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Simfuel Approaches to Understanding Spent Fuel Behaviour

I. Farnan

A. Popel, F. Lord, Z. Heizl [(1)], W.E. Lee[(1)], R. Grimes [(1)], M. Cooper [(1)]
C. Boxall [(2)], N. Rauff-Nishtar [(2)], C. Anwyl [(2)], D.I. Hambley [(3)]

[1] Department of Materials Science, Imperial College London
[2]Department of Nuclear Engineering, Lancaster University
[3]National Nuclear Laboratory, UK

Department of Earth Sciences & Cambridge Nuclear Energy Centre

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Behaviour of UK Specific Spent Fuel Under Conditions Relevant to Geological Disposal

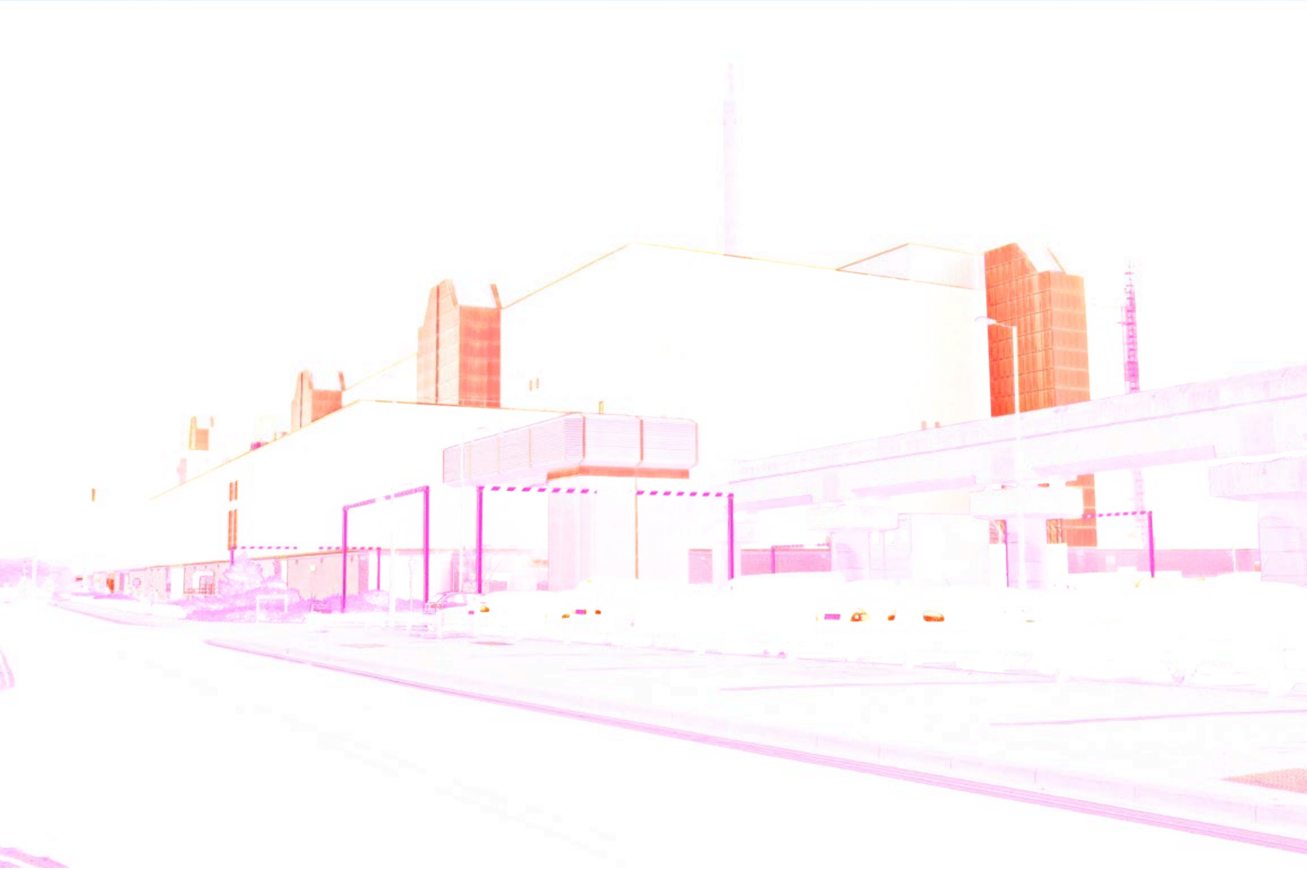
Deepen understanding of dissolution processes of AGR spent fuel

- develop a simfuel approach to understand the location and effect of fission products on the behaviour of AGR SNF (UO_2).

- 5 Investigators, 6 PhD students - 4 year project

Robin Grimes, Bill Lee (Imperial College)
Colin Boxall (University of Lancaster)
David Hambley (UK National Nuclear Laboratory)

Disposal of Spent Fuel in the UK



THERMAL OXIDE REPROCESSING FACILITY (THORP)

Due to close in 2018

UK will not re-process all AGR spent fuel

Some AGR spent fuel will be directly disposed in Geological Disposal Facility (GDF)

Case for direct disposal of PWR and BWR fuels in Europe and USA is well-developed.

Large body of international knowledge on the behaviour of spent fuel under the conditions expected in a GDF

Disposal safety case can use international work, but needs to understand the differences between AGR fuel and LWR spent fuel.

Because of the history of re-processing in the UK there is a lack of expertise in spent nuclear fuel disposal.

UK Advanced Gas Reactor (AGR) Fuel

Comparison with LWR fuel

Temperature

The elevated operating temperature of an AGR reactor compared with a PWR or BWR reactor (825˚C vs ~ 300˚C);

Geometry

The AGR fuel pellet is annular while the PWR is a disc.

Cladding

AGR fuels are clad in niobium-stabilised, high Cr/Ni austenitic stainless steel rather than zircalloy for LWR fuels;

Carbon

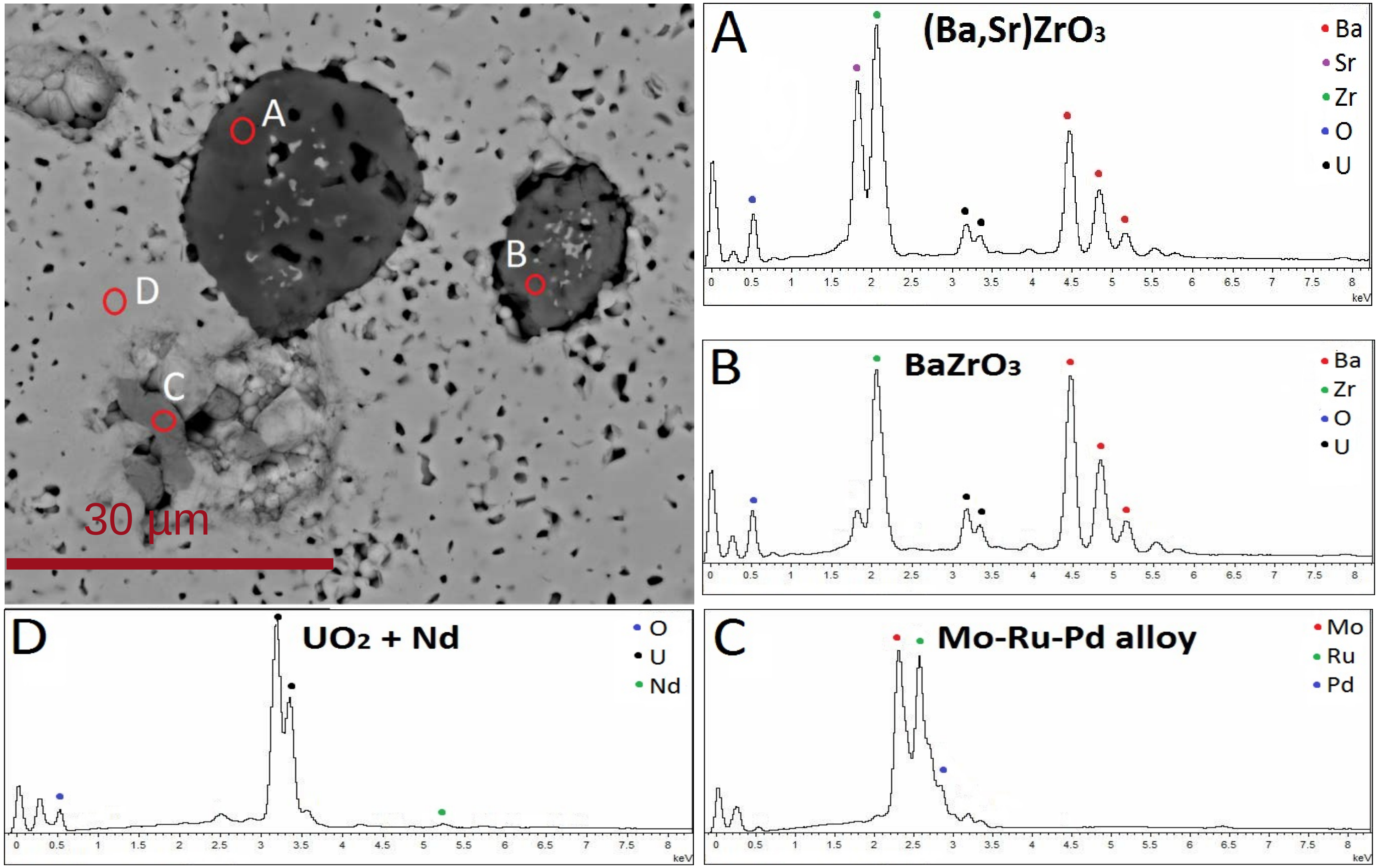
The steel cladding has acquired a carbon deposit due to deposition from additives in the CO_2 coolant.

SimFuel production (WP2)

Phase 1 AGR SimFuel

Chemically representative

spatially features are too large



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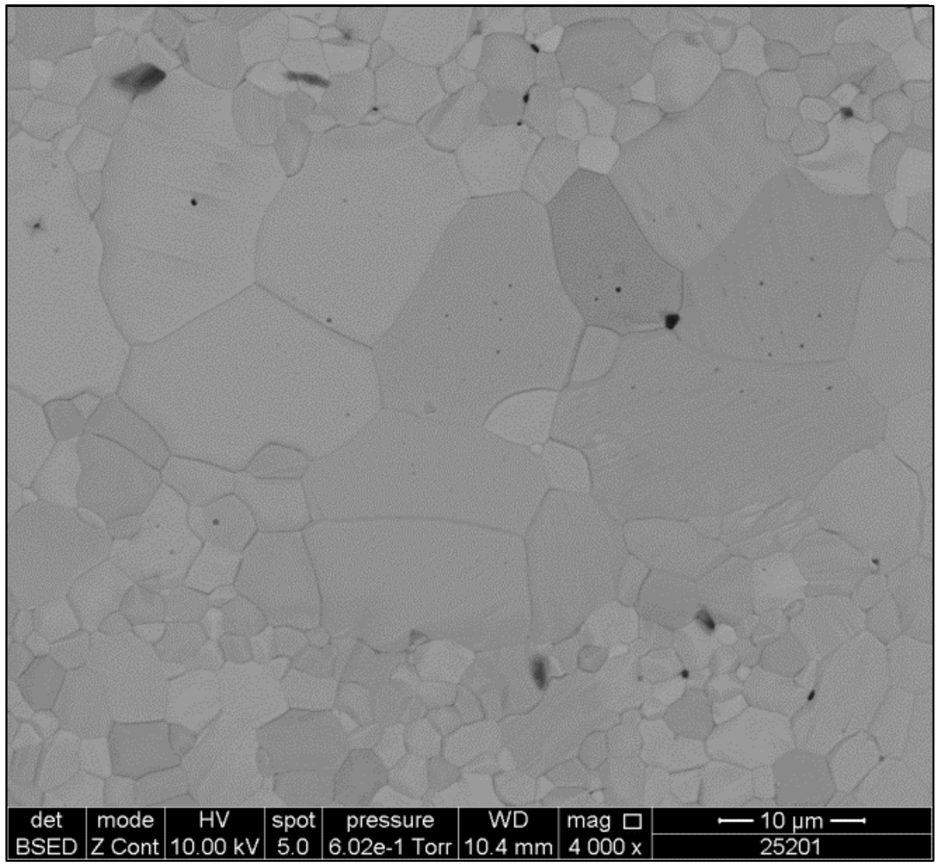
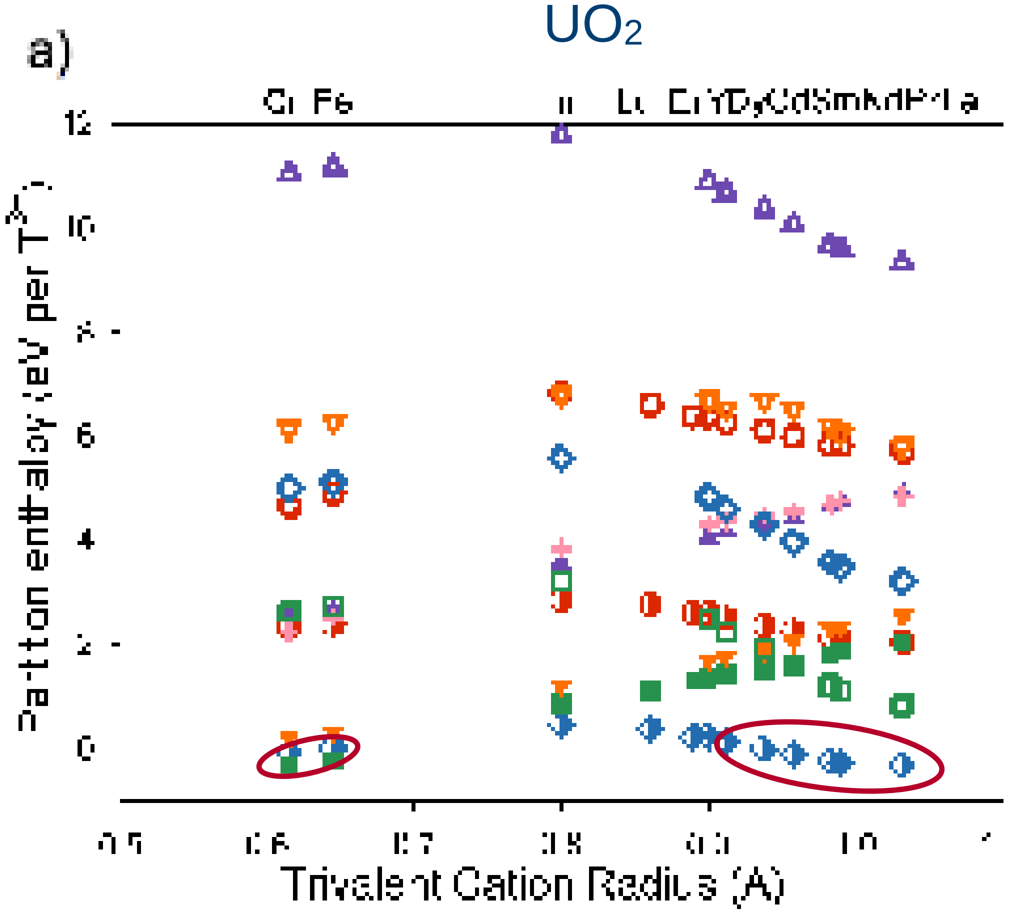
SimFuel production (WP2)

- Two batches of SIMFuel were successfully prepared.
- Grain sizes are smaller than those measured for AGR SNF, but this is due to longer time at elevated temperature.
- Pores are larger in AGR SNF than in SIMFuel, but the overall porosity is higher for the latter. Significant improvement for the 2nd batch.
- SEM-EDX revealed metallic and oxide precipitate:
- Metallic precipitates are mainly Mo, Rh, Ru and Pd,
- Grey-phase is mostly Ba, Zr, Sr and O.
- Several FP surrogates dissolved in UO_2 matrix, such as Ce and Nd.
- The presence of these second phases correspond to literature references.



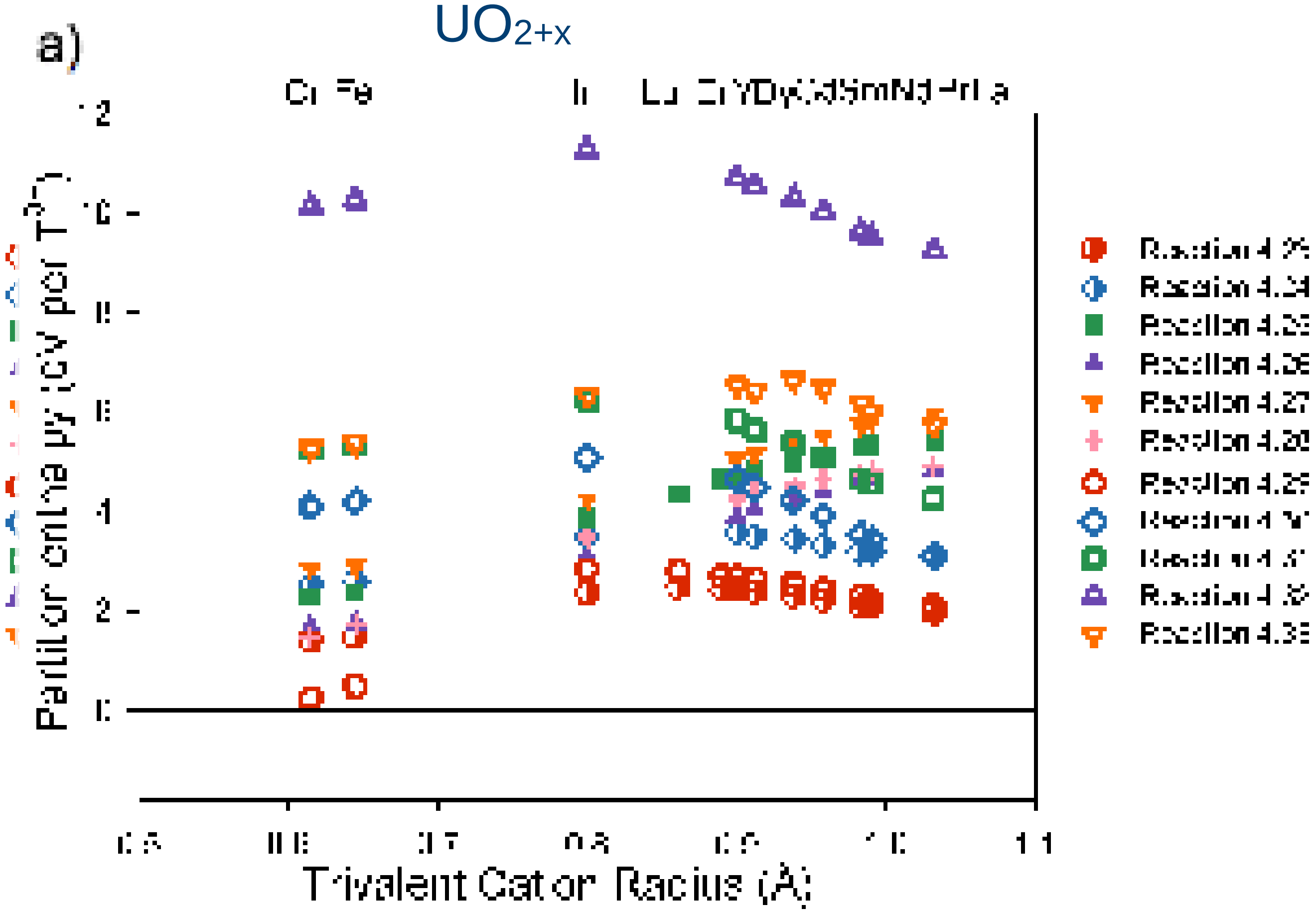
SimulatingFP incorporation into AGR fuel (WP3)

UO$_2$



Some fission products segregate to barium zirconate under stoichiometric conditions

UO$_{2+x}$



BUT not from hyper-stoichiometric UO$_{2+x}$

Full results found here: M.W.D. Cooper, S.C. Middleburgh, R.W. Grimes, *Prog. Nucl. Energ.* ***72*** *33* (2014)

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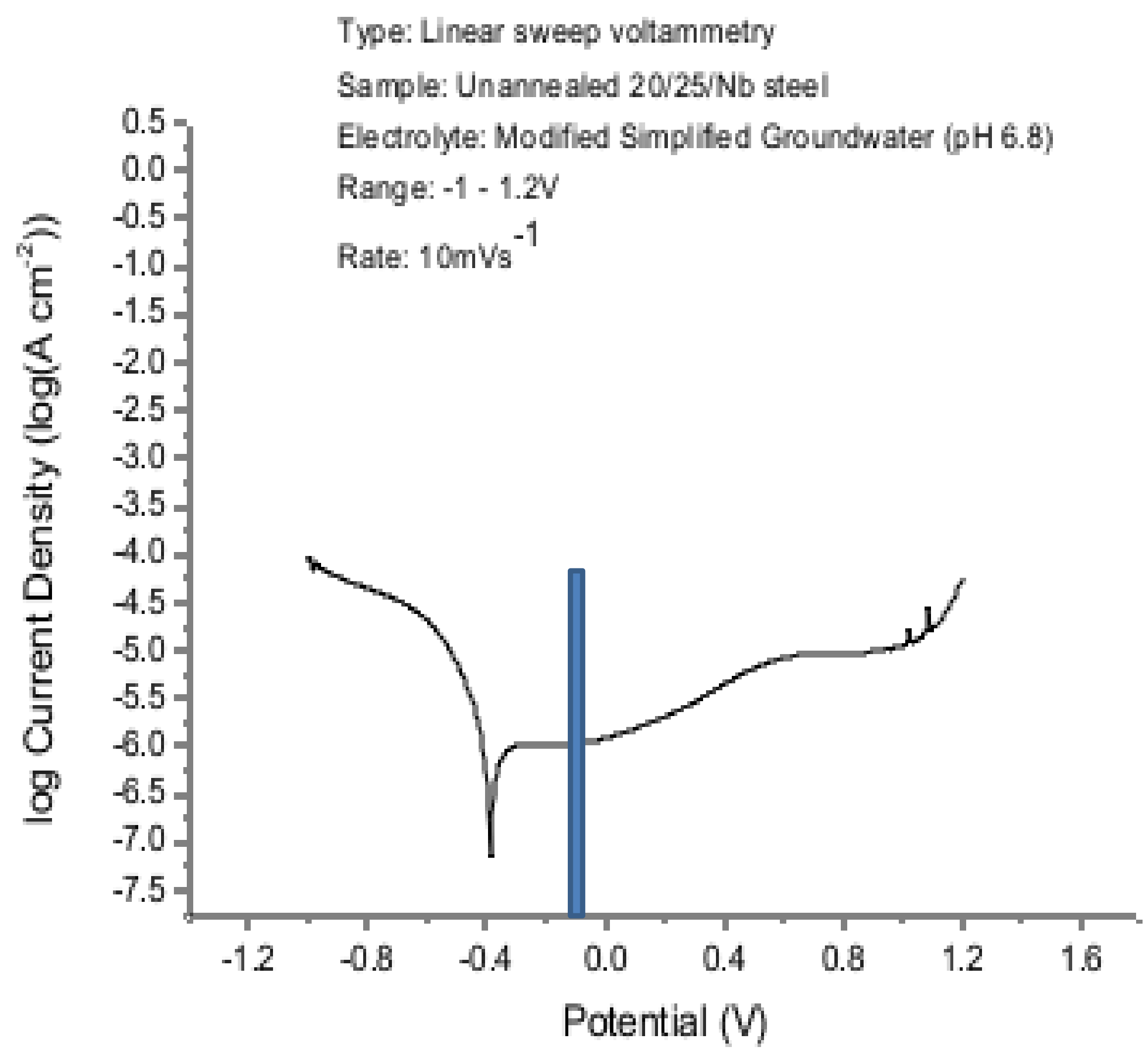
Corrosion of AGR steel clad (WP6)

•20/25/Nb steel has strong corrosion resistance

•In low-chloride electrolyte such as the "modified simplified" Studsvik ground water (10mM NaCl), OCP sits at low potential (-165mV)

•Stable and passive in the absence of H_2O_2 and without coupling to the UO_2 spent fuel



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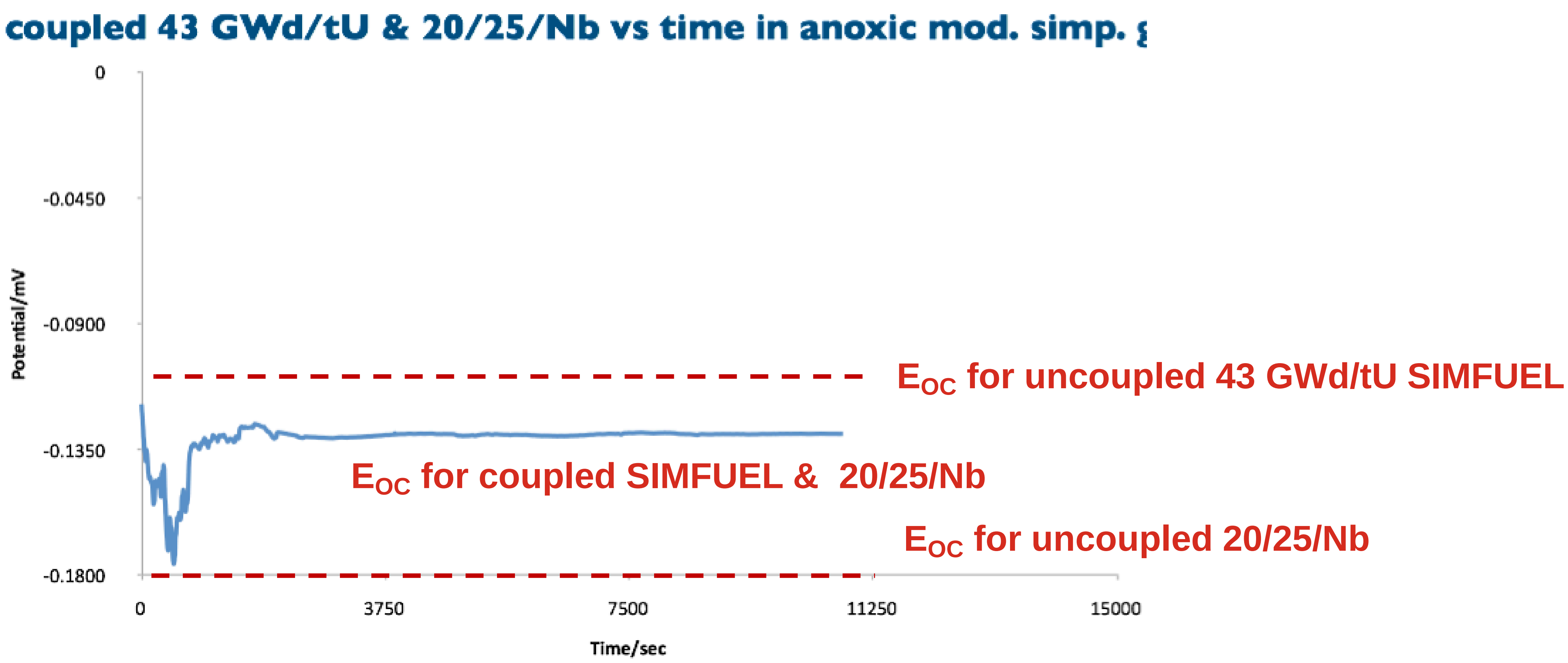
Corrosion of UO_2 SimFuel (WP5)



- E_{OC} measurements on 43 GWd/tU AGR SIMFUELs samples in intimate contact with 20/25/Nb steel in modified simplified groundwater show a mixed potential of ~-0.12 V vs SCE.
- Corresponds to nearly a quarter of the way up the oxidation wave for in-grain UO_2 to UO_{2+x} process in the associated SIMFUEL CV – lower than uncoupled SIMFUEL in groundwater – implying that UO_2/steel coupling **protects** UO_2 matrix against corrosion

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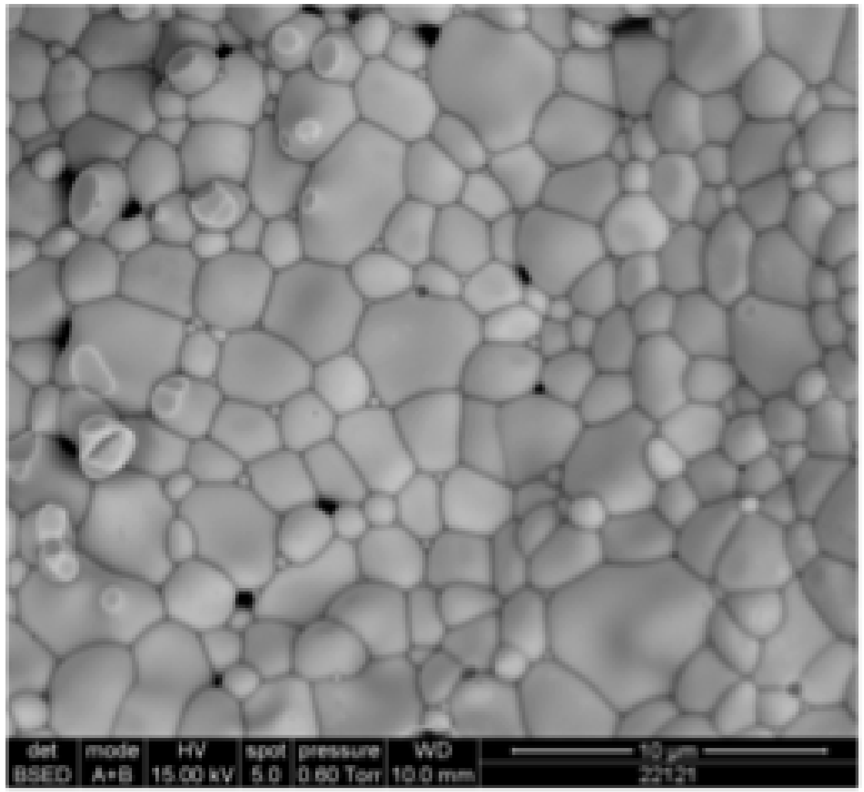
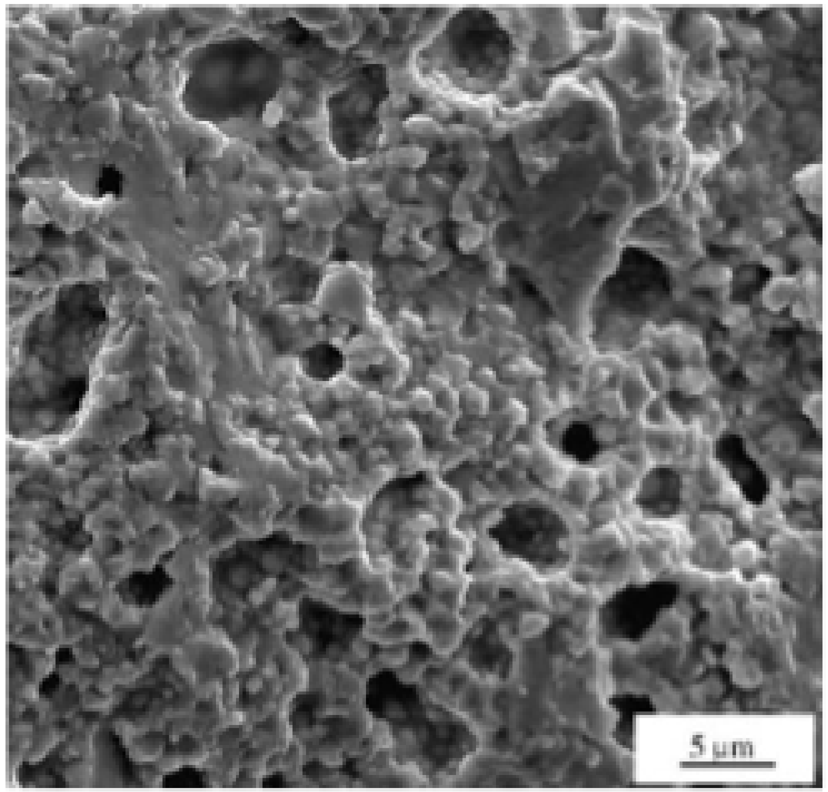
SimFuel vs UO_2

Scanning Electron Microscopy



SEM UO_2 SimFuel pellet



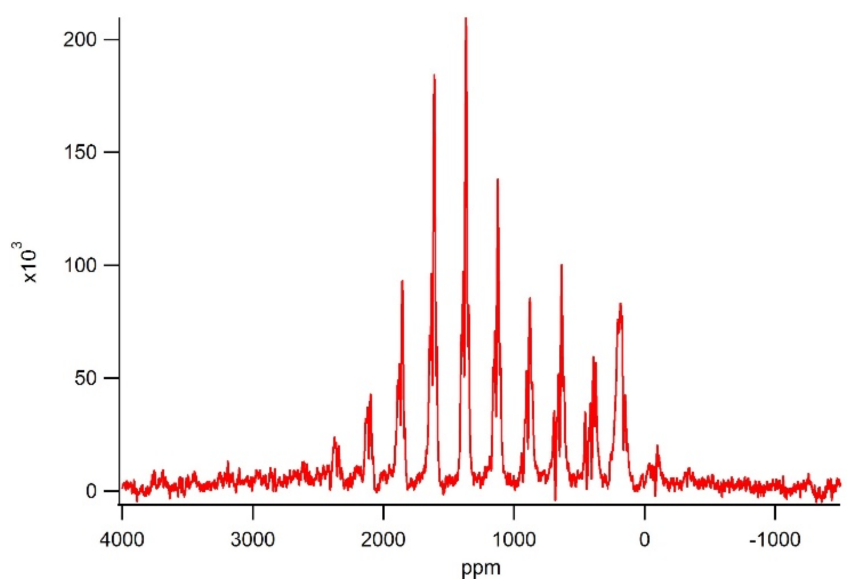
SEM Spent Nuclear Fuel (UO_2)

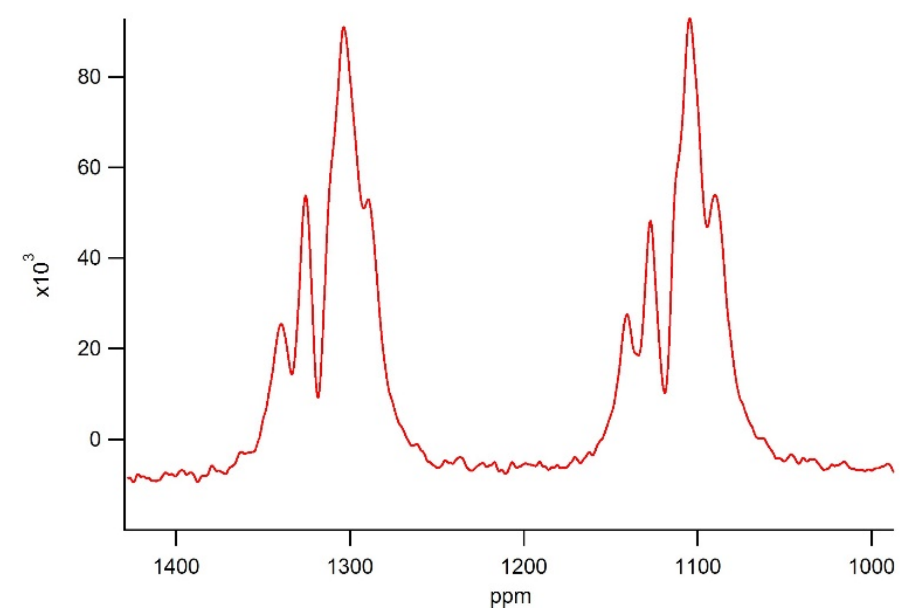
Thesis: A. Popel

Secondary Mineralisation of UO_2 SimFuel (WP7)

^{17}O NMR

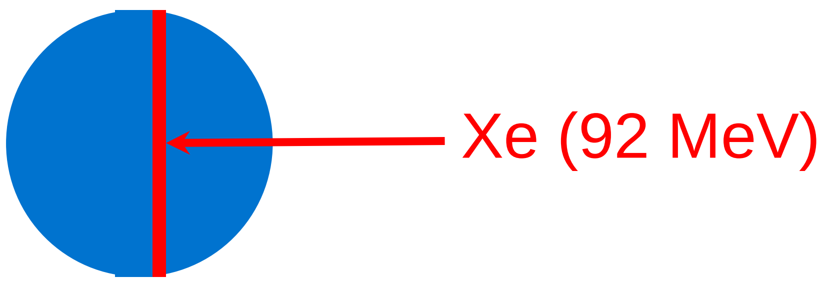
- Samples precipitated from ^{17}O enriched solutions
- Overall oxygen enrichment around 25%
- Very strong uranyl signal; can refine at least 4 environments in metaschoepite
- Expect equal intensity from bridging O and interlayer water, but uranyl dominates.





Irradiation of SimFuel and UO_2 with 92 MeV Xe

1 mm disks



7µm

GRAND ACCELERATEUR NATIONAL D'IONS LOURDS

I. Monnet & C. Grygiel

11 disks irradiated at GANIL

Total fluence of $4.8 \times 10^{15}/cm^2$ 92 MeV Xe^{23+}

The only study of the effect of radiation damage on UO_2 solubility is by Matzke.
Used 40 keV krypton and saw one order of magnitude increase in U solubility.
Here we use fission fragments of appropriate energy for in-reactor damage.

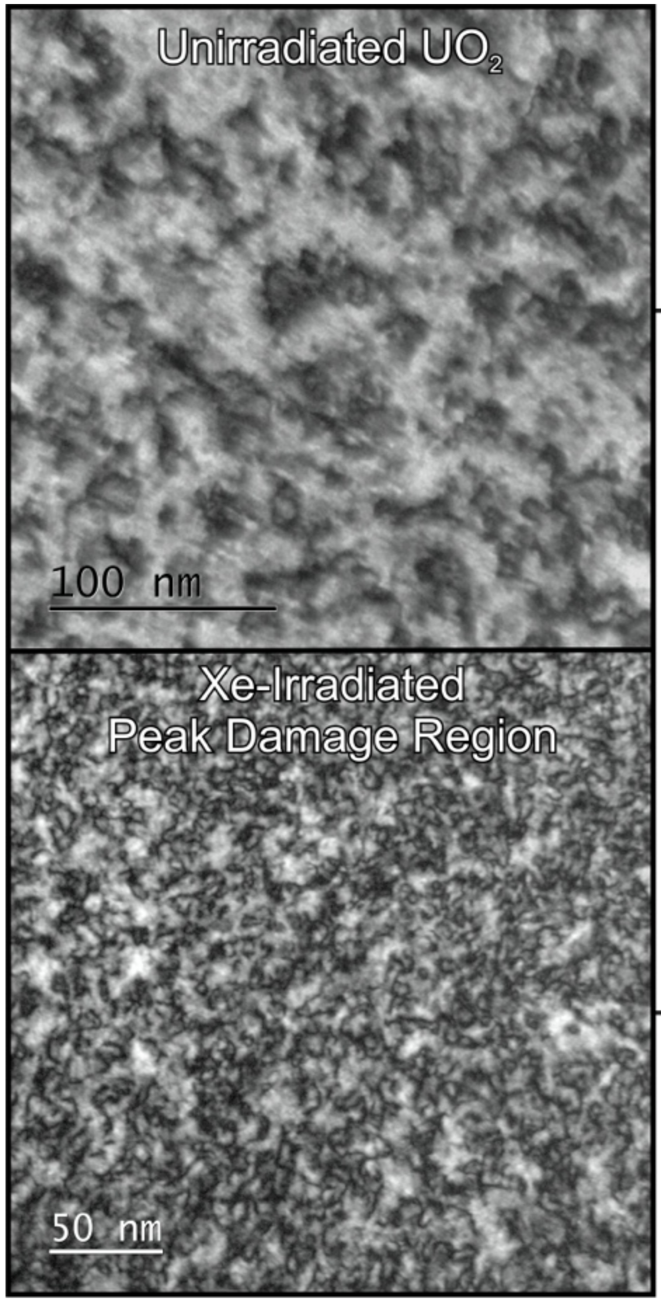
Matzke, H. (1992). "Radiation damage-enhanced dissolution of UO_2 in water." J. Nucl. Mat. 190:101-106

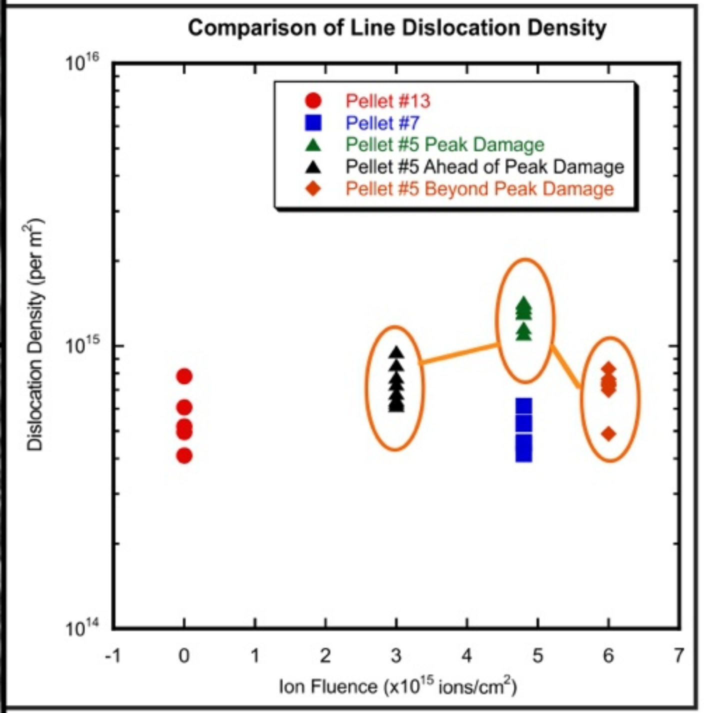
Irradiation of SimFuel and UO_2 structural effects

Small 10 µm sections lifted out of pellets by FIB-SEM

Irradiated samples FIB section spanned the peak damage position, penetration ~7 µm (TRIM)

Density of both line and loop dislocations higher at damage peak than at either side also higher than unirradiated and irradiated 43GWd/THM SimFuel

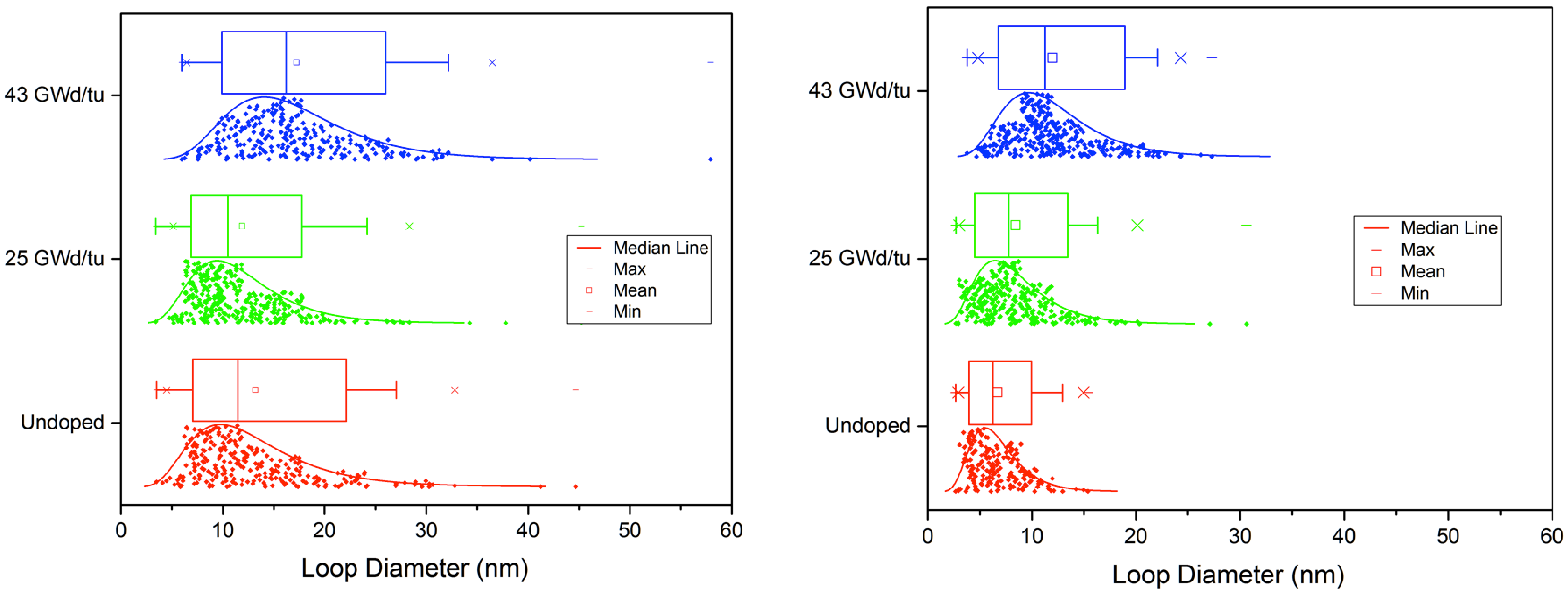




Danny Edwards (PNNL)

Irradiation of SimFuel and UO_2 structural effects

Loop dislocation distributions in SimFuel

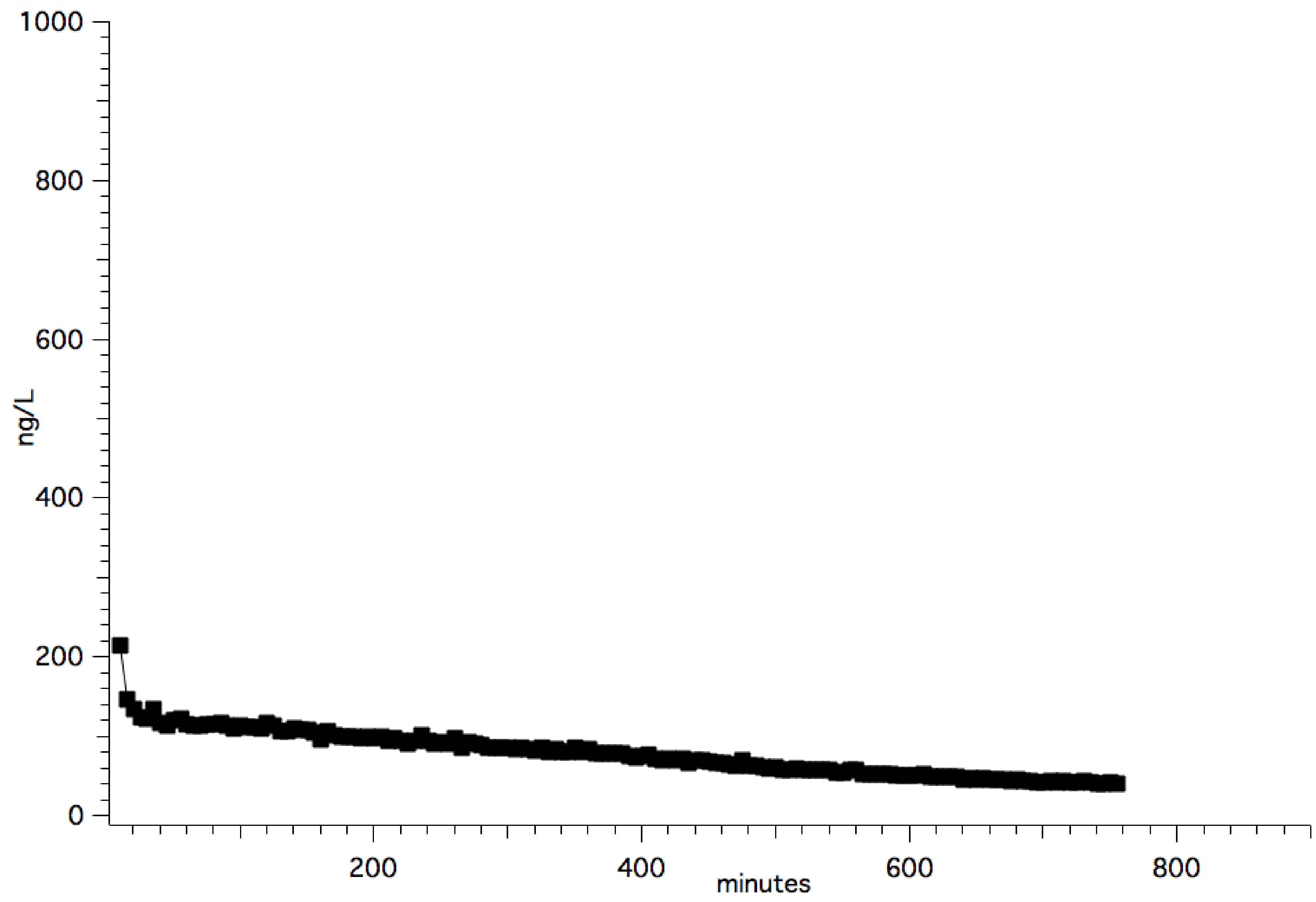


Dissolution of SimFuel - undoped UO_2

Undoped UO_2 12hr dissolution experiment

Initial loss of oxidised layer, settles quickly to a linear behaviour

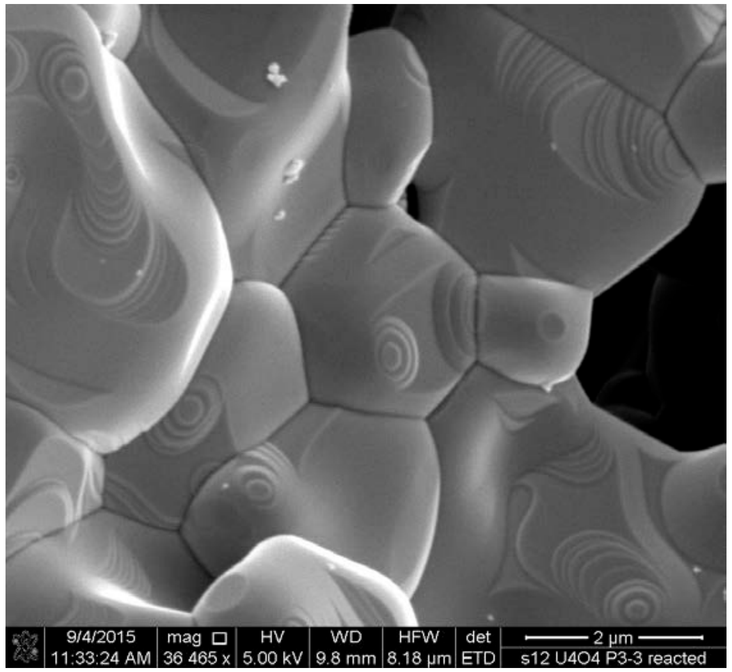
irradiated UO_2 sample much greater concentration of U in solution. Not a simple removal of oxidised layer.



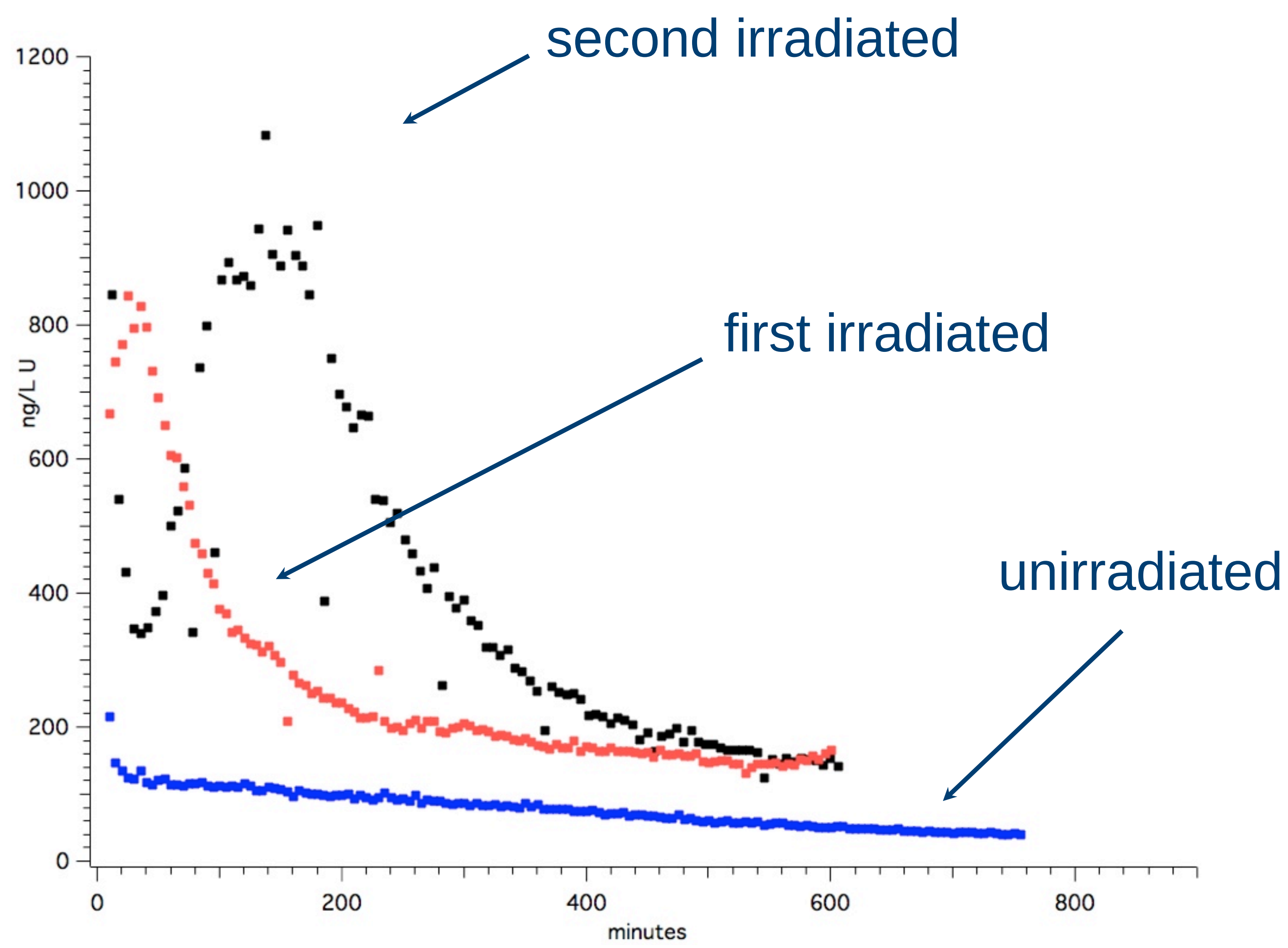
Dissolution of SimFuel - undoped UO_2

Undoped UO_2 12hr dissolution experiment

2nd irradiated UO_2 pellet has initial loss (of oxidised layer?) and then peak as seen for 1st irradiated sample.

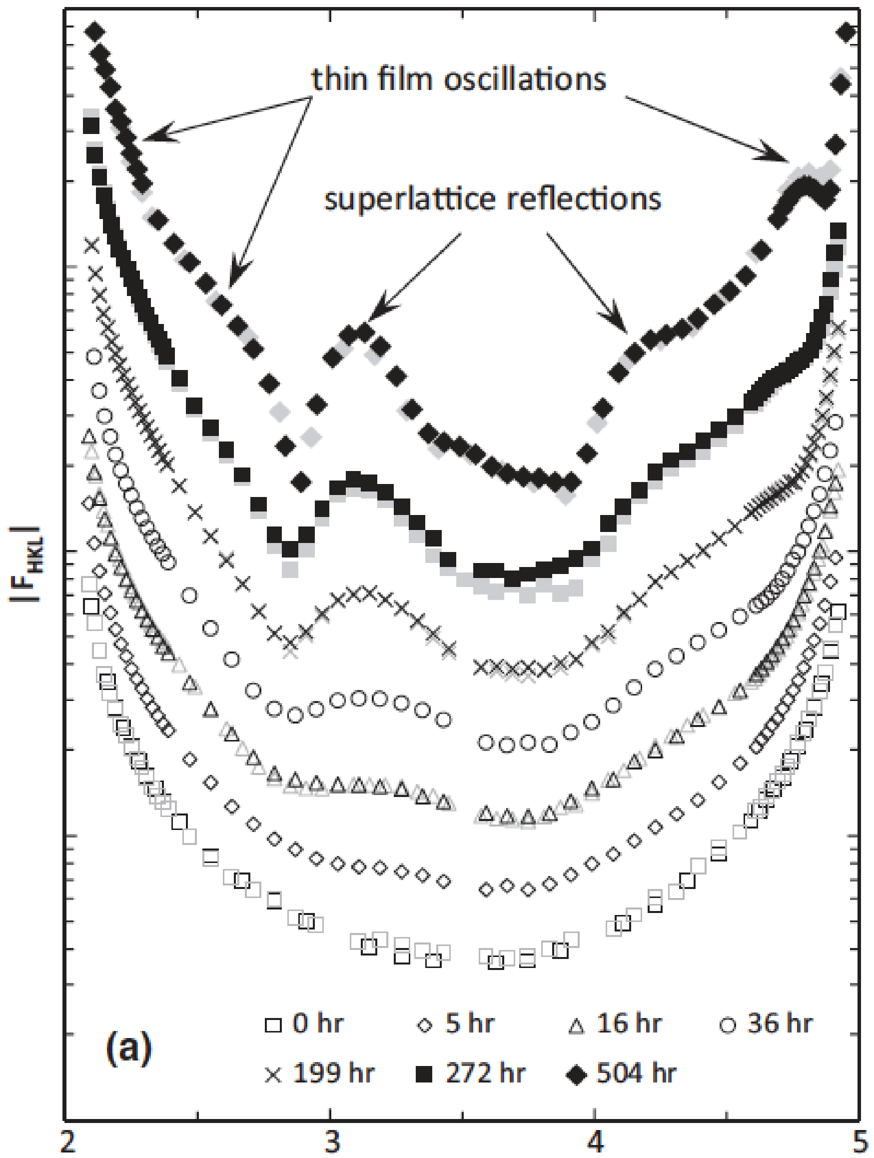


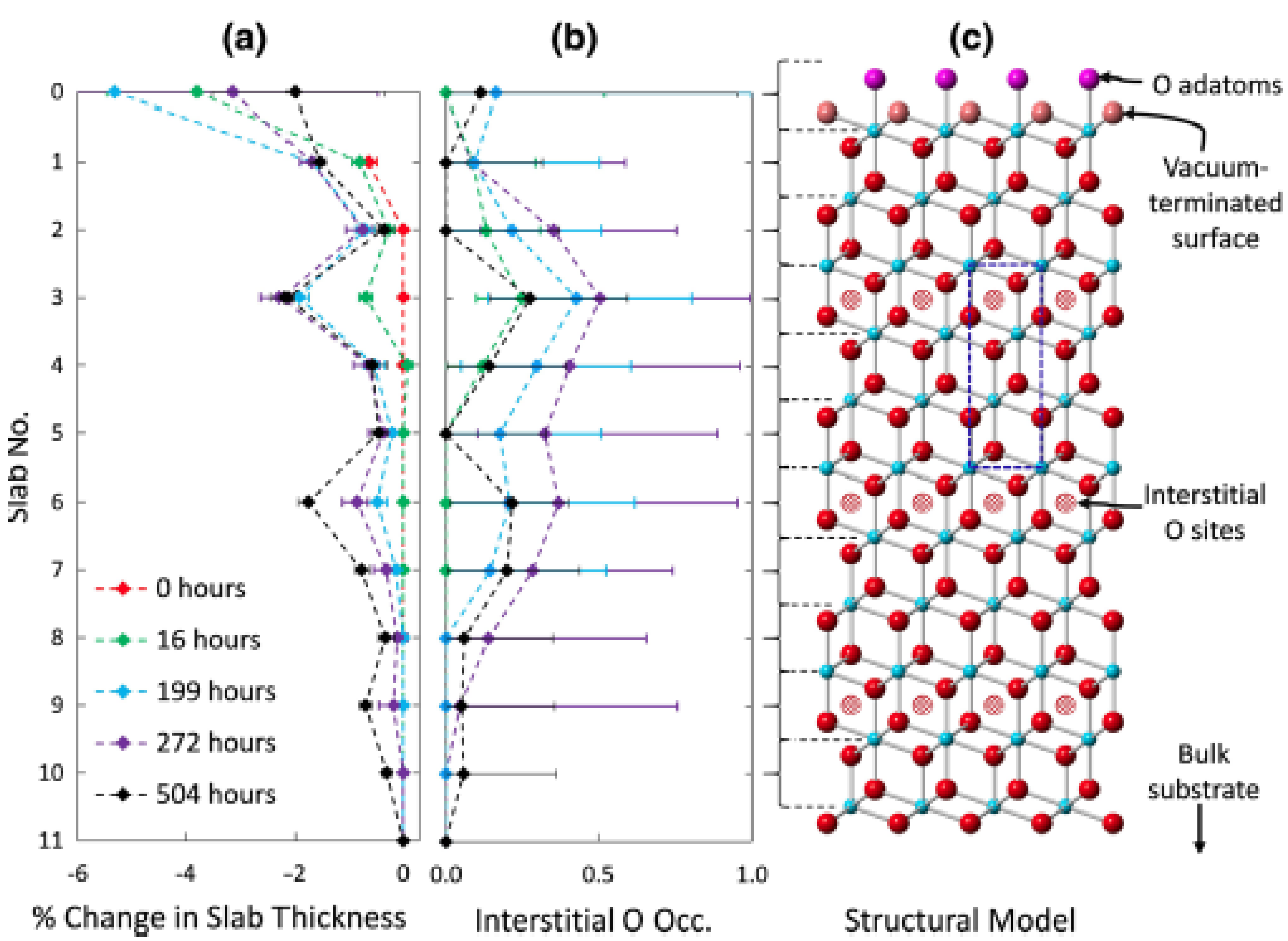
SEM 2nd irradiated UO_2 (after)



Early Stage Oxidation of UO_2

CTR Diffraction & DFT





Stubbs et al, PRL 114, 246103 (2015)

Suitability of UK Spent Nuclear Fuel for Disposal

Summary

Produced two batches of DU SIMFuels -
- chemically representative of AGR SNF
- can control topological/spatial representation
- ‘radiation damage’ simulated with accelerated ions

Producing atomistic models that predict solution/ex-solution FPs in UO_2

Producing interatomic potentials that describe UO_2 and MAs at fuel operating temperatures.

Electrochemical corrosion of clad
- elemental release, conditions for pit corrosion established
- determined corrosion of UO2 SimFuel
- coupling with clad corrosion carried out. Safety effect demonstrated.

U minerals grown in lab
-dentification of key secondary mineralisation features in amorphous and crystalline alteration products, - incorporation of transuranics ‘demonstrated’

Summary

Can produce AGR SimFuel chemically very similar to real SNF, epsilon-particles, grey phase separation and FP partitioning topologically still a challenge

Can see effects of radiation on structure in SimFuel - potential to understand influence on dissolution

DU SimFuels are ‘easily’ handled and can be used in tandem with FIB-SEMs becoming available in active facilities.

SimFuels can be used to investigate separate effects observed/implied in real spent fuel.

Acknowledgements

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