Theme 2: PuO_2 and Fuel Residues

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(for Colin Boxall, Lancaster University)

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NNL

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Theme 2: The Technical Challenge

- ~250 tonnes of separated Pu currently stockpiled worldwide.
- ~50% in long-term storage in UK whilst the government develops its options….

1. Reuse as fuel in modern reactors (*e.g.* as MOX or in a fast reactor)
2. Prompt immobilisation for disposal
3. Continued long term storage (prior to disposition)

Focus of this theme is on options 2 & 3. R&D needs are pressing:

- for option 3 due to it being the current default;
- for option 2 due to comparative lack of R&D on Pu conditioning & packaging due partly to policy uncertainty (GDF or not?)

Addressing these needs is complicated by Pu's radioactivity, decay heat & radiotoxicity, nuclear safeguards requirements and, for some PCM targeted for disposal, poor inventory – so we need R&D on characterisation methods for Pu bearing materials.

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Theme 2: Aims & Objectives

Aim

- To provide technical underpinning to the options for the UK's civil Pu inventory

Objectives

- To understand how the structure and properties of PuO_2 change with time in the presence of H_2O, and to understand the roles these processes play in gaseous product evolution from PuO_2 in storage.

- To understand radiation induced amorphisation & dissolution kinetics of Pu wasteforms.

- To develop novel, fast neutron based radiometric methods for quantification, isotopic composition assessment & remote imaging of Pu bearing materials.

Theme 2: WPs, Resource, Team

Work Packages (WPs):

- WP 2.3.1: Behaviour of PuO_2 during Interim Storage (PuO_2/H_2O)
- WP 2.3.2: Behaviour of Pu Bearing Wasteforms & Encapsulants
- WP 2.3.3: Methods for Characterisation of Stored Pu, PCMs & Pu Contaminated Facilities

Resource:

- 3 PDRA (EPSRC)
- 7 PhD (2 NDA, NNL, Manchester, Lancaster, Sheffield, UCL)

Team:

LANCASTER UNIVERSITY
MANCHESTER 1824 The University of Manchester
UCL
THE UNIVERSITY OF BIRMINGHAM
The University Of Sheffield.
Sellafield Ltd
NDA Nuclear Decommissioning Authority
NATIONAL NUCLEAR LABORATORY

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WP2.3.1: PuO_2 during Interim Storage

Interim storage of PuO_2 involves sealing in inert steel containers. Under certain circumstances, these cans may pressurise; must be avoided in practice.

> "*worker performing general housekeeping and relocating storage cans in the interim storage vault noticed plutonium bearing storage can was **bulging on both ends*** " – Lawrence Livermore National Laboratory 1994

5 routes to gas production have been suggested:

(i) Helium accumulation from α decay;

(ii) Decomposition of polymeric packing material;

(iii) H_2O desorption (steam) from hygroscopic PuO_2;

(iv) Radiolysis of adsorbed water;

(v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

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

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WP2.3.1: PuO_2 during Interim Storage

Thus, this WP will seek to:

a) Understand how the structure and properties of PuO_2 change with time in the presence of H_2O;
b) Attribute these changes to fundamental chemical, physical, and radiation-driven processes at the PuO_2 surface;
c) Understand He (α) generation, retention & release from within PuO_2 matrix;
d) Understand the roles these processes play in gaseous product evolution at Pu oxide surfaces;
e) Understand how above are affected by Pu ageing, inc. Pu isotopics

We will also study chloride surface adsorption mechanisms on PuO_2 and how effects such as radiation, temperature and adsorbed H_2O affect surface speciation and consequently desorption of chloride species under conditions to be employed in likely treatment processes.

WP2.3.1: PuO_2 during Interim Storage

Three tasks:

1. Physicochemical interactions between PuO_2 and H_2O
2. Radiation-induced effects on chemical processes in H_2O–PuO_x systems, inc. hydrogen generation mechanisms at PuO_2 surface
3. Modelling bulk and surface PuO_2 structure, molecular level chemistry and radiation damage

WP2.3.1: PuO_2 during Interim Storage

Task 1: Physicochemical interactions between PuO_2/H_2O

- Seems to be evidence for species that may be PuO_{2+x} or PuO_2OH
- Haschke has suggested a reaction

$$PuO_2 + H_2O \rightarrow PuO_{2+x} + H_2$$

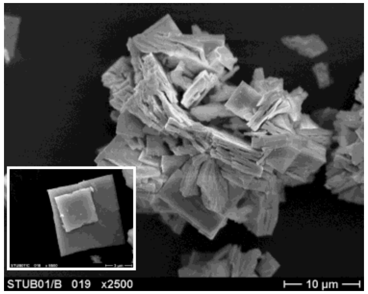
- Has been disputed on thermodynamic grounds

$\Rightarrow$ Quantification of H_2O adsorption

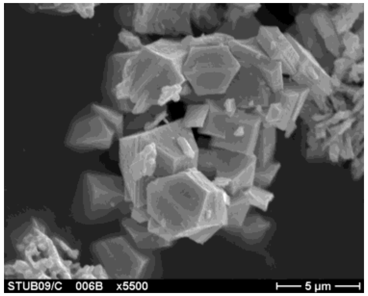
H_2 evolution as f(T, RH, [O_2], Pu isotopics)

Electrochemical studies analogous to UO_{2+x}

Colin Boxall



Thorp PuO_2



Magnox PuO_2

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WP2.3.1: PuO_2 during Interim Storage

Task 2: Mechanistic understanding of radiation-induced effects on chemical processes in H_2O/PuO_x systems

H_2O/PuO_x

- Porosity & Adsorption
- Surface & Over-gas Chemistry
- Hydrogen Production
- Oxygen / ROS Formation
- Radiation Damage to Solid Oxide

Simon Pimblott

MANCHESTER 1824
The University of Manchester

Carolyn Pearce

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WP 2.3.1 PuO_2 during Interim Storage

Task 3: Modelling projects - 1

Targets:

- geometric and electronic structure of PuO_2 bulk & surfaces
- band structure
- water chemi- / physi-sorption
- H_2 generation from reactions of radiolytically generated radical species such as OH• and H•
- recombination of H_2 and O_2 on surfaces
- effects of presence of chloride ion (from PVC degradation)
- close links with experimental studies at Manchester, Lancaster & NNL

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WP 2.3.1 PuO_2 during Interim Storage

Task 3: Modelling projects - 2

How?

- UCL/Lancaster (Nik Kaltsoyannis and Andy Kerridge; PDRA and PhD): quantum mechanical (density functional theory) modelling (two approaches: periodic boundary conditions, periodic electrostatic embedded cluster method) of bulk and surface structure, water absorption and reaction chemistry.

- Birmingham (Mark Read; PhD): atomistic (force field) modelling of stoichiometric PuO_2, including surface energies. Defects and surface structure (feed into UCL DFT studies). Molecular dynamics simulations of water on PuO_2 surfaces.

- Manchester (Simon Pimblott; PhD): stochastic modelling of radiation damage of water above PuO_2 surfaces.

WP 2.3.2 Pu Wasteforms & Encapsulants

Key issue: atomic displacements induced by α recoil result in amorphisation of crystallisation, potentially detrimental to long term wasteform performance (swelling and cracking).

► Relevant to Sellafield Pu, MOX residue immobilisaton

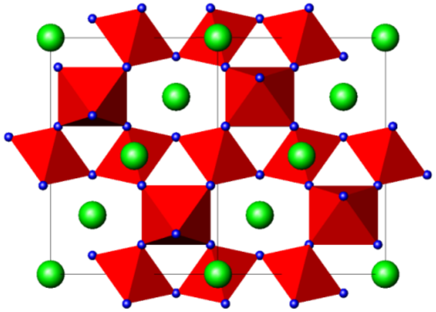
Project will focus on model actinide ceramic wasteforms, *e.g.* pyrochlore $An_2Ti_2O_7$, perovskite $An_{2/3}TiO_3$

Key questions:

► Can we develop mechanism-based rules to predict radiation sensitivity / tolerance in classes of compounds?

► To what extent does amorphisation impact on long-term aqueous durability?

Pu storage can, NNL.



Pyrochlore structure, $An_2Ti_2O_7$

Neil Hyatt
John Provis
Karl Whittle
Claire Corkhill

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WP 2.3.2 Pu Wasteforms & Encapsulants

Aim: to develop new design rules for radiation tolerance

1. Ion beam induced amorphisation

Produces surface amorphised layer (10^2-10^3 nm)

Apply XAS to probe structure in damaged surface layer

e.g. $Gd_2Ti_2O_7$: XAS shows ion beam amorphised phase stabilised by formation of TiO_4 polyhedra

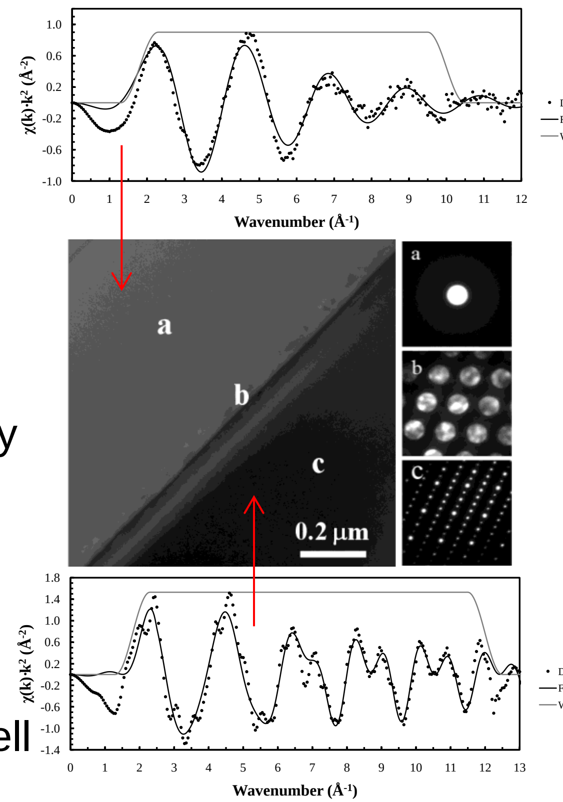
Systematic study of model materials to develop new design rules

2. Investigation of historic Pu doped ceramics at NNL

Study c. 30y old ^{238}Pu doped Synroc specimens fabricated at Harwell

TEM investigation of radiation damage expected during storage

Use EELS to investigate correspondence with ion beam amorphised structures; attempt μ-XAS, XRD at *e.g.* DLS, ANKA



Comparison of Ti XAS data from ion beam amorphised / pristine material showing different co-ordination environments.

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WP2.3.3 Characterisation of stored Pu, PCMs & Pu contaminated facilities

2 PhD projects at Lancaster

Project 1: how does the isotopic composition of Pu in storage change with time as the result of radioactive decay such as ^{241}Am in-growth and the presence of ^{244}Cm?

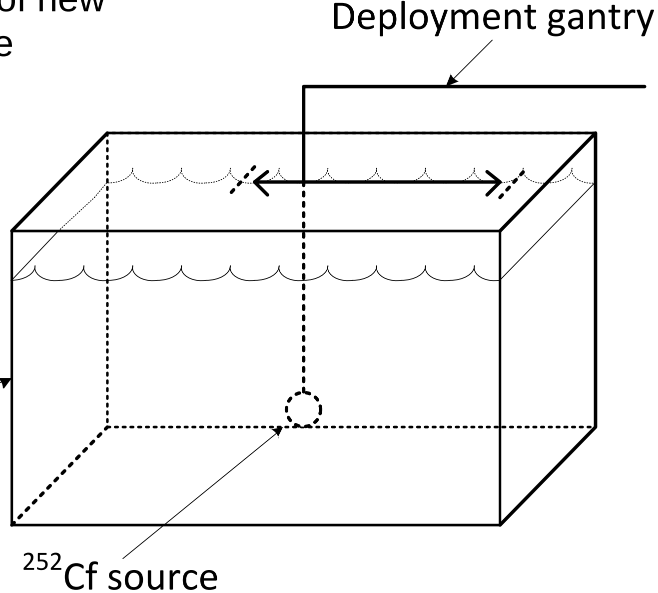
Project 2: develop an imaging system for *in situ* characterisation of Pu distribution in heavily contaminated α facilities

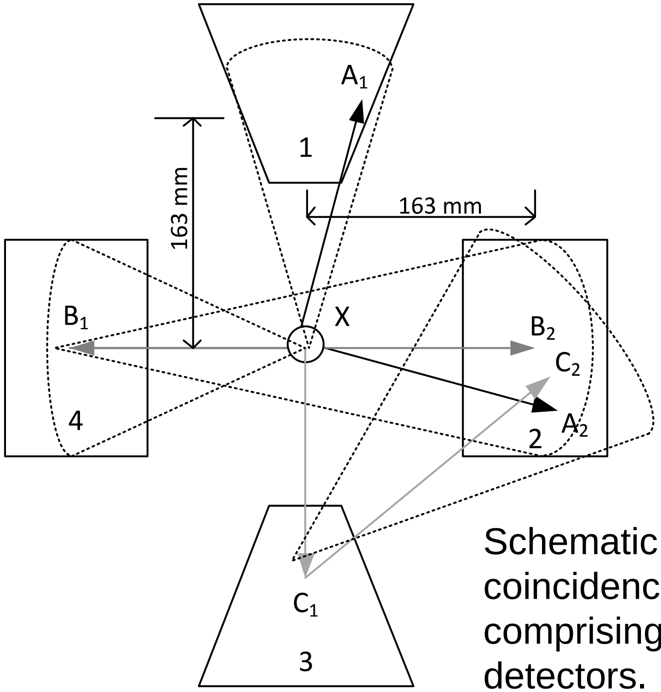
Malcolm Joyce

WP2.3.3 Characterisation of stored Pu, PCMs & Pu contaminated facilities

- Research to date has focussed on:
  - The installation of a ^{252}Cf source at Lancaster.
  - Understanding scattering dynamics between detectors used in the proposed assay.
  - Liaison with experts at Sellafield and advertisement of the studentships.

Schematic of new ^{252}Cf source installation





Schematic of coincidence setup comprising 4 detectors.

Malcolm Joyce