TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

TRANSCEND: Collaborative Research Programme in Transformative Science and Engineering for Nuclear Decommissioning

Theme 4: Nuclear Materials – Meeting #1

Theme leads
Colin Boxall, University of Lancaster
Nik Kaltsoyannis, University of Manchester

Energy
For a Low Carbon Future

Background

- EPSRC Nuclear Consortia Follow-on Funding call 3rd January 2018, submission 16th March, interview 5th June, offer letter 31st August
- Project started 1st October 2018 to 30th September 2022
- £4.59 M EPSRC → total £5.73 M (FEC), plus £3.70 M from industry = £9.43 M
- World-class University network:

Imperial College London
Lancaster University
Queen's University Belfast
University of Birmingham
University of Bristol
University of Leeds
Manchester 1824 The University of Manchester
The University Of Sheffield.
University of Southampton
University of Strathclyde Glasgow
University of Surrey

- Key project partners:

AWE
cavendish nuclear
LLWR Ltd
National Nuclear Laboratory
NDA Nuclear Decommissioning Authority
Radioactive Waste Management
Sellafield Ltd
TÜV SÜD
Nuclear Technologies

Research Themes

Theme 1: Integrated Waste Management (Leads: Claire Corkhill / Joe Hriljac):

- New Materials and Methods for Decontamination of Effluent
- Modelling and Experiments for Understanding Pond and Silo Sludge Behaviour
- Wasteform Science

Theme 2: Site Decommissioning and Remediation (Leads: Becky Lunn / Luc Vandeperre):

- Colloidal-Silica Grout
- Electrokinetic Ground Remediation
- Non-Invasive Monitoring of Soil Contamination, Structural Degradation, Assessment and Repair

Theme 3: Spent Fuels (Leads: David Read / Tom Scott):

- Properties and Reactivity of Bulk Corrosion Products
- Pressing Fuel Barrier Corrosion
- In-Situ Identification of Nuclear Fuel Materials and Surface Corrosion Products
- Prediction of Long-Term SNF Behaviour

Theme 4: Nuclear Materials (Leads: Colin Boxall / Nik Kaltsoyannis):

- Surface Chemistry of PuO_2 under Conditions Relevant to Interim Storage
- Plutonium Immobilisation in Advanced Ceramic Wasteforms

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Theme 4: Nuclear Materials

Partner organisations

Lancaster University

MANCHESTER 1824
The University of Manchester

UNIVERSITY OF BIRMINGHAM

The University Of Sheffield.

EPSRC
Engineering and Physical Sciences Research Council

Sellafield Ltd

NATIONAL NUCLEAR LABORATORY

Radioactive Waste Management

NDA
Nuclear Decommissioning Authority

Theme 4: Nuclear Materials

Introduction, Aims & Objectives, Work Packages

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

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

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

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

Objectives.

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

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

$\Rightarrow$

WP4.2: Plutonium Immobilisation in Advanced Ceramic Wasteforms

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Theme 4: Nuclear Materials

Projects in WP4.1

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

PDRA project (EPSRC): "Fundamental Surface Chemistry of PuO_2" Dom Laventine (Colin Boxall)

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

PhD project (Lancaster): "Quantum chemical simulation of Am incorporation in PuO_2" William Neilsen (Sam Murphy)

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

PhD project (Sellafield/NNL): "Radiolysis of Water on Uranium Oxides and ThO_2" ? (Fred Currell)

PhD project (Sellafield/NNL/NDA): "Hydrogen / Oxygen Recombination at Metal Oxide Surfaces" ? (Colin Boxall)

Theme 4: Nuclear Materials

Projects in WP4.2

WP4.2: Plutonium Immobilisation in Advanced Ceramic Wasteforms

PDRA project (EPSRC): "Plutonium immobilisation" Shi-Kuan Sun (Neil Hyatt)

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

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Theme 4 Meeting #1: Agenda

11:00	*Welcome and overview of Theme 4*
11.10	*Water absorption onto Plutonium Dioxide by piezo-electric crystal nano-balance and contact angle measurements* **Dominic Laventine (U. Lancaster)**
11:35	*Atomistic simulation of Am incorporation into PuO_2* **William Neilson (U. Lancaster)**
11.45	*DFT+U study of $U_{1-y}An_yO_{2-x}$ (An = Np, Pu, Am and Cm) surfaces* **Jia-Li Chen (U. Manchester)**
12:10	*Computational Modelling of PuO_2: Ageing and Storage Phenomena* **Eleanor Murray (U. Birmingham)**
12:30	*Lunch and posters*
14:00	*Characterisation of long-stored Magnox PuO_2 packages* **Robin Orr (NNL)**
14:30	*Underpinning plutonium immobilization in advanced ceramic wasteforms* **Shi-Kuan Sun (U. Sheffield)**
14:55	*Disposability of waste-forms for plutonium immobilisation and efficacy of surrogates* **Clemence Gausse (U. Sheffield)**
15:05	*Quantum chemical modelling of ThO_2 surface chemistry* **Xiaoyu Han (U. Manchester)**
15:15	*Gas generation from the radiolysis of water on uranium oxides and ThO_2* **Fred Currell (DCF / U. Manchester)**
15:25	*The Recombination of Hydrogen and Oxygen on Metal Oxide Surfaces* **Dominic Laventine (U. Lancaster) / Colin Boxall (U. Lancaster)**
15:35	*General Q&A session / discussion*

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Safe Interim Storage of plutonium: Water absorption onto thin-layer plutonium analogues

Transcend Research Consortium

Dr. Dominic Laventine, Prof. Colin Boxall
Lancaster University

Energy For a Low Carbon Future

Lancaster University

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Lloyd's Register Foundation

- Introduction to UK plutonium interim storage
- Synthesis of thin-layer actinide coatings
- Contact angle measurements
- Piezo-crystal nano-balance experiments

- **Introduction to UK plutonium interim storage**
- Synthesis of thin-layer actinide coatings
- Contact angle measurements
- Piezo-crystal nano-balance experiments

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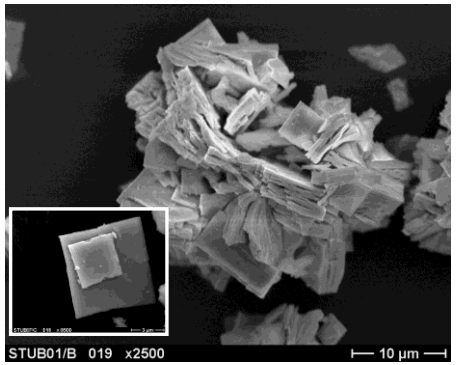
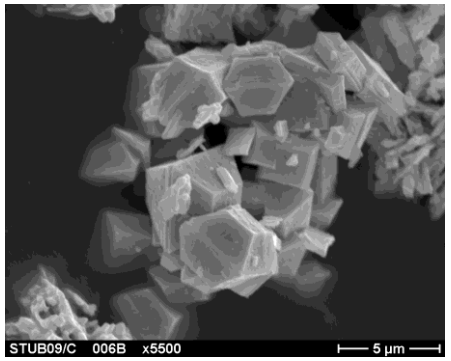
Separation and Reprocessing in the UK

- Reprocessing of spent fuel allows the separation of plutonium from uranium and other species
- PUREX process co-extracts Pu and U as nitrates into an acidified raffinate.
- In the UK, further separation of Pu from the U performed at:
  - THORP reprocessing plant (due to close 2018) by hydrazine reduction of the plutonium
  - Magnox reprocessing plant (due to close 2020)





- *Ca.* 250 tonnes of separated Pu currently stockpiled worldwide. Approx. 137 tonnes is in interim storage in UK whilst the Government "develops its options".

Plutonium interim storage in the UK

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

During storage the radioactivity of the plutonium results in heating of the canisters to an estimated central line temperature of 600°C.

PuO_2 is hydroscopic and picks up water during the packaging process. The disposition of this water under the storage conditions is unclear: It may exists in a gaseous state, or be weakly or strongly bound to the PuO_2 surface. Radiolytic and catalytic processes may also result in formation of radicals and other chemical species.

Need to understand how the structure and properties of PuO_2 change with time under storage condition and how this affects water absorption.

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Cannister pressurisation

Over time a small number of cannisters have been observed to deform due to pressurisation: this makes storage and efficient heat transfer difficult 5 routes to gas production have been suggested that could contribute to this pressurisation:

(i) Helium accumulation from a decay
(ii) Decomposition of polymeric packing material
(iii) H_2O desorption (steam) from hygroscopic PuO_2
(iv) Radiolysis of adsorbed water
(v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a PuO_{2+x} phase.

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

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

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

- Introduction to UK plutonium interim storage
- **Synthesis of thin-layer actinide coatings**
- Contact angle measurements
- Piezo-crystal nano-balance experiments

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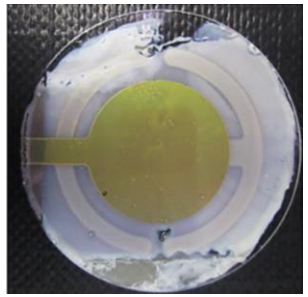
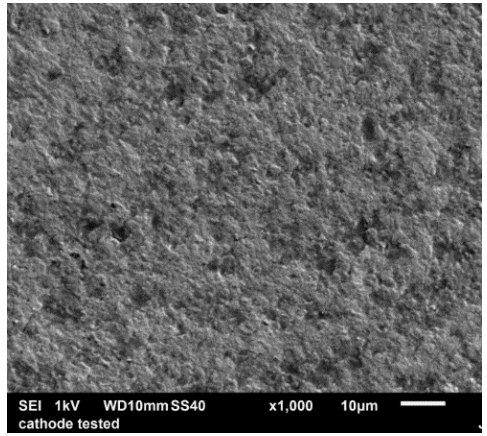
Actinide thin layer synthesis

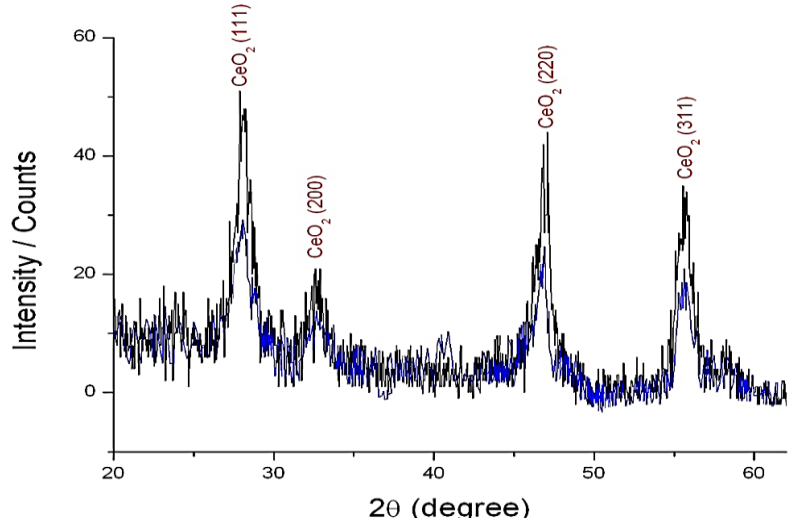
Thin (10-100s nm thick) layers of metal oxide synthesised by drop-coating of salt solutions with surfactant followed by evaporation and calination. Allows surface characteristics to be investigated while using only small amounts of radioactive material.

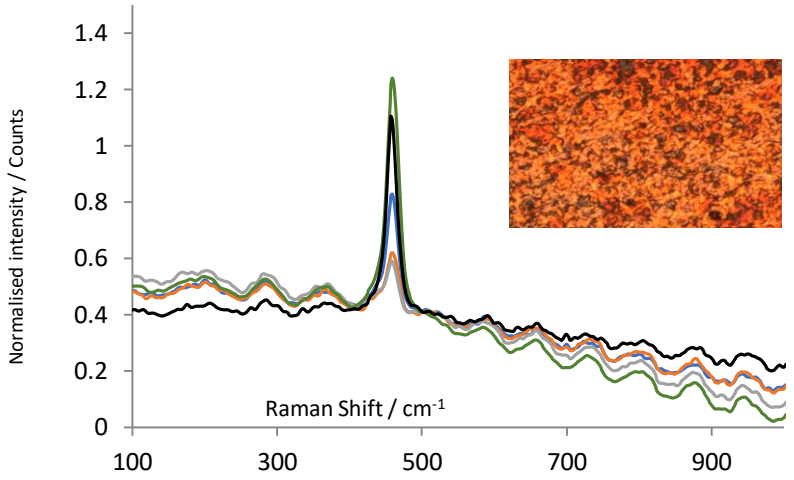
Cerium, Thorium, and Uranium oxides used as analogues of plutonium oxide due to their similar structures and atomic radii.

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









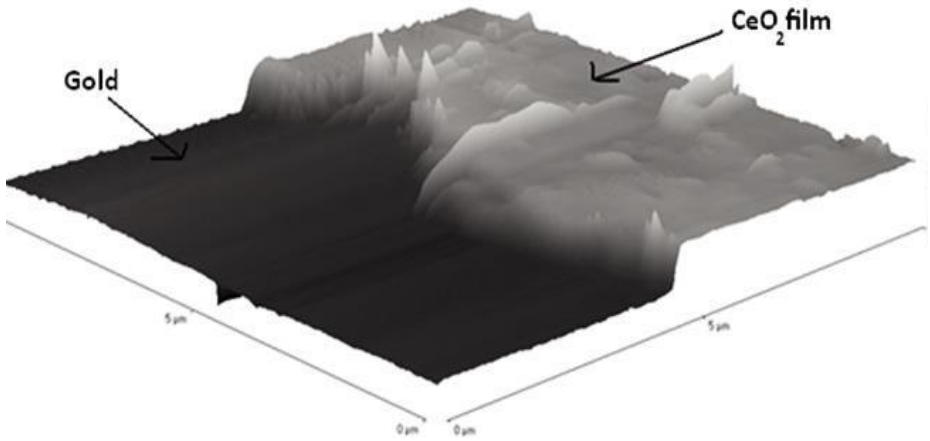
Thin layer depth analyses

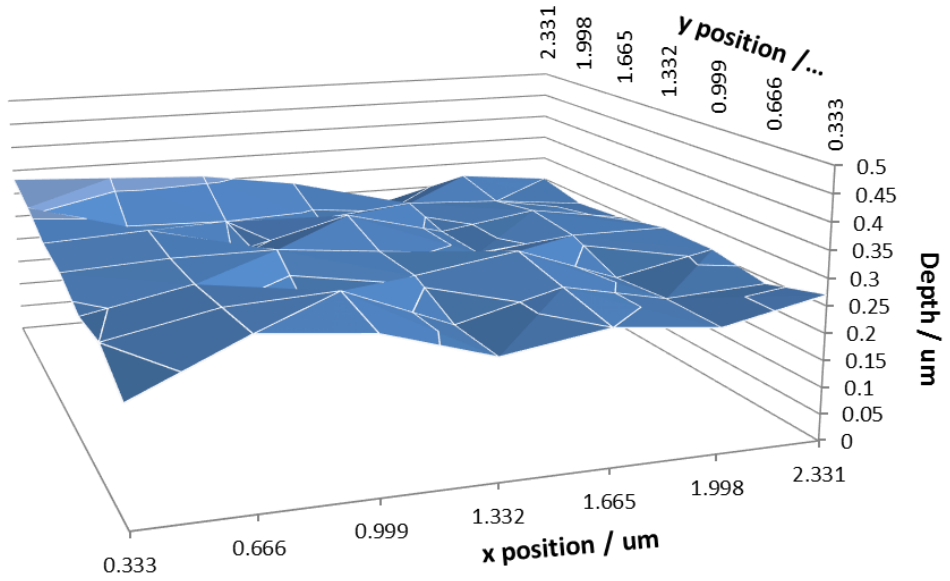
Uncoated crystal $F_{25°C}$ = 5833918 Hz
Coated crystal $F_{25°C}$ = 5826468 Hz
D $F_{25°C}$ = –7450 Hz
D m = 42 ug
vol = 5.5 x 10^{-6} cm^3
Thickness = 125 nm

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

ρ_q = 3.570 $g.cm^{-1}$ n = 1
μ_q = 2.147 x 10^{11} $g.cm^{-1}s^{-2}$
Coated area = 1.33 cm^2
Active area = 0.46 cm^2
d_{CeO_2} = 7.65 $g.cm^{-3}$

XRD thickness is ~250 nm, indicating a porisity of 50%





- Introduction to UK plutonium interim storage
- Synthesis of thin-layer actinide coatings
- Contact angle measurements
- **Piezo-crystal nano-balance experiments**

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Microbalance water absorption

- Study the interactions of plutonium oxide and analogues with water.
  - -- Ceria (CeO_2)
  - -- Thoria (ThO_2)
  - -- Urania (UO_2 / U_3O_8)
  - -- Plutonium oxide (PuO_2) @ NNL Central Lab

- Use of quartz crystal microbalance methodology to experimentally determine:
  - -- The number of monolayers of water bound to the surface
  - -- The enthalpy of binding of the different layers.

- The QCM measures in-situ mass changes at the surface of a piezoelectrode. Changes in mass due to absorption or desorption at the electrode surface result in resonant frequency changes of the quartz crystal, and can be directly related via the Sauerbrey equation:

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

- Through control of temperature and partial pressure of the absorbed gas, the amount of water and enthalpy of absorption can be calculated.

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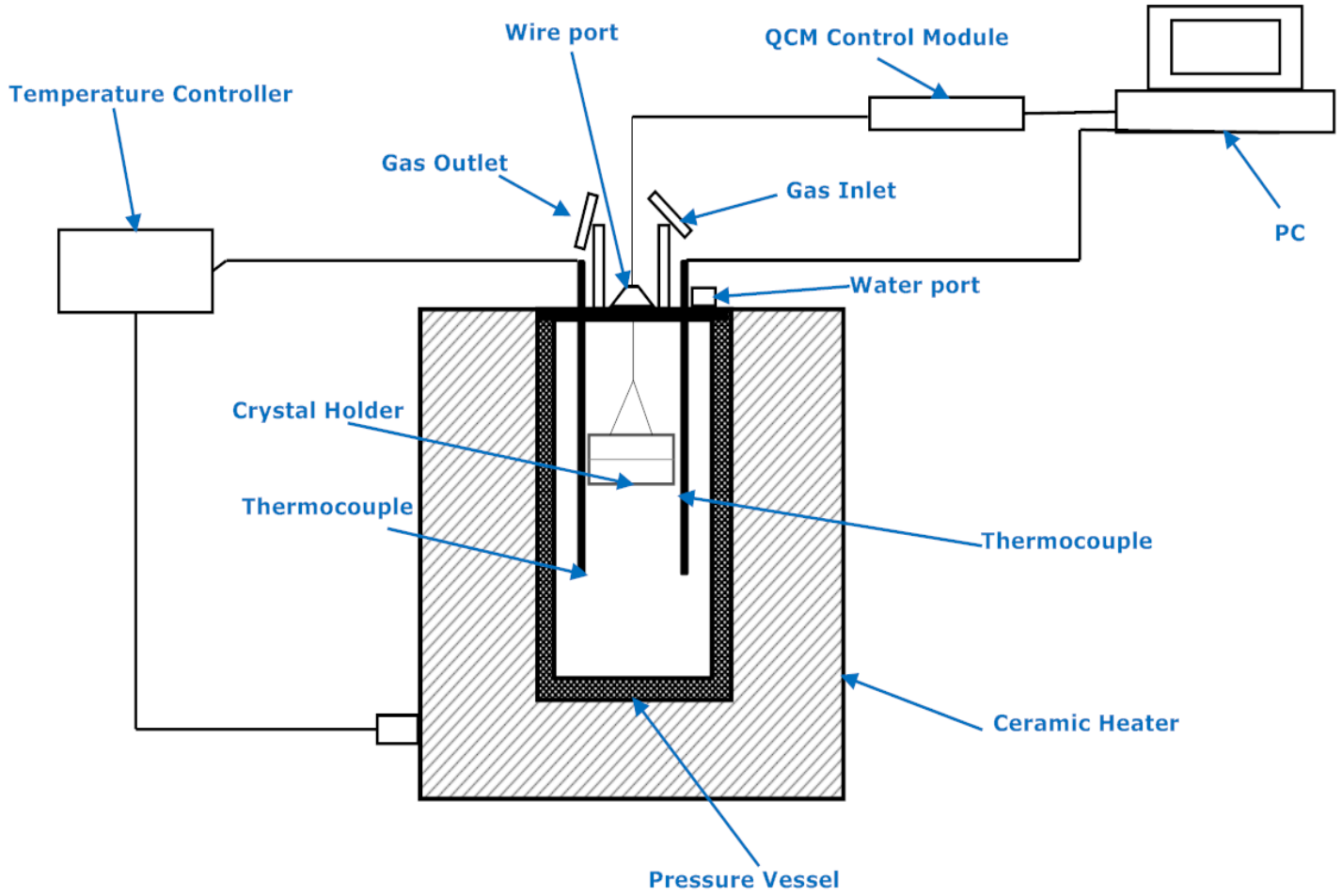
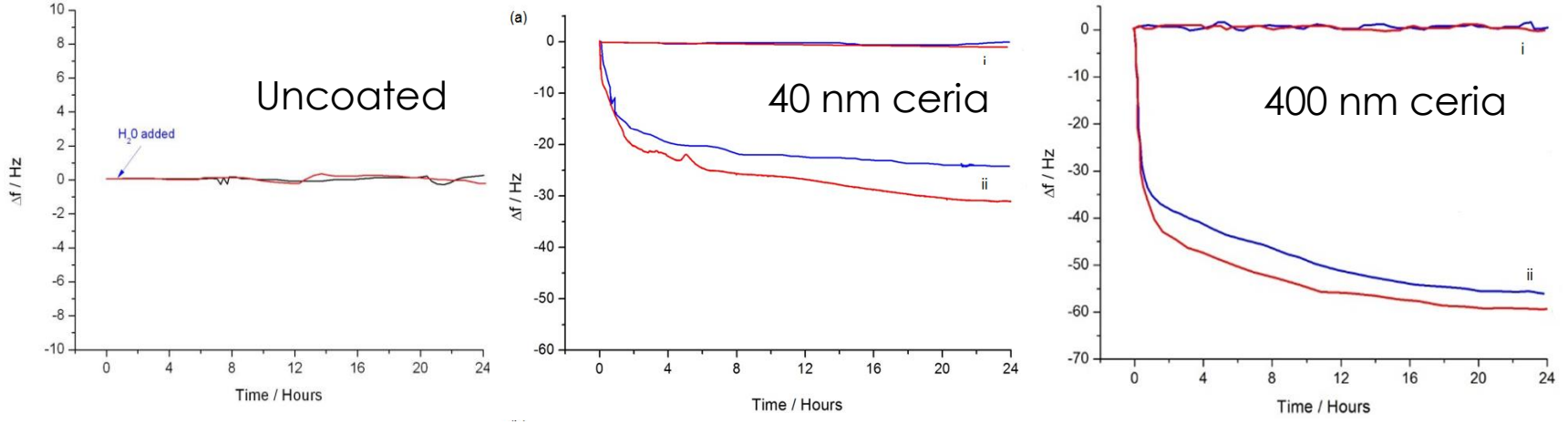
Piezo-crystal nano-balance

Metal crystal transducer and $GaPO_4$ piezo-electric crystals allow higher temperature measurements compared to typical QCM.



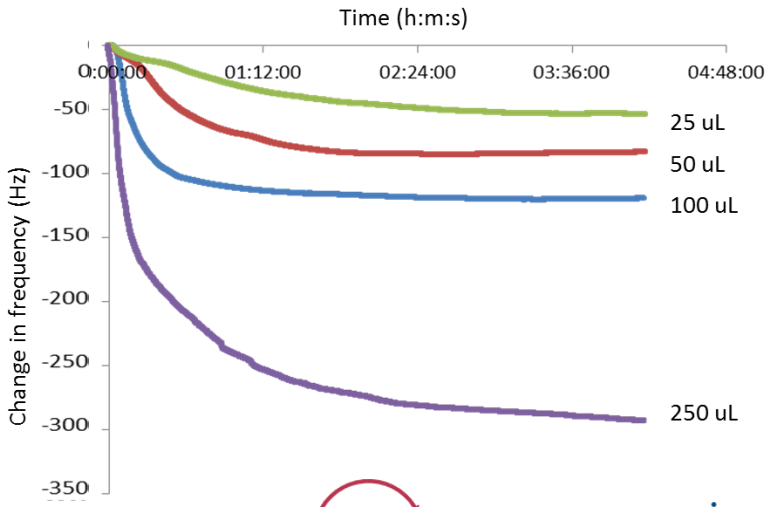
Water absorption: Pilot experiments



Frequency changes due water adsorption onto quartz crystals at 25°C, 10% humidity.
Uncoated crystals showed no appreciable water absorption.
Ceria-coated crystals showed a reduction in frequency due to absorption of water.

Different amounts of water were added to the pre-dried system at RT and equilibrated for 4 hours.

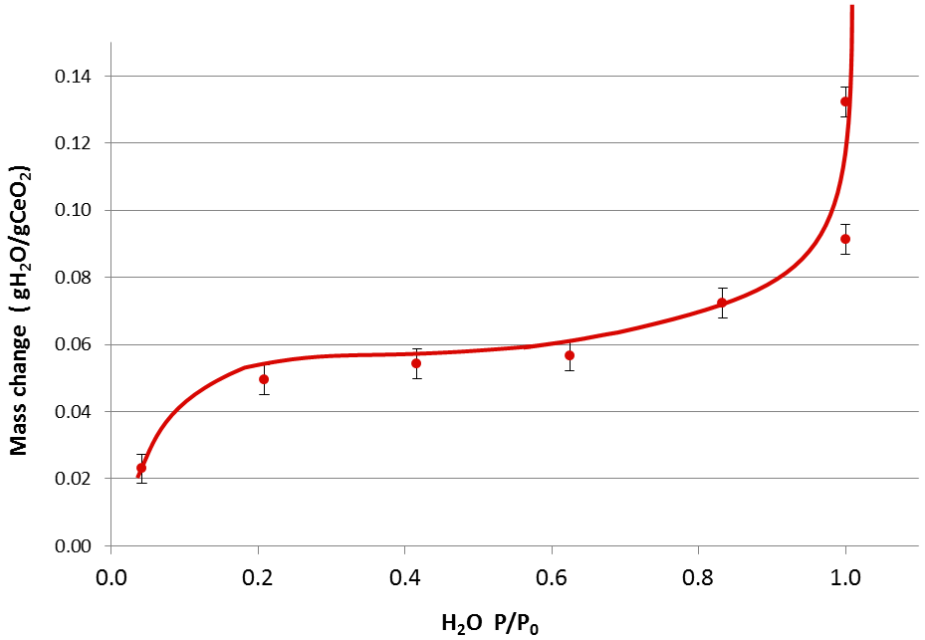
The change in frequency is proportional to the mass of water absorbed onto the ceria, and increased as the amount of water increased.

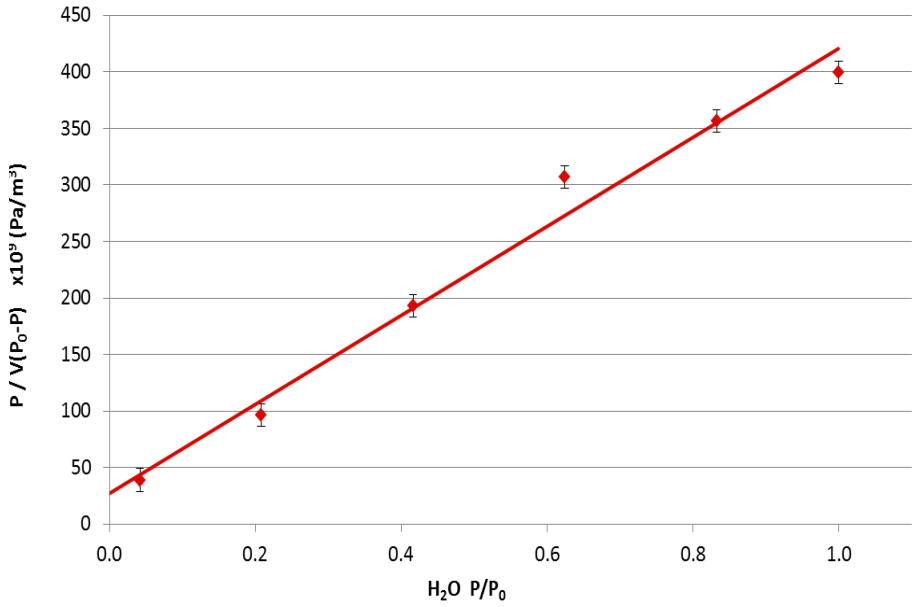


Ceria films on $GaPO_4$ crystals: Humidity variation

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

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





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

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

ΔH_{abs} = 44.3 $kJmol^{-1}$ ΔH_{bind} = 2.5 $kJmol^{-1}$

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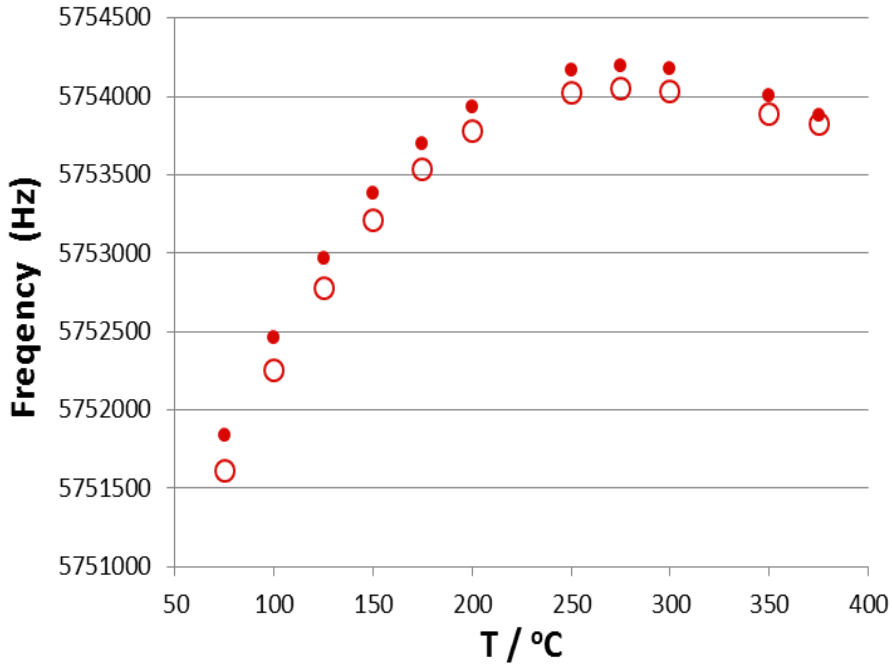
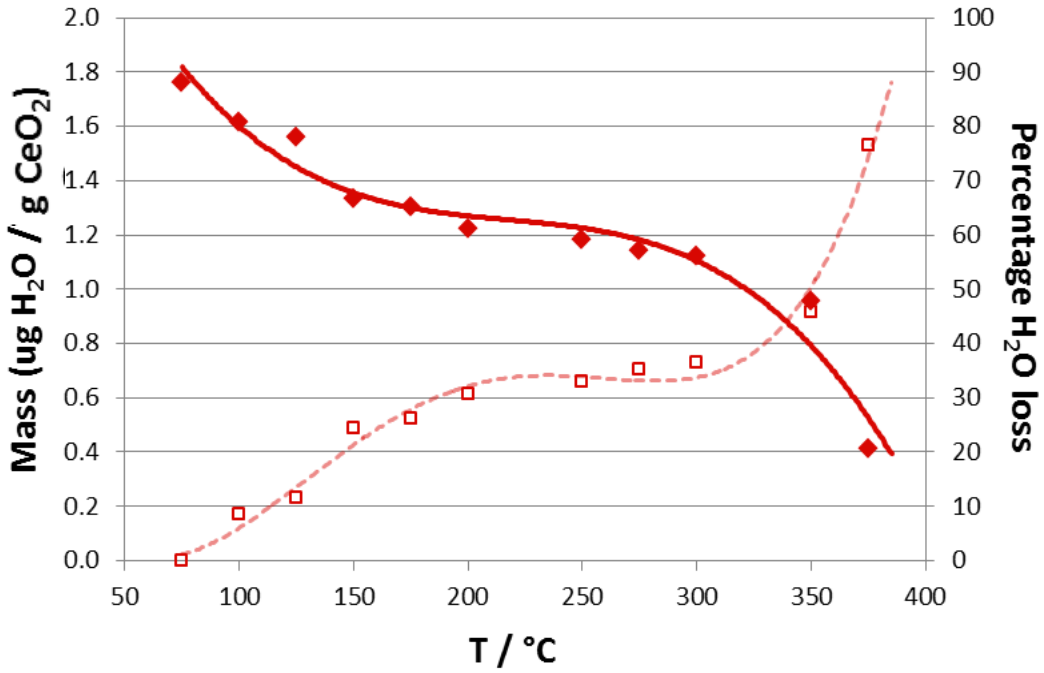
Ceria water absorption: Temperature variation

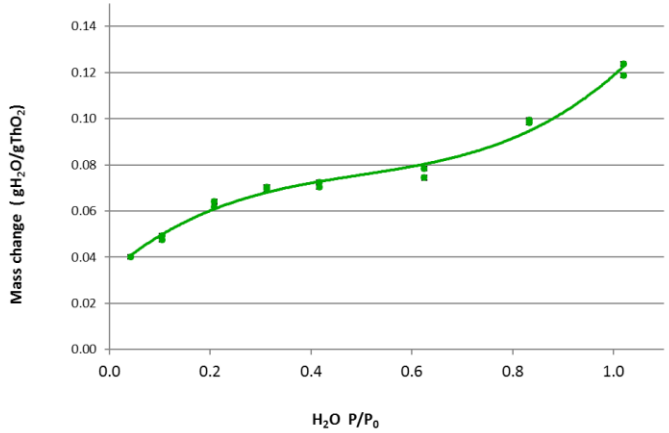
The water saturated system (75°C, 100% rel. humidity) was then heated to approx. 400°C, causing the bound water to desorb as the relative humidity drops.

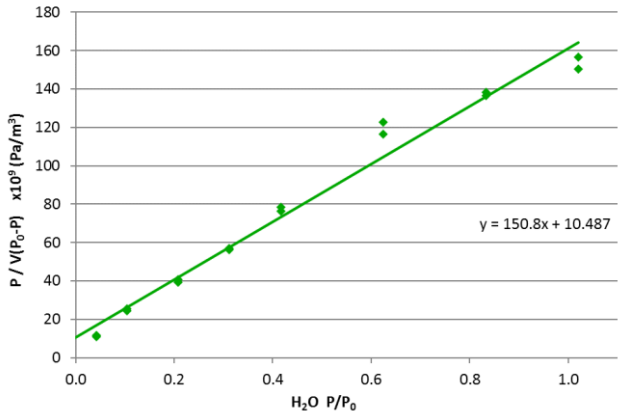




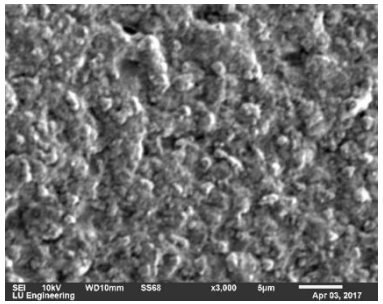
Approximately 20% of the water remains bound to the surface at 375°C.

Thoria films on $GaPO_4$ crystals: BET

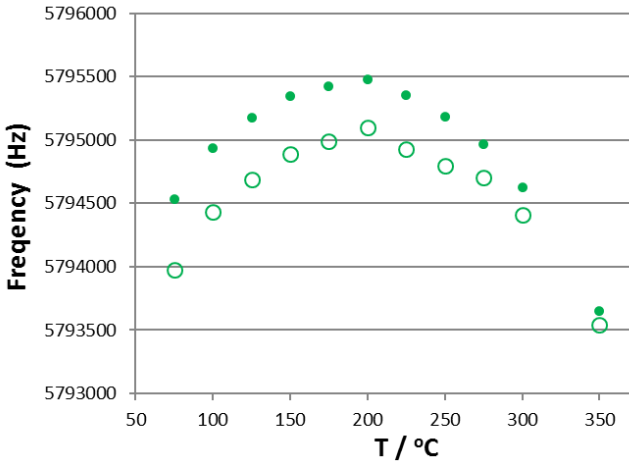


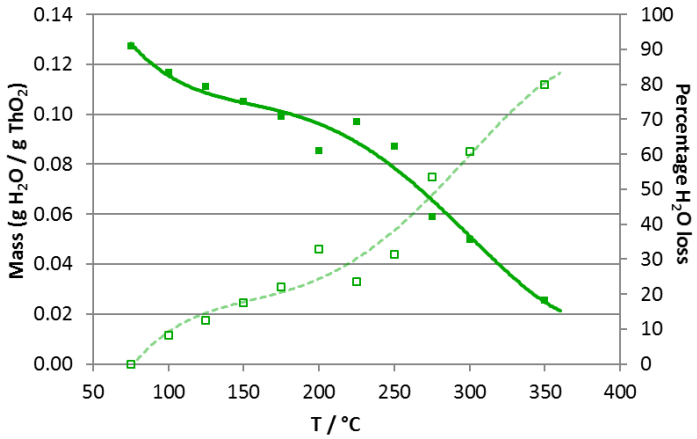


Calc.: 500°C
$V_m = 6.22 \times 10^{-12}$ m^3
SA = 88.5 m^{2}g^{-1}
ΔH_{abs} = 49.4 kJmol^{-1}
ΔH_{bind} = 7.8 kJmol^{-1}

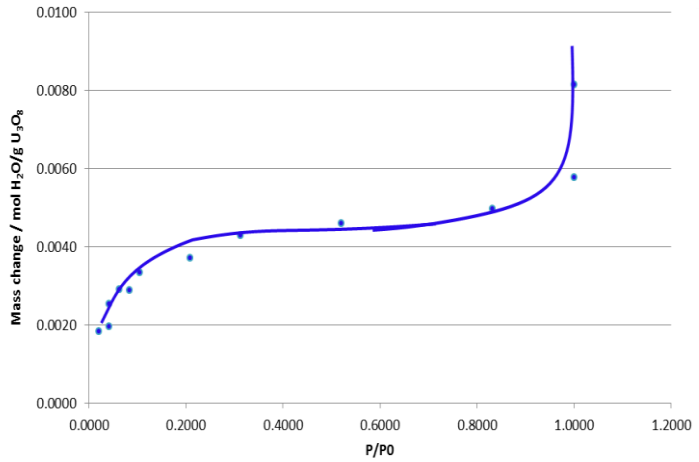


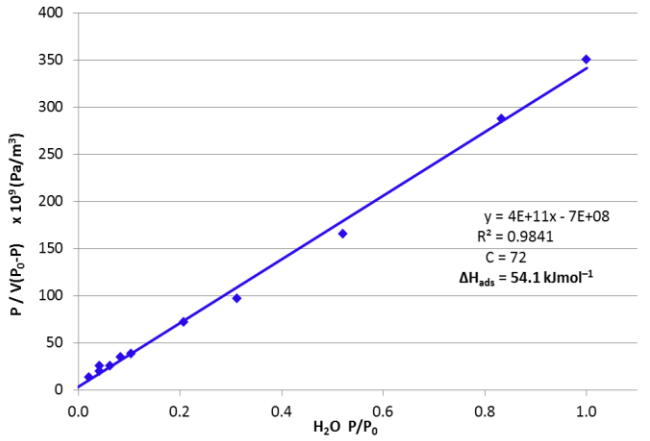
50 ug $Th(oxal)_2$
Calc.: 1000°C
34 ug ThO_2 (QCM)





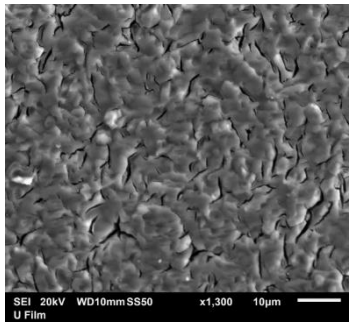
Urania films on $GaPO_4$ crystals: BET



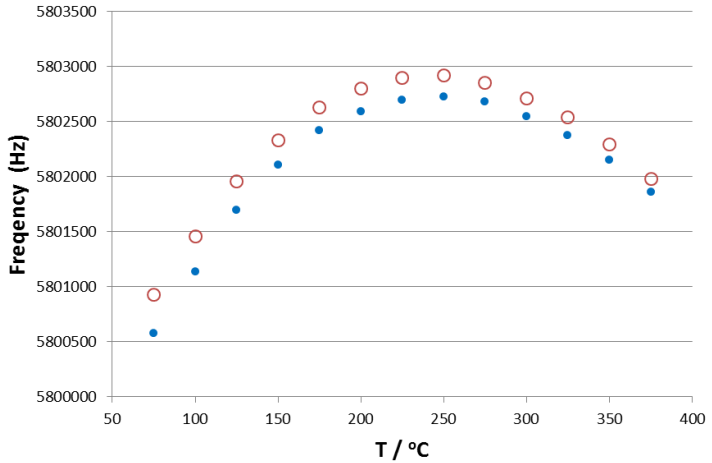


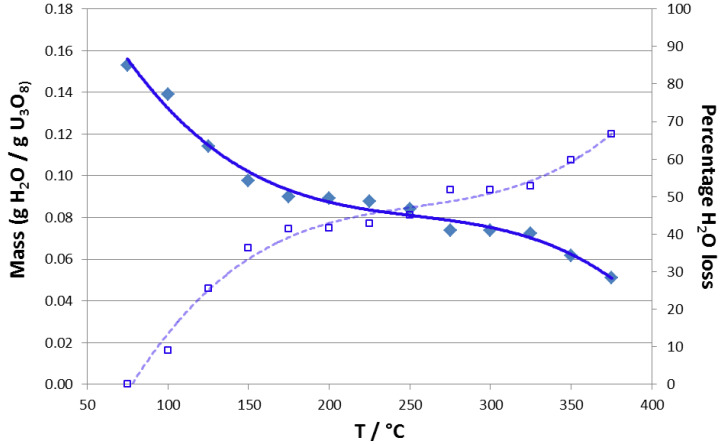
Calc.: 500°C
$V_m = 3.10 \times 10^{-12}$ m^3
SA = 80.9 m^{2}g^{-1}
DH_{abs} = 54.1 kJmol^{-1}
DH_{bind} = 12.5 kJmol^{-1}

Calc: 1000°C
$V_m = 1.50 \times 10^{-12}$ m^3
SA = 42.7 m^{2}g^{-1}
DH_{abs} = 48.1 kJmol^{-1}
DH_{bind} = 6.5 kJmol^{-1}



25 ug $U(NO_3)_3$
Calc.: 1000°C
18 ug U_3O_8 (QCM)
42 nm (XRF)





- Introduction to UK plutonium interim storage
- Synthesis of thin-layer actinide coatings
- **Contact angle measurements**
- Piezo-crystal nano-balance experiments

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Macroscopic water absorption: contact angle measurements

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

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

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

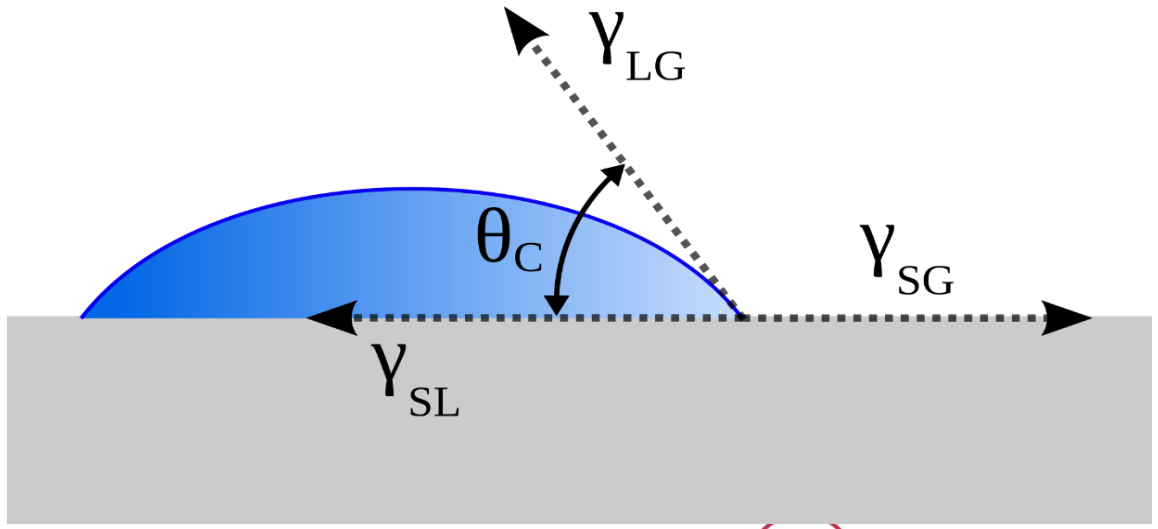
Θ_c = *contact angle*

r: roughness factor

γ_{LG}: surface tension

γ_{SL}: solid-liq IE

γ_{SG}: solid-gas IE



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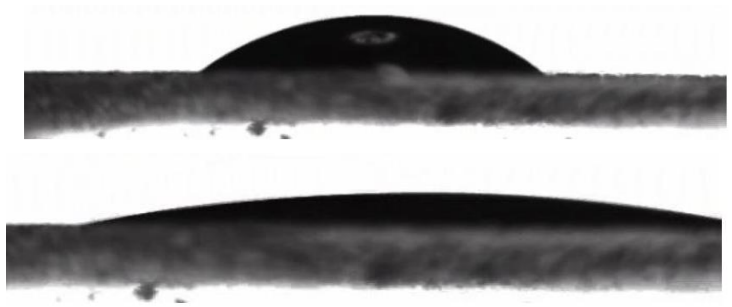
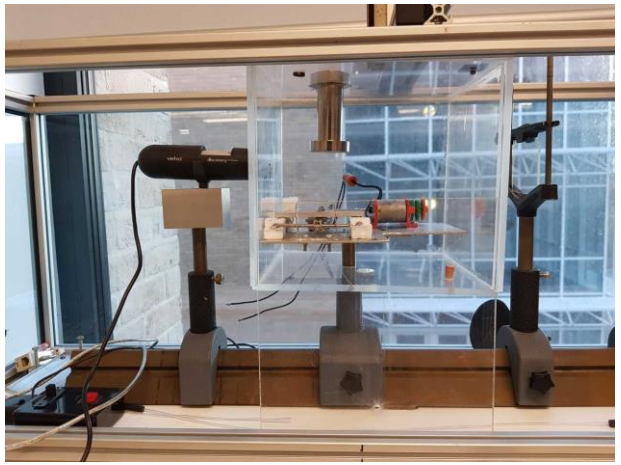
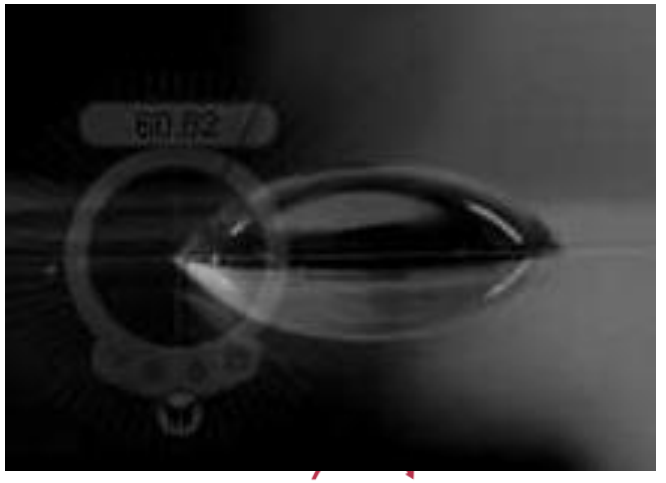
Contact angle measurements: method



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

- Measure contact angles of plutonium oxide analogues (CeO_2, ThO_2, UO_2, $Ce_{1-x}Eu_xO_2$) produced at a range of calcination temperatures.
- Vary humidity of the environment.
- Measure initial contact angles and variation in contact angle during evaporation.
- Automate droplet measurements using image recognition / machine learning.



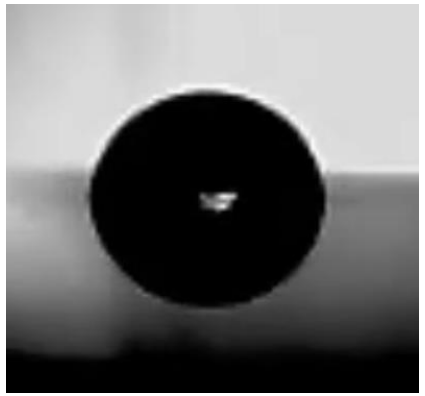


TRANSCEND NATIONAL NUCLEAR LABORATORY Lancaster University

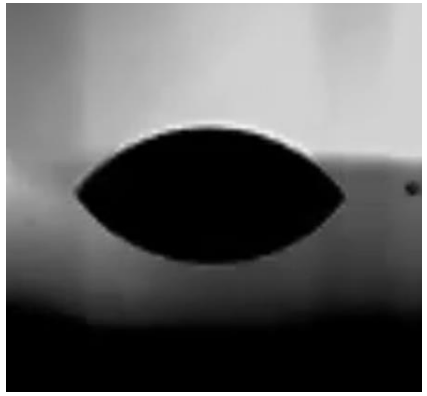
Contact angle measurements calcination temperature

- Higher calcination temperatures result in more hydrophilic surfaces, and lower contact angles.

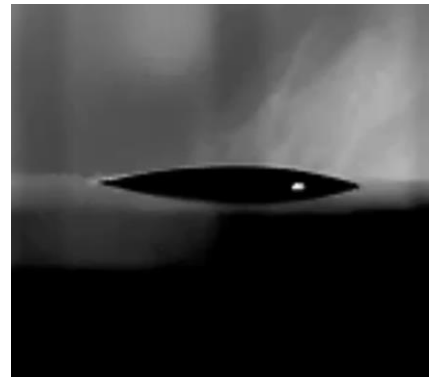
UO_2: 300°C



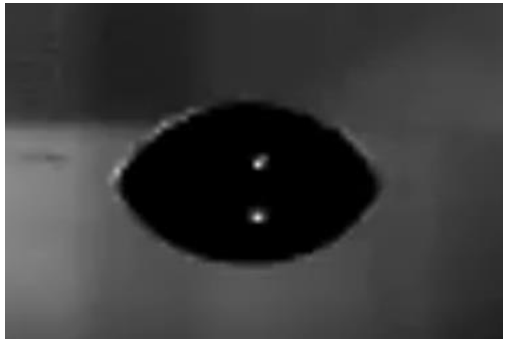
UO_2: 400°C



UO_2: 500°C

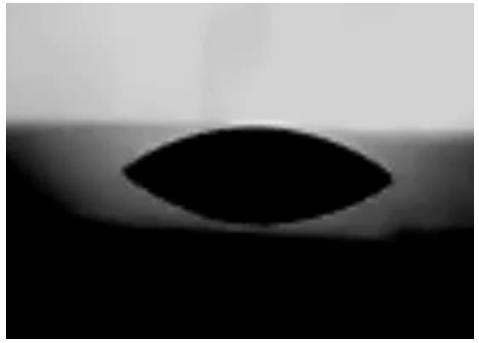


ThO_2: 300°C



ThO_2: 400°C

ThO_2: 500°C

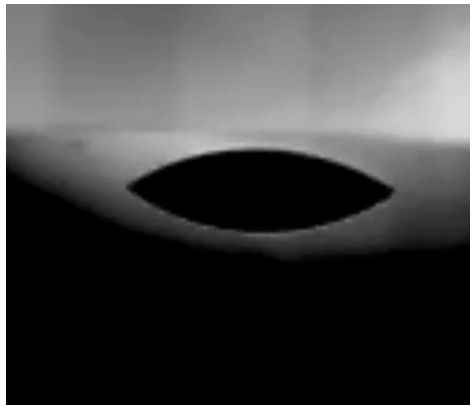


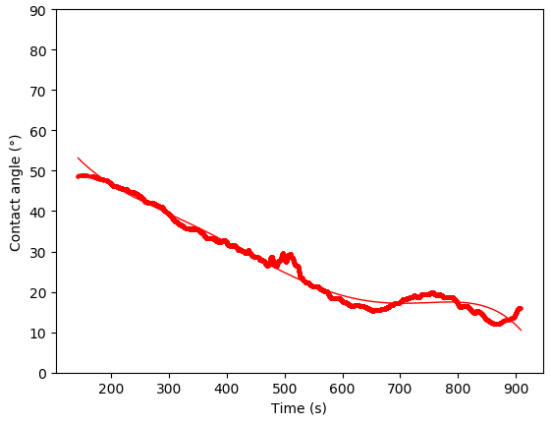
Contact angle measurements: humidity

- Increased humidity (before droplet deposition) results in less wettable surface and greater contact angle. Evaporation time increased.

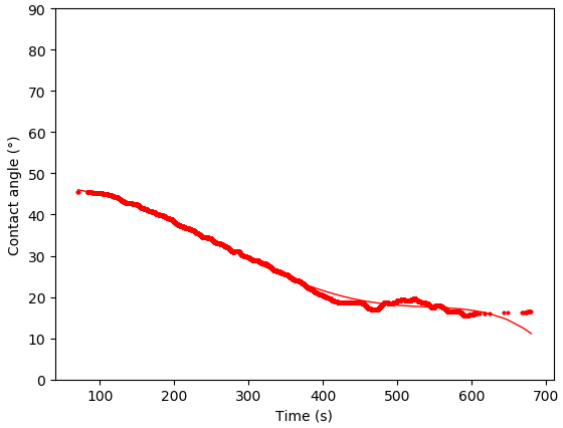
ThO_2 calcined at 400°C

40% hum.



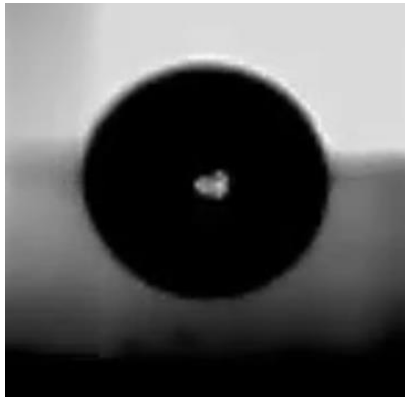


5% hum.

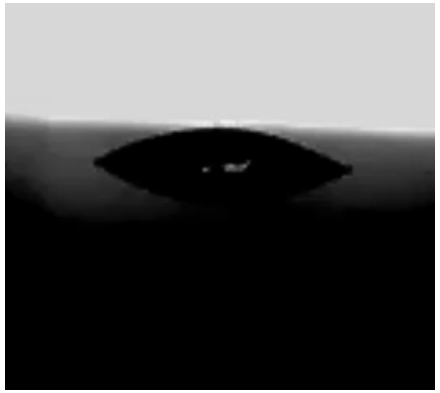


UO_2 calcined at 300°C

70% hum.



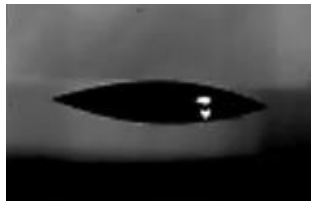
40% hum



Macroscopic water absorption: contact angle measurements

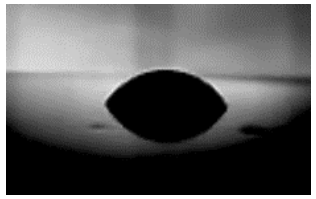
- metal oxide layer on glass substrate (~ 10 ug metal / cm^2), calcined at 300˚C
- water droplet (1 uL) deposited at initial 40% humidity

ThO_2

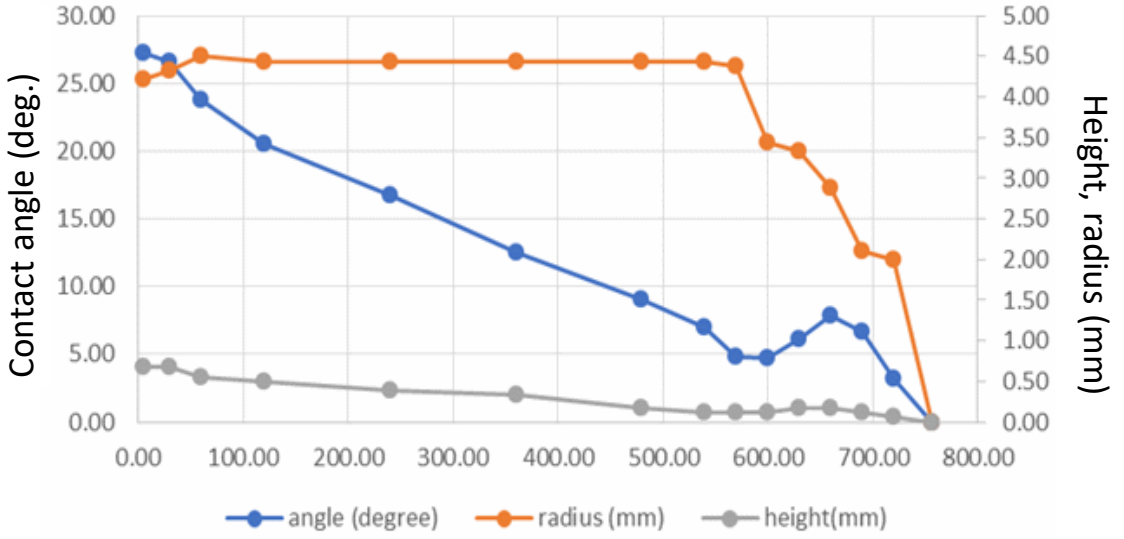


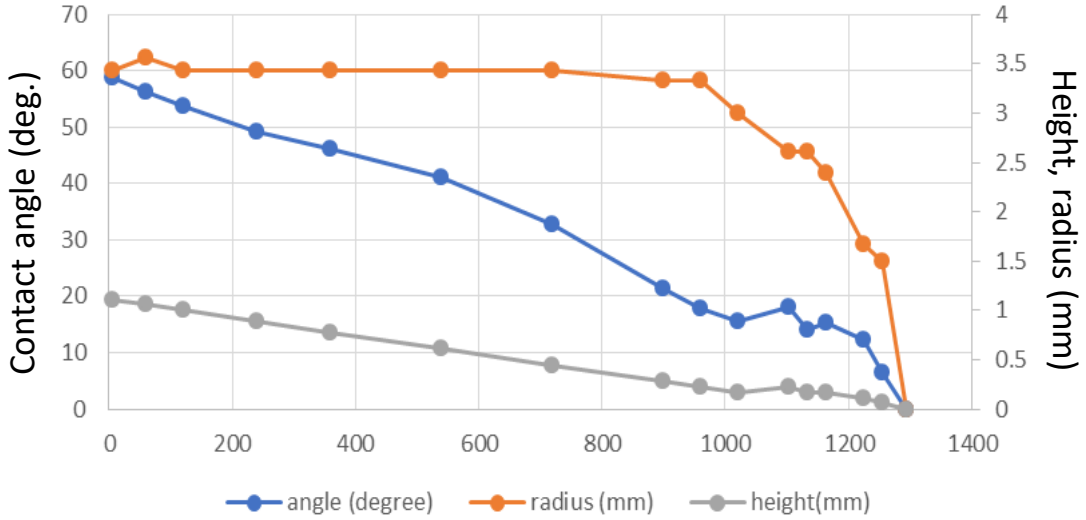
Init. contact angle = 27°

CeO_2



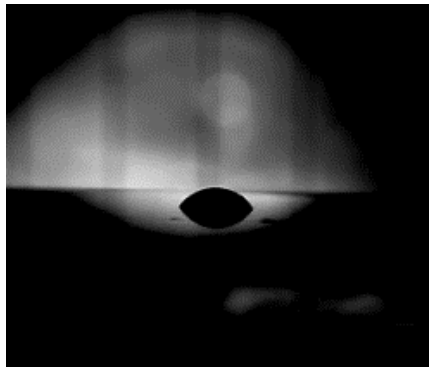
Init. contact angle = 58°





23

Macroscopic water absorption: contact angle measurements

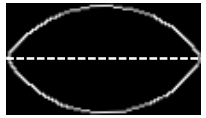


1. Greyscale
2. Blur
3. Edge detect
4. Dilate
5. Erode

Image contour

6. Adjust to horizontal
7. Select largest contour
8. Crop, bisect

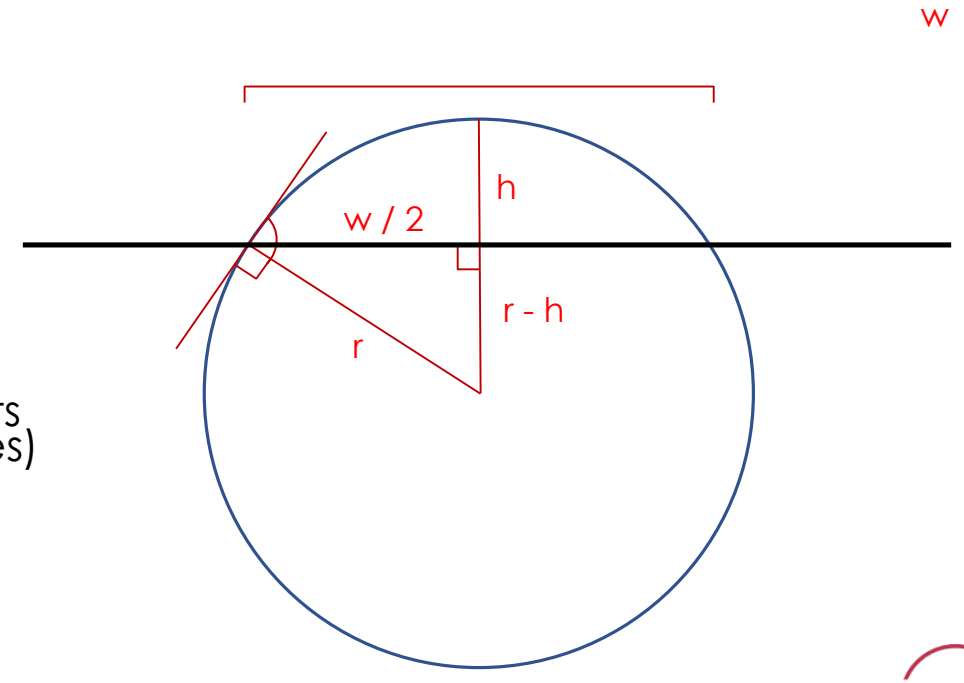
droplet contour



$r = (h / 2) + (w / (8 * h))$

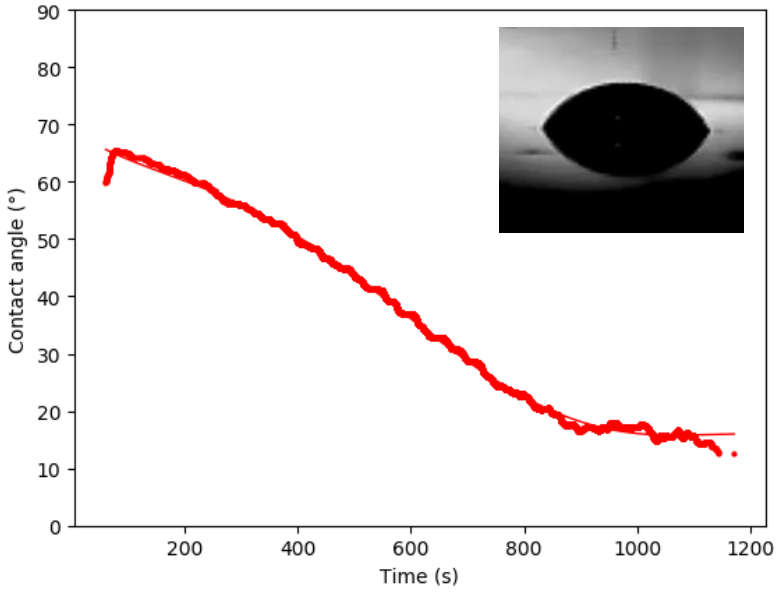
$CA = 90 - \sin^{-1}(r-h / r)$

As the drop evaporates and flattens, the modelled circle gets bigger (w increases, h decreases) and the CA decreases

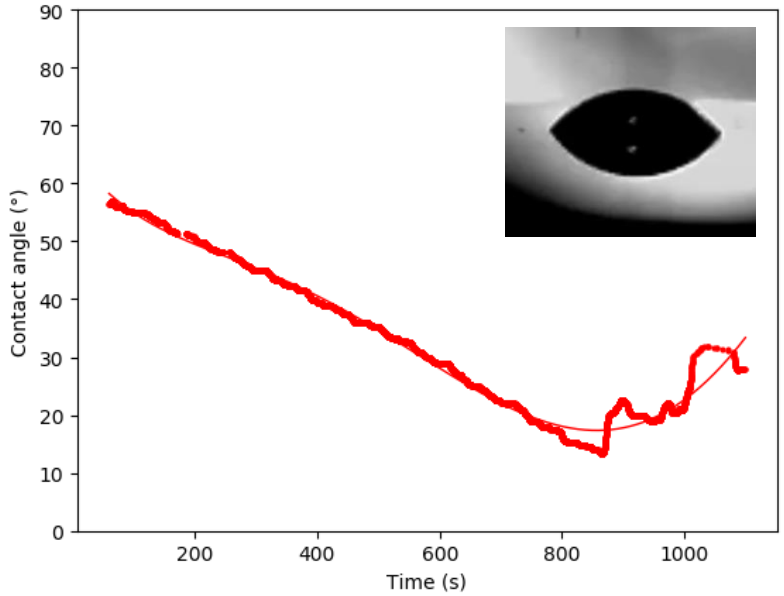


Macroscopic water absorption: contact angle measurements

UO_2 calcined at 300°C, 40% hum.



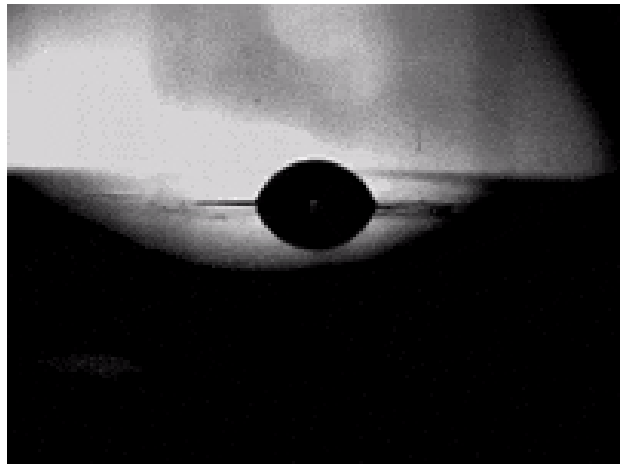
UO_2 calcined at 400°C, 40% hum.



- Calcination at higher temperature gives a lower initial contact angle.
- Rate of evaporation remains approx. the same.
- More contraction events seen for more hydrophilic surface.

Contact angle measurements: Further work

- Reduce size of equipment to fit through glove-box port.
- Improve camera / lighting to give better illumination and resolution.
- Improve automated image recognition.



- Collect more data at different humidities and calcination temperatures, of CeO_2, ThO_2, UO_2.
- Change pH and ionic strength (e.g. salt content) of droplets.
- Measure repeatability of on dry versus pre-wetted surfaces.

Conclusions

- Thin-layers of ceria and thoria (and Urania and plutonia) produced through drop-coating process onto glass and metal surfaces.
- Oxide-coated piezoelectric crystal electrodes used to measure the extent of water absorption onto the oxide surface via changes in frequency.
- Temperature and humidity of the system altered to produce isotherms and the energy of water binding determined.
- Contact angle measurement of water droplets on the oxide layers indicate the wettability and hydrophilicity of the surfaces. Pilot studies indicate significant differences between ceria and thoria, and effects due to calcination temperature and humidity.

Acknowledgments

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- Pat Murphy
- Richard Wilbraham
- Fabrice Andrieux

ITU

- Detlef Wegen

NNL

- Robin Taylor
- Robin Orr
- Dave Woodhead

Thanks for your attention

TRANSCEND

Transformative Science and Engineering for Nuclear Decommissioning

Atomistic simulation of Am incorporation into PuO_2

William Neilson, Lancaster University

w.neilson@lancaster.ac.uk

Supervisor: Dr Samuel T. Murphy

TRANSCEND Thematic Meeting

12th Nov 2019
Lancaster

Energy
For a Low Carbon Future

INTRODUCTION

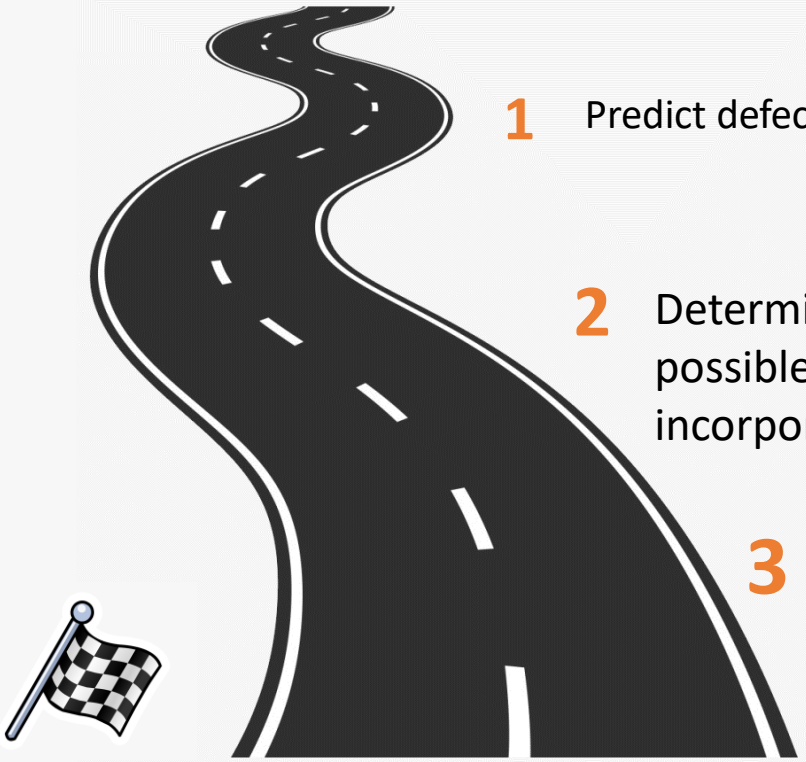
This project will use atomistic simulation to understand the defect chemistry of PuO_2, and how incorporation of Am into PuO_2 may contribute to canister corrosion.

MOTIVATION

- Want to understand if canisters used to hold PuO_2 are vulnerable to corrosion. This could potentially result in the evolution of hydrogen gas from corrosion of the surface by entrained water.
- The conditions do not appear to be sufficiently oxidising to promote corrosion, however experiments have indicated the existence of a hyperstoichiometric PuO_{2+x} that could act as the precursor to corrosion.
- Oxidation may be being driven by changes in the defect chemistry of PuO_2 due to radioactive decay, in particular, the accumulation of Am.
- Americium exhibits complex chemistry with multiple oxidation states, some of which may promote the formation of PuO_{2+x}.

Ref B. Ao, R. Qiu, H. Lu, X. Ye, P. Shi, P. Chen, X. Wang, New Insights into the Formation of Hyperstoichiometric Plutonium Oxides, The Journal of Physical Chemistry, **119**, 101-108 (2015)

PLAN



1 Predict defect chemistry in PuO_2 as function of environmental variables.

2 Determine energies of Am incorporation into PuO_2 lattice for all possible oxidation states, allowing prediction of mode of incorporation.

3 Study whether the Am incorporation is capable of electrically activating PuO_2, informing whether this is a contributor to corrosion.

1 PREDICTING DEFECT CHEMISTRY IN PuO_2 AS FUNCTION OF ENVIRONMENTAL VARIABLES

i Determine formation energies for intrinsic defects in PuO_2:

- $O_i'', V_O^{\cdot\cdot}, Pu_i^{\cdot\cdot\cdot\cdot}, V_{Pu}''''$ + variations of these at varying charge states.
- Utilise LDA + U functional in *ab initio* simulation.

ii Combine DFT data with thermodynamics to predict defect chemistry in PuO_2 as function of environmental variables:

- Defect concentration:

$$c_i = m_i \exp\left(\frac{-\Delta G_f^i}{k_B T}\right)$$

Where:

$$\Delta G_f^i = \Delta E - T\Delta S + \sum_\alpha n_\alpha \mu_\alpha + q_i \mu_e$$

- The vibrational entropy change due to introduction of defects, ΔS, is obtained with empirical calculations, and combined with DFT effect energies.
- With UO_2, this approach led to improved replication of experimental data and the solving of the 'uranium vacancy problem' when combined with interstitial clusters.

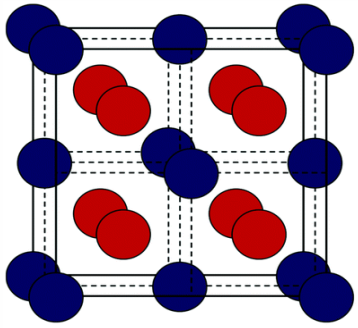
Ref A.Soulie, F. Bruneval, M. Marinica, S. T. Murphy, J. Crocombette, Influence of vibrational entropy on the concentrations of oxygen interstitial clusters and uranium vacancies on nonstoichiometric UO_2, Physical Review Materials, **2**, 083607 (2018)

1 PREDICTING DEFECT CHEMISTRY IN PuO_2 AS FUNCTION OF ENVIRONMENTAL VARIABLES

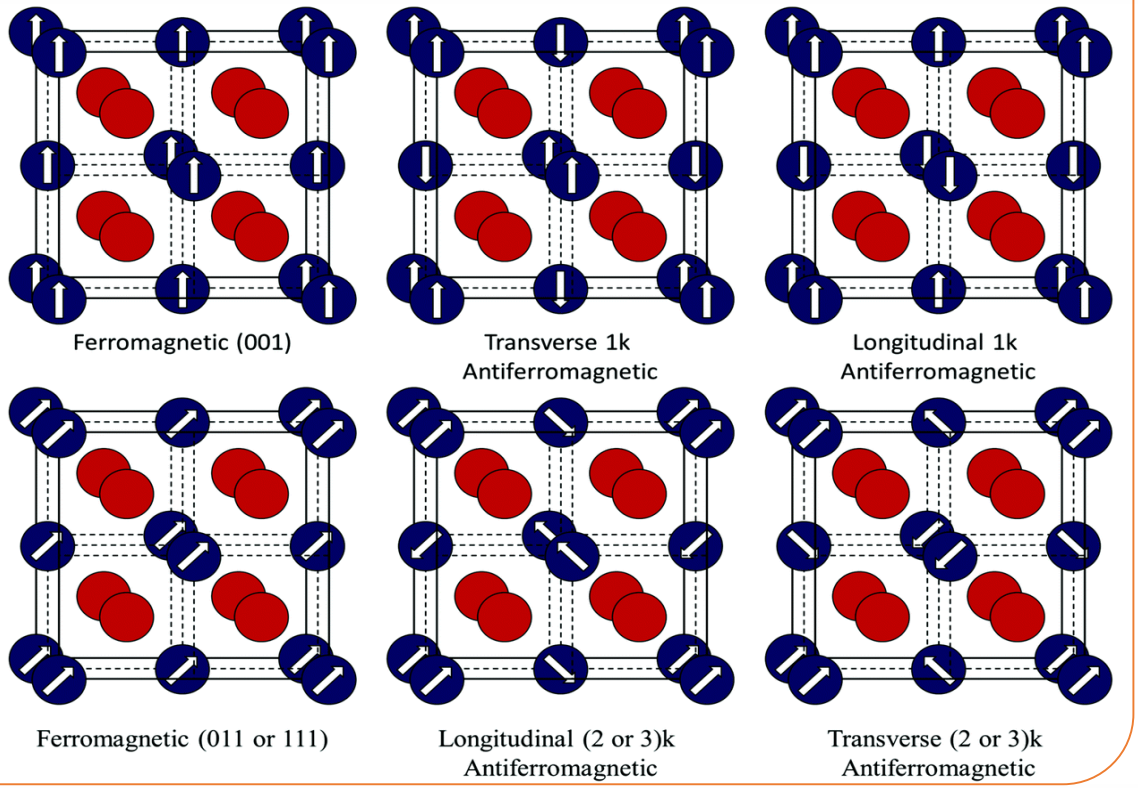
Considerations

- 2 x 2 x 2 supercells to be used, simulating 96 atoms.
- Magnetic order of PuO_2 to be considered.

- Diamagnetic ground-state traditionally inferred, however Pegg *et al* (2018) propose longitudinal 3k antiferromagnetic ground-state.



Diamagnetic



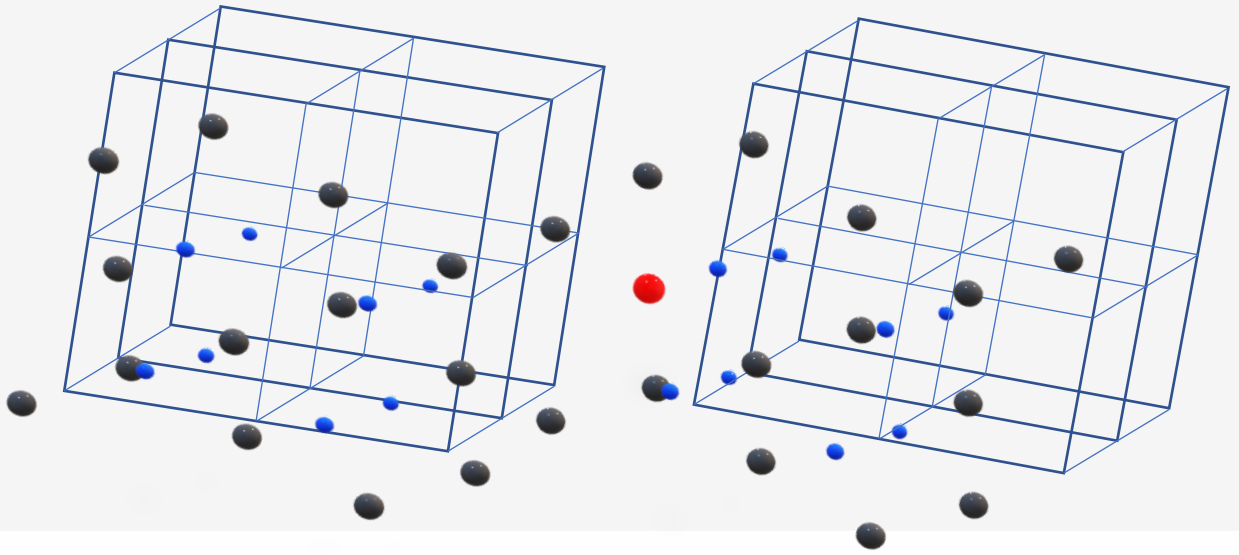
Ref J. T. Pegg, A. E. Shields, M. T. Storr, A. S. Wills, D. O. Scanlon, N. H. de Leeuw, Hidden magnetic order in plutonium dioxide nuclear fuel, Physical Chemistry Chemical Physics, **20**, 20943 (2018)

2 DETERMINE ENERGIES OF Am INCORPORATION INTO PuO_2 LATTICE

The energies of Am incorporation will be determined for all possible oxidation states, allowing prediction of:

- The mode of Am incorporation.
- Its oxidation state.
- The presence of charge compensating defects.

Depiction of PuO_2 fluorite cell:

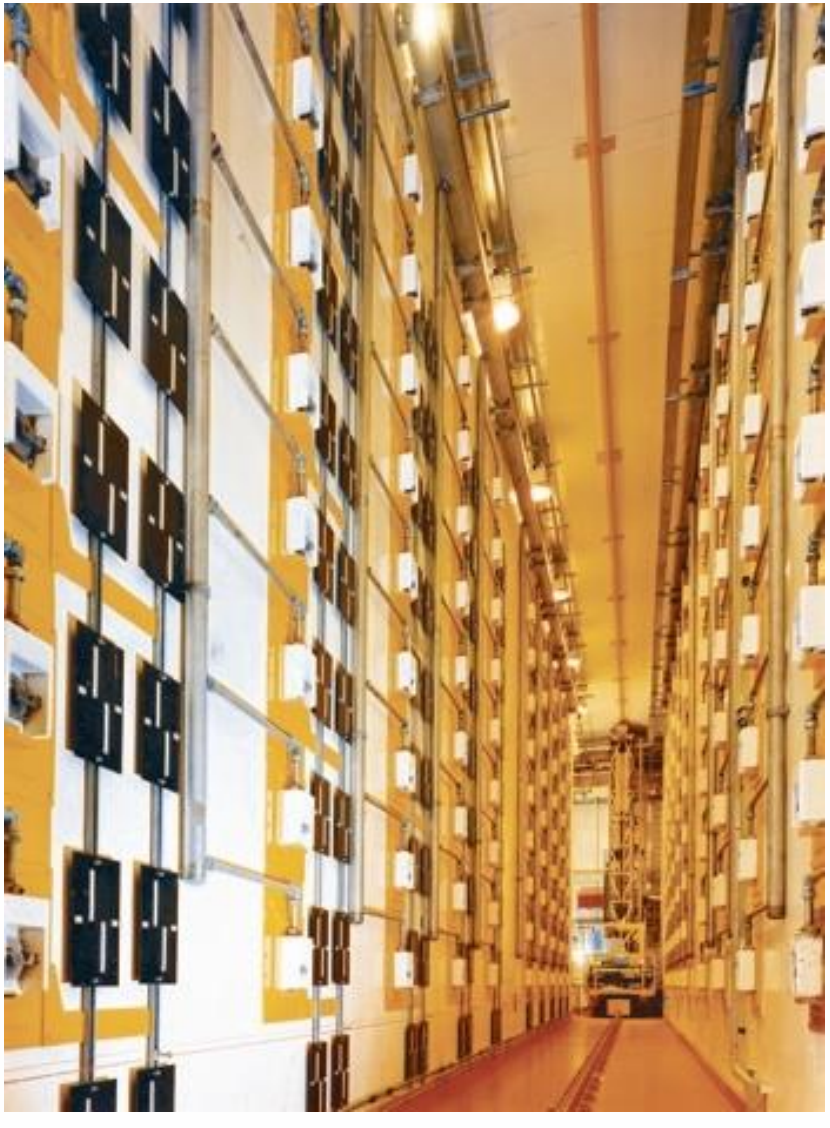


Black = Pu
Blue = O
Red = Am

3 IS INCORPORATION OF Am CAPABLE OF ELECTRICALLY ACTIVATING PuO_2

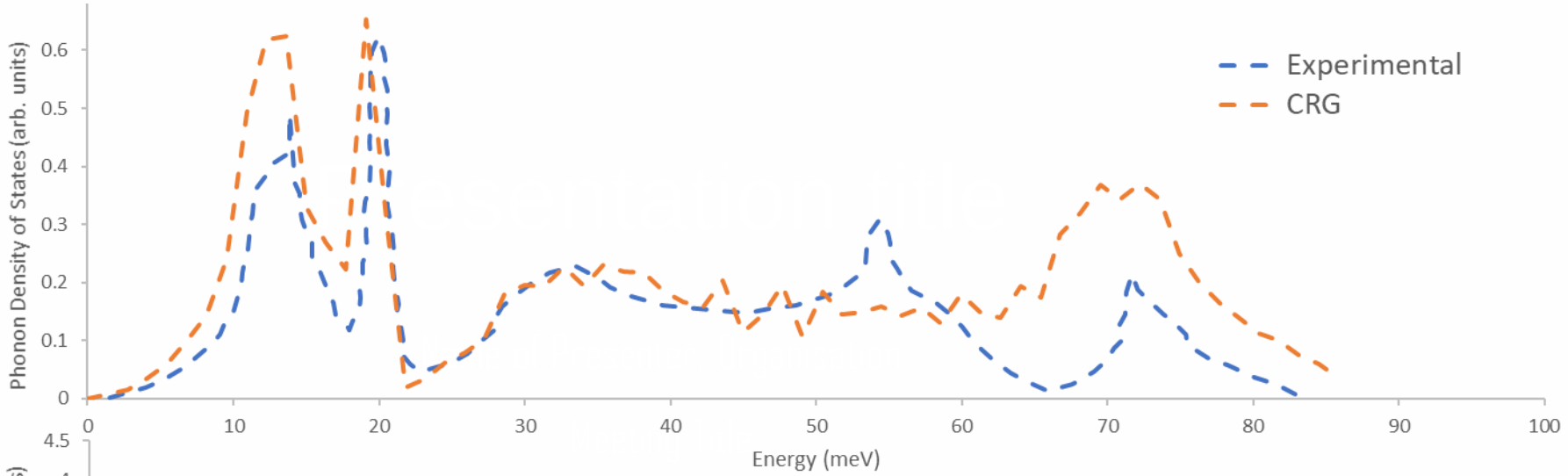
If Am incorporation found to be capable of electrically activating PuO_2, can begin to ask the following questions:

- What is the corrosion rate?
- What is the gas production rate?
- How does this impact the lifetime of the canisters?

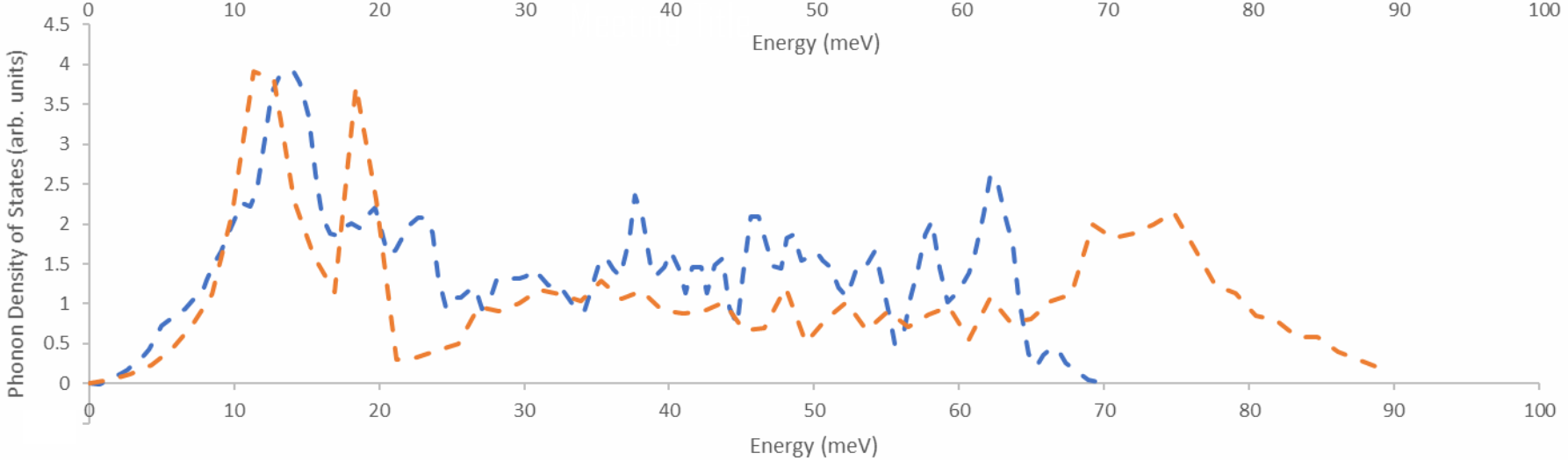


MODEL VALIDATION: Phonon DOS from experiment compared with the Cooper-Rushton-Grimes (CRG) potential

UO_2



PuO_2



UO_2 DATA W. K. Kim, J. H. Shim, M. Kaviany, UO_2 bicrystal phonon grain-boundary resistance by molecular dynamics and predictive models, International Journal of Heat and Mass Transfer, **100**, 243-249 (2016)
PUO_2 DATA M. E. Manley, J. R. Jeffries, A. H. Said, C. A. Marianetti, H. Cynn, B. M. Leu, M. A. Wall, Measurement of the phonon density of states of PuO_2 (+2% GA): A critical test of theory, Physical Review B, **85**, 132301 (2012)

MODEL VALIDATION: Lattice parameters & elastic constants of PuO_2

	Lattice constant (Å)	Bulk modulus (GPa)	Crystal Symmetry (Space group number)	Magnetic configuration
This work **(Empirical pair potential)**	5.38	225.16	$Fm\bar{3}m$ (225)	Diamagnetic
Experiment	5.395-5.398[1]	178-379[2]	$Fm\bar{3}m$ (225)	Exp.
PBEsol +U[2] **(Density Functional Theory with Hubbard correction)**	5.415	215	$Fm\bar{3}m$ (225)	Longitudinal 3k antiferromagnetic

[1] J. T. Pegg, A. E. Shields, M. T. Storr, A. S. Wills, D. O. Scanlon, N. H. de Leeuw, Hidden magnetic order in plutonium dioxide nuclear fuel, Physical Chemistry Chemical Physics, **20**, 20943 (2018)
[2] J. M. Haschke, T. H. Allen, L. A. Morales, Reaction of Plutoonium Dioxide with Water: Formation and Properties of PuO_{2+x}, Science, **287**, 285-287 (2000)

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Transformative Science and Engineering for Nuclear Decommissioning

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Transformative Science and Engineering for Nuclear Decommissioning

Atomistic Simulation of the ageing of PuO_2

Elanor Murray, University of Birmingham

TRANSCEND Theme meeting

12th November 2019
Lancaster

Energy
For a Low Carbon Future

About me…

- BSc Natural Sciences: Physics and Chemistry
- MSc Nuclear Decommissioning and Waste Management
- MSc project at Tradebe in Winfrith

- Now: ‘Atomistic Simulation of the ageing of PuO_2’

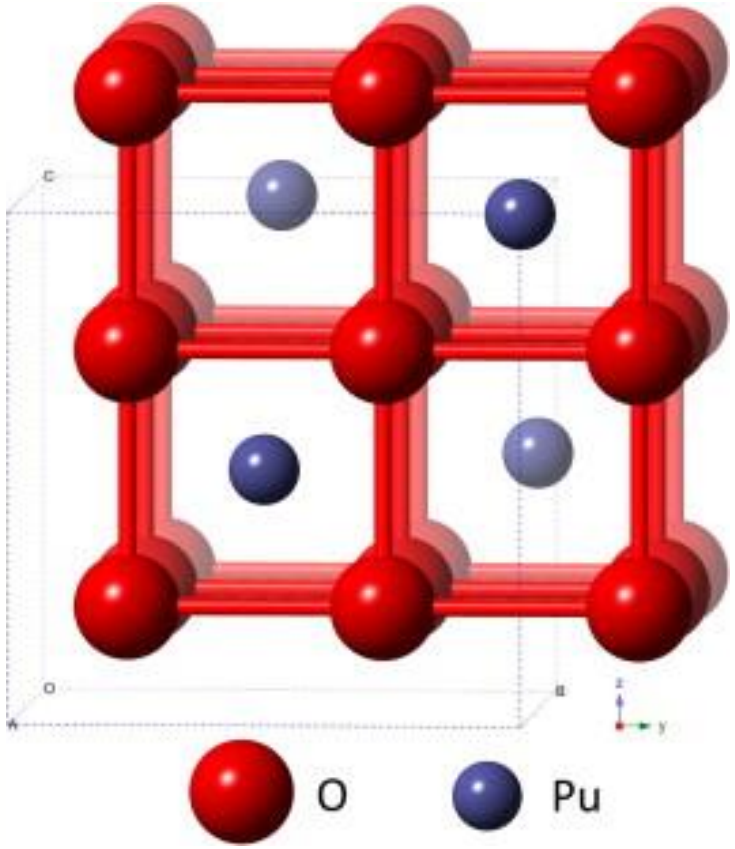
  Supervisor: Dr Mark Read

  School of Chemistry

Stockpile


HOUSES OF PARLIAMENT
PARLIAMENTARY OFFICE OF SCIENCE & TECHNOLOGY
POSTNOTE
Number 531 September 2016
Managing the UK Plutonium Stockpile
93
Np
[237]
plutonium
94
Pu
[244]
americium
95
Am
[243]
Overview
The UK is storing the largest 'separated' civil plutonium stockpile in the world. This poses safety, security and cost challenges.
The Nuclear Decommissioning Authority is assessing long term options for managing the stockpile with industry pushing for a timetable for the selection and delivery of an

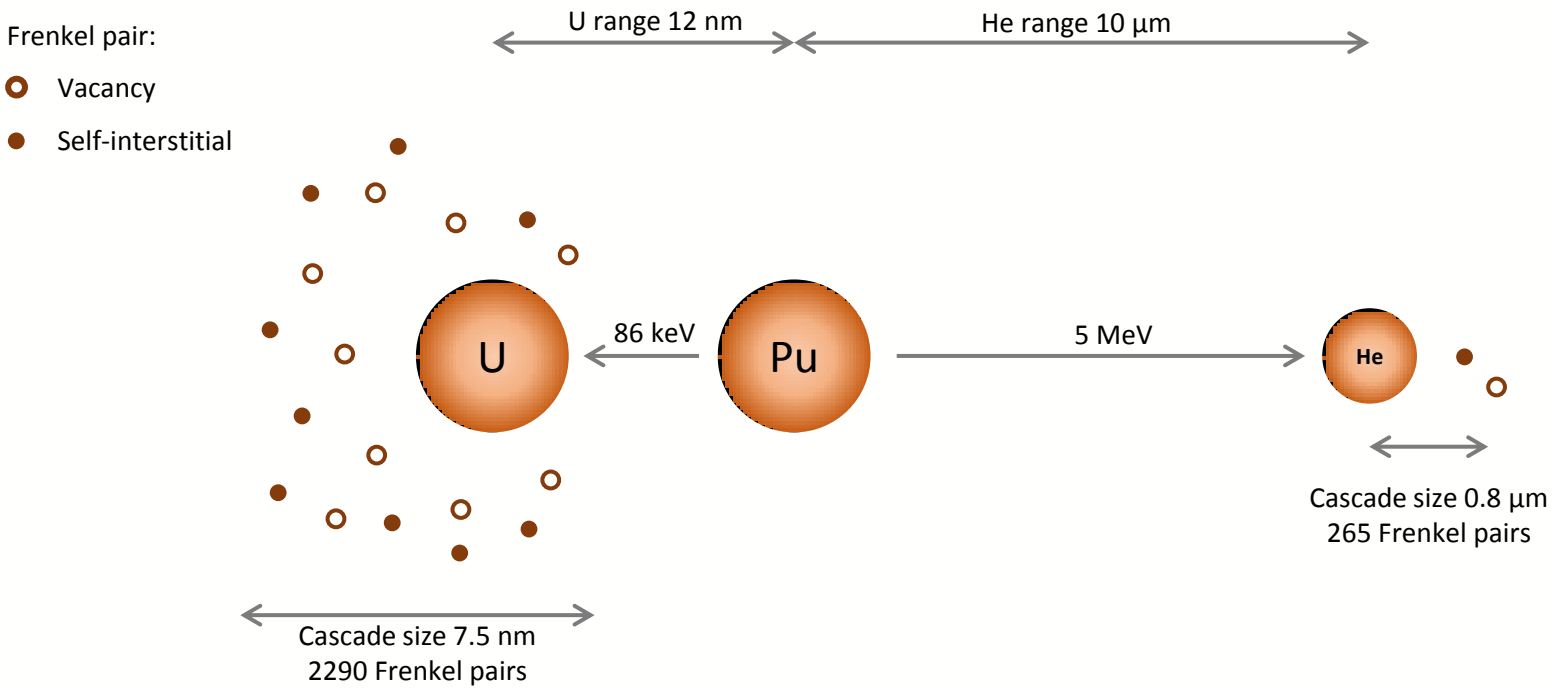
Plutonium Dioxide



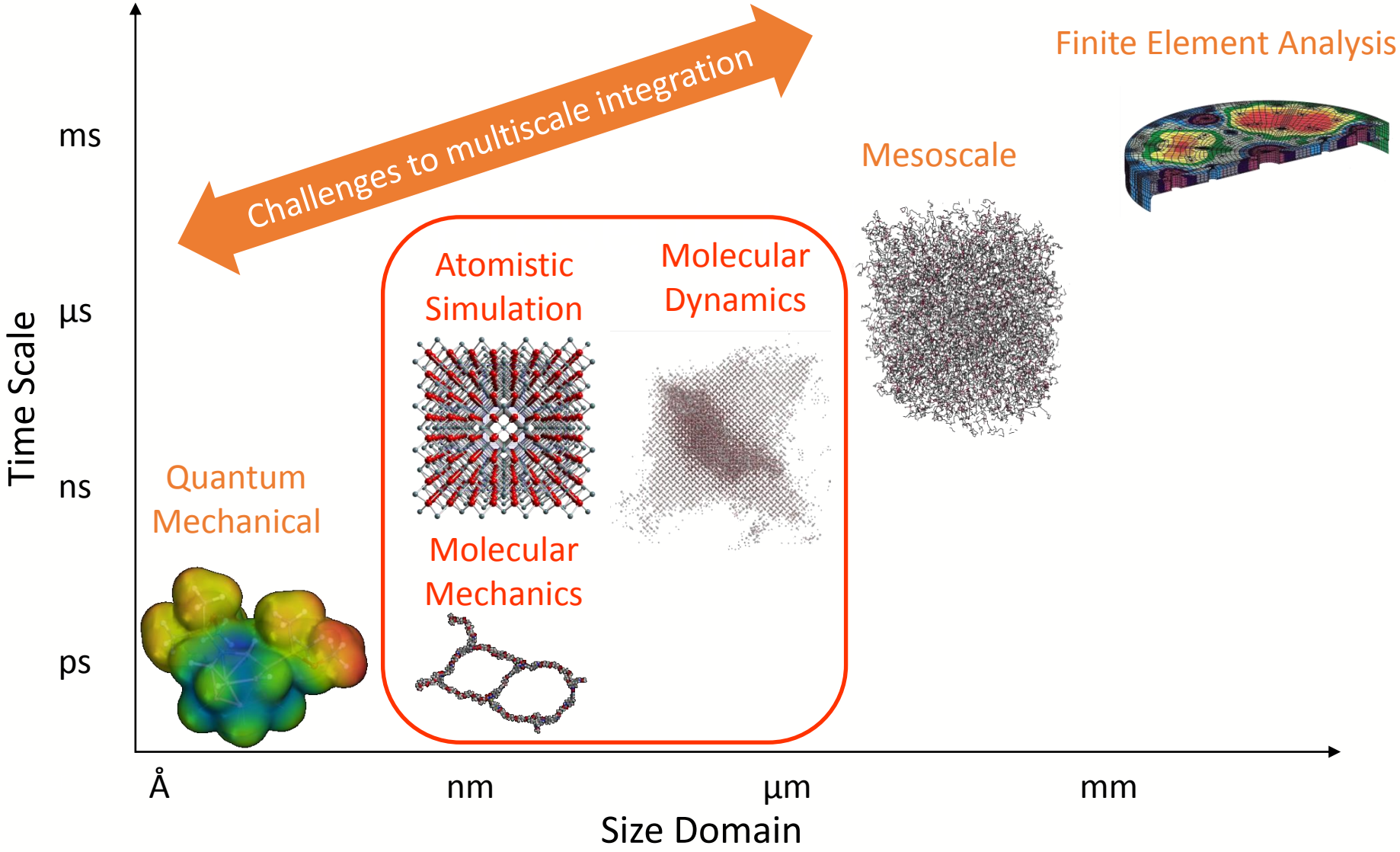
Ref: *Read MSD, Jackson RA. Journal of Nuclear Materials. 2010;**406(3)**:293*

Ageing Effects in Plutonium

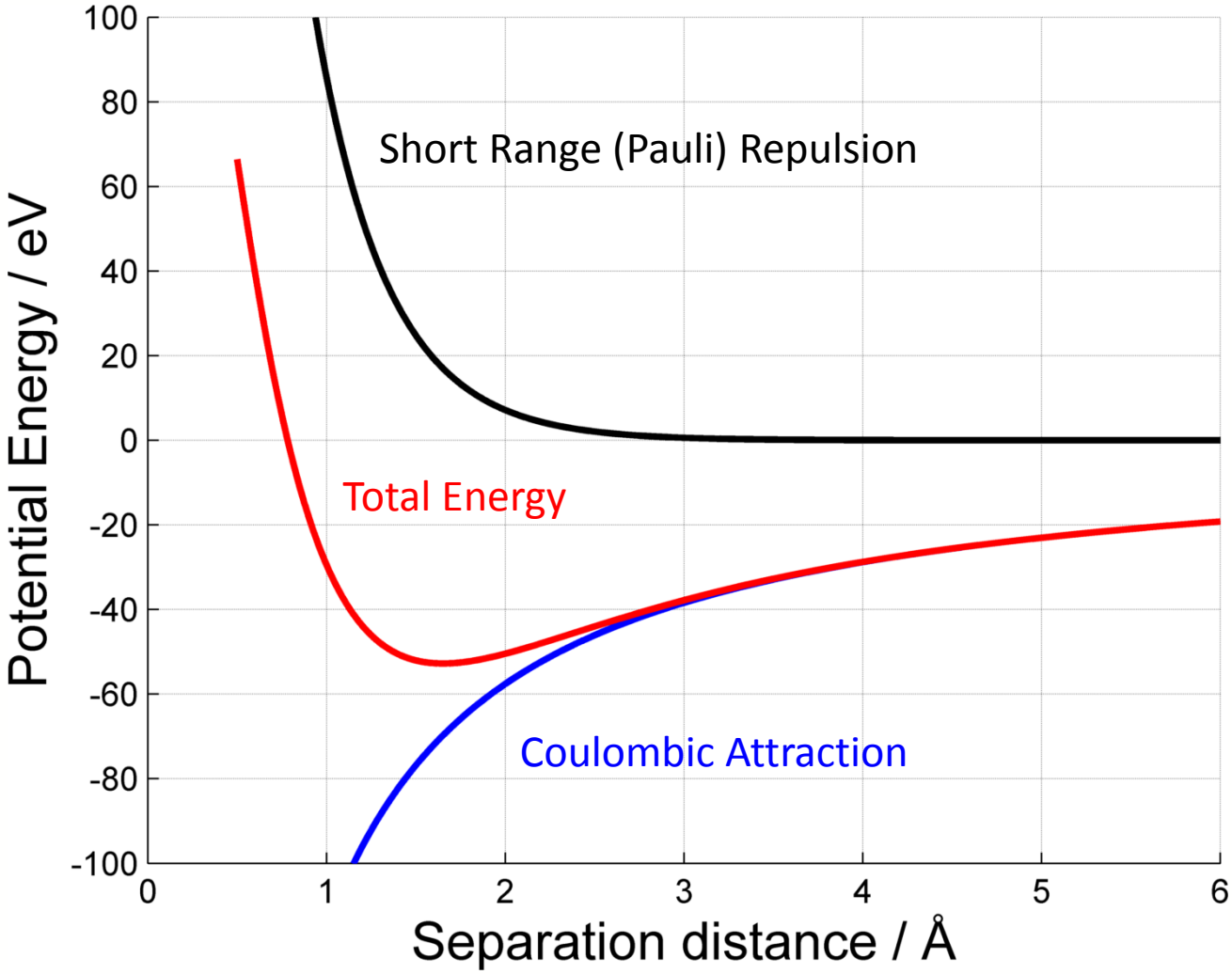
- Lattice damage
- Helium bubble in-growth
- Potential void swelling



Modelling scales and regimes



The Potential Model



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

The Potential Model

- The short range potential

The Lennard-Jones Potential:

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

The Morse Potential:

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

Buckingham potential:
Suitable for ionic solids

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

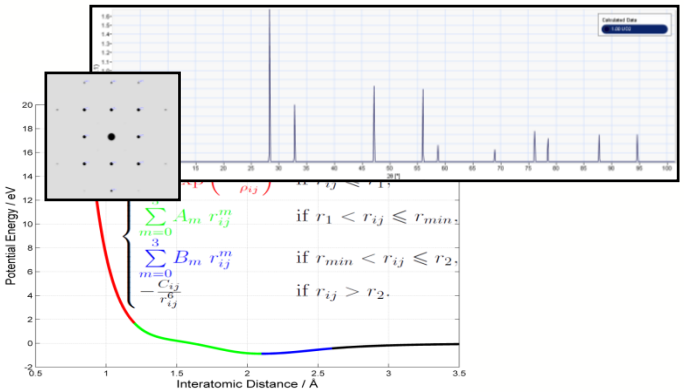
GULP overview

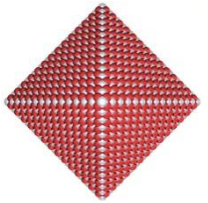
Crystal Structure
'Force Field'

Initial position of ions
Forces acting between them

GULP

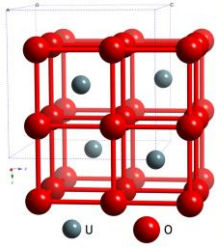
Geometry optimise
Final position of ions
Predict properties





Geometry Optimised
Crystal Structure

Physical Properties:
Mechanical
Optical



Potential Evaluation for PuO_2

Property		Calculated	Experimental	Δ%
Lattice Constant	a_0 (Å)	5.398117	5.39819[a]	-0.001
Ionic Distances	Pu^{4+} - Pu^{4+} (Å)	3.817	3.816[b]	0.026
	Pu^{4+} - O^{2-} (Å)	2.3375	2.337[b]	0.021
	O^{2-} - O^{2-} (Å)	2.6991	2.698[b]	0.041
Elastic Constant Matrices	C_{11} (GPa)	408.557	430.6[b]	-5.119
	C_{12} (GPa)	130.2112	128.4[b]	1.411
	C_{44} (GPa)	67.3014	67.3[b]	0.002
Bulk Modulus	B (GPa)	222.99314	-	-
Shear Modulus	K (GPa)	84.8231	-	-
Youngs Moduli	Y (GPa)	345.6173	-	-
Static dielectric constant tensor	ε_0	15.91823	-	-
High frequency dielectric constant tensor	ε_∞	3.22557	-	-

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

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

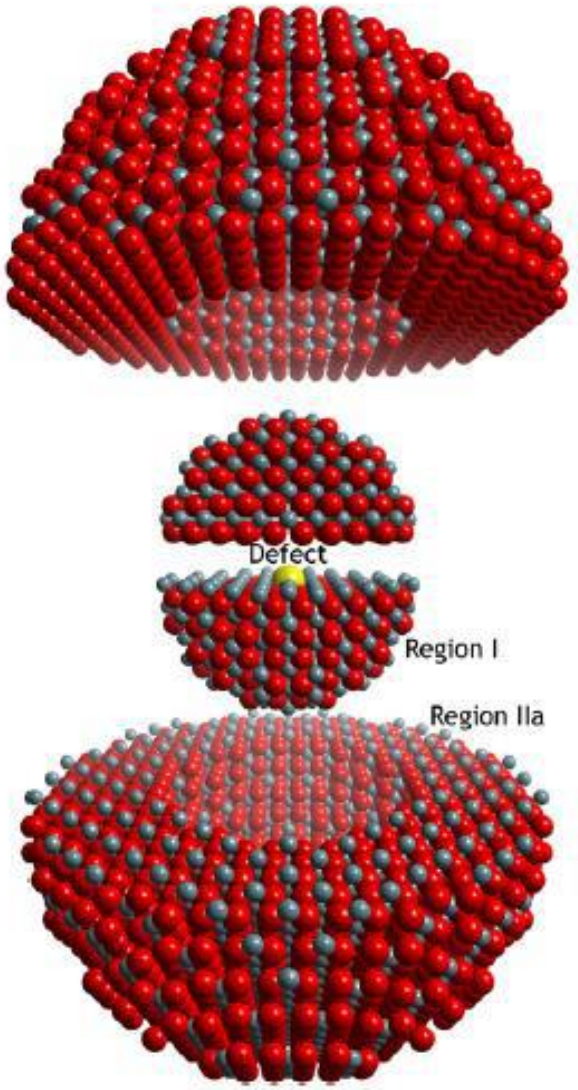
Mott - Littleton

Divide the defective lattice into two regions:

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

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

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



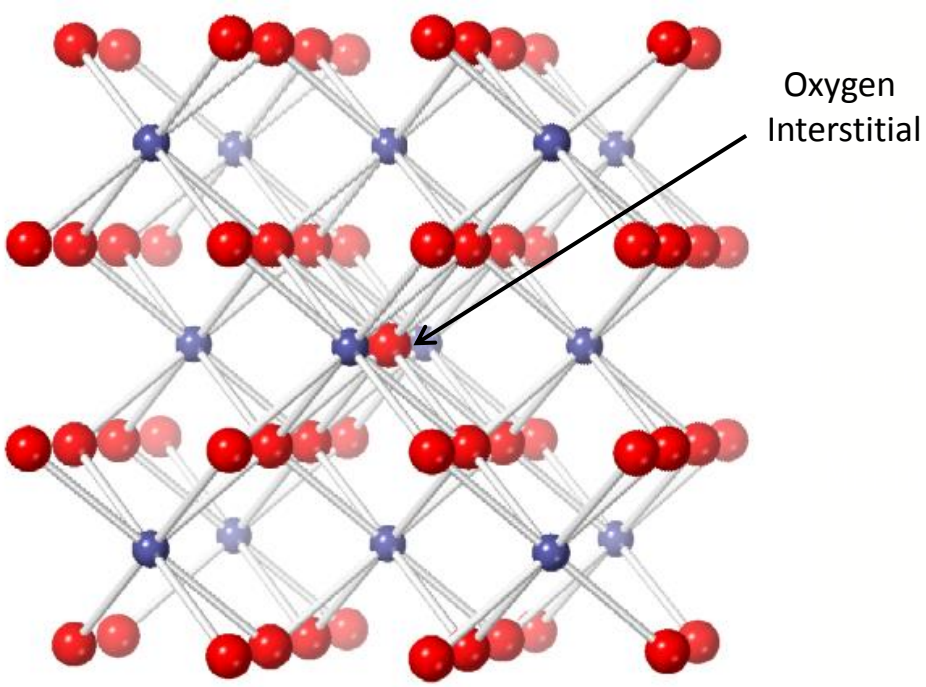
Ref: *Read MSD, Jackson RA. Journal of Nuclear Materials. 2010;**406(3)**:293*

Defect Formation Energies for Isolated Defects

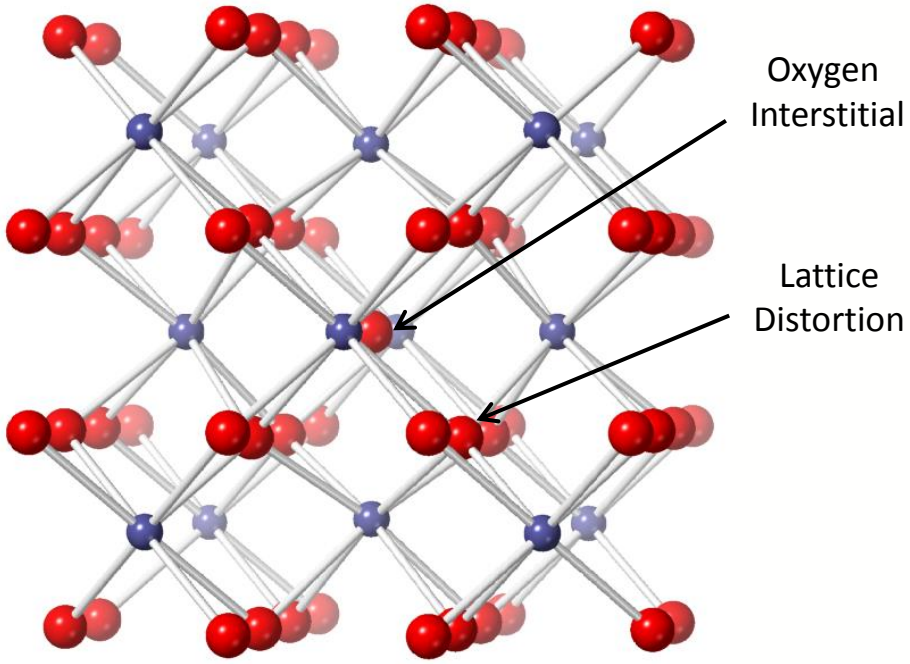
Point Defect		Position	Formation energy (eV)
Plutonium vacancy	$V_{Pu}^{''''}$	(0, 0, 0)	80.03
Oxygen vacancy	$V_O^{\bullet\bullet}$	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	17.09
Plutonium interstitial	$Pu_i^{\bullet\bullet\bullet\bullet}$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	-59.97
Oxygen interstitial	O_i''	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	-11.75

Plutonium and Oxygen interstitials were placed in octahedral holes.

Oxygen Interstitial Visualisation



Unrelaxed structure



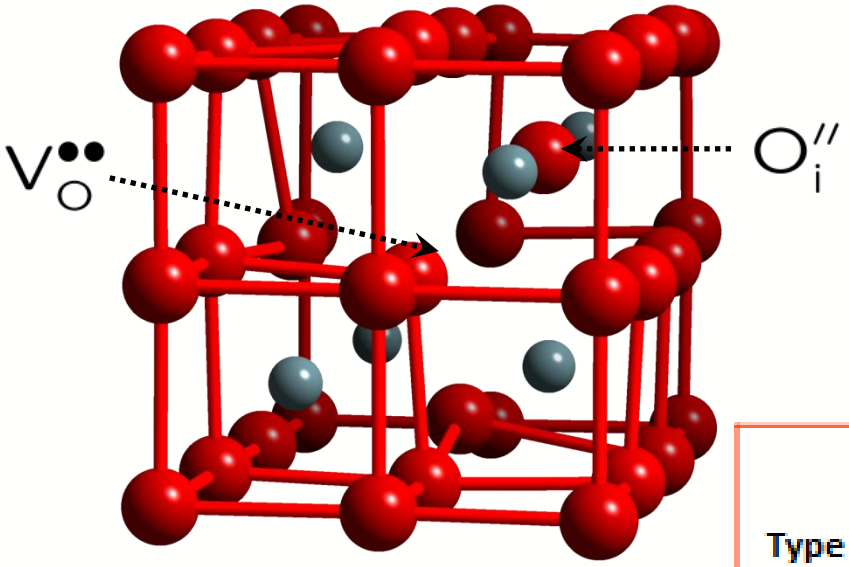
Relaxed structure

Unbound Defect Formation Energies

Bound Defect	Formation reaction	Formation Energy (eV/Defect)
Schottky Trio	$Pu_{Pu}^{x} + 2O_o^{x} \rightleftharpoons V_{Pu}^{''''} + 2V_o^{\bullet\bullet} + PuO_{2\ (surface)}$	3.545
Oxygen Frenkel Pair	$O_o^{x} \rightleftharpoons V_o^{\bullet\bullet} + O_i^{''}$	2.668
Plutonium Frenkel Pair	$Pu_{Pu}^{x} \rightleftharpoons V_{Pu}^{''''} + Pu_i^{\bullet\bullet\bullet\bullet}$	10.029

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

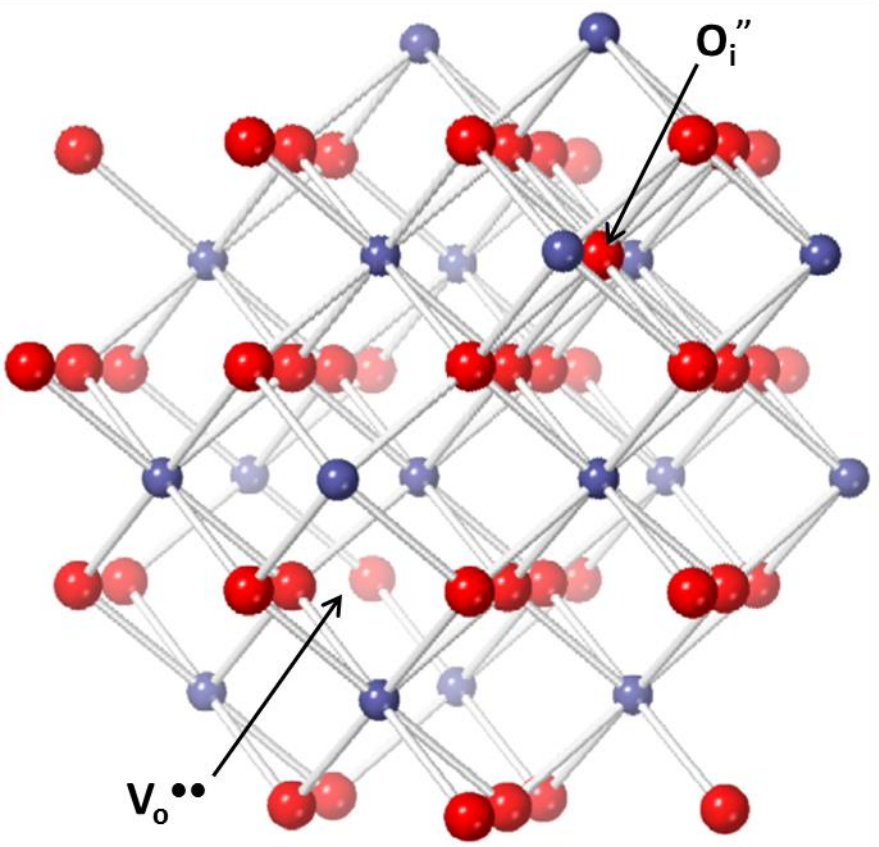
Oxygen Frenkel Pair Configurations



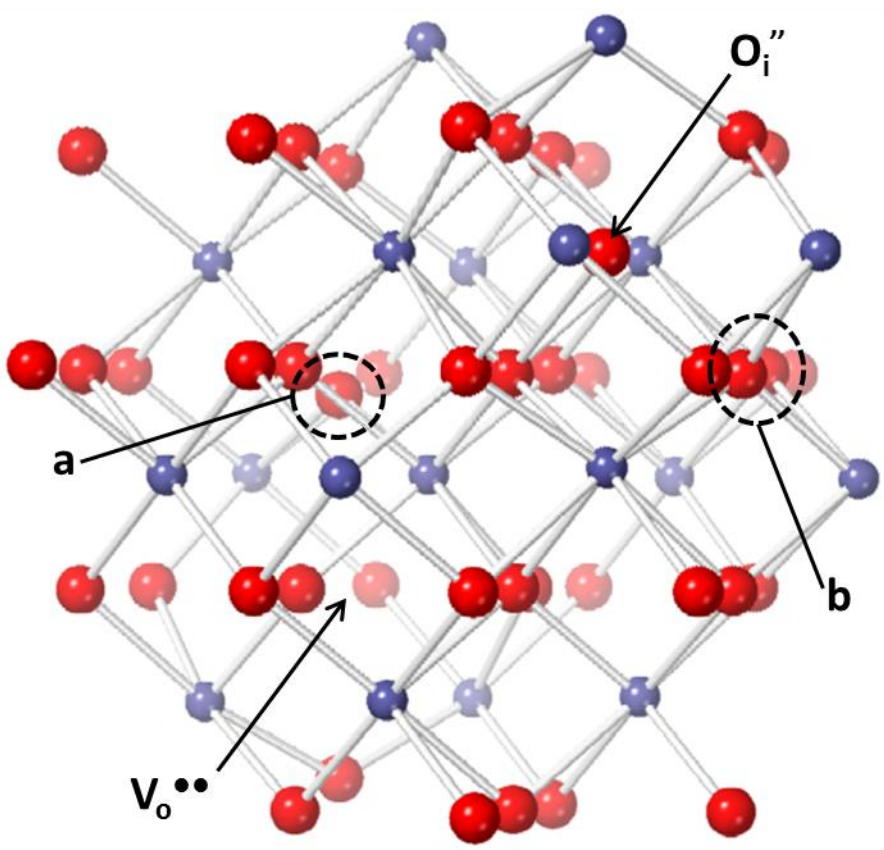
To prevent recombination, oxygen defects are separated by a plutonium ion.

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

Oxygen Frenkel Pair Configurations

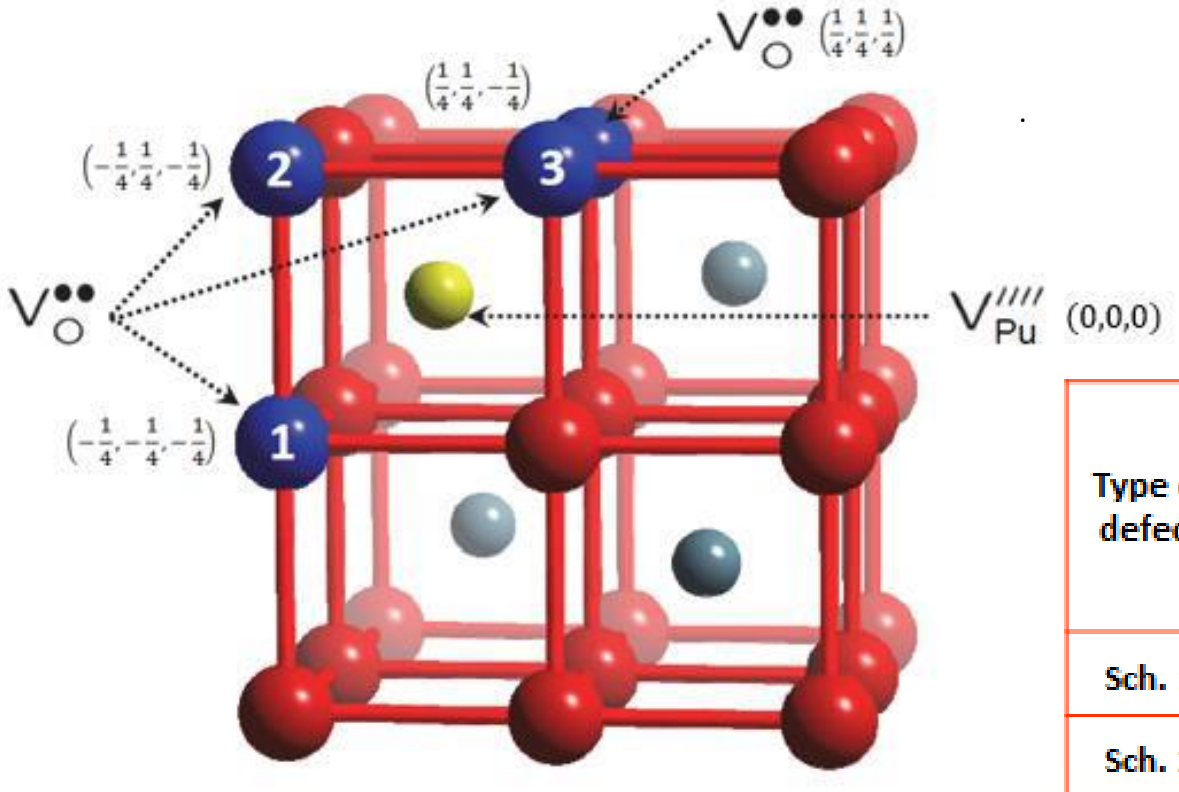


Unrelaxed structure



Relaxed structure

Schottky Defect Configurations

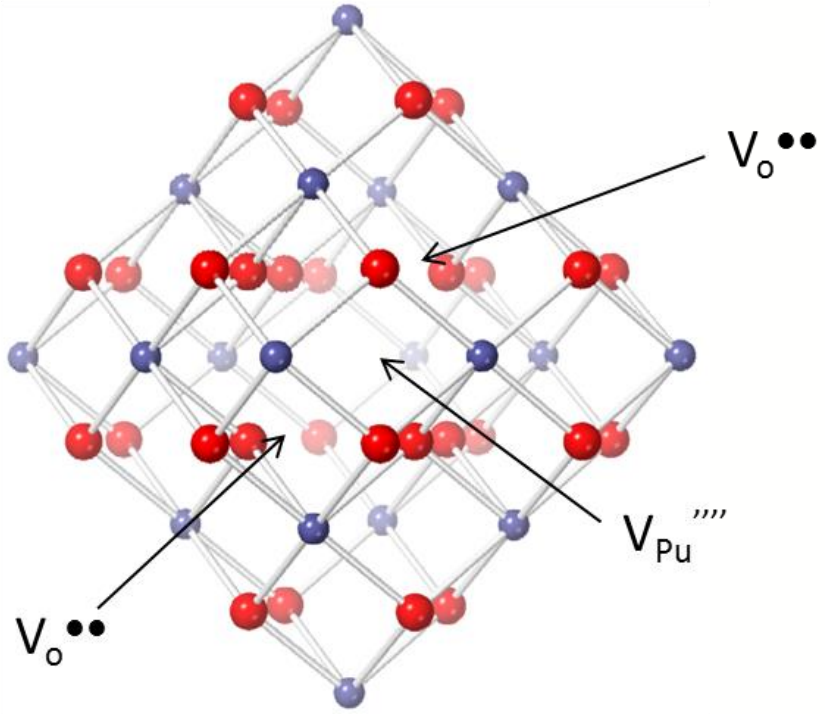


Compared the three different Schottky configurations.

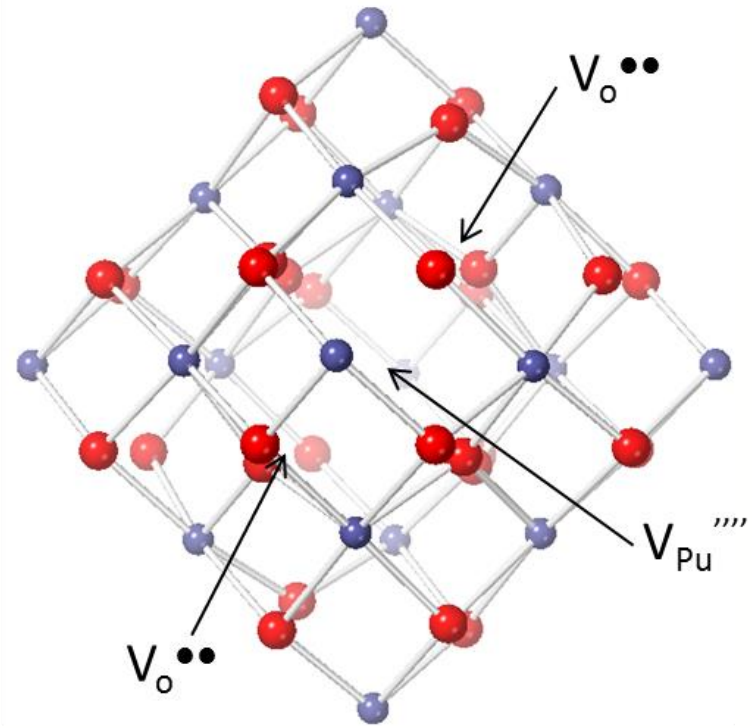
Type of defect	Second $V_O^{\bullet\bullet}$ position	Formation energy (eV)	Formation energy (eV/Defect)	Binding energy (eV/Defect)
Sch. 1	$(-\frac{1}{4},-\frac{1}{4},-\frac{1}{4})$	109.363	1.929	-1.616
Sch. 2	$(-\frac{1}{4},\frac{1}{4},-\frac{1}{4})$	109.369	1.931	-1.614
Sch. 3	$(-\frac{1}{4},\frac{1}{4},\frac{1}{4})$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

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

Schottky Defect Configurations



Unrelaxed structure



Relaxed structure

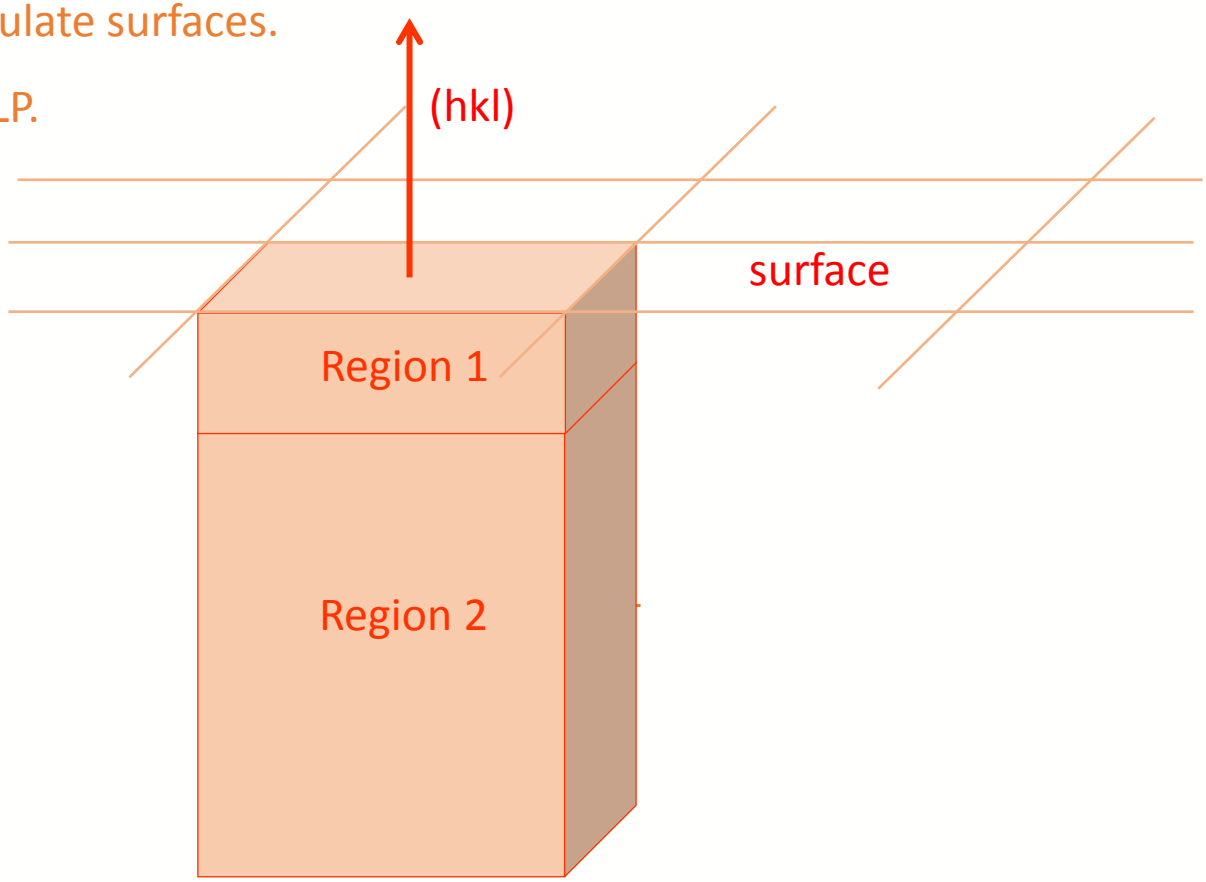
Intrinsic Defect Energies

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

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

Surface Simulations

- Have begun using METADISE to simulate surfaces.
- Using the same potentials as in GULP.



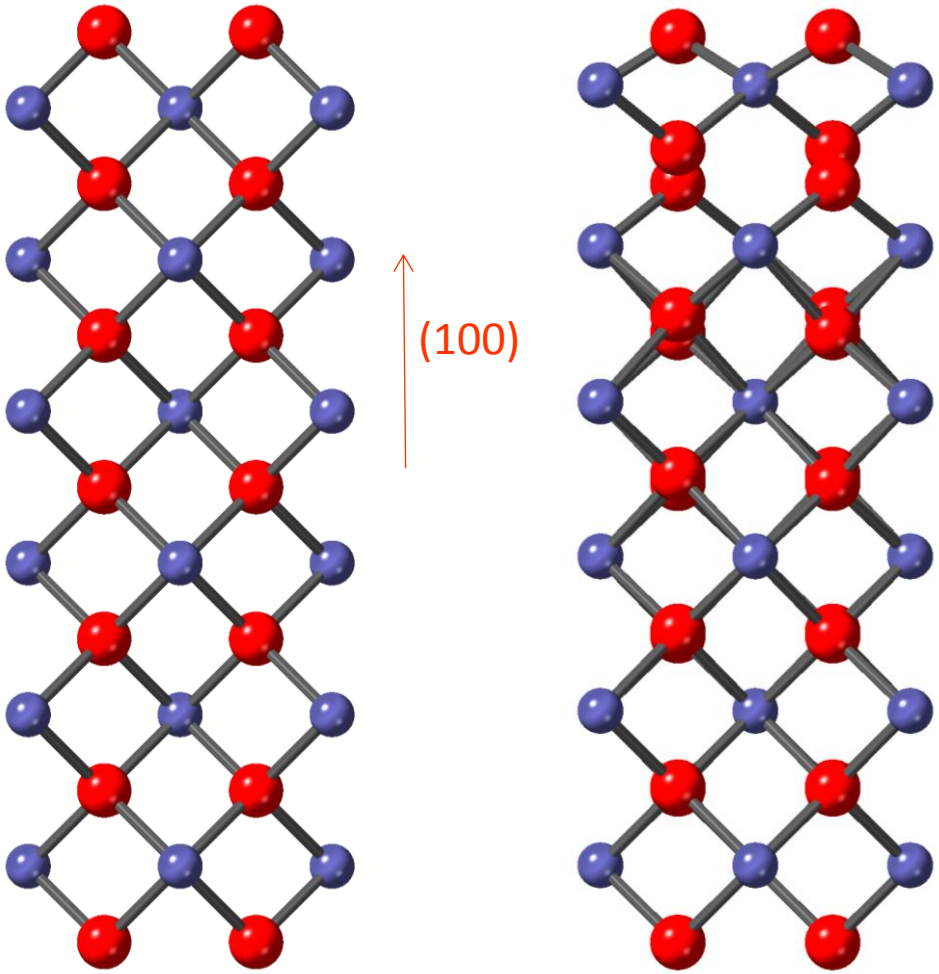
Pure Surface Simulations

h	k	l	Unrelaxed E_{surf} (Jm^{-2})	Relaxed E_{surf} (Jm^{-2})	% ΔE_{surf} relaxation
1	0	0	6.3092	2.40634	-61.86
1	1	0	3.36026	1.79074	-46.71
1	1	1	1.67001	1.20452	-27.87
2	1	0	10.1207	2.57971	-74.51
2	1	1	6.55974	2.02959	-69.06
2	2	1	6.84231	1.94249	-71.61
3	1	0	11.10917	2.79665	-74.83
3	1	1	7.45802	2.29264	-69.26
3	3	1	2.91388	1.53115	-47.45

- Modelled the {*n*10}, {*n*11} and {*nn*1} surfaces. Where *n*=1,2,3.
- Found the {*nn*1} surfaces to be the most energetically stable.

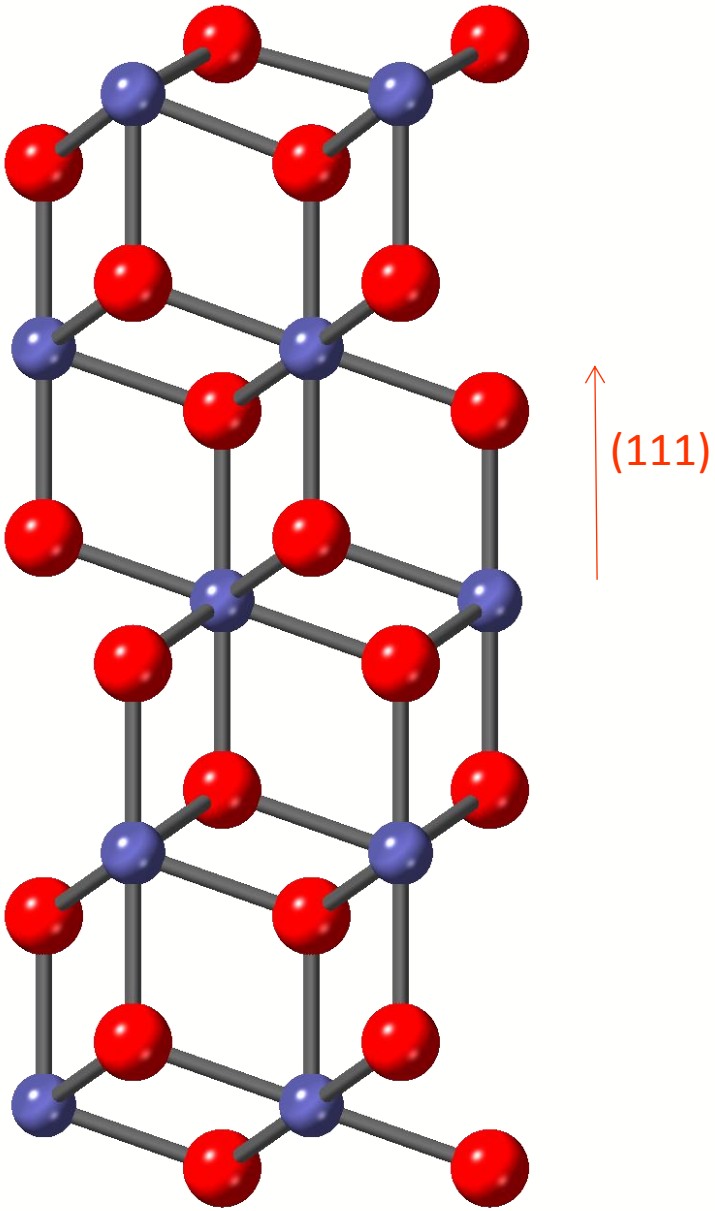
100

- Less stable surfaces had greater surface relaxation.



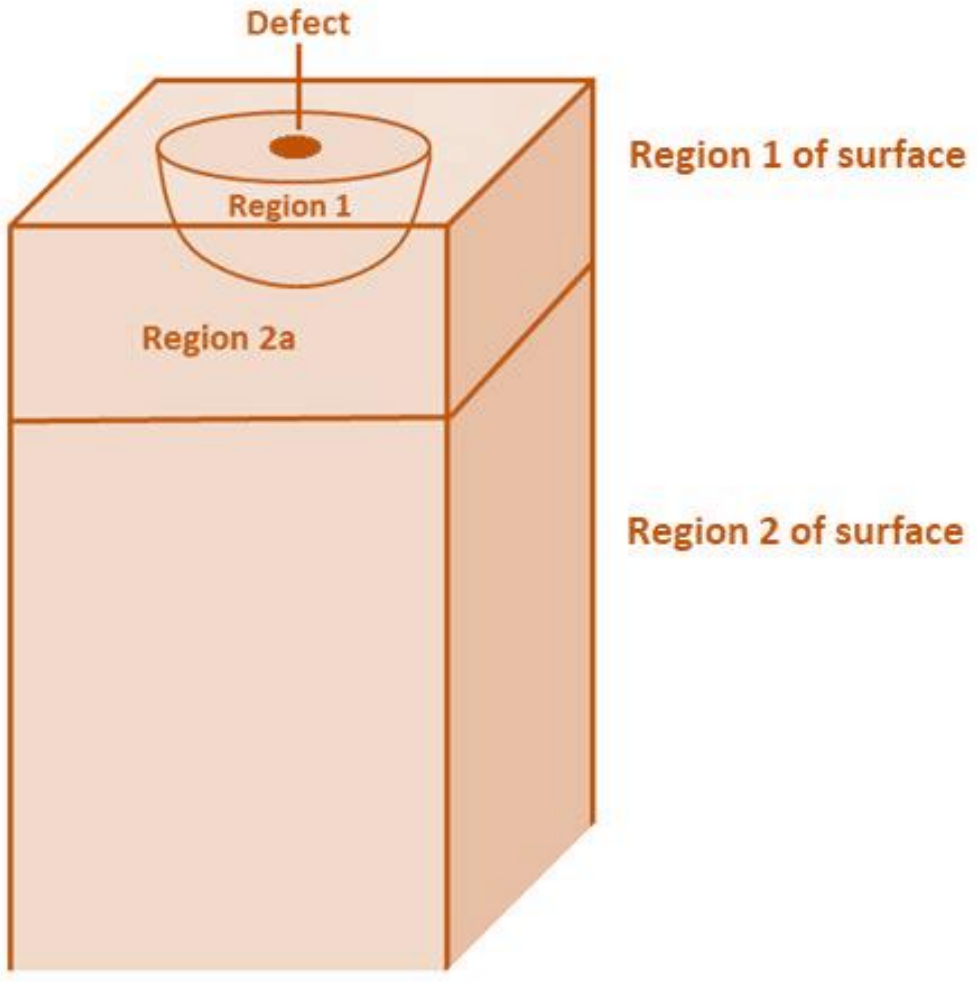
111

- Structure of the (111) surface which is the most energetically stable surface.



Defective Surfaces

- Run defect calculations for surfaces.
- Calculate segregation energies.
- Investigate extended defects such as grain boundaries.



Future work

- Begin simulation of defective surface structures.
- Investigate helium migration pathways.

Thanks to

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Safe Interim Storage of plutonium:

Helium sequesteration onto PuO_2 analogues

Oxygen and hydrogen recombination on PuO_2 surfaces

Transcend Research Consortium

Dr. Dominic Laventine, Prof. Colin Boxall
Lancaster University

Energy For a Low Carbon Future

UTGARD LABORATORY

Lancaster University

NATIONAL NUCLEAR LABORATORY

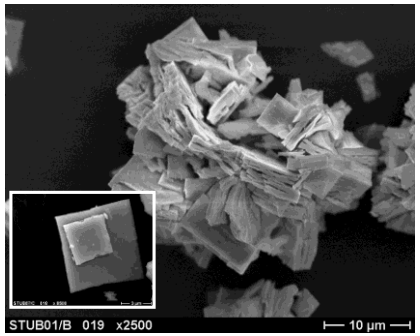
Lloyd's Register Foundation

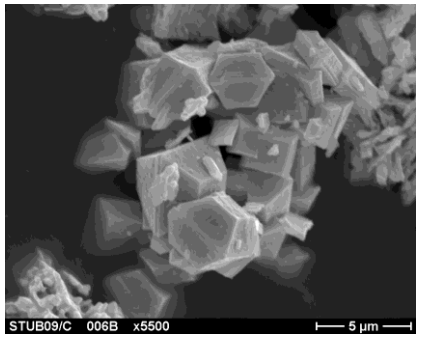
- Introduction to UK plutonium interim storage
- Helium sequesteration onto PuO_2 analogues
- Oxygen and hydrogen recombination on PuO_2

- **Introduction to UK plutonium interim storage**
- Helium sequesteration onto PuO_2 analogues
- Oxygen and hydrogen recombination on PuO_2

Separation, Reprocessing and Interim Storage in the UK

- Reprocessing of spent fuel allows the separation of plutonium from uranium and other species
- PUREX process co-extracts Pu and U as nitrates into an acidified raffinate.
- In the UK, further separation of Pu from the U performed at:
  - THORP reprocessing plant (due to close 2018) by hydrazine reduction of the plutonium
  - Magnox reprocessing plant (due to close 2020)





- *Ca.* 250 tonnes of separated Pu currently stockpiled worldwide. Approx. 137 tonnes is in interim storage in UK whilst the Government "develops its options".
- Interim storage of PuO_2 involves sealing in nested steel containers, under a partial argon atmosphere with (PVC) packing material.
- During storage the radioactivity of the plutonium results in heating of the canisters to an estimated central line temperature of 600°C.

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Cannister pressurisation

Over time a small number of cannisters have been observed to deform due to pressurisation: this makes storage and efficient heat transfer difficult 5 routes to gas production have been suggested that could contribute to this pressurisation:

(i) Helium accumulation from a decay
(ii) Decomposition of polymeric packing material
(iii) H_2O desorption (steam) from hygroscopic PuO_2
(iv) Radiolysis of adsorbed water
(v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a PuO_{2+x} phase.

PuO_2 is hydroscopic and picks up water during the packaging process. The disposition of this water under the storage conditions is unclear: It may exists in a gaseous state, or be weakly or strongly bound to the PuO_2 surface.

Radiolytic and catalytic processes on bound water may also result in formation of radicals (e.g. H., HO.) and other chemical species (e.g. H_2, O_2, H_2O_2).

Gaseous O_2 and H_2 may also be consumed by catalytic processes, or absorbed into the PuO_2 matrix.

- Introduction to UK plutonium interim storage
- **Helium sequesteration onto PuO_2 analogues**
- Oxygen and hydrogen recombination on PuO_2

He sequesteration: introduction

(i) Helium accumulation from a decay
(ii) Decomposition of polymeric packing material
(iii) H_2O desorption (steam) from hygroscopic PuO_2
(iv) Radiolysis of adsorbed water
(v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a PuO_{2+x} phase.

Alpha decay of Pu produces alpha particles, which can then be trapped as He.

Pu-238 → U-235 + He
Pu-239 → U-235 + He
Pu-240 → U-235 + He
Pu-242 → U-235 + He
Pu-241 → Am-241 → Np-237 + He

The total amount of helium produced over time can be easily calculated if the isotopic ratio of Pu sample is known. However, some proportion of the He will be sequestered within: 1) interstitial spaces 2) pores

This entrapped He does not contribute to pressurisation, therefore the amount sequested needs to be known to predict canister pressures.

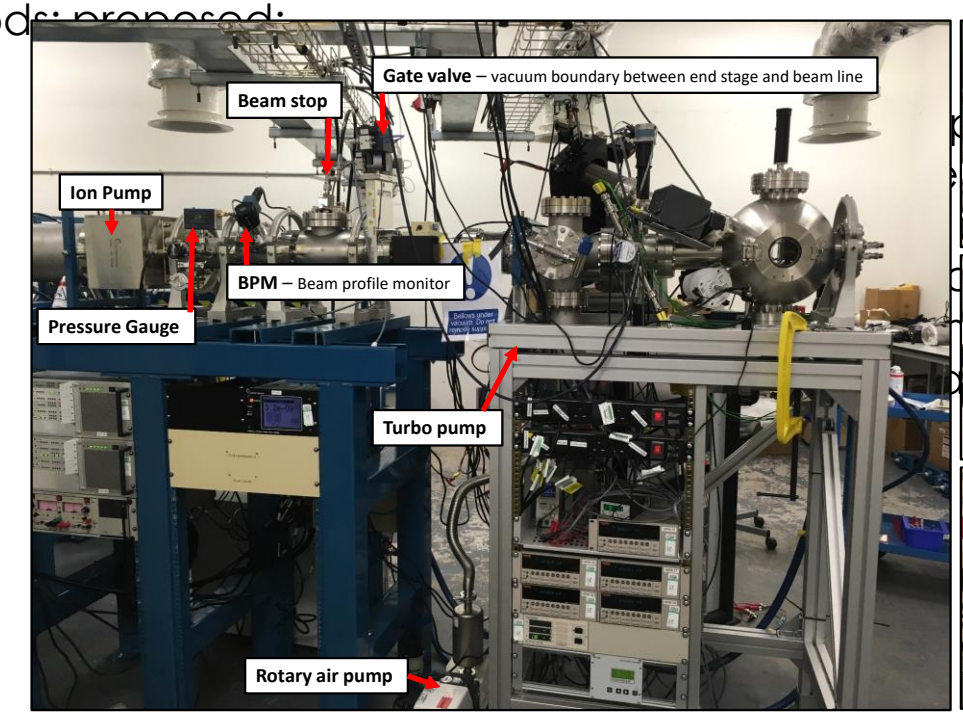
Some of the sequestered He could possibly escape over time, with the thermodynamics and kinetic of these desorption processes will deirmine the eventual pressures developed.

He sequesteration: implantation methods

In order to measure He desorption, first need to implant He into samples

CeO_2 used as a non-active surrogate for PuO_2

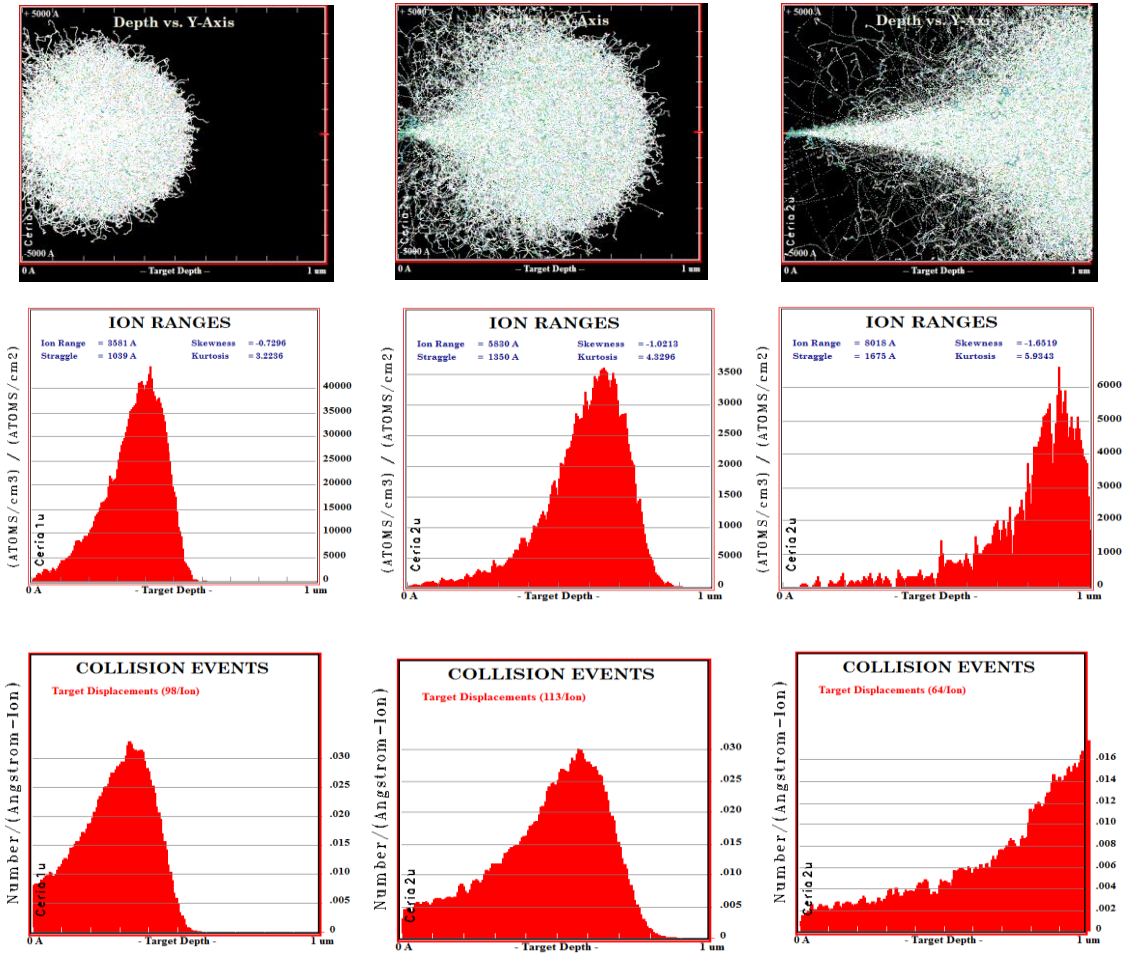
Two methods proposed:

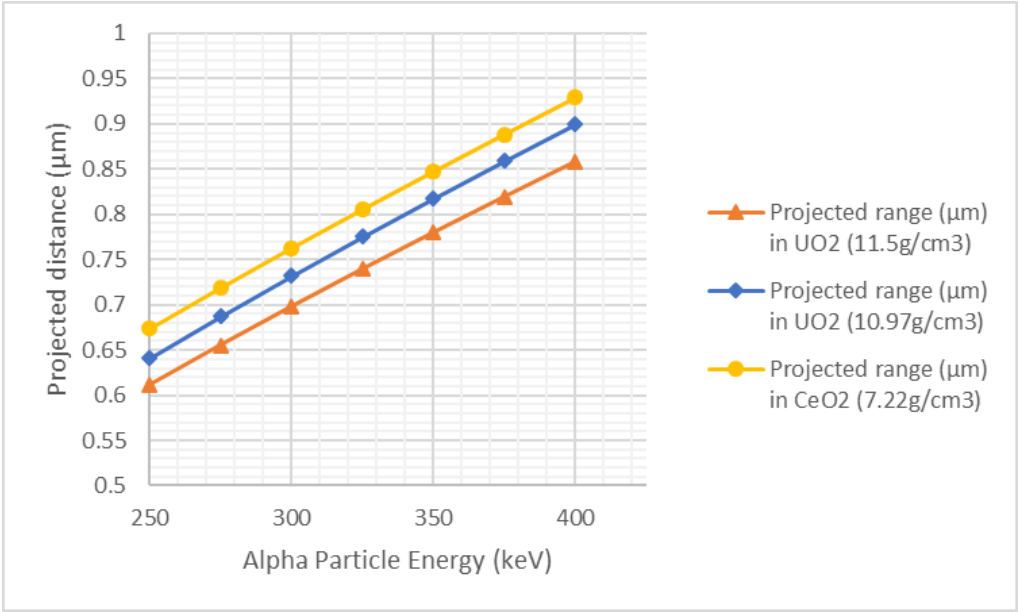


Elements of the beamline, including the high vaccum pumps

He sequesteration: Turing ion beam energies

100 keV 200 keV 500 keV





He sequesteration: implantation methods

Measure desorption rates as a function of temperature and pressure.

Two methods: proposed:

1) TGA-MA. Powder samples implanted with He can be heated to up to 1100°C and the amounts of He (or other gases) released monitored by MS.

2) QCM. Thin layer samples can be heated to 600°C and the change in mass due to He desorption directly measured.

- Introduction to UK plutonium interim storage
- Helium sequesteration onto PuO_2 analogues
- **Oxygen and hydrogen recombination on PuO_2**

O_2 / H_2 recombination: introduction

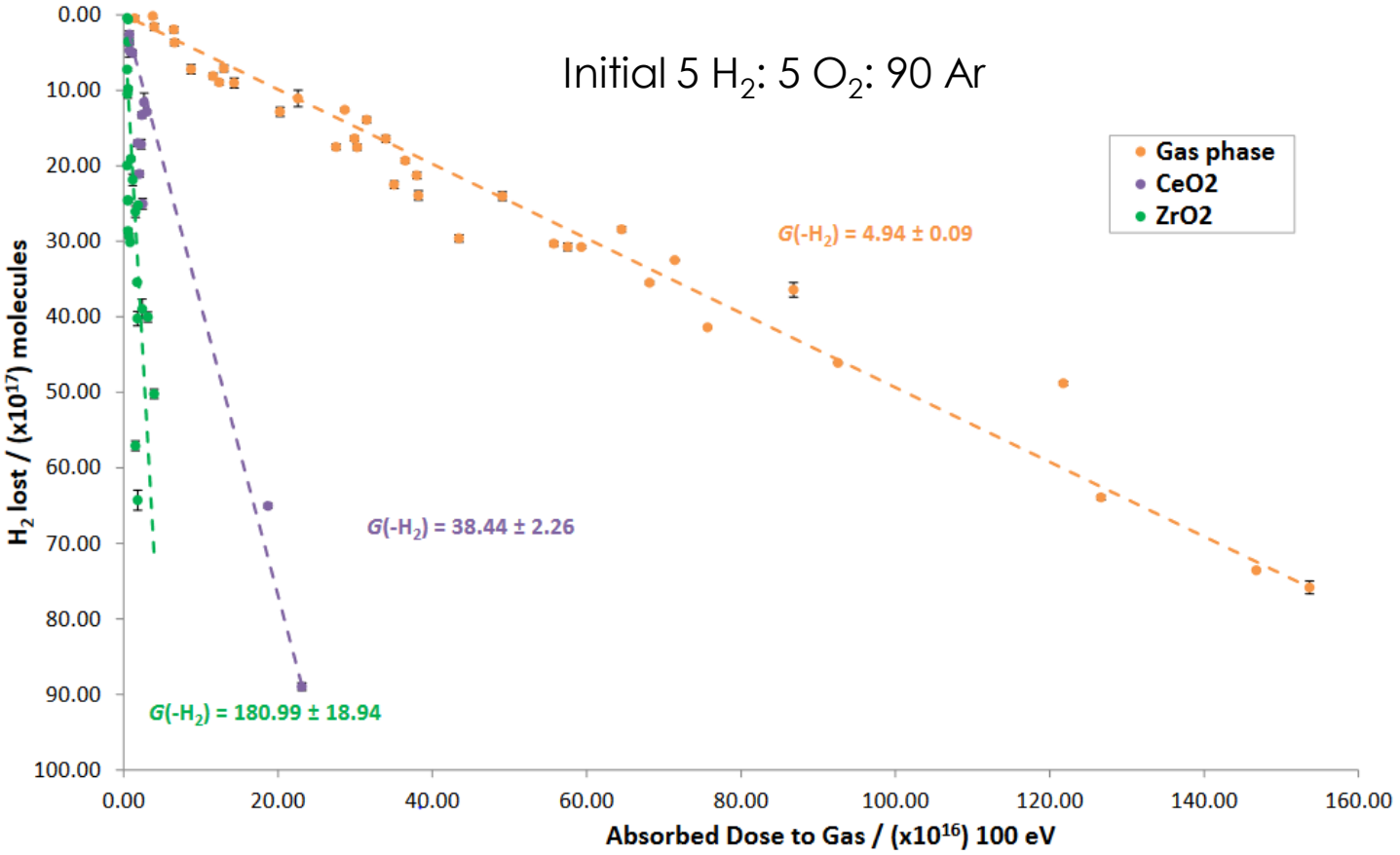
- Simple radiolysis of H_2O would be excepted to produce H_2 and O_2 species. Small scale studies of PuO_2 packages suggest that gaseous hydrogen and oxygen is formed.
- Cannister headspace atmospheres are hydrogen rich but contain no oxygen.

Where has the O_2 gone?

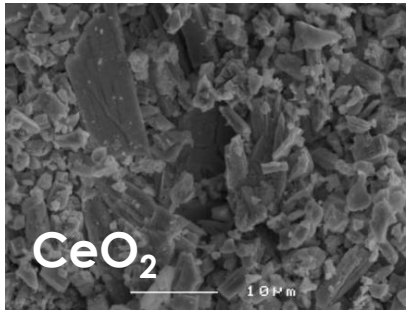
- Reduced catalytically, then O^{2-} absorbed into metal oxide?
- Radiolytic or catalytic recombination of H_2 and O_2?

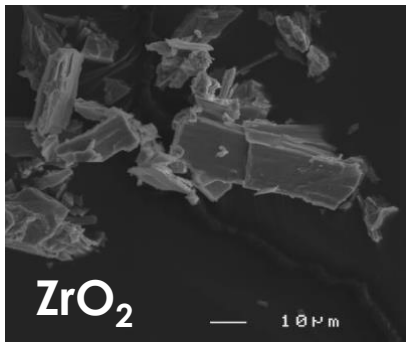
O_2 / H_2 recombination: prelim studies

Preliminary studies* indicate that irradiation of gas phase mixtures of hydrogen and oxygen with helium ions or gamma rays can lead to **loss of hydrogen**, presumably through radiation-induced reaction with oxygen to form water. This loss of hydrogen is found to be accelerated by the presence of zirconium and cerium oxides.



* Luke Jones, Dalton Cumbria Facility, Manchester University





O_2 / H_2 recombination: methods

- Simulate storage conditions in a vessel with varied temperature, pressure.
- Seal metal oxide (ceria or zirconia)powder in the vessel, with different initial partial pressures of H_2 and O_2
- Periodically sample head space gas and measure the partial pressures of H_2, O_2, H_2O and other likely species formed (H_2O_2)
- Use MS-gas analyser or GC
- Method developed will be transferred to NNL central lab to apply to PuO_2 samples

Conclusions

- 2 PhD projects; 1 Transcend-funded, 1 NGN / Transcend affiliated
- Helium implantation to be investigated using ion beam at DCF, followed by measuring desorption by GC or TGA-MS.
- O_2 / H_2 mixtures over PuO_2 analogue powders to be investigated, monitoring headspace gases produced or depleted.
- O_2 / H_2 experiments to be replicated at NNL with actual PuO_2 samples

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