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
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:

Key project partners:
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
Theme 4: Nuclear Materials

Partner organisations
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

⇒

**WP4.2:** Plutonium Immobilisation in Advanced Ceramic Wasteforms
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)
<table>
<thead>
<tr>
<th>Time</th>
<th>Topic</th>
<th>Presenter</th>
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</thead>
<tbody>
<tr>
<td>11:00</td>
<td>Welcome and overview of Theme 4</td>
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<tr>
<td>11:10</td>
<td>Water absorption onto Plutonium Dioxide by piezo-electric crystal nano-balance and contact angle measurements</td>
<td>Dominic Laventine (U. Lancaster)</td>
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<tr>
<td>11:35</td>
<td>Atomistic simulation of Am incorporation into PuO₂</td>
<td>William Neilson (U. Lancaster)</td>
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<td>11:45</td>
<td>DFT+U study of U₁₋ₓAnₓO₂₋ₓ (An = Np, Pu, Am and Cm) surfaces</td>
<td>Jia-Li Chen (U. Manchester)</td>
</tr>
<tr>
<td>12:10</td>
<td>Computational Modelling of PuO₂: Ageing and Storage Phenomena</td>
<td>Eleanor Murray (U. Birmingham)</td>
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<td>12:30</td>
<td>Lunch and posters</td>
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<td>14:00</td>
<td>Characterisation of long-stored Magnox PuO₂ packages</td>
<td>Robin Orr (NNL)</td>
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<tr>
<td>14:30</td>
<td>Underpinning plutonium immobilization in advanced ceramic wasteforms</td>
<td>Shi-Kuan Sun (U. Sheffield)</td>
</tr>
<tr>
<td>14:55</td>
<td>Disposability of waste-forms for plutonium immobilisation and efficacy of surrogates</td>
<td>Clemence Gausse (U. Sheffield)</td>
</tr>
<tr>
<td>15:05</td>
<td>Quantum chemical modelling of ThO₂ surface chemistry</td>
<td>Xiaoyu Han (U. Manchester)</td>
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<td>15:15</td>
<td>Gas generation from the radiolysis of water on uranium oxides and ThO₂</td>
<td>Fred Currell (DCF / U. Manchester)</td>
</tr>
<tr>
<td>15:25</td>
<td>The Recombination of Hydrogen and Oxygen on Metal Oxide Surfaces</td>
<td>Dominic Laventine (U. Lancaster) / Colin Boxall (U. Lancaster)</td>
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<tr>
<td>15:35</td>
<td>General Q&amp;A session / discussion</td>
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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
• 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
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”.
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 exist 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.
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) \( \text{H}_2\text{O} \) desorption (steam) from hygroscopic \( \text{PuO}_2 \)
(iv) Radiolysis of adsorbed water
(v) Generation of \( \text{H}_2 \) by chemical reaction of \( \text{PuO}_2 \) with \( \text{H}_2\text{O} \), producing a \( \text{PuO}_{2+x} \) phase.

The last 3 processes all involve \( \text{PuO}_2/\text{H}_2\text{O} \) interactions and are complex, inter-connected & poorly understood.

- Experimental methods have been employed to determine extent of \( \text{H}_2\text{O} \) 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
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(NO₃)₃
10 uL H₂O
10 uL MeOH
5% Triton-X
Calc.: 350°C
Thin layer depth analyses

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

$$\Delta f = -\left(\frac{nf_0^2}{A\sqrt{\rho_q\mu_q}}\right)\Delta m$$

$\rho_q = 3.570 \text{ g.cm}^{-1}$  $n = 1$
$\mu_q = 2.147 \times 10^{11} \text{ g.cm}^{-1}\text{s}^{-2}$
Coated area = 1.33 cm$^2$
Active area = 0.46 cm$^2$
$d_{\text{CeO}_2} = 7.65 \text{ g.cm}^{-3}$

XRD thickness is $\sim$250 nm, indicating a porosity of 50%
• Introduction to UK plutonium interim storage

• Synthesis of thin-layer actinide coatings

• Contact angle measurements

• Piezo-crystal nano-balance experiments
Microbalance water absorption

• Study the interactions of plutonium oxide and analogues with water.
  -- Ceria (CeO$_2$)  -- Urania (UO$_2$ / U$_3$O$_8$)
  -- Thoria (ThO$_2$)  -- 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.
Metal crystal transducer and GaPO$_4$ piezoelectric 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:

$$\frac{1}{[V a \left(\frac{P_0}{P} - 1\right)]} = \left(\frac{C-1}{V_mC}\right)\left(\frac{P}{P_0}\right) + \frac{1}{V_mC}$$

$$C = e^{\left(\Delta H_{ads} - \Delta H_{liq} / RT\right)}.$$

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

- $V_m = 2.43 \times 10^{-12}$ m$^3$
- $\Delta H_{abs} = 44.3$ kJmol$^{-1}$
- $\Delta H_{bind} = 2.5$ kJmol$^{-1}$

SA = 28 m$^2$g$^{-1}$
The water saturated system (75°C, 100% rel. humidity) was then heated to approx. 400°C, causing the bound water to desorb as the relative humidity drops. Approximately 20% of the water remains bound to the surface at 375°C.
Thoria films on GaPO₄ crystals: BET

Calc.: 500°C

\( V_m = 6.22 \times 10^{-12} \text{ m}^3 \)

SA = 88.5 m²g⁻¹

\( \Delta H_{\text{abs}} = 49.4 \text{ kJmol}^{-1} \)

\( \Delta H_{\text{bind}} = 7.8 \text{ kJmol}^{-1} \)

50 ug Th(oxal)₂
Calc.: 1000°C
34 ug ThO₂ (QCM)
Urania films on GaPO$_4$ crystals: BET

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

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

25 ug U(NO$_3$)$_3$
Calc.: 1000°C
18 ug U$_3$O$_8$
(QCM)
42 nm (XRF)
• Introduction to UK plutonium interim storage
• Synthesis of thin-layer actinide coatings
• Contact angle measurements
• Piezo-crystal nano-balance experiments
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.

\[ r \cos \theta_c = \cos \theta_m \]
\[ \gamma_{LG} \cos \theta_c = \gamma_{SL} - \gamma_{SG} \]
\( \theta_c = \) contact angle

\( r \): roughness factor
\( \gamma_{LG} \): surface tension
\( \gamma_{SL} \): solid-liq IE
\( \gamma_{SG} \): solid-gas IE
Water droplet on oxide nano-thick layer at 100% humidity, before and after UV irradiation.

- Measure contact angles of plutonium oxide analogues (CeO$_2$, ThO$_2$, UO$_2$, Ce$_{1-x}$Eu$_x$O$_2$) 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.
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.

\[ \text{ThO}_2 \text{ calcined at } 400^\circ \text{C} \]
40% hum.  5% hum.

\[ \text{UO}_2 \text{ calcined at } 300^\circ \text{C} \]
70% hum.  40% hum
Macroscopic water absorption: contact angle measurements

- metal oxide layer on glass substrate (~ 10 ug metal / cm²), calcined at 300°C
  - ThO₂
    - Init. contact angle = 27°
  - CeO₂
    - Init. contact angle = 58°

- water droplet (1 uL) deposited at initial 40% humidity
Macroscopic water absorption: contact angle measurements

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

\[ r = \frac{h}{2} + \frac{w}{8h} \]

\[ CA = 90 - \sin^{-1}\left(\frac{r-h}{r}\right) \]
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

Lancaster University
   Pat Murphy
   Richard Wilbraham
   Fabrice Andrieux

ITU
   Detlef Wegen

NNL
   Robin Taylor
   Robin Orr
   Dave Woodhead

Thanks for your attention
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
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$_{2+x}$.

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\textsubscript{2} AS FUNCTION OF ENVIRONMENTAL VARIABLES

**i** Determine formation energies for intrinsic defects in PuO\textsubscript{2}:

- \(O_{i}^{\prime\prime}, V_{O}^{\prime\prime}, Pu_{i}^{\prime\prime\prime}, V_{Pu}^{\prime\prime\prime} \) + 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\textsubscript{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, \(\Delta S\), is obtained with empirical calculations, and combined with DFT effect energies.
- With UO\textsubscript{2}, this approach led to improved replication of experimental data and the solving of the ‘uranium vacancy problem’ when combined with interstitial clusters.

1 PREDICTING DEFECT CHEMISTRY IN PuO₂ AS FUNCTION OF ENVIRONMENTAL VARIABLES

Considerations

- 2 x 2 x 2 supercells to be used, simulating 96 atoms.
- Magnetic order of PuO₂ to be considered.

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

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
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

UO₂

PuO₂

**MODEL VALIDATION: Lattice parameters & elastic constants of PuO$_2$**

<table>
<thead>
<tr>
<th></th>
<th>Lattice constant (Å)</th>
<th>Bulk modulus (GPa)</th>
<th>Crystal Symmetry (Space group number)</th>
<th>Magnetic configuration</th>
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<tr>
<td><strong>This work</strong></td>
<td>5.38</td>
<td>225.16</td>
<td>$Fm\bar{3}m$ (225)</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>(Empirical pair potential)</td>
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<tr>
<td><strong>Experiment</strong></td>
<td>5.395-5.398$^{[1]}$</td>
<td>178-379$^{[2]}$</td>
<td>$Fm\bar{3}m$ (225)</td>
<td>Exp.</td>
</tr>
<tr>
<td><strong>PBEsol +U$^{[2]}$</strong></td>
<td>5.415</td>
<td>215</td>
<td>$Fm\bar{3}m$ (225)</td>
<td>Longitudinal 3k antiferromagnetic</td>
</tr>
<tr>
<td>(Density Functional Theory with Hubbard correction)</td>
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Thank you
Atomistic Simulation of the ageing of PuO$_2$

Elanor Murray, University of Birmingham

TRANSCEND Theme meeting
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
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

Frenkel pair:
- Vacancy
- Self-interstitial

Cascade size 7.5 nm
2290 Frenkel pairs

U range 12 nm
He range 10 µm

Cascade size 0.8 µm
265 Frenkel pairs
Modelling scales and regimes

Time Scale

- ms
- µs
- ns
- ps

Size Domain

- Å
- nm
- µm
- mm

Challenges to multiscale integration

- Quantum Mechanical
- Molecular Mechanics
- Atomistic Simulation
- Molecular Dynamics

Finite Element Analysis

Mesoscale
The Potential Model

\[ U_L = \sum_{ij} \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} + \sum_{ij} \Phi_{ij}(r_{ij}) \]

- Short Range (Pauli) Repulsion
- Coulombic Attraction
- Total Energy

Transformative Science and Engineering for Nuclear Decommissioning
The Potential Model
- The short range potential

The Lennard-Jones Potential:
\[ \phi_{ij}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \]

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

Buckingham potential:
\[ \phi(r_{ij})_{Buck} = A_{ij} \exp \left( \frac{-r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} \]

Suitable for ionic solids
GULP overview

Initial position of ions
Forces acting between them

Crystal Structure
‘Force Field’

Geometry optimise
Final position of ions
Predict properties

Geometry Optimised
Crystal Structure

Physical Properties:
Mechanical
Optical
Potential Evaluation for PuO$_2$

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

The potentials used for PuO$_2$ provide agreement with elastic constants and crystallographic data.

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

<table>
<thead>
<tr>
<th>Region</th>
<th>Size (Å)</th>
<th>Number of Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region I</td>
<td>14</td>
<td>1888</td>
</tr>
<tr>
<td>Region IIa</td>
<td>28</td>
<td>12344</td>
</tr>
</tbody>
</table>

Ref: Read MSD, Jackson RA. Journal of Nuclear Materials. 2010;406(3):293
Defect Formation Energies for Isolated Defects

<table>
<thead>
<tr>
<th>Point Defect</th>
<th>Position</th>
<th>Formation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plutonium vacancy</td>
<td>$V_{\text{Pu}}^{****}$</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>Oxygen vacancy</td>
<td>$V_{\text{O}}^{**}$</td>
<td>($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)</td>
</tr>
<tr>
<td>Plutonium interstitial</td>
<td>$\text{Pu}_i^{****}$</td>
<td>($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)</td>
</tr>
<tr>
<td>Oxygen interstitial</td>
<td>$O_i^{**}$</td>
<td>($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)</td>
</tr>
</tbody>
</table>

Plutonium and Oxygen interstitials were placed in octahedral holes.
Oxygen Interstitial Visualisation

Unrelaxed structure

Relaxed structure

Oxygen Interstitial

Lattice Distortion
## Unbound Defect Formation Energies

<table>
<thead>
<tr>
<th>Bound Defect</th>
<th>Formation reaction</th>
<th>Formation Energy (eV/Defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky Trio</td>
<td>$\text{Pu}<em>x \overset{\text{Pu}}{\text{Pu}} + 2O_x \rightleftharpoons V</em>{\text{Pu}'''} + 2V_o \cdot \cdot + \text{PuO}_2 \text{(surface)}$</td>
<td>3.545</td>
</tr>
<tr>
<td>Oxygen Frenkel Pair</td>
<td>$O_o^{x} \rightleftharpoons V_o \cdot \cdot + O_i^{''}$</td>
<td>2.668</td>
</tr>
<tr>
<td>Plutonium Frenkel Pair</td>
<td>$\text{Pu}<em>x \overset{\text{Pu}}{\text{Pu}} \rightleftharpoons V</em>{\text{Pu}'''} + \text{Pu}_i \cdot \cdot \cdot \cdot$</td>
<td>10.029</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Type of defect</th>
<th>$V_0$ position</th>
<th>$O_i$ position</th>
<th>Formation energy (eV)</th>
<th>Formation energy (eV/Defect)</th>
<th>Binding energy (eV/Defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFP 1</td>
<td>$(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$</td>
<td>$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$</td>
<td>4.138</td>
<td>2.069</td>
<td>-0.599</td>
</tr>
<tr>
<td>OFP 2</td>
<td>$(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$</td>
<td>$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$</td>
<td>4.2321</td>
<td>2.116</td>
<td>-0.552</td>
</tr>
</tbody>
</table>
Oxygen Frenkel Pair Configurations

Unrelaxed structure

Relaxed structure
Schottky Defect Configurations

Compared the three different Schottky configurations.

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

Unrelaxed structure

Relaxed structure
### Intrinsic Defect Energies

<table>
<thead>
<tr>
<th>Bound Defect</th>
<th>Formation reaction</th>
<th>Defect Formation Energy</th>
<th>Binding Energy (eV/Defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky Trio</td>
<td>$\text{Pu}<em>x^+ + 2\text{O}<em>x^+ \Leftrightarrow {\text{V}</em>{\text{Pu}}'': 2\text{V}</em>{\text{O}}''}^x + \text{PuO}_2(\text{surface})$</td>
<td>3.545</td>
<td>1.929</td>
</tr>
<tr>
<td>Oxygen Frenkel Pair</td>
<td>$\text{O}<em>x^x \Leftrightarrow {\text{V}</em>{\text{O}}'': \text{O}_{\text{i}}''}^x$</td>
<td>2.668</td>
<td>2.069</td>
</tr>
<tr>
<td>Plutonium Frenkel Pair</td>
<td>$\text{Pu}<em>x^x \Leftrightarrow {\text{V}</em>{\text{Pu}}'': \text{Pu}_{\text{i}}'\prime\prime\prime}^x$</td>
<td>10.029</td>
<td>7.868</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>Unrelaxed $E_{\text{surf}}$ (Jm$^{-2}$)</th>
<th>Relaxed $E_{\text{surf}}$ (Jm$^{-2}$)</th>
<th>% $\Delta E_{\text{surf}}$ relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>6.3092</td>
<td>2.40634</td>
<td>-61.86</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>3.36026</td>
<td>1.79074</td>
<td>-46.71</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.67001</td>
<td>1.20452</td>
<td>-27.87</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>10.1207</td>
<td>2.57971</td>
<td>-74.51</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>6.55974</td>
<td>2.02959</td>
<td>-69.06</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>6.84231</td>
<td>1.94249</td>
<td>-71.61</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
<td>11.10917</td>
<td>2.79665</td>
<td>-74.83</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>7.45802</td>
<td>2.29264</td>
<td>-69.26</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2.91388</td>
<td>1.53115</td>
<td>-47.45</td>
</tr>
</tbody>
</table>

- Modeled the $\{n10\}$, $\{n11\}$ and $\{nn1\}$ surfaces.
  Where $n=1,2,3$.
- Found the $\{nn1\}$ surfaces to be the most energetically stable.
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
Thank you
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
• 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

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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 PuO₂ 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.
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) \( \text{H}_2\text{O} \) desorption (steam) from hygroscopic \( \text{PuO}_2 \)  
(iv) Radiolysis of adsorbed water  
(v) Generation of \( \text{H}_2 \) by chemical reaction of \( \text{PuO}_2 \) with \( \text{H}_2\text{O} \), producing a \( \text{PuO}_{2+x} \) phase.

\( \text{PuO}_2 \) is hydroscopic and picks up water during the packaging process. The disposition of this water under the storage conditions is unclear: it may exist in a gaseous state, or be weakly or strongly bound to the \( \text{PuO}_2 \) surface.

Radiolytic and catalytic processes on bound water may also result in formation of radicals (e.g. \( \text{H} \), \( \text{HO} \)) and other chemical species (e.g. \( \text{H}_2 \), \( \text{O}_2 \), \( \text{H}_2\text{O}_2 \)).

Gaseous \( \text{O}_2 \) and \( \text{H}_2 \) may also be consumed by catalytic processes, or absorbed into the \( \text{PuO}_2 \) matrix.
• Introduction to UK plutonium interim storage

• Helium sequesteration onto PuO$_2$ analogues

• Oxygen and hydrogen recombination on PuO$_2$
(i) **Helium accumulation from a decay**
(ii) Decomposition of polymeric packing material
(iii) H$_2$O desorption (steam) from hygroscopic PuO$_2$
(iv) Radiolysis of adsorbed water
(v) Generation of H$_2$ by chemical reaction of PuO$_2$ with H$_2$O, producing a PuO$_{2+x}$ phase.

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

\[
\begin{align*}
\text{Pu-238} & \rightarrow \text{U-235} + \text{He} \\
\text{Pu-239} & \rightarrow \text{U-235} + \text{He} \\
\text{Pu-240} & \rightarrow \text{U-235} + \text{He} \\
\text{Pu-242} & \rightarrow \text{U-235} + \text{He} \\
\text{Pu-241} & \rightarrow \text{Am-241} \rightarrow \text{Np-237} + \text{He}
\end{align*}
\]

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 sequestered 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 determine the eventual pressures developed.
In order to measure He desorption, first need to implant He into samples of CeO$_2$ used as a non-active surrogate for PuO$_2$.

Two methods: proposed:

1. High temperatures and pressures to physically force He gas into CeO$_2$ powders to be heated within furnace.

2. He implantation by alpha particle bombardment, using the beam at DCF. Requires samples that can be uniformly implanted by scanning beam across the surface. Tune beam energy to ensure maximal implantation with minimal damage to any underlying substrate.

Elements of the beamline, including the high vacuum pumps.
He sequestration: Turing ion beam energies

100 keV       200 keV       500 keV
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

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O₂ / H₂ recombination: introduction

- Simple radiolysis of H₂O would be expected to produce H₂ and O₂ species. Small scale studies of PuO₂ packages suggest that gaseous hydrogen and oxygen is formed.

- Cannister headspace atmospheres are hydrogen rich but contain no oxygen.

  Where has the O₂ gone?

- Reduced catalytically, then O²⁻ absorbed into metal oxide?

- Radiolytic or catalytic recombination of H₂ and O₂?
O₂ / H₂ 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
O₂ / H₂ 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 H₂ and O₂.
- Periodically sample head space gas and measure the partial pressures of H₂, O₂, H₂O and other likely species formed (H₂O₂).
- Use MS-gas analyser or GC.
- Method developed will be transferred to NNL central lab to apply to PuO₂ 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.

• O₂ / H₂ mixtures over PuO₂ analogue powders to be investigated, monitoring headspace gases produced or depleted.

• O₂ / H₂ experiments to be replicated at NNL with actual PuO₂ samples
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ITU
Detlef Wegen

NNL
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Robin Orr
Dave Woodhead

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