H_2 Generation from Radiolysis of Adsorbed Water on the Surface of PuO_2

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DISTINCTIVE Theme Meeting, Rheged Center
17th October 2017

Research Councils UK Energy For a Low Carbon Future

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This Work

- Investigate H_2 production
- Thorp and Magnox material 'as received'
- Range of %RH conditions
- Argon glovebox
- Parallel samples in N_2 glovebox

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Sample Humidification

- H_2SO_4 solutions used to achieve a range of %RH (25-95%RH)
- Samples weighed periodically until a constant weight is achieved
- 0.21 mg m^{-2} per monolayer of H_2O used to calculate water monolayer coverage

J.M. Haschke and T.E. Ricketts, *J. Alloy Compd.*, 1997, **252** (1-2), 148-156

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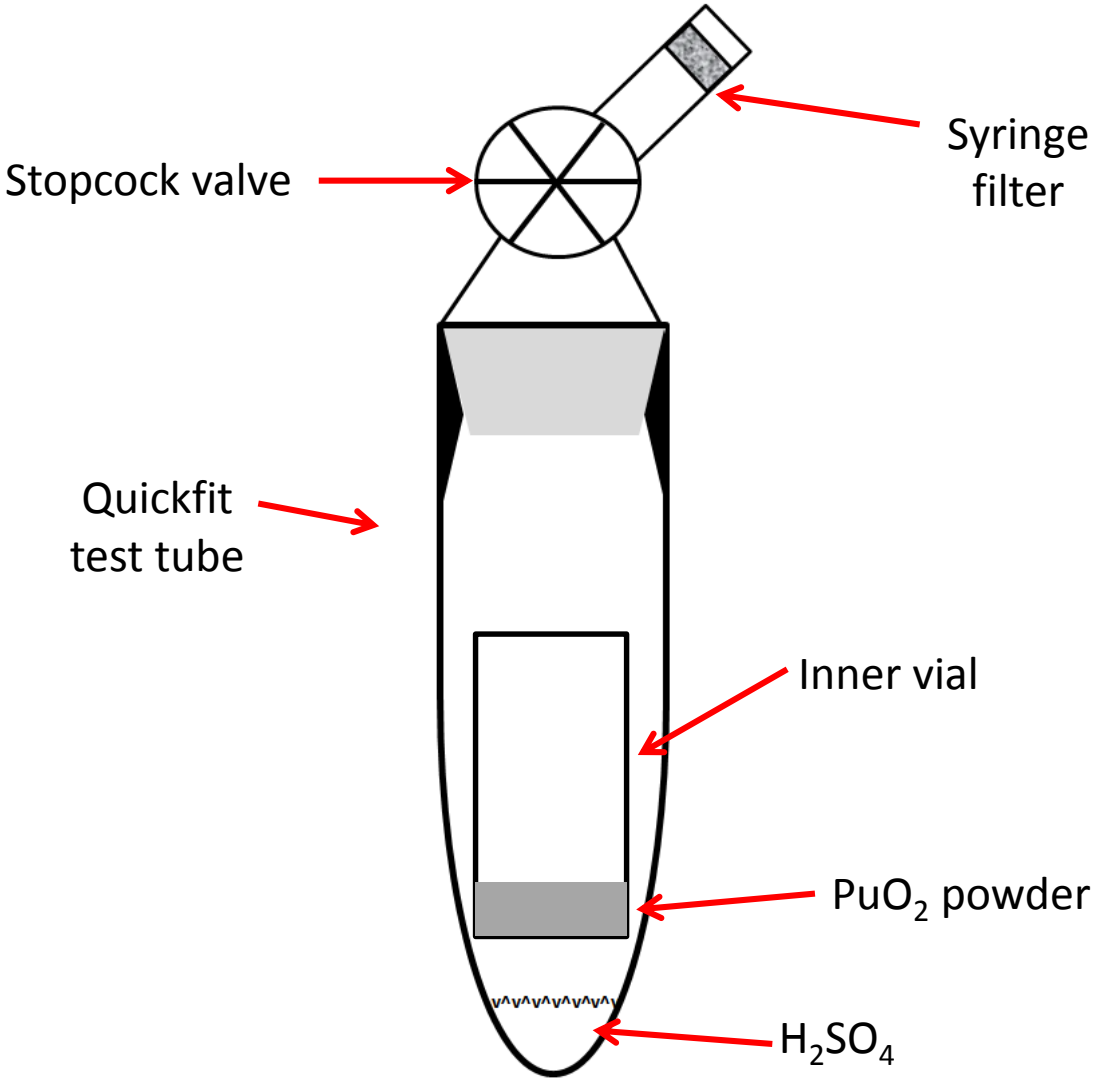
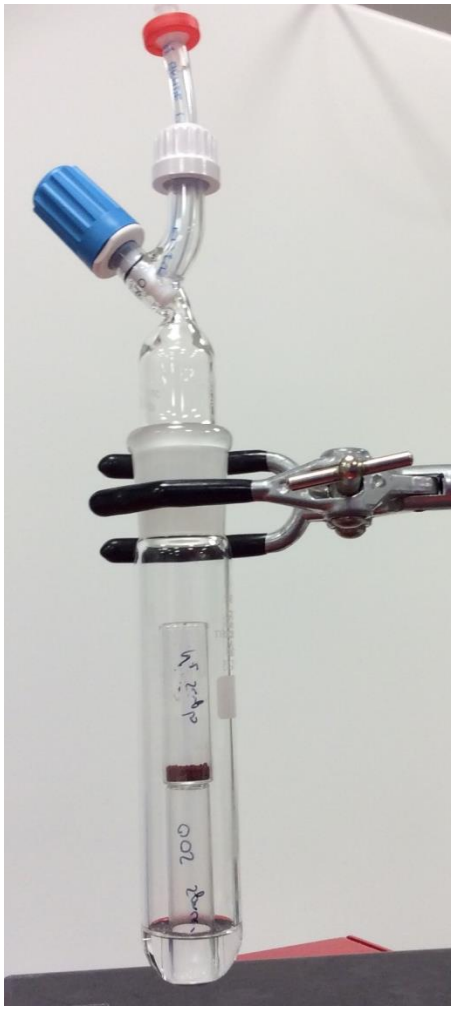
Experimental Set-up





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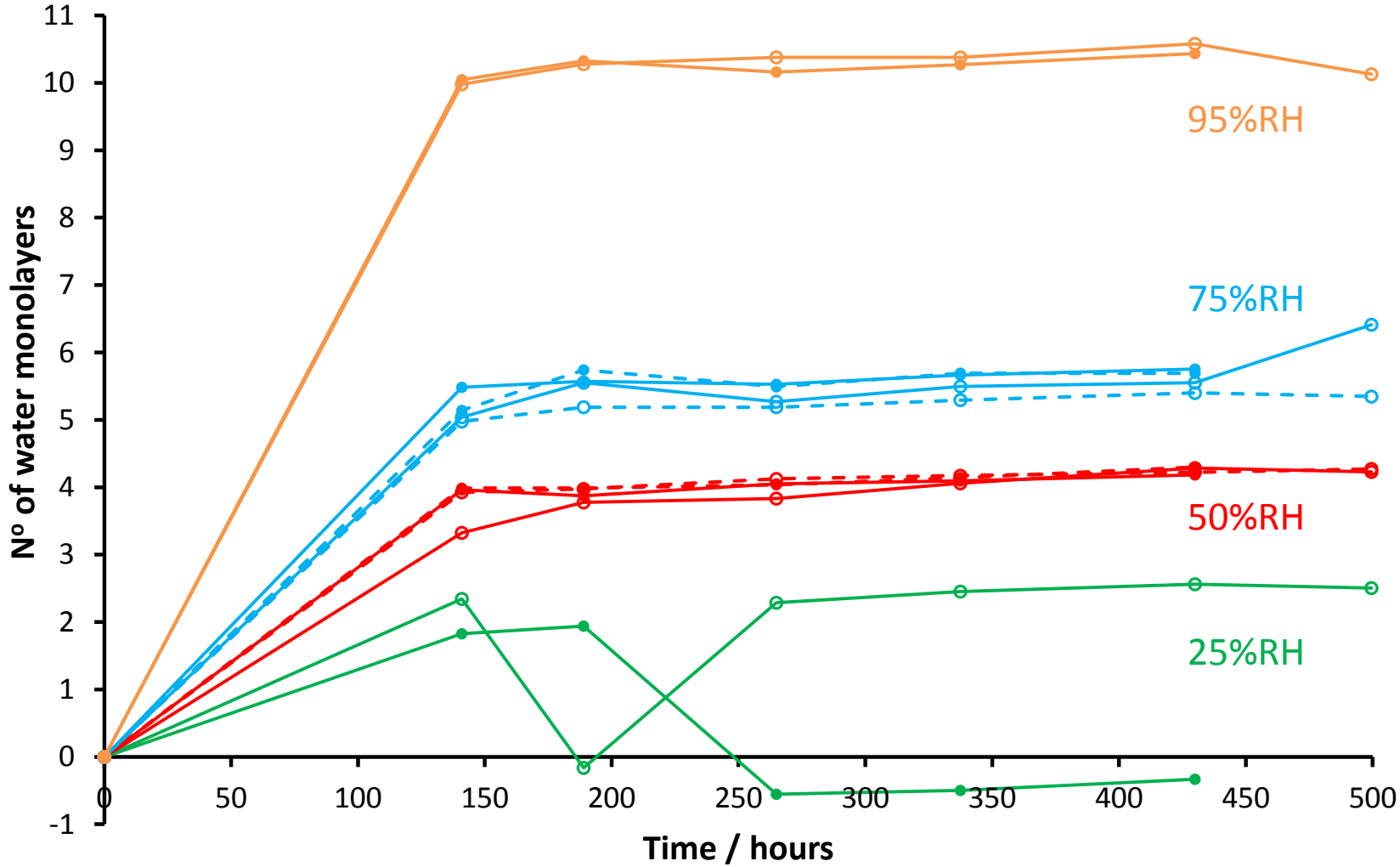
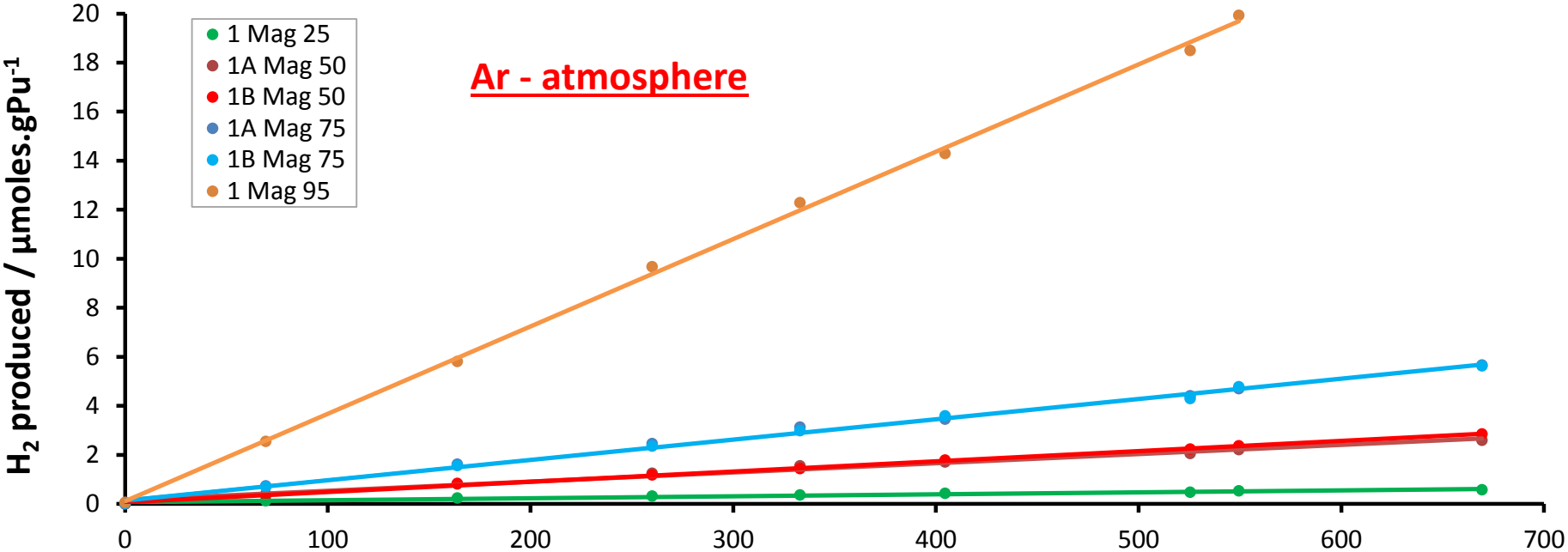
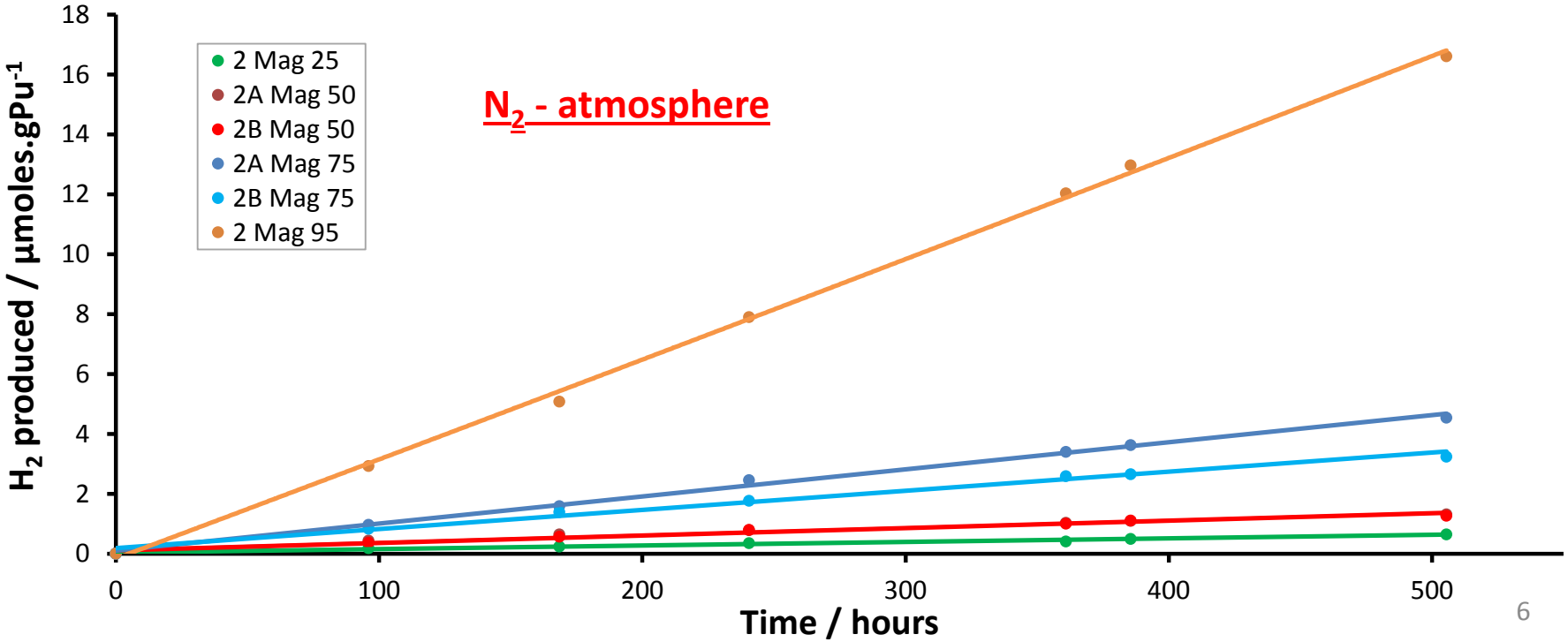
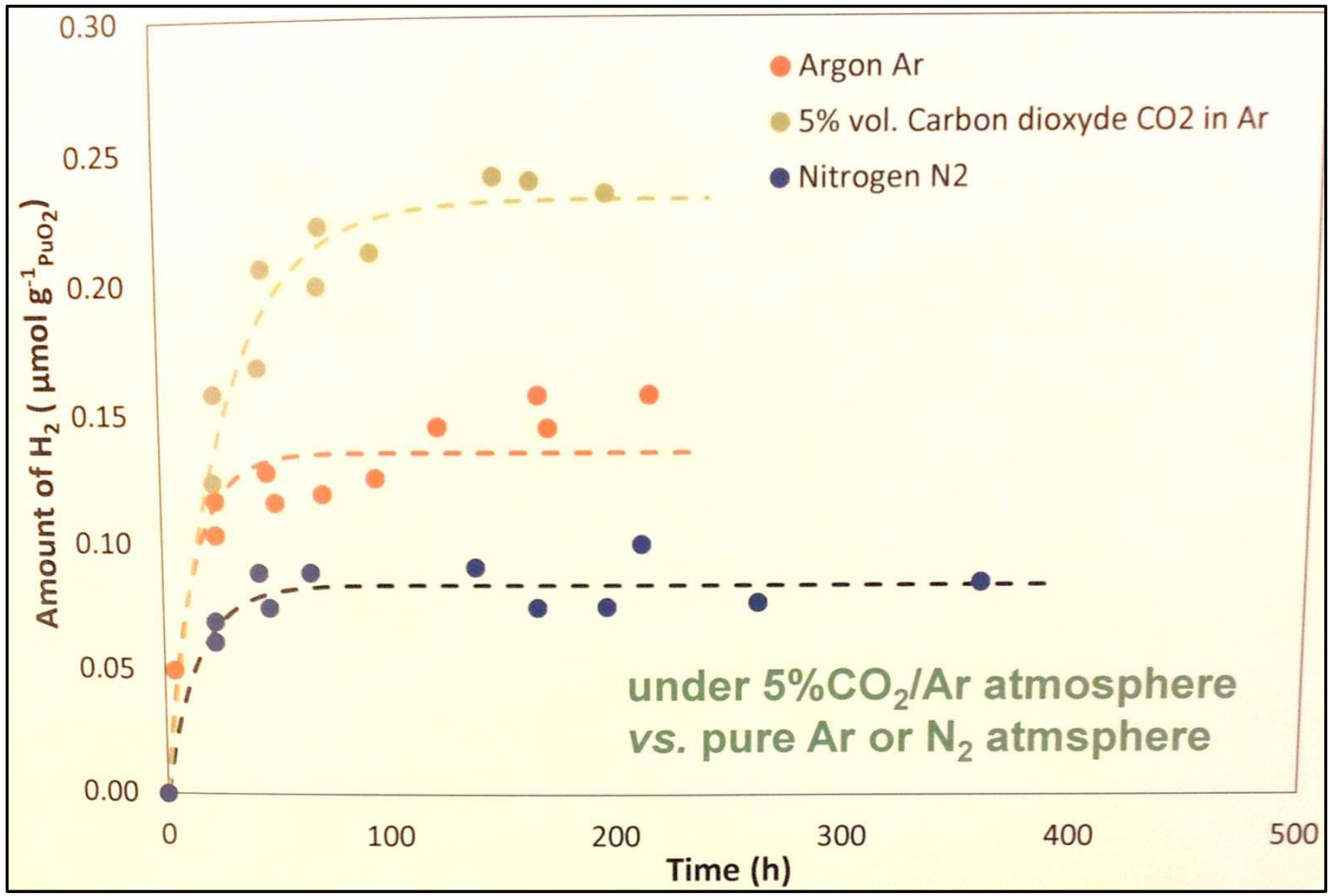
Magnox Humidification



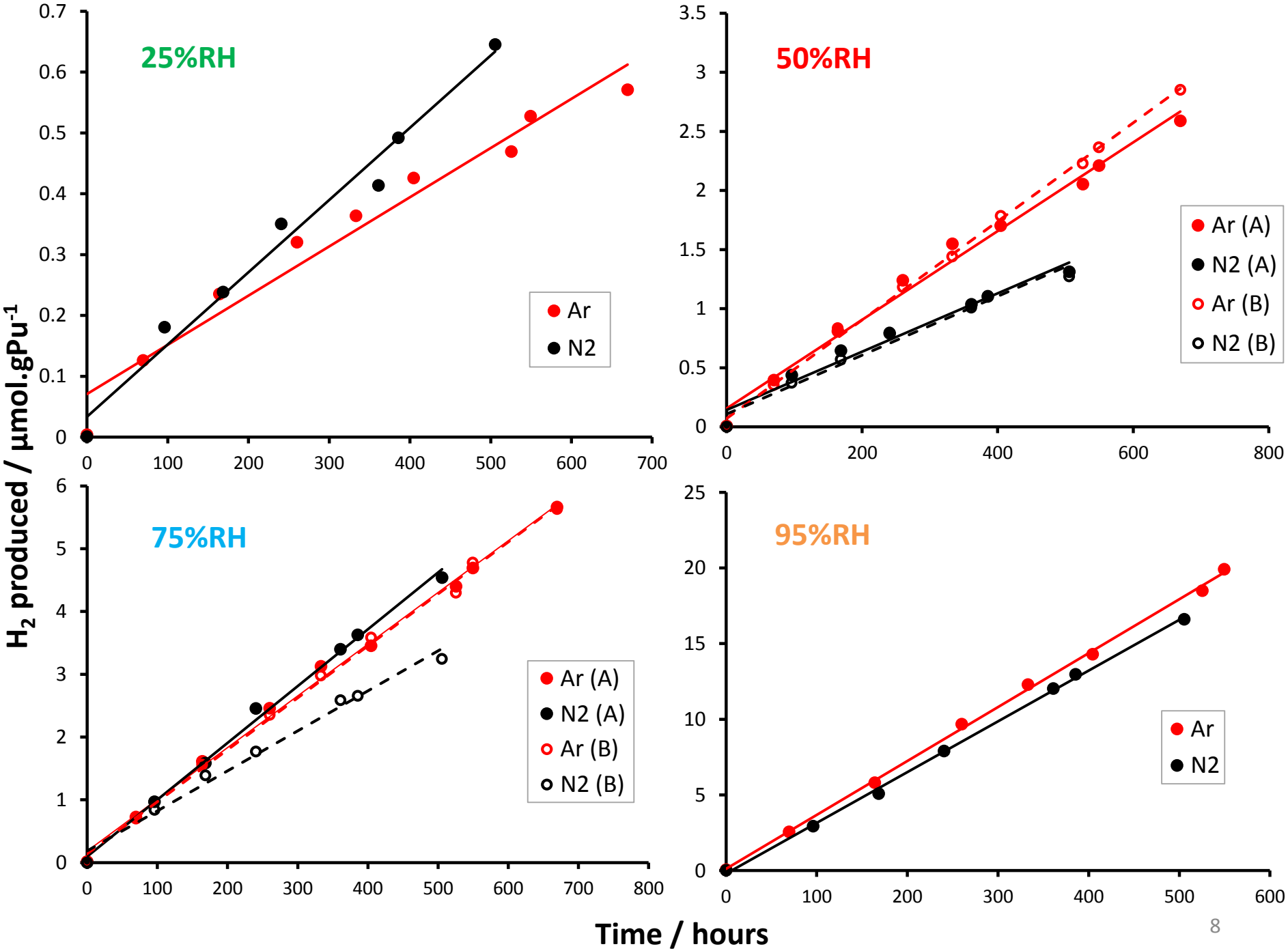
Magnox PuO_2 SSA: 9.2 ± 1.2 $m^2\ g^{-1}$


Ar - atmosphere
1 Mag 25
1A Mag 50
1B Mag 50
1A Mag 75
1B Mag 75
1 Mag 95
H2 produced / µmoles.gPu-1
0
2
4
6
8
10
12
14
16
18
20
0
100
200
300
400
500
600
700


N2 - atmosphere
2 Mag 25
2A Mag 50
2B Mag 50
2A Mag 75
2B Mag 75
2 Mag 95
H2 produced / µmoles.gPu-1
0
2
4
6
8
10
12
14
16
18
0
100
200
300
400
500
Time / hours



L. Venault et.al., CEA, poster presented at 30th Miller Conference, Sicily, Oct. 2017


25%RH
Ar
N2
50%RH
Ar (A)
N2 (A)
Ar (B)
N2 (B)
75%RH
Ar (A)
N2 (A)
Ar (B)
N2 (B)
95%RH
Ar
N2
H2 produced / µmol.gPu-1
Time / hours

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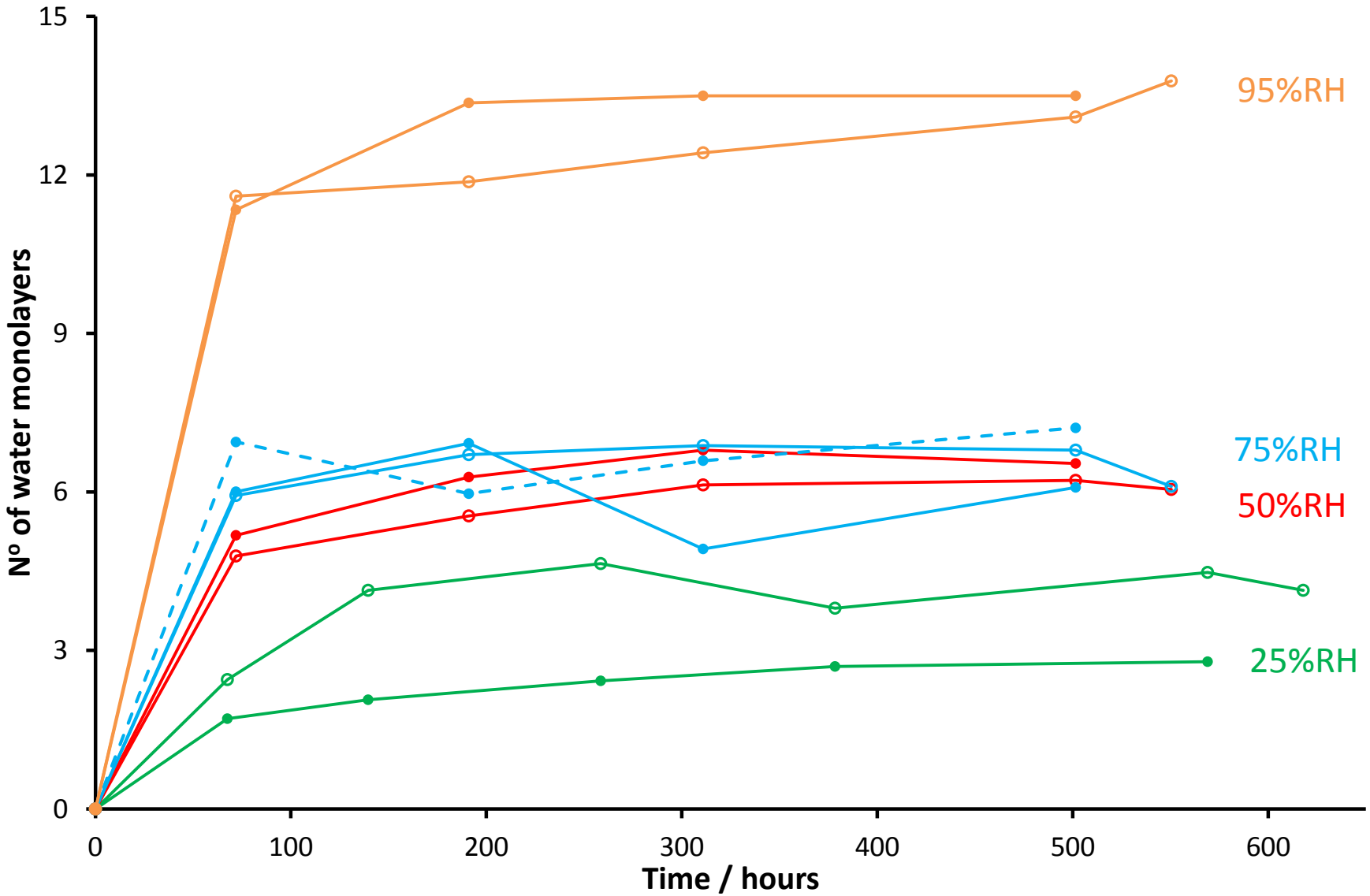
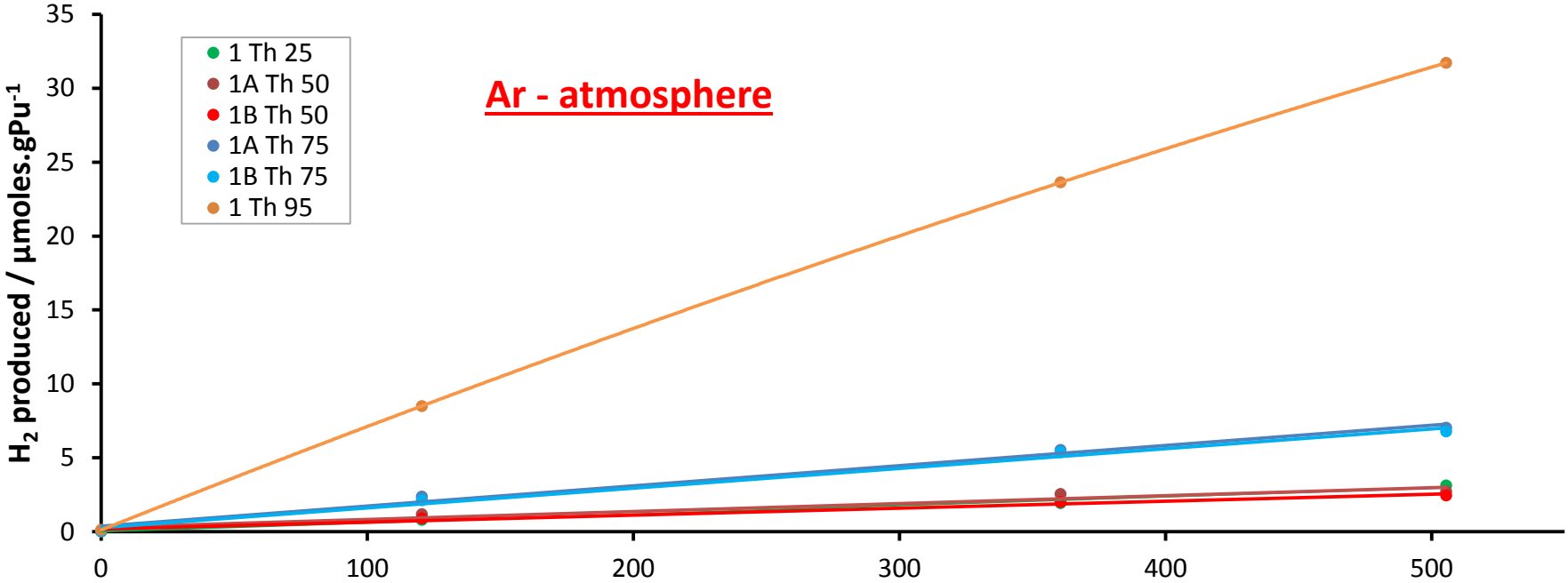
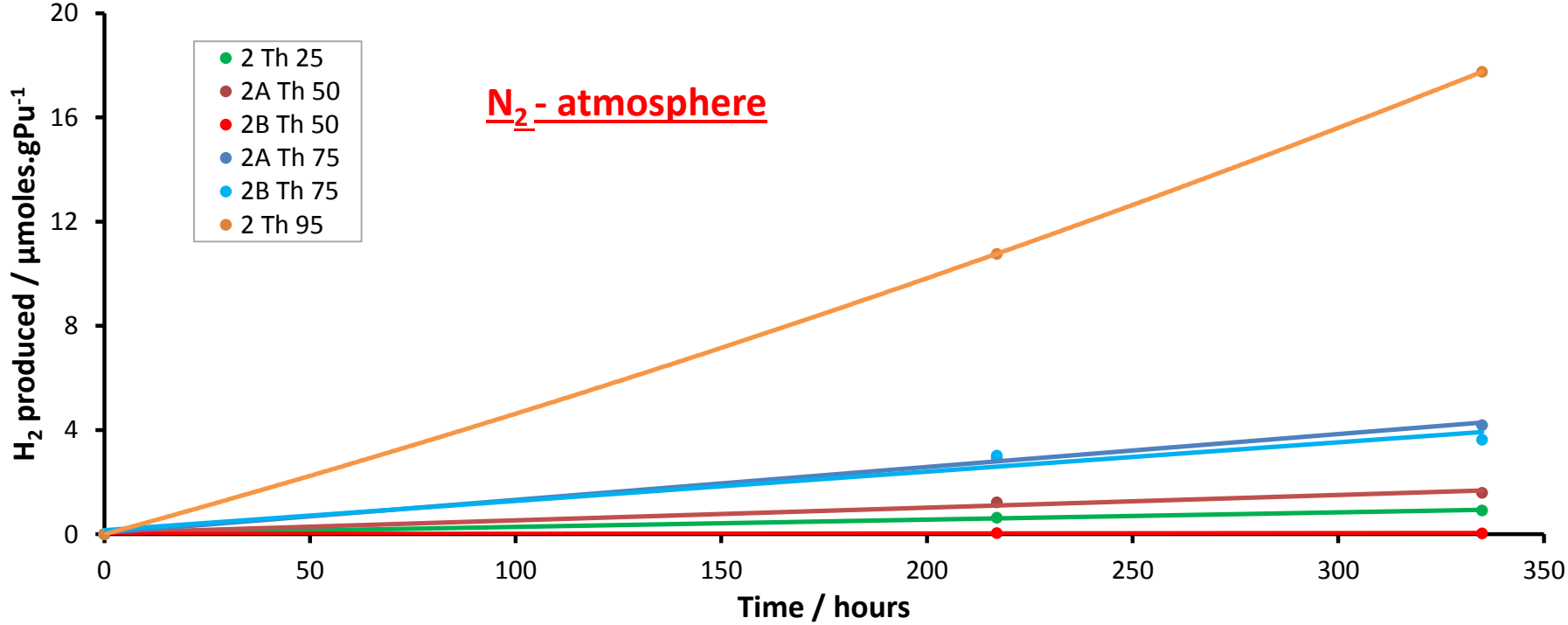
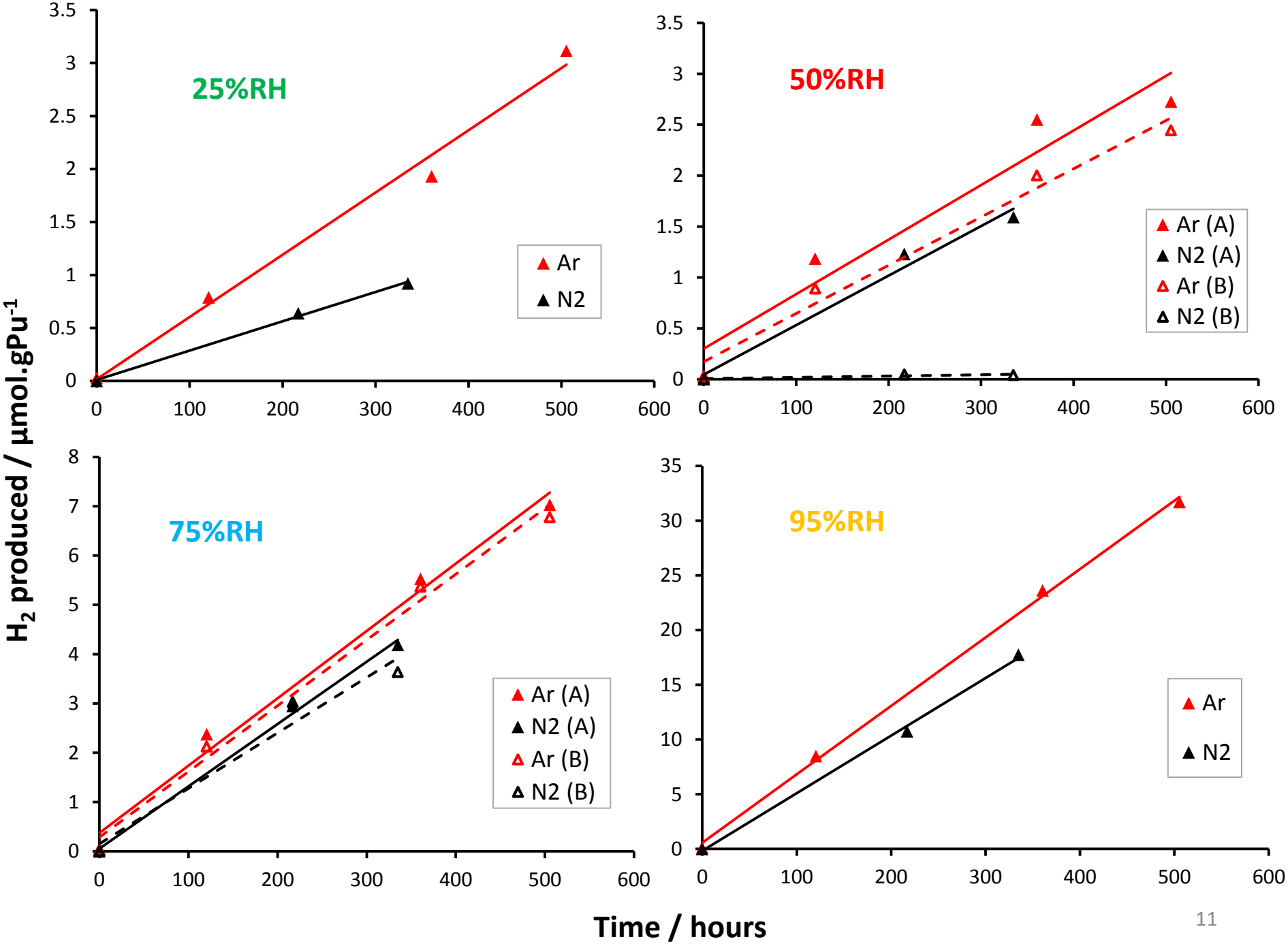
Thorp Humidification



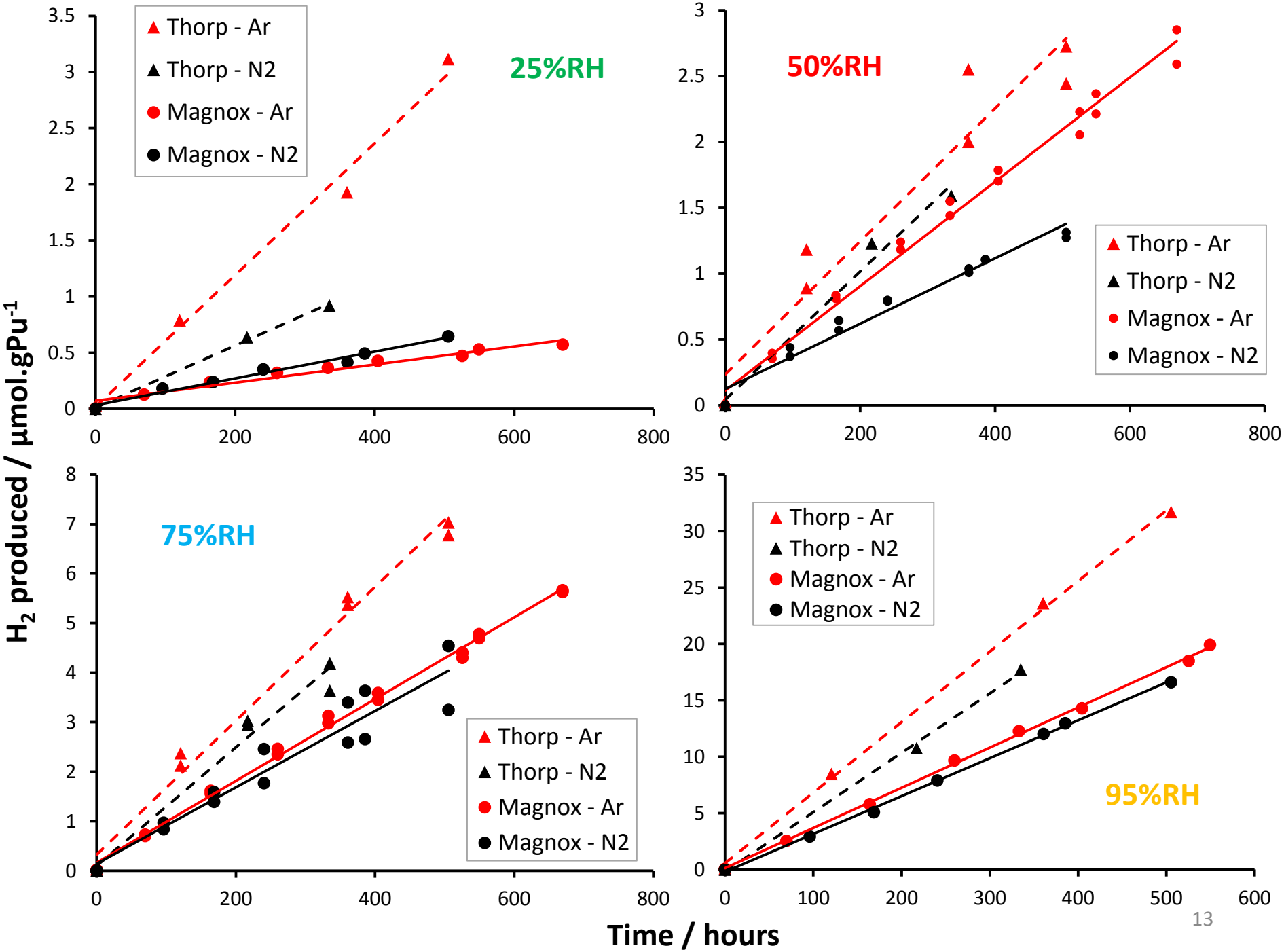
Thorp PuO_2 SSA: ~7 $m^2\ g^{-1}$


Ar - atmosphere
1 Th 25
1A Th 50
1B Th 50
1A Th 75
1B Th 75
1 Th 95
H2 produced / µmoles.gPu-1
0
5
10
15
20
25
30
35
0
100
200
300
400
500


N2 - atmosphere
2 Th 25
2A Th 50
2B Th 50
2A Th 75
2B Th 75
2 Th 95
H2 produced / µmoles.gPu-1
0
4
8
12
16
20
0
50
100
150
200
250
300
350
Time / hours


25%RH
Ar
N2
50%RH
Ar (A)
N2 (A)
Ar (B)
N2 (B)
75%RH
Ar (A)
N2 (A)
Ar (B)
N2 (B)
95%RH
Ar
N2
H2 produced / µmol.gPu-1
Time / hours

Material Comparison


25%RH
50%RH
75%RH
95%RH
Thorp - Ar
Thorp - N2
Magnox - Ar
Magnox - N2
H2 produced / µmol.gPu-1
Time / hours

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Conclusions

- Linear H_2 production (both materials) – no steady state as seen by other groups
- Increasing H_2 with increasing ML coverage (both materials)
- Magnox samples – little difference between Ar and N_2
- Thorp samples – greater H_2 produced in Ar atmosphere than in N_2
- Thorp generates more H_2 than comparative Magnox samples across all %RH conditions

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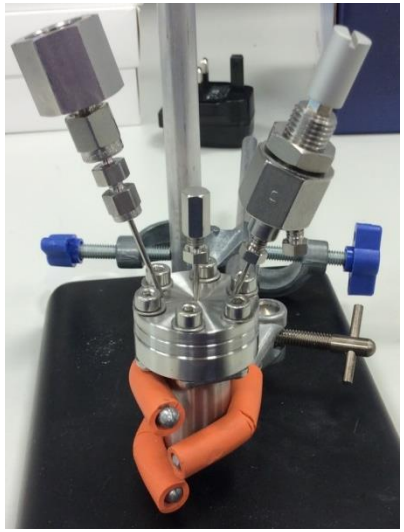
Further Work

- Determine absorbed dose and $G(H_2)$
- Lower %RH
- Longer timescales
- Increase S/V ratio to better simulate canisters
- Quantification of O_2



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Acknowledgements

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- Kevin Webb
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- Simon Pimblott

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- DISTINCTIVE EPSRC grant code - EP/L014041/1

Previous Work

- Undertaken by NNL Radiochemistry team
- Investigating H_2 production
- PuO_2 from Thorp and Magnox product streams
- Different RH environments
- N_2 and air glovebox atmospheres

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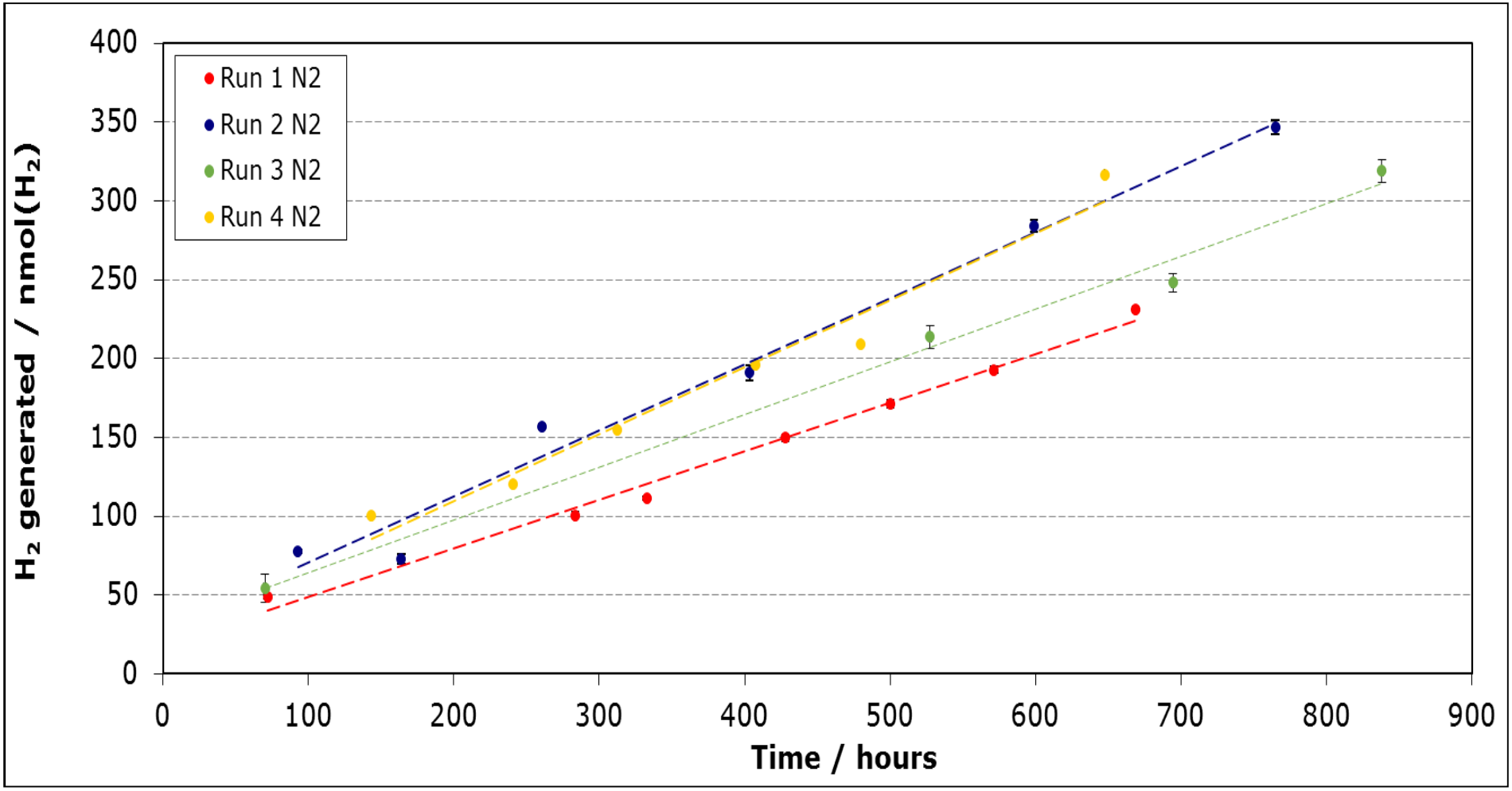
Trend 1 – Linear H_2 production



Magnox PuO_2 calcined at 950 °C in 50%RH

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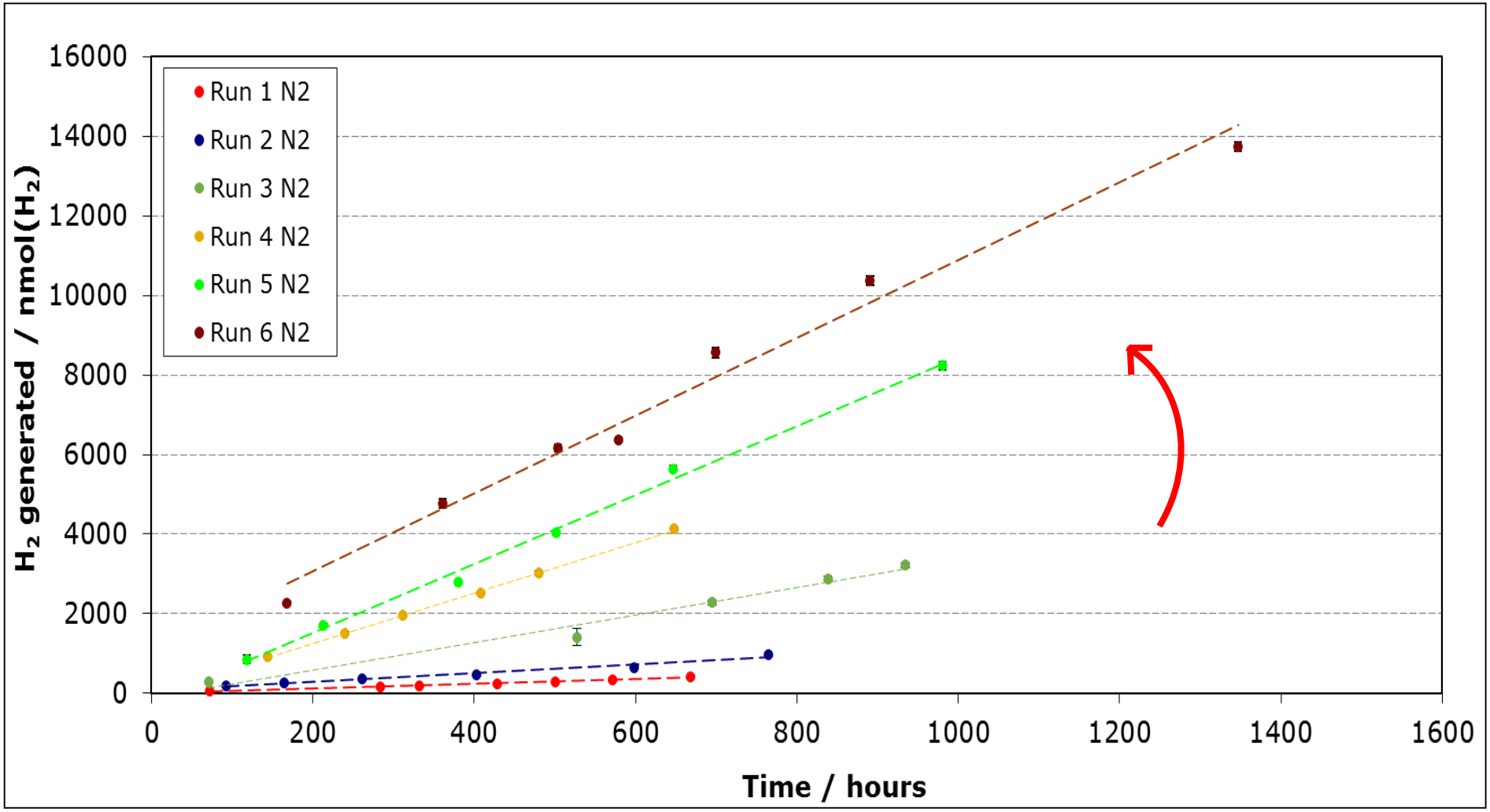
Trend 2 – Anomalous H_2 production



Magnox PuO_2 calcined at 800 °C in 50%RH

Run 1: 0.37 x10^{-19} cm^3 (H_2). MeV (total)$^{-1}$ m^{-2}

Run 6: 6.02 x10^{-19} cm^3 (H_2). MeV (total)$^{-1}$ m^{-2}

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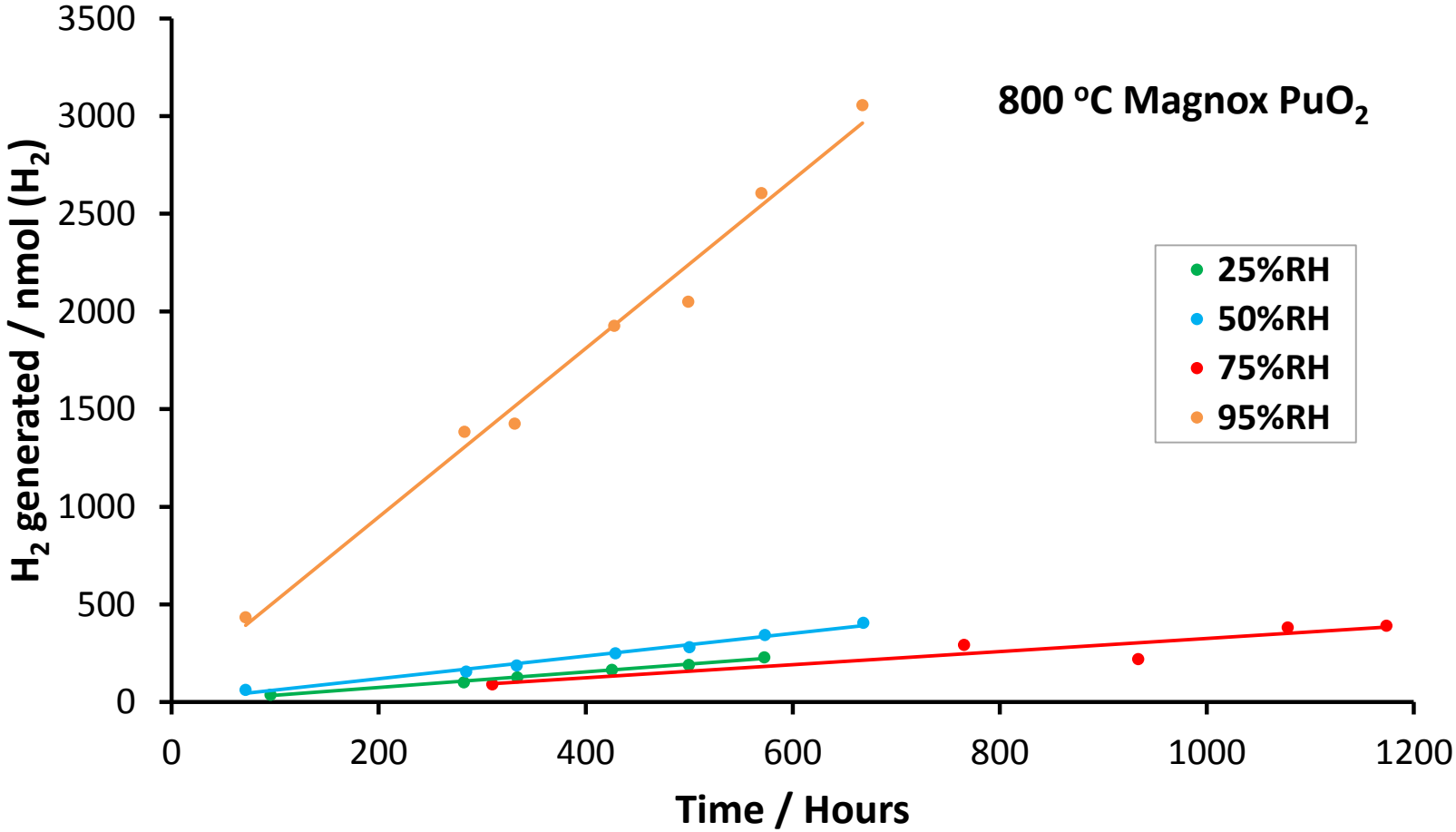
H_2 production vs. %RH



Conclusions

- Linear H_2 production
- Increased H_2 production rate with increasing RH
- Anomalous hydrogen production observed at low %RH

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Material Isotopics

isotope	$t_{1/2}$	α -decay energy	Magnox PuO_2	Thorp PuO_2
	Yrs.	MeV	Wt. fraction	Wt. fraction
Pu-238	86.4	5.487	0.23	1.39
Pu-239	24,360	5.101	73.26	50.95
Pu-240	6,580	5.155	22.26	36.14
Pu-241	13.2	-	3.25	5.62
Pu-242	3.79×10^5	4.89	1	5.9
Am-241	460	5.48	t.b.d.	0.0528
SSA / $m^2\ g^{-1}$			9.2 ± 1.2	t.b.d.
			Correct to 12/10/16	Correct to 18/9/16

Experimental Matrix

Ar glovebox

%RH	25	50	75	95
Magnox	x	xx	xx	x
Thorp	▲	▲▲	▲ ▲	■

x 1 g
▲ 0.8 g
■ 0.5 g

N_2 glovebox

%RH	25	50	75	95
Magnox	x	xx	xx	x
Thorp	▲	▲ ▲	▲ ▲	■

Theme Two Meeting

17th October 2017

Atomistic Simulations of PuO_2 Ageing and Fuel Residues

By Nathan A. Palmer

School of Chemistry

The University of Birmingham

UNIVERSITY OF BIRMINGHAM

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Contents

- Background of project
- Methods and testing of interatomic potentials
- Defect simulations in PuO_2
- Pure PuO_2 surface simulations
- Simulations of helium in PuO_2
- Simulations of Pu doped UO_2 (MOX)
- Summary and future work

Background

- The UK has the largest stockpile of civil plutonium (Pu) in the World currently ~126 tonnes, stored at Sellafield, Cumbria in oxidised form as plutonium dioxide, PuO_2.

- Storage symptoms have been identified related to poorly understood radiochemistry: gas pressurisation in storage cans, hydrogen generation and can swelling.

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POSTNOTE

Number 531 September 2016

Managing the UK Plutonium Stockpile

Overview

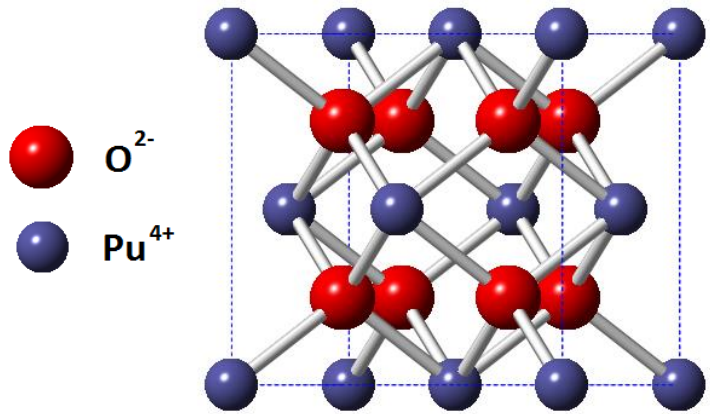
- The UK is storing the largest 'separated' civil plutonium stockpile in the world. This poses safety, security and cost challenges.
- The Nuclear Decommissioning Authority is assessing long term options for managing the stockpile with industry pushing for a timetable for the selection and delivery of an

- There is no current strategy on usage only proposals.

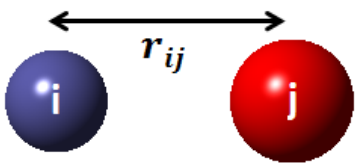
- Hence, a fundamental understanding is needed of the complex ageing behaviour of the stockpile for long-term storage.

The force-field method

- A computational approach to modelling materials on the atomistic scale based on derivation and application of interatomic potentials.
- Knowing the crystal structure and basic mechanical and optical properties of a compound, interatomic potentials are derived by empirical fitting to this data.
- Having derived sufficient potentials, they are used as fundamental basis of predicting other properties of a material through energy minimisation of its bulk structure and surfaces.



Unit cell of Pu(IV) O_2



$$V(r_{ij}) = \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} + \phi(r_{ij}) \text{ with}$$

$$\phi(r_{ij})_{Buck} = A_{ij}\, exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

Potential evaluation for PuO_2

Property	Read et al. (2014) potentials	Arima et al. (2005) potentials	Reported
a_0 (Å)	5.39817	5.38005, 5.39538[1]	5.39819[a]
C_{11} (GPa)	408.6	467.1	430.6[b]
C_{12} (GPa)	130.2	117.1	128.4[b]
C_{44} (GPa)	67.3	109.0	67.3[b]
B (GPa)	223.0	233.7	178.0[c], 218.0[d]
ε_0	15.92	-	19.27[b]
ε_∞	3.2	-	3.0[e]

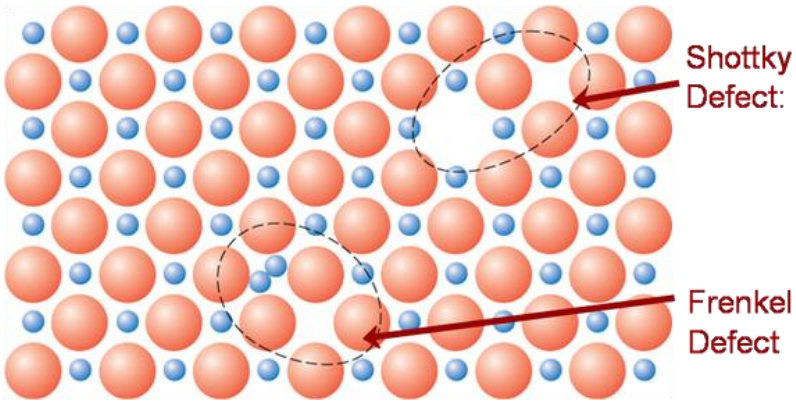
1- from molecular dynamics.

Refs: a- Belin et al. (2004), b- Meis et al. (1998), c- Idiri et al. (2004), d- Li (DFT, 2002), e- Haire (2000).

Intrinsic defects in PuO_2

Intrinsic defect	E_{defect}^{form} (eV)		
	Read et al. (2014) potentials	Arima et al. (2005) potentials	Reported energies
Schottky defect	5.79	5.71	7.51[a]
O Frenkel pair	3.65	7.03	3.48[a], 2.72-2.92[b]
Pu Frenkel pair	15.74	16.27	15.19[a]

Refs: a- Lu et al. (DFT, 2015), b- Murch et al. (exp, 1987).



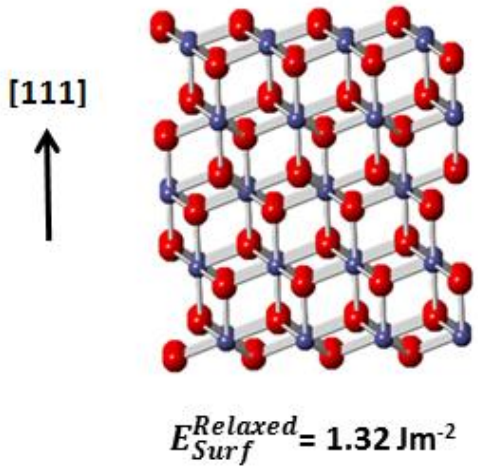
⇒ O Frenkel pairs and Schottky defects are energetically preferred intrinsic defects in PuO_2.

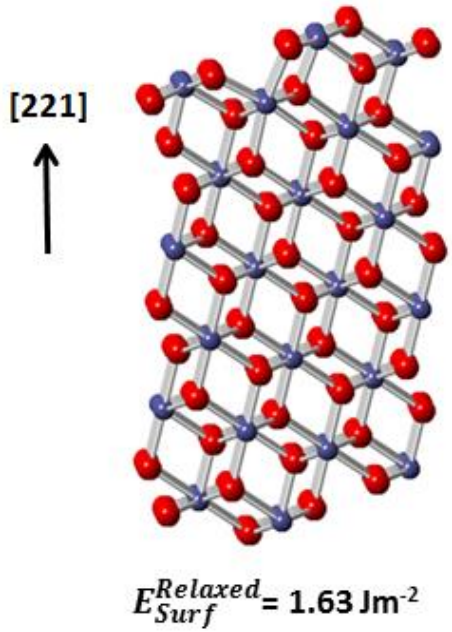
Pure PuO_2 surfaces

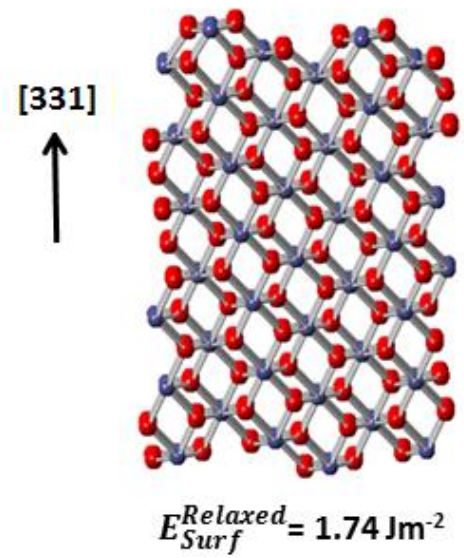
Surface	$\overline{E}_{Surf}^{Unrel}$ (Jm^{-2})	E_{Surf}^{Rel} (Jm^{-2})	ΔE_{Surf} (Jm^{-2})
(100)	2.42	549.24	546.82
(110)	3.32, 3.148[a]	2.07, 1.539[a]	-1.24, -1.609[a]
(111)	1.65, 1.479[a]	1.32, 1.069[a], 1.33[b]	-0.32, -0.41[a]
(210)	11.64	3.06, 3.35[b]	-8.58
(211)	7.38	2.30	-5.09
(221)	2.41	1.63, 1.65[b]	-0.78
(310)	18.28	3.09, 3.30[b]	-15.19
(311)	8.95	2.62, 2.94[b]	-6.32
(331)	2.61	1.74, 1.76[b]	-0.87

Refs: a- Tasker et al. (1979), b- Williams et al. (2015) -(both for UO_2).

Lowest energy PuO_2 surfaces





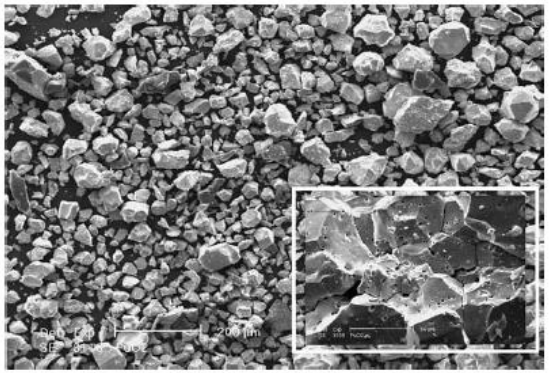


Surface	Calc. d spacing (Å)	Exp. d spacing * (Å)	Δ % (×10^{-2})
(111)	3.1166	3.5144	4.00
(221)	1.7994	1.7987	3.87
(331)	1.2384	1.2379	4.28

*Ref: Belin et al. (2004)

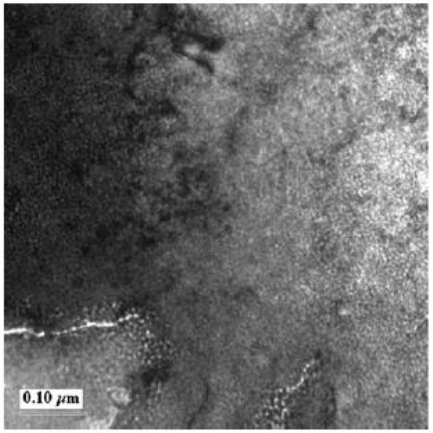
Helium behaviour in PuO_2

- Helium gas is generated in PuO_2 due to the spontaneous alpha decay of Pu, a high - energy process, releasing an alpha particle (helium nucleus) and a U recoil nucleus, causing lattice damage.
- Half-life of Pu-239 is 24, 100 years, Pu-238 it is 87.7 years (source: nndc).
- Helium gas accumulation can be detrimental to PuO_2 mechanical and structural properties through their complex behaviour.
- Also helium gas is a possible contributor cause for pressurisation in storage cans if it is released in the head-space.
- Hence, atomistic simulations are needed to enhance understanding of helium behaviour in PuO_2.



SEM micrograph of a disintegrated PuO_2 pellet after 40 years storage in N_2.

Ronchi et al. (2004)



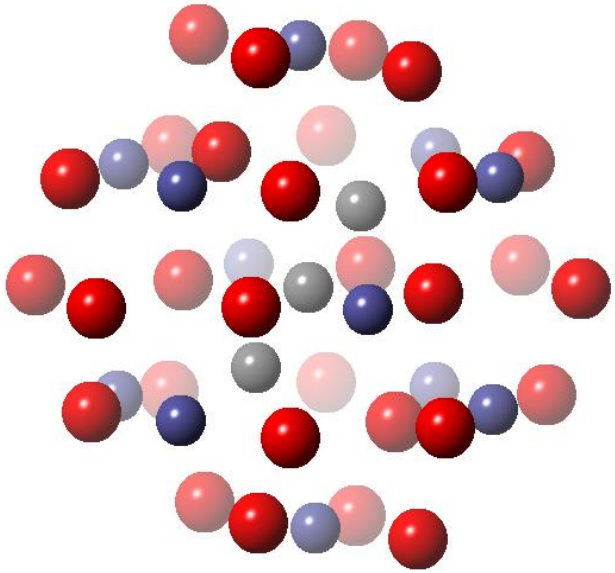
TEM image of clusters and strings of He bubbles in a natural uranium oxide sample.

Roudil et al. (2008)

Helium atom trapping in PuO_2 lattice

Helium trapping site	E_{He}^{incorp} (eV)	
	Read and Grimes et al. potentials	Arima and Grimes et al. potentials
Octahedral interstitial site	-0.07	-0.05
O vacancy	-0.55	-0.26
Pu vacancy	-0.24	-0.24
O Frenkel pair[1]	-	-
Pu Frenkel pair	0.08	0.07
Schottky defect	-0.52	-0.75

1- Not energy optimised.

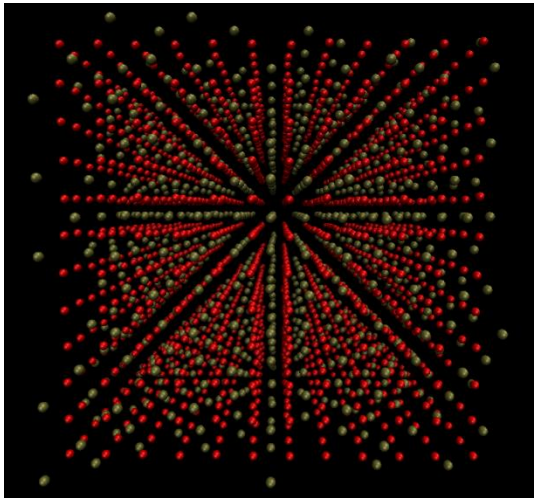


3 He atoms (grey spheres) in a Schottky defect.

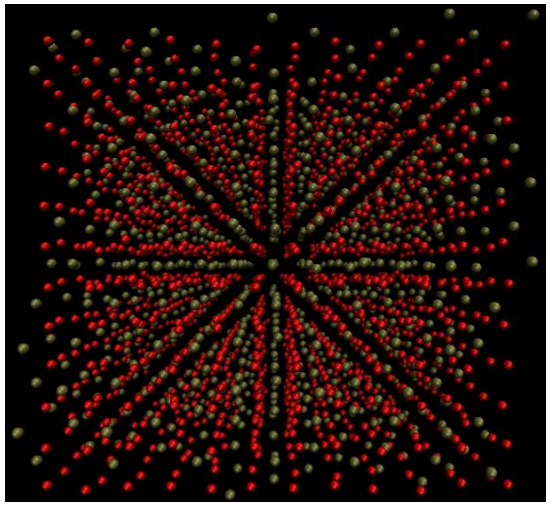
⇒ Vacancy sites and octahedral interstitial sites are typically suitable trapping sites of helium atoms.

Molecular dynamics

- A computational method in which there is time evolution of a physical system based on Newton's laws of motion, to calculate particle trajectories over time and hence to predict dynamical properties.
- Thermal, electrical and mechanical properties are typically calculated for a wide range of materials.
- The forces are calculated from the potentials through $F = -\frac{\partial V}{\partial r}$ and calculations are every time step, Δt, typically 1 femto-second (10^{-15} sec).
- The timescales are up to tens of pico-seconds (10^{-12} sec), length scales up to tens of nano-meters (10^{-9}m).



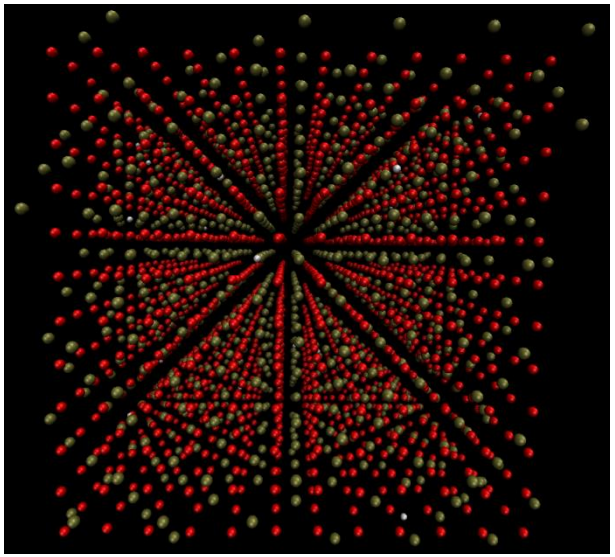
PuO_2 666 supercell, 298K



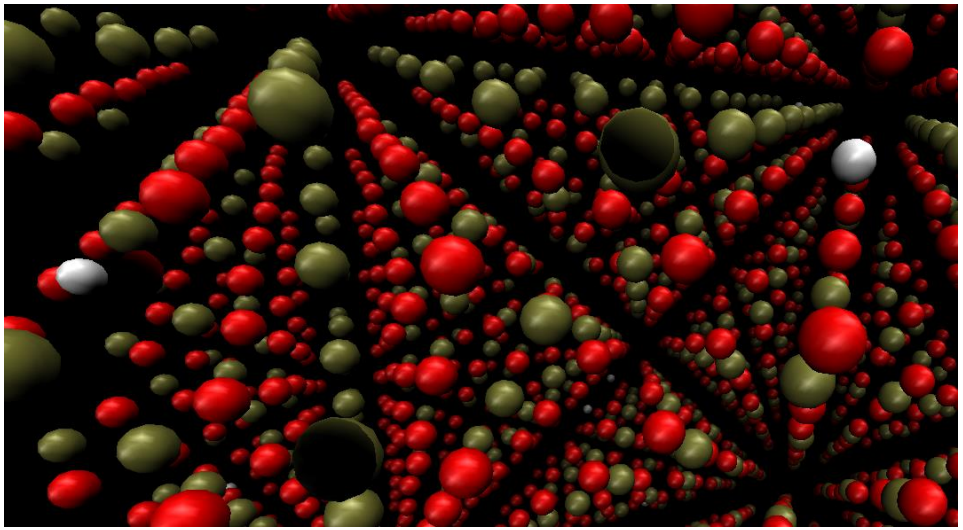
PuO_2 666 supercell, 2000K

Helium effects in PuO_2

- Modelling helium atoms in a 6 by 6 by 6 PuO_2 supercell, varying temperature and helium concentration.
- Helium atoms are added randomly in the octahedral interstitial sites.
- Equilibrate supercell first to correct temperature, then evolve in 'production run' to obtain data.

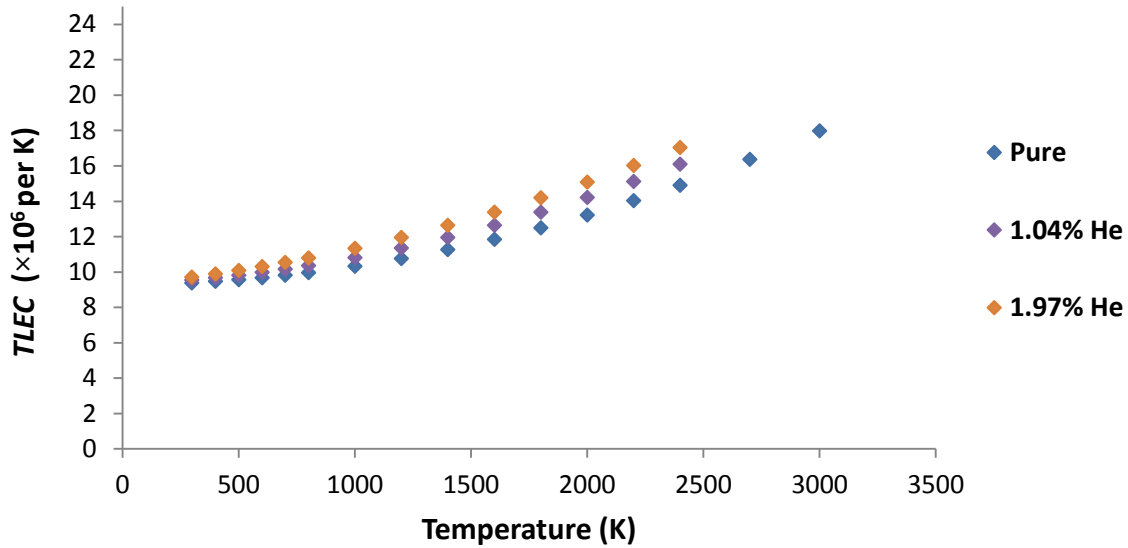


Helium in a 6 by 6 by 6 PuO_2 supercell, 298K.



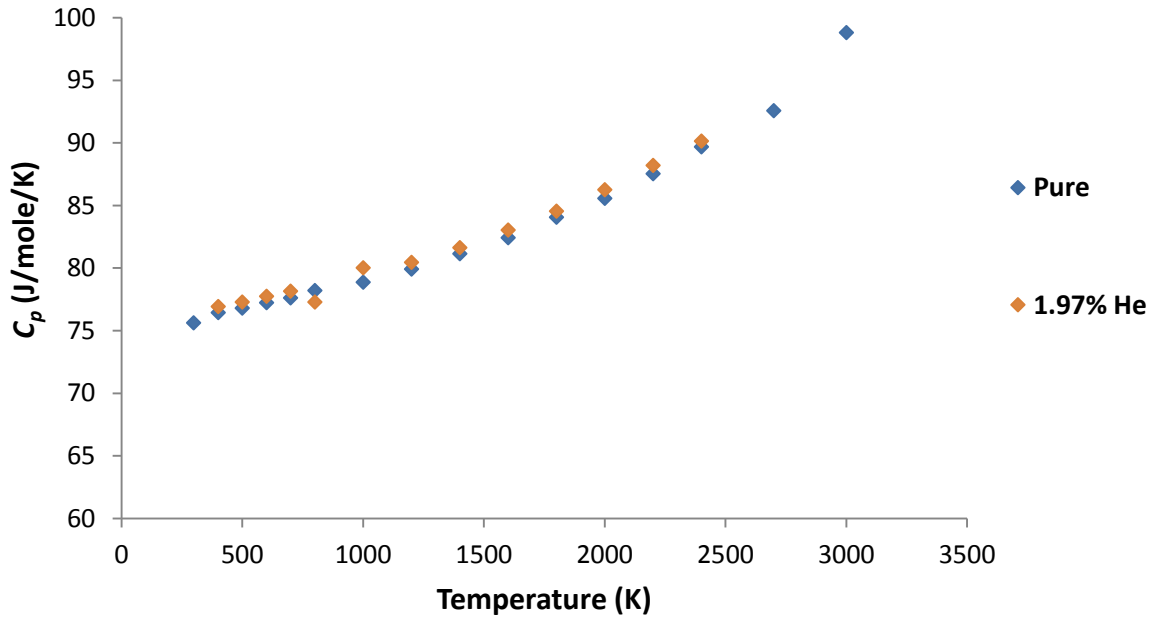
Helium (grey spheres) in octahedral interstitial sites.

Helium effects in PuO_2



$$TLEC = \frac{1}{a_{0\,(298K)}}\left(\frac{\partial a_0}{\partial T}\right)$$

⇒ Predicted to be an increase in the TLEC due to helium, which increases with temperature.

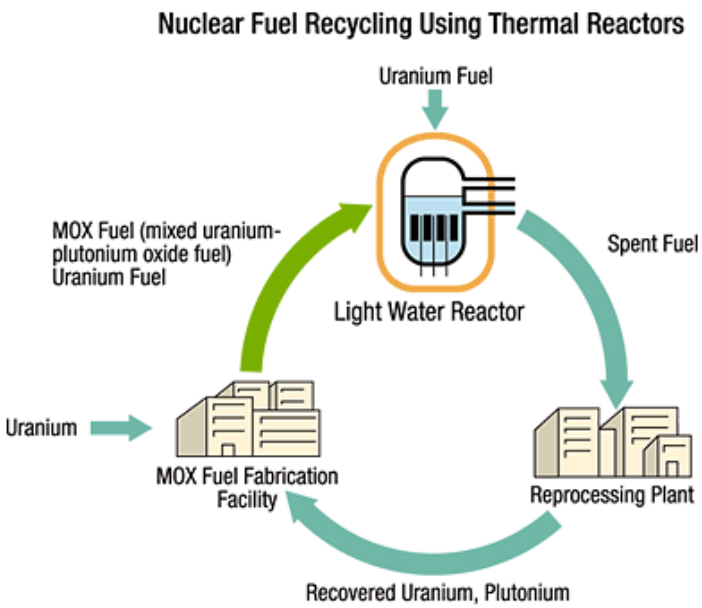


$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

⇒ Small effect of helium on heat capacity.

Simulations of Pu doped UO_2 (MOX)

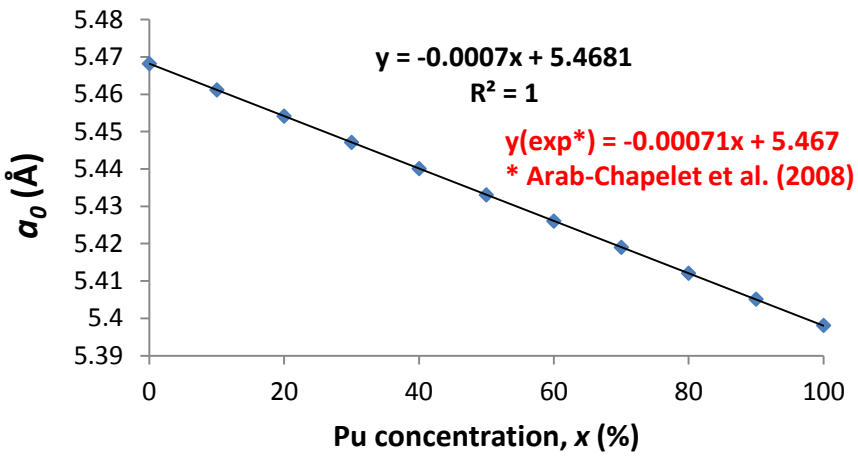
- Currently, MOX fuel provides approximately 5% of all nuclear fuel used worldwide.
- Considered as a solid solution of UO_2 doped with Pu, MOX = $Pu_xU_{1-x}O_2$.
- Typically Pu concentration is ~ 5-10% for fresh MOX fuel.
- Pu usage in MOX fuel is a key preferred option for use of the Pu stockpile, UK.
- To simulate MOX, a 'mean-field' approach and a supercell method have both been used.



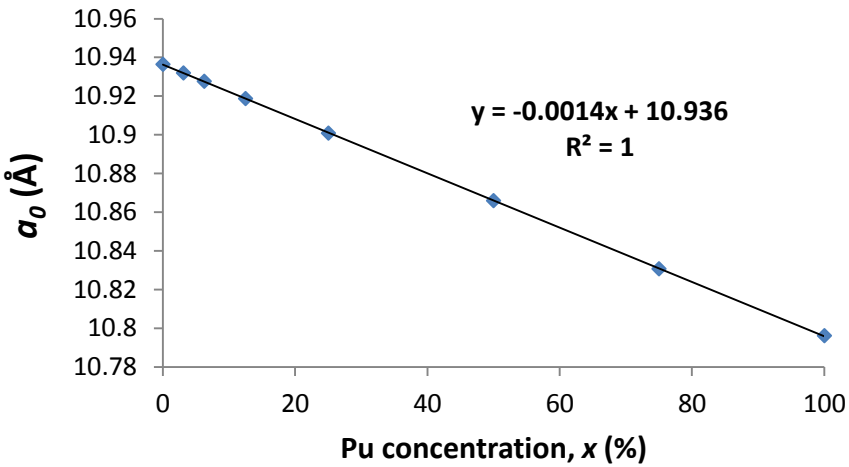
MOX fuel cycle

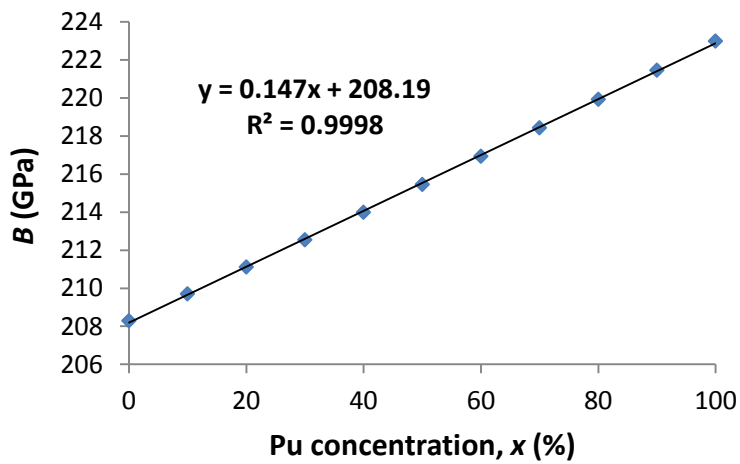
Properties of MOX- Lattice parameter and bulk modulus

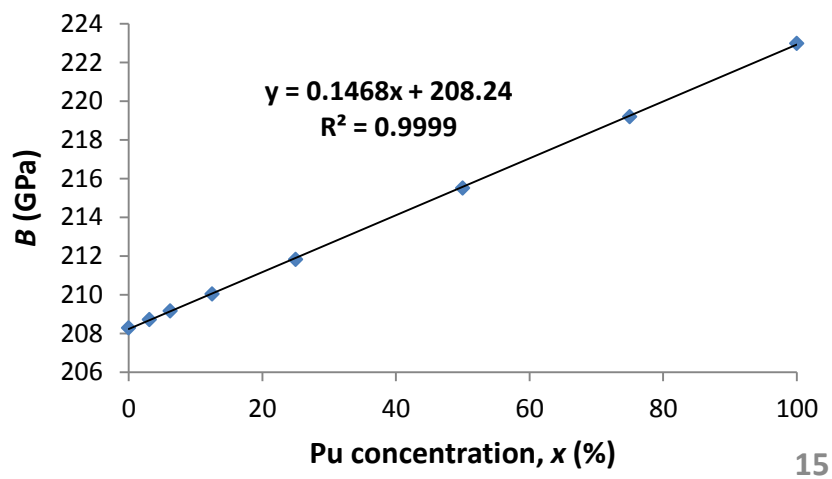
Mean-field Approach



Supercell Method

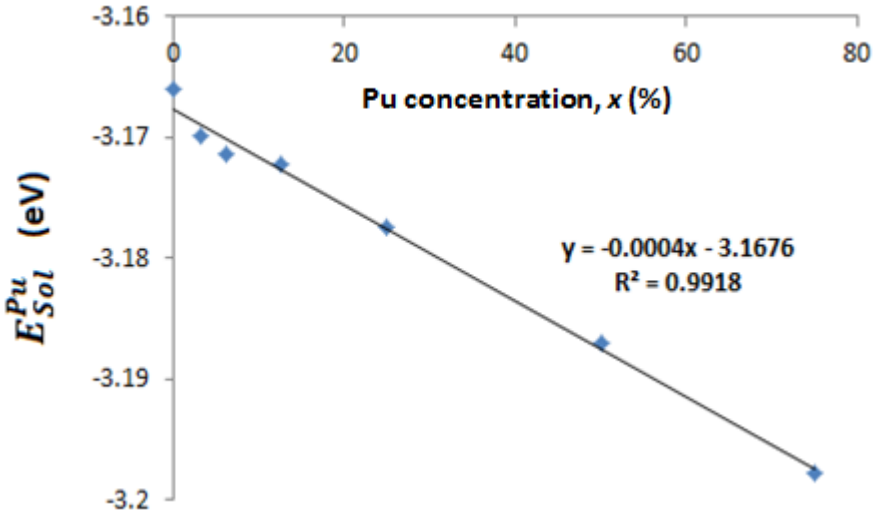






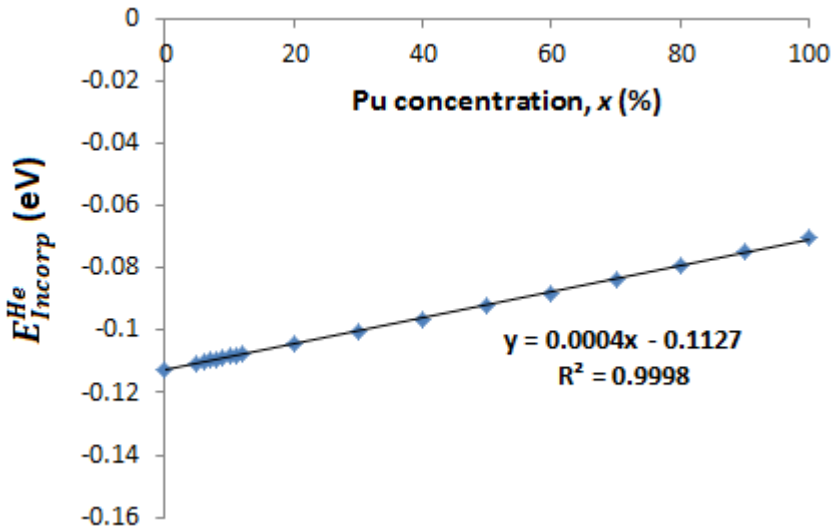
Incorporation of Pu and He in MOX

Pu incorporation in UO_2



⇒ Linear trend with Pu incorporation energetically favourable (exothermic) in UO_2, becoming more so with increasing Pu concentration.

Helium incorporation in MOX



⇒ Linear trend with He incorporation is modestly energetically favourable in MOX, becoming less so with increasing Pu concentration.

Summary of results

- Arima et al. potentials deemed suitable for molecular dynamics simulations at elevated temperatures, although Read et al. set better for static lattice simulations.
- The (111) surface is the dominant, lowest energy surface of pure PuO_2.
- Lattice vacancies (individual and Schottky) and octahedral interstitial sites are the most favourable helium traps.
- Low concentrations of helium in octahedral interstitial sites over 298-2400K is stable, with very small effects on bulk thermal properties.
- Vegards Law holds for MOX fuel, with Pu and helium incorporation favourable.

Future work…..

- Molecular dynamics of helium in defective PuO_2.
- Modelling of radiation damage in PuO_2.
- Simulations of defective PuO_2 surfaces.

Acknowledgements

- Dr Mark S.D. Read- Supervisor, University of Birmingham.
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- Professor Steve C. Parker, University of Bath.
- Drs Robin Orr (NNL) and Helen Steele (SL).
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- NDA, NNL and DISTINCTIVE Consortium for funding.

UNIVERSITY OF BIRMINGHAM

NDA Nuclear Decommissioning Authority

NATIONAL NUCLEAR LABORATORY

DISTINCTIVE

Thank you for your attention

Any questions?

DISTINCTIVE

REAL-TIME DETERMINATION OF ROSSI-α DISTRIBUTION, ACTIVE FAST NEUTRON MULTIPLICITY, NEUTRON ANGULAR DISTRIBUTION AND NEUTRON SPECTRUM

using organic liquid scintillators

Last Update: October 17, 2017

Rashed Sarwar[1]

V. Astromskas[1], C. Zimmerman[2], R. Mills[2], S. Croft[3] & M. Joyce[1]

[1] **Engineering** Department, **Lancaster** University
[2] **UK National Nuclear** Laboratory, **UK**
[3] **Safeguard & Security** Technology, **Oak Ridge** National Laboratory

PROJECT OVERVIEW

THE PROJECT

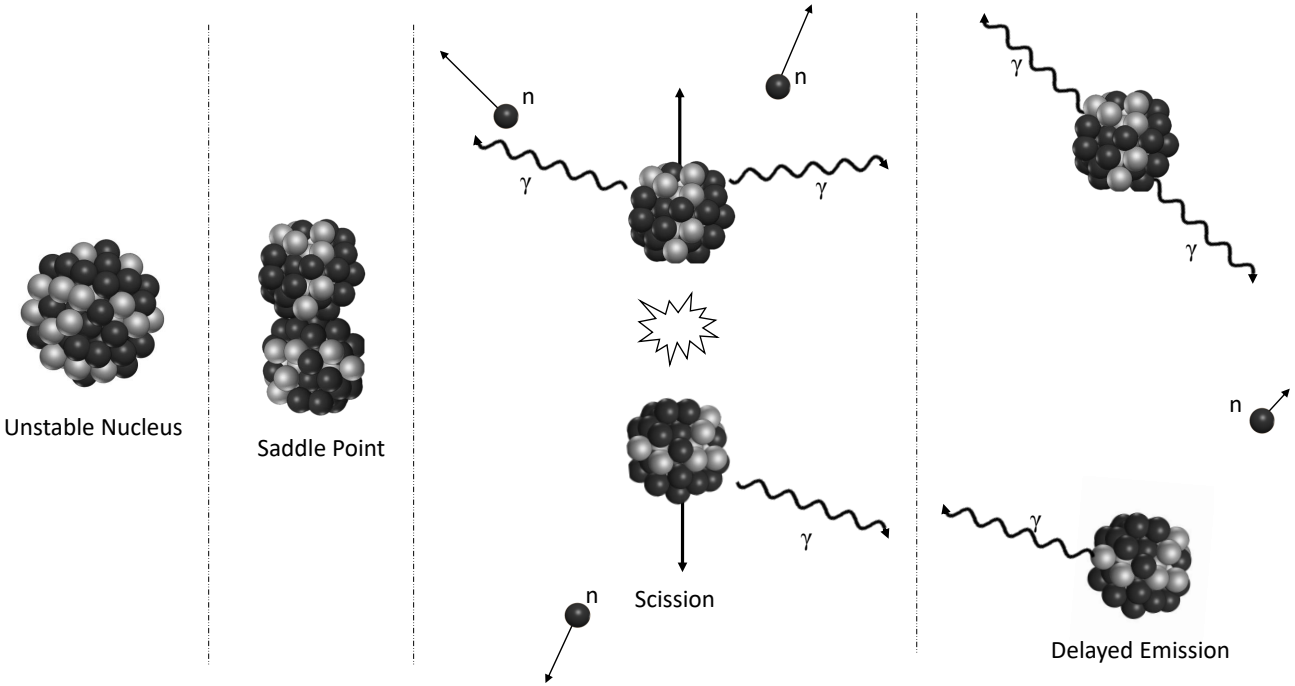
→ **Objective:**

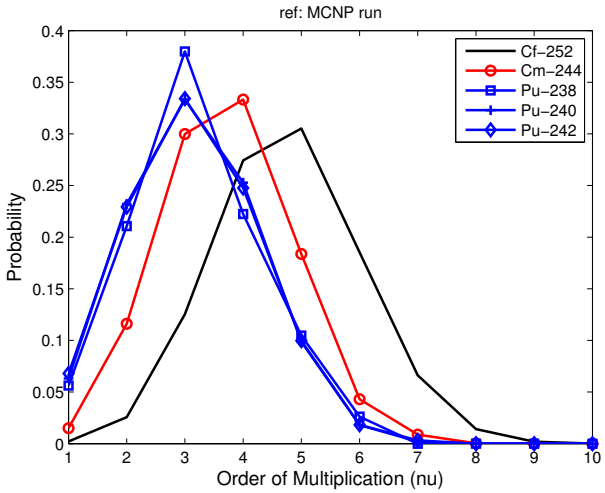
1. Development of a real-time algorithm that can determine Rossi-α distribution, neutron multiplicity, neutron angular distribution and neutron spectrum
2. Develop a model to discern contamination of Rossi-α distribution due to neutron scatter in the environment
3. Develop a model to correct for neutron crosstalk and photon breakthrough for the neutron multiplicity distribution

→ **Motivation:**

1. Exploit the excellent timing characteristics of liquid scintillation detectors to determine high order neutron multiplicity
2. Enable development of small in-situ instrumentation
3. Correct inaccuracy arising from neutron crosstalk and photon breakthrough to avoid over/under estimation of samples being examined

MULTIPLICITY



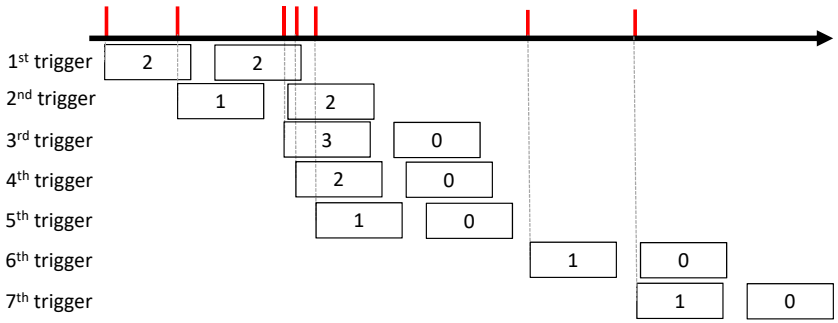


INSTRUMENTATION

ALGORITHM

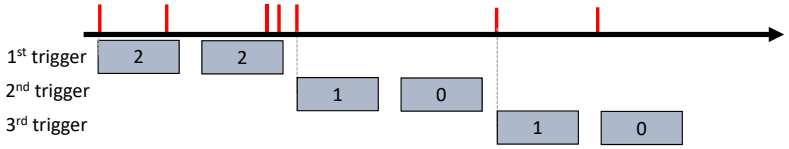
Shift register algorithm

- → Open a new acquisition window for every incoming particle
- → Generates a reduced factorial moment distribution (i.e. singles, doubles, triples, etc.)



Event triggered algorithm

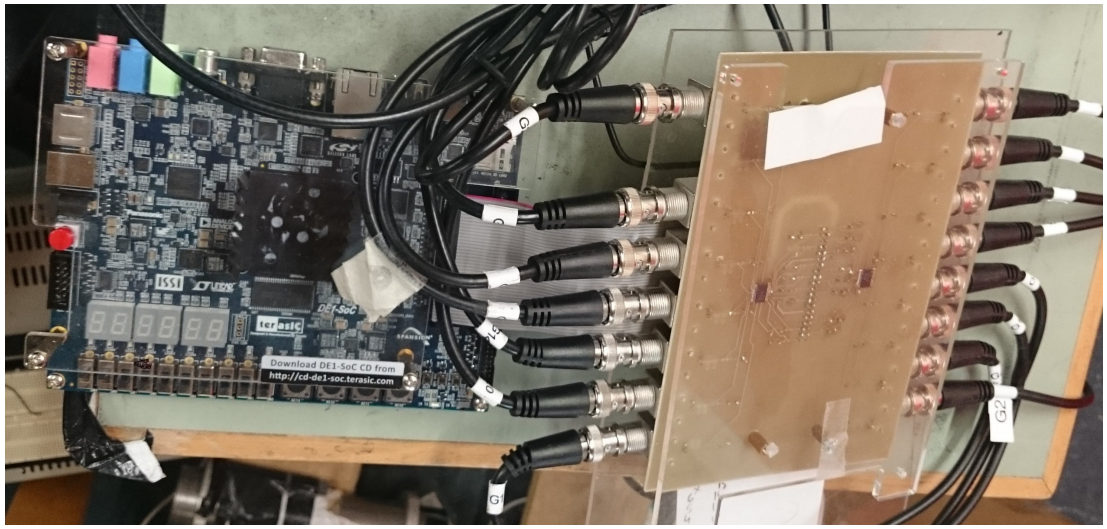
- → Only starts new acquisition window for 'new' particles
- → Generates a distribution that corresponds to the size of cluster of incoming particles (i.e. singlets, doublets, triplets, etc.)



IMPLEMENTATION

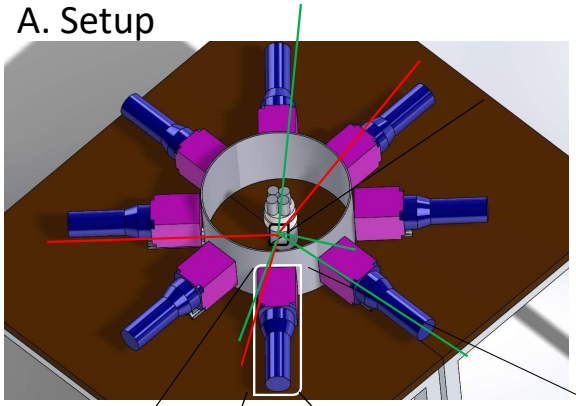
Based on Altera DE1-SoC FPGAs

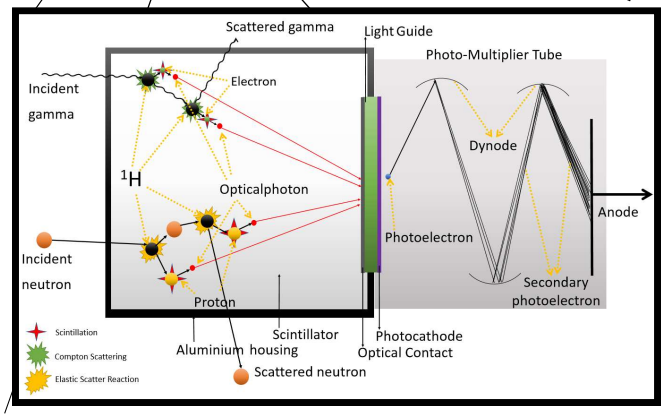
- → Runs linux kernel to allow user to connect monitor and keyboard to use device as a standalone system.
- → Rossi-α & Feynman-Y using shared circuit
- → Time-of-flight analysis



HARDWARE INTERLINK

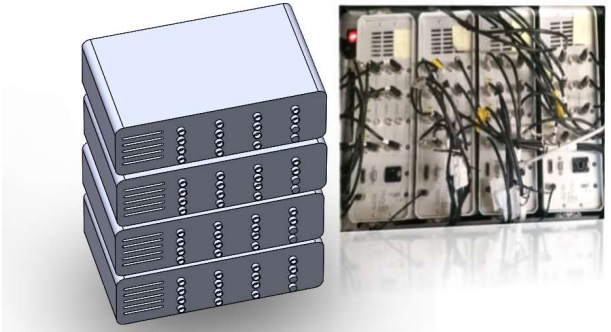
A. Setup

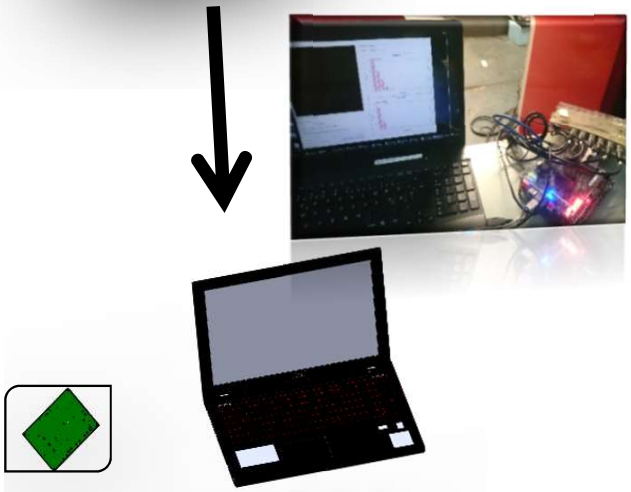




B. Liquid Scintillators

C. Mixed Field Analyser



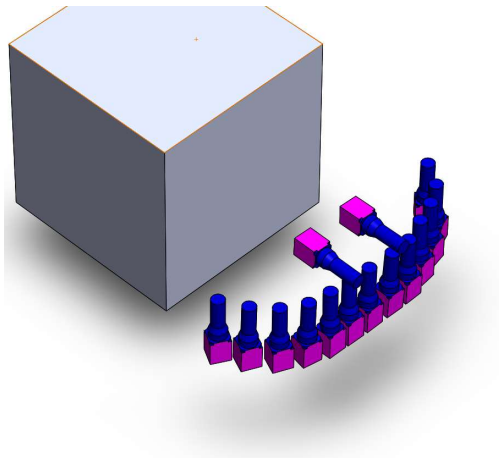


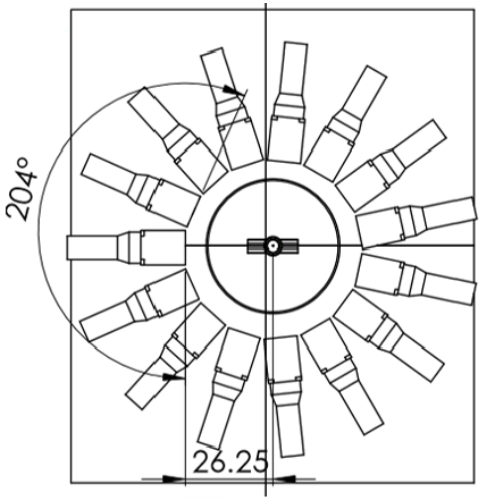
D. FPGA-SoC Multiplicity Analyser

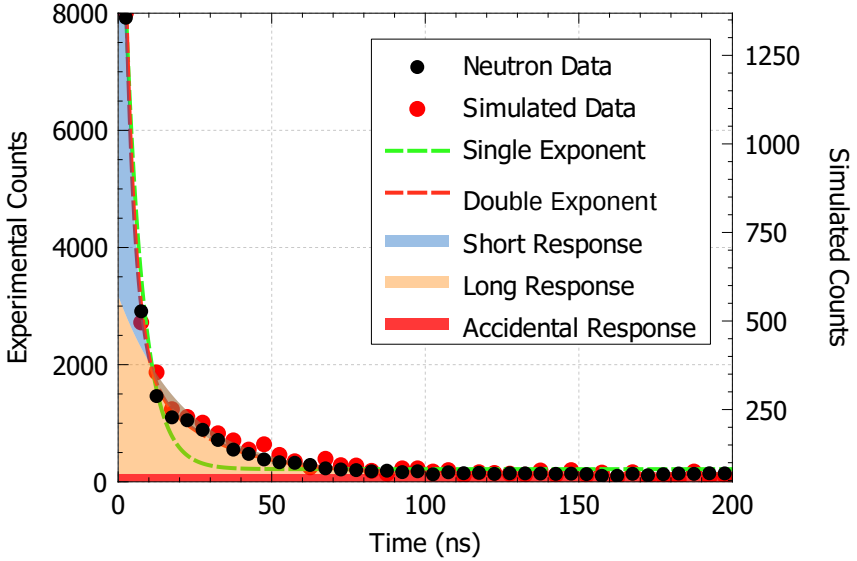
EXPERIMENTS & RESULTS

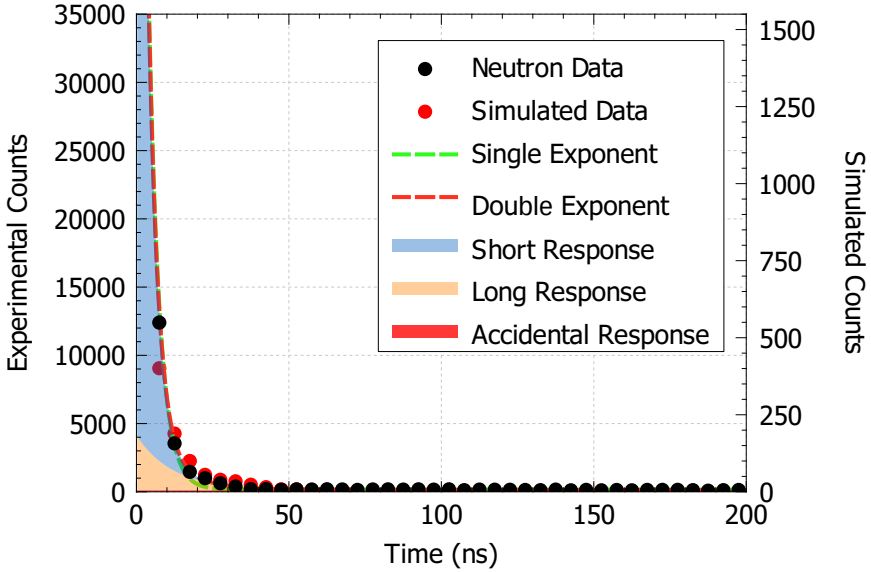
ROSSI-α DISTRIBUTIONS

- **Short Gate-width:** about 12 ns for gamma and 18 ns for neutron distribution
- **Long Gate-width:** almost no contribution from long scattered events in gamma distribution compared to the neutron distribution
- **Model:** single exponential models fails to predict LSD response
- **Strength of source:** 10,000,000 n/s & 331,541 n/s
- **Simulator:** Geant4.10.3 with LLNL FREYA Library



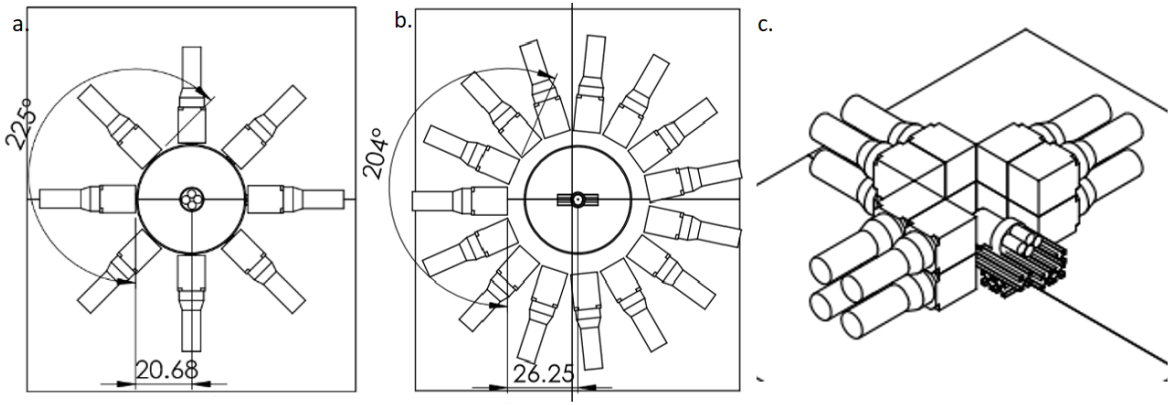


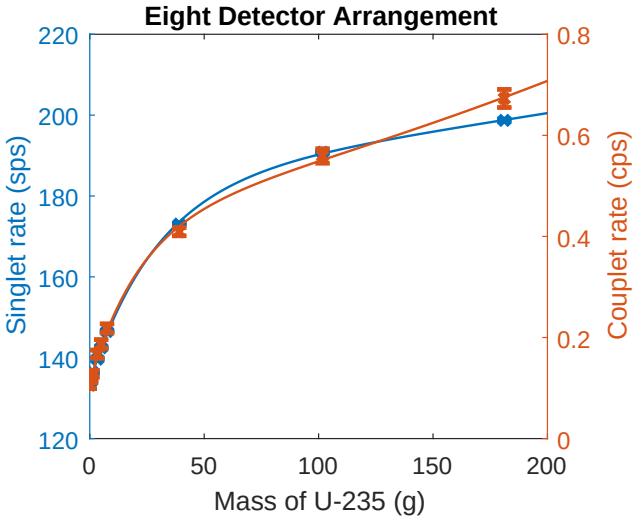


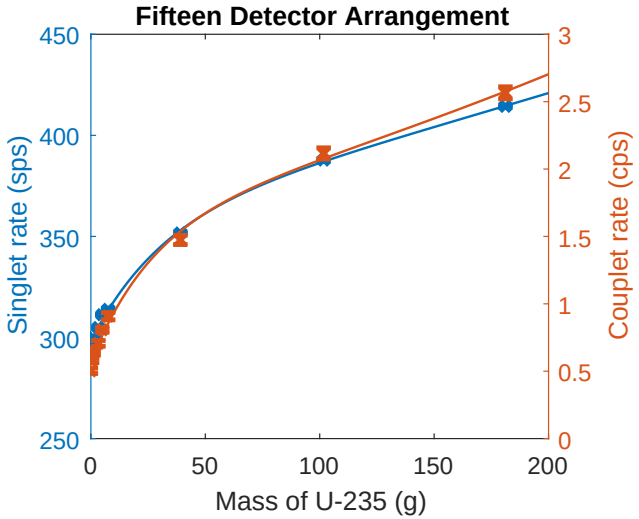


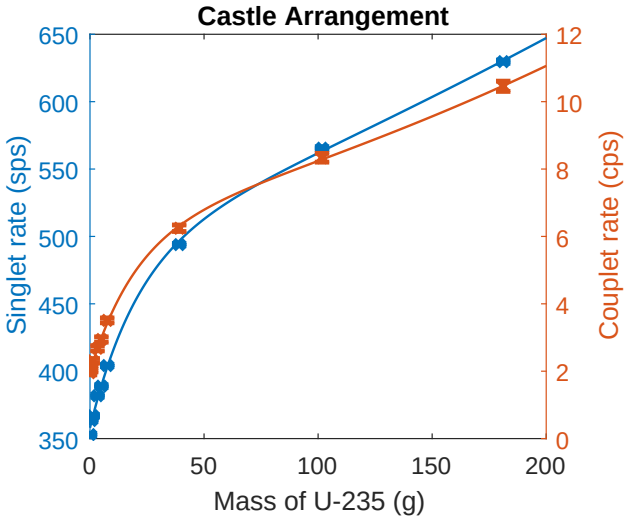
ACTIVE NEUTRON MULTIPLICITY

- **Strength of AmLi:** 167,000 n/s
- **Size of moderator:** 3.75 cm
- **Range of U235 mass for sample:** 0.5 g to 200 g



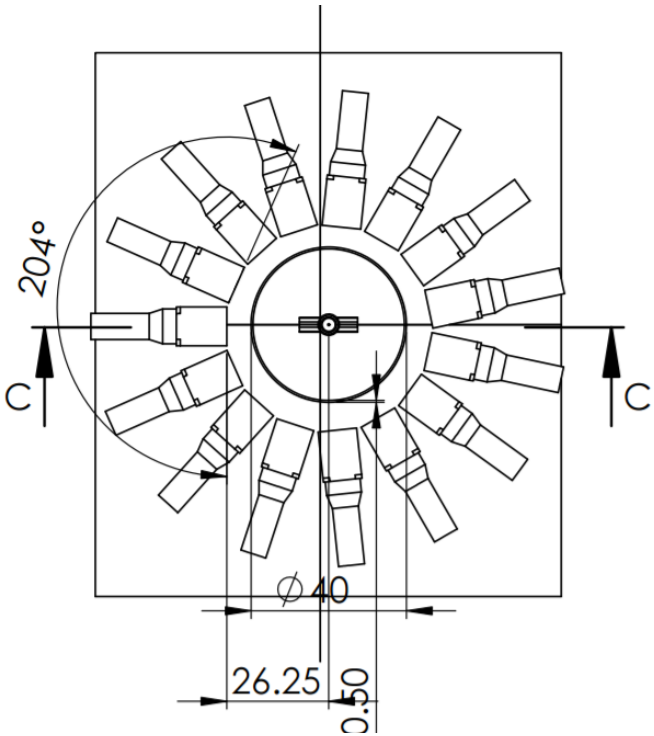


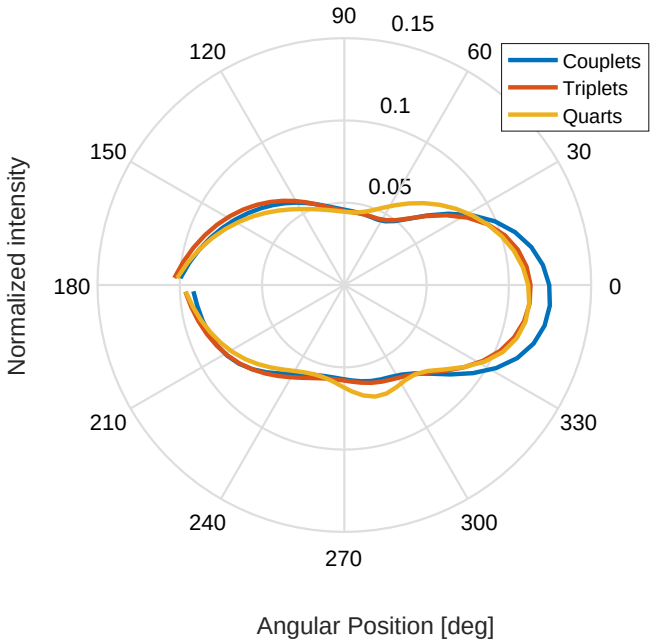




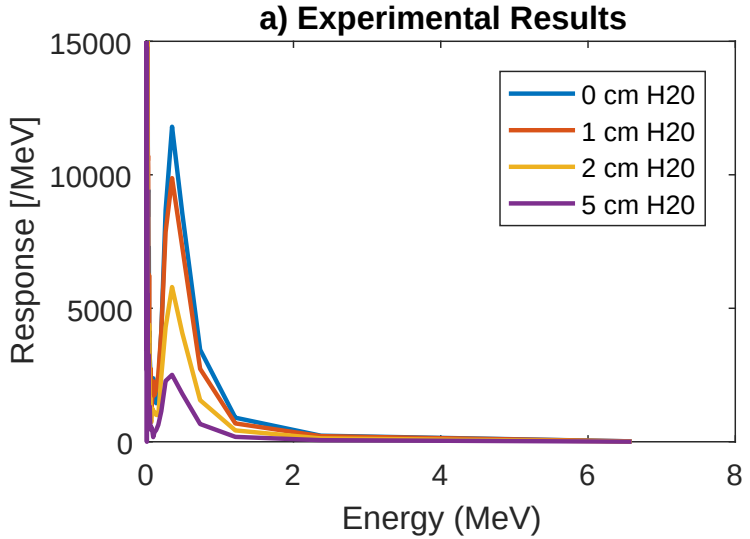
NEUTRONS ANGULAR DISTRIBUTION: CF252

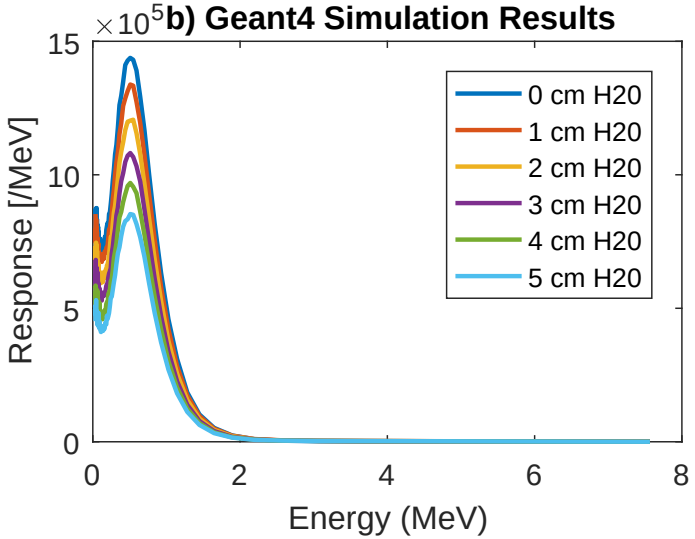
- **Trigger:** Neutron Trigger
- **Strength of source:** 331,541 n/s
- **Angular Distribution:** Determine the angular distribution using LSD.
- **Higher order angular distribution:** Deviation from accepted trend noticed which is beyond the scope of experimental uncertainty.



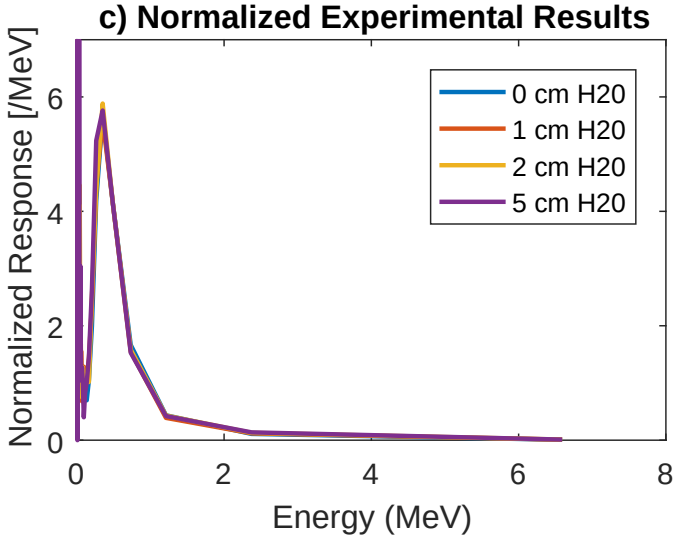


NEUTRON SPECTROSCOPY: CF252



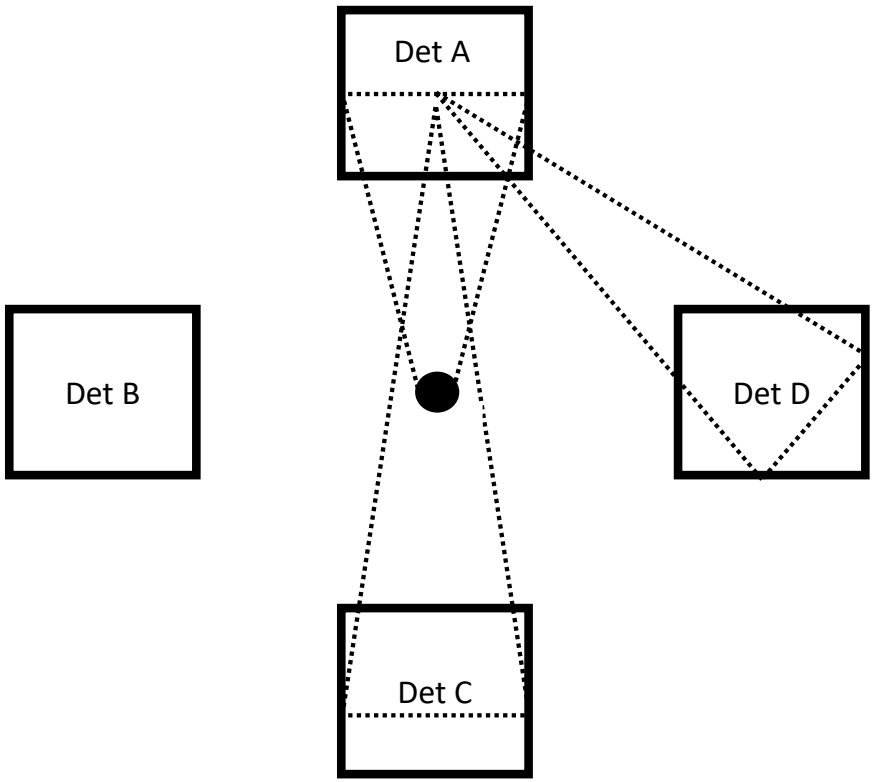


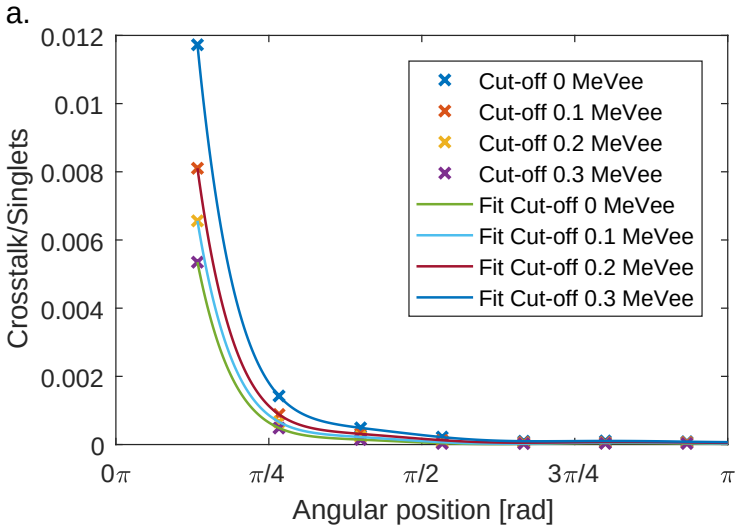
- **Trigger:** Photon Flash
- **15-detector arrangement:** with the source placed inside cylindrical water tanks of different radius of 1, 2 and 5cm. 0cm represents no water.

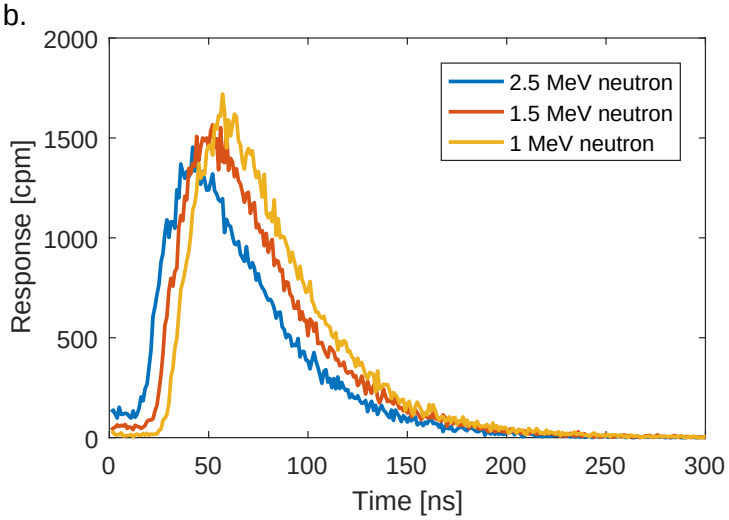


CROSSTALK AND PHOTON BREAKTHROUGH

CROSSTALK


Det A
Det B
Det C
Det D

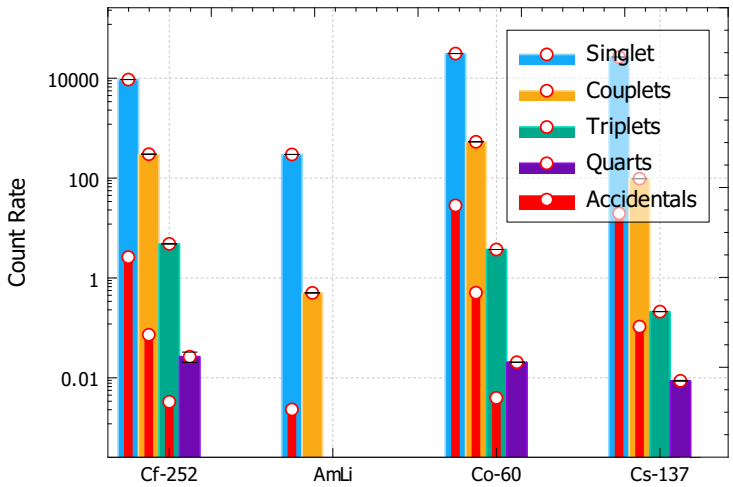

a.
Crosstalk/Singlets
0.012
0.01
0.008
0.006
0.004
0.002
0
0π
π/4
π/2
3π/4
π
Angular position [rad]
Cut-off 0 MeVee
Cut-off 0.1 MeVee
Cut-off 0.2 MeVee
Cut-off 0.3 MeVee
Fit Cut-off 0 MeVee
Fit Cut-off 0.1 MeVee
Fit Cut-off 0.2 MeVee
Fit Cut-off 0.3 MeVee


b.
Response [cpm]
2000
1500
1000
500
0
0
50
100
150
200
250
300
Time [ns]
2.5 MeV neutron
1.5 MeV neutron
1 MeV neutron

CORRECTION MODEL

When a cross-talk event takes place:

- **Updraft Crosstalk:** the singlet bin loses one count.
- **Downdraft Crosstalk:** couplet and potentially the higher-order bins gain one count.
- **Crosstalk Correction Model:**



$$F_x(n)' = \underbrace{F_x(n)\left(1+\sum_{k=1}^{\infty}\right)}_{\text{(correction term for updraft)}} - \underbrace{\sum_{m=n-k}^{\infty}\left(F_x(m)\sum_{k=1}^{\infty}XT(k)\right)}_{\text{(correction term for downdraft)}} \quad (1)$$

- **Photon Breakthrough Correction Model:**

$$F'_n = F_n(1) - B_x\sum_{k=1}^{\infty}F_g(k) \quad (2)$$

VALIDATION

→ **Validation:**

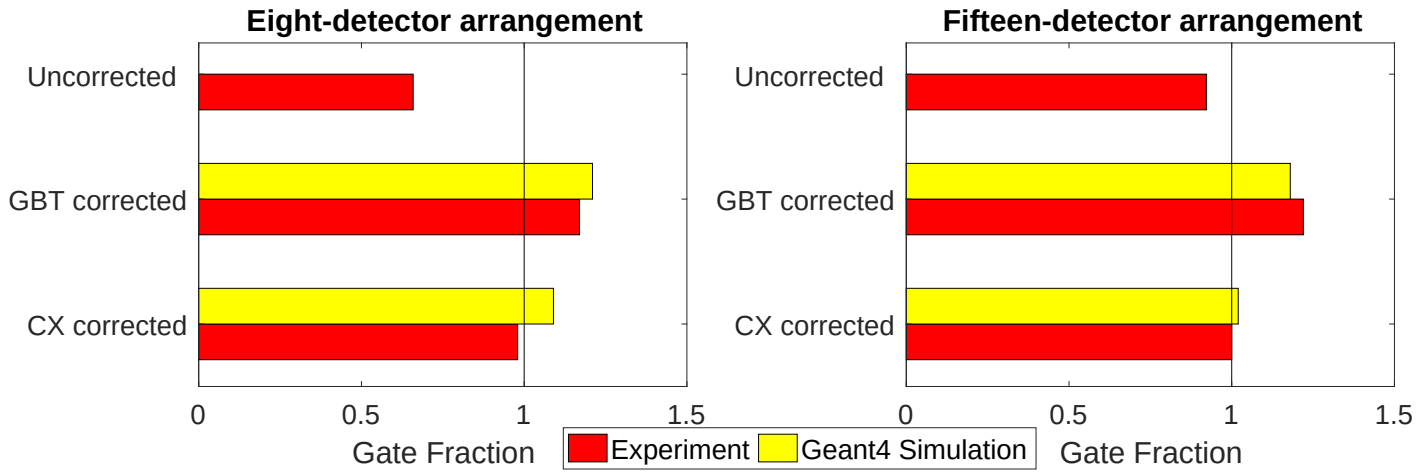
$$S = F\epsilon\nu_{s1}(1+\alpha)$$

$$D = \frac{F\epsilon^2 f_d M \nu_{s2}^2}{2!}$$

$$f_d = \exp^{-t_{pd}/\tau}(1-\exp^{-t_g/\tau})$$

		8- detector arrangement			
		Experiment		Simulation	
		Value	f_d	Value	f_d
	Time	1202	N/A	1	N/A
Foreground Distribution	$F_n(1)$	931633 ± 3052	0.659 ± 0.004	N/A	
	$F_n(2)$	177903 ± 422			
	$F_n(3)$	1755 ± 42			
Foreground Distribution (/sec)	$F_n(1)$	7750.7 ± 2.5			
	$F_n(2)$	148.0 ± 0.4			
	$F_n(3)$	1.46 ± 0.03			
Photon corrected Foreground Distribution (/sec)	$F_n(1)$	6275 ± 147	1.17 ± 0.03	6730 ± 82	1.21,± 0.09
	$F_n(2)$	148.0 ± 0.4		261 ± 16	
	$F_n(3)$	1.46 ± 0.03		3 ± 2	
Photon and XT corrected Foreground Distribution (/sec)	$F_n(1)$	6299 ± 148	0.98 ± 0.03	6756 ± 92	1.09,± 0.08
	$F_n(2)$	124.3 ±1.1		235 ± 15	
	$F_n(3)$	0.95 ± 0.16		2.07 ± 1.75	

→ **Percentage of correction applied:**
- Singlets: 19.6%
- Couplets: 19.4%
- Triplets: 47.84%



CONCLUSION

CONCLUSION

Conclusion

1. Implementation of an real-time system for multiplicity and spectroscopy using scintillation detectors based on time-of-flight method
2. Characterization of scatter component in Rossi-α distribution
3. Determination of angular correlation and neutron spectroscopy of ^{252}Cf
4. Characterization of neutron crosstalk between detectors and validation of a correction model using gatefraction

Future Work

1. Compare results with different models of nuclear fission and the associated fast neutron emission i.e. CEF, CGMF, FREYA and FIFRELIN approaches
2. Determine coincidence in non-homogeneous packaging to determine sample information

END OF FILE

The University Of Sheffield.

Department Of Materials Science & Engineering

NucleUS
Immobilisation Science Laboratory

Radionuclide interactions with cementitious materials for radioactive waste management

Antonia Yorkshire, Dr Claire Corkhill, Prof John Provis

DISTINCTIVE

EPSRC
Engineering and Physical Sciences Research Council

NATIONAL NUCLEAR LABORATORY

midas

THE 1ST STUDENT EXPERIENCE SURVEY 2014-15

The University Of Sheffield.
Department Of Materials Science & Engineering

Cementitious encapsulation of ILW

NucleUS
Immobilisation Science Laboratory

- Intermediate level waste: 4 GBq tonne^{-1} alpha; 12 GBq tonne^{-1} of beta/gamma[1]
- Amount: 450 000 m^3
- Current management: encapsulation in Portland cement grouts

Fly ash: Plutonium contaminated materials (PCM)

Blast furnace slag: Magnox fuel cladding

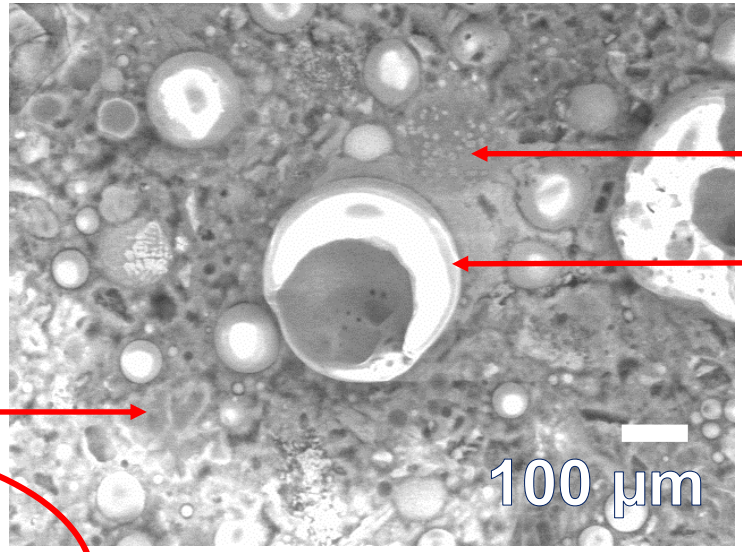
[1] "The 2010 UK Radioactive Waste Inventory: Main report," Nuclear Decommissioning Authority, URN 10D/985 NDA/ST/STY(11)0004, 2011

The University Of Sheffield.
Department Of Materials Science & Engineering

Project objectives

NucleUS
Immobilisation Science Laboratory

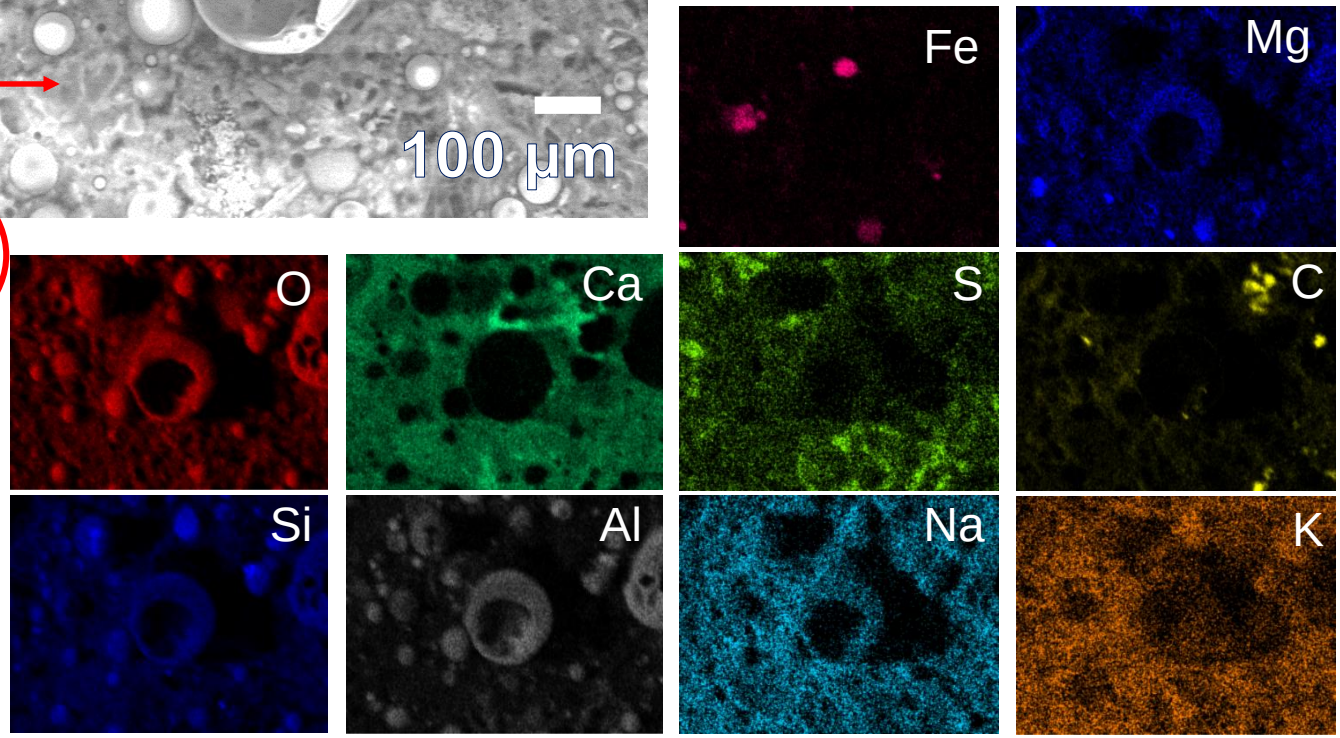
1:1 FA/PC
28 days curing
w/s = 0.33



Portlandite: $Ca(OH)_2$

Fly ash particle

C-S-H: bulk of the cement matrix

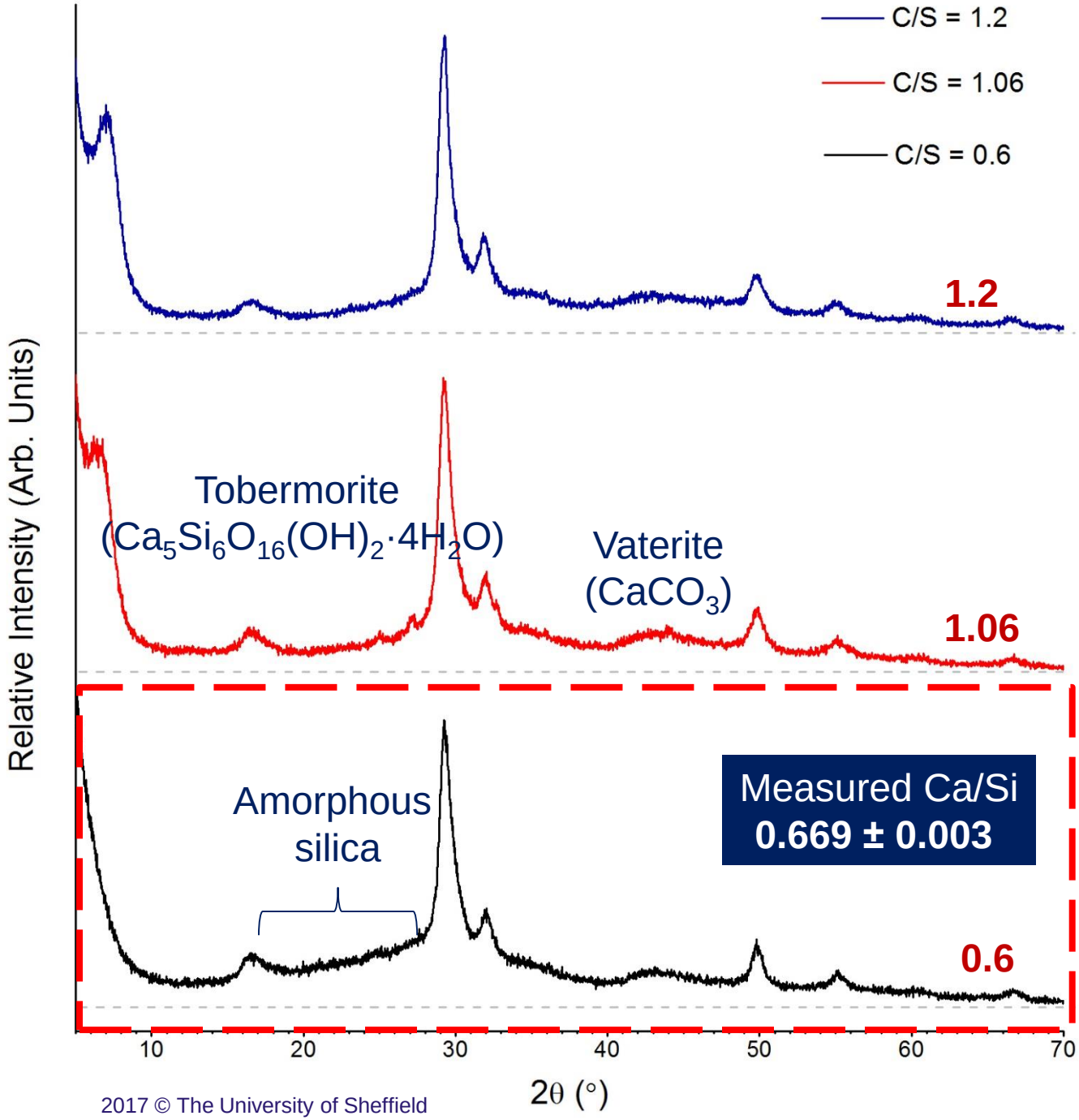


Ettringite:
$Ca_6(Al_2O_6)(SO_4)_3.32H_2O$

Monosulfate:
$Ca_4(Al_2O_6)(SO_4).12H_2O$

NucleUS
Immobilisation Science Laboratory

Synthesis of C-S-H



- $CaO:SiO_2$ slurries were mixed at w/s = 15 in weight ratios of 3:1, 1:1 and 1:3 for 7 days
- Theoretical **Ca/Si** ratios of **1.2, 1.06** and **0.6**

Tajuelo Rodriguez, E., Garbev, K., Merz, D., Black, L. & Richardson, I. G. "Thermal stability of C-S-H phases and applicability of Richardson and Groves' and Richardson C-(A)-S-H (I) models to synthetic C-S-H." *Cem. Concr. Res.* **93,** 45–56 (2017)

Uranium sorption and co-precipitation

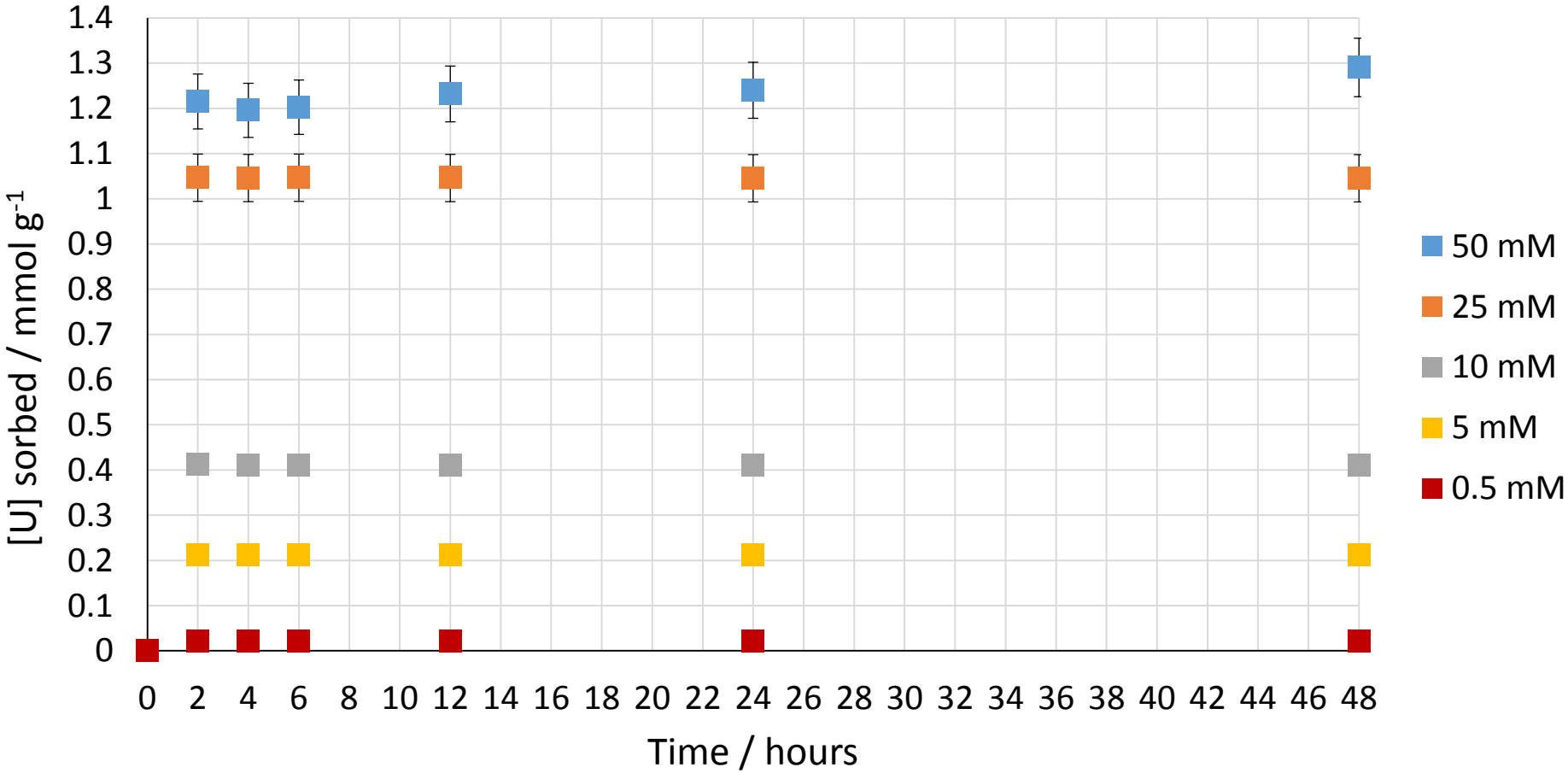
Sorption experiments

- Uranium as uranyl nitrate ($UO_2(NO_3)_2$) at 50, 25,10, 5 and 0.5 mM
- C-S-H(0.6) at 25 g L^{-1}
- Sampled at 2, 4, 6, 12, 24 and 48 hours
- U, Ca and Si concentrations in solution measured

Co-precipitation

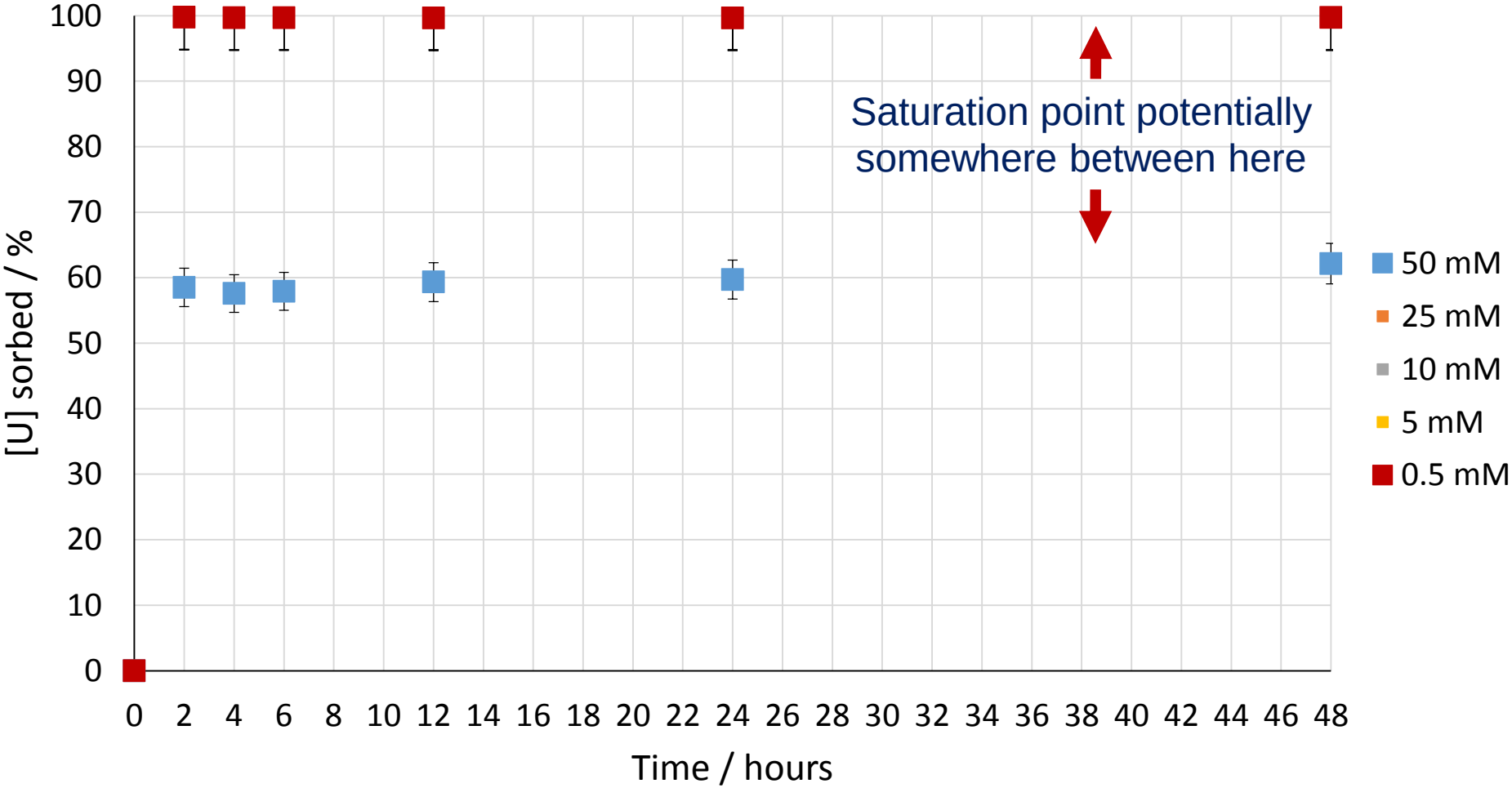
- C-S-H(1.06) synthesised presence of uranyl nitrate
- Thermally treated to induce crystallisation

Uranium uptake

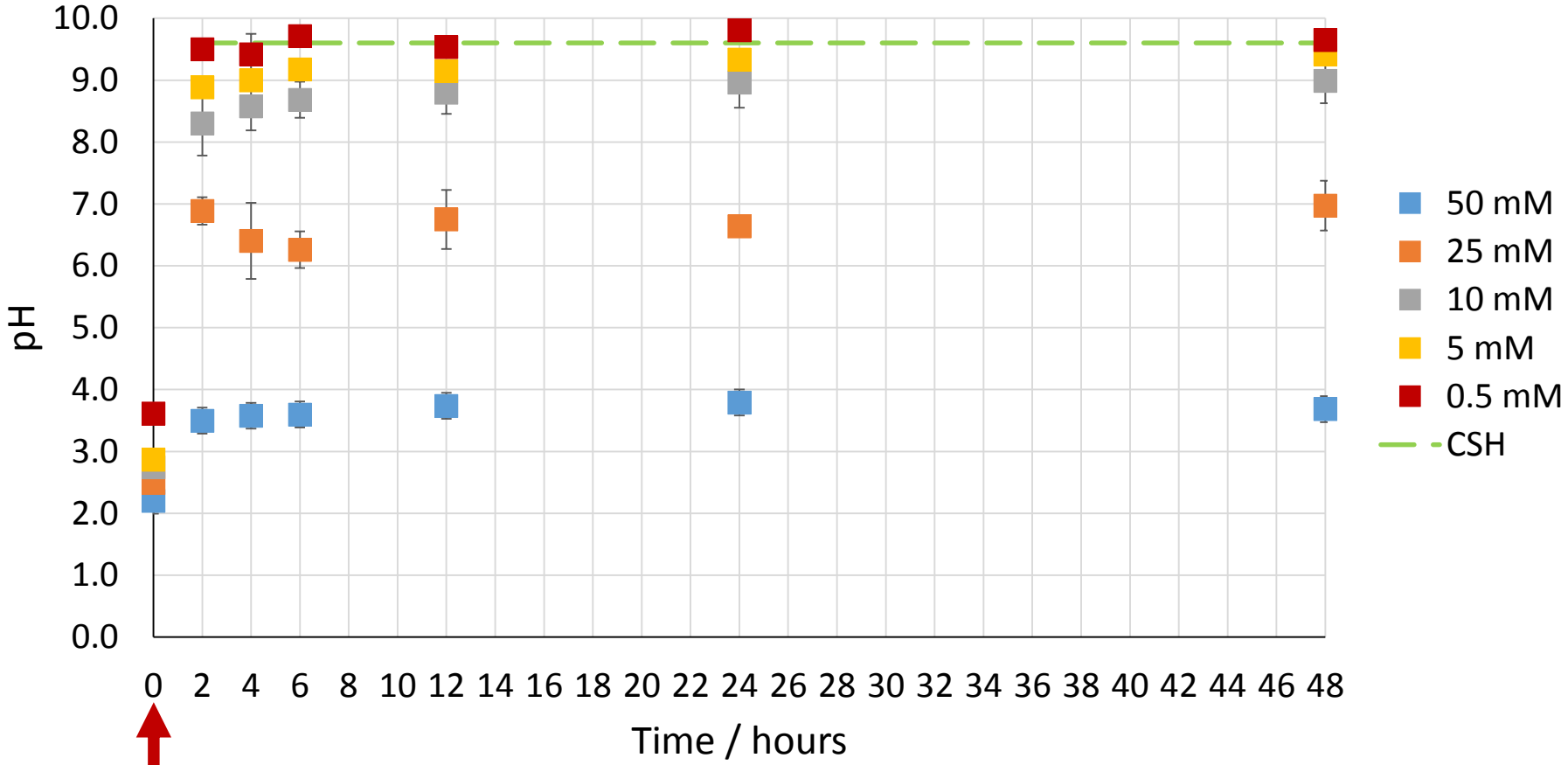


- Uranium uptake is rapid – achieved within 2 hours

Uranium uptake



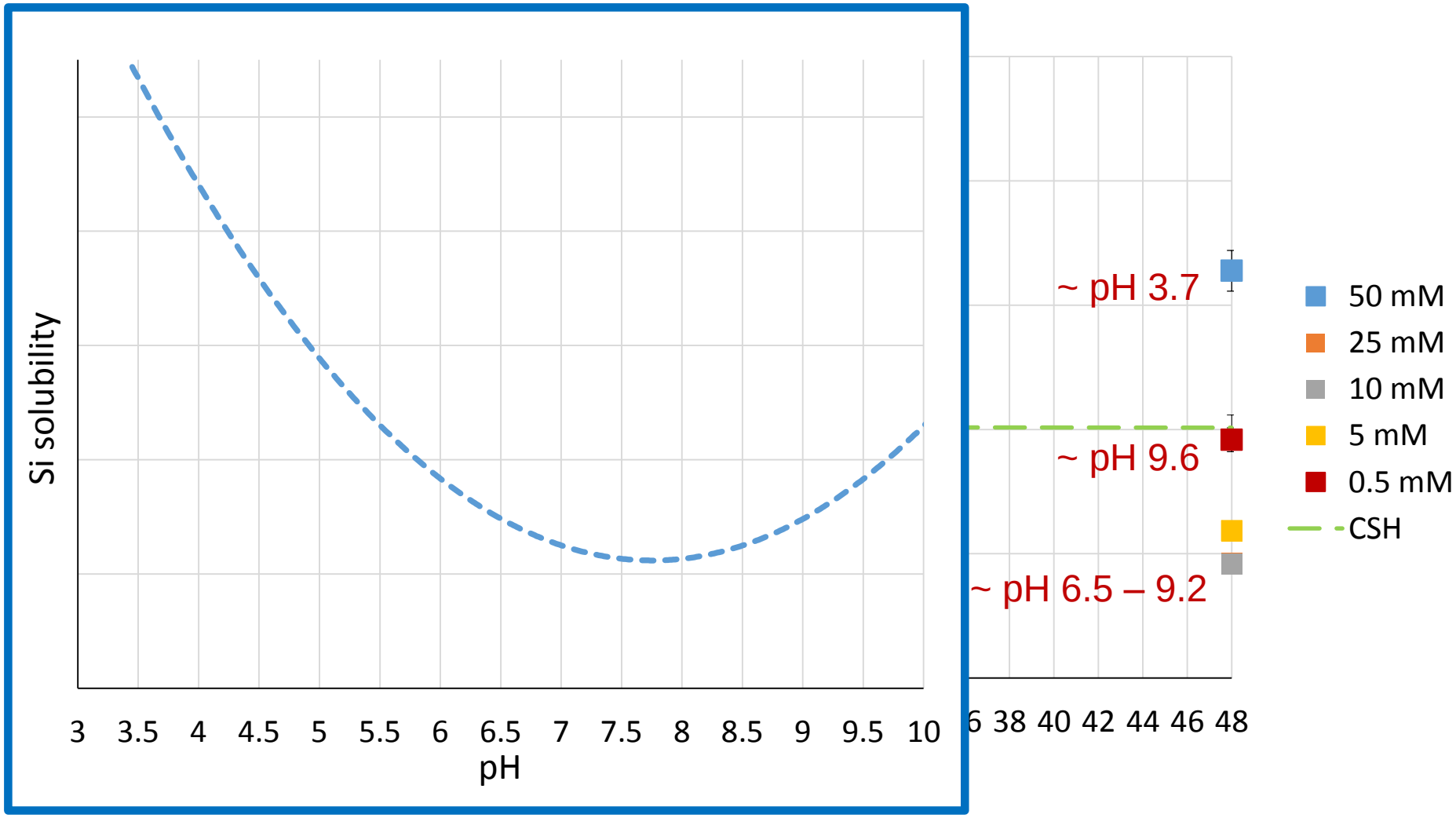
pH measurements



pH before addition of C-S-H: **2-4**

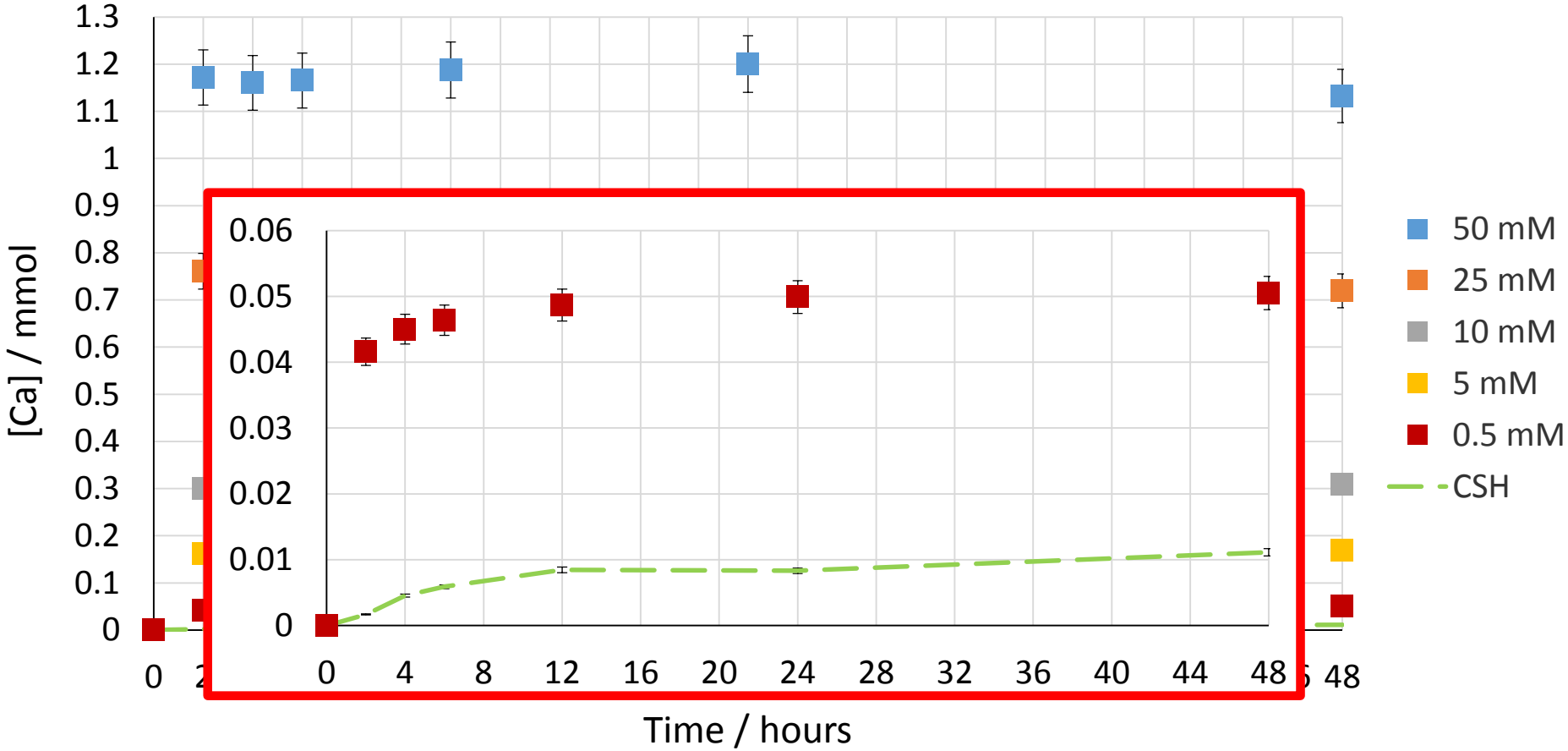
- Large pH increase due to addition of C-S-H to uranyl nitrate

Silicon release



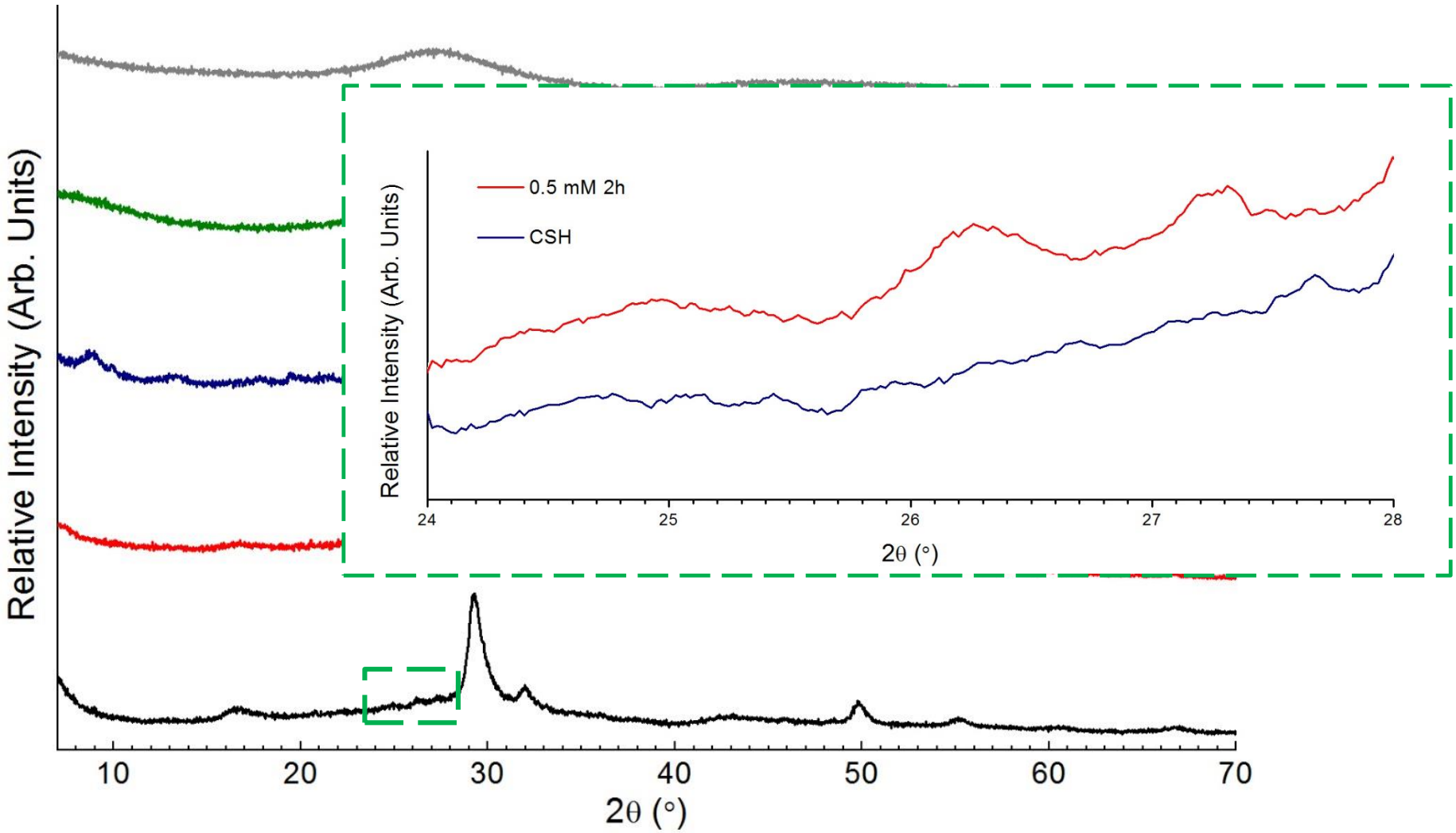
- Correlates with the maximum pH of the solutions

Calcium release

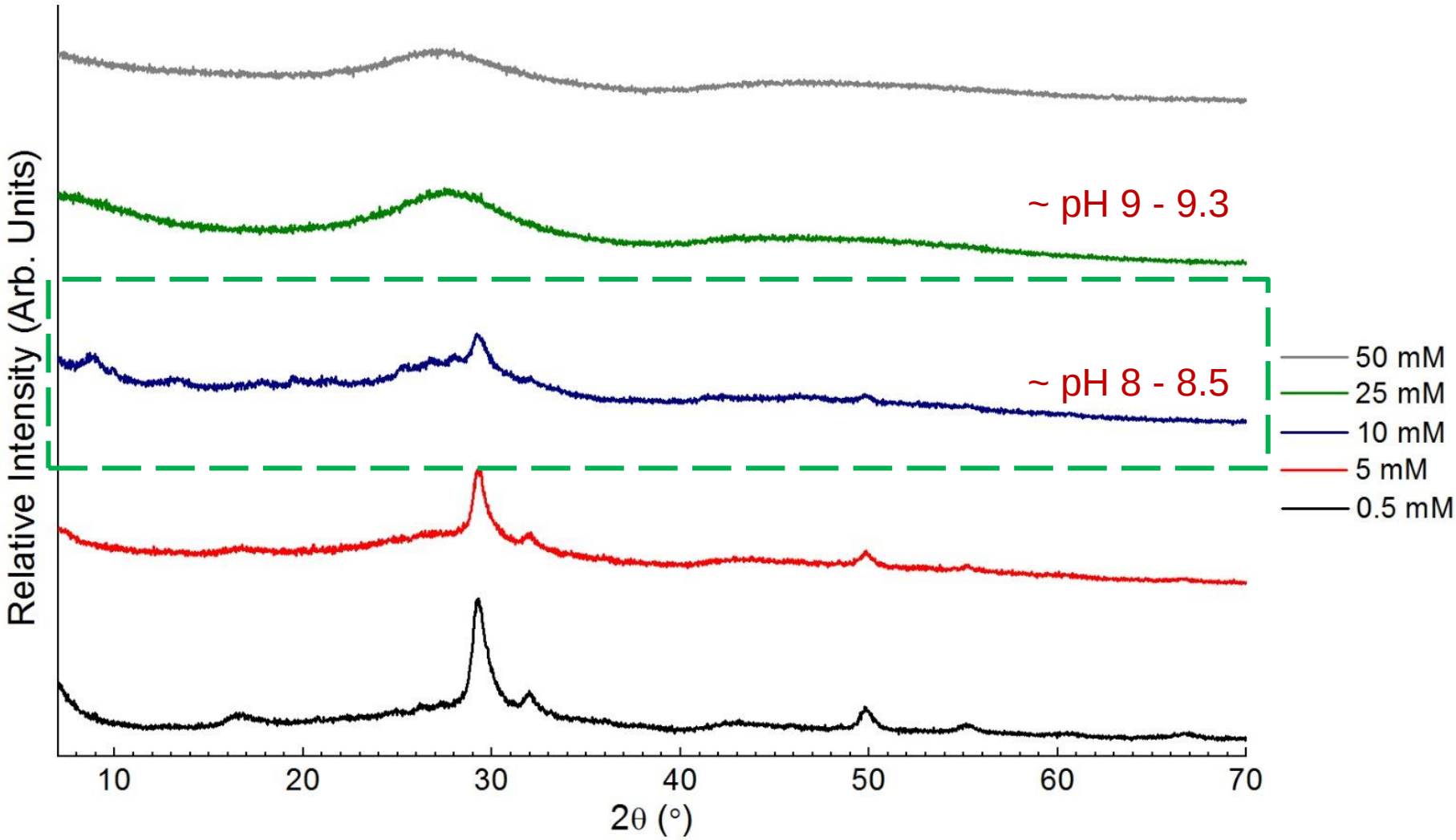


- Higher pH shows a higher Ca release – correlates with uranium uptake

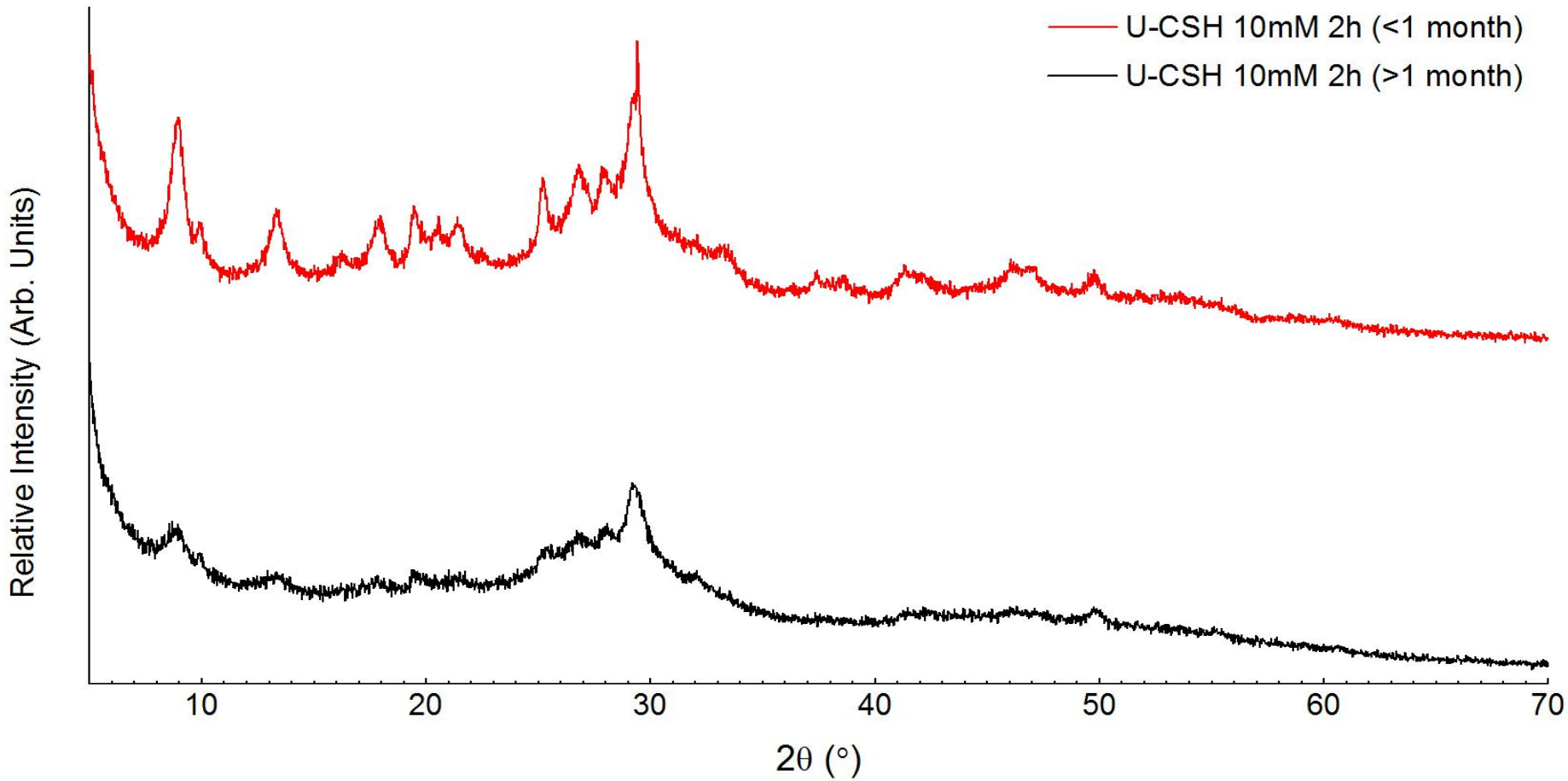
XRD results



XRD results

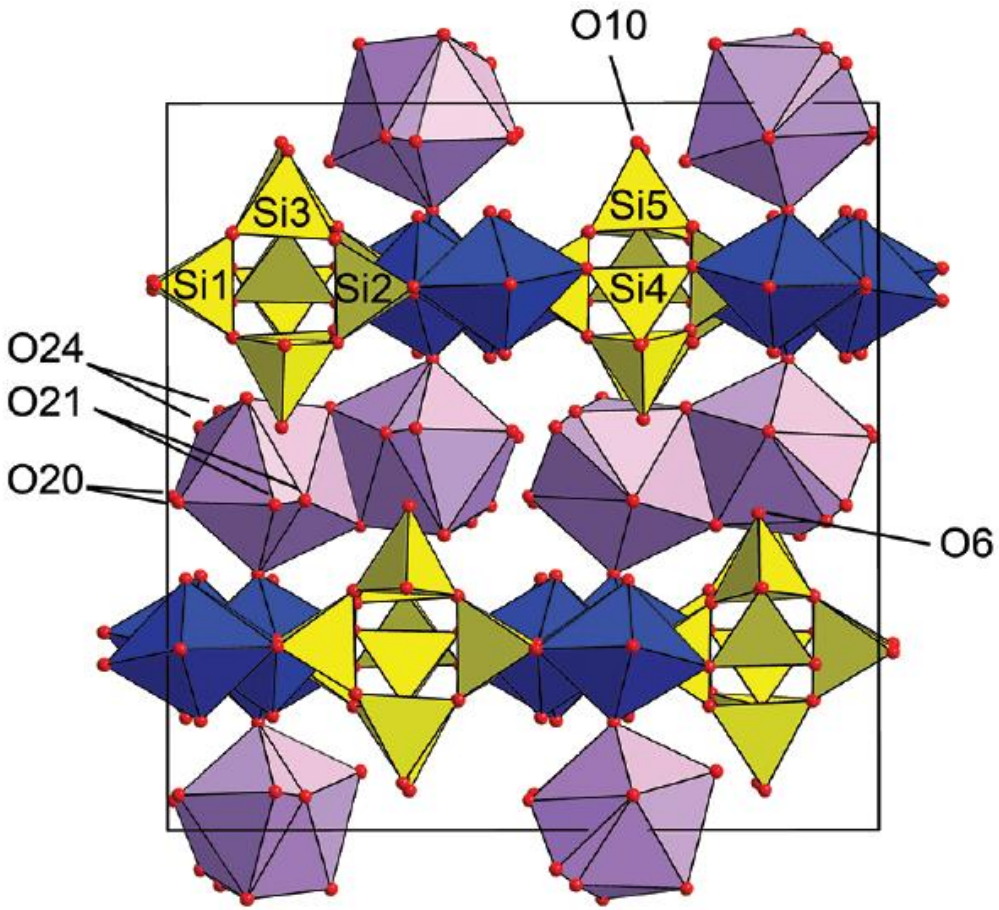


XRD results



- Formation of *Haiweeite*, with an ideal formula of $Ca[(UO_2)_2Si_5O_{12}(OH)_2].3(H_2O)$

Haiweeite



- Forms at 10 mM uranyl nitrate and 25 g L^{-1} C-S-H.
- A uranyl sheet silicate with dimers of calcium polyhedra.
- Formation of which shows evidence that uranium can incorporate into the C-S-H structure by the formation of a new phase.

Plasil, J., Fejfarova, K., Cejka, J., Dusek, M., Skoda, R. & Sejkora, J., "Revision of the crystal structure and chemical formula of haiweeite, Ca(UO2)2(Si5O12)(OH)2·6H2O." *Am. Mineral.* **98,** 718–723 (2013)

U sorption and co-precipitation

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Co-precipitation

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Co-precipitation experiments

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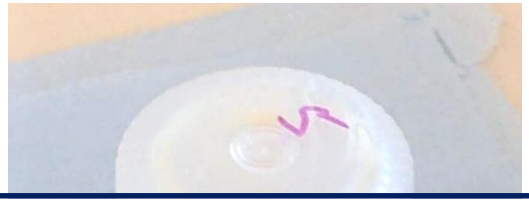
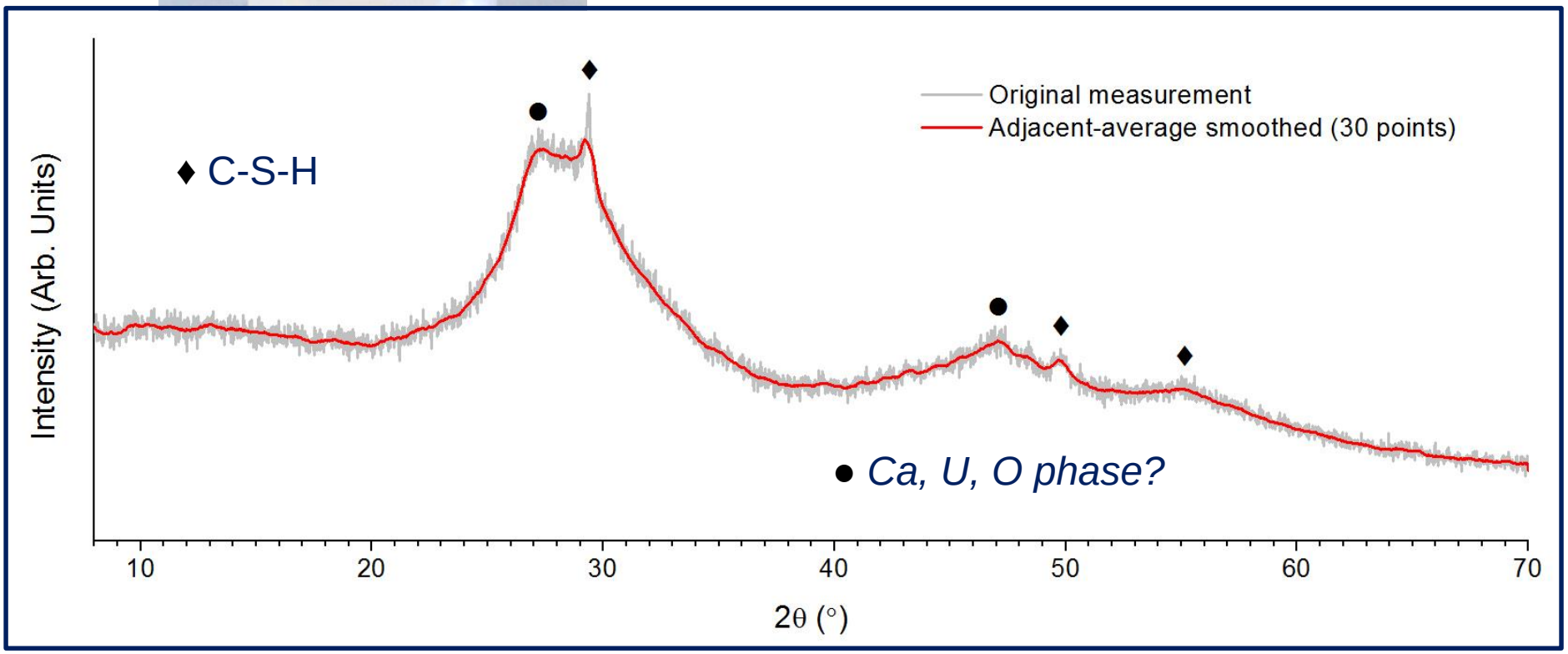
Immobilisation Science Laboratory



- 100 mM $UO_2(NO_3)_2$ solution
- 1:1 $CaO:SiO_2$ ratio by mass (theoretical Ca/Si = 1.06)



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Thermal treatment up to 1000 °C

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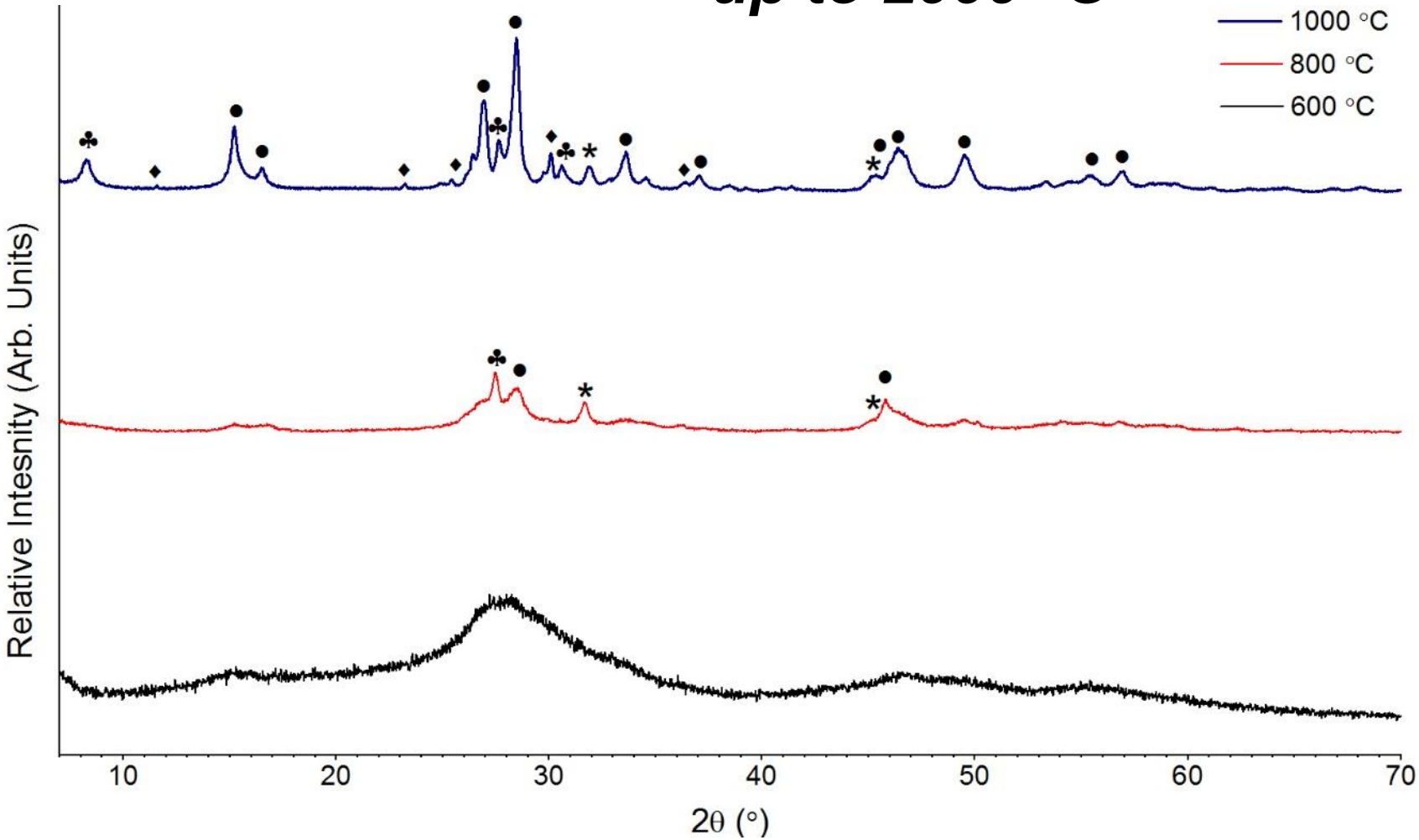

♦ Wollastonite

● *Calcium uranate*

♣ Unidentified phase(s)

* *Unidentified phase – U, Si, O?*

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Thermal treatment: Comparison to C-S-H

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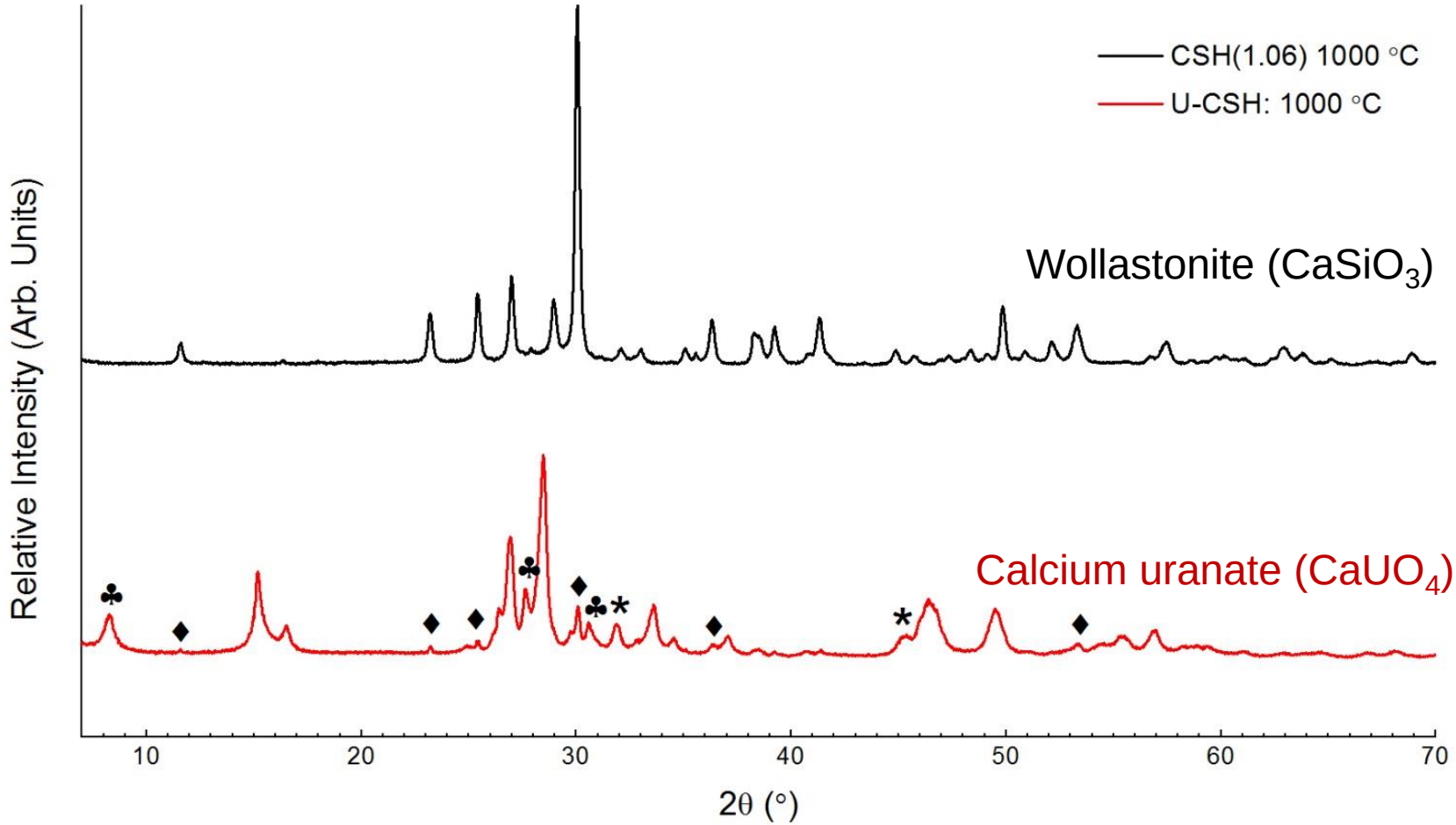

♦ Wollastonite

♣ Unidentified phase(s)

* *Unidentified phase – U, Si, O?*

Summary of uranium work

- Uranium uptake by C-S-H is **rapid** and occurs within 2 hours
- pH of the starting solution is affecting the **C-S-H structure** due to Ca and Si solubility
- Evidence to show that uranium can be incorporated into the C-S-H structure - haiweeite
- However we do see the potential for sorption of uranium by calcium and silicon - calcium uranate and soddyite
- Early thermodynamic geochemical modelling shows that these phases are favourable to form
- Currently studying this with plutonium

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Plutonium containing cements

NucleUS
Immobilisation Science Laboratory

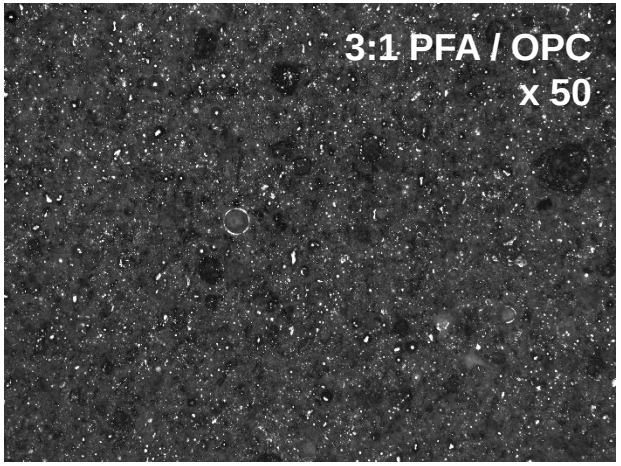
NATIONAL NUCLEAR LABORATORY

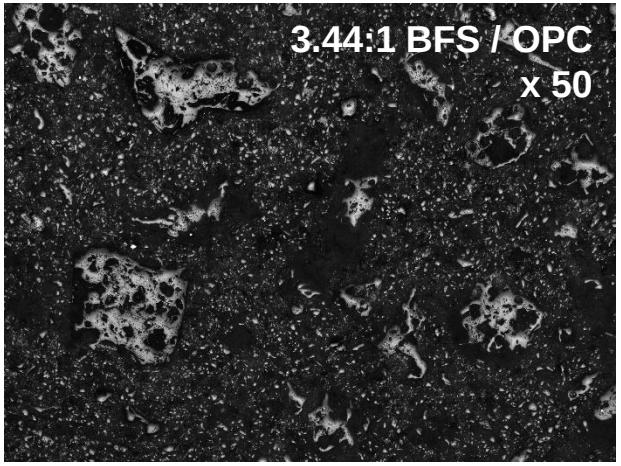
Sarah Kearney, Mike Angus & Robin Orr

August 2017

Fly ash / Portland cement

Blast furnace slag / Portland cement





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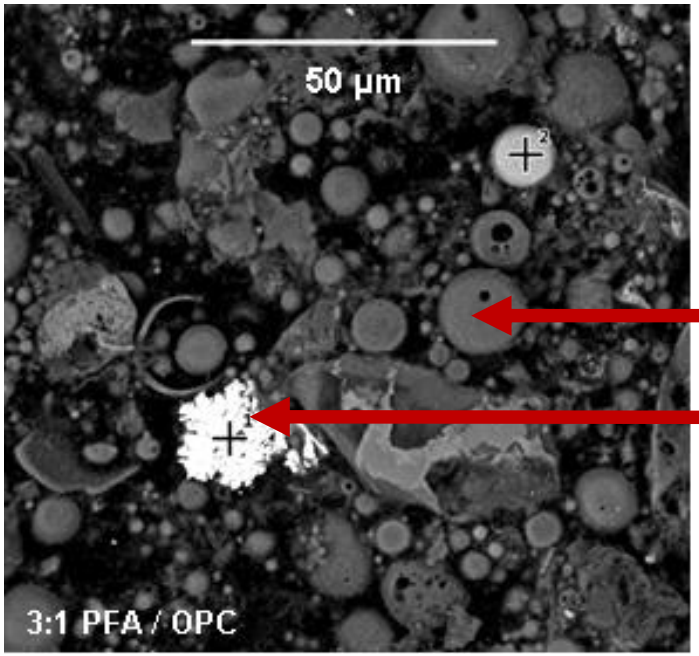
Plutonium containing cements

NucleUS
Immobilisation Science Laboratory

NATIONAL NUCLEAR LABORATORY

Sarah Kearney, Mike Angus & Robin Orr

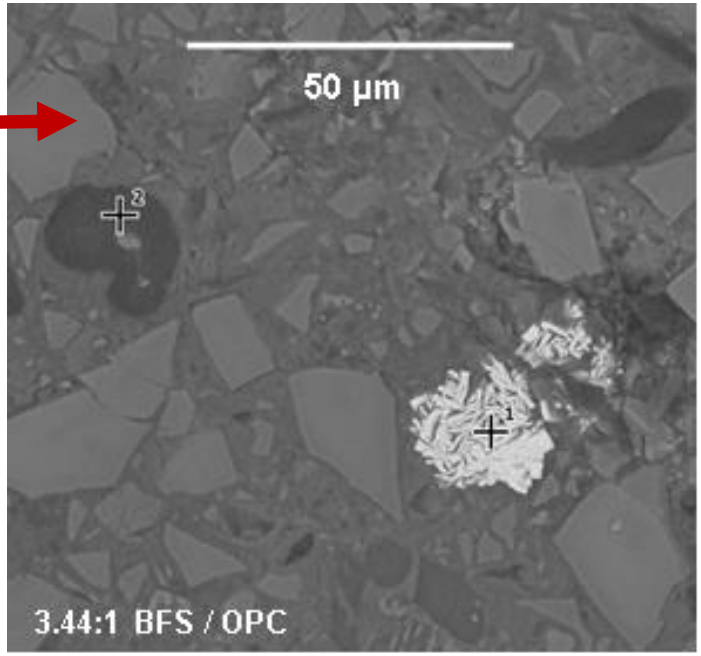
August 2017



Calumite

Fly ash

PuO_2



	Weight Concentration (%)	
Element	*Spot 1*	*Spot 2*
Pu	76.2 ± 0.5	-
O	9.7 ± 0.4	58.9 ± 0.0
Ca	4.4 ± 0.9	4.4 ± 0.3
Si	2.1 ± 0.3	17.3 ± 0.1
Al	-	12.2 ± 0.0

	Weight Concentration (%)	
Element	*Spot 1*	*Spot 2*
Pu	76.2 ± 0.7	-
O	12.5 ± 0.0	80.2 ± 0.2
Ca	2.8 ± 0.3	14.3 ± 0.2
Si	1.8 ± 0.2	5.5 ± 0.3

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Conclusions & Further work

Conclusions

- Uranium uptake by C-S-H is **rapid** and occurs within 2 hours - need to buffer the solution for further experiments, as the pH will also have an effect on the **uranyl speciation** as well as the C-S-H structure
- Co-precipitation yields separate calcium and silicon based products, showing the potential for both **incorporation** and **sorption**
- C-S-H is an important cement phase for uranium retention in ILW
- Thermodynamic modelling will be an import tool to determine the phases that are likely to from in these systems

Conclusions & Further work

Further work

- Contact experiments for Tc and Pu with C-S-H, hydrotalcite and AFt/AFm phases
- Thermodynamic modelling to determine phase speciation and solubility
- Further structural refinement:

  Rietveld refinement and PDF-XRD of phases

  Synchrotron experiments: EXAFS, XANES and XRD

  NMR proposal submitted

U	**C-S-H**
Tc →	**Hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}.4H_2O$)**
Pu	**Ettringite ($Ca_6(Al_2O_6)(SO_4)_3.32H_2O$)**

diamond

THE 1ST STUDENT EXPERIENCE SURVEY 2014-15

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Sarah Kearney
Martin Stennett
Colleen Mann
Dan Bailey & Sarah O'Sullivan

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