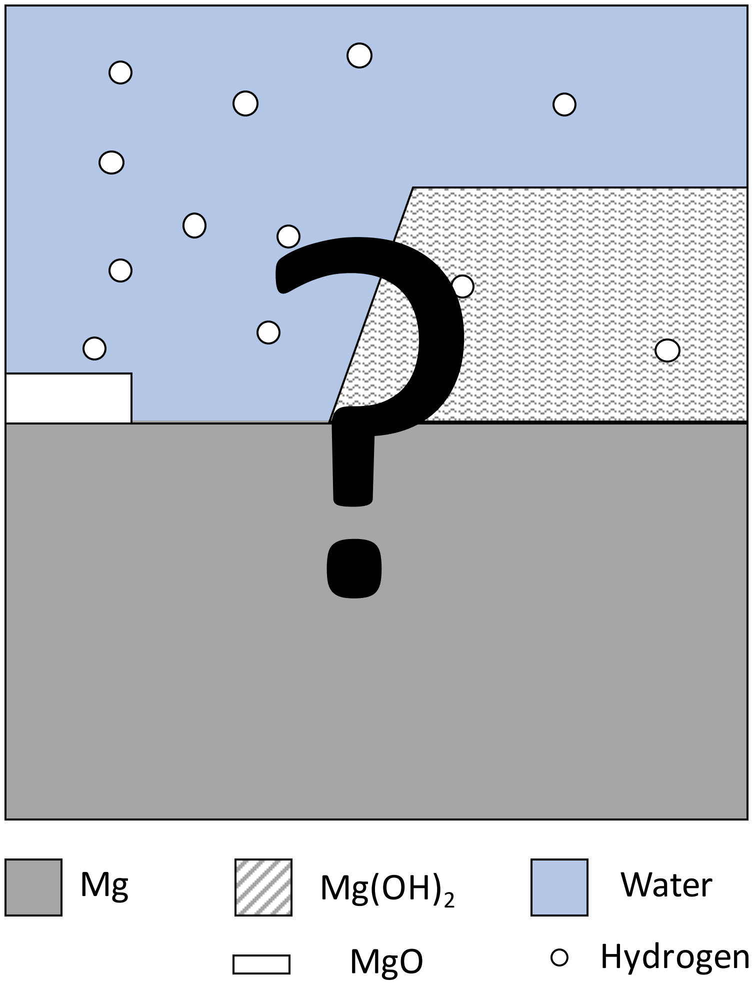
$$= 5Mg + MgCl_2 + 18H_2O \rightarrow 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O + H_2$$

Magnesium (Hydr)Oxychlorides – Thermodynamics and Speciation



- Begin to precipitate with in brines >1.5M with sufficient additional Mg
- $Mg(OH)_2$ also known as Brucite is sparingly soluble and buffers to pH ≈10.5
- High concentrations of $MgCl_2$ increase solubility – 100x greater at 4.5M
- Cement phases 3 and 5 (metastable) precipitate as solids with pH ≈12.5

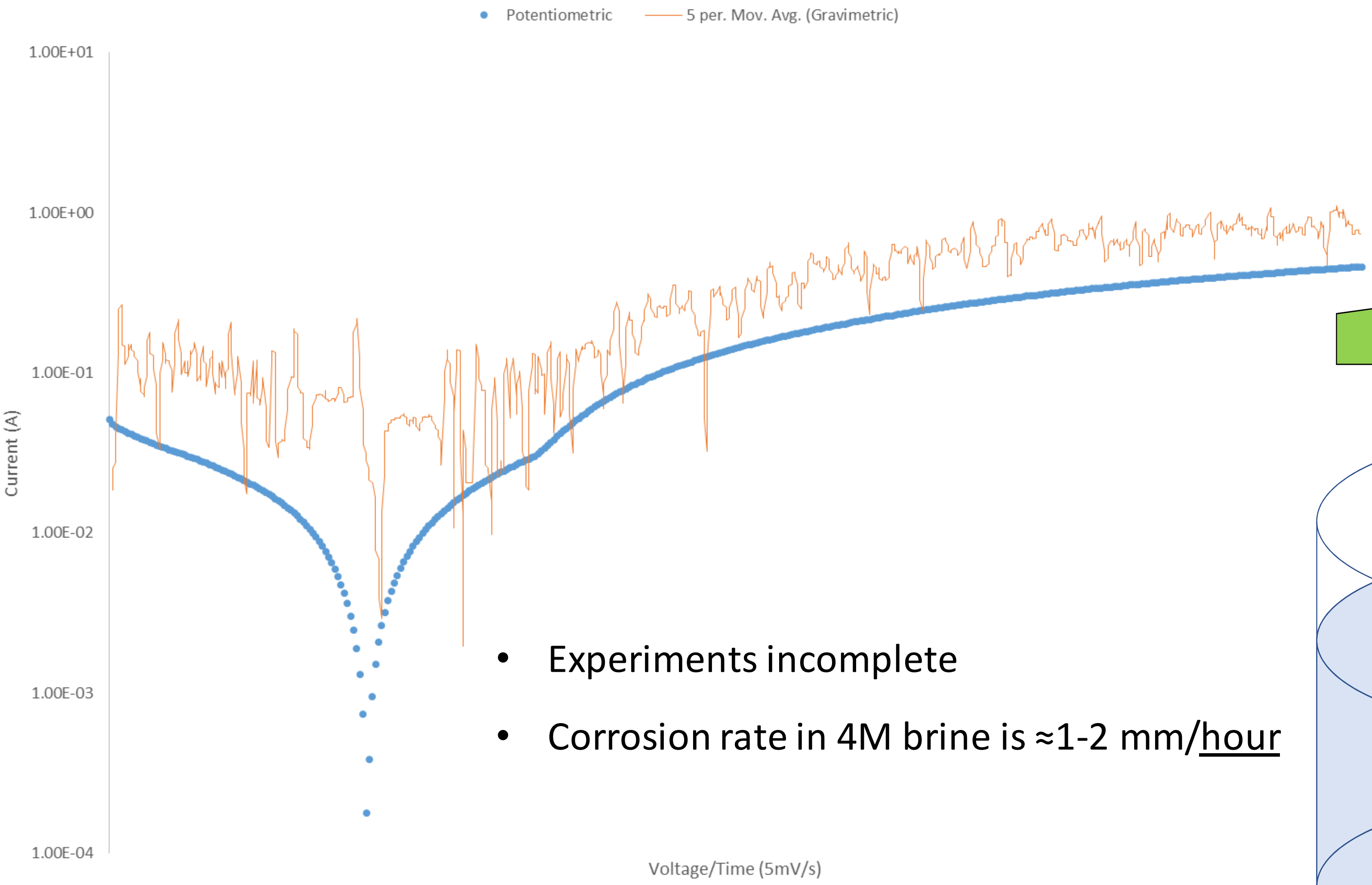
Magnesium Corrosion Behaviour



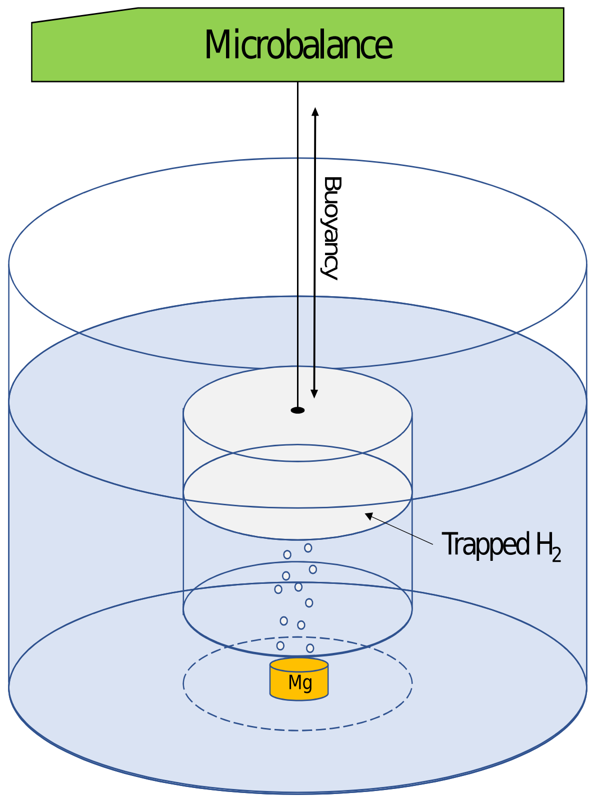
- Extremely cathodic (-2.37V vs. SHE)
- Generates H_2 gas as by-product of oxidation
- Passive metal with poorly-protective $Mg(OH)_2$ surface layer stabilised at high pH
- Surface film formation can be inhibited in buffered solutions where the solubility of $Mg(OH)_2$ is increased
- Fine detail of corrosion mechanism still not fully understood (read: controversial!)
- Note: While Magnox and pure Mg have different corrosion behaviour, they are mechanistically comparable

Transformative Science and Engineering for Nuclear Decommissioning

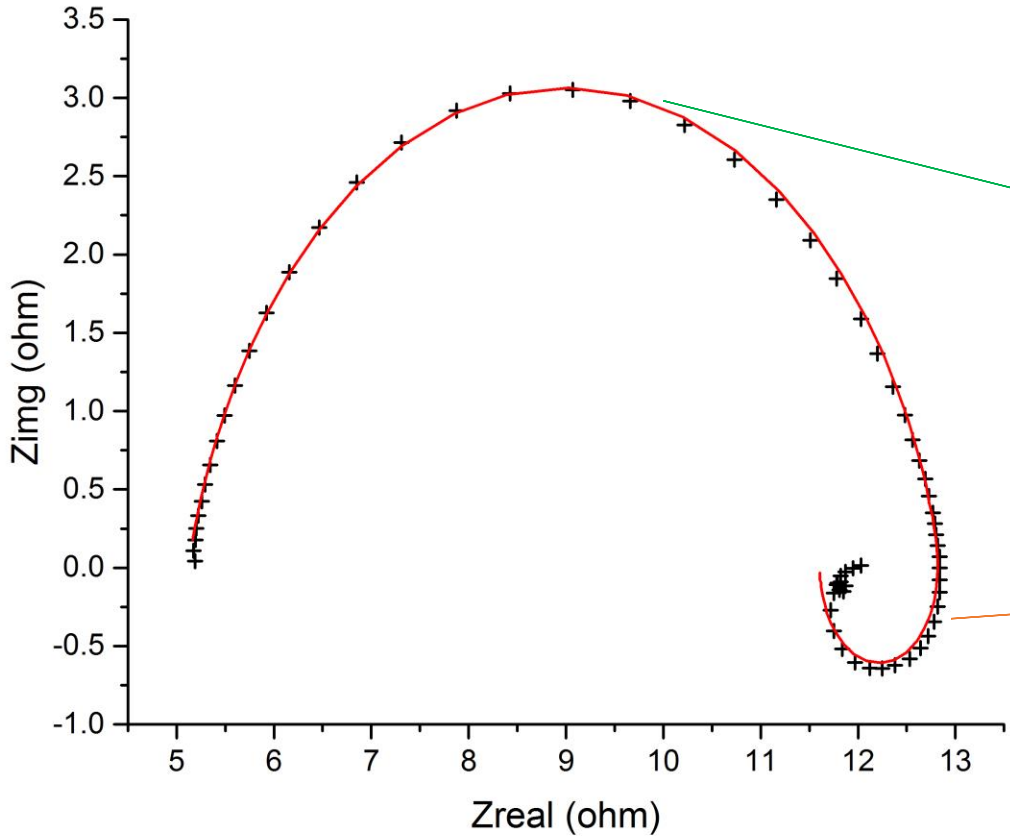
Polarization Measurements with Gravimetric H_2 Collection

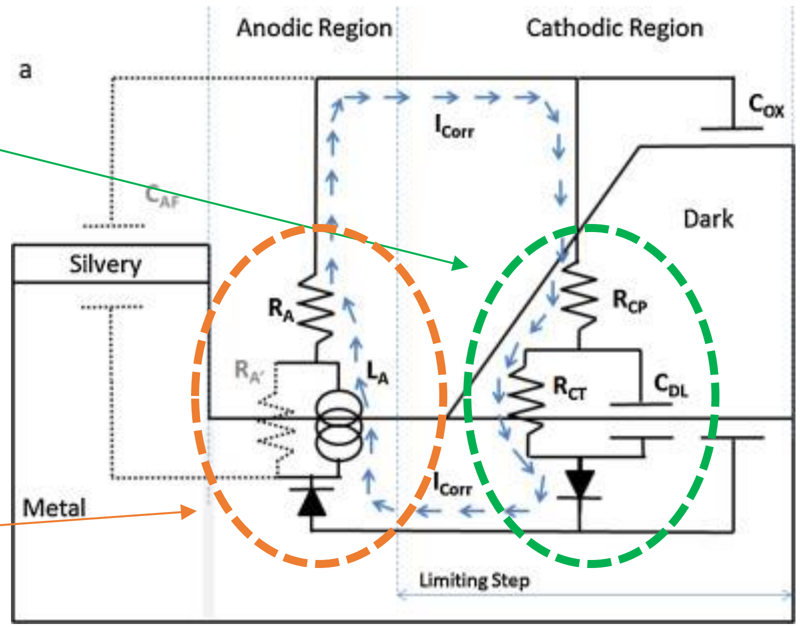


- Experiments incomplete
- Corrosion rate in 4M brine is ≈1-2 mm/<u>hour</u>



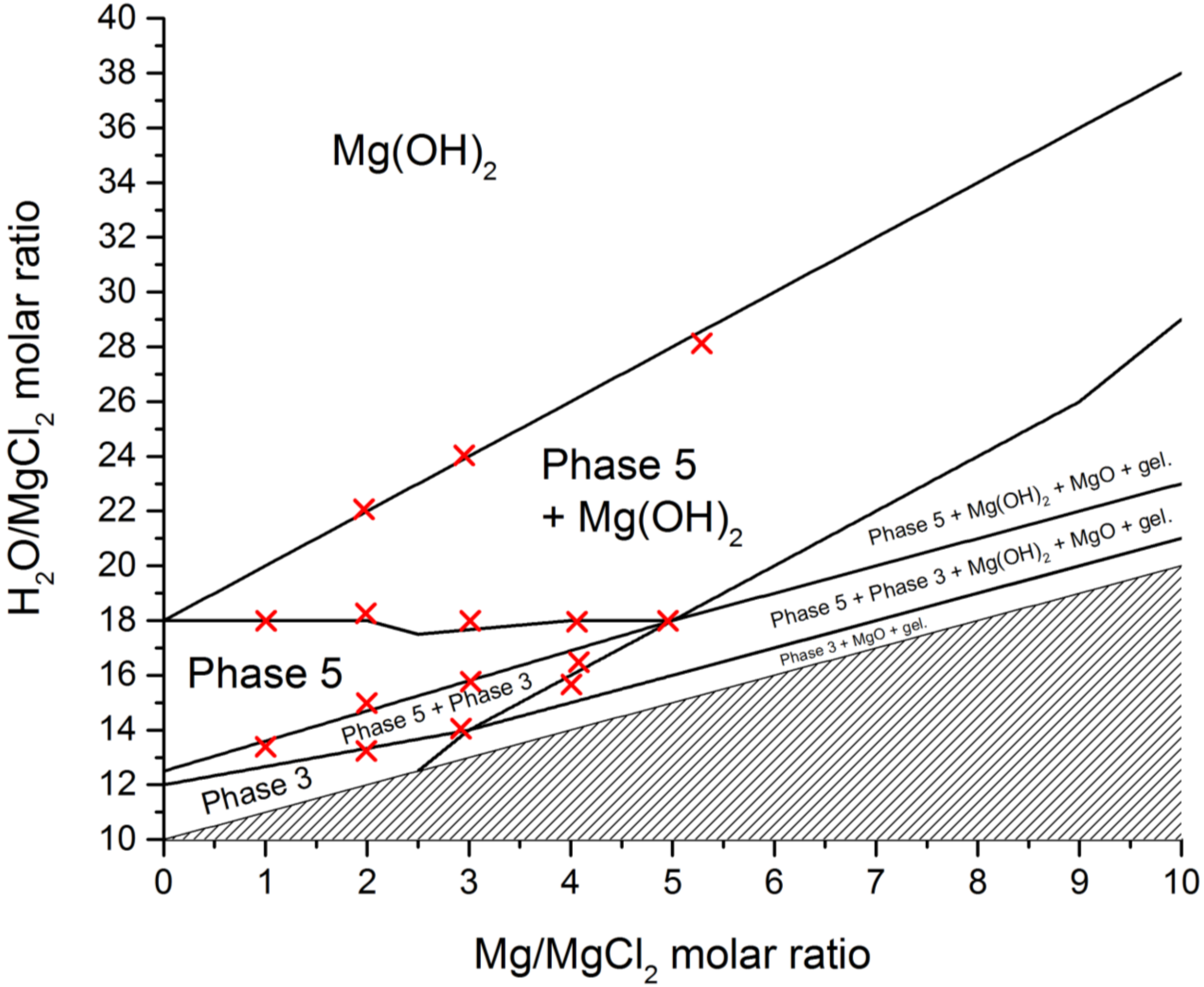
Impedance Spectroscopy in Saturated $MgCl_2$ Brine





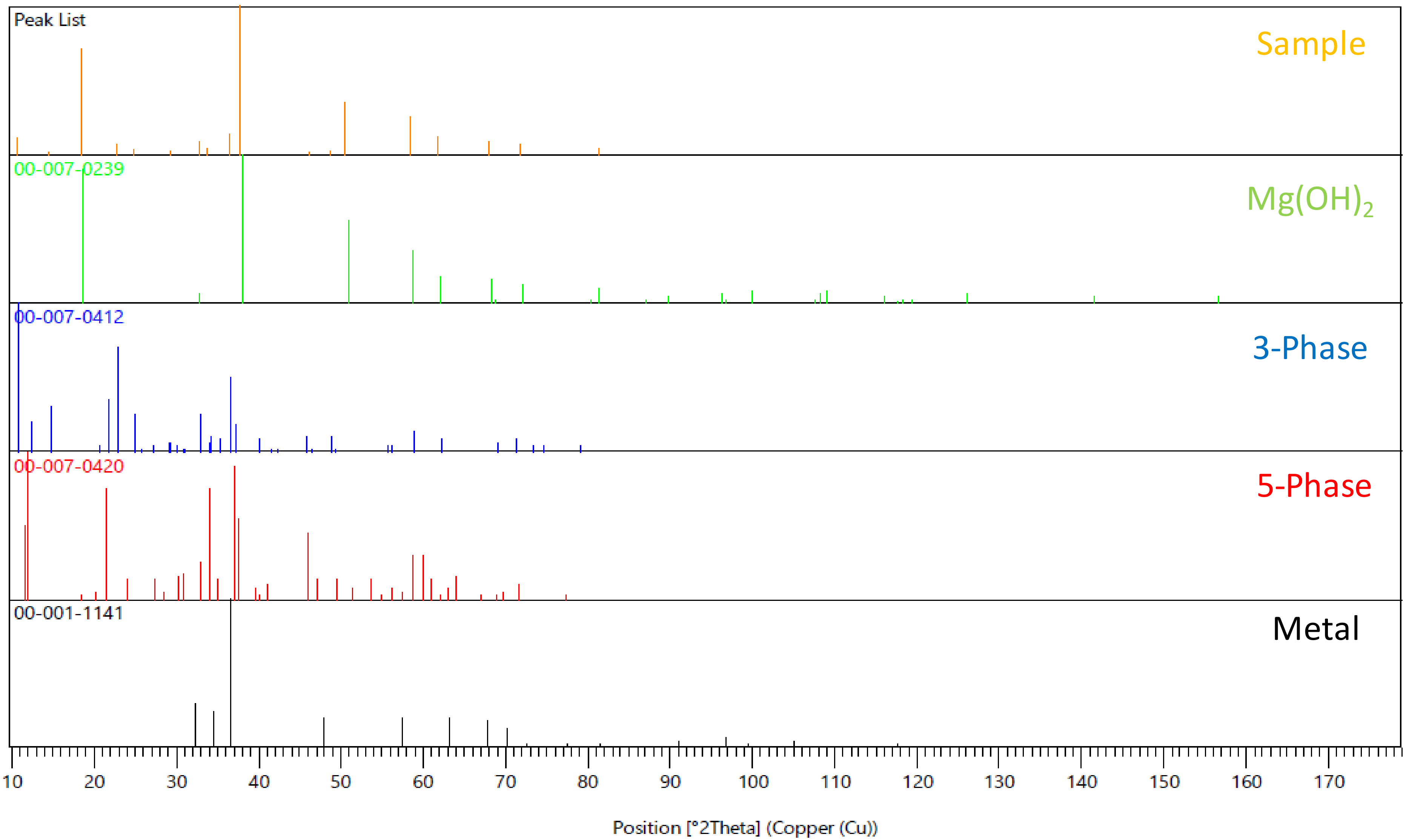
from Curioni et al. (2015)

Synthesising Cement from Metal Powders



Adapted from Liu et al. (2015)

Phase Identification using X-Ray Diffraction

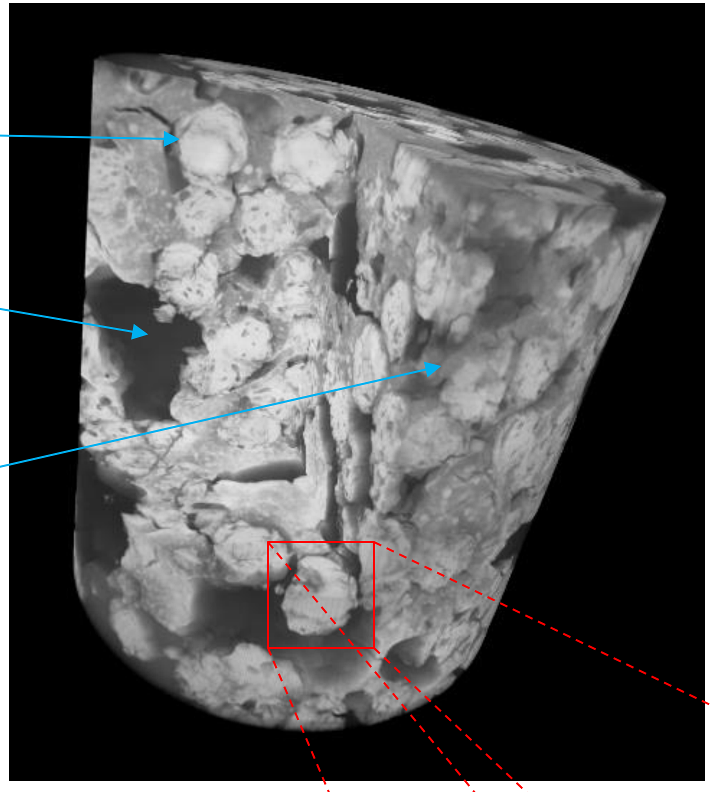


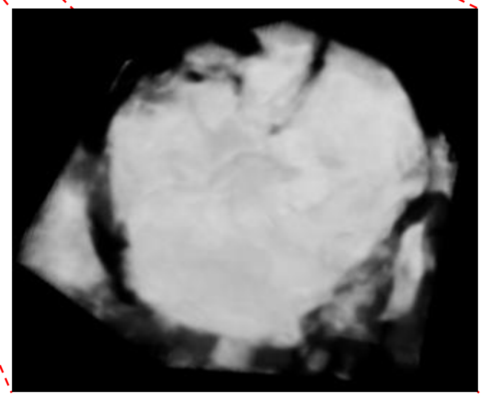
Internal Imaging of Cements using Computed Tomography (uCT)

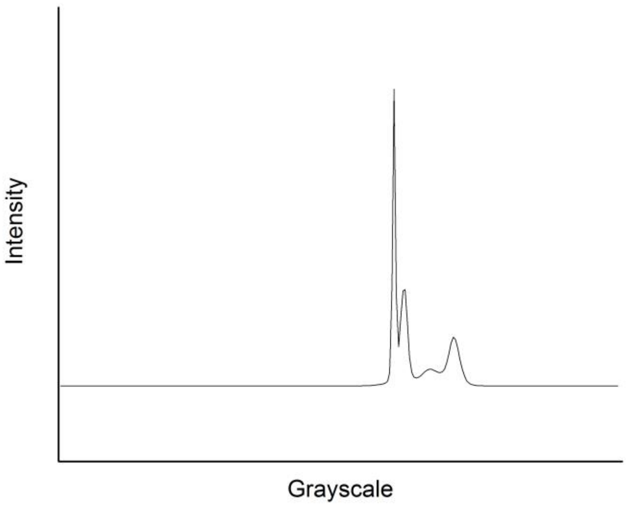
Nucleation sites ~500µm dia.

Large voids created by H_2 Holdup

Interstitial material – unhydrated $Mg(OH)_2$







TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

Thank you

pmjav@leeds.ac.uk

Transformative Science and Engineering for Nuclear Decommissioning

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

Victoria L. Frankland [1], Nathan Thompson [2], Antoni Milodowski [1], Joshua Bright [1], Neil Hyatt [2] and David Read [1,3]

[1)] University of Surrey, Guildford, UK; [2)] Materials Science and Engineering, University of Sheffield, Sheffield, UK; [3)] National Physical Laboratory, Teddington, UK

12th November 2019
TRANSCEND Theme Meeting Lancaster University

For a Low Carbon Future

Alteration of Spent Nuclear Fuel

Oxidation mechanism of U metal is unclear

Reaction path 1 [1]:

Uranium metal, U

↓

Uraninite, UO_2

↓

U_3O_7/U_4O_9

↓

U_3O_8

↓

Uranium trioxide, UO_3

Reaction path 2 [2]:

Uranium metal, U

↓

Uraninite, UO_2

↓

Ianthinite, $U^{4+}(U^{6+}O_2)_5O_7 \cdot 10(H_2O)$

↓

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

Studtite, $UO_2O_2(H_2O)_2 \cdot H_2O$

↓

Metal-UOHs

↓

Metal uranyl complexes (e.g. phosphates)

1) McEachern and Taylor, (1998); 2) Baker, (2014)

Possible Remote Operation Characterisation Techniques

TRLFS

Raman

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

Alteration of Spent Nuclear Fuel

Reaction path:

Uranium metal, U

↓

Uraninite, UO_2

↓

Ianthinite, $U^{4+}(U^{6+}O_2)_5O_7 \cdot 10(H_2O)$

↓

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

Studtite, $UO_2O_2(H_2O)_2 \cdot H_2O$

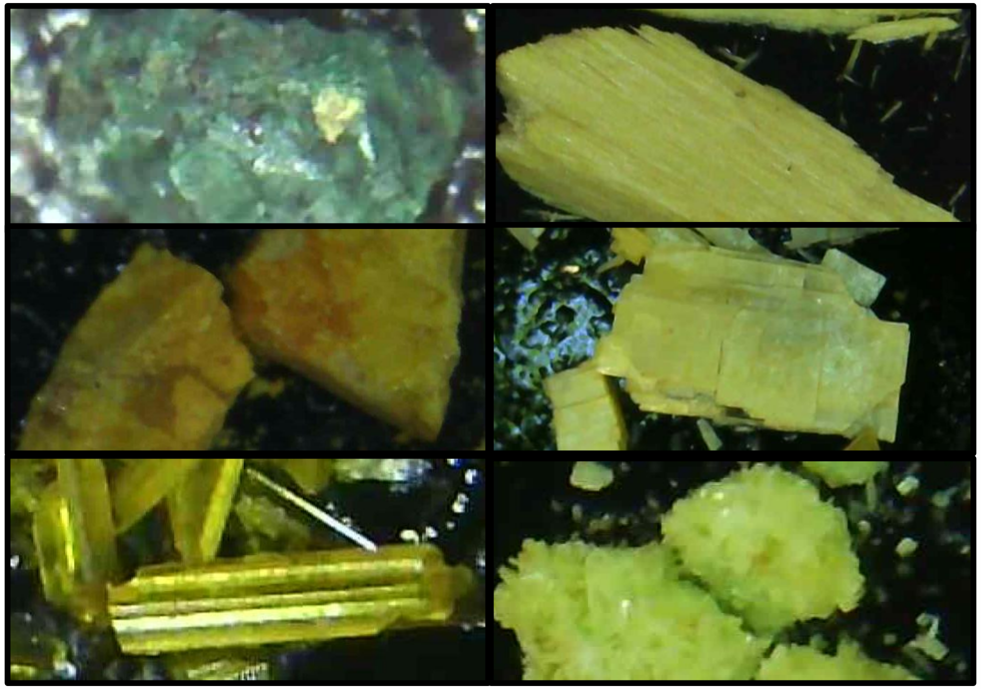
↓

Metal-UOHs

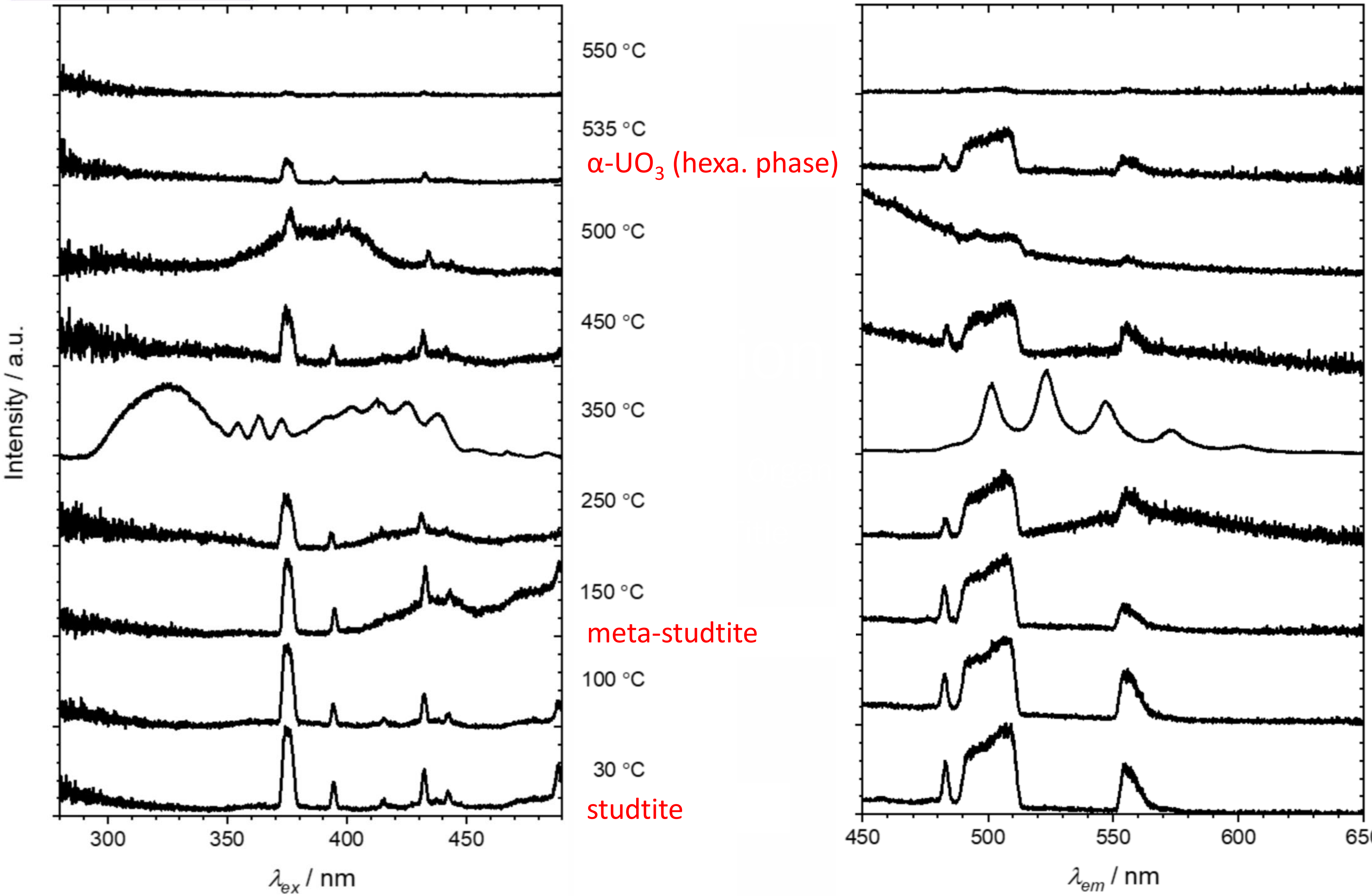
↓

Metal uranyl complexes (e.g. phosphates)

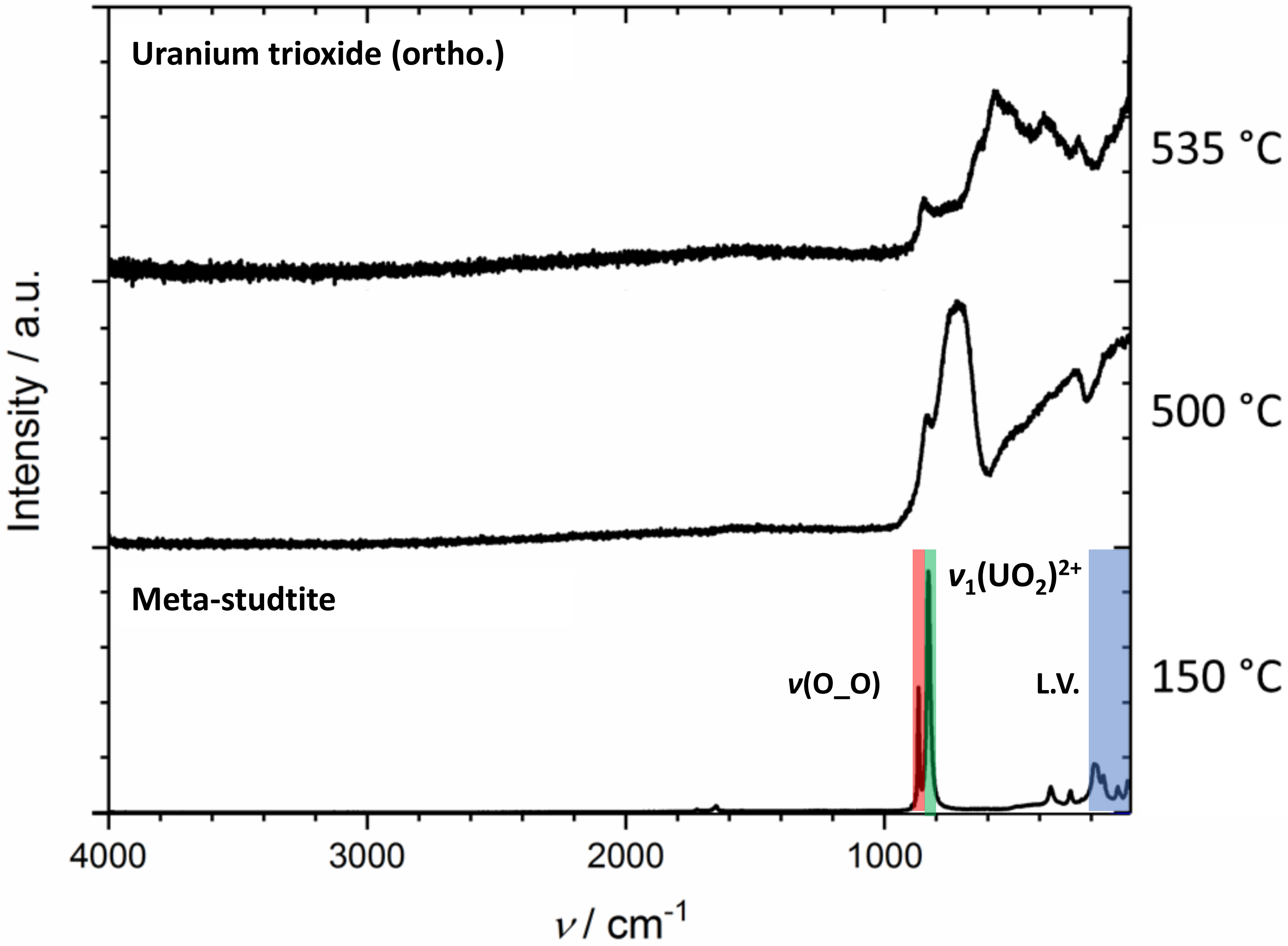
Spectral data from high quality type U-bearing minerals and synthetic species required.



Heated Studtite Fluorescence Spectra



Heated Studtite Raman Spectra



Alteration of Spent Nuclear Fuel

Reaction path:

Uranium metal, U

↓

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↓

Ianthinite, $U^{4+}(U^{6+}O_2)_5O_7 \cdot 10(H_2O)$

↓

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

Studtite, $UO_2O_2(H_2O)_2 \cdot H_2O$

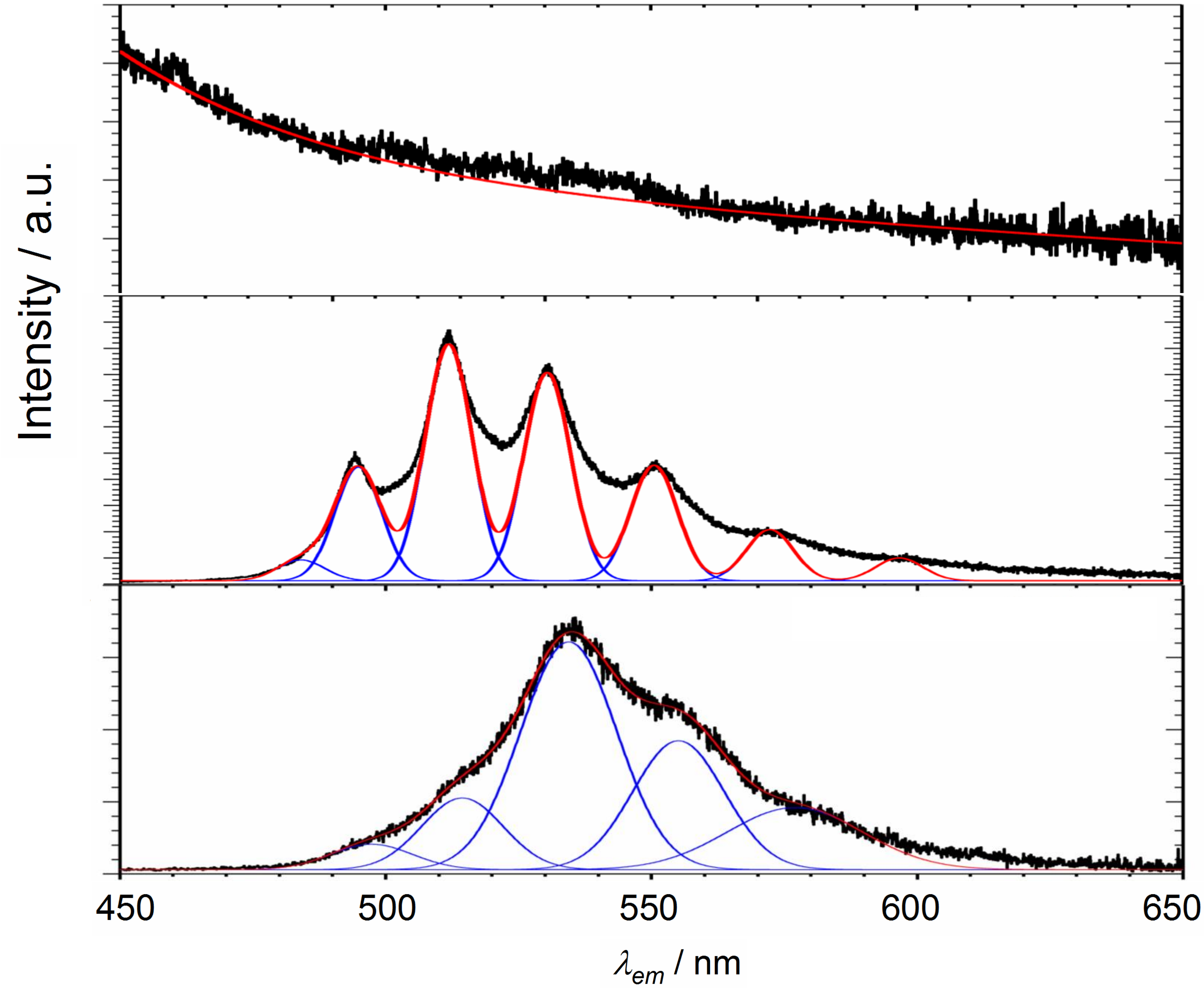
↓

Metal-UOHs

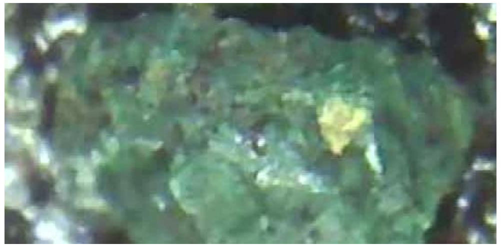
↓

Metal uranyl complexes (e.g. phosphates)

Fluorescence Emission Spectra



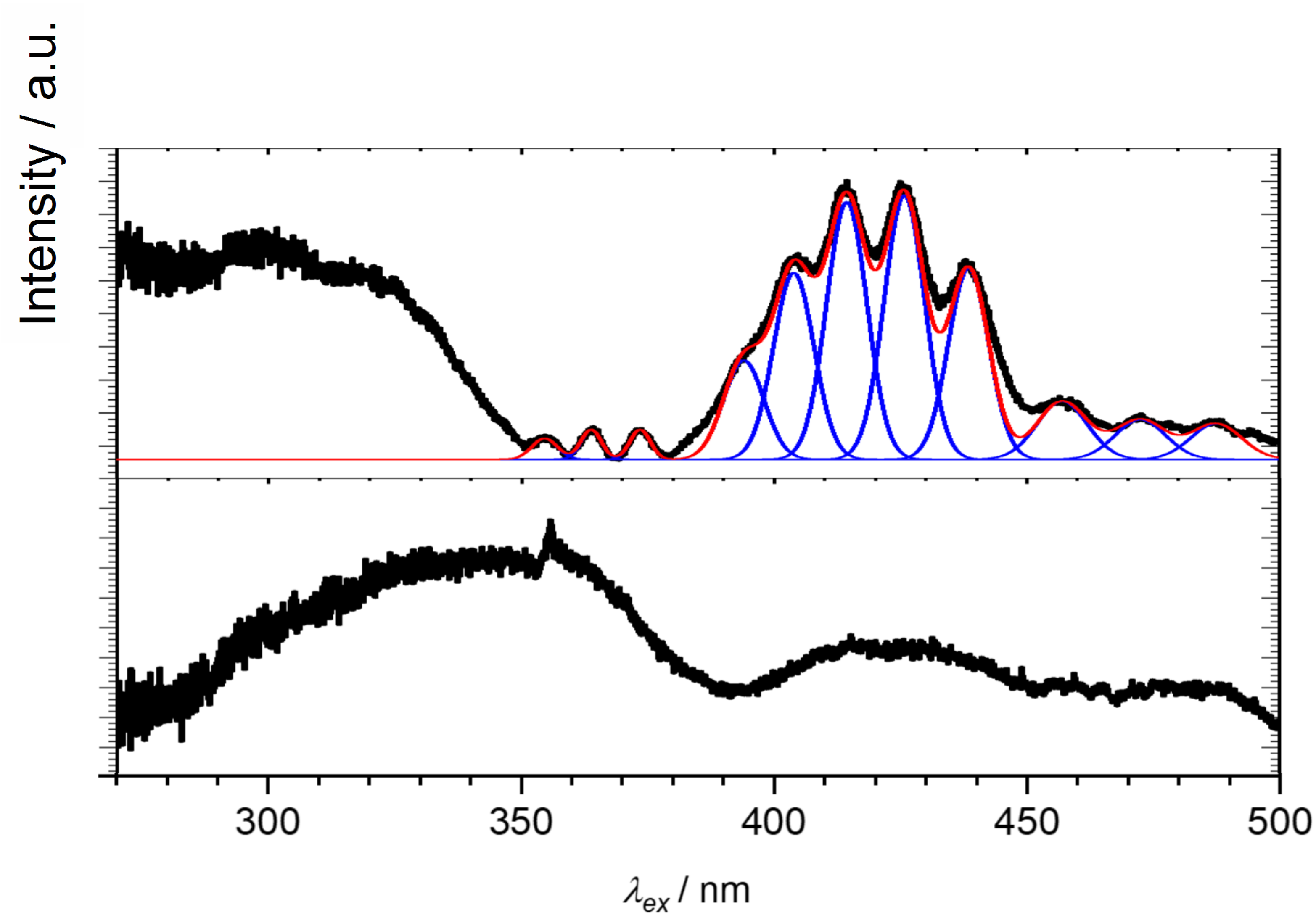
Vandenbrandeite
$CuUO_2(OH)_4$



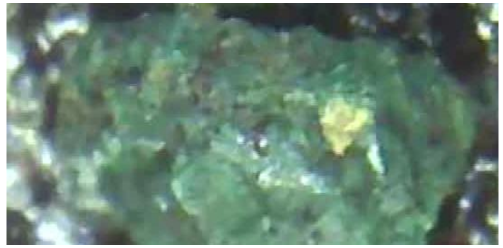
Vandendriesscheite
$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11}\cdot 11(H_2O)$

Becquerelite (?)
$Ca(UO_2)_6O_4(OH)_6\cdot 8(H_2O)$

Fluorescence Excitation Spectra



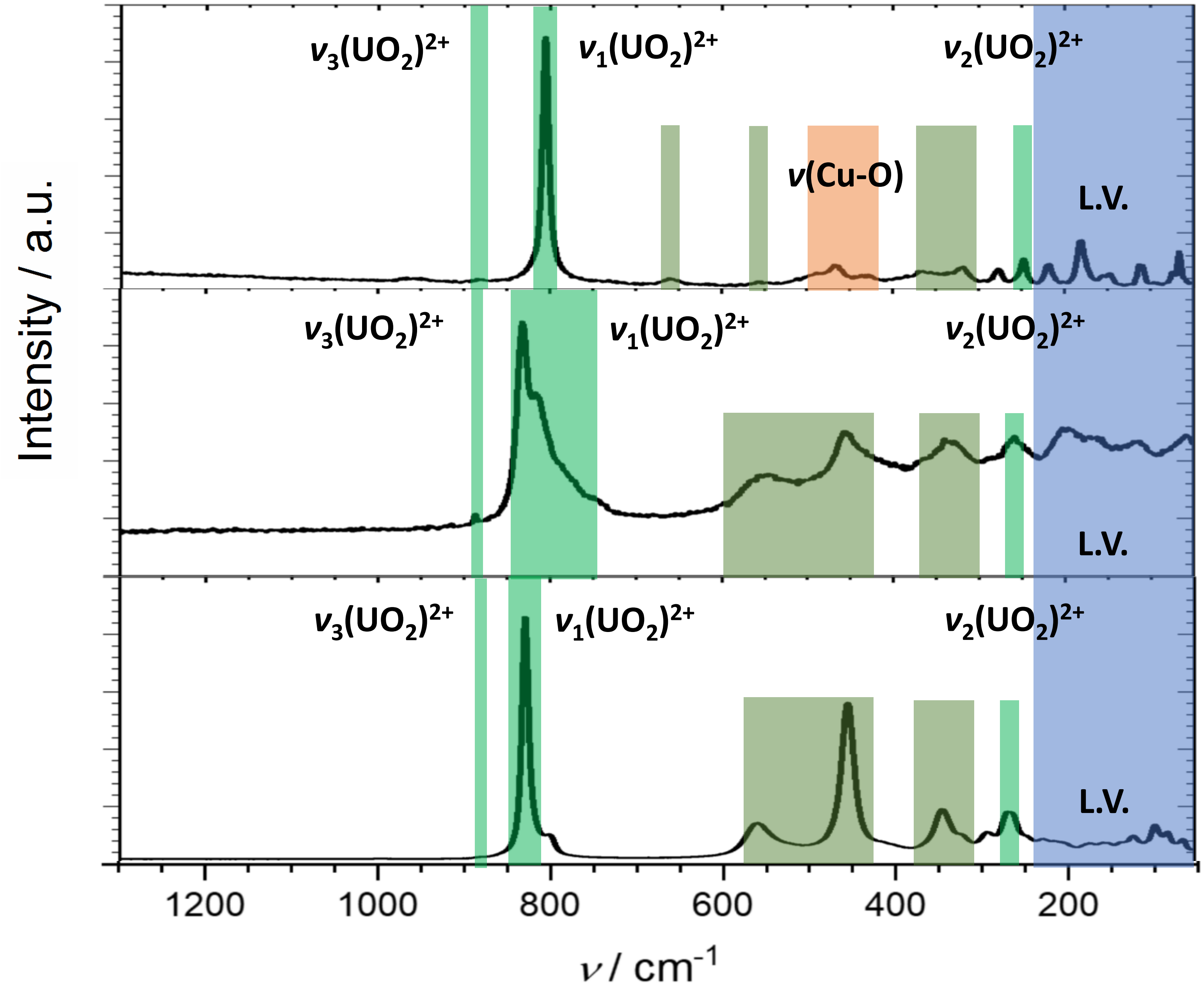
Vandenbrandeite
$CuUO_2(OH)_4$



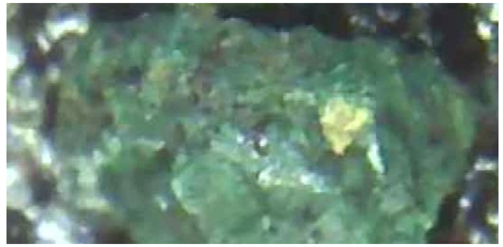
Vandendriesscheite
$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11}\cdot 11(H_2O)$

Becquerelite (?)
$Ca(UO_2)_6O_4(OH)_6\cdot 8(H_2O)$

Raman Spectra



Vandenbrandeite
$CuUO_2(OH)_4$



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

Becquerelite (?)
$Ca(UO_2)_6O_4(OH)_6\cdot 8(H_2O)$

Alteration of Spent Nuclear Fuel

Reaction path:

Uranium metal, U

↓

Uraninite, UO_2

↓

Ianthinite, $U^{4+}(U^{6+}O_2)_5O_7 \cdot 10(H_2O)$

↓

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

Studtite, $UO_2O_2(H_2O)_2 \cdot H_2O$

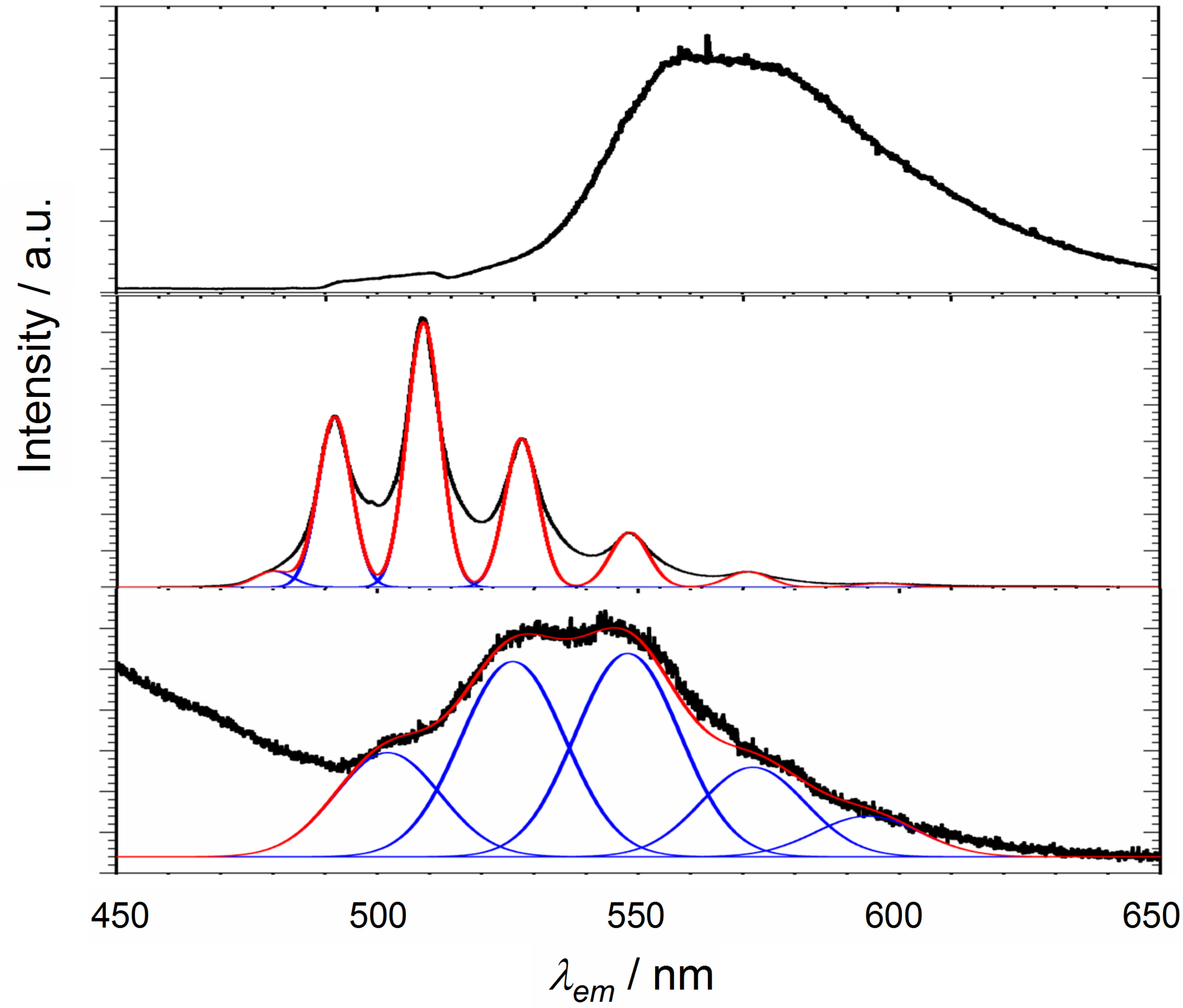
↓

Metal-UOHs

↓

Metal uranyl complexes (e.g. phosphates)

Fluorescence Emission Spectra

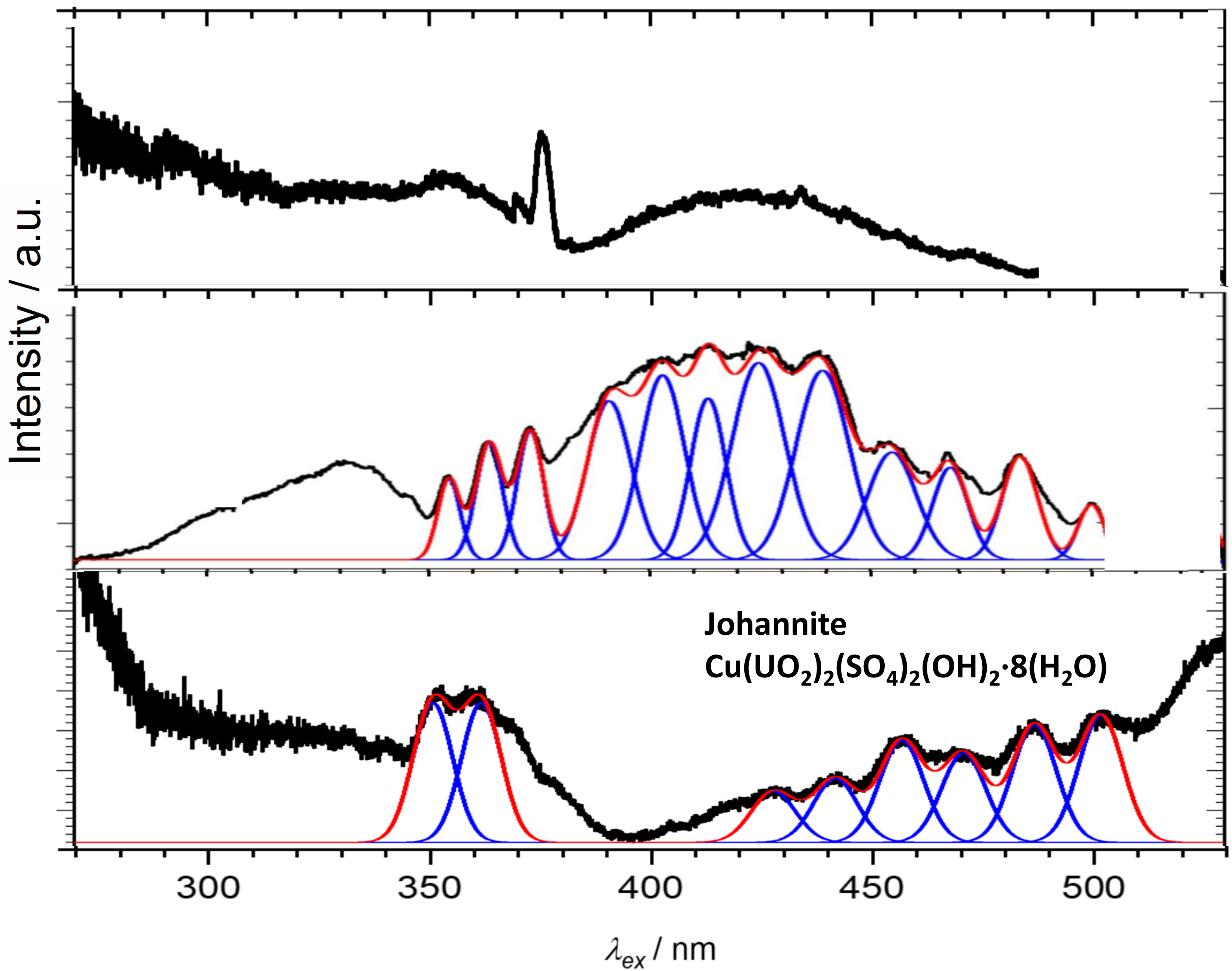


Boltwoodite
$K_2(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5(H_2O)$

Sr-rich meta-autunite
$Sr(UO_2)_2(PO_4) \cdot 6\text{-}8(H_2O)$

Johannite
$Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 8(H_2O)$

Fluorescence Excitation Spectra



Boltwoodite
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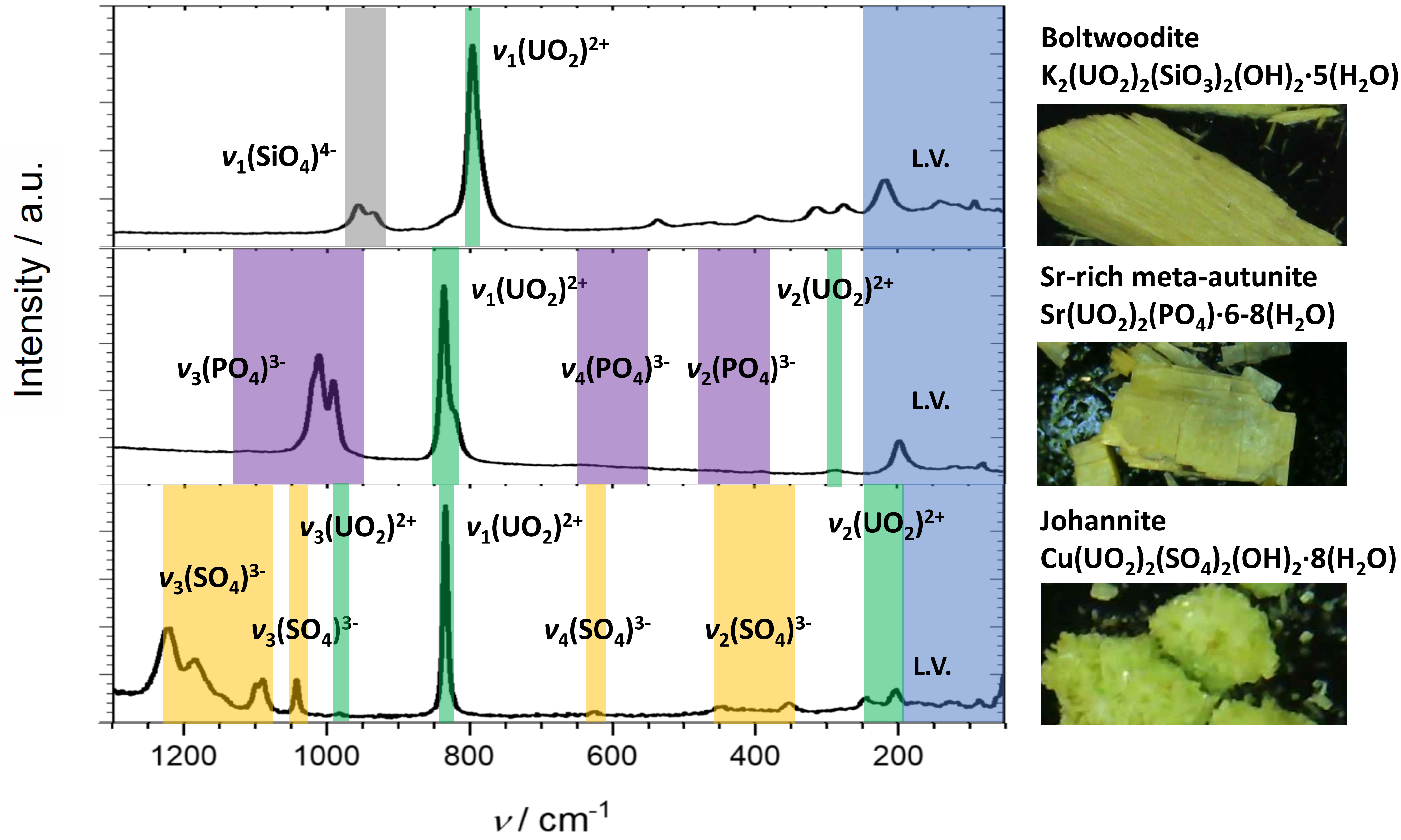
Johannite
$Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 8(H_2O)$

Raman Spectra



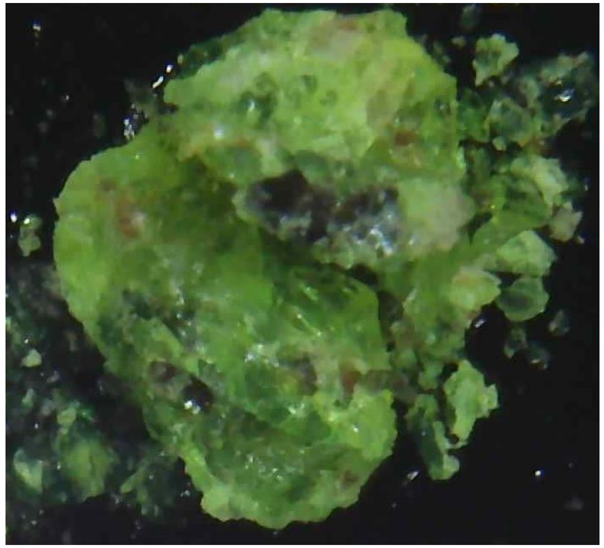
Conclusions

- Characterisation by Raman spectroscopy works well
- Characterisation by fluorescence spectroscopy is dependent on uranium-bearing species
- Some ligands and cations appear to promote fluorescence
  - Phosphate and sulfate ligands
  - Pb^{2+} cation
- Some cations appear to quench fluorescence
  - Cu^{2+}

Future Work

- **TRLFS and Raman spectroscopy**
  - **Analytical grade U compounds**
  - **Natural History Museum collection**
  - **U-bearing solutions**
  - **Reference Collection Database**

- **Guide *in situ*, real time experimental simulations of the corrosion/alteration process**

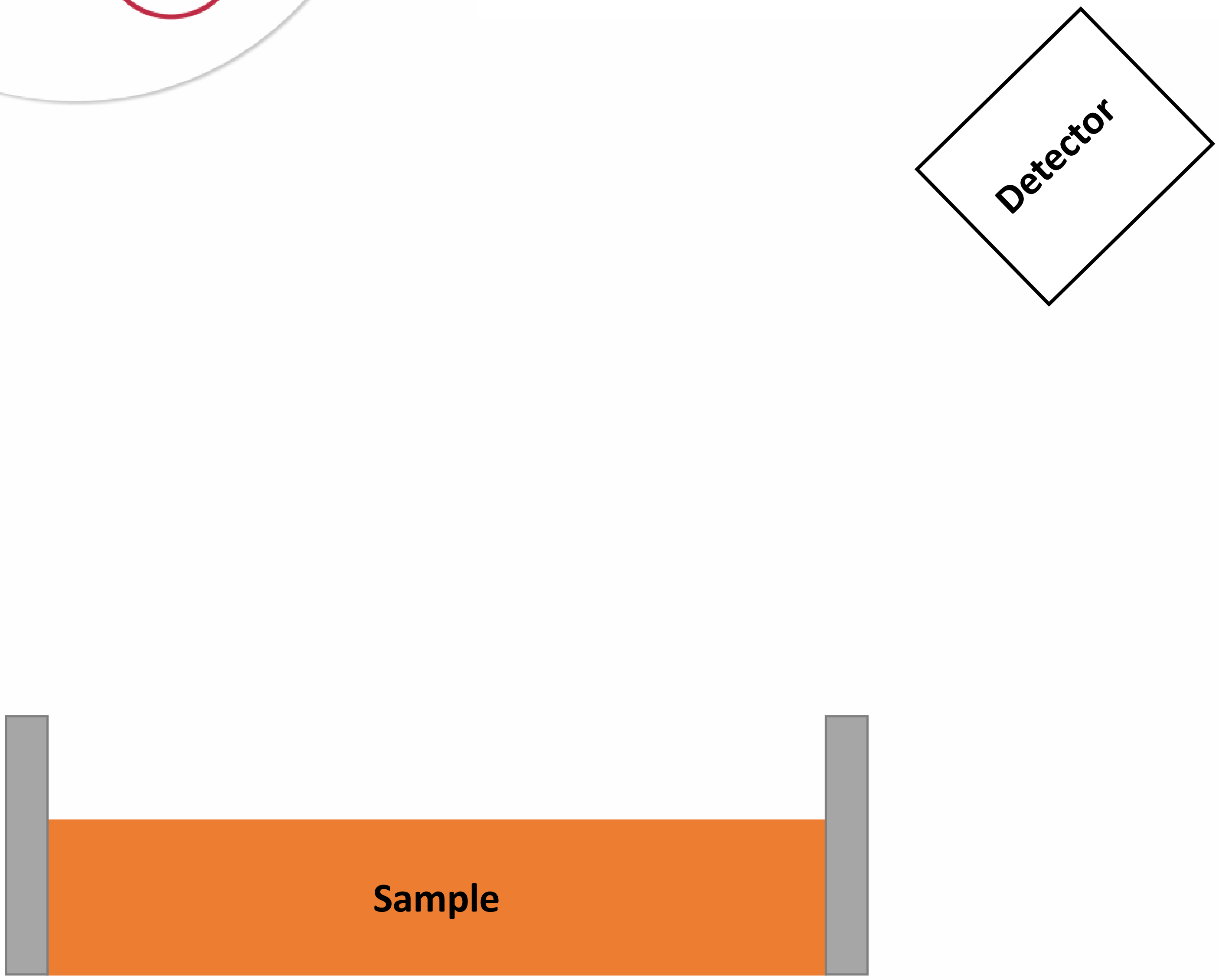


LIBS-LA- ICP-MS Funding Accepted

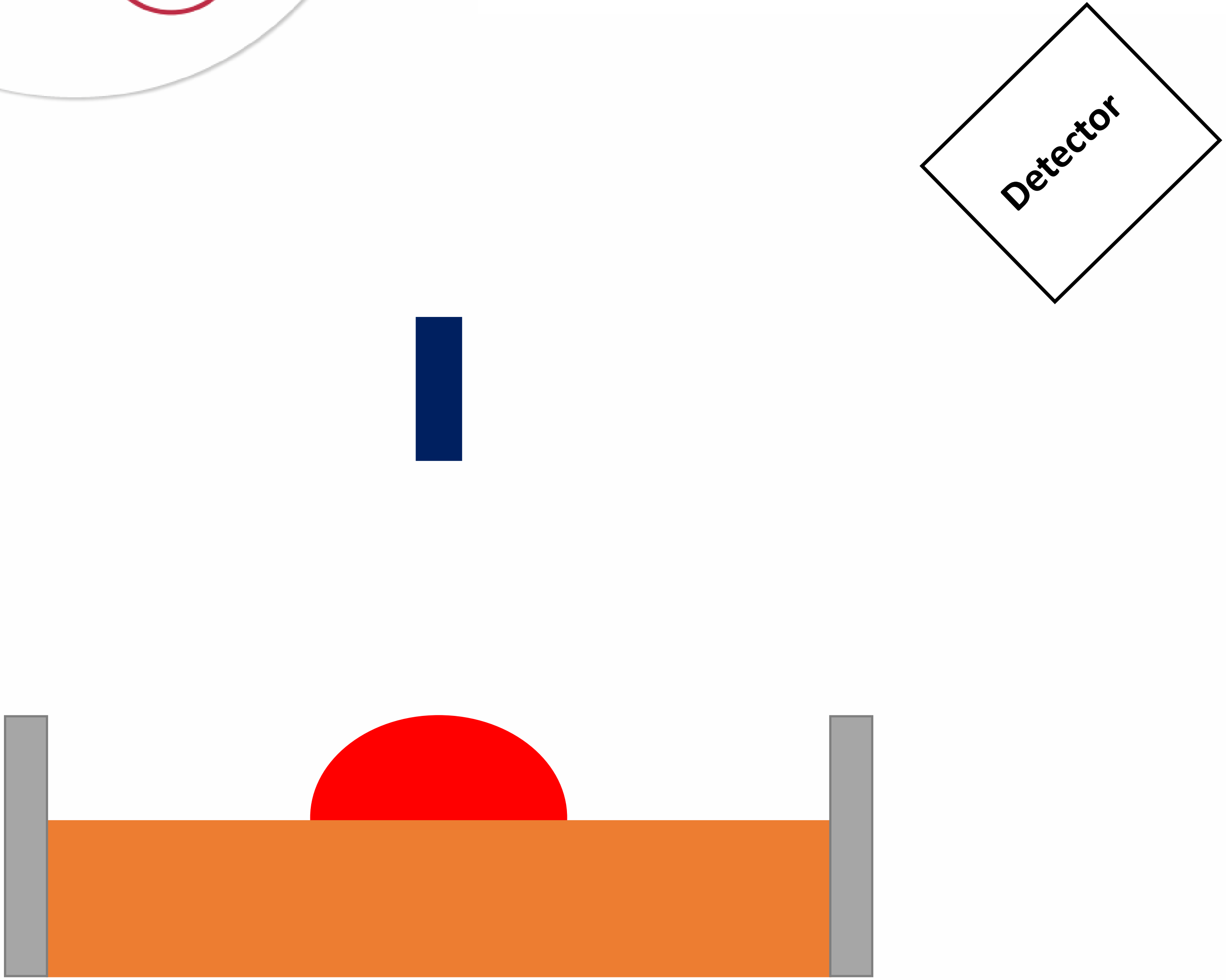
Laser-induced breakdown spectroscopy (LIBS) tandem with laser ablation (LA) system coupled to an existing (ICP-MS) system.

Applied Spectra.com

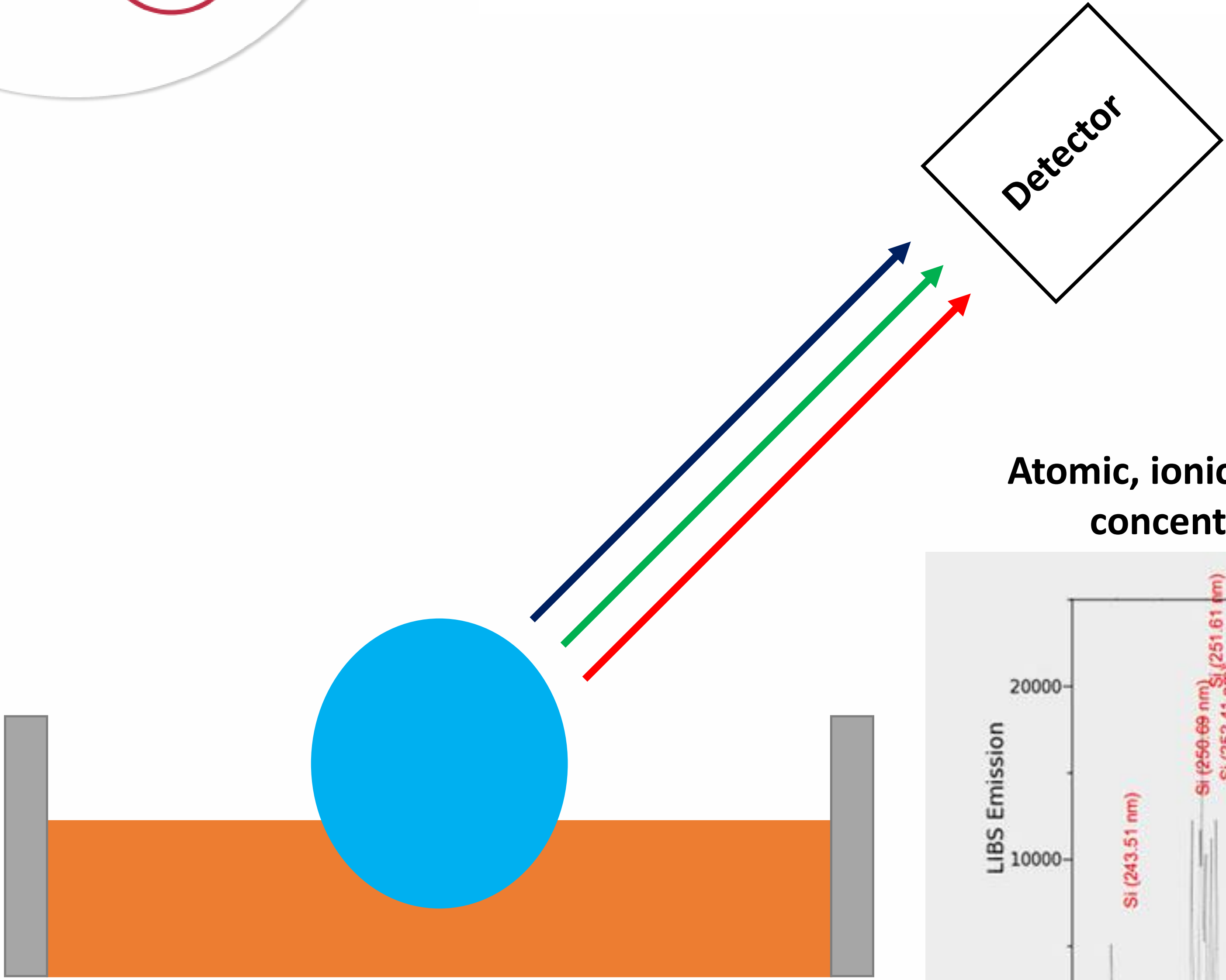
LIBS



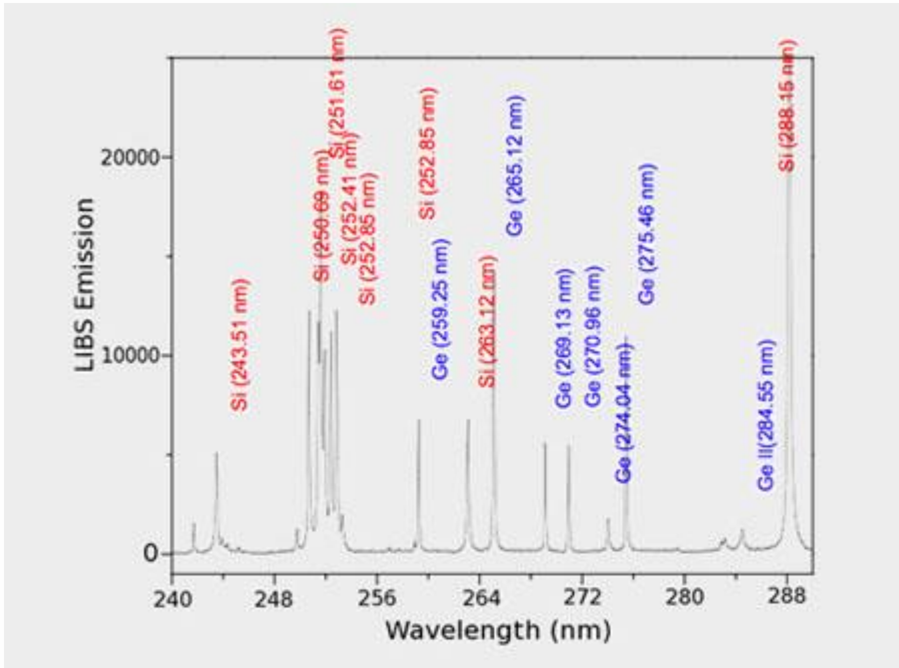
LIBS



LIBS

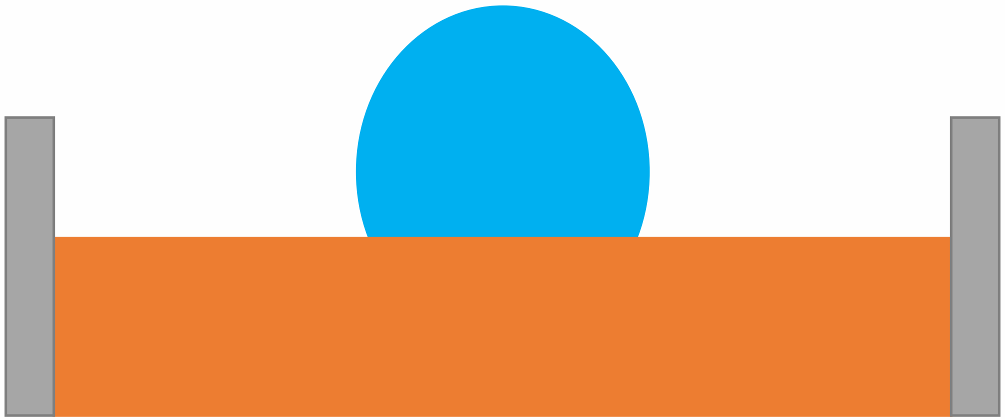


Atomic, ionic and molecular relative concentration abundances

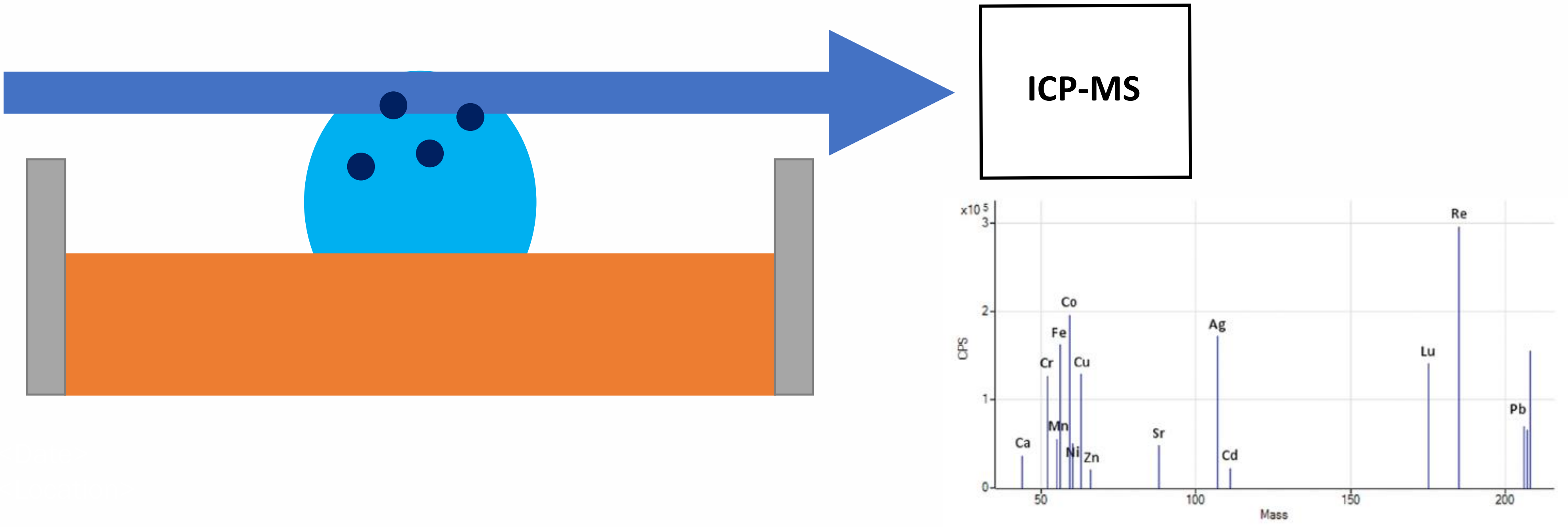


Applied Spectra.com

LA-ICP-MS



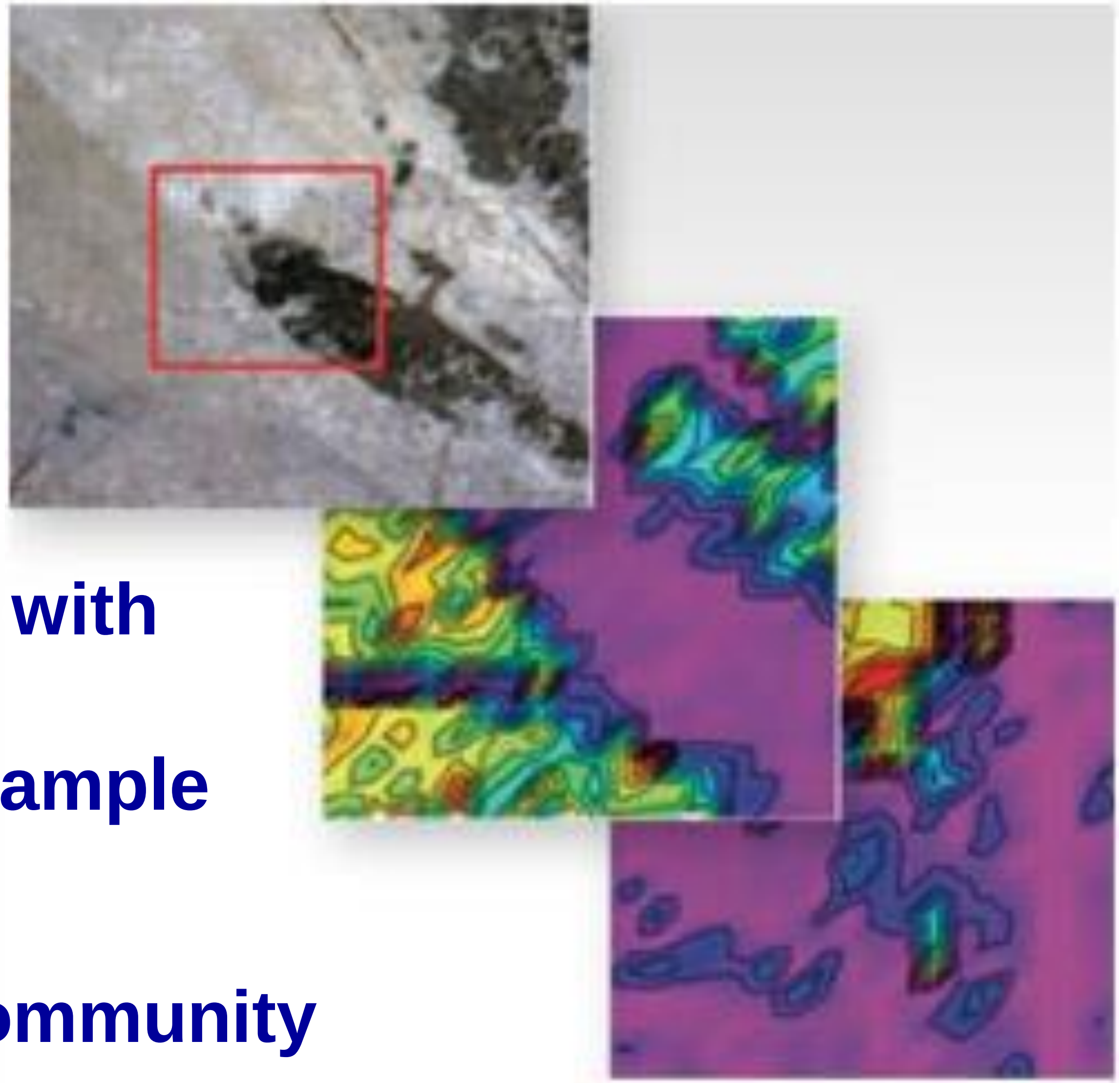
LA-ICP-MS



LIBS-LA- ICP-MS

Combined LIBS and LA-ICP-MS enables:

- **Determine elemental abundance**
- **Chemical mapping (2D and 3D)**



Combining LIBS-LA-ICP-MS with SEM-EDX, XRD and Raman spectroscopy will improve sample identification

Available to TRANSCEND community

Applied Spectra.com

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

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
Nathan Thompson
Prof Neil Hyatt

BGS 1835 · national museum wales amgueddfa cymru · NATURAL HISTORY MUSEUM · The University Of Sheffield.

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TRANSCEND · Research Councils UK Energy For a Low Carbon Future · DISTINCTIVE

Thank you

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Transformative Science and Engineering for Nuclear Decommissioning

Predicting the Alteration of Spent Nuclear Fuels

Joshua W. G. Bright[1], Victoria L. Frankland[1], Robert Lawrence[1], Marco Sacchi[1] and David Read[1,2]

Transcend Theme Meeting

12 November 2019
Lancaster University

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[2] Nuclear Metrology Group, National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom

Energy
For a Low Carbon Future

About Me

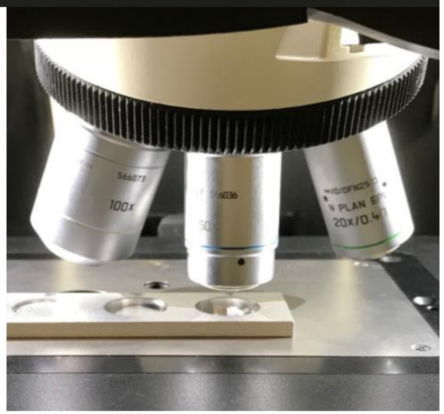
- Masters project at University of Surrey
  - Characterisation of UOH's and Brucite
- New PhD student at University of Surrey
  - Predicting the corrosion of spent nuclear fuels

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

- Alteration of MAGNOX fuel known to form Brucite.

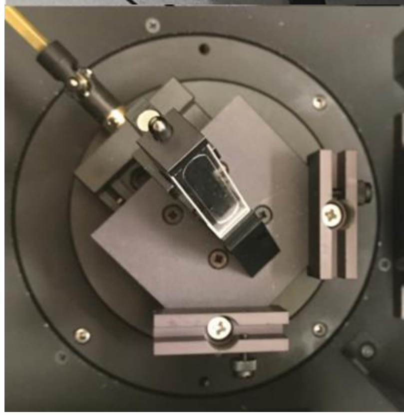
- Experiment and computational modelling to determine structures, spectra and reaction mechanisms.

- Use of laser based techniques allow for stand off analysis and monitoring in real time.



Raman Spectroscopy

- 245, 457, 532, 633 and 785 nm lasers



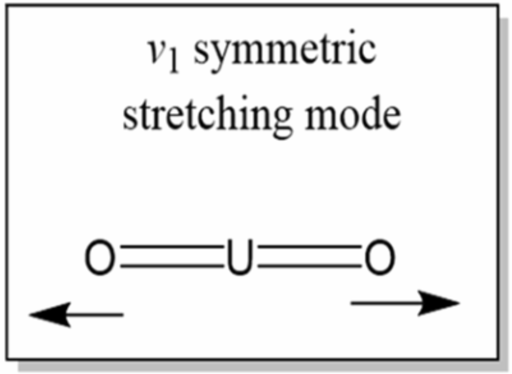
TRLFS

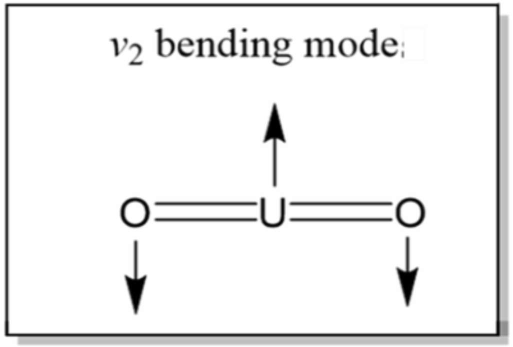
- Xenon Lamp (250 – 1000 nm)
- Supercontinuum (400 – 3000 nm)
- Pulse picosecond laser (357.32 nm)

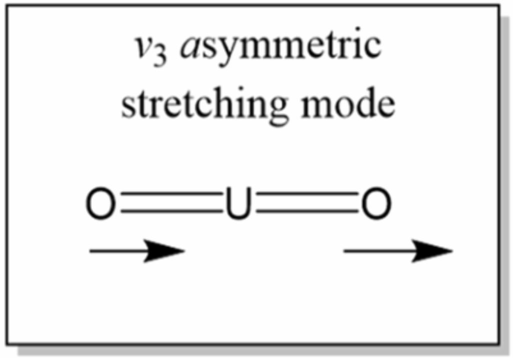
Raman

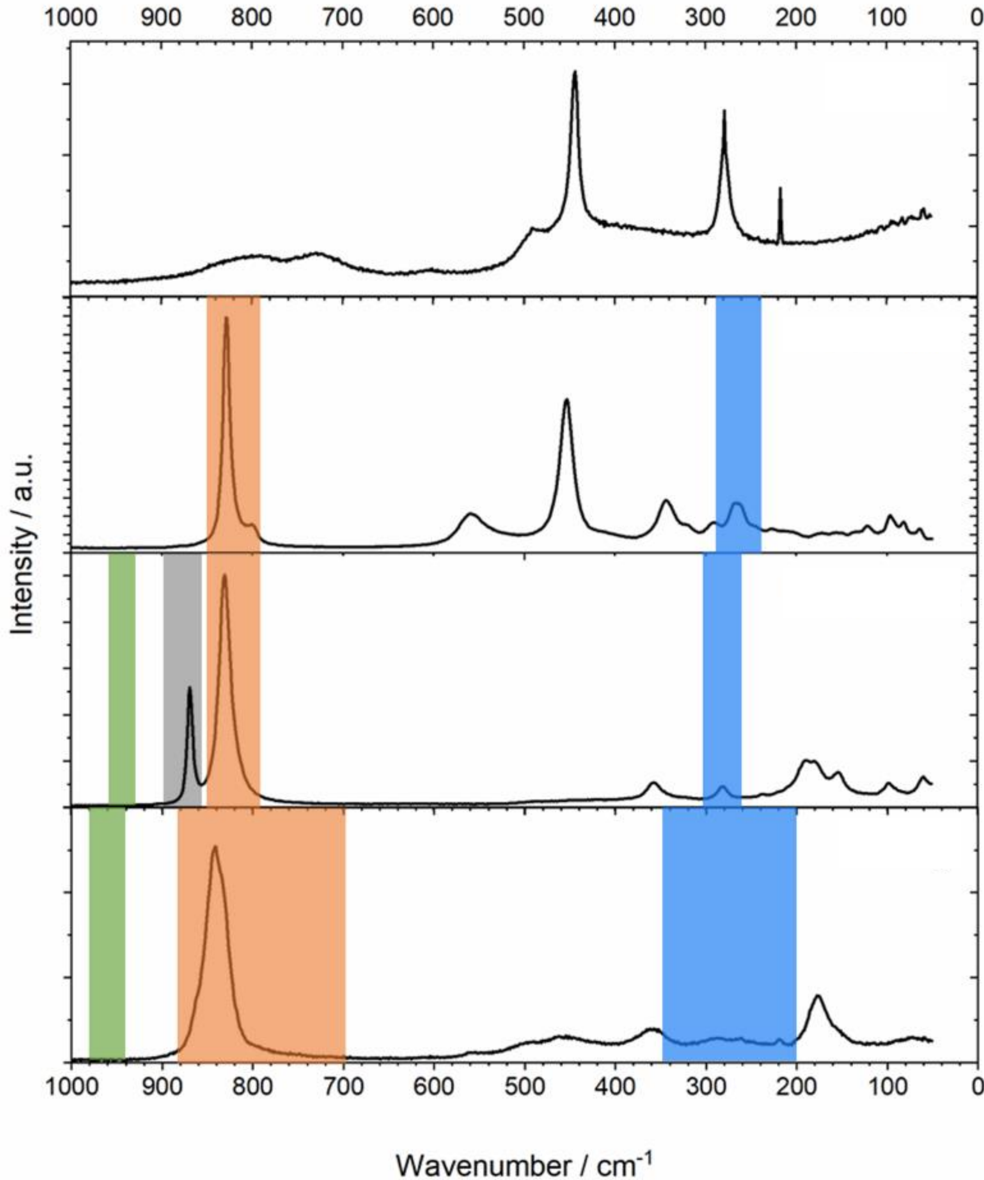
Highlighted regions

$v_1(UO_2)^{2+}$
$v_2(UO_2)^{2+}$
$v_3(UO_2)^{2+}$
v(O-O)



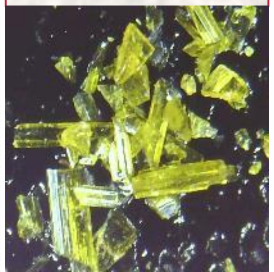






Brucite

$Mg(OH)_2$



Becquerelite

$Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$

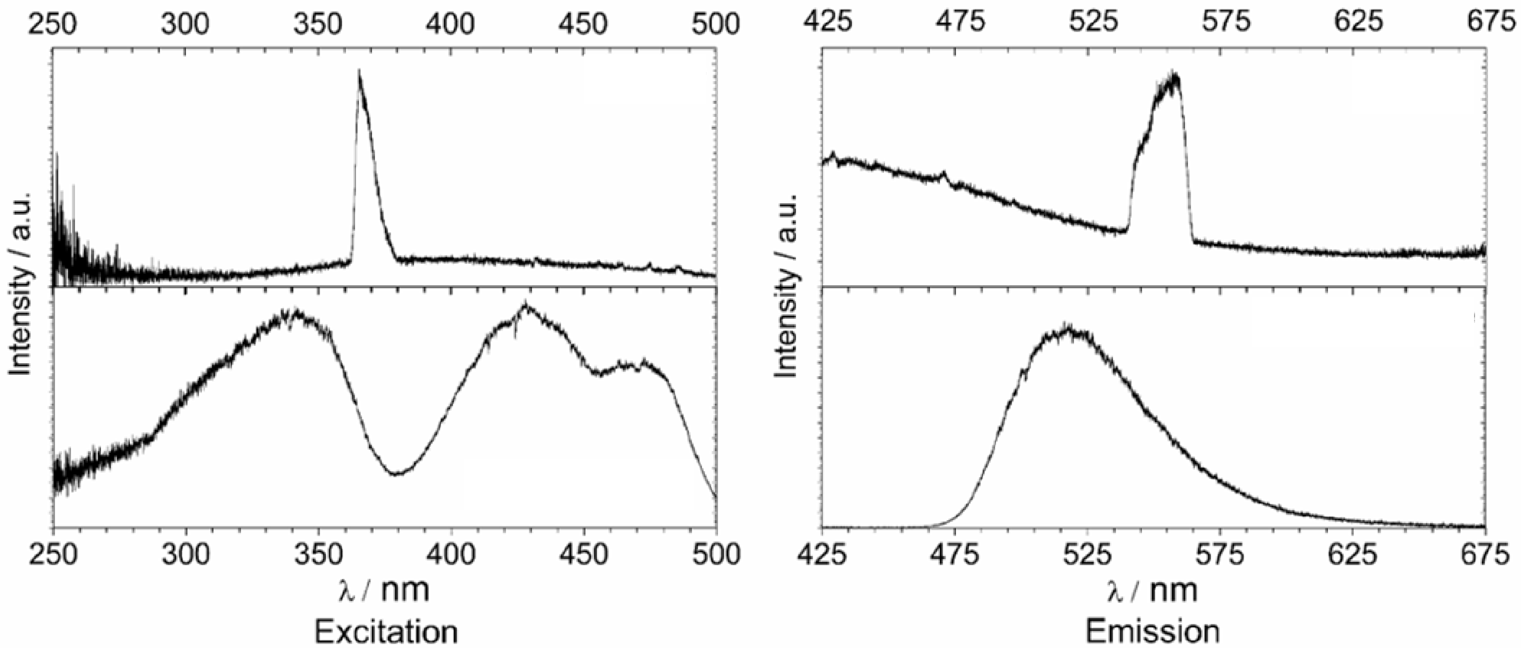
Metastudtite

$UO_4 \cdot 2H_2O$

Uranium trioxide

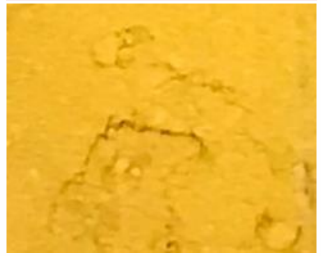
UO_3

Time Resolved Laser Fluorescence



Brucite

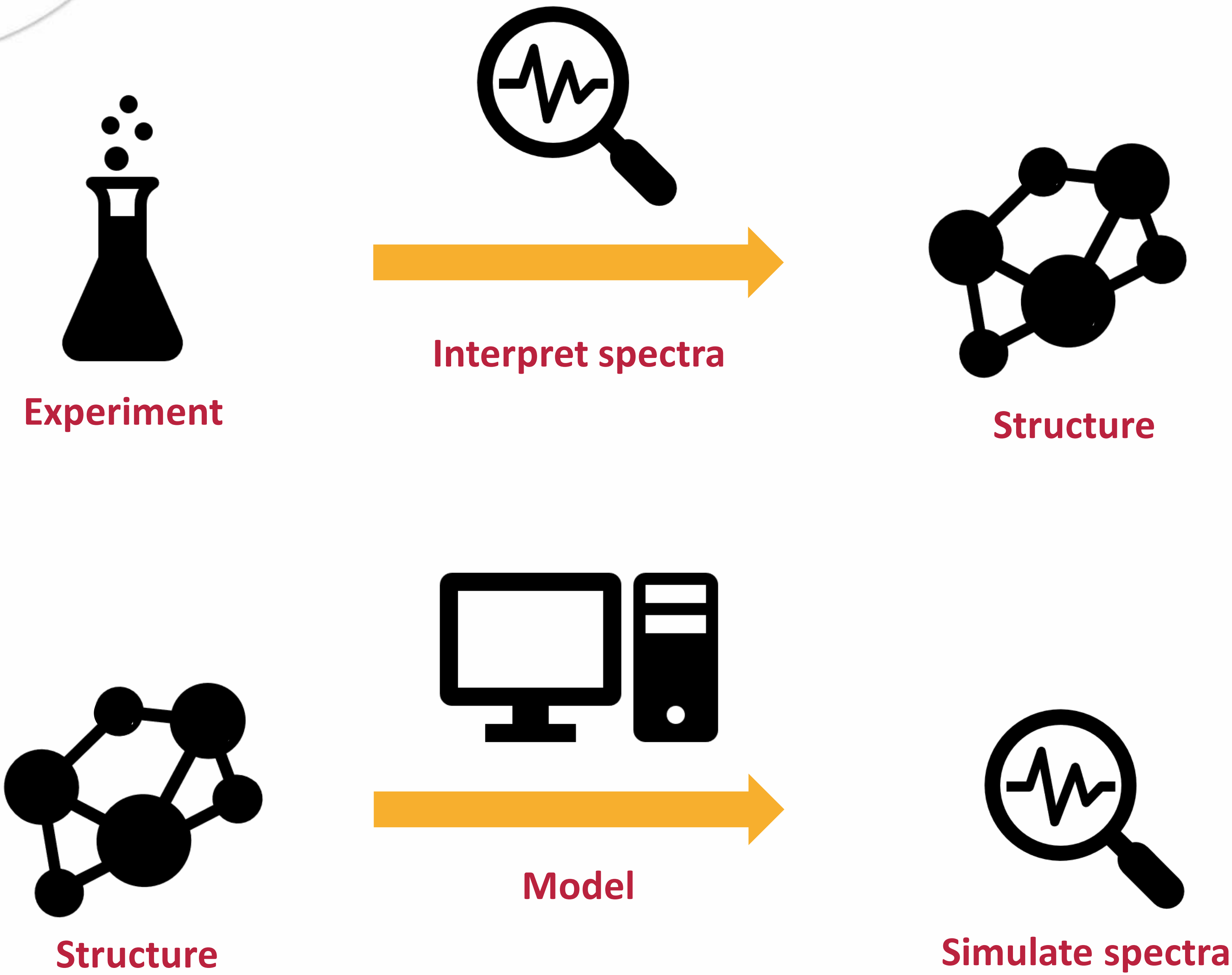
$Mg(OH)_2$



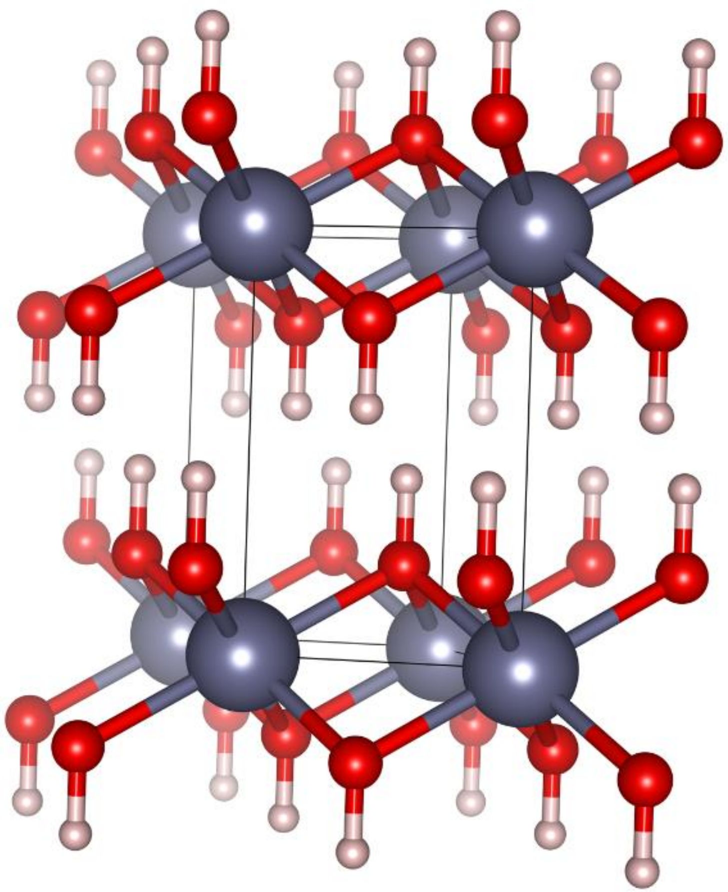
Uranium trioxide

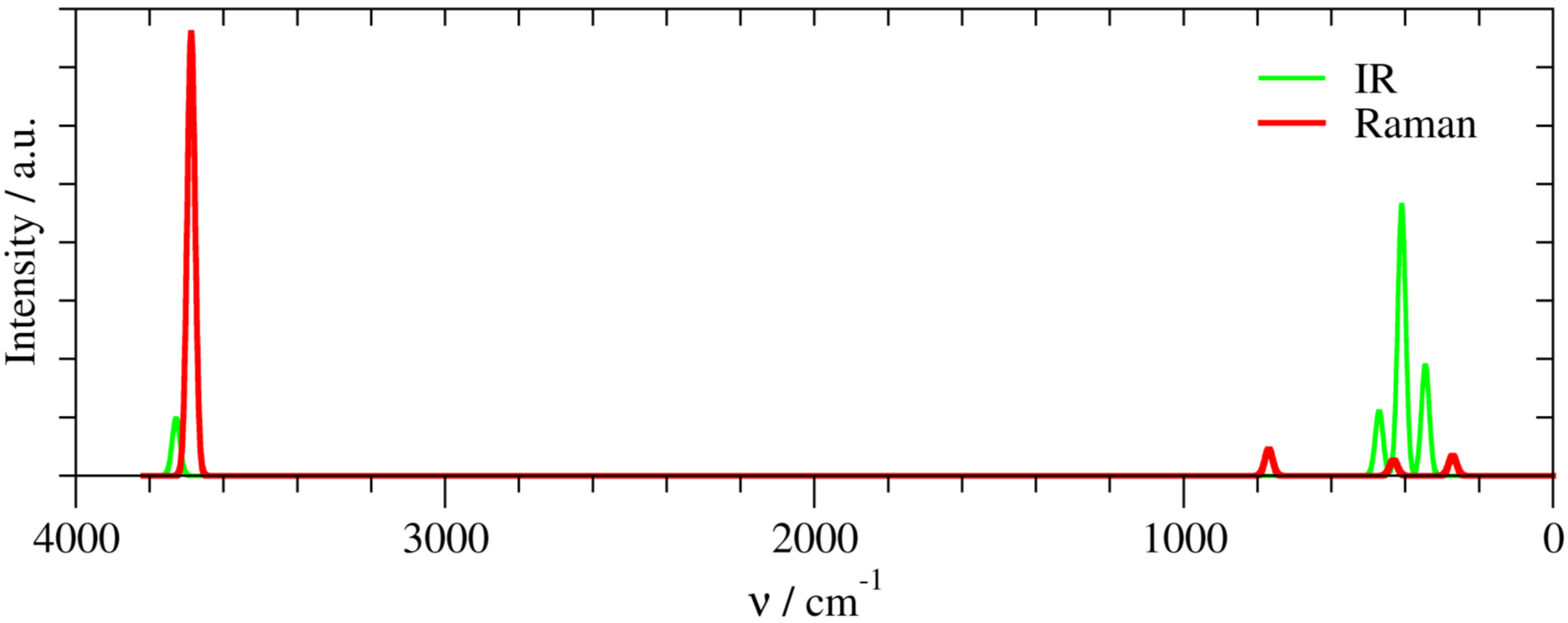
UO_3

Transformative Science and Engineering for Nuclear Decommissioning



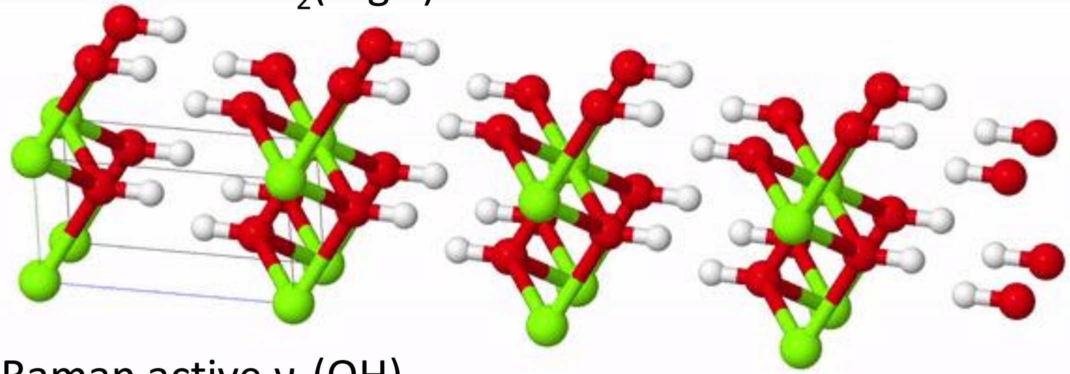
- Computational modelling of brucite
- PBE functional used
- Raman and IR and simulated with DFT
- Fluorescence and electronic spectra aim to simulate in future



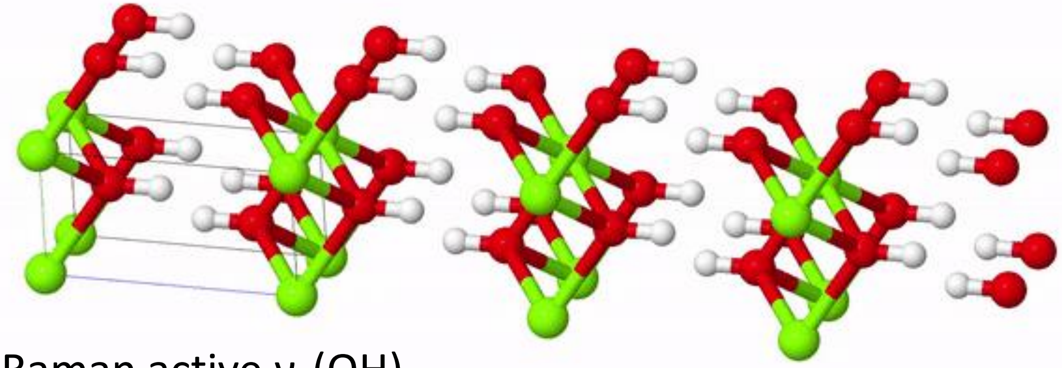

IR
Raman
Intensity / a.u.
4000
3000
2000
1000
0
ν / cm-1

Simulated Raman Modes

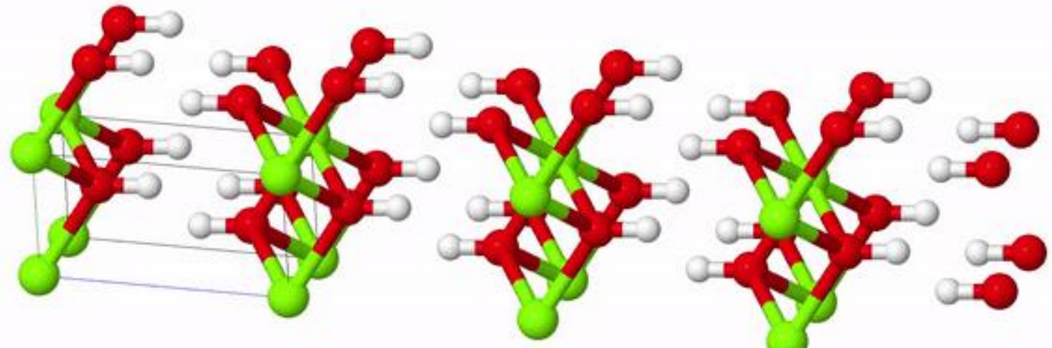
Raman active ν_2(MgO)



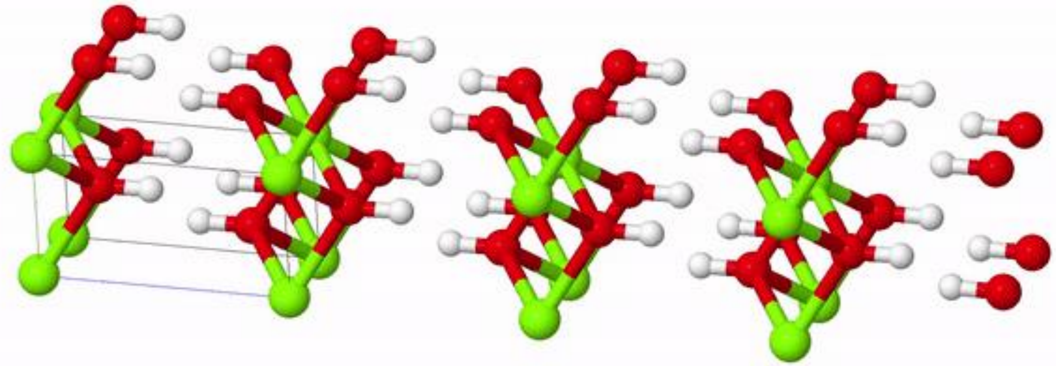
Raman active ν_1(MgO)



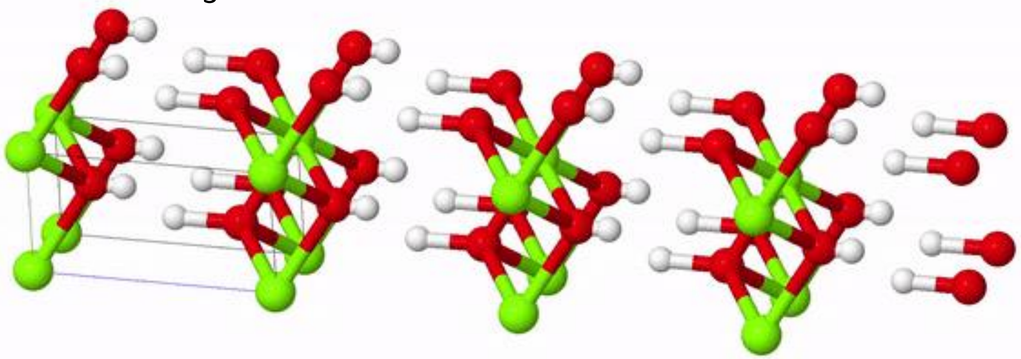
Raman active ν_2(OH)



Raman active ν_1(OH)

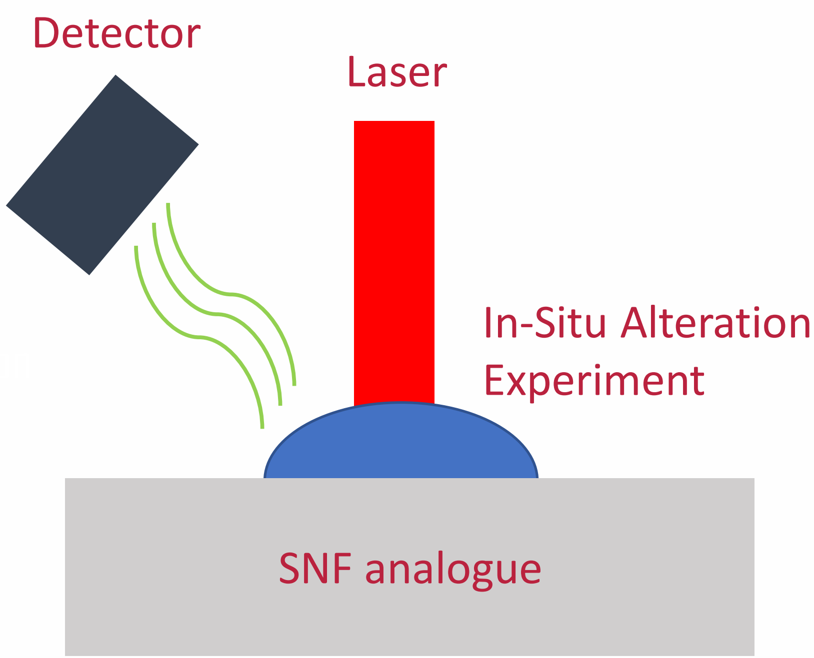


IR active ν_3(OH)



Future Work

- Model Raman, IR and electronic spectra of UOH's
- In-situ Raman experiments with thin films of U, UO_2 and UC
- Model reactions of thin films
- Determine mechanism of alteration



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Sarah Heisig

John-William Brown

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Kay Green

Dr Matthew Horstwood

University of Sheffield

Nathan Thompson

Thank you

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