

Gas generation from radiolysis of water on Uranium and Thorium oxides

Project update

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Section 1: Project introduction





Okay well.. who cares?



Probably sites like Sellafield do..

- As we all know, Sellafield has a lot of PuO_2 In storage
- Significant humidity during packing could lead to pressurisation
- Pressurisation doesn't currently occur at Sellafield but other storage areas around the world have witnessed this





Why Thorium and Uranium Oxides?

Biggest reason – May turn out to be useful surrogates for PuO₂





Primary project goals

(why this project exists)





Section 2: Experimental setup

Old method of radiolysis at DCF..

Co-60 Irradiator



It works but needs modernising..



If you remember my last presentation: Small MOdular Radiation Experimental Systems





Methodically turning the 3D cad drawings into physical objects





Methodically turning the 3D cad drawings into physical objects







Scale version of the irradiator





Gas syringe system







Okay well.. who cares?



Hopefully anyone wanting to do radiolysis experiments does..

Advantages over previous method:

- Fully autonomous (everything is designed to eventually take care of itself)
- You'll be able to monitor gas production as it happens rather than 15 minutes later
- Modularity of the system ensures future proofing and flexibility
- Forerunners of the system have successfully been used with active materials



Section 3: Experiments

How to answer the previous unknowns..





How to answer the previous unknowns..





Interfacial Energy Transfer during Gamma Radiolysis of Water on the Surface of ZrO_2 and Some Other Oxides

N. G. Petrik, A. B. Alexandrov, and A. I. Vall

Focuses on Hydrogen production from many different oxides which is expressed as "G"

G value - µmol J-1 of a product produced per 100eV of energy absorbed

Water produces ~0.45 molecules per 100eV (for reference)



Interfacial Energy Transfer during Gamma Radiolysis of Water on the Surface of ZrO₂ and Some Other Oxides

N. G. Petrik, A. B. Alexandrov, and A. I. Vall

Group 1 - Reduced H ₂ Yield		Group 2 - H ₂ Yield Close to Control		Group 3 - Enhanced H ₂ Yield	
Oxide	G(H ₂)(molecules/100eV)	Oxide	G (H ₂)(molecules/100eV)	Oxide	G (H ₂)(molecules/100eV)
MnO2	0.002 to 0.04	MgO	1.3 to 1.9	Ga ₂ O ₃	30
Co3O4	0.001 to 0.06	CaO	0.2 to 1.4	Y ₂ O ₃	4 to 20
	0.001 to 0.08	SrO	0.4 to 2.4	La ₂ O ₃	10
	0.001 to 0.00	BaO	0.3 to 3.3	Nd ₂ O ₃	3.0 to 5.5
Fe2O3	0.09	ZnO	0.1 to 1.8	Sm2O₃	3 to 15
Main focus of the paper			0.1101.0	Eu ₂ O ₃	6 to 40
		CaO	0.2 to 3.0	Gd ₂ O ₃	4 to 6
		Cu ₂ O	0.2 to 3.0	Yb ₂ O ₃	6 to 10
		NiO	0.3 to 0.4	Er ₂ O ₃	10 to 140
		Cr ₂ O ₃	0.1 to 2.0	HfO ₂	10
		Al2O ₃	0.2	ZrO ₂	10 to 80
		CeO ₂	2.6		
		SiO ₂	1.0 to 3.0		
		TiO ₂	0.3 to 0.5		
		V2O5	0.2 to 1.0		
		Nb ₂ O ₅	0.2 to 0.4		
		WO ₃	0.4		



But why is there enhancement?

Interfacial Energy Transfer during Gamma Radiolysis of Water on the Surface of ZrO₂ and Some Other Oxides

N. G. Petrik, A. B. Alexandrov, and A. I. Vall

 \triangle Group I \square Group 2 \bullet Group 3





Nanoparticle doping

Zirconia nanoparticles have been doped with varying quantities of Ti

Titanium Ions Dispersed into the ZrO₂ Matrix: Spectroscopic Properties and Photoinduced Electron Transfer

S. Livraghi, F. Olivero, M. C. Paganini,* and E. Giamello

Dipartimento di Chimica IFM, Università di Torino and NIS, Nanostructured Interfaces and Surfaces Centre of Excellence, Via P. Giuria 7, I-10125 Torino, Italy

Received: July 6, 2010; Revised Manuscript Received: September 10, 2010

Doping can drastically change the band gap energy (if the literature is correct – as low as 1.3 eV)

H₂ production to be measured and compared to stock ZrO₂

Experiment still in planning, more details and results will be on the next presentation!



What about Thorium and Uranium?



Plan for Uranium and Thorium Experiments

- Thorium has the greater interest due to lack of literature for radiolysis
- Experiments to be conducted when:
- A. Experimental setup is complete
- B. Travel restrictions lift
- All the oxides to be ran at a range of doses and humidity's
- Both using alpha and gamma

I have already secured Thoria, If anyone has any Uranium oxides lying about please contact me!





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Assessment of zirconolite glass-ceramic as a suitable waste-form for Pu immobilisation: Comparison with zirconolite full ceramic

<u>Clémence Gausse</u>, Ellie Ormerod, Laura J. Gardner, Neil C. Hyatt, Martin C. Stennett and Claire L. Corkhill NucleUS Immobilisation Science Laboratory, University of Sheffield, United Kingdom

18th May 2021 Virtual meeting













Context

- Upon completion of fuel reprocessing, the UK will have a stockpile >140t of PuO₂
- Dual track strategy of immobilisation & reuse by MOX fabrication for LWR

- Not all Pu will be suitable (Am-241 ingrowth) for MOX

- Commercial case for MOX utilisation uncertain
- Wasteform selected for Pu immobilisation will need to play a functional role in supporting safe disposal

- Retaining Pu and its daughters for over 100,000 years

- Hot Isostatic pressing identified as possible thermal treatment for PuO₂ wastes
 - ✓ Uniform incorporation of radionuclides
 ✓ Batch process (inventory control)
 ✓ No off-gas production
 ✓ Minimal secondary wastes produced
 ✓ Hermetically sealed wasteform
 ✓ Facilitates high waste-loadings
 - ✓ Facilitates high waste-loadings
 - ✓ Significant cost saving







• Natural mineral present in a wide variety of localities in Earth

- Demonstrates a good chemical flexibility (incorporation of various cations)

- High durability and radiation tolerance

- Full ceramic suitable for relatively pure Pu-residues
- Glass-ceramic suitable for higher impurity Pu-residues

1. Synthesis & characterisation of the zirconolite ceramic & glass-ceramic

2. Investigate the zirconolite *durability* via dissolution experiments











Time (days)

150 200 250 300 350

Time (days)



1. HIPed zirconolite glass-ceramic & ceramic synthesised

2. HIP resulted in an uniformly dense structure with little secondary phases

3. First results in dissolution evidenced a great durability in zirconolite glassceramic & full ceramic in GDF conditions

4. The SI shows an over-saturation for TiO_2 and $AlHO_2$

Future work

- Characterisation of the samples post-dissolution
- Dissolution test in more aggressive conditions (0.01 M HNO₃)
- Synthesis & durability of HIPed U-doped zirconolite glass-ceramic



HADES



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Thank you!

Special thanks to:

Laura Gardner Lewis Blackburn Dan Bailey Amber Mason Paul Heath **Claire Corkhill** ISL team



Radioactive Waste Management













Atomistic Simulation Helium Incorporation in PuO_2

Elanor Murray

University of Birmingham

19th May 2021 Teams





Atomistic Simulation of Helium Incorporation in PuO₂



Transformative Science and Engineering for Nuclear Decommissioning



How much helium can the lattice accommodate?

What are the likely trapping sites?

Is helium diffusion vacancy assisted?

How does helium aggregate?

What is the mechanism for bubble formation?




Atomistic Simulation of Helium Incorporation in PuO₂



He in

 PuO_2

Bulk

Molecular Dynamics

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Bulk PuO2

$$\Phi_{ij}(r_{ij}) = A e^{\left(rac{-r_{ij}}{
ho}
ight)} - rac{C}{r_{ij}^6}$$

Buckingham potential of Read et al.







Mott-Littleton methodology for finding defect energies

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Found Schottky and Oxygen Frenkel Pairs to be most energetically favourable defects

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Surface PuO₂

Pu Frenkel Pair has highly negative segregation energy, so there is a thermodynamic drive for it to form at the surface rather than in the bulk.



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Wulff construction of PuO2



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



R. W. Grimes, NASO ASI Series B, vol. 279, 1991.V. Dremov, et al. Phys. Rev. B, vol. 77, p. 224306, 2008.

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He in PuO₂

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Helium Incorporation











Y. Yun, O. Eriksson, and P. M. Oppeneer, Journal of Nuclear Materials, vol. 385, no. 3, pp. 510 – 516, 2009. N. Kuganathan, P. Ghosh, A. Arya, and R. Grimes, Journalof Nuclear Materials, vol. 507, pp. 288 – 296, 2018.

Six He surrounding a Vacancy He in PuO2 Oxygen ۲ Atomic vacancy relaxation • • Helium atoms initially in OIS Plutonium vacancy Atomic relaxation ۲ 0 He 0 Pu

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12

Energetically favourable for He to occupy Pu vacancies and related defects

For O vacancy and FP the He atoms remained in the initial OIS

Above 6 He atoms, in Pu defects, the He atoms remain in the OIS surrounding the octahedral configuration of He atoms

5 He surrounding Pu vacancy





Atomistic Simulation of Helium Incorporation in PuO₂

> Molecular Dynamics

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Molecular Dynamics

Cell Size	Nº. Atoms	a _{av} (Å)	σ (Å)
2x2x2	96	5.438755	0.017347
4x4x4	768	5.436541	0.009991
6x6x6	2592	5.431079	0.003779
8x8x8	6144	5.43198	0.002638
10x10x10	12000	5.435528	0.001923

4x4x4

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60

50



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Molecular Dynamics

Potential Evaluation

 $\Phi_{ij}(r_{ij}) = ???$

For molecular dynamics, CRG potential is most suitable



Read potential is a shell model





Molecular Dynamics

Diffusivity

Calculating MSD over range of temperatures for 2ns simulations

 $D = \frac{MSD}{6t}$







Molecular Dynamics

Arrhenius Plot

 $D = Ae^{\frac{-Ea}{RT}}$



Oxygen Trajectory 2000K



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0% 0.5%

2%

4%

5.5

6

 $imes 10^{-4}$

Molecular Dynamics

Total Energy (eV)

Schottky Incorporation





Atomistic Simulation of Helium Incorporation in PuO₂



Molecular Dynamics

He in PuO₂

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He in PuO₂

Helium Incorporation

He in OIS, 500K, 1ns

Defect	Trajectory	
Pure		
Oxygen Vacancy		
Plutonium Vacancy	0.	





Trajectory of 27 He in OIS over 1ns



He in PuO₂ He Incorporation in Defective PuO₂



2% Schottky





Atomistic Simulation of Helium Incorporation in PuO₂



Bulk

PuO₂

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He at

Surfaces

Migration

Pathways

He

clustering



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Thank you

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Helium behaviour in non-stoichiometric PuO₂

William Neilson, Lancaster University

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Supervisor: Dr Samuel T. Murphy

TRANSCEND Thematic Meeting





INTRODUCTION

This project has studied the defect chemistry of bulk PuO_2 to understand the ageing of the material, investigating how Am and He are accommodated into PuO_2 and what impact they have on the defect chemistry.

Defect chemistry:

- The formation of defects (the addition or removal of atoms from the perfect lattice) can accommodate deviations from stoichiometry in PuO₂, resulting in PuO_{2+x}
- Can examine the defect chemistry as a function of temperature and oxygen partial pressure.
- Describes how impurities, such as Am & He, are incorporated into the lattice .
- Help in understanding how PuO₂ continues to evolve when kept in storage.
- May help identify hazards, such as potential pressurisation mechanisms in the canisters used for storage.



Presentation overview

- Methodology
- Intrinsic defects
- Americium
- Helium
- Combined effect of Americium and Helium



Adding intrinsic defects

Create supercell



Study intrinsic defects

<u>REMOVE OXYGEN ATOMS</u> Oxygen vacancies: V_0^{\times} , V_0^{1+} and V_0^{2+}

 $\frac{\textbf{ADD PLUTONIUM ATOMS}}{\textbf{Plutonium interstitials:}} Pu_i^{\times}, Pu_i^{1+}, Pu_i^{2+}, Pu_i^{3+} \text{and } Pu_i^{4+}$

 $\frac{\textbf{REMOVE PLUTONIUM ATOMS}}{\textbf{Plutonium vacancies: } V_{Pu}^{\times}, V_{Pu}^{1-}, V_{Pu}^{2-}, V_{Pu}^{3-} \text{ and } V_{Pu}^{4-}}$

2 x 2 x 2, 96 atoms



Adding extrinsic defects

\bigcirc	Study americium	ADD AMERICIUM ATOMS
		Americium interstitials:
		Am_i^{\times} , Am_i^{1+} , Am_i^{2+} , Am_i^{3+} and Am_i^{4+}
		Oxygen substitutions:
		Am_0^{\times} , Am_0^{1+} , Am_0^{2+} , Am_0^{3+} , Am_0^{4+} , Am_0^{5+} and Am_0^{6+}
		Plutonium substitutions:
		Am_{Pu}^{4-} , Am_{Pu}^{3-} , Am_{Pu}^{2-} , Am_{Pu}^{1-} , Am_{Pu}^{2+} , Am_{Pu}^{2+} , Am_{Pu}^{3+} , Am_{Pu}^{4+} and Am_{Pu}^{5+}
Study helium		
\bigcirc	Study helium	ADD HELIUM ATOMS
\bigcirc	Study helium	ADD HELIUM ATOMS Helium interstitials:
\bigcirc	Study helium	$\frac{\text{ADD HELIUM ATOMS}}{\text{Helium interstitials:}}$ He_{i}^{\times}
\bigcirc	Study helium	ADD HELIUM ATOMS Helium interstitials: He_i^{\times} Oxygen substitutions:
	Study helium	ADD HELIUM ATOMSHelium interstitials: He_i^{\times} He_i^{\times} Oxygen substitutions: He_0^{\times} , He_0^{1+} and He_0^{2+}
	Study helium	ADD HELIUM ATOMSHelium interstitials: He_i^{\times} Oxygen substitutions: He_0^{\times} , He_0^{1+} and He_0^{2+} Plutonium substitutions:



Computational details

Simulate with DFT. Obtain the energy of defect containing PuO₂ supercells.

Apply model.

The Defect Analysis Package (DefAP) is a thermodynamic code that predicts the defect chemistry of a system.

- Calculates defect formation energies.
 - DFT energies of defect.
 - Vibrational entropy contribution.
 - Chemical potentials of host atoms and their temperature and pressure dependence.
 - Finite size corrections.
- Calculates electron and hole concentrations.
- Calculates Fermi level (and defect concentrations) that result in the entire system being charge neutral.
- Allows for control of total Am and He concentration.
- Automatically creates the plots seen throughout this presentation.



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Brouwer diagram - Defect concentrations in ${\rm PuO}_2$ as a function of oxygen partial pressure. Temperature: 1000 K



- Oxygen defects dominant
- Hyper-stoichiometry negligible
- Hypo-stoichiometry much more favourable



Brouwer diagram - Defect concentrations in $Pu_{0.999}Am_{0.001}O_{2\pm x}$ as a function of oxygen partial pressure. Temperature: 1000 K



$Pu_{0.999}Am_{0.001}O_{2\pm x}$

- Oxygen defects are the dominant intrinsic defect and control the stoichiometry in Pu_{1-y}Am_yO_{2±x}. Hyper-stoichiometry always found negligible.
- Am is accommodated in Pu substitutions under all conditions.
- At * Am reduced from +IV to +III as partial pressure decreases, in agreement with experimental observation



Comparison with experiment



Values of x in $Pu_{1-y}Am_yO_{2\pm x}$ as a function of oxygen partial pressure at y values of a) 0.09 and b) 0.072, with comparison to experimental results

M. Osaka, K. Kurosaki, S. Yamanaka, Oxygen potential of (Pu0:91Am0:09)O2-x, J. Nucl. Mater. 357 (2006) 69–76. doi:10.1016/j.jnucmat.2006.05.044.

T. Matsumoto, T. Arima, Y. Inagaki, K. Idemitsu, M. Kato, K. Morimoto, T. Sunaoshi,

Oxygen potential measurement of (Pu0:928Am0:072)O2-x at high temperatures, J. Nucl.

Sci. Technol. 52 (2015) 1296–1302. doi:10.1080/00223131.2014.986243.



Defect concentrations in $Pu_{1-y}Am_yO_{2\pm x}$ as a function of temperature. Oxygen partial pressure: 0.01 atm.





Defect concentrations in $Pu_{1-y}Am_yO_{2\pm x}$ as a function of Am concentration. Oxygen partial pressure: 0.01 atm, temperature 800 K.





Investigating helium

No vibrational entropy contribution

DFT + D

Accommodation of helium

He on interstitial site very favourable



Defect formation energies for Helium defects in PuO₂ as a function of the Fermi energy. Calculated at 1000 K and an oxygen partial pressure of 10⁻¹⁰ atm. Only the charge state with the lowest formation energy for a given Fermi level is shown for each defect, represented with a numeric label.



Defect concentrations in $PuO_{2\pm x}$ as a function of oxygen partial pressure. Temperature: 1000 K.





Role of americium

- Americium was found to act as a p-type dopant, promoting charged oxygen vacancies.
- Hypothesise that Am promotes He accommodation on oxygen vacancies.
- Prevented from directly studying both americium and helium at the same time with DFT + D.
- But do know the impact of Am: A high concentration of Am 3+ that brings about a high concentration of charge in the system with a magnitude of -1.





We therefore deposit a high concentration of charge with a magnitude of -1 in the Helium system to replicate the presence of Am.


Defect concentrations in $PuO_{2\pm x}$ as a function of concentration of artificially added charge (λ^{-1}). Oxygen partial pressure: 10⁻³⁰ atm, temperature 1000 K.



0.000001% Am 3+



Defect concentrations in $PuO_{2\pm x}$ as a oxygen partial pressure with a fixed He concentration of 0.001 atoms per PuO_2 molecule. Temperature 500 K.





Next steps





Thank you

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The Radiolysis of Water over Plutonium Dioxide: A Study of H_2/O_2 Recombination

Processes

Cameron Williams, Lancaster University TRANSCEND Theme 4

19th May 2021



- The UK currently stores a vast quantity of Pu at it's Sellafield site
- Discussions are ongoing regarding the future of this material

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• The material is stored in a range of chemical forms though this project will focus on material in the form of PuO₂ powder







- Current storage methods are only designed as a stopgap until a decision is made regarding permanent storage options
- It is possible that the current storage canisters could be in use until the middle of this century or beyond
- Concerns have been raised in literature regarding the risk of can pressurisation

LA-UR-98-4557 Title: Literature Search on Hydrogen/Oxygen Recombination and Generation in Plutonium Storage Environments Author(s): Jane A. Lloyd and P. Gary Eller (Corresponding Author) Los Alamos National Laboratory Los Alamos, NM 87545 Lee Hyder (Retired) Savannah River Site Aiken, SC 29808 Submitted to:



- Following the Lloyd paper of 1999 a paper published by Bailey et al. in 2000 suggested methods of can pressurisation
- Temperature Induced Pressurisation
- Build up of Helium
- Desorption of Adsorbed Species
- Decomposition of Adsorbed Species
- Pressure Pulses





- Examination of canisters of a range of ages reveals lower than anticipated levels of pressurisation
- This could suggest that the impact of the pressurisation processes has been over exaggerated
- Or another counter process could be present







- Morales of Los Alamos National Laboratory published a paper examining the rates of this recombination process over PuO₂
- In this paper he makes notes on the standard used for the packaging of waste canisters stating:

"The pressure equation contains two major assumptions (1) that hydrogen and oxygen generated from radiolysis do not react to form water and (2) that the oxygen generated by radiolysis reacts with the oxide material and does not contribute to the pressure in the container. With regard to the first assumption, if the formation of water from hydrogen and oxygen is important, then the calculated pressures would be dramatically reduced. The formation of water is thermodynamically favoured."

 Morales made use of PVT apparatus to allow for collection of rate determining data

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- He observed that the final gas phase was approximately stoichiometric consistent with H₂O formation although water was not observed within the gas phase
- The rate was shown to plateau over time indicating the blocking of reaction sites
- This suggests that PuO₂ powder is used as the reaction site within the recombination reaction mechanism



"Figure 5a – Plots of the pressure-time curves measured for both the pure and impure oxides as a function of moles of hydrogen consumed during the experiments" – taken from Preliminary Report on the Recombination Rates of Hydrogen and Oxygen over Pure and Impure Plutonium Oxides by Morales - 1999

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- It is possible to perform concentration based experiments to determine if one of these mechanisms is in use
- By holding H₂ concentration and varying O₂ concentration the observed rate should rise through a maximum at 2:1 H₂:O₂
- If the L-H mechanism is in use the rate should fall after the maximum
- If the rate plateaus after the maximum it is indicative of the E-R mechanism





- An alternative mechanism was highlighted by Thomas Donoclift based on work by Mullins of Oak Ridge National Laboratory
- Cerium in Cerium Oxide is capable of attaining both a sub- and super-stoichiometric form
- Donoclift proposed that the Mars van Krevelen mechanism could therefore be used to facilitate the recombination reaction





- Donoclift conducted concentration based experiments to determine whether the MvK mechanism was in effect in a cerium oxide powder system
- The concentration of O₂ was varied whilst H₂ was held at a constant 4.3 x10⁻⁴ mol dm⁻³. This was also repeated with a constant O₂ concentration and a varied H₂ concentration



Experimental Planning

 Experimental preparation has been carried out over the last few months and initial calibration and testing of the experimental set up should be underway in a few months time

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 Experimental work at this stage will focus on Donoclift's experimental theme and will aim to gain a more complete understanding of the potential mechanisms





Experimental Planning

- There are minor differences between the experimental set ups though they shouldn't fundamentally change to the nature of the system
- The main difference is the change from a continuous flow reactor to a batch reactor this was done to better simulate the sealed "batch-like" conditions of a canister
- A batch reactor will be connected to a GC equipped with a TCD via a gas sampling rig
- Cerium Oxide powder will be used initially though there are plans to examine a range of simulants over time
- Experimental Parameters: Temperature – 350°C
 Pressure – 3 bar
 Mass of Powder – 0.01 mol (1.72 g CeO₂)
 Maintained Concentration of Gas – 0.4%
 Varied Range of Gas – 0-1% (0.1%
 increments)



"Figure 1 – Flammability Diagram for Hydrogen/Air/Nitrogen at 400°C and 1 bar" – taken from Molnárné at al. – 2018

Future Work

 Moving on from here there are multiple options for further experimentation and data collection

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- There are plans to utilise a range of simulants to isolate different redox chemistries to determine if this has an impact on the mechanism
- Options to examine powder morphology and powder stoichiometry to determine whether changes to reaction sites could also impact the employed mechanism



"Figure 1 – Single water molecule adsorbed molecularly on the 2x2 UO {111} surface" – taken from Water Adsorption on AnO₂ {111} {110} and {100} Surfaces (An = U and Pu): A Density Functional Theory + U Study by B. Tegner -2018



"Figure 17 – Dissociative adsorption of a single water molecule on the UO {100} slab, at the oxygen vacancy. The positon of the oxygen vacancy is indicated with a black circle" – taken from Oxygen Vacancy Formation and Water Adsorption on Reduced AnO₂ {111} {110} and {100} Surfaces (An = U and Pu): A Computational Study by J. Wellington - 2018



Thank You

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The U-factor on the simulations of PuO_2 and its interaction with water

Xiaoyu Han, Nik Kaltsoyannis University of Manchester Nuclear Materials



19 May, 2021





The Sellafield nuclear reprocessing site in Cumbria © Redharc Images/Alamy

UK has the world's largest stockpile of the PuO_2 .

- Sellafield in Cumbria
- 2 "Magnox" research sites and 10 nuclear power stations

Inside of the PuO_2 storage container, water and other small molecules might interact with PuO_2

A major barrier to making progress --- lack of knowledge about the retired facilities.



Choices on the Hubbard U

- <u>The experimental data on lattice parameter</u>, **bandgap**, bulk modulus, etc.
- 1.8 eV; electronic band gap;¹ Calcined plutonium oxalatc; 20-1000 C; linear fitting for intrinsic bandgap.
 2.80 eV; optical band gap;²
 - PAD thin film; RT
- <u>A linear response approach</u> to the calculation of the effective interaction parameters in the DFT+U method



• <u>The redox reaction from the experiment</u>

a small added potential on f electron (0.2 eV) could change the number of f electron by nearly 2 e.

How PuO₂ responds to U value and its surface chemistry?

¹C.E. McNeilly, J. of Nuclear Materials, 11, 53, (1964) ² T. Mark McCleskey, J. of Appl. Phys. 113, 013515 (2013);





Computational settings

- VASP
- PAW-PBE Duddarev +U method
- 500 eV cutoff
- $5 \times 5 \times 5$ and $15 \times 15 \times 15$ k point mesh for bulk geometry relaxation and pDOS, respectively
- For the slab, 2×2 supercell with 5 layers, the bottom 2 layer fixed.
- Dipole correction along the surface direction
- 15 Å vacuum slab
- DFT- D3 correction for the vdW correction





• Larger U, bigger the bandgap

PBE0

• Smaller U, more close to the lattice P

 $(n \cdot e) = (n \cdot$

Which U could mimic the electronic character?



the degeneracy of the plutonium 5f and oxygen 2p bands ARPES for PuO_2 on a PAD film at 40.8 eV (enhance 5f character)*



Fig. 4. PDOS of bulk AnO₂ (An = U (top), Np, Pu (bottom)) modelled as $An_{16}O_{32}$ clusters with the PEECM and the PBEO functional. Vertical line shows the Fermi level. Vertical scale in arbitrary units.

Pu 5f **hybridization** with O 2p orbital at valence band is the KEY.





neering for Nuclear Decommissioning

XES :Two shoulders with width of 1.8 eV



- Small U leads to metallic;
- a charge-transfer insulator in large Hubbard U;
- a Mott insulator in small Hubbard U

U=3 preserved the **hybridization** and **the peaks width**

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2

(a)

U=1

с 5-Е_f (eV)

-4

2

-2

(b)

E-E_f (eV)

(c)

E-E_f (eV)

U=3

2

0

-2

Г

ΧU

κ

Г

LWX

Х

U

Г

Κ

Г

U=2



wx

L

indirect bandgap ---- direct bandgap





W: How hard to remove an electron from the surface



$Pu_1 \xrightarrow{O_1}{O_2}$

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	U=1	U=2	U=3	U=4	U=5	U=6
O ₁ (6)	7.17	7.19	7.20	7.21	7.24	7.24
Pu ₁ (16)	13.69	13.62	13.61	13.60	13.52	13.55
O ₂	7.17	7.18	7.19	7.21	7.24	7.23
O ₃	7.16	7.22	7.21	7.21	7.26	7.23
Pu ₂	13.64	13.58	13.55	13.53	13.50	13.49
Pu (bulk)	14.03	13.67	13.60	13.65	13.66	13.68
O (bulk)	6.98	7.17	7.20	7.18	7.17	7.16



- **U=3** is more close to PBE0;
- When U>3, the surface Pu is more oxidized than bulk.

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H₂O@PuO₂ (111)



Charge difference



- Pu-O_{water} bond length is decrease with U value.
- Both surface energy and adsorption energy is oscillate with U





E_{ad} is more related with the charge transfer of water and the O₃ Not Bonded Pu



E_f (eV)

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Summary

- Systematic studied the U value affect on the PuO_{2;}
- Compared with experiment and hybrid functionals, <u>U=3</u> is the best to mimic the electron characters at the conduction band;
- Lattice parameter, bandgap, band alignments, work functions, bond length with water are almost <u>linear responds</u> to the U;
- However, the effective charge, charge transfer, surface energy and water adsorption energy are <u>oscillated</u> with the U.
- E_{ad} is more related with the charge transfer of water and the O₃, as well as the Fermi level allocation.



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Thank you

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