Transitioning of Spent AGR Fuel from Wet to Dry Storage

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Introduction

- Large quantities of nuclear fuel has accumulated in storage ponds.
- Fuel can not be stored in ponds indefinitely.
- In many countries dry storage of spent nuclear fuel (SNF) is used as an interim measure.
- Key requirements for dry storage are criticality prevention, integrity maintenance and retrievability.
- All of these are affected by corrosion and hence the interaction with water.

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Types of Water

ASTM C1553 identifies 2 forms of water.

Bound Water

- Chemisorbed water-Water that is bound to other species by forces whose energy levels approximate those of a chemical bond.
- Physisorbed water-Water that is physically bound to internal or external surfaces of solid material.

Unbound Water

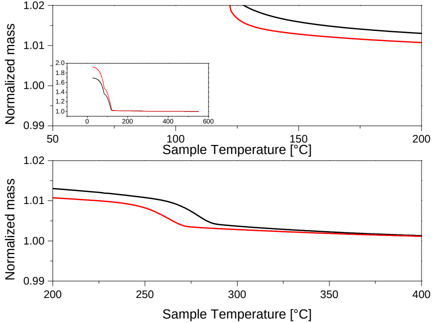
- Free water-Water that in the solid, liquid or vapour state that is not chemically bound to another species
- Trapped water-Unbound water that is physically trapped or contained by the surrounding matrix.

Bound Water

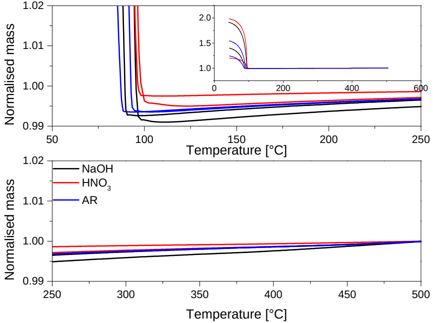
TGA drying of corroded metal.

- Aluminium shows a clear mass drop as the oxide dehydrates.
- No similar peak apparent for SS.

Aluminium



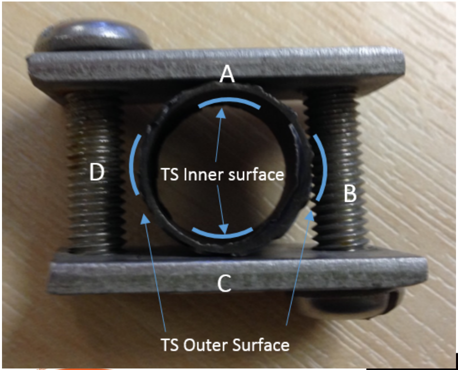
Stainless Steel (SS)

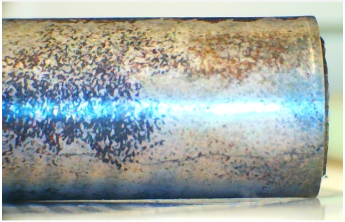


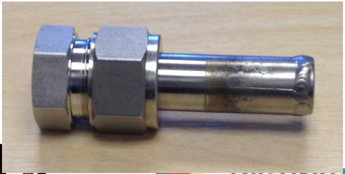
Trapped Water

Sample Production

- Failures of AGR fuel have been attributed to IGSCC.
- A test piece (TP) was produced which had SCC cracks.







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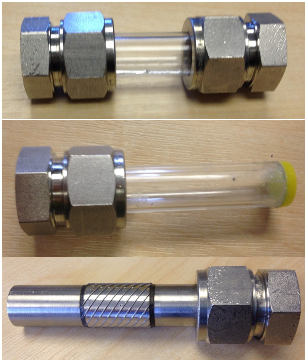
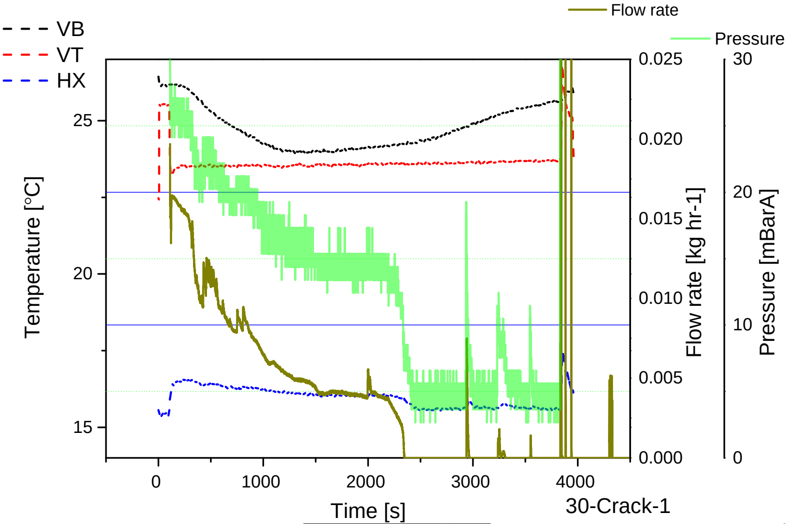
Macro Scale Drying Rig



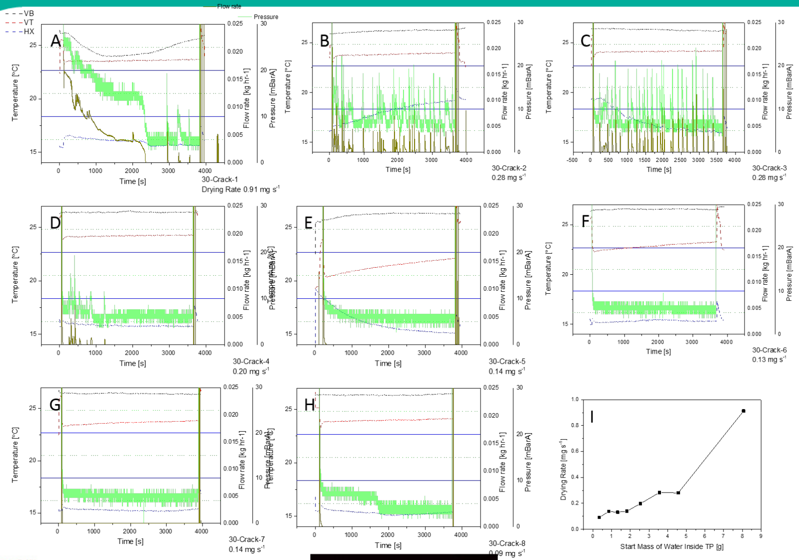
Typical Data Plot



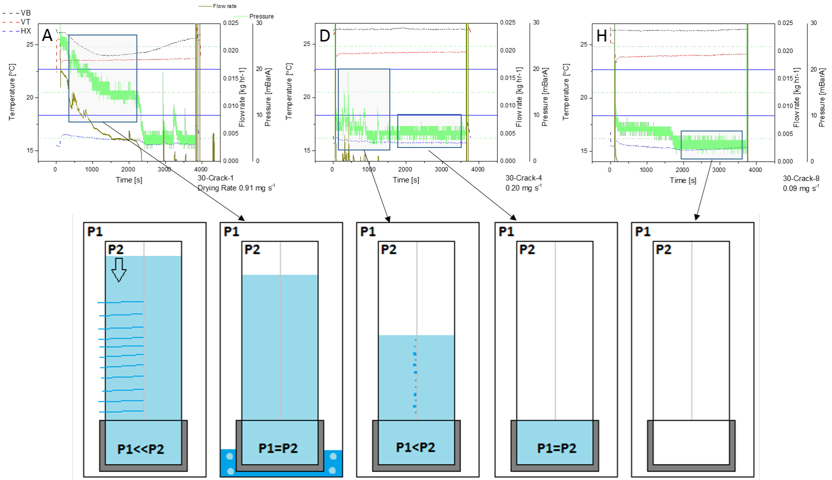
30-Crack-1

Drying Rate 0.91 mg s^{-1}

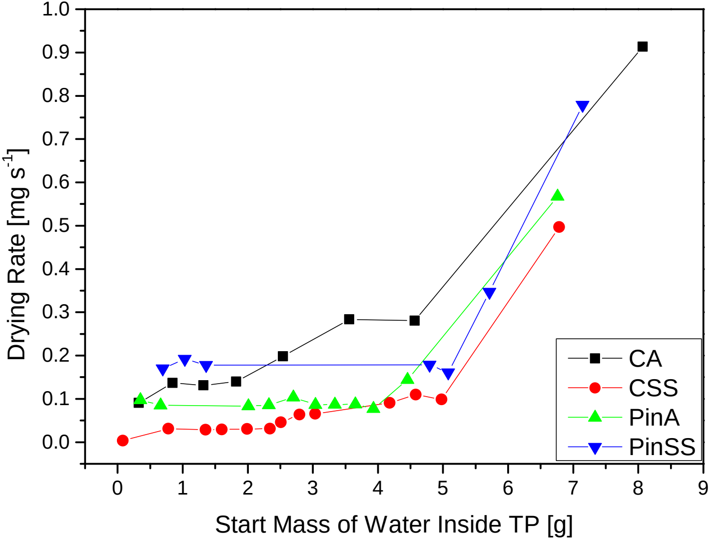
Drying Regimes



Drying Regimes



Drying Regimes



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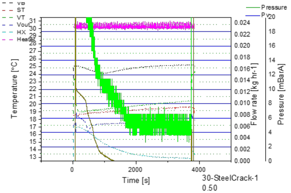
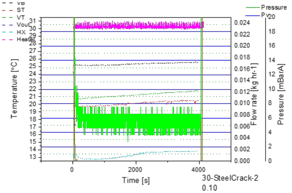
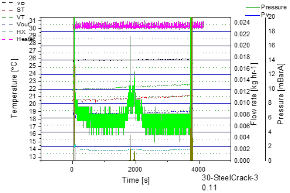
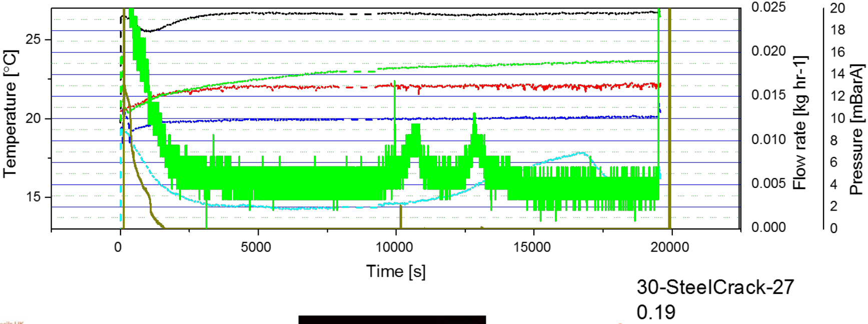
Drying Regimes









Next Steps

Macro Scale Drying

- Reconfigure rig for flowed gas drying.
- End point determination.

Other

- Long term corrosion work.
- Creation and drying of carbon deposits.

Thank you!

Smart cements for chloride / moisture sensing in nuclear concrete assets

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MSc Decommissioning and Radwaste Management, University of Oriental Piedmont, Italy
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DISTINCTIVE 3rd Annual Meeting
5th - 6th April 2017
York, UK

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Summary

- ***Introduction*:**
  - → *Issue: Structural integrity in nuclear context*
  - → *Corrosion of steel rebars in concrete*
    - ➢ *Role of chloride and moisture*
  - → *Monitoring of chloride and moisture*
- ***Overview of the project:***
  - → *Novel solution proposed*
  - → *Steps of the project*
- ***Experimental work:***
  - → *Methodology details*
  - → *Preliminary results*
- ***Conclusions and future work***

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Introduction

→ *Issue: Structural integrity in nuclear context*

Structural integrity and stability:

- Important for all types of buildings;
- In particular, structures in nuclear context:
  - Are usually coastal;
  - Underpin safety-critical structures and radiation barriers;
  - Are irradiated by ionizing radiation;
  - Play the role of phisical barrier between radioactive materials and the external environment.

→ ✓ Are made of reinforced concrete

↓

Corrosion of steel rebars

Figure 1 – Temporary waste storage D1, Nuclear power Plant of Garigliano (Ce), Italy.

Figure 2 – Consequences of rebar corrosion.

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Introduction

→ *Corrosion of steel rebars in concrete*

➤ *Role of chloride and moisture*

In the normal highly alkaline environment of concrete:

- ✓ pH > 11.5;
- ✓ the surface of steel rebars is protected from corrosion by a **thin passive oxide film**.

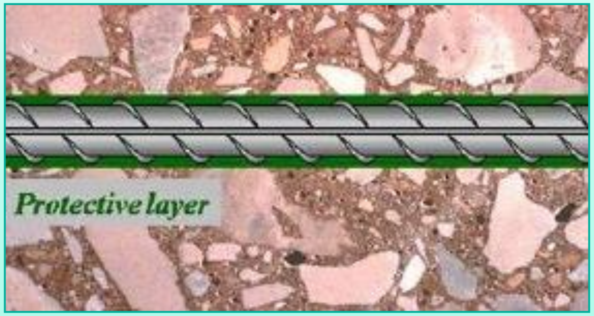

Figure 3 – Reinforcing steel covered with the protective oxide film in concrete.

Under certain conditions, **the passive film breaks**, leading to corrosion.

DEPASSIVATION of steel rebars

CARBONATION

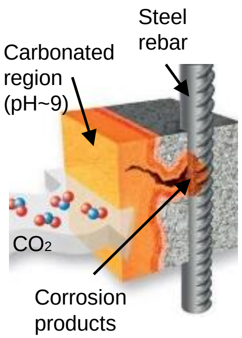

Figure 4 – Carbonation measurement, by means of phenolphthalein solution.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (1)

CHLORIDE CONTAMINATION

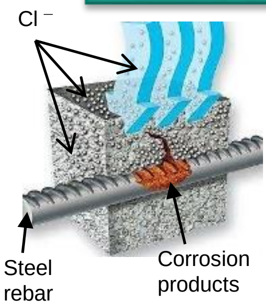

Figure 5 – Example of 'pitting corrosion' of steel rebars, due to chloride penetration.

Cl^- concentration > 'threshold' value (2)

IMPORTANT ROLE OF WATER

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Introduction

→ *Monitoring of chloride and moisture*

➢ *Existing methods*

Chloride
- Ion selective electrodes enbedded in concrete;
- Fibre optic sensors.

Moisture
- Humidity sensors;
- Electrical resistance sensors;
- Dielectric permittivity sensors.

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Chloride

- Ion selective electrodes enbedded in concrete;
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Moisture

- Humidity sensors;
- Electrical resistance sensors;
- Dielectric permittivity sensors.

Disadvantages:

❖ Not suitable for long term monitoring;

❖ Not accurate enough;

❖ Don't provide protection and repair to concrete.

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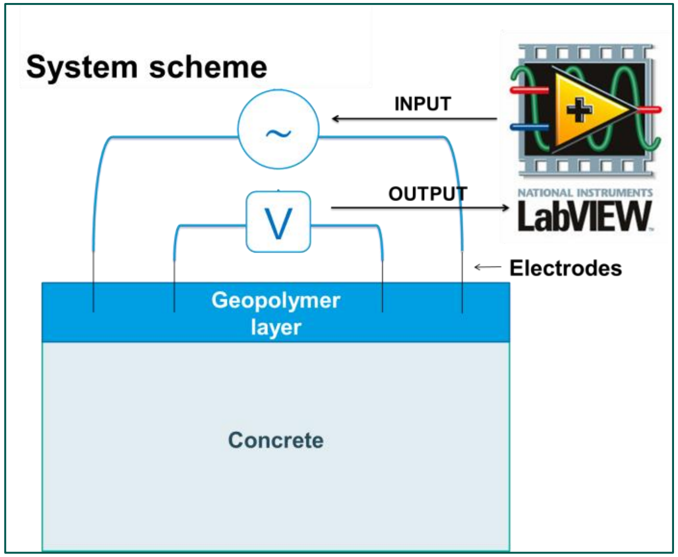
Overview of the project

→ *Novel solution proposed*

- *New sensing system*

Coupled system:

- Smart cements = fly ash geopolymers
- Electrical system = Electrodes, LabVIEW



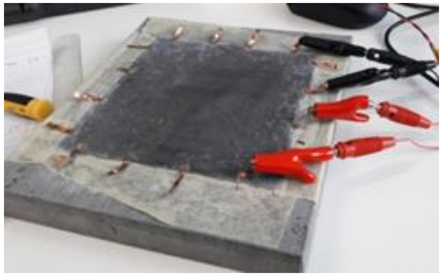


Figure 6 - Diagram and photograph of the scheme of the whole sensing system, showing a geopolymer surface layer on concrete substrate and the electrodes linked to the LabVIEW software.

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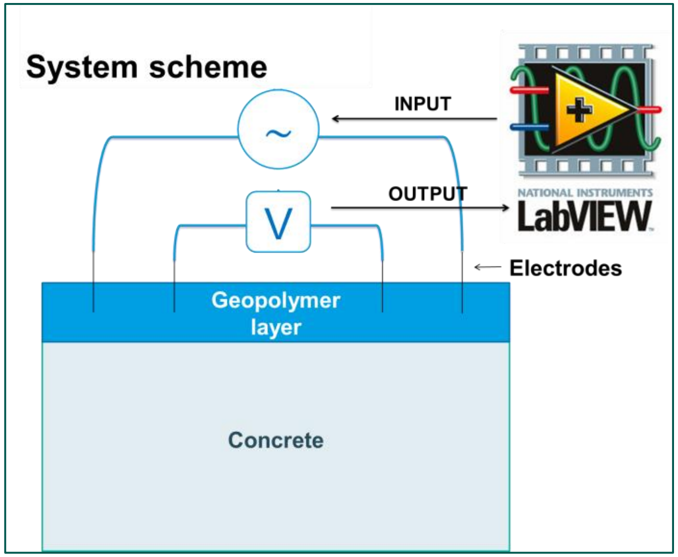
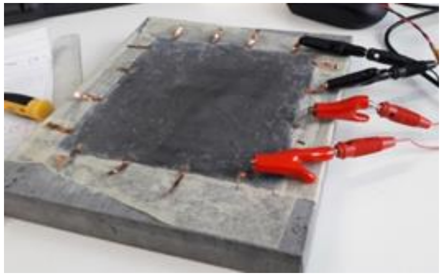
- **Highly-adhesive binders**
- **Durable**
- **Chemically resistant**
- **Electrically conductive**





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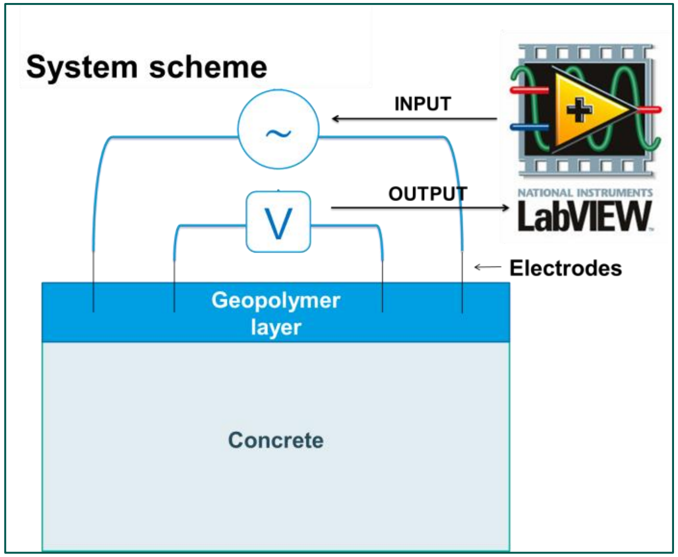

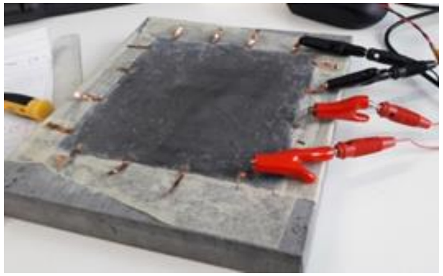

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Advantages:

- Affordable;
- Suitable for long term monitoring;
- Non-destructive;
- Combined monitoring and maintenance technology.

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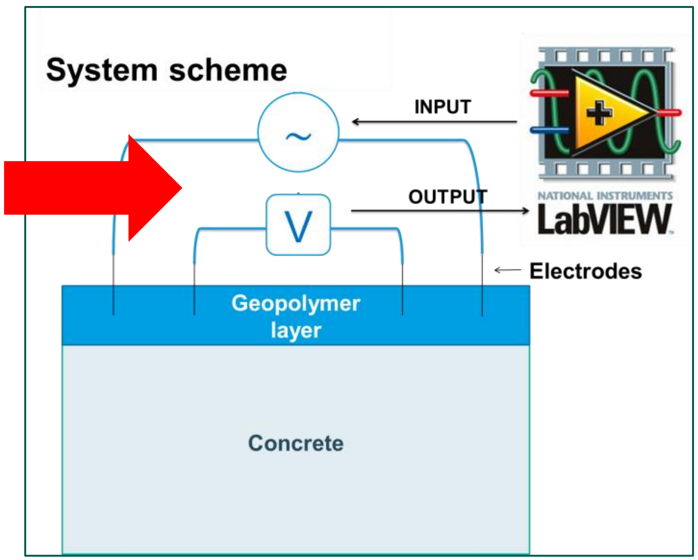

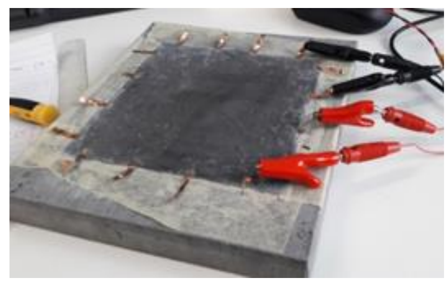

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Overview of the project

→ *Novel solution proposed*

- *New sensing system*

Electrochemical Impedance Spectroscopy (EIS)

→ **High information**

→ **Non destructive**

$$Z = \frac{V_t}{I_t} = \frac{V_0 \sin(\omega t)}{I_0 \sin(\omega t + \varphi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} \qquad (3)$$

Z = Impedance	V = Potential	I = Current
ω = Frequency	φ = Phase	t = Time

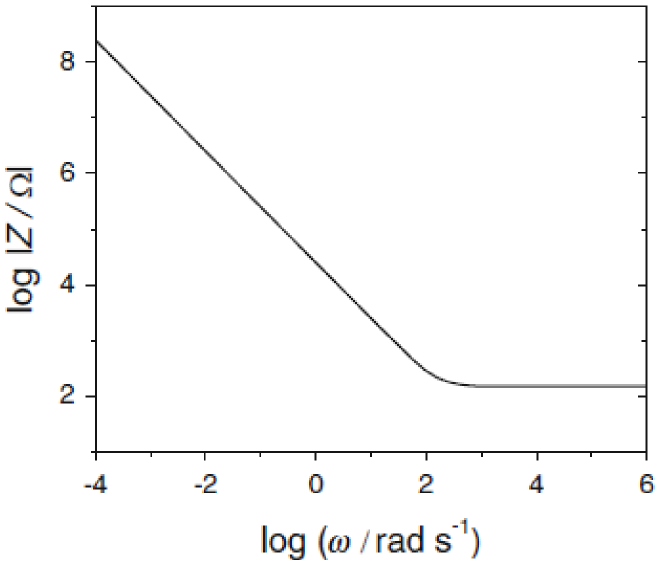

Figure 7 – Bode plot with the log of the absolute value of impedance versus the values of frequency.

Overview of the project

→ *Novel solution proposed*

➢ *New sensing system*

Electrochemical Impedance Spectroscopy (EIS)

→ **High information**

→ **Non destructive**

Variations of Impedance

ΔZ :

- **Temperature**
- **Strain**

Previous studies (Temperature, Strain)

- **Concentration of chloride ions**
- **Moisture**

Object of study in this work (Concentration of chloride ions, Moisture)

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Overview of the project

→ *Novel solution proposed*

- *New sensing system*

Electrochemical Impedence Spectroscopy (EIS)

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Variations of Impedence

ΔZ :

- **Temperature**
- **Strain**

} *Previous studies*

- **Concentration of chloride ions**
- **Moisture**

} ***Object of study in this work***

← **Radiation**

↑

- Radiolysis
- Ionization
- ***Interference?***

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Overview of the project

→ *Steps of the project*

1^{st} ⇨

- **Making the most suitable geopolymer binder;**
- **Putting it in a layer on concrete, with embedded electrodes;**
- **Curing it to an uncracked layer.**

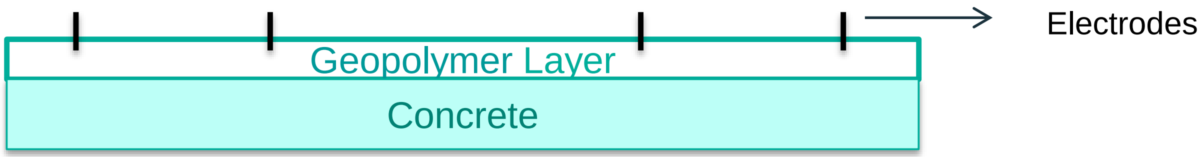

Figure 8 – Scheme of geopolymer layer put on a concrete samples, with electrodes embedded.

2^{nd} ⇨

- **Implementing a LabVIEW code, that could allow to do preliminary tests and measurements.**

3^{rd} ⇨

- **Doing different tests in laboratory and field trials varying variables:**
  - Chloride and moisture concentration;
  - Ionizing radiation.

Overview of the project

→ *Steps of the project*

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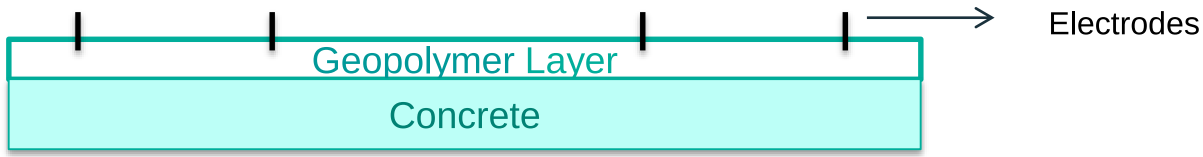

Figure 8 – Scheme of geopolymer layer put on a concrete samples, with electrodes embedded.

PRELIMINARY EXPERIMENTS

→ PRELIMINARY RESULTS

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Experimental work

→ *Methodology details*

Geopolymer synthesis

- ***Mixing***
  - *Fly ash (A)*
  - *Alkali activator solution (L):*
    - Sodium Hydroxide (SH)
    - Sodium Silicate (SS)

$$\frac{L}{A} = 0.50$$

$$\frac{SH}{SS} = 0.40$$

$$SH\ solution = 10\ M$$

Figure 9 – Mixing procedure of geopolymer binder, and ratios between the components.

Sample preparation

- ***Putting geopolymer binder on concrete samples of different ages:***
  - ***Less than 3 months old;***
  - ***Over 3 months old;***
  - ***Over 3 years old.***
- ***Putting copper electrodes in some samples: 0.1 mm thick.***

Figure 10 – Procedure of putting geopolymer layers on concrete surface.

Curing procedure

- ***Curing samples:***
  - *In the Environmental Chamber at 40°C for 3 days;*
  - *At room temperature at 23 °C for 28 days.*

Figure 11 – Samples in the Environmental chamber.

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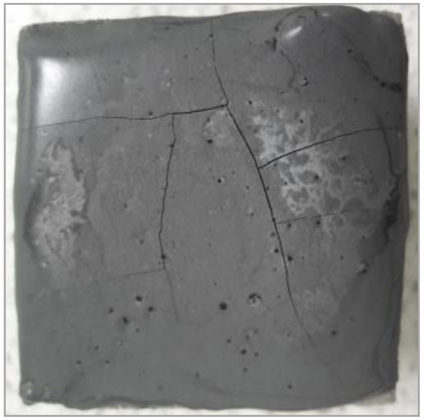
Experimental work

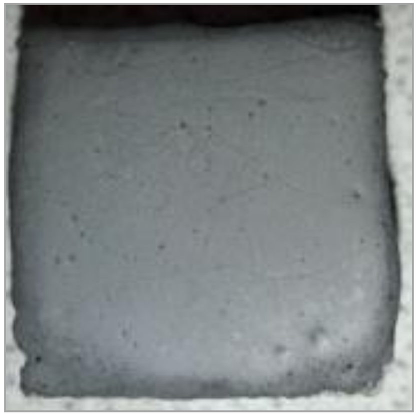
→ *Preliminary results*

- **Samples cured at room temperature (23°C) for 28 days.**

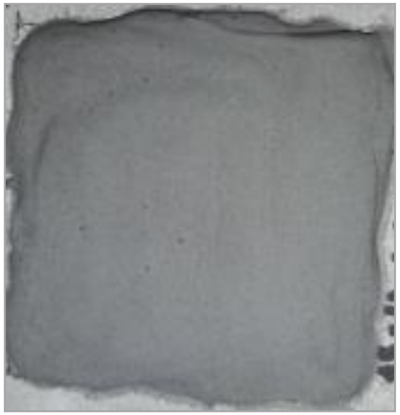
Geopolymer layer put on:



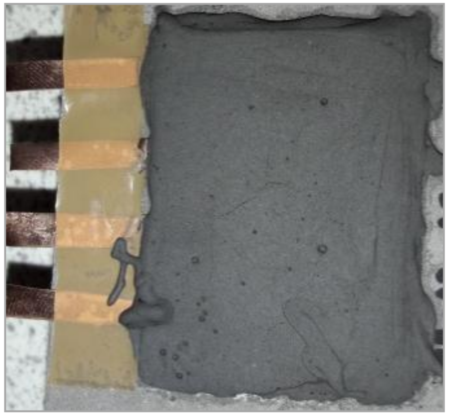
a) Less than 3 months old concrete sample.



b) Over 3 months old concrete sample.



c) Over 3 years old concrete sample.



d) Over 3 years old concrete sample, with copper electrodes (0.1 mm thick).

Deep and evident cracks	Slight cracks	No cracks	Slight cracks

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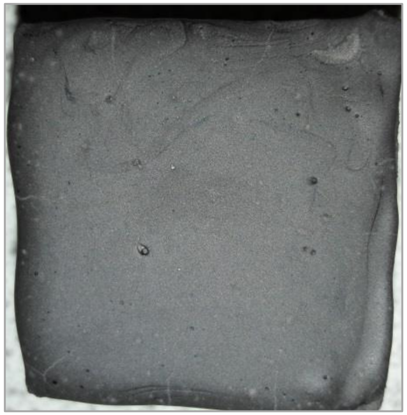
Experimental work

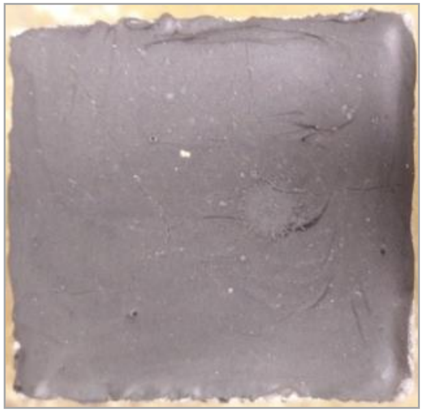
→ *Preliminary results*

- ➢ **Samples cured in the Environmental Chamber at 40°C for 3 days.**

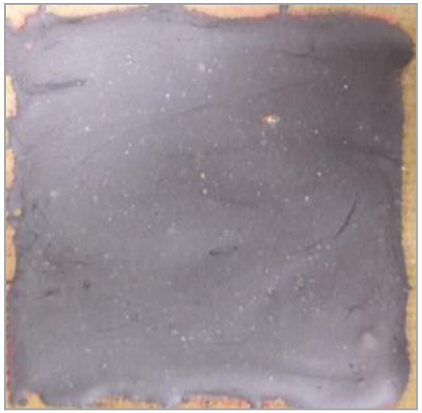
Geopolymer layer put on:



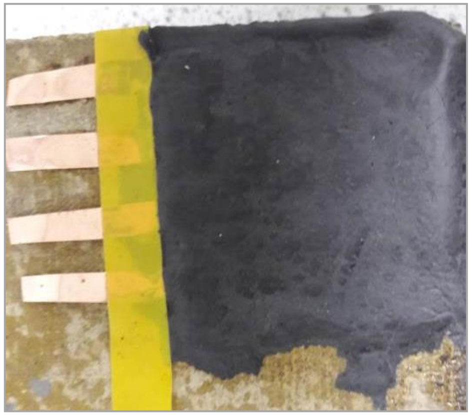
e) Less than 3 months old concrete sample.



f) Over 3 months old concrete sample.



g) Over 3 years old concrete sample.



h) Over 3 years old concrete sample, with copper electrodes (0.1 mm thick).

Evident cracks	Slight cracks	No cracks	Slight cracks

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Experimental work

→ *Preliminary results*

Cracking could occur in geopolymers placed on newer concretes **due to a combination of**:

1) **Increased water transport away from the geopolymer:**
   - ➢ Dry shrinkage of the top layer
     - → Young concrete is porous and gets less porous as it matures.

2) **Expansion of the concrete substrate due to water uptake:**
   - ➢ Swelling;
   - ➢ A small increase in hydration if there are reaction products left over.

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Conclusions and future work

→ *Conclusions*

- **Optimistic results:**

  - uncracked geopolymer surface layer on old concrete.

    → **Advantage** for application in existing structures (e.g. nuclear facilities, radwaste repositories, etc…).

- **Preliminary qualitative** analysis.

Conclusions and future work

→ *Conclusions*

- **Optimistic results:**
  - uncracked geopolymer surface layer on old concrete.
    → **Advantage** for application in existing structures (e.g. nuclear facilities, radwaste repositories, etc…).
- **Preliminary qualitative** analysis.
- **Quantitative tests and measurements** necessary.

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Conclusions and future work

→ *Future work*

1. Quantitative measurements on the geopolymer + concrete samples:

- Electrical conductivity;
- Porosity;
- Sorptivity;
- Strength;
- Adhesion;
- Imaging.

2. Tests varying variables:

- Ratios between components of geopolymer;
- Molarity of SH;
- Curing temperature;
- Curing time;
- Curing humidity level;
- Radiation (type, activity, distance from the source).

3. Developing the associate EIS interrogation and data processing system in LabVIEW.

4. Assessing the final system in field:

- Beta and gamma radiation;
- Chloride and moisture contamination.

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Thank you!

THANK YOU FOR YOUR TIME!

Biondi Lorena
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Thank you!

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Insights

→ *EIS system*

Current applied: 10 μA ÷ 100 μA → Voltage measured: 1 V ÷ 10 V

Invar, kovar or plastics electrodes

⇩

Very low thermal expansion or compression with Temperature

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Insights

→ *EIS theory*

In a **linear** or **pseudo-linear** system:

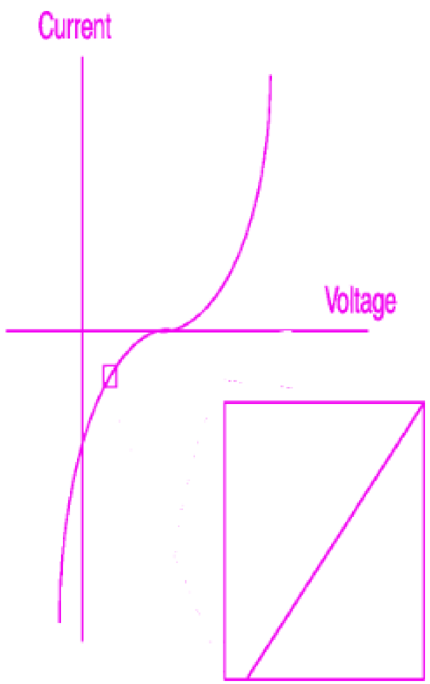

Figure 12 – Current versus voltage curve showing pseudo-linearity.

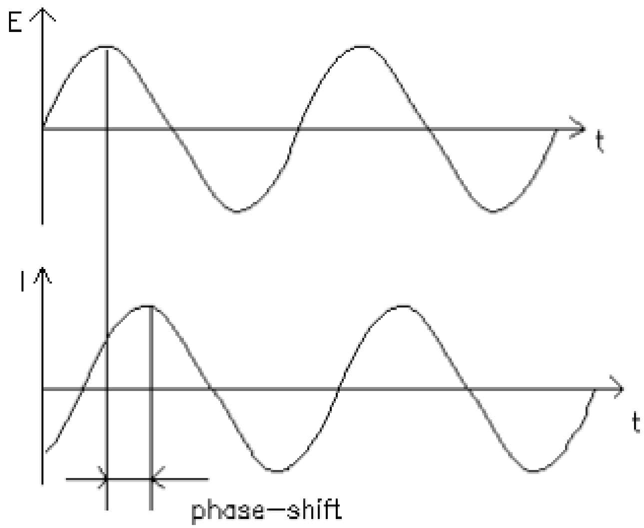

Figure 13 – Sinusoidal current response in a linear system.

$$V_t = V_0 \sin(\omega t) \qquad (4)$$

$$I_t = I_0 \sin(\omega t + \phi) \qquad (5)$$

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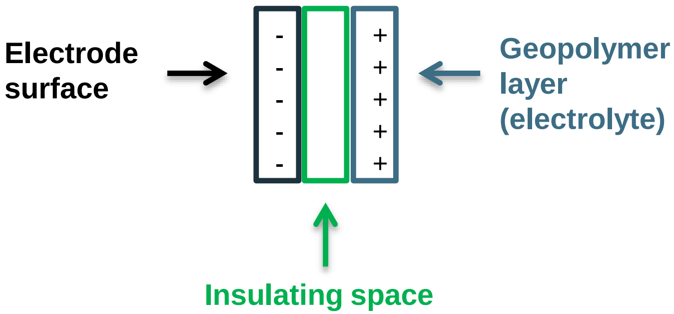
Insights

→ *EIS theory*

An electrical double layer exists on the interface between an electrode and its surrounding electrolyte. This double layer is formed as ions from the solution adsorb onto the electrode surface. The charged electrode is separated from the charged ions by an insulating space, often on the order of angstroms.
Charges separated by an insulator form a capacitor so a bare metal immersed in an electrolyte will behave like a capacitor.



The **resistance of an ionic solution** depends on:

- the ionic concentration;
- the type of ions;
- the temperature;
- the geometry of the area in which current is carried.

In a bounded area with area A, length l, the solution resistivity equal to ρ, and carrying a uniform current, the resistance is defined as:

$$R = \rho \frac{l}{A} \qquad (6)$$

Component	Current Vs.Voltage	Impedance
resistor	E= IR	Z = R
inductor	E = L di/dt	Z = jωL
capacitor	I = C dE/dt	Z = 1/jωC

Figure 14 – Common electrical elements of a circuit.

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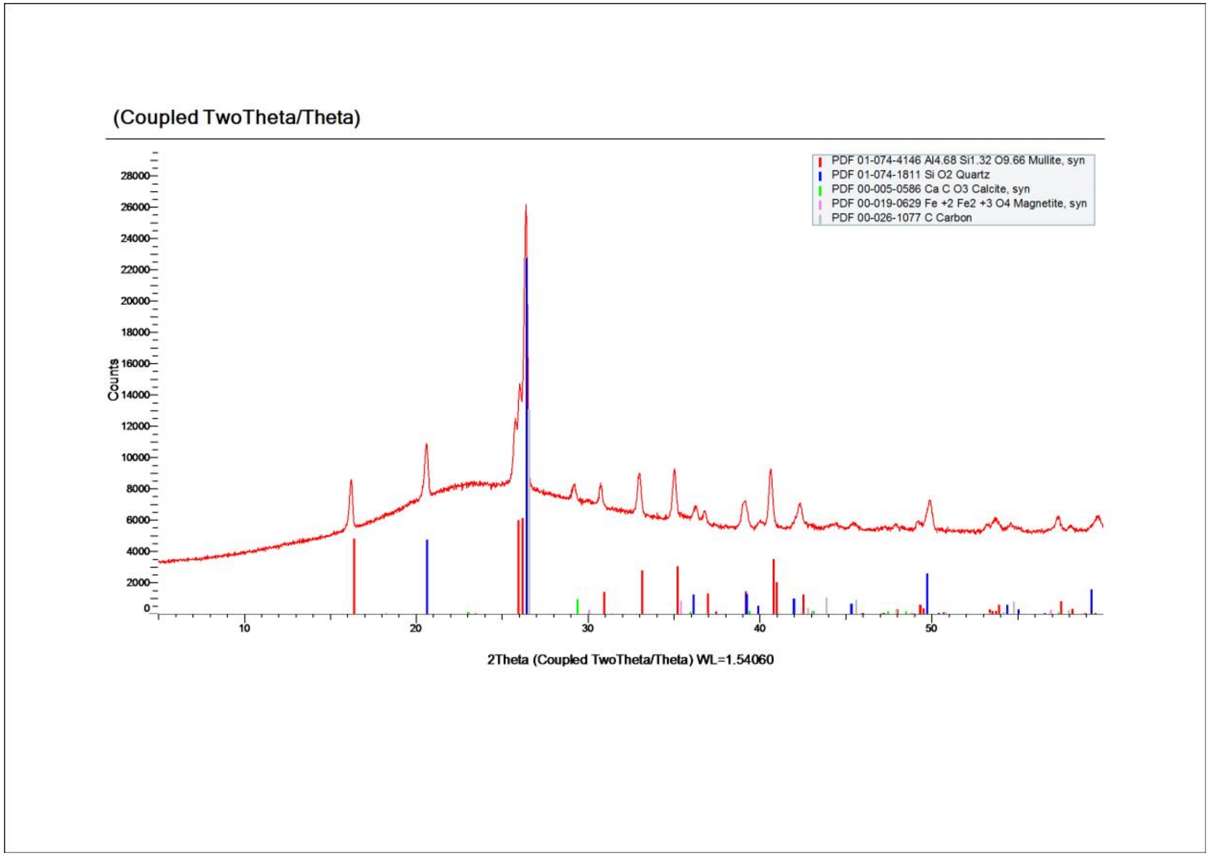
DISTINCTIVE

Insights

→ *XRD spectrum*



Sample of geopolymer put in concrete, cured in the environmental chamber at 40 °C.

	Class F %	Class C Lignite based (%)
SiO_2	47.2 to 54	18 to 24.8
Al_2O_3	27.7 to 34.9	12.1 to 14.9
Fe_2O_3	3.6 to 11.5	6.3 to 7.8
CaO	1.3 to 4.1	13.9 to 49
Free lime content	0.1	18 to 25
MgO	1.4 to 2.5	1.9 to 2.8
SO_3	0.1 to 0.9	5.5 to 9.1
Na_2O	0.2 to 1.6	0.5 to 2
K_2O	0.7 to 5.7	1 to 3

Figure 15 – Chemical composition for fly ashes.

Phase	Mean %	Min. (%)	Max (%)
Amorphous	59	30	78
Mullite	19	7	46
Haematite	7	2	15
Magnetite	6	2	10
Quartz	5	1	12
Carbon	4	1	13

Figure 16 – Phase composition of UK fly ashes.

Insights

→ *Novel solution proposed*

- *New sensing system*

Intelligent monitoring:

- Automated measurement of
  - the status of a structure;
  - the components of a structure.

→

- surface mounted sensors
- embedded sensors

↓

‘Smart’ structures, materials (sensors)

←

Their status changes in response to environmental conditions.

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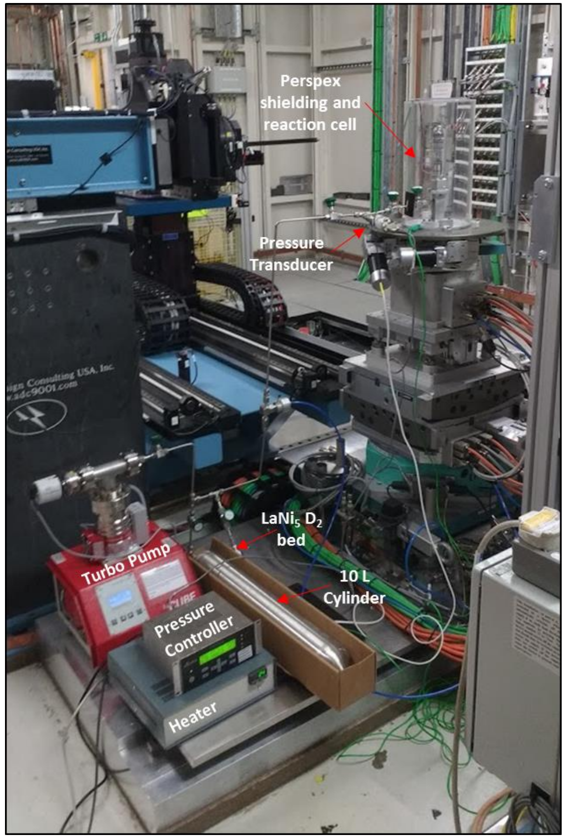
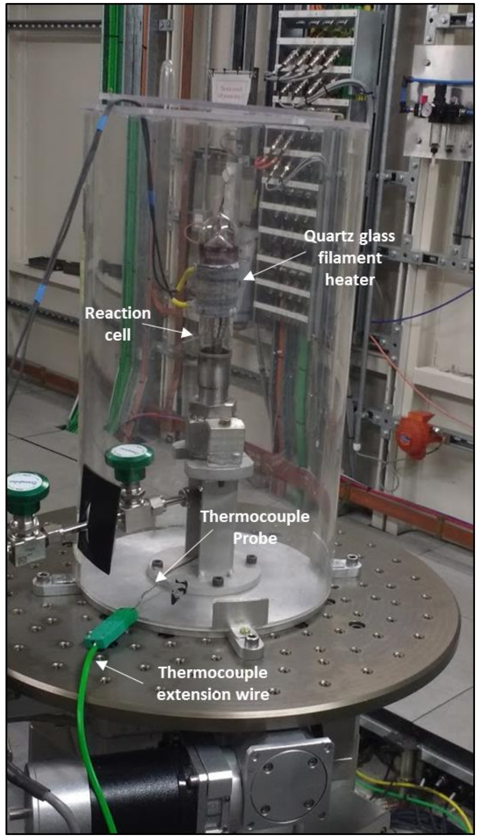
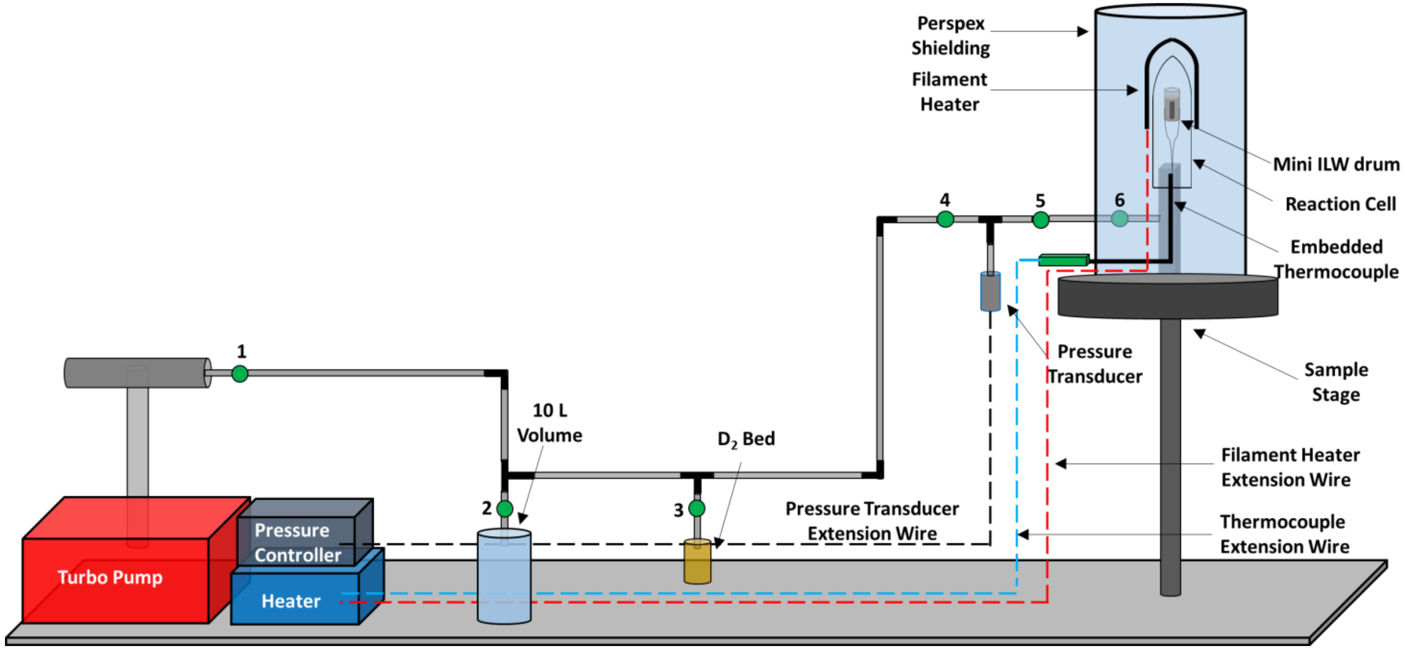
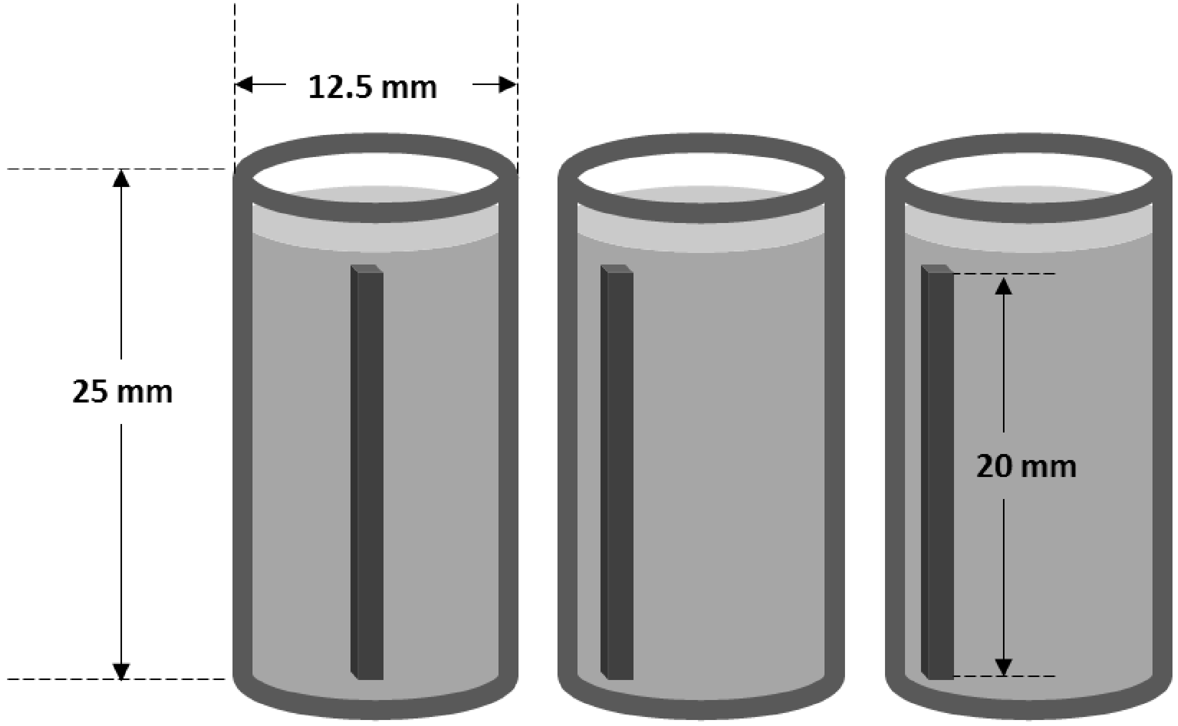
Online synchrotron–based uranium corrosion experiments

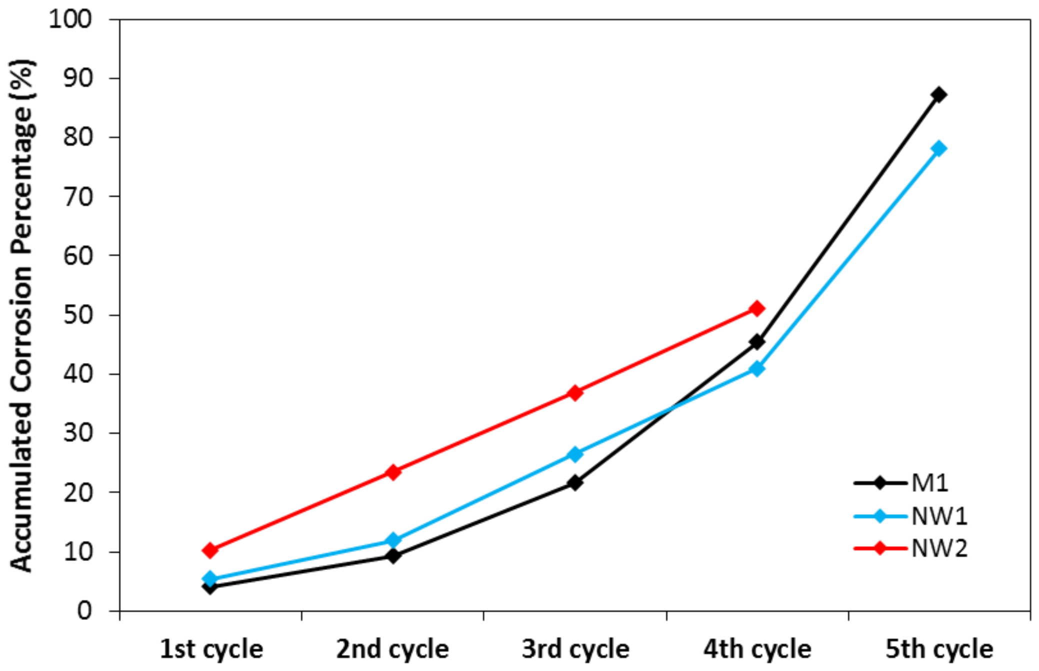






Online synchrotron–based uranium corrosion experiments



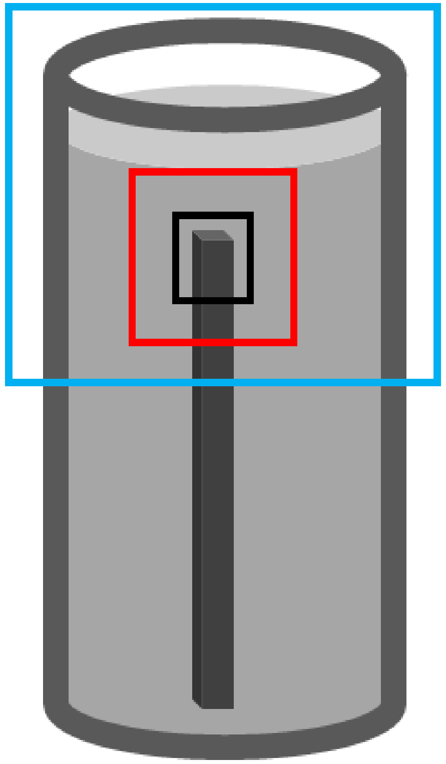


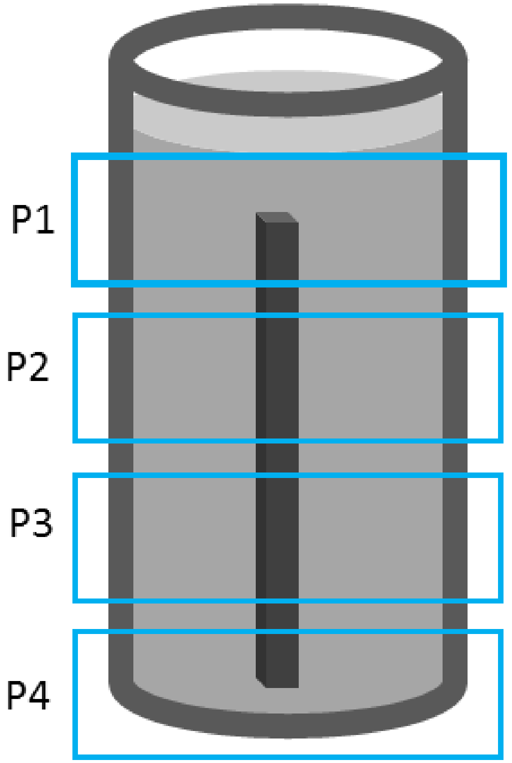
Online synchrotron–based uranium corrosion experiments

Camera 2 – 20.3 mm x 17.1 mm, 7.9 µm/pixel

Camera 3 – 8.3 mm x 7.0 mm, 3.2 µm/pixel

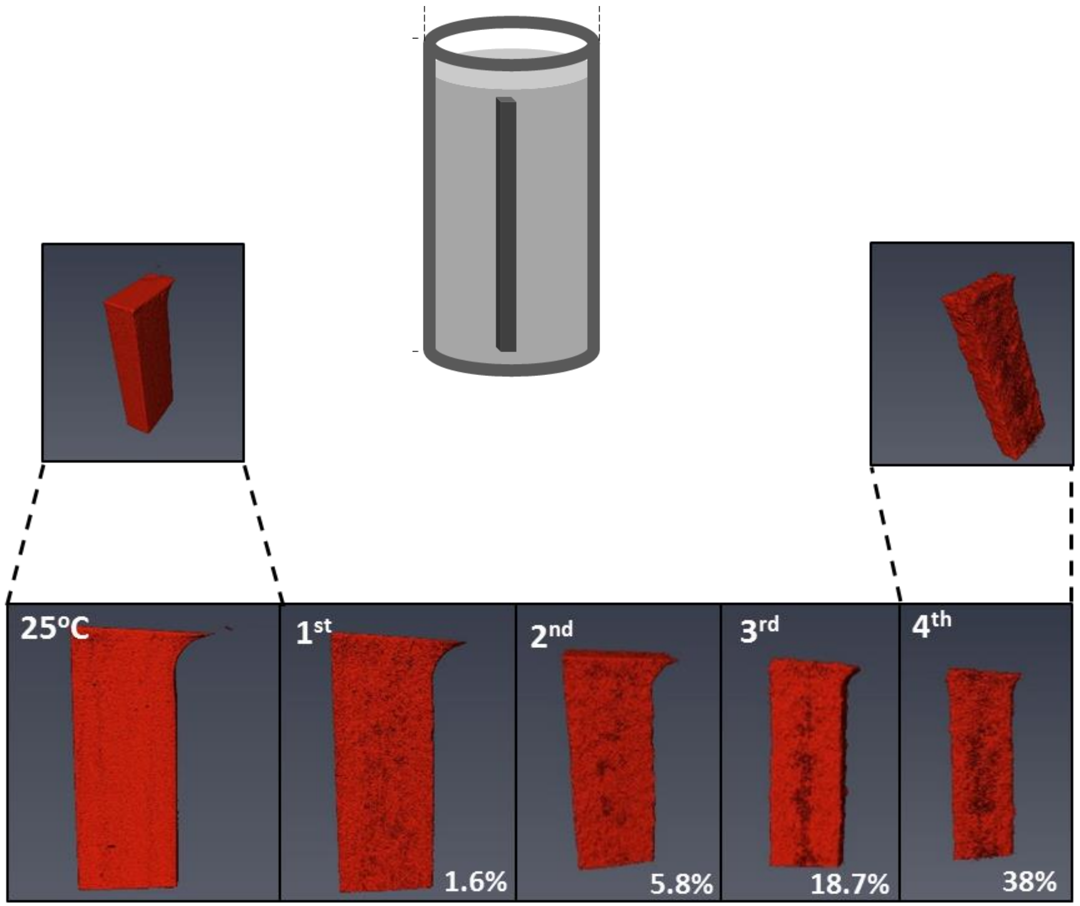
Camera 4 – 3.3 mm x 2.8 mm, 1.3 µm/pixel





Profile of corroding uranium – Camera 4

Sample M1



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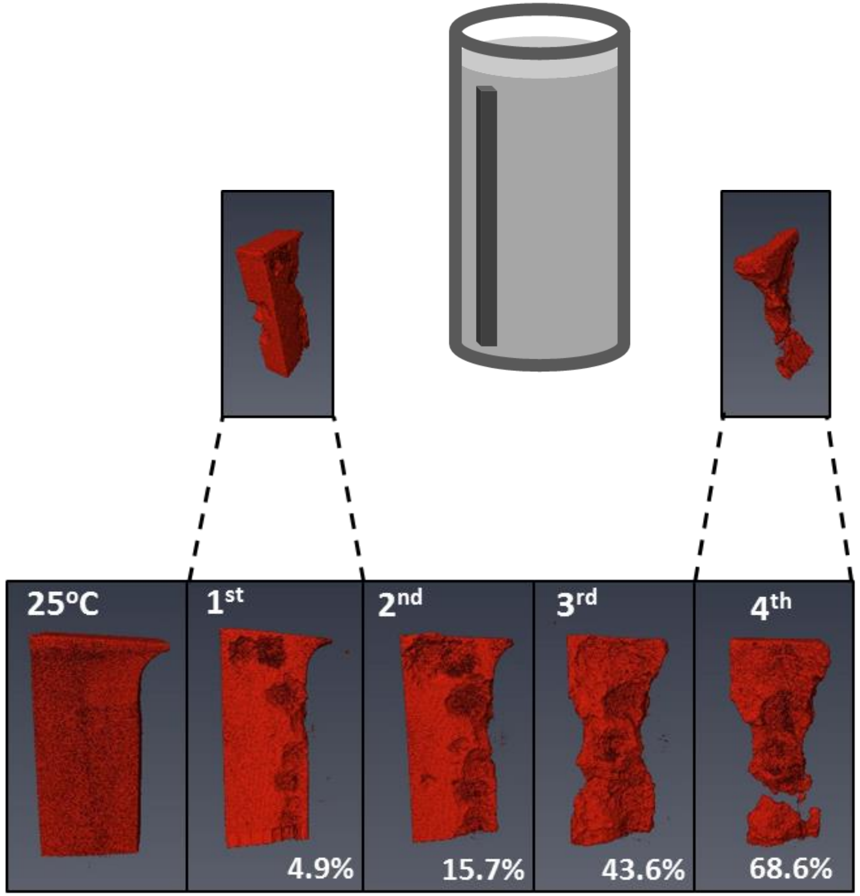
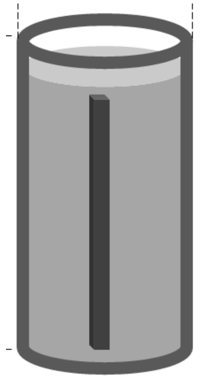
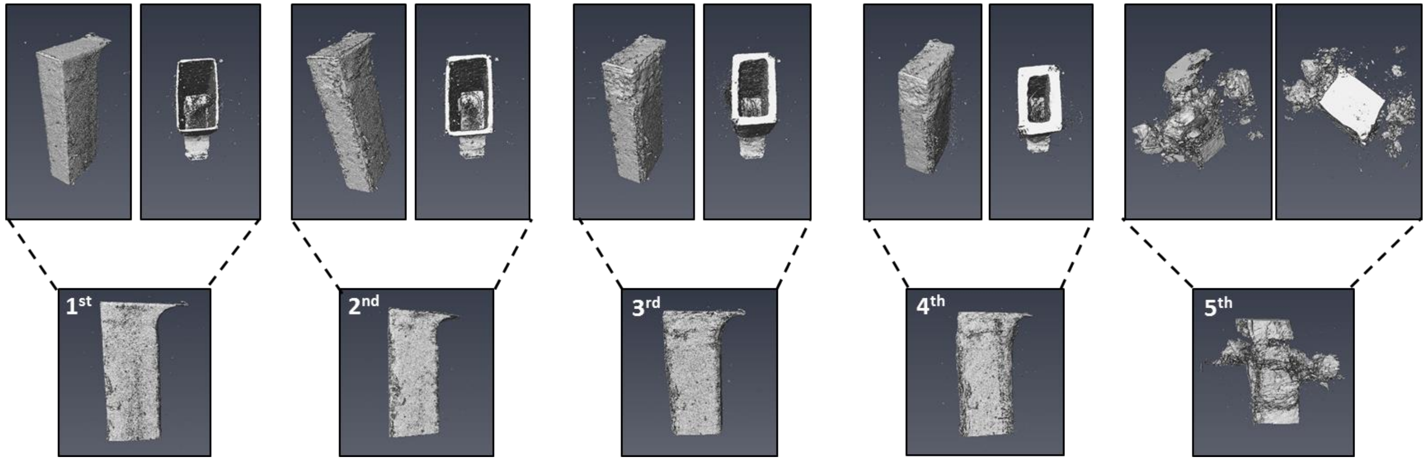


Online synchrotron–based uranium corrosion experiments

Profile of corrosion products – Camera 4

Sample M1





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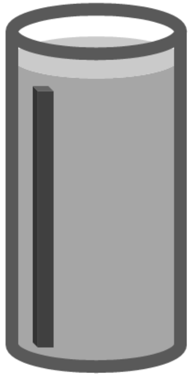
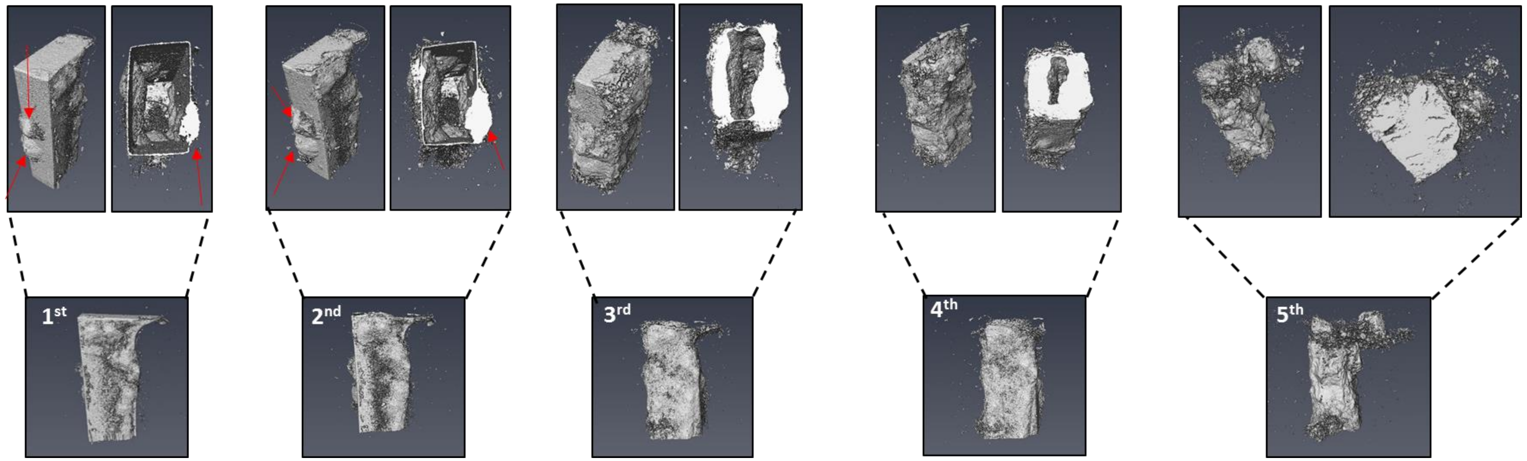
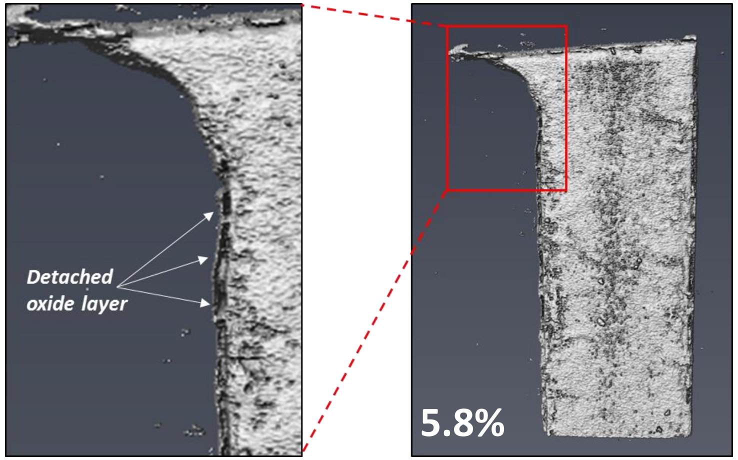




Online synchrotron–based uranium corrosion experiments

Sample M1



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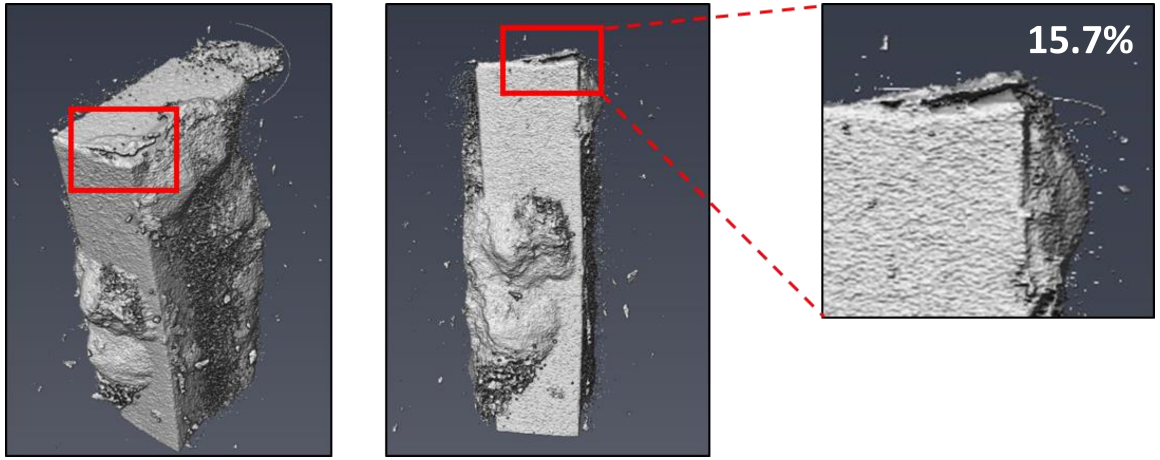

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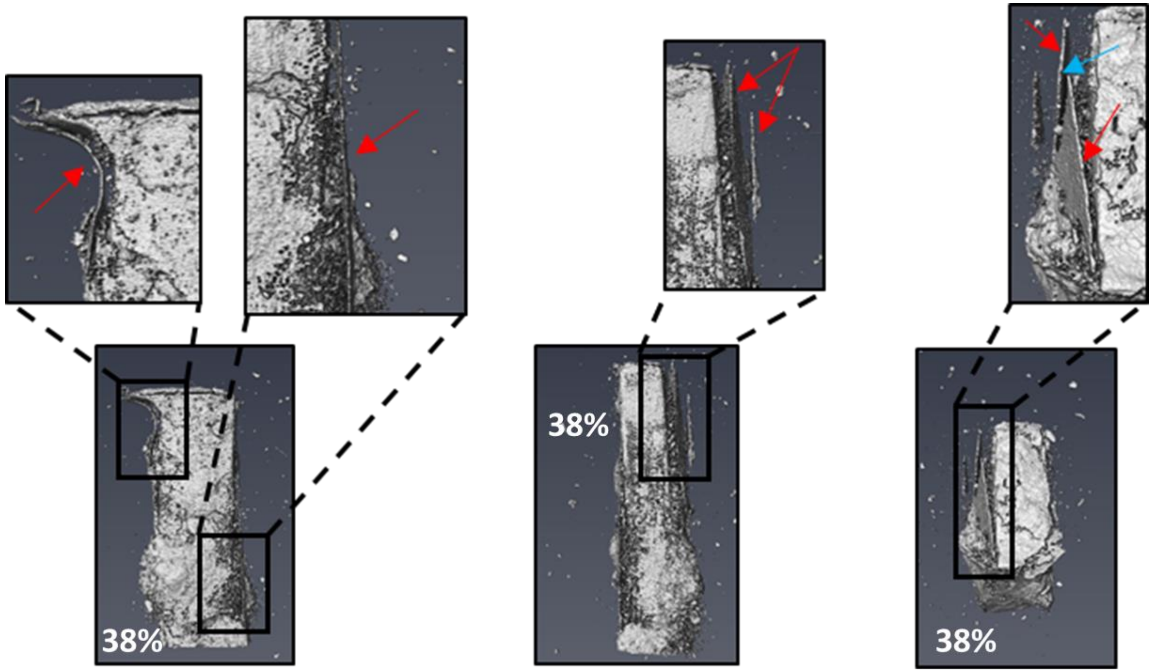
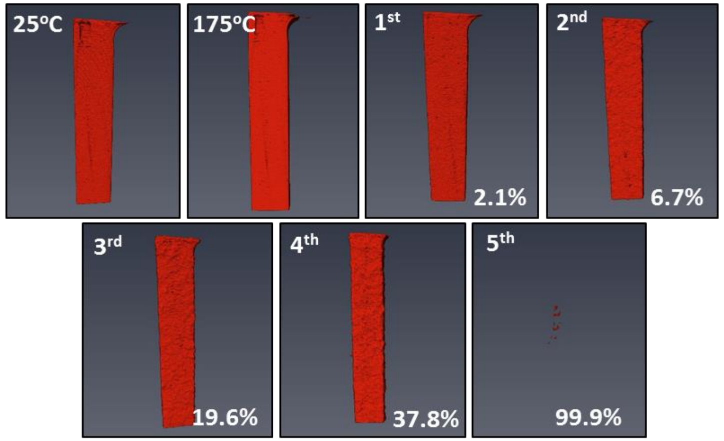


Online synchrotron–based uranium corrosion experiments

Sample M1



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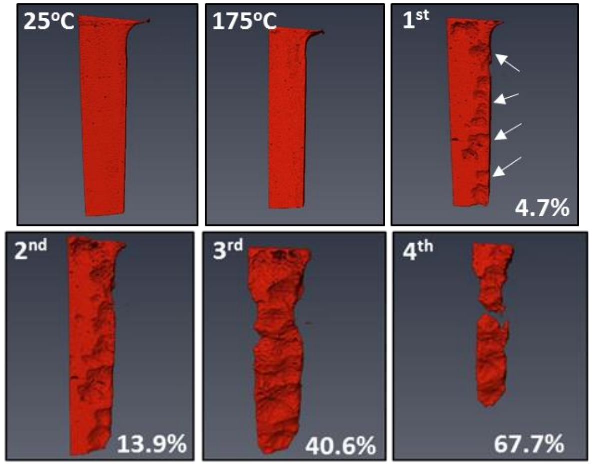

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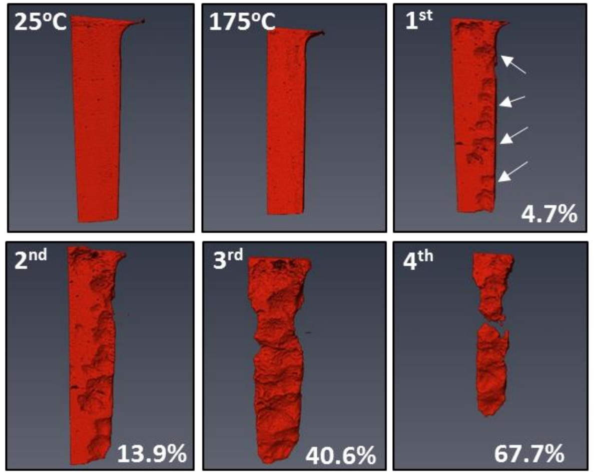
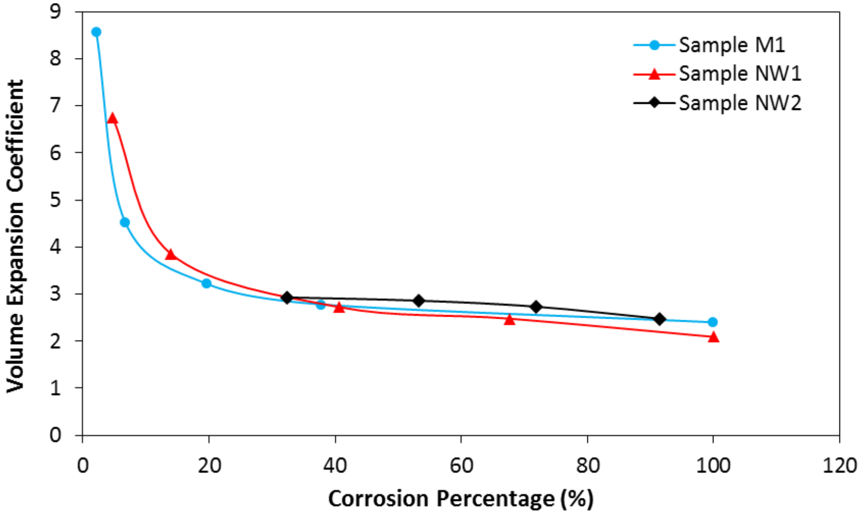
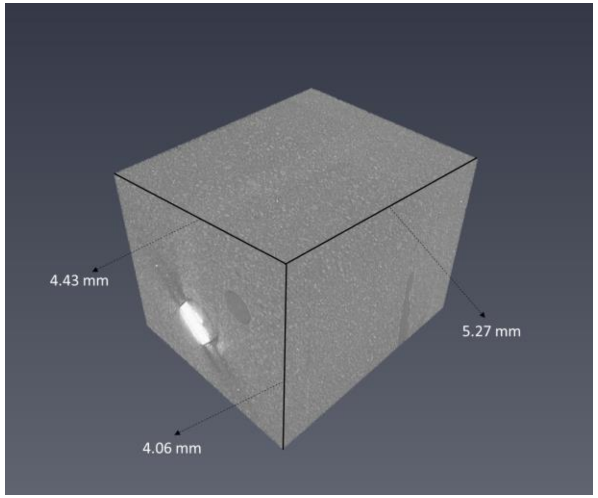
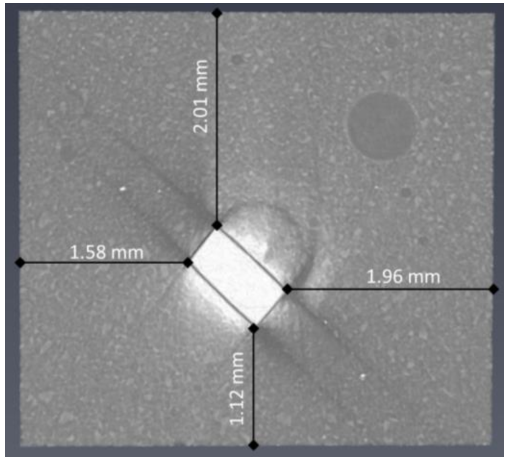




Online synchrotron–based uranium corrosion experiments

Sample M1





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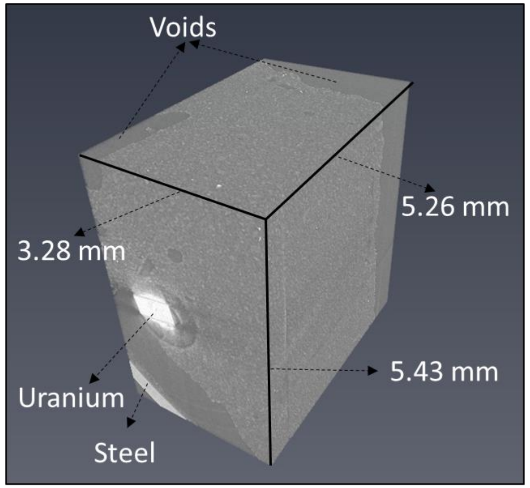

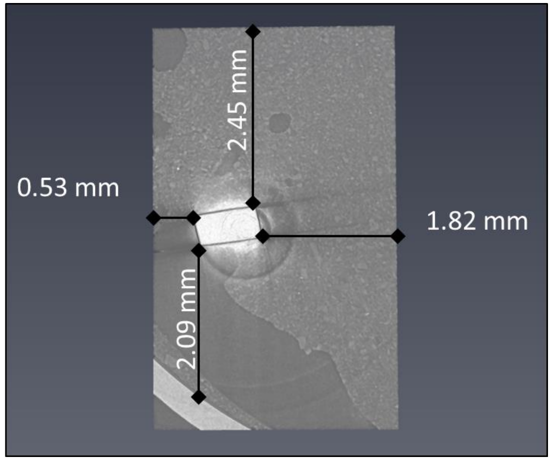

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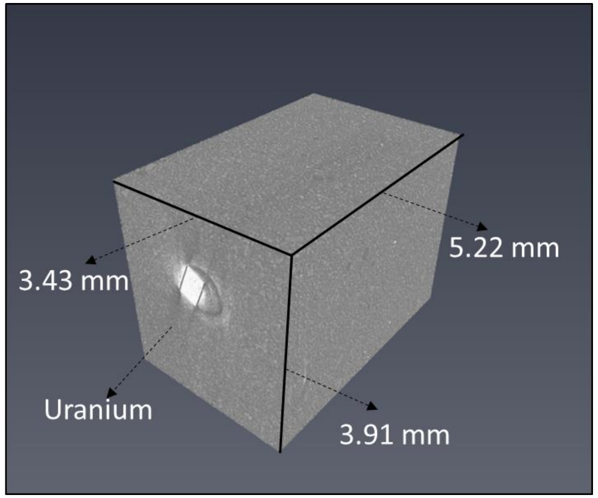

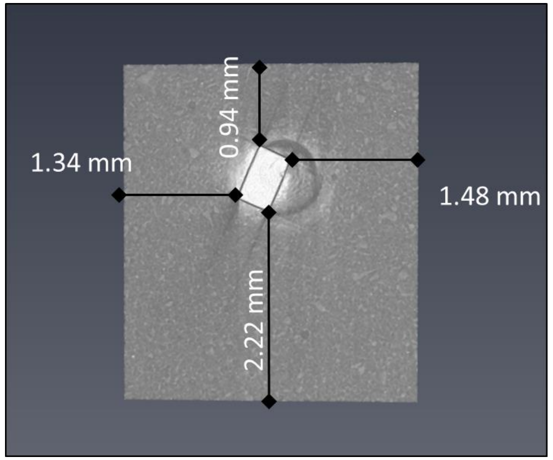

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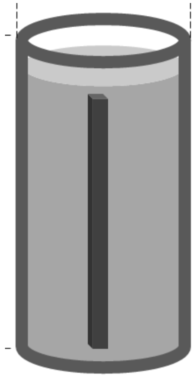
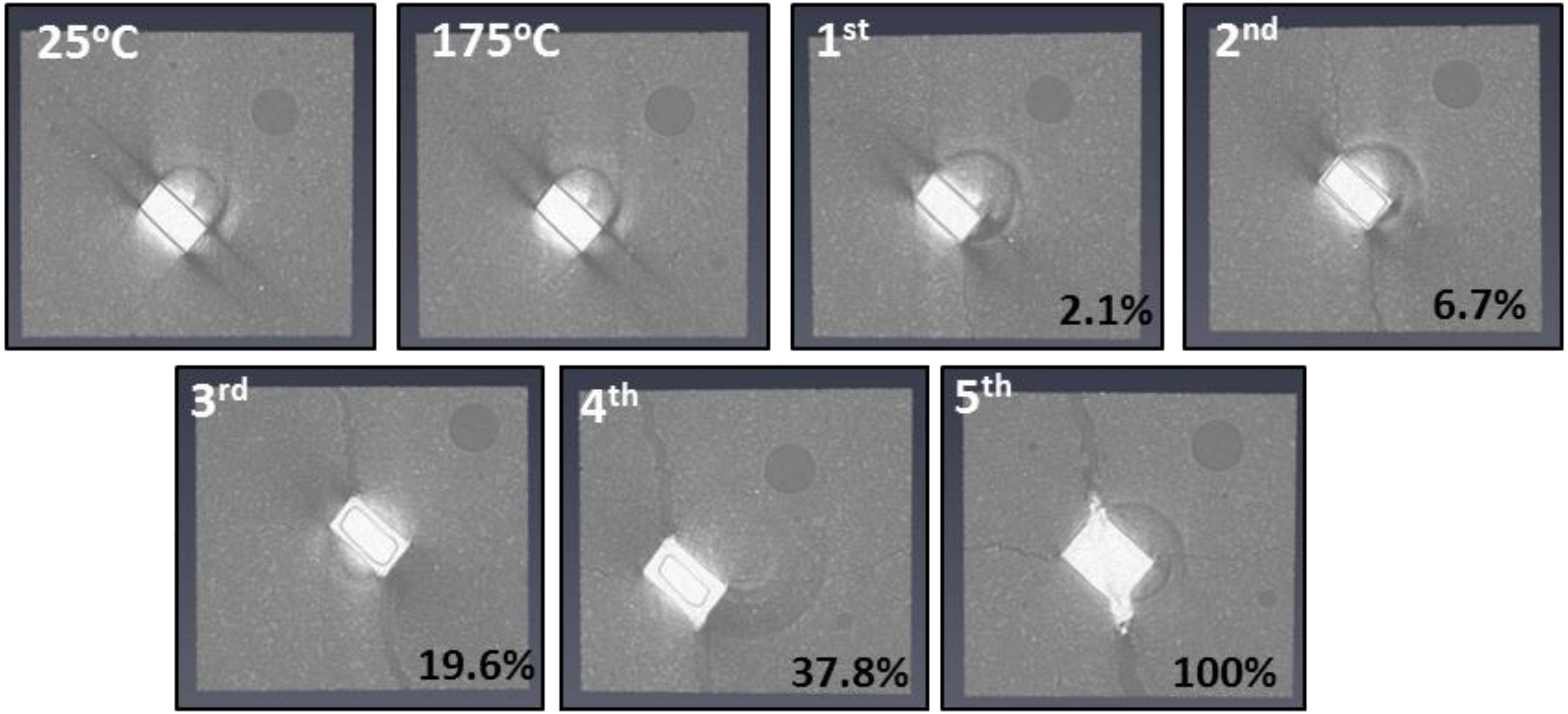
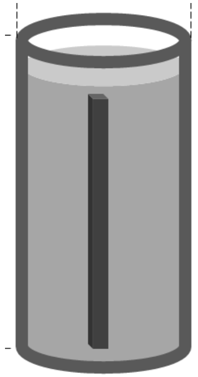




Online synchrotron–based uranium corrosion experiments

Sample M1

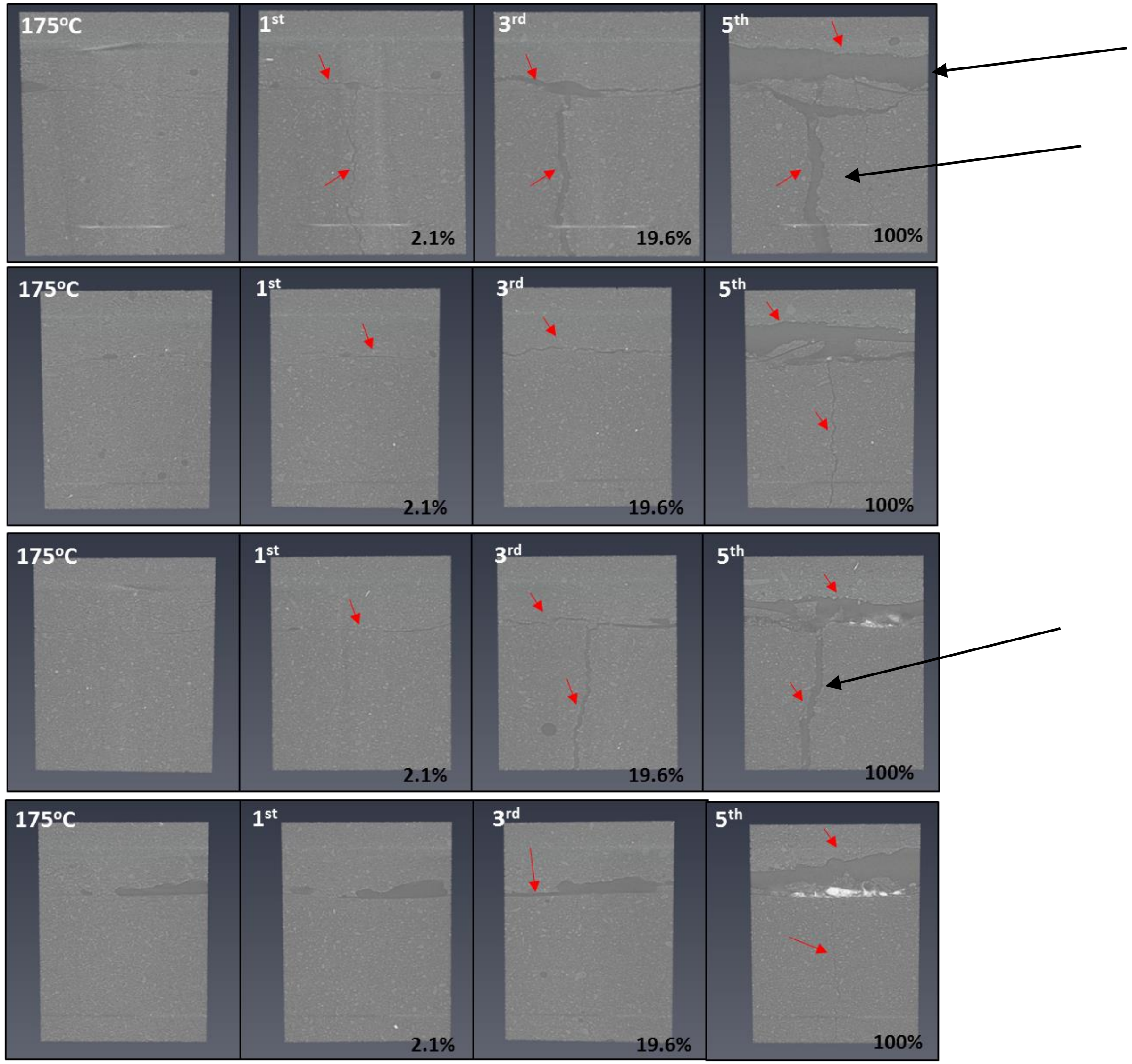


Side A

Side B

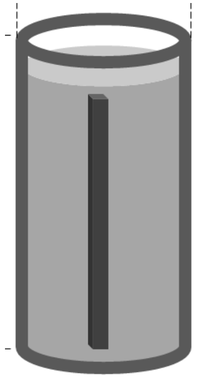
Side C

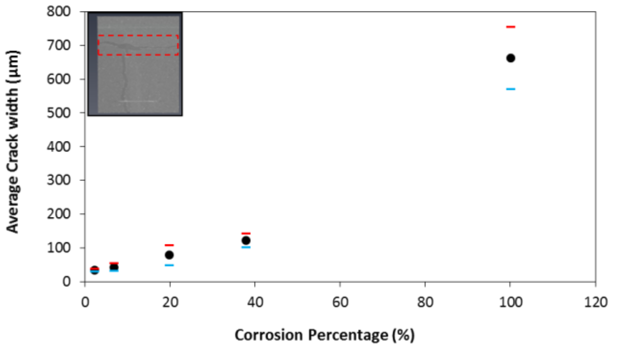
Side D

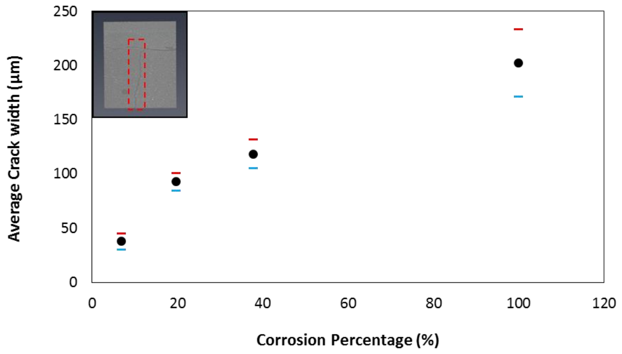


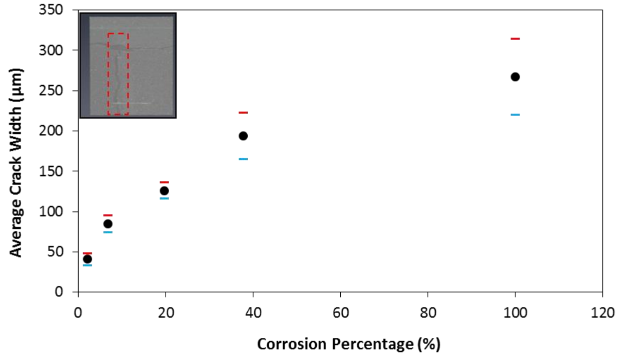
Online synchrotron–based uranium corrosion experiments

Sample M1

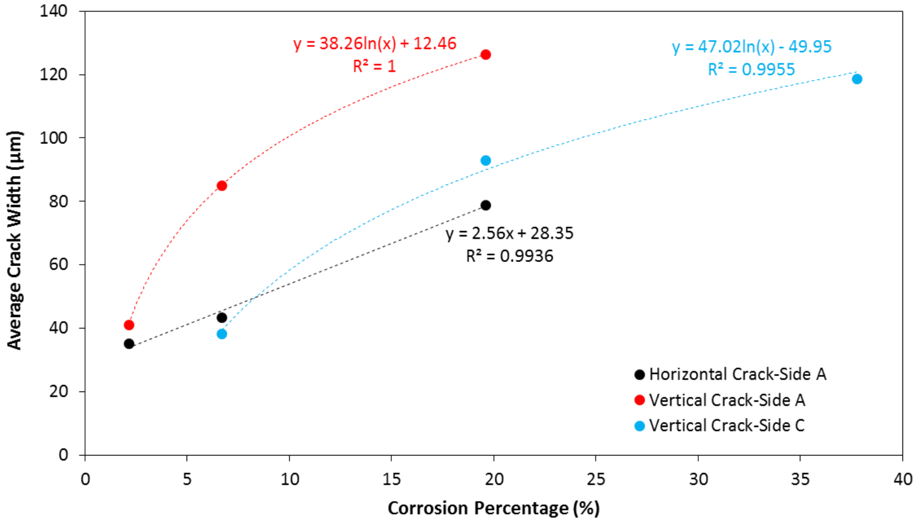






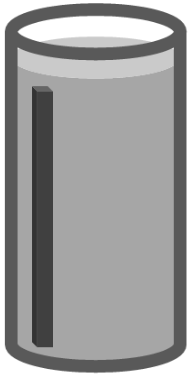


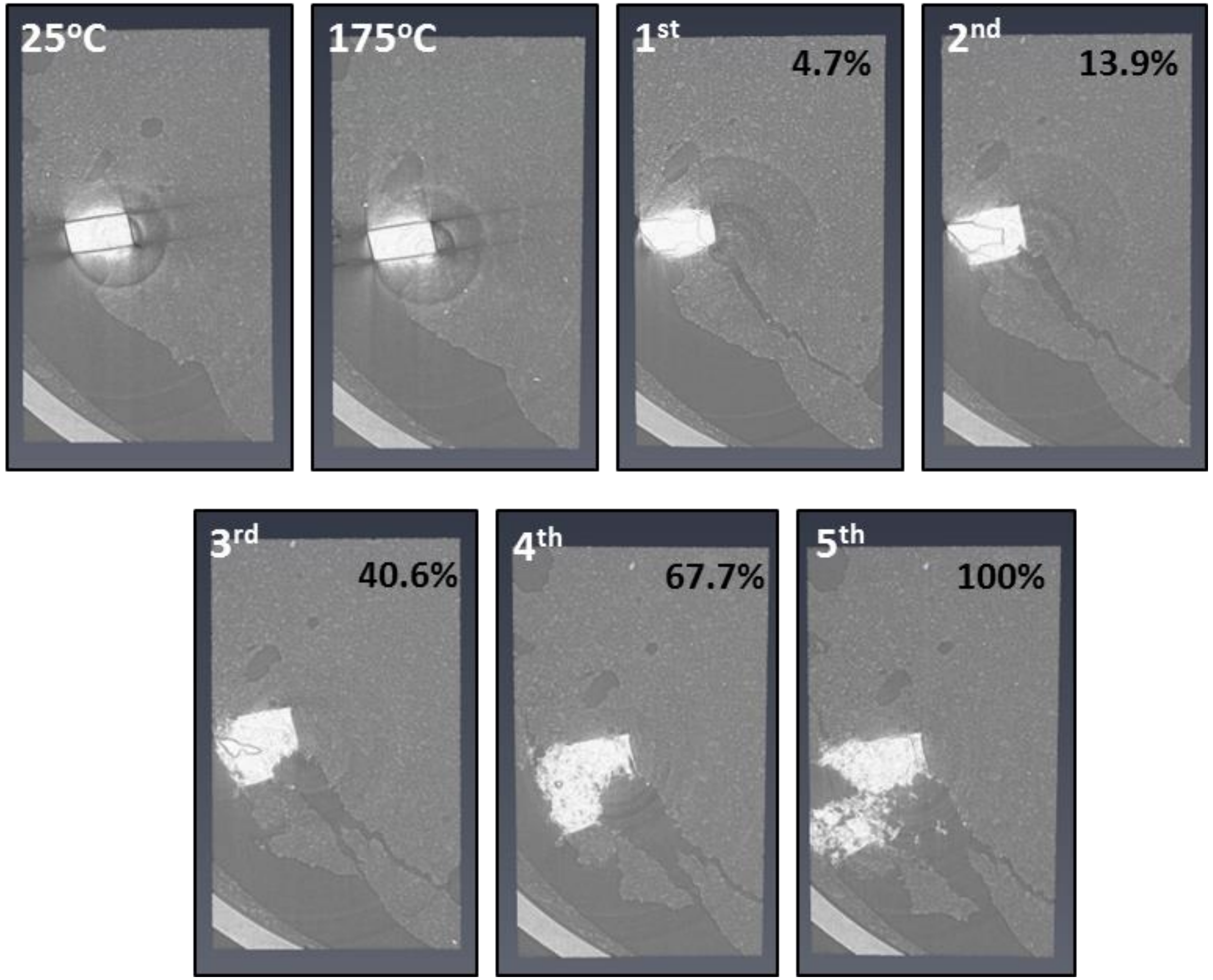
Grout Fracture Initiation: 0.57%



Online synchrotron–based uranium corrosion experiments

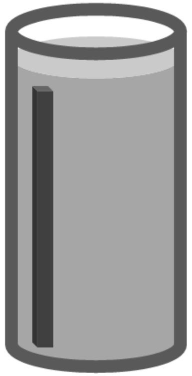
Sample NW1

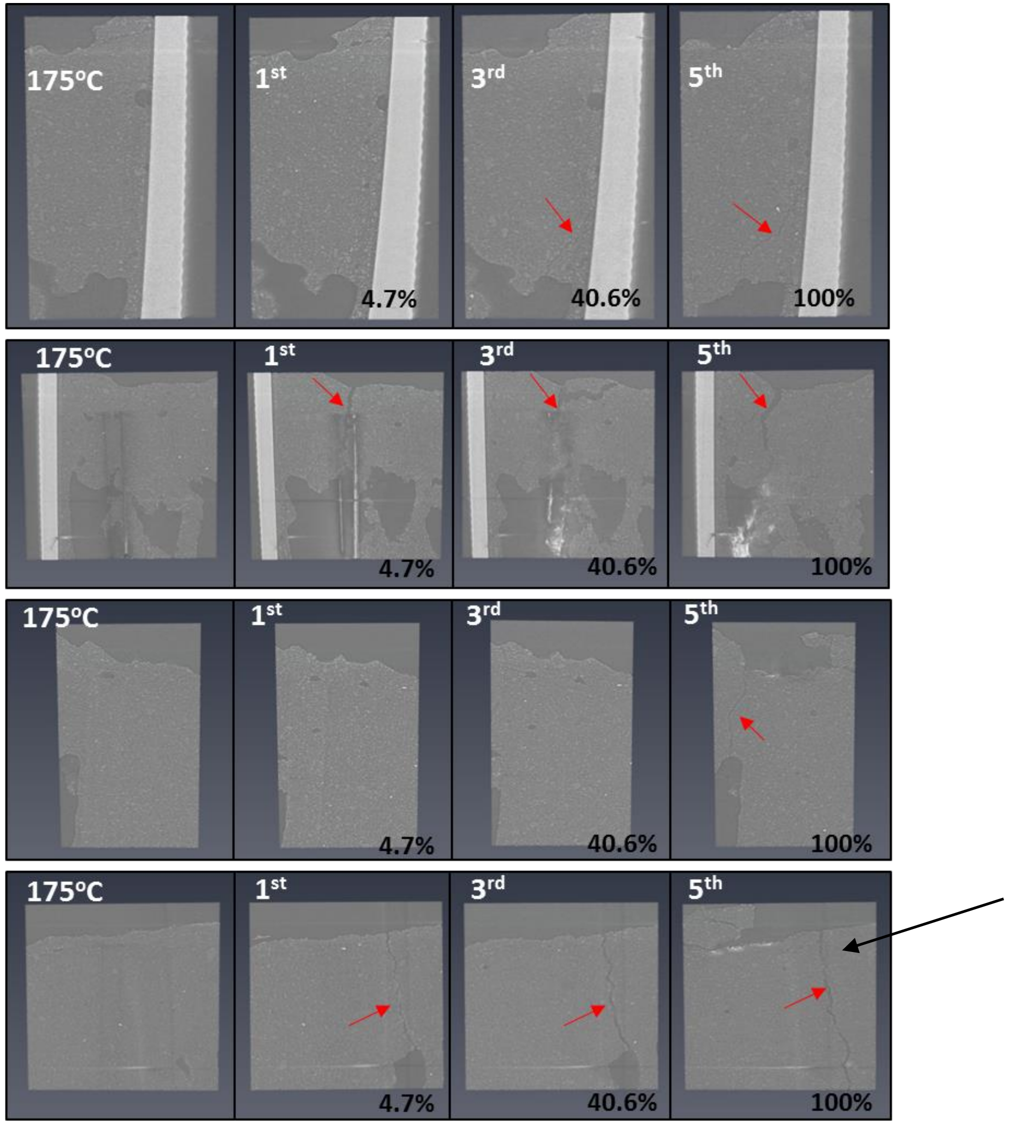




Online synchrotron–based uranium corrosion experiments

Sample NW1





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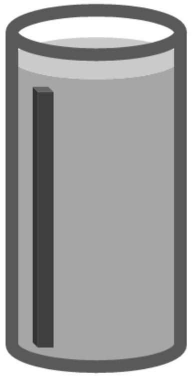
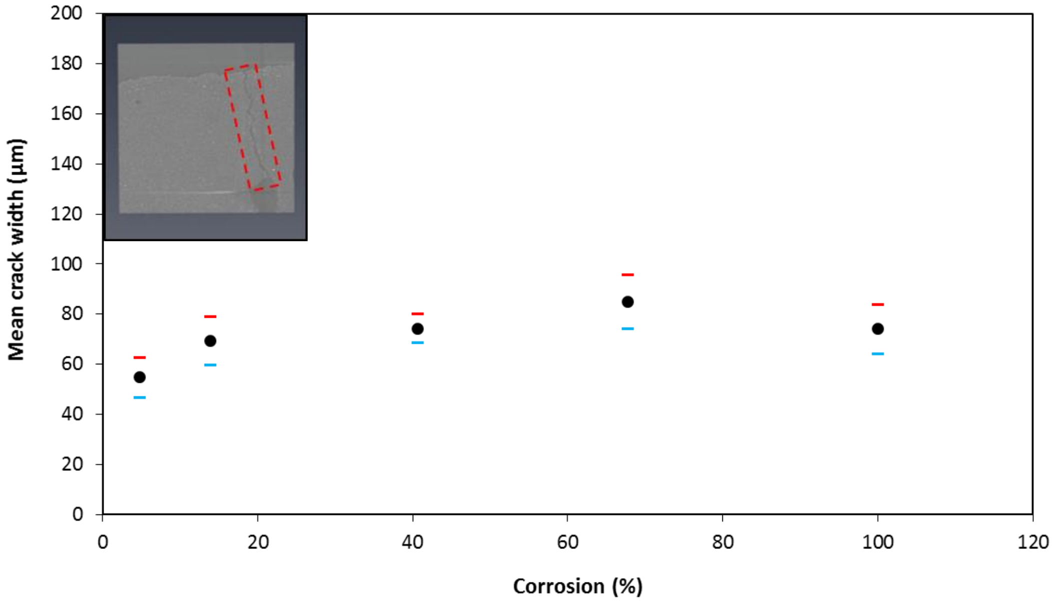
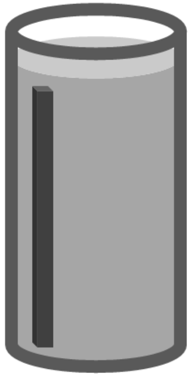
Sample NW1

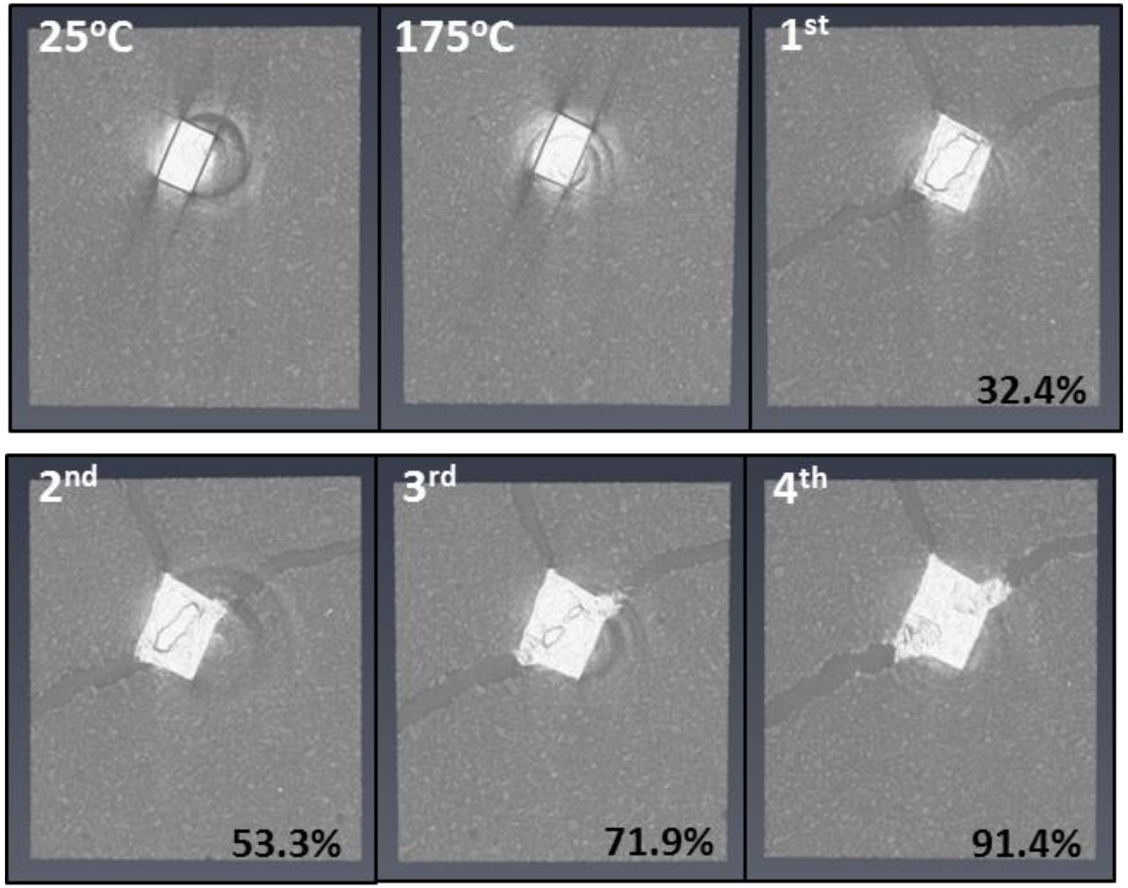




Online synchrotron–based uranium corrosion experiments

Sample NW2





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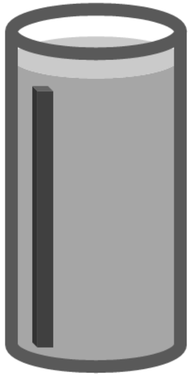
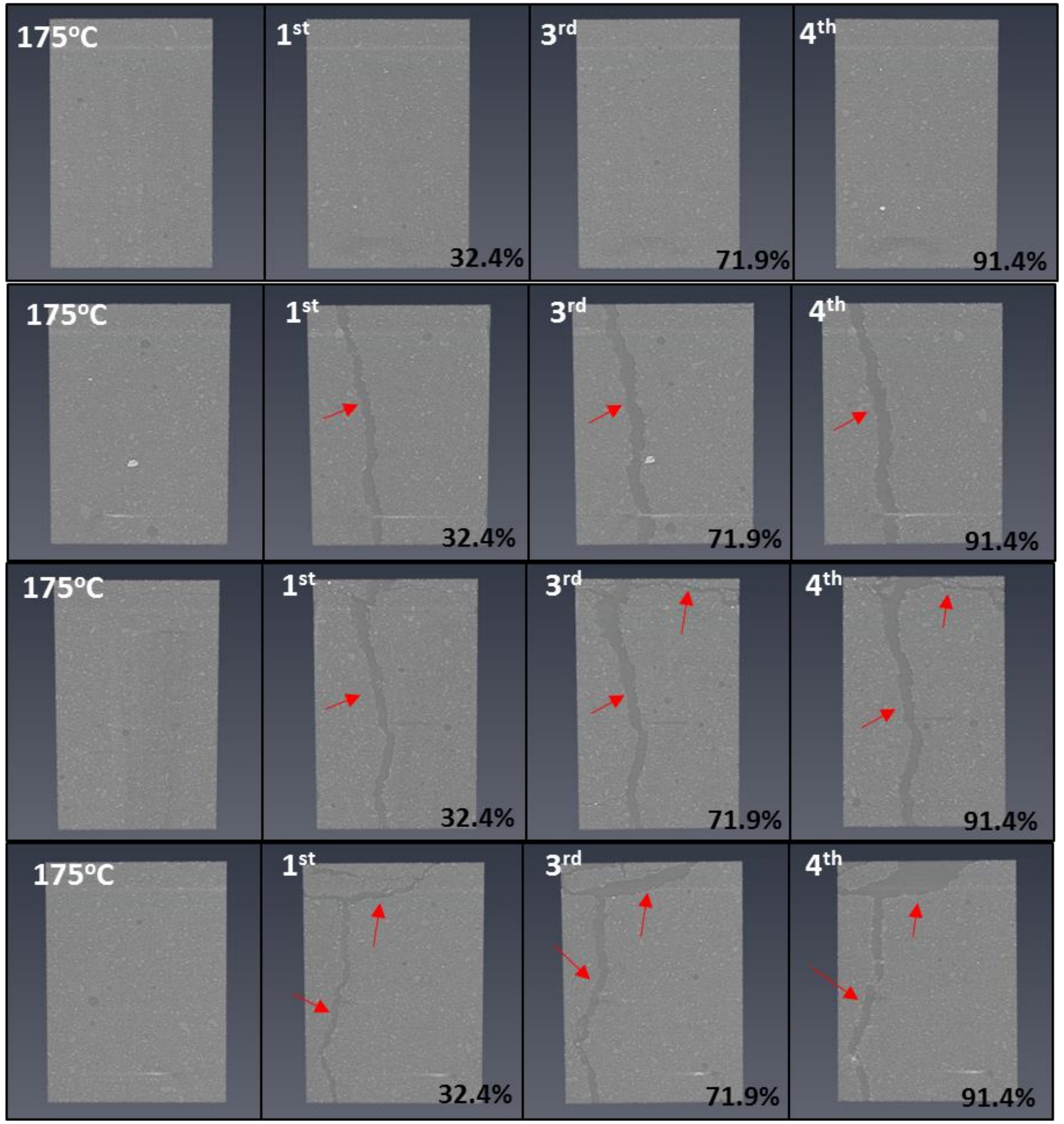
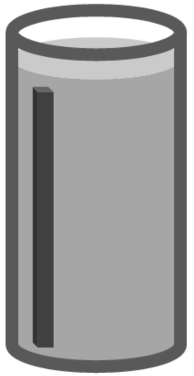
Sample NW2

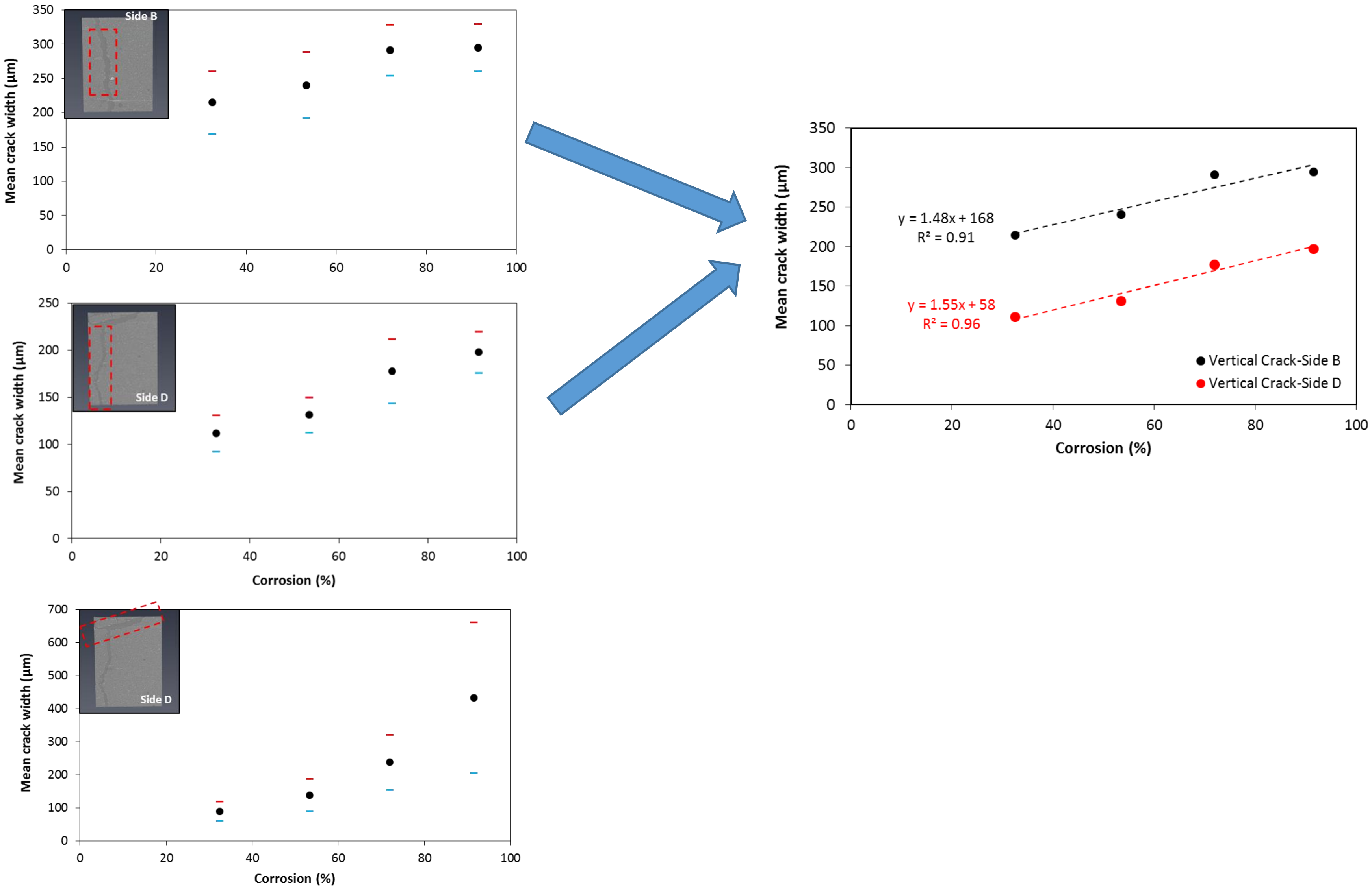




Online synchrotron–based uranium corrosion experiments

Sample NW2





The effects of colloidal silica based grouts on Sr and Cs speciation – present and future research

Pieter Bots[1], Rebecca Lunn[1], Grainne El Mountassir[1], Matteo Pedrotti[1], Timothy Payne[2] and Joanna Renshaw[1]

[1] Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, G1 1XJ, UK
[2] Australian Nuclear Science and Technology Organisation, Kirrawee DC, New South Wales 2232, Australia

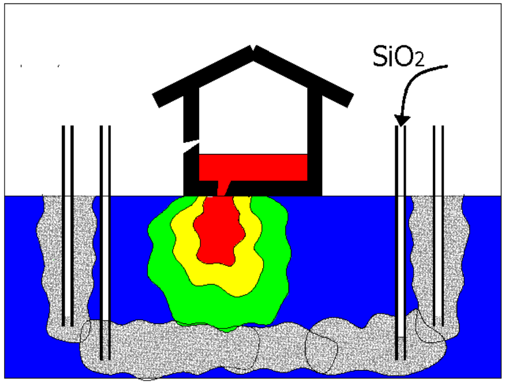
DISTINCTIVE Annual Meeting
5th/6th April 2017
York

Containment of legacy wastes

- Around the world sites exist with radioactive wastes such as
  - Sellafield (UK)
  - Hanford (USA)
  - Little Forest Legacy Site (Australia)
- For long term management radionuclide migration through the subsurface need to be inhibited
- Grouts have large potential for applications in the long term management of such legacy sites
  - Such grouts need to decrease the potential for radionuclide migration

GROUT APPLICATIONS

- Vertical and horizontal hydraulic barriers
- Waste encapsulation
- Ground sealing
- Mechanical improvement
- Combinations



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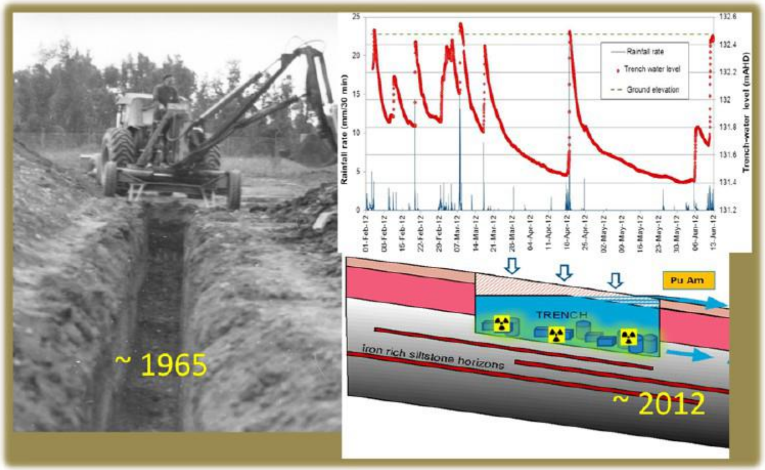
The Little Forest Legacy Site (LFLS)

- Operational for low level waste disposal: 1960-1968
- Unlined trenches covered with ~1m soil
- Low levels of radioactivity found in surface runoff, soil and vegetation



Payne et al. *Environmental Science & Technology* (2013) **47** 13284-13293

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Strontium and Caesium

- Caesium-137 and strontium-90 are short lived fission products
- Have been detected in soil, surface runoff and vegetation

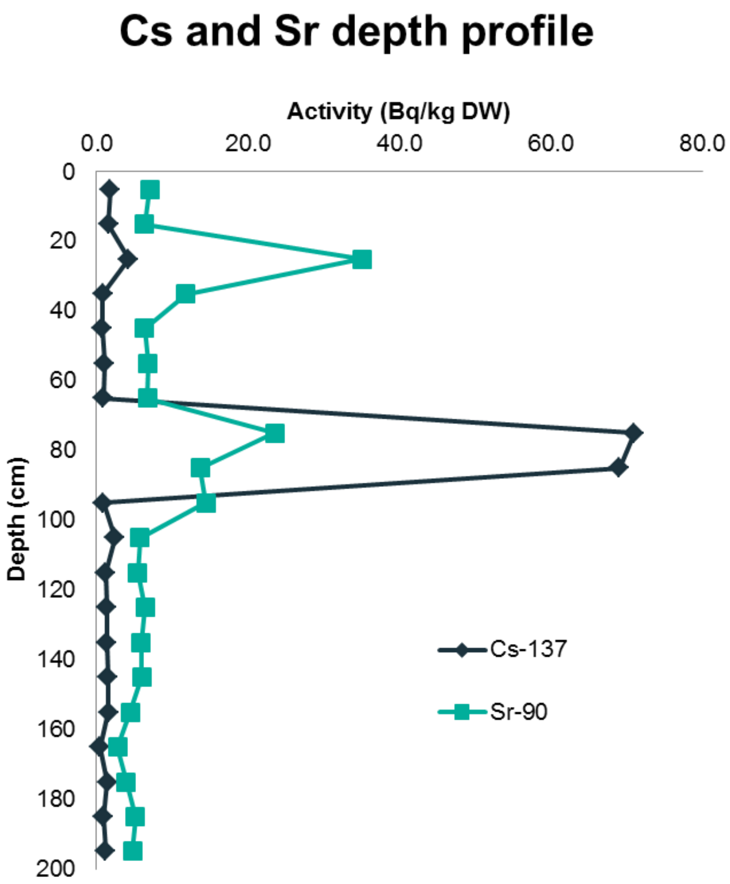
Cs and Sr geochemistry

Cs

- Cs^+ interacts with illite and other clays
  - into the hydrated interlayer
  - surface complexes on basal plane

Sr

- Sr^{2+} adsorption onto metal oxides and silicates
- $SrCO_3$ precipitates under alkaline conditions



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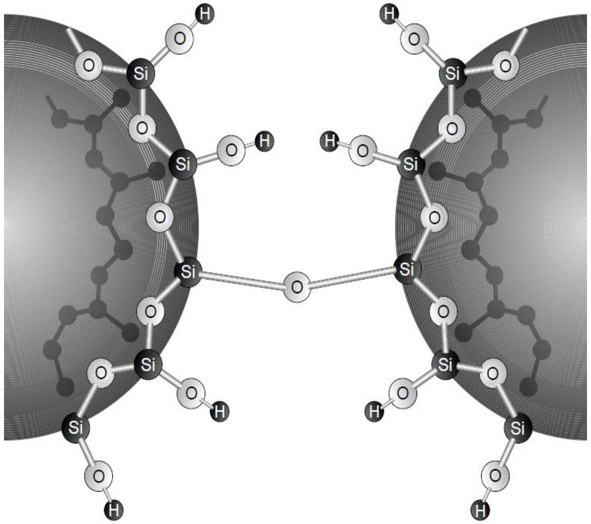
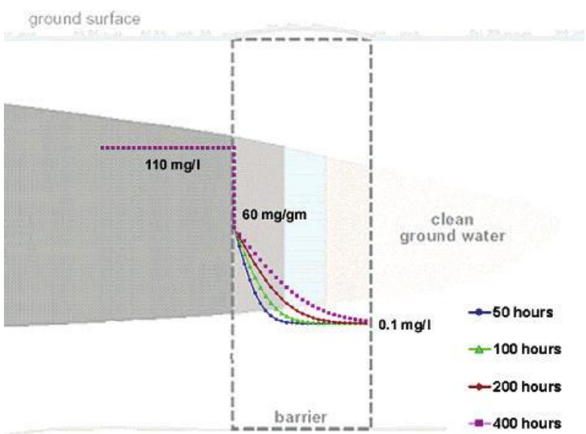
Colloidal Silica Grouts

- Silica sol:
  - 2 – 150 nm SiO_2 nanoparticles; 15 – 40 wt%
- Gelling induced by accelerant:
  - NaCl, $CaCl_2$, KCl
- Grouted colloidal silica gel creates hydraulic barrier
- Limited immobilization of anions such as CrO_4^{2-}
- How do these grouts affect the geochemistry and mobility of radionuclides:
  - Cs-137, Sr-90, Uranium etc.



Moridis et al. (1995) Containment Technology Workshop.



Tantemsapya and Meegoda *Environmental Science and Technology* (2004) **38** 3950-3957

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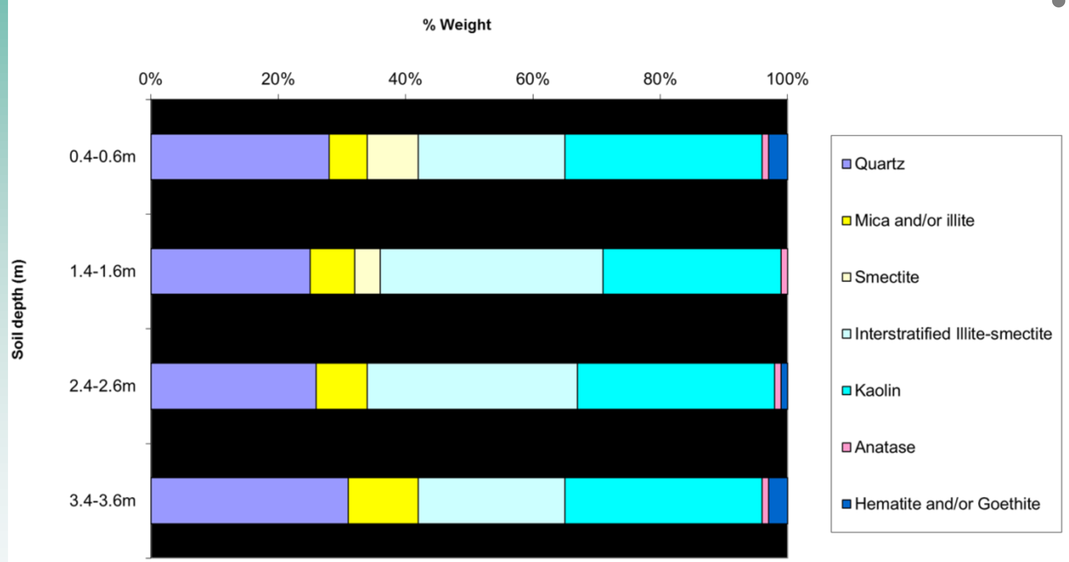
Adsorption Experiments

- Soil and waste components based on XRD and historical waste records:
  - **Soil:** Illite/smectite, Kaolinite, Anatase (TiO_2), Goethite (FeOOH), Quartz
  - **Waste:** Cellulose, Magnetite (Fe_3O_4), Gibbsite ($Al(OH)_3$), PVC
- Geochemistry (to represent the groundwater at LFLS):
  - 10 mM NaCl; pH 4 – 8



- Procedure:
  - Equilibration of 10g/l with solutions until pH stable
  - Spiking the experiment with Sr, Cs or Sr and Cs
  - After 48h, solutions were sampled and analysed by IC for Cs^+ and Sr^{2+}

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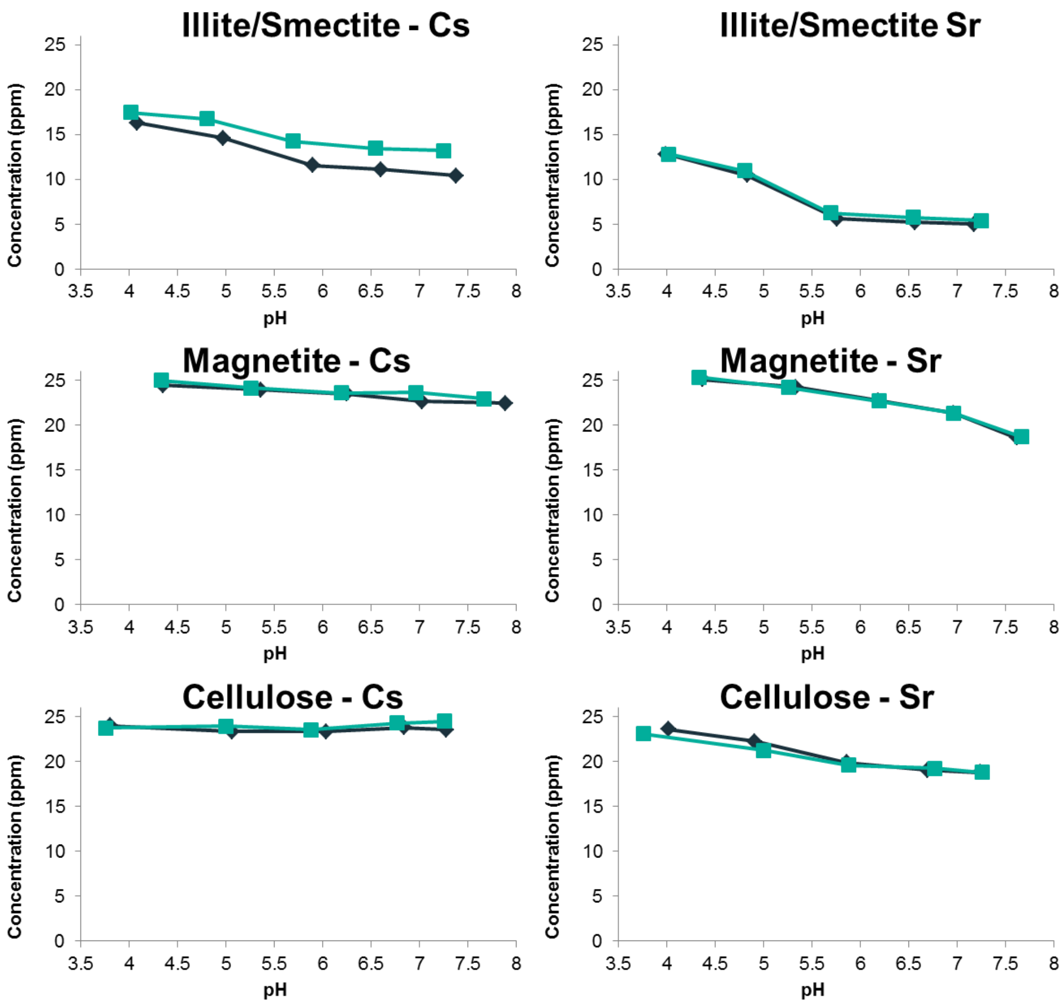
DISTINCTIVE

Cs and Sr adsorption

- Neither Sr nor Cs adsorbed to PVC, goethite, gibbsite or quartz
- Strontium:
  - Illite/smectite > Anatase > Kaolinite = Magnetite = Cellulose
- Cesium:
  - Illite/smectite > Kaolinite > Anatase = Magnetite ≥ Cellulose
- More Sr adsorbed than Cs
- Decreased Cs adsorption in the presence of Sr



Concentration of Cs and Sr after 48h equilibration. Dark symbols and lines: Cs or Sr; light symbols and lines: Cs and Sr

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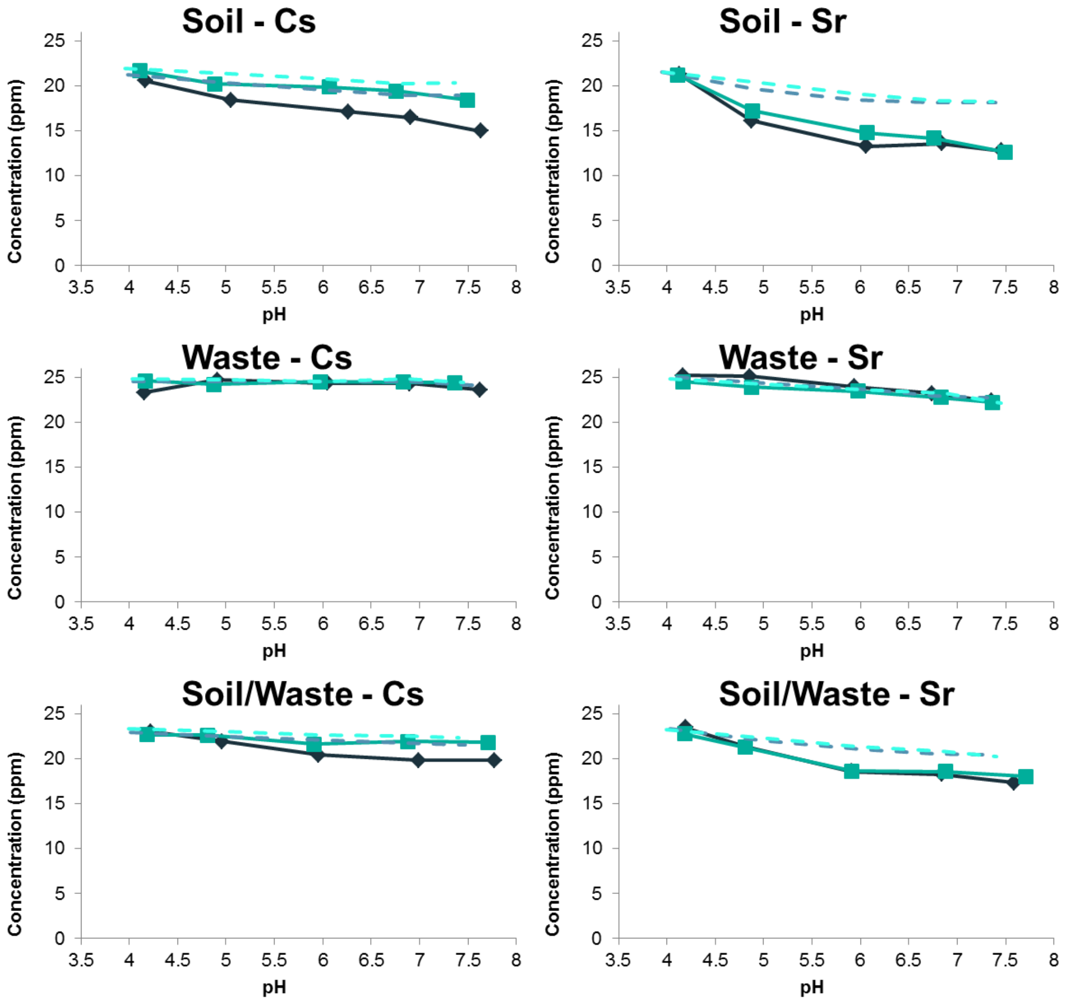
Cs and Sr in soil and wastes

- Adsorption of Sr and Cs to soil
- Limited Cs adsorption to waste
- Weighted averages (dashed lines) did not simulate the experiments
  - No easy prediction of behaviour of Sr and Cs at LFLS
  - No natural organic matter in experiments



Concentration of Cs and Sr after 48h equilibration. Dark symbols and lines: Cs or Sr; light symbols and lines: Cs and Sr

Future work 1

- Adsorption and Desorption
- Adsorption of uranium(VI)
- Effects of Cs and Sr on the adsorption of U(VI) (and vice versa)
- Desorption of Sr, Cs and U(VI) from selected solids and mixtures
- Desorption of Sr, Cs and U(VI) from soil and waste mixtures embedded in colloidal silica grout

Future work 1

- Adsorption experiments performed
    - Simulated soil
    - pH 7
- After 48h of equilibration:
    - Adding 30 ml:

      Accelerant based on a 3h gel time
        - 0-233 mM NaCl
        - 0-33 mM $CaCl_2$
        - 0-138 mM KCl

      Colloidal silica
        - 0-7 wt%
- Method development analysing ≤ 20ppm Cs and Sr in such saline solutions is ongoing

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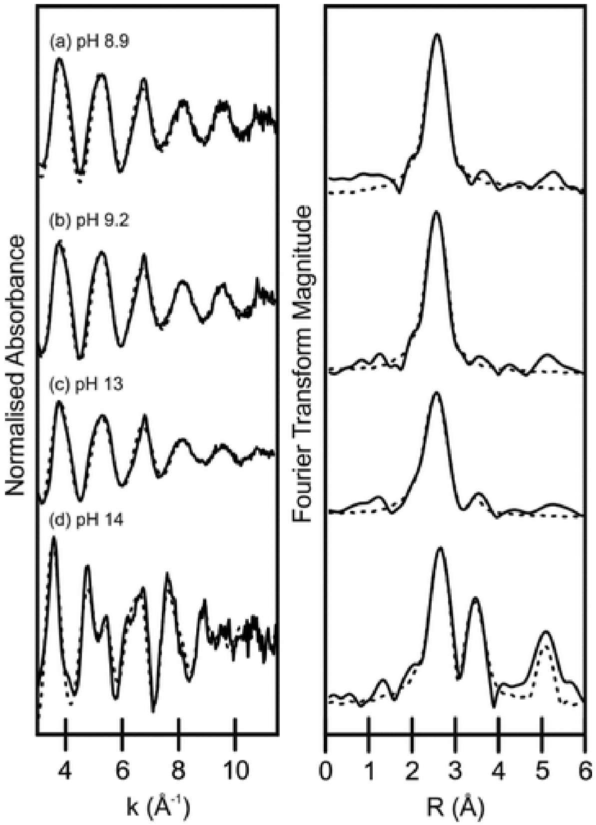
Future work 2

- X-ray absorption spectroscopy (XAS)
- XAS
  - Synchrotron radiation technique
  - Non-destructive
  - Element specific
  - Provides information on the local coordination environment
- Proposal for beamtime has been resubmitted for XAS experiments on Sr and Cs
  - Adsorbed to soil and waste components
  - Adsorbed to soil and waste mixtures
  - Soil and waste mixtures embedded in grout



Fuller et al. *Langmuir* (2016) **32** 2937-2946

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Future work 3

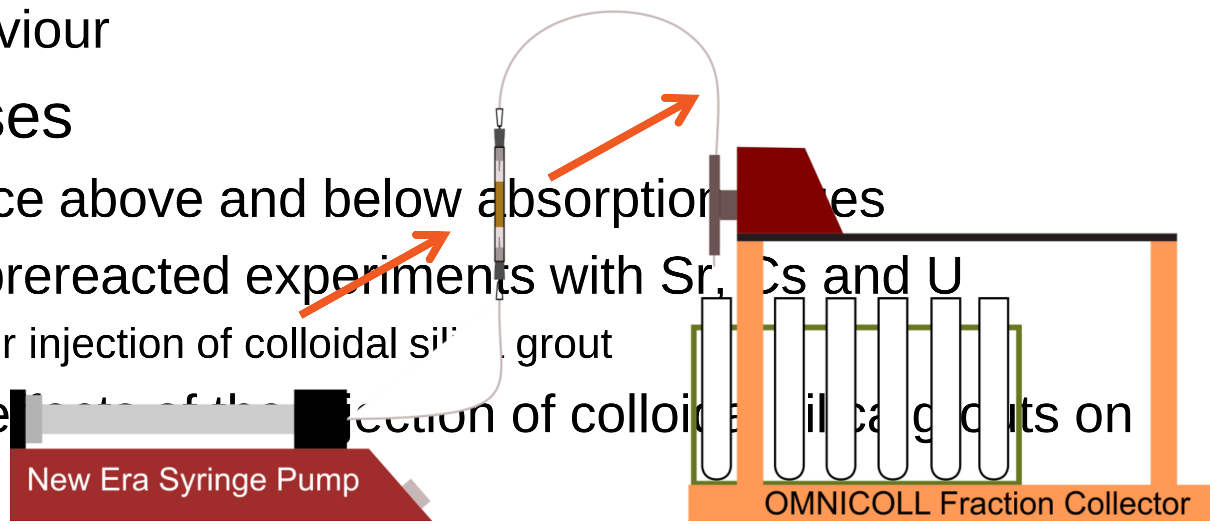
- Synchrotron based X-ray CT experiments
  - Beamtime proposal funded by Diamond Light Source (5 days)
  - 3D imaging technique based on density diffences

In-situ time resolved experiments

- Real-time imaging of injection of colloidal silica grout
- Determining the effects of solid matrix and porewater on injection behaviour

Elemental analyses

- Using fluorescence above and below absorptio… …es
- Experiments on prereacted experiments with Sr, …s and U
  - Before and after injection of colloidal si… grout
- Determining the e… …ection of colloi… …ts on the distribution of



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Future work 4

Test trenches at the Little Forest Legacy Site
Trenches with similar dimensions to the legacy site to:

- Improve understanding of hydrology of trenches, particularly the presence of an excavated trench, loosely filled, and covered with soil
- Understand the evolution of the waste materials
  - Changes in chemical and physical properties of these components and radionuclides in them
  - What could cause subsidence in the trenches
- Understand the effects of the trench (excavation) on the local hydrology, including its behaviour when saturated
- Test proposed options for remediation, e.g.:
  - Engineered cover
  - In-situ grouting

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Summary and conclusions

- Comprehensive adsorption experiments performed
- Illite/smectite is the strongest adsorbent
- Understanding the adsorption in complex soils requires further understanding

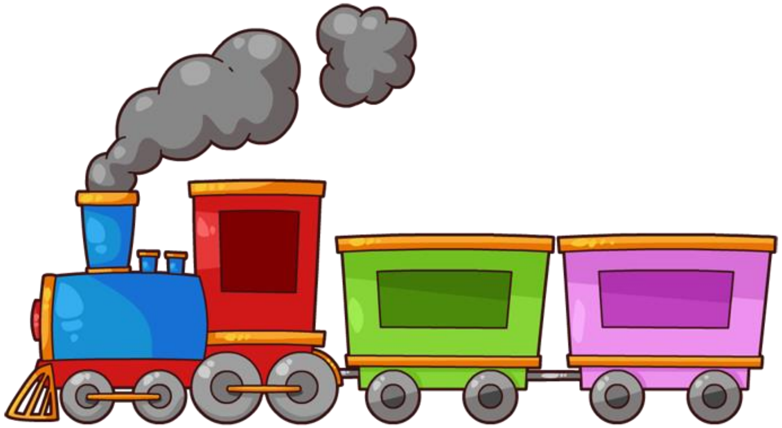
Ongoing and future work

- Desorption
- Imaging
- X-ray Absorption Spectroscopy
- Test trenches at the Little Forest Legacy Site

Thank you for your attention

Gas Generation from Water on the Surface of PuO_2

Luke Jones
University of Manchester



DISTINCTIVE 3rd Annual Meeting
5-6th April 2017
National Railway Museum, York

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The University of Manchester
Dalton Nuclear Institute

Outline

- Background
- Previous experimental work
- This project
- Further work

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Dalton Nuclear Institute

Theme 2 Background

- Decades of reprocessing SNF leads to Pu stockpile
- Stored in multi canister system as PuO_2
- Different fuel sources / different storage conditions
- Several mechanisms for canister pressurisation:
    - He accumulation
    - Radiolytic degradation of organics
    - Steam generation
    - Radiolysis of adsorbed water
    - H_2 generation from PuO_2/H_2O chemical reaction

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Previous Work

- Investigating H_2 production
- Undertaken by NNL Radiochemistry team
- PuO_2 from Thorp and Magnox product streams
- Magnox product calcined to reduce specific surface area
- Different RH environments
- N_2 and air glovebox atmospheres
- Ambient temperature
- Al foil cap for select experiments

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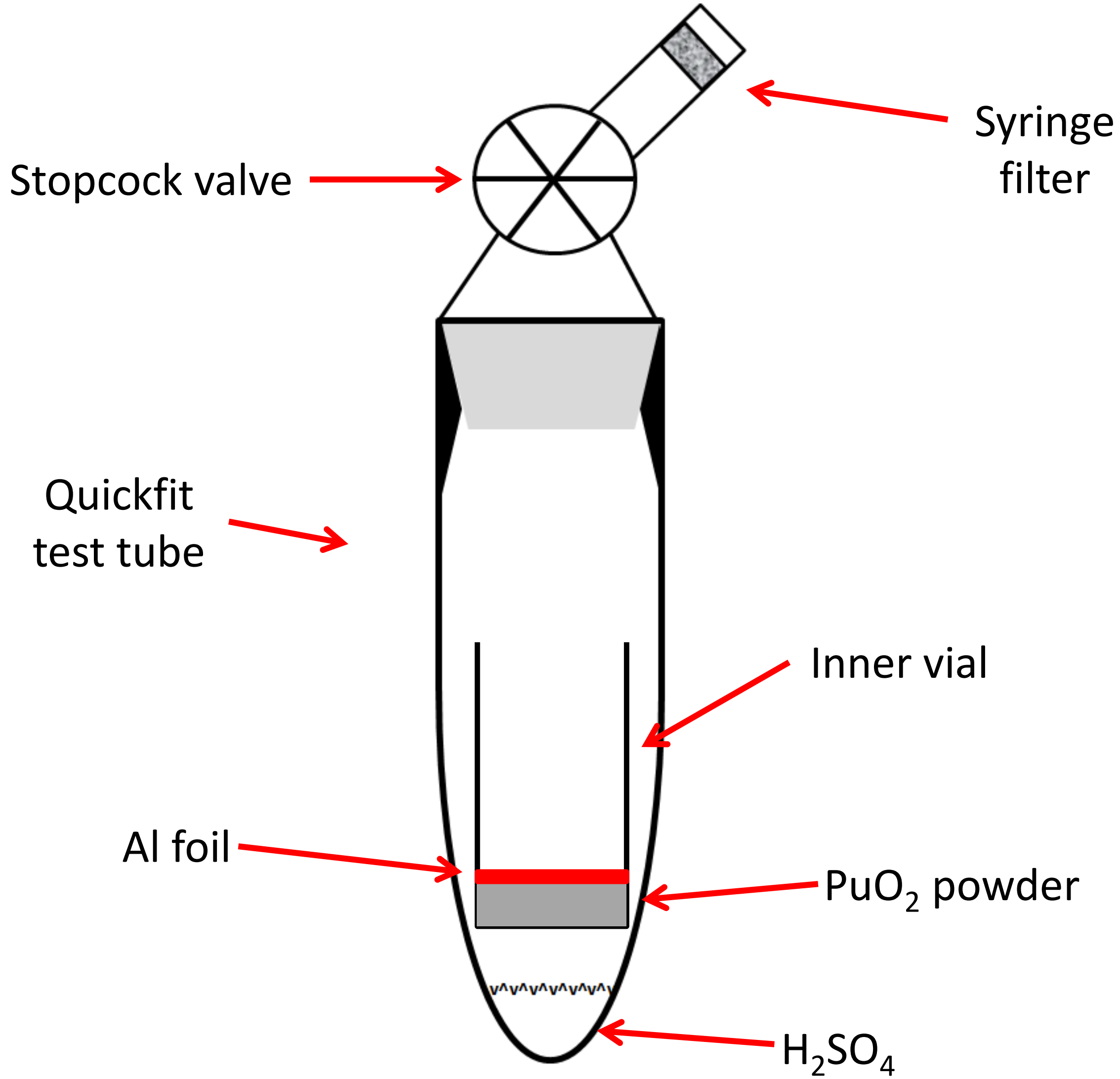
Dalton Nuclear Institute

Experimental Set-up



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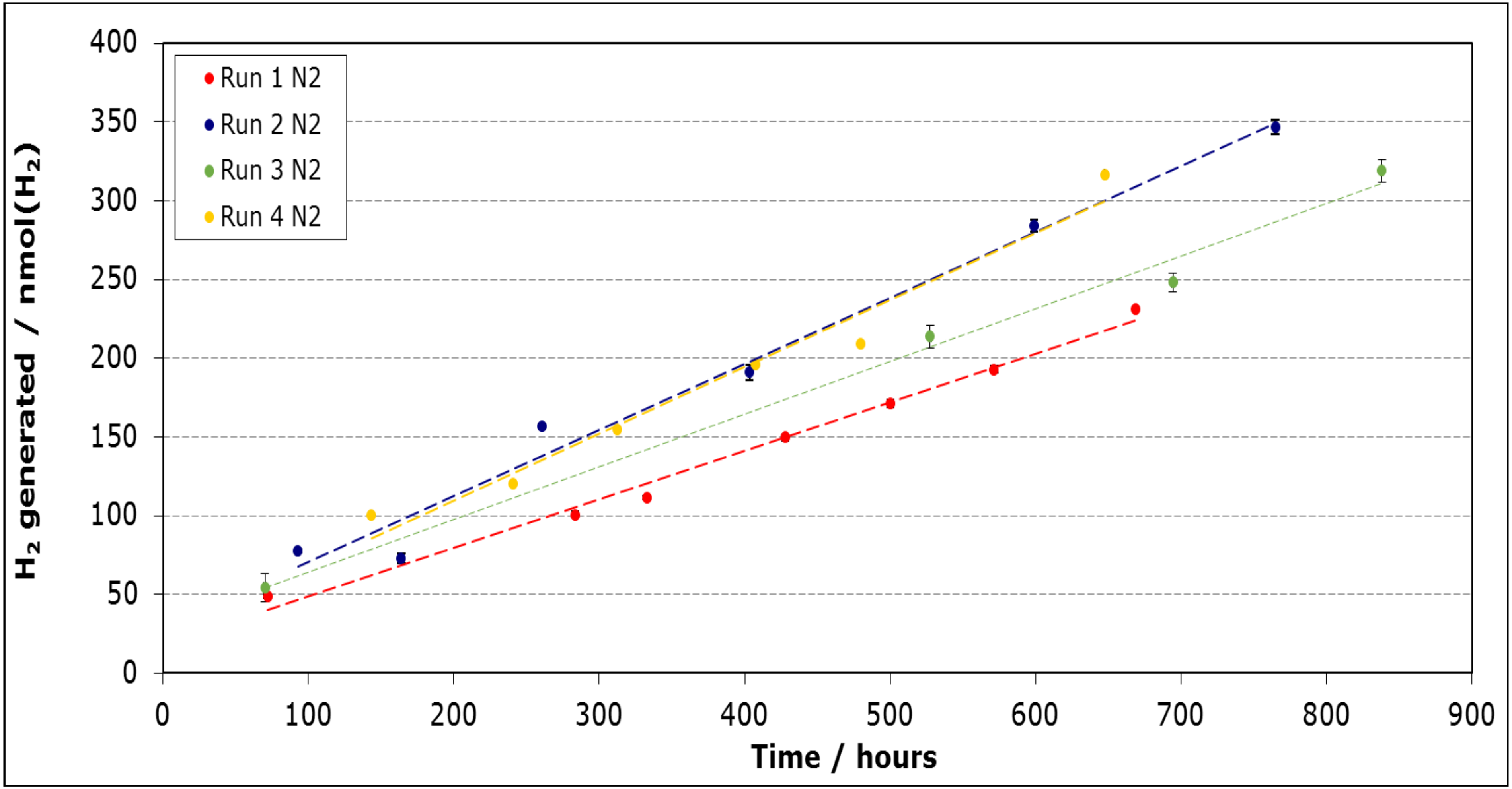
Trend 1 – Linear H_2 production



Magnox PuO_2 calcined at 950 °C in 50 %RH

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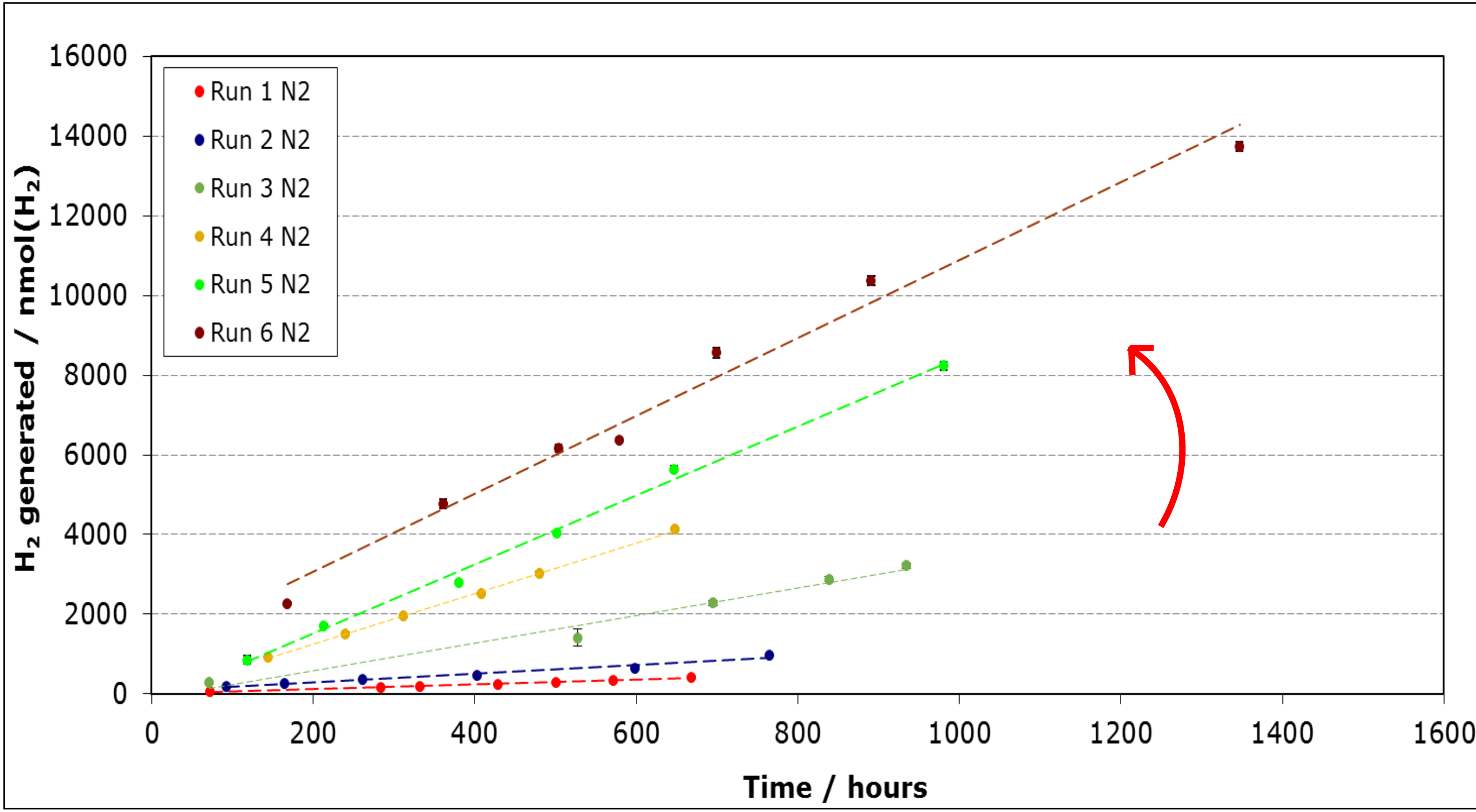
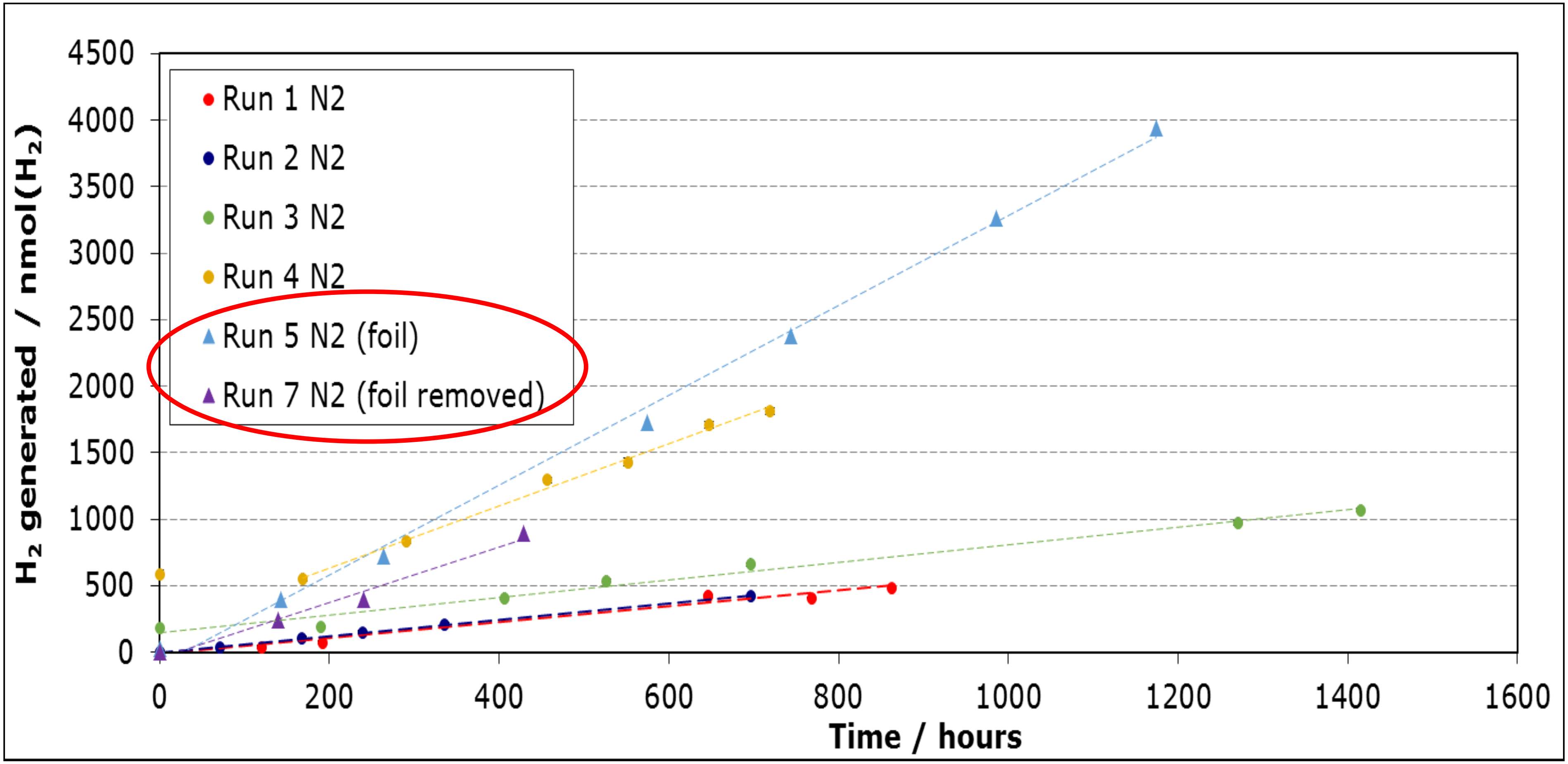
Trend 2 – Anomalous H_2 production



Magnox PuO_2 calcined at 800 °C in 50 %RH

Run 1: 0.37 $\times 10^{-19}$ cm^3 (H_2). MeV (total)$^{-1}$ m^{-2}
Run 6: 6.02 $\times 10^{-19}$ cm^3 (H_2). MeV (total)$^{-1}$ m^{-2}

Trend 3 – Effect of Al foil



Magnox PuO_2 calcined at 900 °C in 25 % RH

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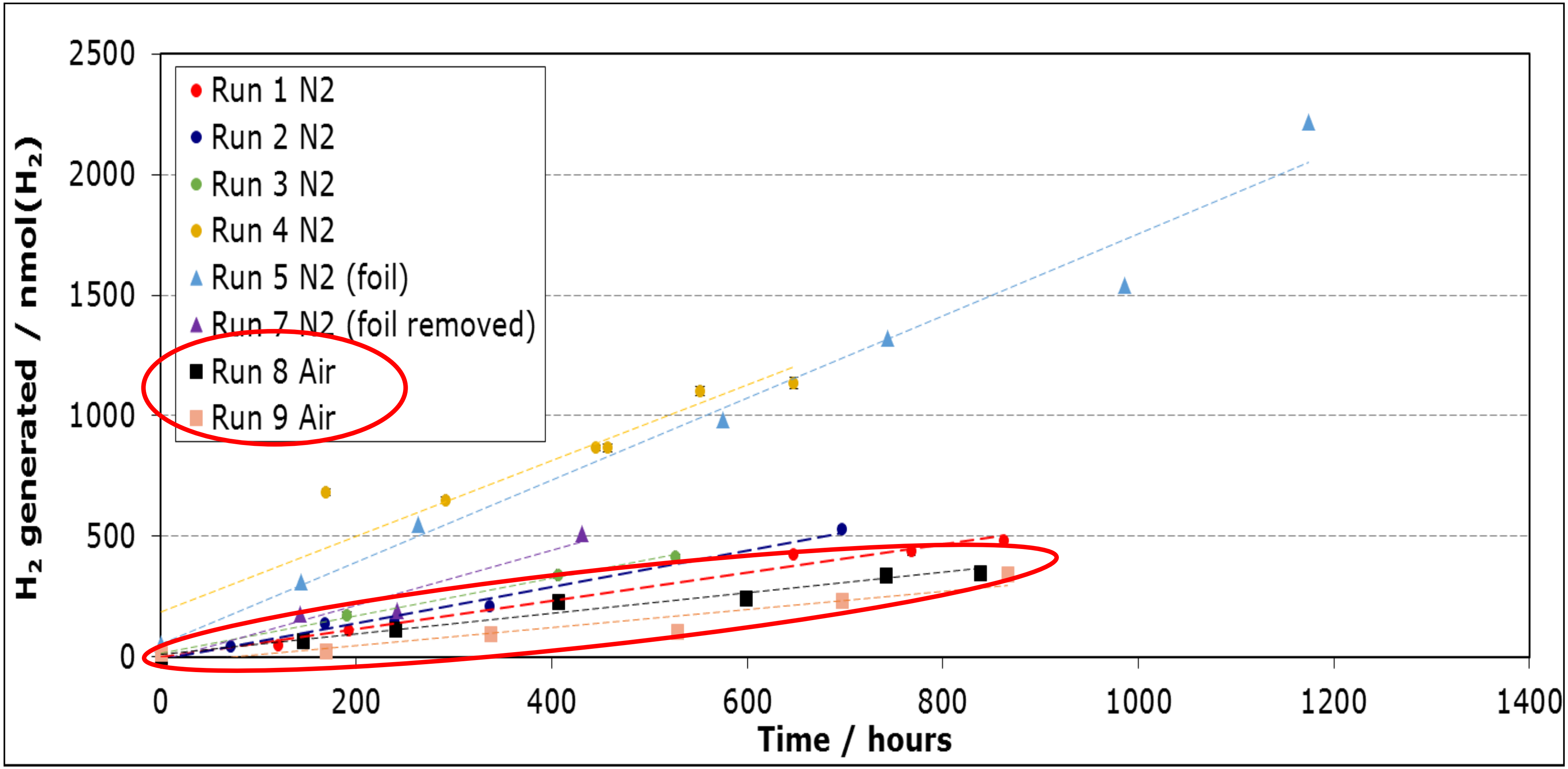
Trend 4 – Effect of glovebox atmosphere



Magnox PuO_2 calcined at 900 °C in 50 %RH

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Conclusions

- Linear H_2 production
- Increased H_2 production rate with increasing RH
- AHP observed at low RH
- Al foil increased H_2 rate for high RH samples
- Changing atmosphere has different effects on each product

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This Work

- Thorp and Magnox product ‘as received’
- Argon glovebox
- Parallel samples in air/N_2 glovebox
- Au foil experiments
- Characterisation of oxide powder
- Aged PuO_2 samples (potentially)

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Experimental Matrix (tbc)

Ar glovebox

RH %	25	50	75	95
Magnox	x	x	x	x
Thorp	x	x	x	x

Air/N_2 glovebox

RH %	25	50	75	95
Magnox	x	x	x	x
Thorp	x	x	x	x

- another 8 samples to allocate across both g/boxes

Progress

- Material on order from plant
- Paperwork signed off
- *Hands in the box*

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Further Work

- Longer timescale experiments
- Increase S/V ratio to better simulate canisters
- Quantification of O_2
- In-situ gas sampling
- Metal reaction vessels
- Headspace measurements from actual storage cans

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Acknowledgements

- Robin Orr (NNL)
- NNL Radiochem. team
- Howard Sims (NNL)
- Paul Cook, Jeff Hobbs and Helen Steele (SL)
- Simon Pimblott
- NDA for facilities costs
- EPSRC grant code - EP/L014041/1

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NATIONAL NUCLEAR LABORATORY

Adventures in Actinide Science

Dr Tamara Griffiths

DISTINCTIVE Conference

York, UK

06th April 2017

Introduction

NATIONAL NUCLEAR LABORATORY

- Worked at NNL since November 2013

- Research Associate within the Radiochemistry team.

- Based at NNL-Central Laboratory, Sellafield.

Background

NATIONAL NUCLEAR LABORATORY

Centre for Radiochemistry Research

- Masters of Chemistry (2004 – 2008)
  → The University of Manchester
- Interest in radiochemistry stemmed from MChem project

→ Dr Nicholas Bryan

→ Centre for Radiochemistry Research

→ Effect of Humic Substances on Radionuclide Migration

Background

- PhD Inorganic Chemistry (2008-2012)

→ The University of Manchester

→ Dr Clint Sharrad

→ Dr Mark Sarsfield (NNL, Industrial Supervisor)

→ PhD funded by NDA

→ Desire to further study chemistry of the actinides

→ Investigating Heterogeneous Complexes Relevant to Sellafield Waste Ponds and Solvent Reprocessing Techniques.

Sellafield Legacy Waste Ponds

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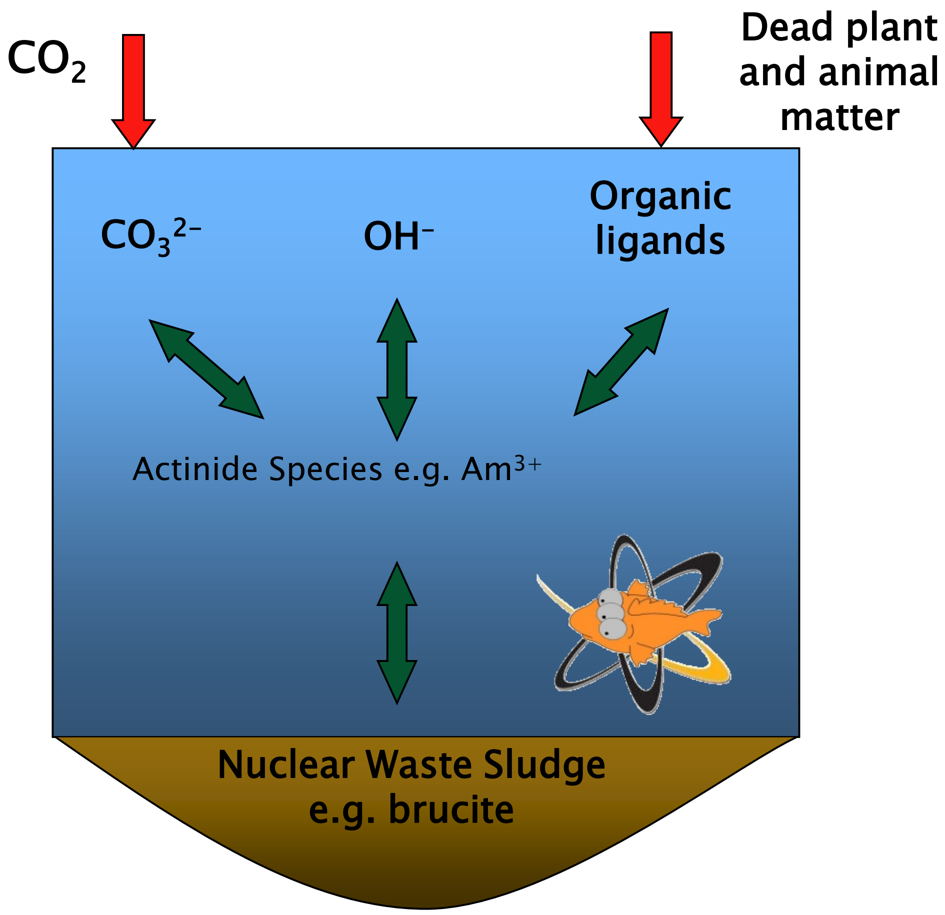
Pond chemistry is complex



Understanding the behaviour of actinide species in solution is important when disposing and processing nuclear waste

Actinide Ternary Complexes

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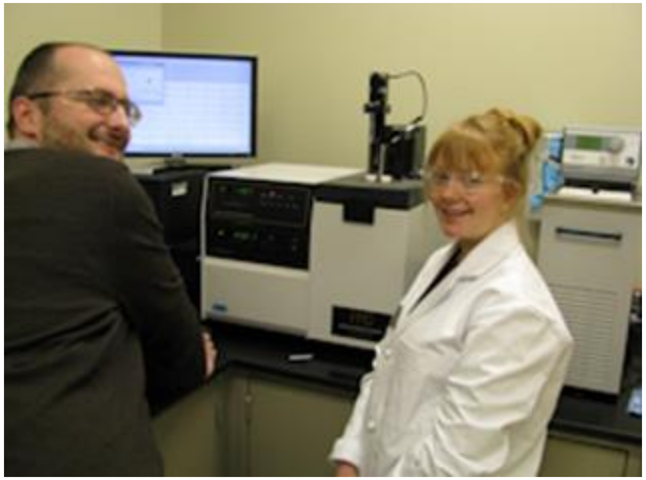


INL Idaho National Laboratory

- Desire to study ‘exotic’ isotopes (^{241}Am and ^{248}Cm)
- Seconded to Idaho National Laboratory
- Seconded to National Nuclear Laboratory

Background

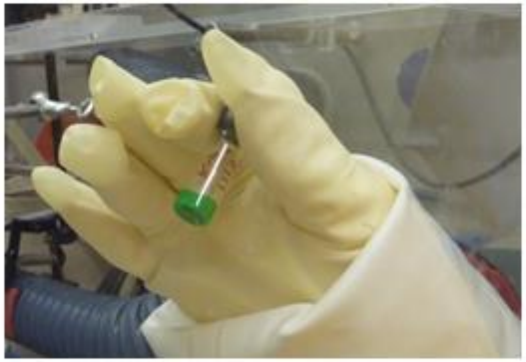
- Post Doctoral Research Associate (2012-2013)

→ Dr Clint Sharrad and Prof. Francis Livens

→ Studying ^{237}Np redox behaviour in PUREX

- Seconded to KIT-INE, Germany

→NMR of plutonium-TBP containing systems



- Seconded to INL, USA

→Gamma radiolysis of neptunium-TBP containing systems

Working at NNL

NATIONAL NUCLEAR LABORATORY

- Applied directly to NNL early 2013

→Impressed with world-class facilities

→Opportunity to work alongside the world-leading experts

→Want to further develop my knowledge/interest in studying chemistry of actinide ions

- Interviewed July 2013
- Commenced November 2013 (direct intake)
- Research Associate within Radiochemistry Team

Radiochemistry Team

NATIONAL NUCLEAR LABORATORY

Chris Mason, Central Laboratory, Sellafield

Team's key capabilities:

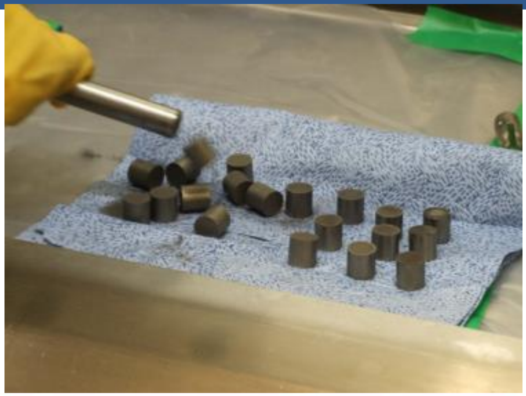
- Suite of Pu gloveboxes
  - → highly skilled glovebox operators
  - → >100 man years of experience
- Actinide Separations, Advanced Reprocessing & Flow Sheet Development
- Plutonium Processing and Storage

Team's facilities and equipment of note:

- PuMA Labs (suite of Pu gloveboxes; fumehoods; spectroscopic and electrochemical capabilities)
- High Inventory Facility (Pu can processing and packaging; SAA; pXRD; SEM; metallography; ceramography; gas chromatography; TGA)

ASGARD

NATIONAL NUCLEAR LABORATORY



- Carbide fuel is being considered for use in Gen IV reactors.

- Two main options for aqueous reprocessing carbide fuel:

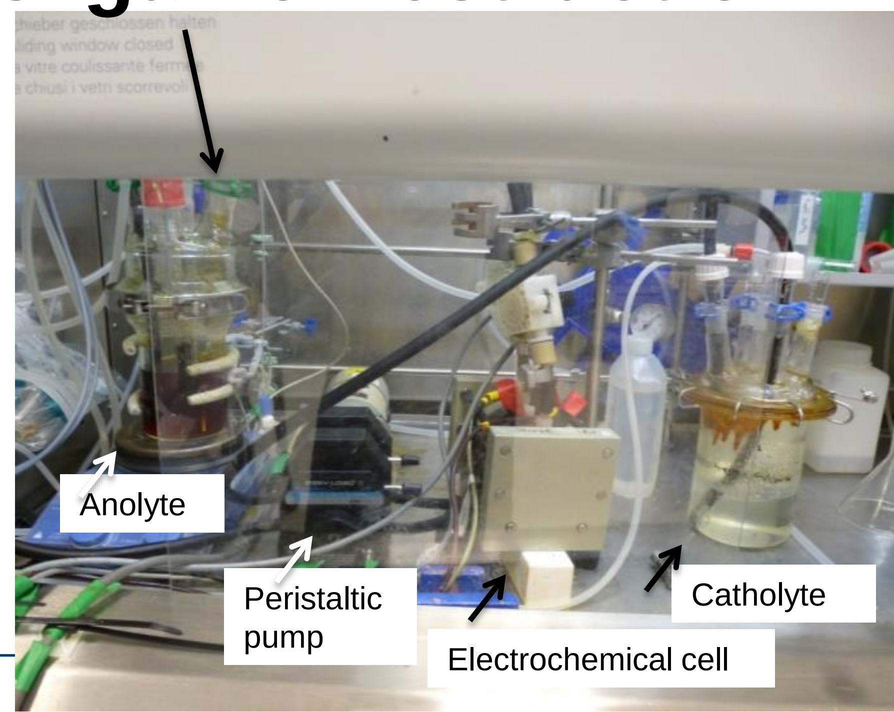
ASGARD

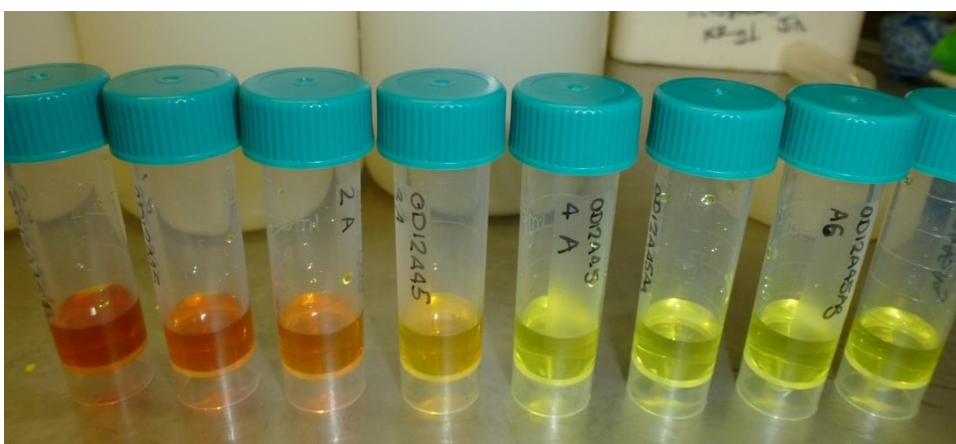
1. Direct dissolution of the carbide.
2. Oxidative pre-treatment to an oxide followed by dissolution.

ASGARD

UC Pellet Dissolution

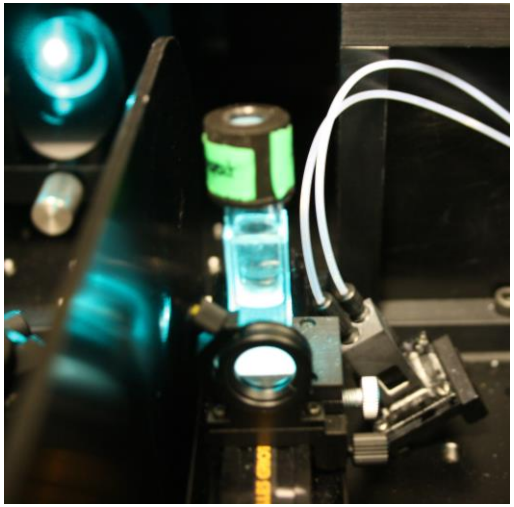
Organic Destruction





Luminescence Spectroscopy

NATIONAL NUCLEAR LABORATORY

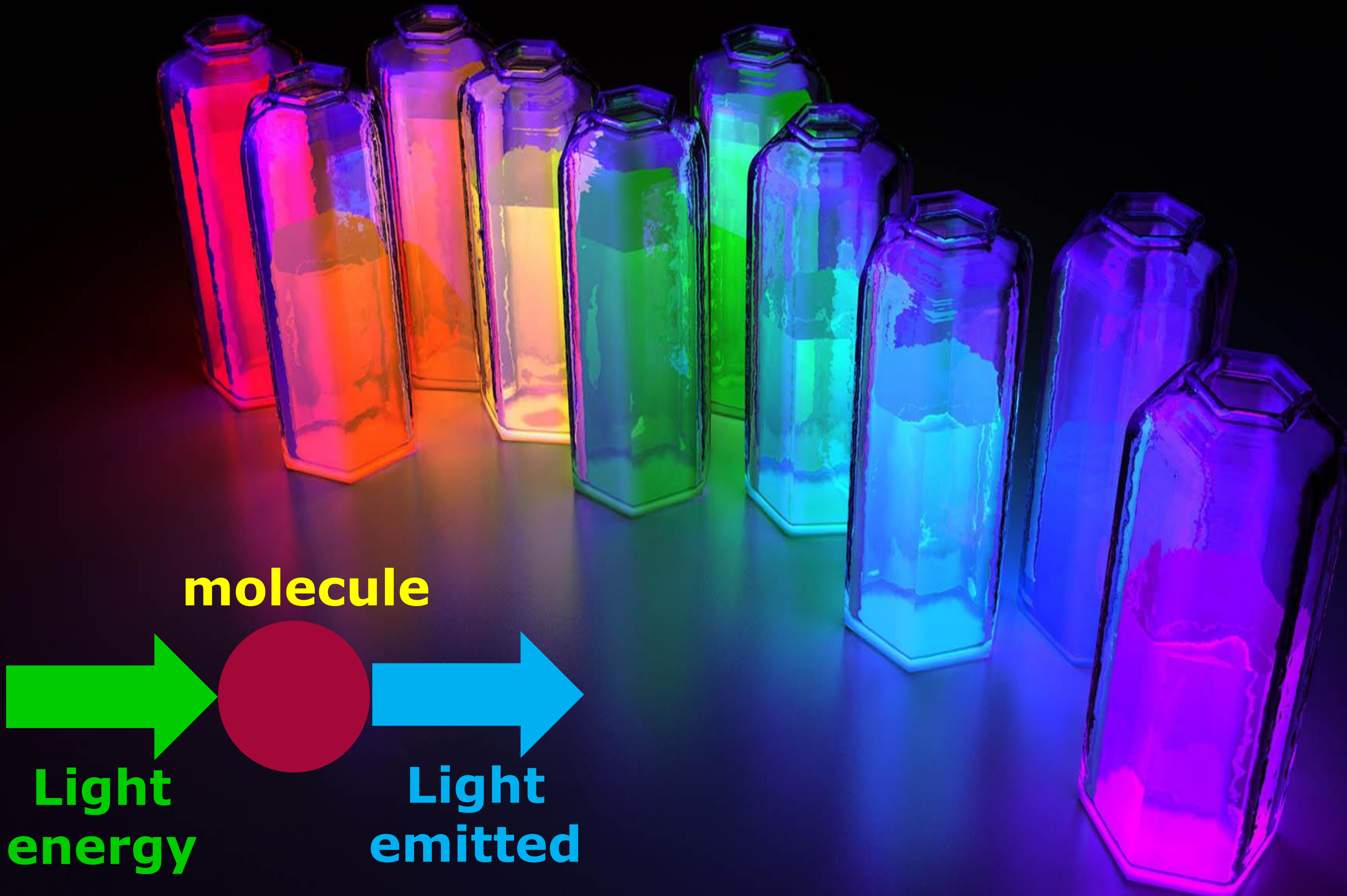


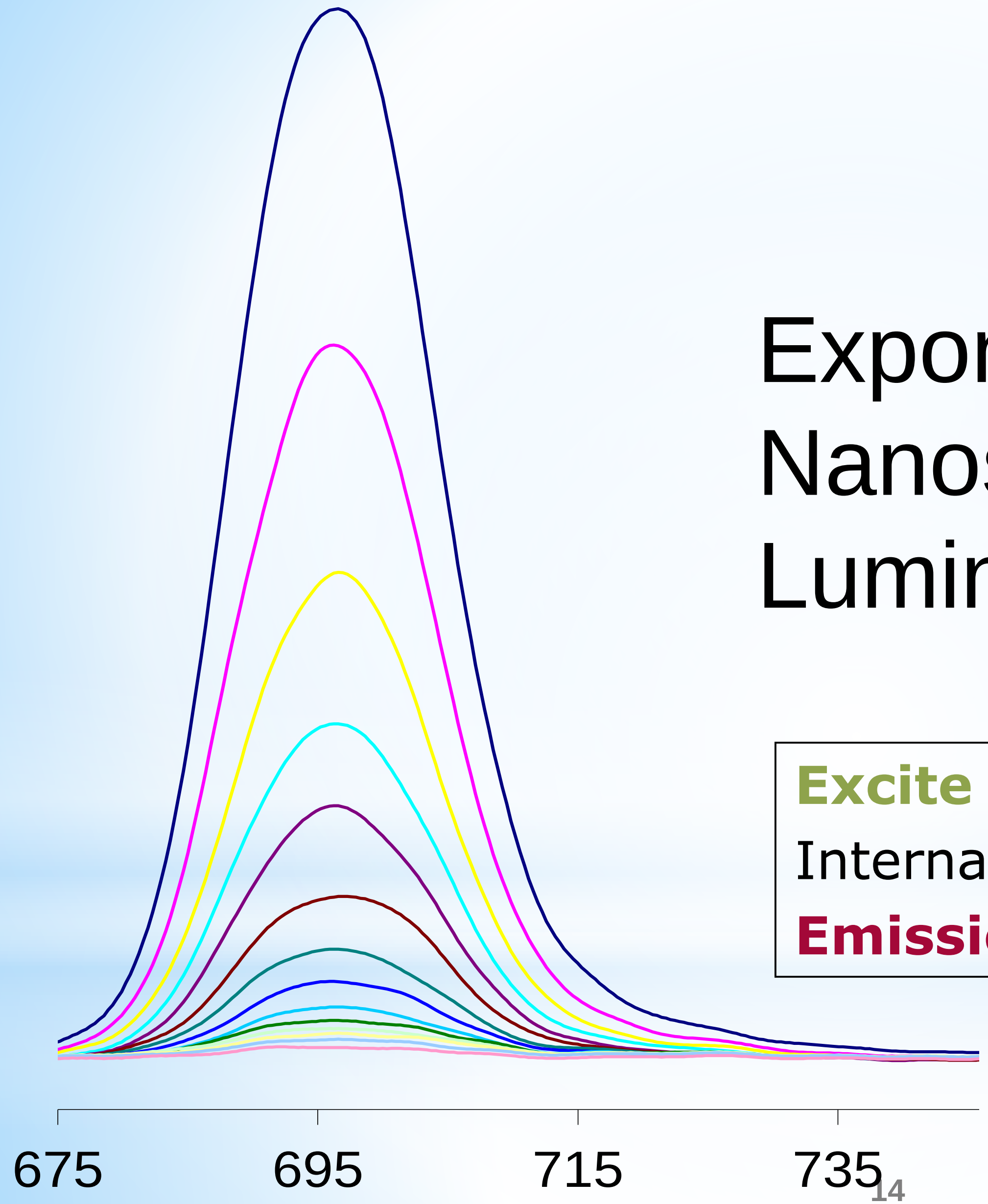
Renew the Luminescence Spectroscopy capability.

Develop tool to study Am(III) speciation with TODGA ligand.

For optimising solvent extraction processes

What is luminescence?





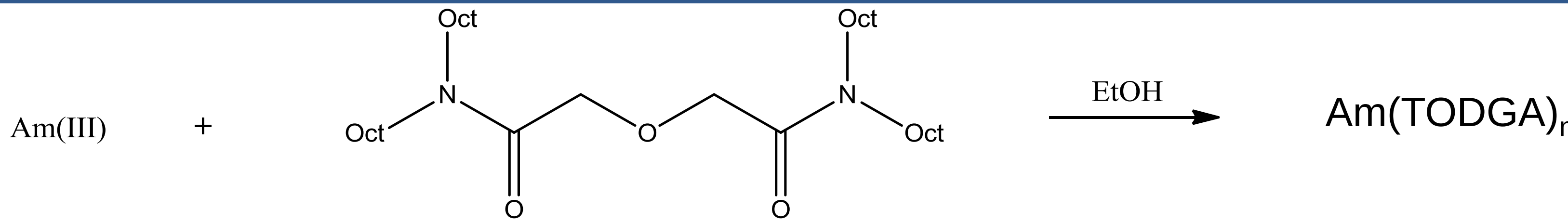
Exponential Decay
Nanosecond Timescale
Luminescence Lifetime

Excite Am(III) ion at 503 nm.

Internal Conversion.

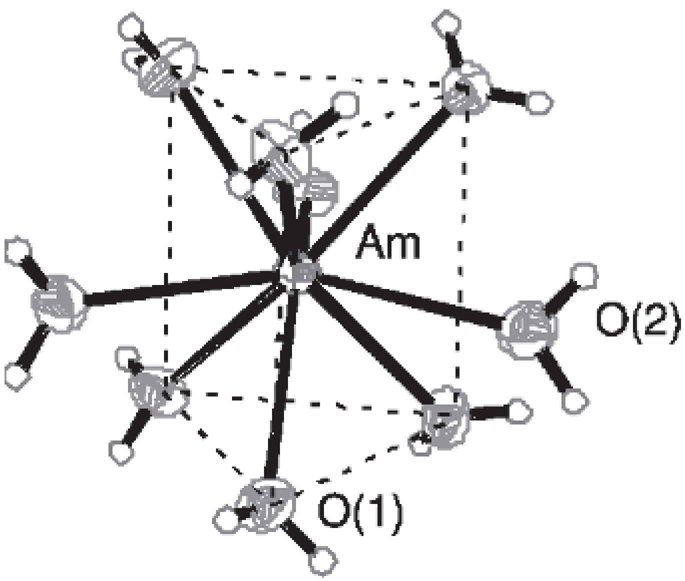
Emission observed at 691 nm.

Am(III)-TODGA Titration



$[Am(EtOH)_9]^{3+}$ λ_{max} = 695.4 nm
τ = 38.6 ns N_{EtOH} = ~ 9

$[Am(TODGA)_3]^{3+}$ λ_{max} = 695.9 nm
τ = 180.0 ns N_{EtOH} = 0



COLLABORATION

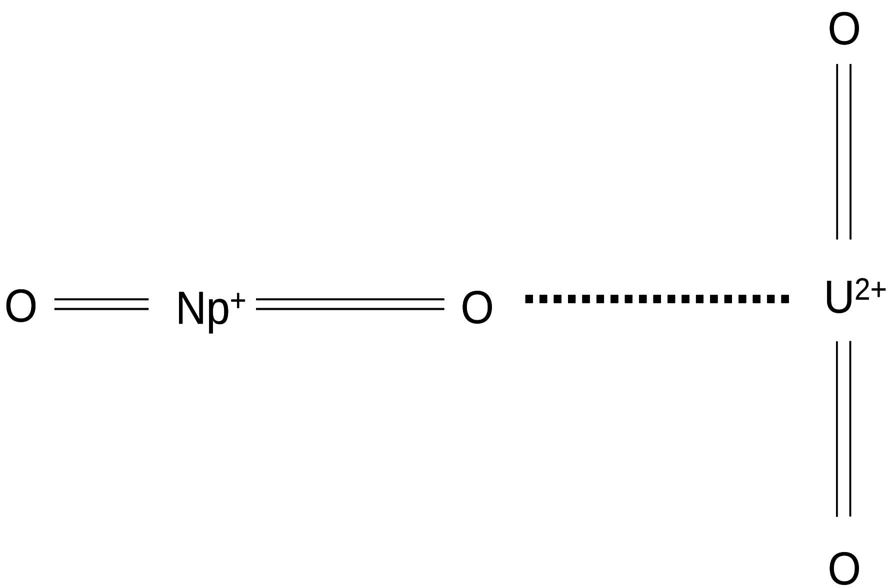
The EU 7th Framework Programme, TALISMAN, enabled a collaboration to be established between NNL and CEA.

3 months secondment for two early career researchers:

- Tamara Griffiths (NNL) to CEA Marcoule Nuclear site.
- Arnaud Deroche (CEA) to NNL Central Laboratory.

Joint NNL-CEA study of Cation-Cation Interactions (CCIs).

CCIs tend to be characteristic of pentavalent actinide ions.



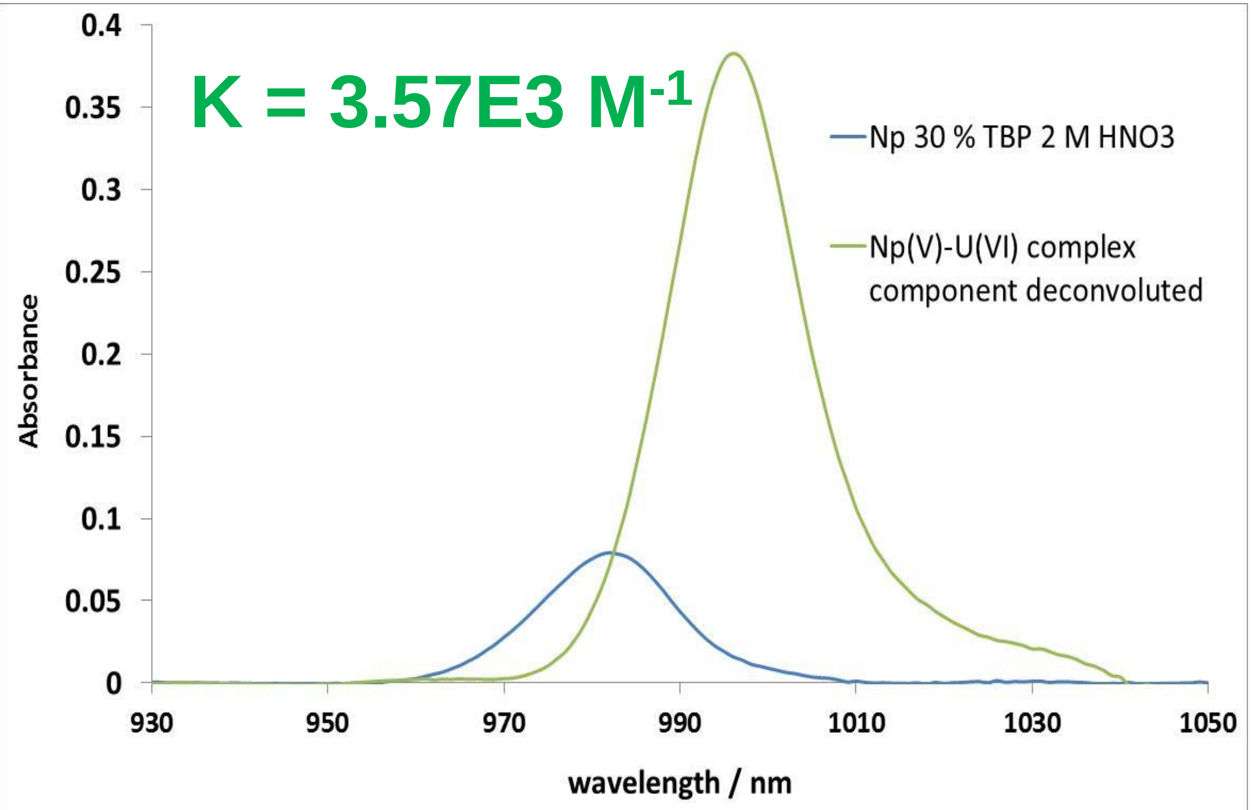
The Np(V)-U(VI) CCI was studied in organic solution (TBP/TPH).

The Np(V)-U(VI) CCI may synergistically enhance the extraction of Np(V).

Overall aim of addressing the control of Np in the development of advanced reprocessing routes.

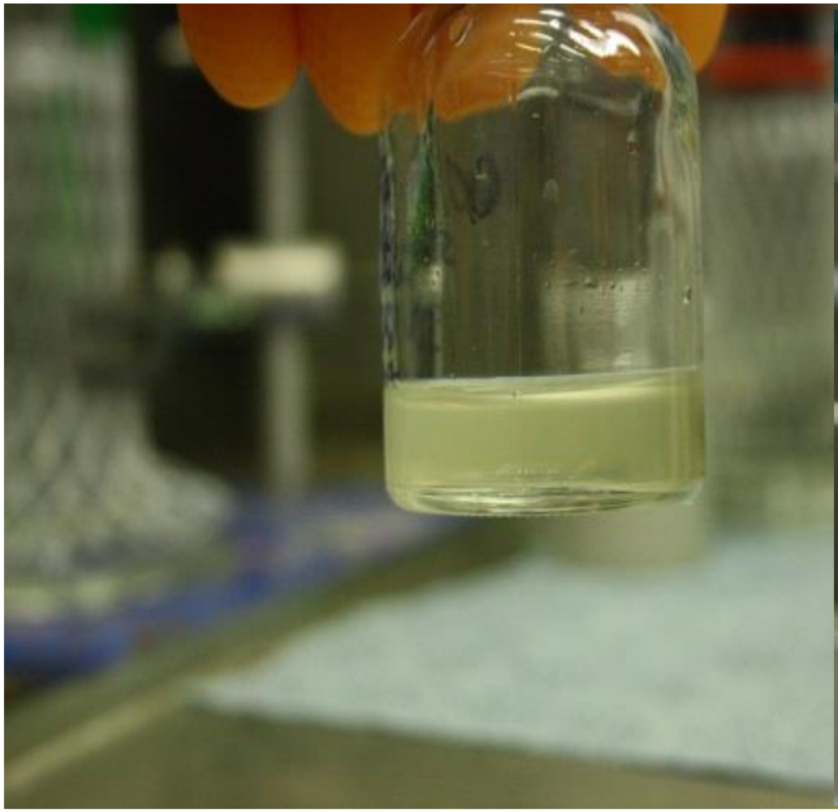
The Np(V)-U(VI) CCI was observed using electronic absorption spectroscopy

Stability Constant Determination for the Np(V)-U(VI) CCI:



Contribute to further understanding of actinide complexation and redox chemistry under solvent reprocessing conditions.

Biogeochemistry



ESA
Space Batteries

Working at NNL

NATIONAL NUCLEAR LABORATORY

- Enjoy working on multiple research projects.
- Enjoy the opportunity to present my work to a national and international audience.
- Opportunity to be industrial PhD supervisor.
- Continue to strengthen links between NNL and universities/other research institutes world-wide.
- Enthusiastic, proactive, continually looking for opportunities to develop.

Acknowledgements

NNL Radiochemistry Team

- Chris Mason
- Dr Mark Sarsfield
- Dr Chris Maher
- Prof. Robin Taylor
- Dr Sean Woodall
- Dr Mike Carrott
- Dr Dan Whittaker
- Stacey Reilly
- Catherine Campbell
- Hannah Colledge
- Louise Walton
- Colin Gregson
- Josh Holt
- Cheryl Carrigan
- Kevin Webb
- Bliss McLuckie

University of Manchester

- Dr Clint Sharrad
- Dr Nick Bryan
- Prof. Francis Livens
- Dr Louise Natrajan
- Dr Kate Tucker
- Prof. Melissa Denecke

INL

- Dr Leigh Martin
- Dr Peter Zalupski

KIT-INE

- Dr Peter Kaden
- Dr Andreas Geist

Engagement and impact with a distinctive edge

Neil Hyatt
University of Sheffield
Email: n.c.hyatt@sheffield.ac.uk

DISTINCTIVE Annual Meeting
04-06 April 2017
York

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE.
Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories

Media & public engagement summer school

Wednesday 22nd – Friday 24th June 2016

Halifax Hall Hotel, Sheffield

For all DISTINCTIVE PhD students & PDRAs

Research Councils UK Energy For a Low Carbon Future

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Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories

Media & public engagement summer school

DISTINCTIVE

Decommissioning, Immobilisation and Storage soluTIons for NuClear wasTe InVEntories

DISTINCTIVE media and public engagement summer school

Halifax Hall, Sheffield, June 2016

Wednesday 22nd June	Thursday 23rd June	Friday 24th June
Participants arrive in time for lunch	0930: **Making the most of our media opportunities** (Mentor Media) Basic Media Skills *The Dining Room (caberet – 40)*	0900: **Engaging with policy makers** Matt Billson (Energy 2050) 0915: **Popular Science Writing** Vikki Cantrill (Freelance Writer) Mary Cruse (Freelance Writer, Diamond) Dan Cooper (The Nuclear Hitchiker) *The Dining Room (caberet – 40)*
	1100: Tea & Coffee	1030: Tea & Coffee
	1130: **"Selling your story" using the T.R.U.T.H. principles** (Mentor Media) *The Dining Room (caberet – 40)*	1100: **Popular Science Writing Exercise** *The Dining Room (caberet – 40)*
1230: LUNCH	1230: LUNCH	1230: LUNCH
1330: **Welcome and setting the scene** 1400: **Public engagement session** Mike Wood (University of Salford) Laura Holland (Diamond Light Source, via skype) *The Dining Room (theatre – 40)*	1330: **Putting the skills into practice** (Mentor Media) *The Dining Room (caberet – 40)*	1400: **"Dragon's Den"** Exercise on public engagement group activity Round 1 *The Dining Room (caberet – 40)*
1500: Tea & Coffee	1500: Tea & Coffee	1500: Tea & Coffee
1530: Hotel check-in 1600: **Group work on public engagement** *Library (caberet - 20); The Dining Room (theatre – 40)*	1530: **Press Conference Exercise** (Mentor Media) *Ennis Room (caberet - 20); Library (caberet - 20)* **Close**	1530: **"Dragon's Den"** Exercise on public engagement group activity Round 2 *The Dining Room (caberet – 40)*
Virtual Chernobyl: Ennis Room	1630: **Q&A with Tom Sheldon, Science Media Centre** *The Dining Room (caberet – 40)* 1700: **Group work on public engagement** *Ennis Room (caberet - 20); Library (caberet - 20)*	1545: **Winners announced**
1830: DINNER	1900: **DINNER** (with after dinner speaker – Tim Yeo)	1600: **CLOSE**
1930: Group work on public engagement *Library (caberet - 20); The Dining Room (theatre – 40)*		

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Media & public engagement summer school

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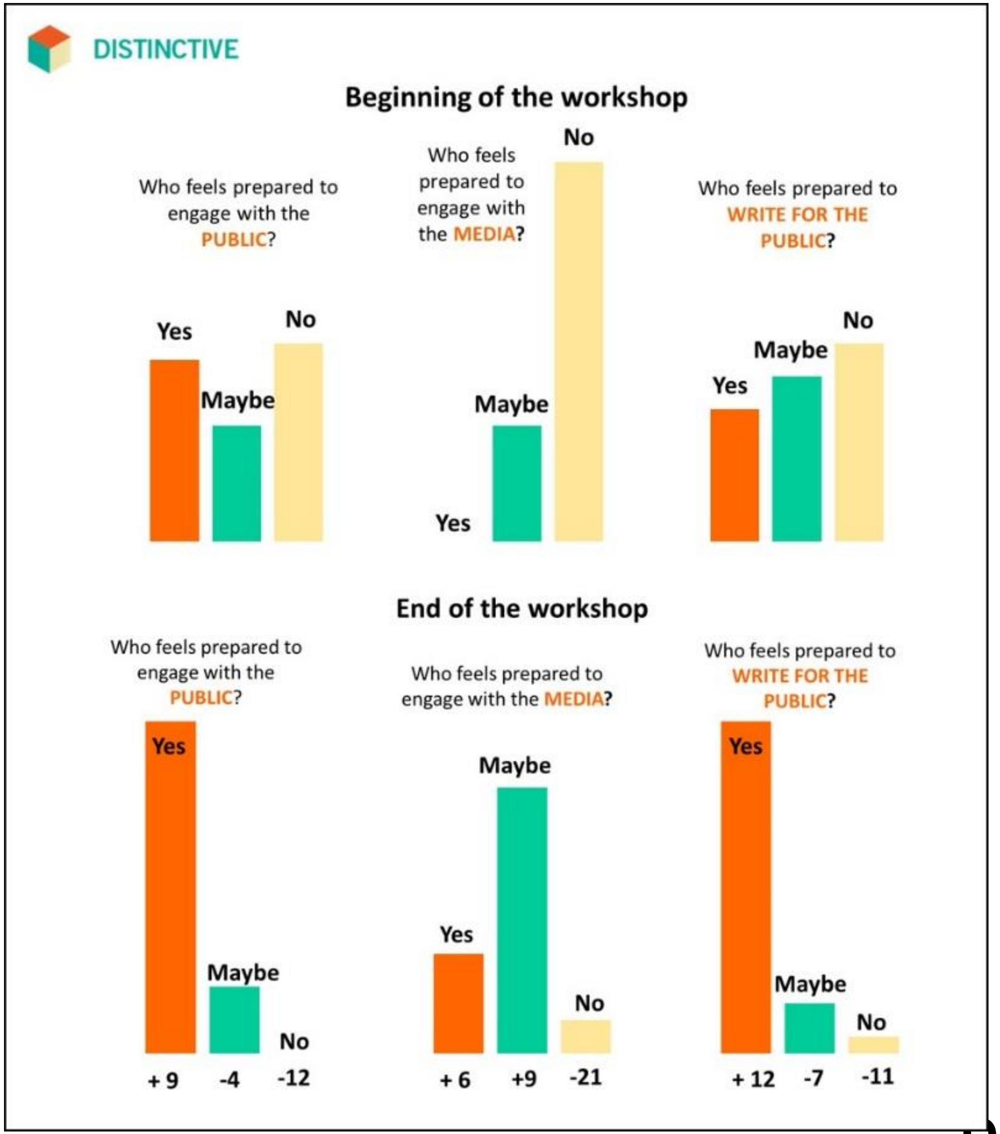

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE.
Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories

Online / real-time stakeholder engagement

- Deliberatorium platform launched in May 2016 but uptake was poor
- The concept was developed at MIT: a social computing platform designed to help people combine their insights to find solutions for complex multi-disciplinary problems.
- It was originally developed for large scale discussions of climate change policy, and we are applying it here to radioactive waste.
- Members of the DISTINCTIVE consortium were strongly encouraged to take part, and engage with a broader network of stakeholders that will also contribute.

Online / real-time stakeholder engagement

- Matthew Cotton (now at York) will be running a face to face Deliberatorium session at the annual meeting
- Participants contribute either by posting *issues* (technical / social questions that need to be answered), *ideas* (possible answers for a question), or *arguments* (statements that support / detract from an *idea* or *argument*).
- These are arranged into branching trees of arguments
- This setup has the advantage of allowing different users different roles. One user can propose an idea, a second raise an issue concerning how some aspect of that idea can be implemented, and a third propose possible resolutions for that issue. .
- Matthew will then produce an 'argument map' which we will report as a deliverable of the project, and work this up into a social science publication (for a journal such as *Science Communication)*

DISTINCTIVE documentary film

Key messages for the film:

• Nuclear decommissioning, waste management and waste disposal is a complex and interdisciplinary science and engineering challenge

• Research needs to be timely and goal oriented, but also of a fundamental nature, of high quality, and independent, to underpin technology selection, optimisation and deployment

• The UK project may take a century to complete, so a pipeline of highly skilled researchers, as delivered by the project, is essential.

Segment	Message	Time?
1	Big picture: UK nuclear decommissioning, waste management, disposal To camera with cutaway and stock footage	1.00
2	AGR, Magnox & Exotic Fuels (9 projects) To camera with lab cutaway footage	1.00
3	PuO2 and Fuel Residues (12 projects) To camera with lab cutaway footage	1.00
4	Legacy Ponds & Silos (21 projects) To camera with lab cutaway footage	1.30
5	Structural Integrity (9 projects) To camera with lab cutaway footage	1.00
6	Research translation and impact (NDA / Sellafield Ltd) To camera with stock cutaway footage	1.00

International Festival of Glass 2017

Bank Holiday weekend: 25-28 August
Footfall of 13,000 visitors per day
Need a presentation team of four volunteers

Invited participation – glass applications for radioactive waste treatment

1. Public lecture:
Prof. Neil Hyatt, Engineering radioactive waste glasses for the future

2. Interactive display:

- Pop up graphic display on radwaste glass
- DISTINCTIVE docu-film
- Radwaste glass educational film
- Table with glass artefacts
- Demonstration – Prince Rupert drops

INTERNATIONAL FESTIVAL OF GLASS STOURBRIDGE UK

US Nuclear Waste Technical Review Board

Invited poster presentation at the US Nuclear Waste Technical Review Board Richland, WA on June 21, 2017.

Expert participants will advise the NWTRB on the state of the art understanding of radioactive waste glass mechanisms

This will shape US radioactive waste disposal strategy and associated research priorities.

Participants will include DOE, the Washington State Department of Ecology and other stakeholders, DOE site contractors, and national laboratories, and the local community which will be the host for the US Low Activity Waste Glass repository (on the Hanford site).

The University of Sheffield has been invited to participate in the meeting and contribute an expert poster on the understanding of nuclear waste glass alteration and its impacts on disposal safety, developed through DIAMOND and DISTINCTIVE

NWTRB
U.S. Nuclear Waste Technical Review Board

Research Councils UK
Energy
For a Low Carbon Future

DISTINCTIVE.

Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories

Engaging with policy makers

Objectives:

► Raise profile of project in government departments and Westminster

► Promote research outcomes and impacts

► Provide opportunity for consortium researchers to engage policy makers

Proposed event

All Party Parliamentry Group on Nuclear Energy (2017)

DISTINCTIVE sponsored discussion / poster event over lunch; sponsor Tim Yeo – discussion ongoing with David Mowatt MP (APPG Vice Chair)