Theme 2: PuO_2 and Fuel Residues

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Industry Road Show
1st July, 2014
Sellafield Ltd. and NNL

Research Councils UK
Energy
For a Low Carbon Future

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Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories

Theme 2: The Technical Challenge

- ~250 tonnes of separated Pu currently stockpiled worldwide.
- ~50% in long-term storage in UK whilst the Govt 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 2 & 3. R&D needs are pressing:

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

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

Theme 2: Aims & Objectives

Aim

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

Objectives

- To understand how the structure and properties of PuO_2 change with time in the presence of H_2O.
- 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
- WP 2.3.2: Behaviour of Pu Bearing Wasteforms & Encapsulants
- WP 2.3.3: Methods for Characterisation of Stored Pu, PCM & Pu Contaminated Facilities

Resource:

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

Team:

WP2.3.1: PuO_2 during Interim Storage

Interim storage of PuO_2 involves sealing in inert steel containers. Under certain circumstances, these gas 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.

WP2.3.1: PuO_2 during Interim Storage

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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, 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, T 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:

- Physicochemical interactions between PuO_2 and H_2O
- Hydrogen generation mechanisms at PuO_2 surface
- Modelling bulk & surface PuO_2 structure, molecular level chemistry and radiation damage

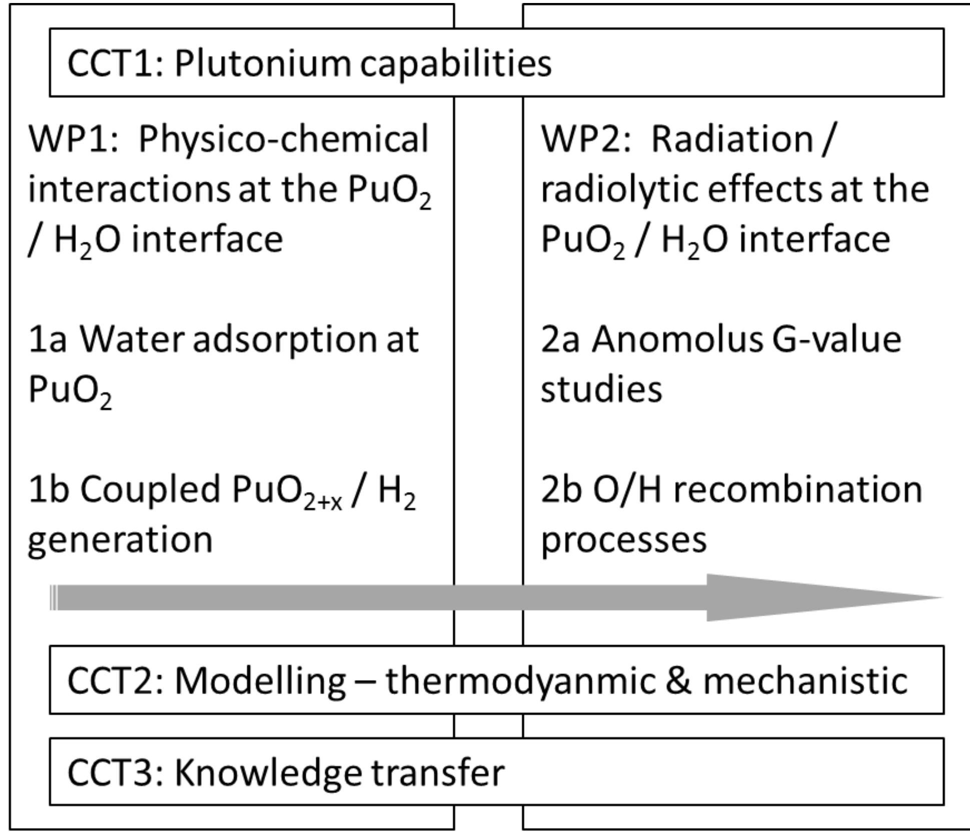


Figure 1: Structure of the work programme

WP2.3.1: PuO_2 during Interim Storage

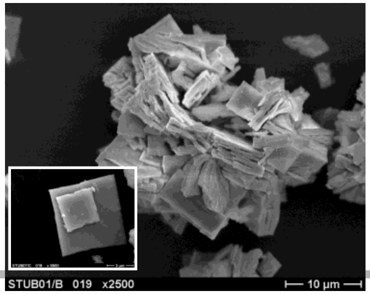
First Task: Chemical interaction between PuO_2/H_2O

- 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.
- Should not change with specific activity

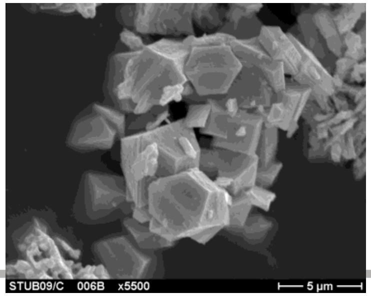
Quantification of H_2O adsorption

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

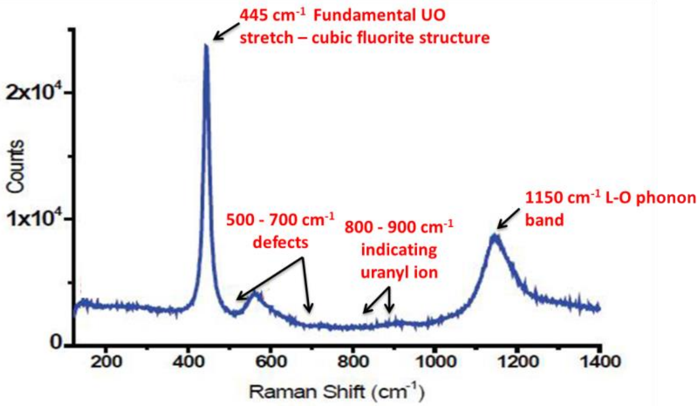
Electrochemical studies analogous to UO_{2+x}



Thorp PuO_2



Magnox PuO_2



WP2.3.1: PuO_2 during Interim Storage

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

Water - PuO_x

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

Simon Pimblott

Carolyn Pearce

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

WP 2.3.1 PuO_2 during Interim Storage

Task 3: Modelling Projects - 2

How?

- UCL (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

Project focus on model actinide ceramic wasteforms

► Relevant to Sellafield Pu, MOX residue immobilisaton

► e.g. pyrochlore $An_2Ti_2O_7$, perovskite $An_{2/3}TiO_3$

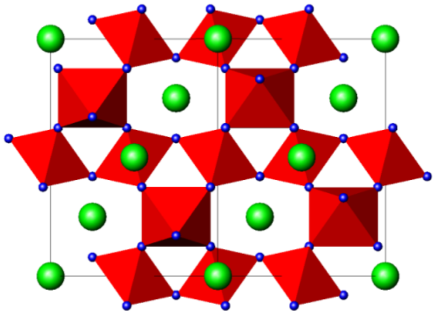
Key issue: atomic displacements induced by daughter recoil result in amorphisation of crystallisation, potentially detrimental to long term performance.

Pu storage can, NNL.

Two 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 aqueous durability?



Pyrochlore structure, $An_2Ti_2O_7$

WP 2.3.2 Pu Wasteforms & Encapsulants

Methodology – first phase

Aim: Develop new design rules for radiation tolerance

1. Ion beam induced amorphisation

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

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 TiO4 polyhedra, cf. TiO6 in crystalline material

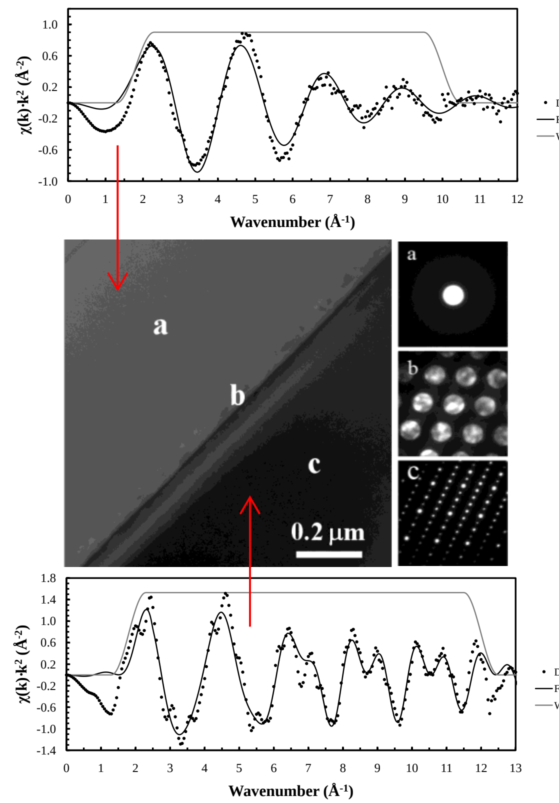
Systematic study of model materials to develop new design rules

2. Investigation of historic Pu doped ceramics at NNL

Unique ca. 30y old 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

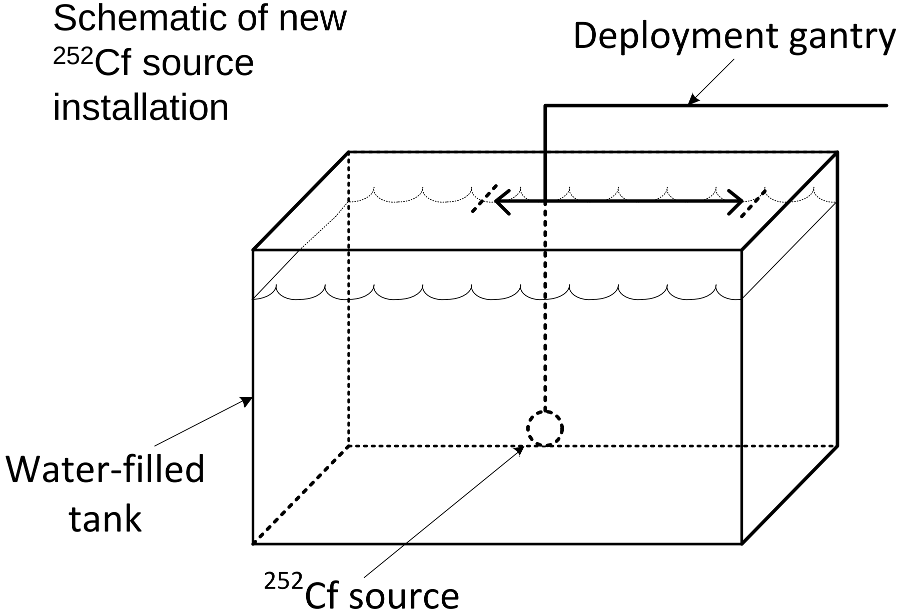


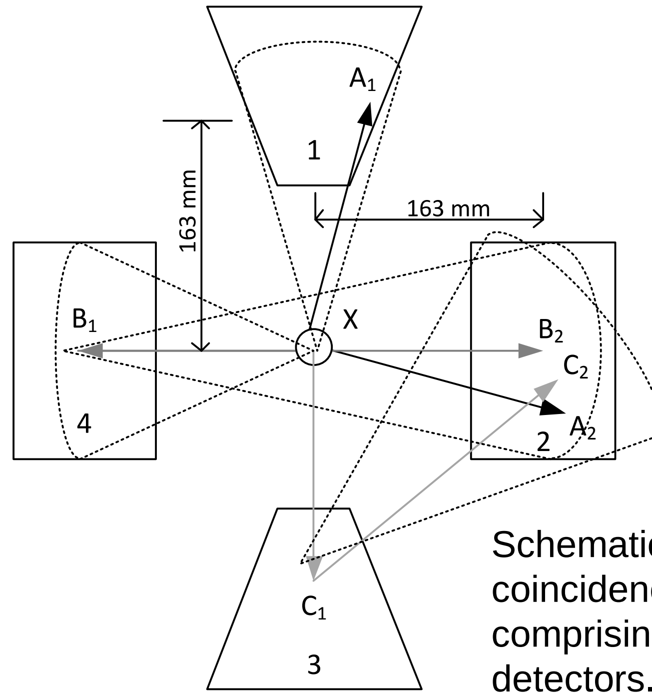
Comparison of Ti XAS data from ion beam amorphised / pristine material showing different co-ordination environments.

WP2.3.3 Characterisation of stored Pu, PCM & 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.