DISTINCTIVE – 4th Annual Meeting

Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories

National Railway Museum, York
11th September 2018

Introduction and Housekeeping, and Overview

Michael Fairweather
University of Leeds

Research Councils UK Energy For a Low Carbon Future

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Acknowledgements

The DISTINCTIVE University Consortium gratefully acknowledges funding from the EPSRC as part of the Research Councils UK Energy programme

The Energy Programme is a Research Councils UK cross council initiative led by EPSRC and contributed to by ESRC, NERC, BBSRC and STFC

Code: EP/L014041/1

We also gratefully acknowledge funding from our key project partners

Sponsorship

The DISTINCTIVE University Consortium would like to say a special thank you to our event sponsors, the NDA, for their support of the PhD Student Poster Award

Nuclear
Decommissioning
Authority

Project Background

- Project started 10th February 2014 to 9th February 2018, although no-cost extension granted to 9th February 2019
- £4.91M EPSRC → total £6.13M, plus £2.23M from industry = £8.36M
- World-class University network:

Imperial College London
Lancaster University
Loughborough University
University of Birmingham
University of Bristol
UCL
University of Leeds
Manchester 1824 The University of Manchester
The University Of Sheffield.
University of Surrey
University of Strathclyde Glasgow

- Key project partners:

National Nuclear Laboratory
NDA Nuclear Decommissioning Authority
Sellafield Ltd
Research Councils UK Energy For a Low Carbon Future

www.distinctiveconsortium.org

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Progress Since Last Annual Meeting

Theme meetings, Rheged Centre, Penrith, 16th and 17th October 2017:

- Held as two parallel oral sessions in addition to poster presentations
- High industry attendance – including representatives from Amec Foster Wheeler, AWE, Cavendish Nuclear, Fraser-Nash Consultancy, Jacobs, LLWR, NDA, NNL, NSG Environmental, Radioactive Waste Management, Sellafield Ltd, Tuv-Sud Nuclear Technologies
- Enabled useful discussions with end-users providing useful direct feedback

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Progress Since Last Annual Meeting

Waste Management 2018, Phoenix, Arizona, 18th-22nd March 2018:

- Pre-eminent international conference on management of radioactive materials, attracting over 2,000 delegates
- DISTINCTIVE held dedicated session showcasing work of consortium
- Session well attended with ~60 people attending
- Focus on key findings to date and achievements, as well as importance of consortium from an industrial point of view
- Many thanks go to Prof Ian Pegg (Catholic University of America) and Dr Laurie Judd (Longenecker & Associates) for chairing session
- Networking event held after session well attended and many new contacts made
- Many thanks go to Longenecker & Associates for once again sponsoring this event
- Six other papers on work carried out by consortium

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Progress Since Last Annual Meeting

Conference attendance:

- Birmingham Research Poster Conference 2017, 15th June 2017, Birmingham, UK
- PETRUS-ANNETTE PhD and Early-Stage Researchers Conference 2017, 26th-30th June 2017, Lisbon, Portugal
- Actinides 2017, 9th-14th July 2017, Sendai, Japan
- Turbulence, Heat and Mass Transfer 9, 10th-13th July 2018, Rio de Janeiro, Brazil

Visits to facilities

- Diamond Light Source, Didcot, UK
- Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia
- Internships at Hitachi-GE Nuclear Energy Ltd (HGNE), Hitachi, Japan
- Numerous other visits associated with active research: British Geological Survey, Dalton Cumbria Facility, GANIL (France), Little Forest Legacy Site (Australia), National Nuclear Laboratory Central Laboratory, Oak Ridge National Laboratory (USA), Photon Factory (Japan) and Surrey University Ion Beam Facility




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Project Impact

Information on Key Findings and Project Impact on Gateway to Research

Impact plan identified three groups of non-academic beneficiaries:

- Site licence companies and associated industrial supply chain
- Society and stakeholder groups
- Government, regulators and implementation authorities

Also discussed:

- Deliberatorium
- Active research fund

http://gtr.rcuk.ac.uk

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Project Impact: Technical Work Packages/Themes

Theme 1 AGR, Magnox and Exotic Spent Fuels (Lead: Tom Scott/David Read):

Addresses UK's spent nuclear fuel inventory, and preferred options for disposal. Includes retrieval of fuel from current storage facilities and repackaging options available. Concerned with Advanced Gas-Cooled Reactor, Magnox and other so-called 'Exotic' spent fuels, with goal to increase knowledge and mechanistic understanding of processes involved during management

Project Title	Type	University
Wet Fuel Storage Issues		
Use of time resolved laser fluorescence spectroscopy to investigate dissolution rates	PDRA	Loughborough / Surrey
Behaviour of used nuclear fuel in wet storage	PhD[a]	Lancaster
Transitions to Dry Fuel Storage		
Investigation of wasteform evolution during wet-recovery and drying of SNF	PDRA	Bristol
UO_2 surface reactivity and alteration	PhD	Bristol
Determination of optimum drying conditions for AGR fuels	PhD	Leeds
Long-Term Storage Effects and Exotic Fuels		
Options for exotic carbide fuels	PhD	Imperial
Grain boundary damage mechanisms in strained AGR cladding under irradiation	PhD	Manchester
Life cycle approach as decision tool for waste management/decommissioning of existing and future plants	PhD	UCL

[a]Associated PhD

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Project Impact: Technical Work Packages/Themes

Theme 1 AGR, Magnox and Exotic Spent Fuels – Notable Achievements:

- Work on transitioning spent AGR fuel from wet to dry storage to inform drying and transitioning of legacy materials from current aged storage facilities at Sellafield assisting development of fuel handling operations. Investigations into behaviour of fuel and cladding materials
- Fuel material behaviour includes U, UC and UO_2, with novel use of thin films to examine behaviour of fuels in water and moist atmospheres (i.e. transition from submerged pond storage to dry storage). Thin film surfaces directly comparable to surfaces on bulk crystals and hence provide test substrate for mimicking spent nuclear fuels
- Detailed experimental and modelling work giving improved understanding of oxidation of UC fuel from Dounreay Fast Breeder, critical step to enable its disposition
- For cladding materials, work resulted in better understanding of corrosion behaviour, quantifying extent of microstructure damage, and developing automated drying techniques. Contributed to change in way ILW material from silos at Sellafield will be packaged which feeds into long term storage strategies for spent fuel being developed by NDA and Sellafield Ltd

Project Impact: Technical Work Packages/Themes

Theme 2 PuO_2 and Fuel Residues (Lead: Colin Boxall/Nik Kaltsoyannis):

Addresses challenge presented by UK's civil plutonium inventory. Plutonium is bi-product of reprocessing spent fuel received from UK's fleet of nuclear power generators, with approximately 125 tonnes of Pu in interim storage in UK. However, no decision has yet been made regarding its final treatment and disposition

Project Title	Type	University
Behaviour of PuO_2 During Interim Storage		
Modelling the surface chemistry of PuO_2 at the molecular level	PDRA	UCL / Manchester
Understanding the interfacial interactions of plutonium dioxide with water	PDRA	Lancaster
Computational modelling of PuO_2 ageing and fuel residues	PhD	Birmingham
Investigation of anomalous hydrogen production from water adsorbed on oxides	PhD[a]	Manchester
Simulation of low-energy electron radiolysis of water adsorbed on oxides	PhD[a]	Manchester
Understanding surface species and interactions between adsorbed chloride and water on stored PuO_2	PhD[a]	Manchester
The interaction of water with PuO_2 surfaces	PhD[a]	UCL / Manchester
Behaviour of Pu-Bearing Wasteforms and Encapsulants		
Ceramic materials for actinide disposition	PDRA	Sheffield
Understanding actinide sorption and binding to cement materials for radioactive waste management	PhD	Sheffield
Development of glass-ceramics for Pu disposition using hot isostatic pressing	PhD	Sheffield
Methods for the Characterisation of Stored Pu, Pu-Contaminated Materials and Pu-Contaminated Facilities		
Real-time fast neutron plutonium assay for plutonium storage and ageing applications	PhD	Lancaster
In-situ characterisation of heavily-contaminated plutonium finishing environments	PhD	Lancaster

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Project Impact: Technical Work Packages/Themes

Theme 2 PuO_2 and Fuel Residues – Notable Achievements:

- Strategy proposed for de-risking Pu management policy by adopting dual track approach: remaining Pu not converted into MOX fuel, or reused, immobilised and treated as waste for disposal. Findings presented to House of Commons, All Party Parliamentary Group on Nuclear Energy
- Input into process design, operational and safety aspects of Sellafield Product and Residue Store Retreatment Plant for retreating and/or repackaging historic Pu and residues for consolidation into store
- Development of glass-ceramic formulations, and hot isostatic pressing process, for immobilisation of plutonium stockpile, supported by hands-on Pu-239 validation at ANSTO. Unique facility and capability developed for hot isostatic pressing of actinides
- New methodology for determination of very slow dissolution kinetics of actinide glass-ceramics through ultra-high resolution optical interferometry and AFM techniques, providing quantitative input data for disposal system safety assessment
- Successful trials on UO_2 and ThO_2 (as PuO_2 simulants) of nanogravimetric device for direct measurement of water entrainment in plutonia powders and subsequent determination of heats of adsorption; instrument transferred to NNL for analogous measurements on PuO_2 powders

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Project Impact: Technical Work Packages/Themes

Theme 3 Legacy Ponds and Silo Wastes (Lead: Joe Hriljac/Bill Lee):

Addresses clean-up of UK's biggest safety and security threat; Sellafield legacy ponds and silos, care and maintenance programme for which currently costs UK tax payer approximately £70M per year to maintain their basic condition

Project Title	Type	University
Wasteform Durability		
Durability of heterogeneous ILW glass/ceramic wasteforms from complex wastestreams	PDRA	Imperial
Novel ceramic wasteforms for Cs and Sr encapsulation	PhD[a]	Birmingham
Corrosion of uranium in water and hydrogen	PhD[a]	Bristol
Evolution of grouted waste forms containing uranium	PhD[a]	Bristol
Glass composite materials for Sellafield LP&S ILW immobilisation	PhD[a]	Imperial
Glass composite materials for Fukushima ILW immobilisation	PhD[a]	Imperial
Thermal treatment of Pu-contaminated materials and ILW	PhD[a]	Sheffield
Interaction of brucite surfaces with uranium and its fission products	PhD[a]	UCL /Manchester
Effluent Treatment and Analysis		
Novel ion exchange materials	PDRA	Birmingham
Magnetic nanoparticles for waste separation or sequestration	PhD	Imperial
Enhanced shear micro- and ultra-filtration without recycle pumping	PhD	Loughborough
New ion exchange materials for effluent clean-up	PhD[a]	Birmingham
Pond and Silo Sludges		
Measurement and modelling of sludge mobilisation and transport	PDRA	Leeds
Gas retention and release from nuclear legacy waste	PhD	Leeds
Development of Raman spectroscopy techniques for the remote analysis of nuclear wastes in storage	PhD	Bristol
Computational simulations of storage pond sludge disturbance	PhD	Lancaster
Characterisation of flocculated waste suspensions with acoustic backscatter	PhD	Leeds
Autonomous systems for nuclear decommissioning in extreme radiation environments	PhD	Manchester
The development of characterisation techniques for intermediate level waste sludges	PhD[a]	Leeds
Modelling hydrogen generation from radioactive sludges	PhD[a]	Queen's Belfast
Irradiated sludges – experimental	PhD[a]	Queen's Belfast

Project Impact: Technical Work Packages/Themes

Theme 3 Legacy Ponds and Silo Wastes – Notable Achievements:

- Prototype acoustic backscatter measurement technique for monitoring suspended sediment particles in water being installed in legacy fuel storage pond at Sellafield to allow improved design of waste processing options
- Modelling and measurement work on slurry transport and deposition providing input to process design (single pipe blockage can take several weeks to recover and can cost tens of millions of pounds). According to Sellafield, technology being developed could accelerate 7 year hazard reduction programme (emptying of tanks) by more than 1 year, with multi-million pound savings
- Technical advice given regarding design of new Sellafield SIXEP (Site Ion Exchange Effluent Plant) Contingency Plant for waste slurry discharges based on slurry modelling and experimental work performed
- Gas hold-up work informing case and operational planning at Sellafield for raw waste storage. Fundamental to maximising store capacity pending geological disposal and underpins waste monitoring strategy. Potential to avoid generation of several hundred waste packages
- Successful knowledge transfer of slag formulation development for treatment of Pu-contaminated materials to industry, and validation of vitrified products from pilot scale melter experiments

Project Impact: Technical Work Packages/Themes

Theme 4 Structural Integrity (Lead: Rebecca Lunn):

Addresses challenge of ageing nuclear infrastructure, and how to ensure continued safety of workforce involved in nuclear decommissioning and management. Aim is to develop reliable systems for nuclear infrastructure characterisation, restoration and preservation

Project Title	Type	University
Physical Ground Barriers for In-Situ Contaminant Containment		
In-situ ground contaminant containment (physical barrier)	PDRA	Strathclyde
In-situ ground contaminant containment (physical barrier)	PhD	Strathclyde
Development of novel, low cost biomineral permeable reactive barriers for radionuclide remediation	PhD[a]	Strathclyde
Remote Crack Detection, Infrastructure Health Prediction and Building Preservation		
Nano-cracking of cement phases: reactivity and dissolution	PhD	Strathclyde
Crack sealing and water transport	PhD	Strathclyde
Monitoring of moisture and chloride in contaminated storage structures	PhD	Strathclyde
Simulating radiation damage in cement	PhD[a]	Queen’s Belfast
Impact of recycled concrete fines on the engineering performance of cementitious infill	PhD[a]	Leeds
Development and Real-time Management of Autonomous Systems for Decommissioning		
Production real-time segmented as-built CAD models for planning/execution remote and human intervention tasks	PhD	Birmingham

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Project Impact: Technical Work Packages/Themes

Theme 4 Structural Integrity – Notable Achievements:

- Developed model of silica grout gelling that enables control of grout gel time from minutes to 10s of hours. Model accounts for in-situ soil and groundwater conditions and provides flexibility for innovative grout use, e.g. injection of horizontal barriers requiring much longer gel times
- Developed grout gelling model validated against data from laboratory-based colloidal silica injection into fine sands at metre scale
- Case submitted to ARPANSA (Australian nuclear regulator) and gained approval to conduct colloidal silica-based field trial for grouting legacy waste trenches at Little Forest Legacy Site, Sydney. Mock waste trench to be constructed and grouted in-situ with colloidal silica. Results of trial will be used to underpin future options for long-term site management
- Developed novel repair strategies for degraded concrete infrastructure. Repair strategy based on application of silica nanoparticles to repair cracks in cement storage ponds. Aim is to restore strength and inhibit water seepage
- Demonstrated that cement structure (C-S-H gel) can be tailored to sorb radionuclides into cement matrix

4th Annual Meeting: Agenda

- Impact-focused technical presentations on each of 4 research themes, and 4 associated technical presentations
- Impact presentation, and industrial perspective of impact of DISTINCTIVE programme
- Technical poster presentations for viewing during breaks
- PhD award for best poster presentation will be presented at end of Wednesday. Don't forget to vote!

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4th Annual Meeting: Objectives

- Facilitate knowledge transfer, enabling our researchers to share advances made, and to engage with industry experts and potential employers
- Provide networking opportunities between academia, industry, government and regulatory authorities
- Promote the uptake of DISTINCTIVE research into the nuclear waste management and decommissioning industry
- Generate new collaborative research ideas

I hope that you enjoy the meeting

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Characterisation of Uranium Mineral Phases by Time-Resolved Laser Fluorescence and Raman Spectroscopy

Victoria L. Frankland[1], Rachida Bance-Soualhi[1] and David Read[1,2]
[1)] University of Surrey, Guildford, UK; [2)] National Physical Laboratories, Teddington, UK

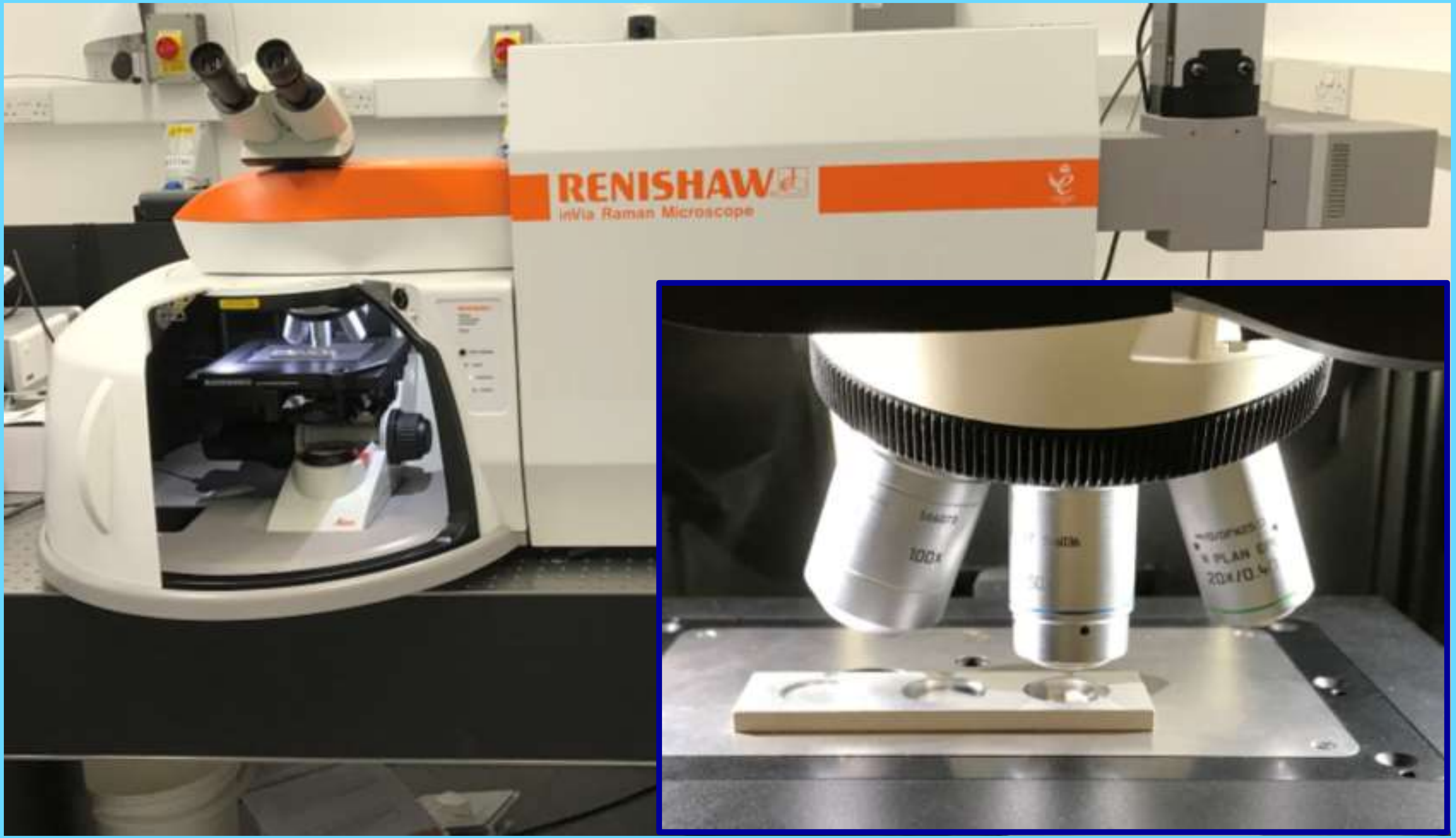
Aim

- Create a spectral database for non-destructive identification of U species from operational & legacy nuclear sites.
  - Reference spectra from high quality type mineral phases
  - Applied to amorphous & ultra-thin surface alteration products
  - Method also capable of characterising aqueous & non-aqueous solutions

- Limitations with conventional techniques for U phase ID:
  XRD - requires good crystallinity
  IR spectroscopy - spectra masked by water features
  Non-(trans)portable techniques

- Techniques chosen:
  - Time-Resolved Laser Fluorescence Spectroscopy (TRLFS)
  - Raman Spectroscopy

Raman Spectroscopy

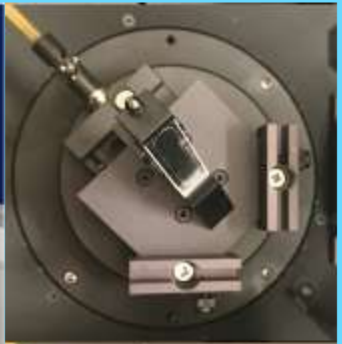


- 5 Lasers:
  - 244 nm (UV)
  - 457 nm (blue)
  - 532 nm (green)
  - 633 nm (red)
  - 785 nm (IR)

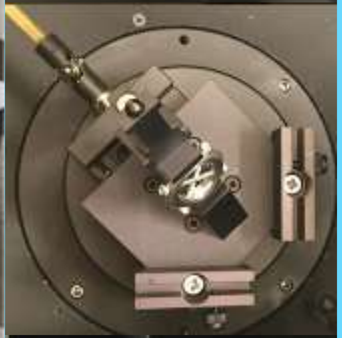
- Powders and Clusters

- Alternative stage for solutions

Time Resolved Laser Fluorescence Spectroscopy (TRLFS)



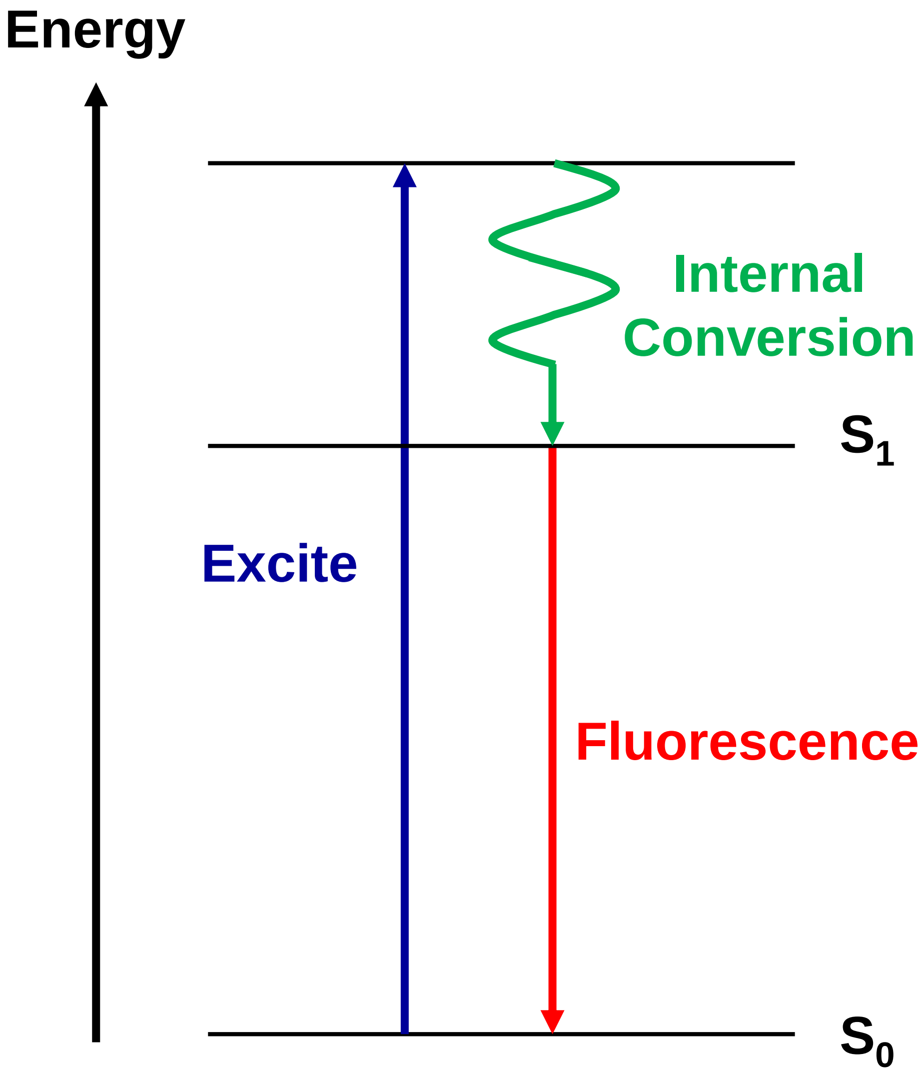
Powders

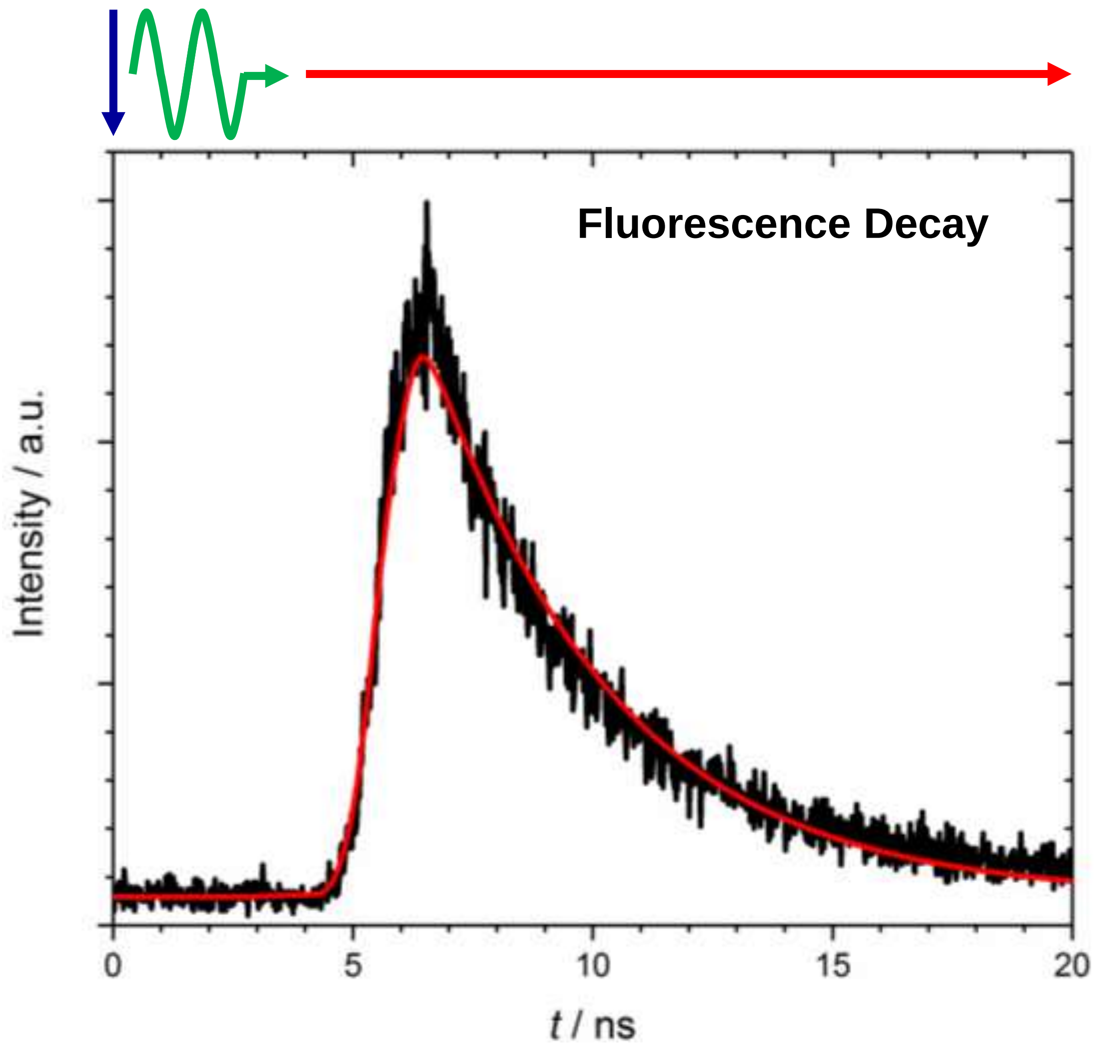


Clusters

Solutions

Fluorescence





U Minerals and Analytical Grade Powders

Oxides:
- Hydrous uranate
- Uraninite
- Uraninite (part oxidised)
- Uranium trioxide

Metal Oxides
- Davidite (La,Ce,Ca,Y,Ti,Fe)
- Fourmarierite (Pb)
- Masuyite (Pb)
- Vandenbrandite (Cu)

Arsenate (AsO_4):
- Novacekite

Carbonates (CO_3):
- Rutherfordine

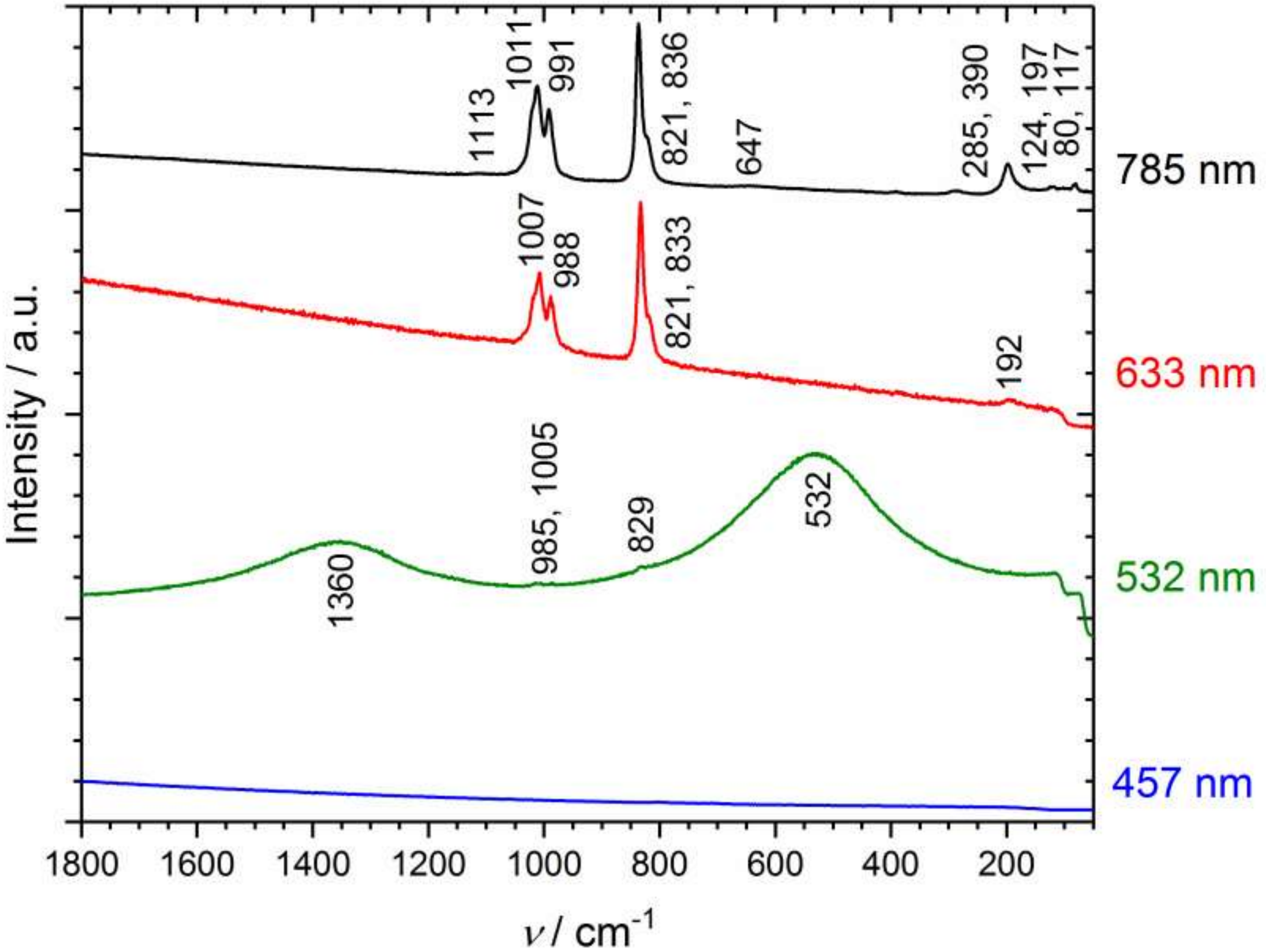
Phosphates (PO_4):
- Bassetite
- Meta-autunite
- Meta-torbernite
- Saleeite

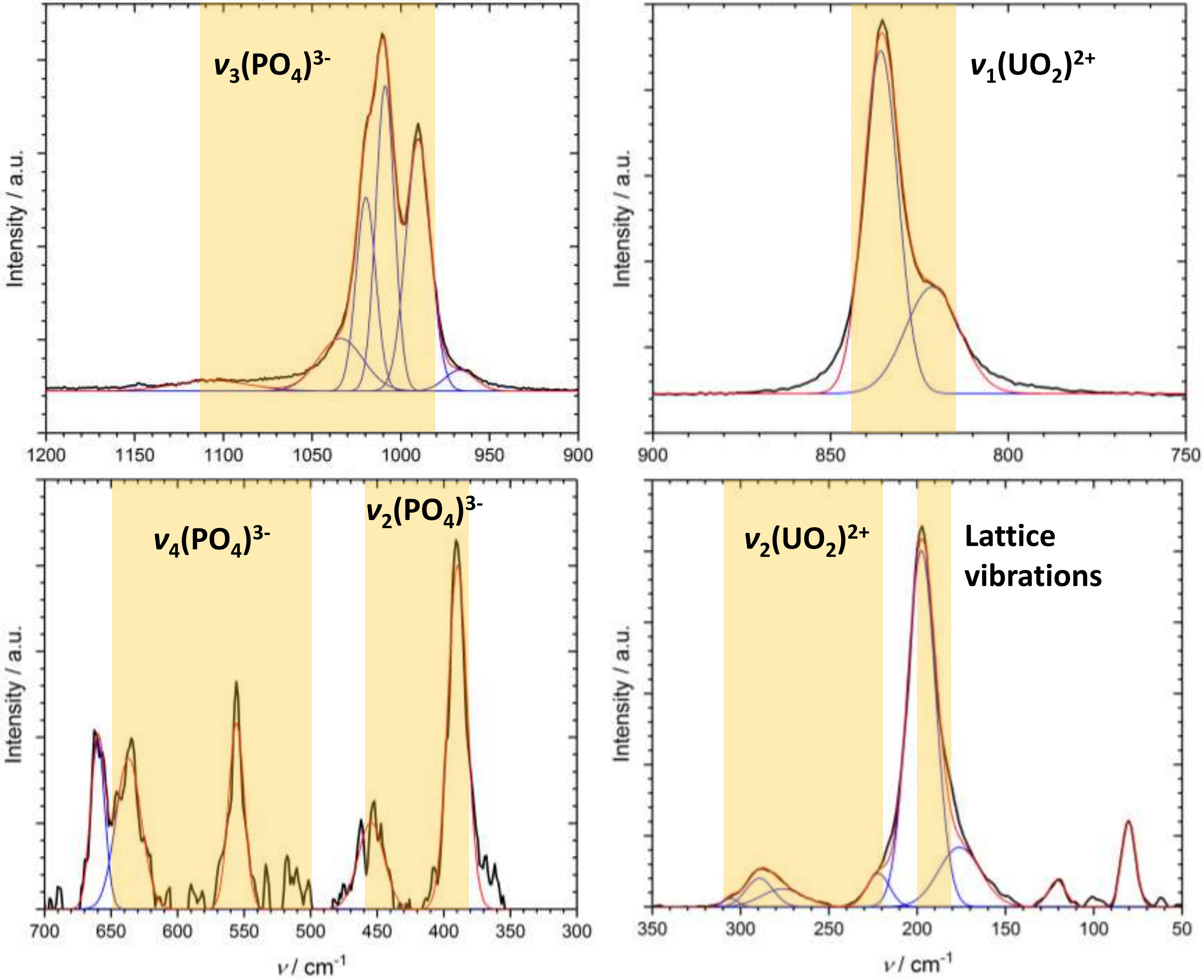
Silicates (SiO_4):
- Boltwoodite
- Cuprosklodowskite
- Kasolite
- Soddyite
- Uranophane - beta

Sulfates (SO_4):
- Johannite
- Uranyl sulfate
- Zippeite

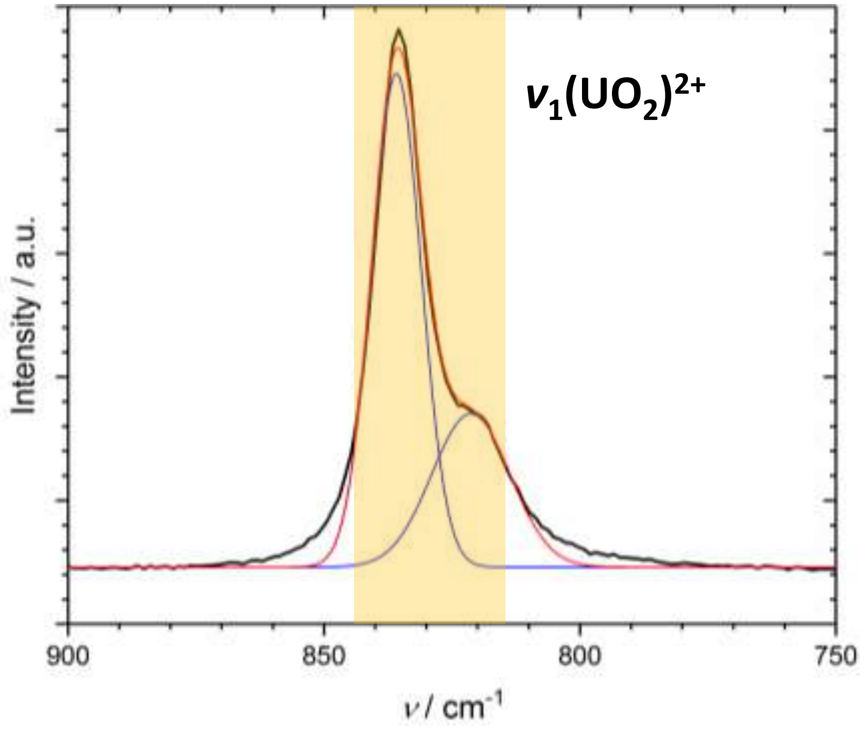
Vanadate (VO_4):
- Carnotite
- Tyuyamunite

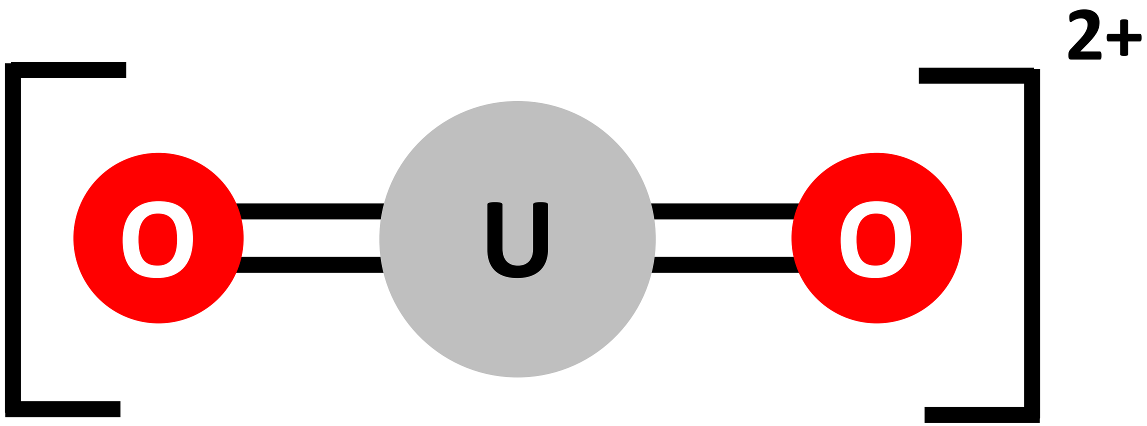
Raman: Meta-autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 6\text{-}8(H_2O)$)





1) Stefaniak, *et al.*, (2009)
2) Frost, (2004)
3) Frost & Weier, (2004)





$d_{U\text{-}O}$ (Å) = 106.5 $[v_1(UO_2)^{2+}]^{-2/3}$ [1]

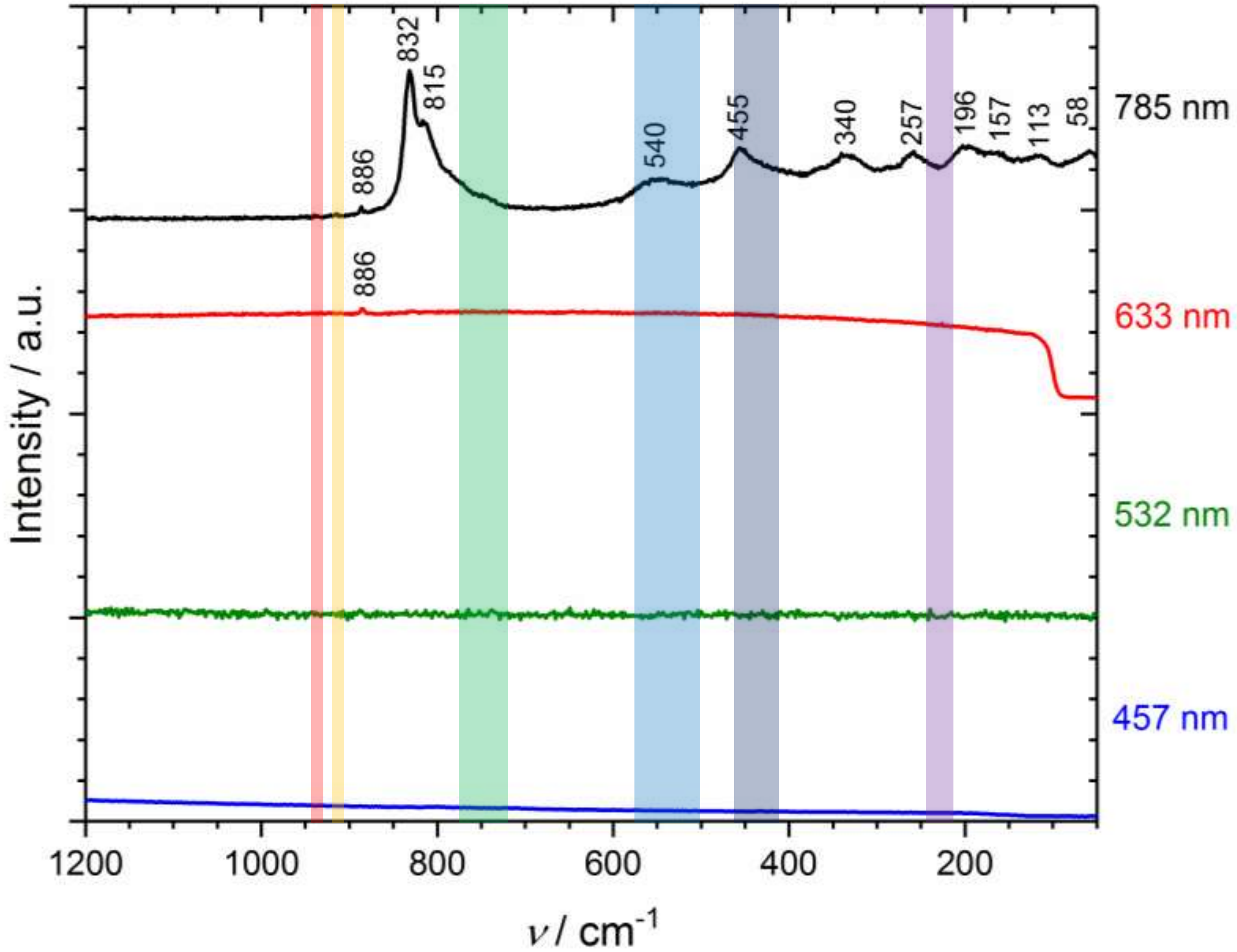
$k_{U\text{-}O}$ (mdyn $Å^{-1}$) = $[1.08 / (d_{U\text{-}O} - 1.17)]^3$ [2, 3]

$v_3(UO_2)^{2+}$ (cm^{-1}) = $[91.41 / (d_{U\text{-}O} - 0.804)]^{3/2}$ [1]

$v_1(UO_2)^{2+}$ / cm^{-1}	836 (dominant)	821 (shoulder)
$d_{U\text{-}O}$ / Å	1.78	1.79
$k_{U\text{-}O}$ / mdyn $Å^{-1}$	5.69	5.29
$v_3(UO_2)^{2+}$ / cm^{-1}	913	893

1) Bartlett & Cooney, (1989); 2) Badger, (1935); 3) Jones, (1959)

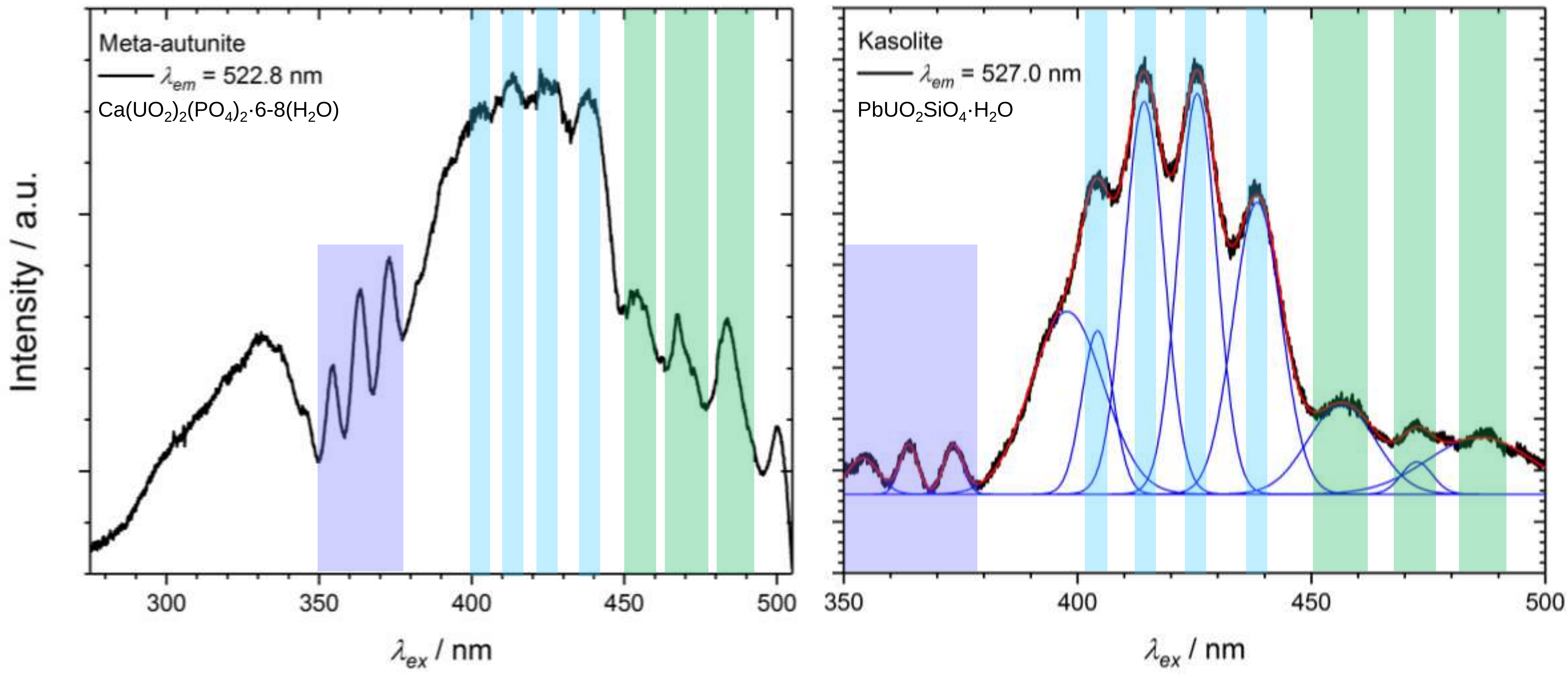
Raman: Kasolite ($PbUO_2SiO_4 \cdot H_2O$)



Assignment	This work	Literature [1-3]
$\nu_3(SiO_4)^{4-}$	-	~ 940
$\nu_1(SiO_4)^{4-}$	-	~ 910
$\nu_1(UO_2)^{2+}$	832 815	750-770 721
$\nu_4(SiO_4)^{4-}$	540	500-575 (multiple)
$\nu_2(SiO_4)^{4-}$	455	415-455
$\nu_2(UO_2)^{2+}$	257	215-240

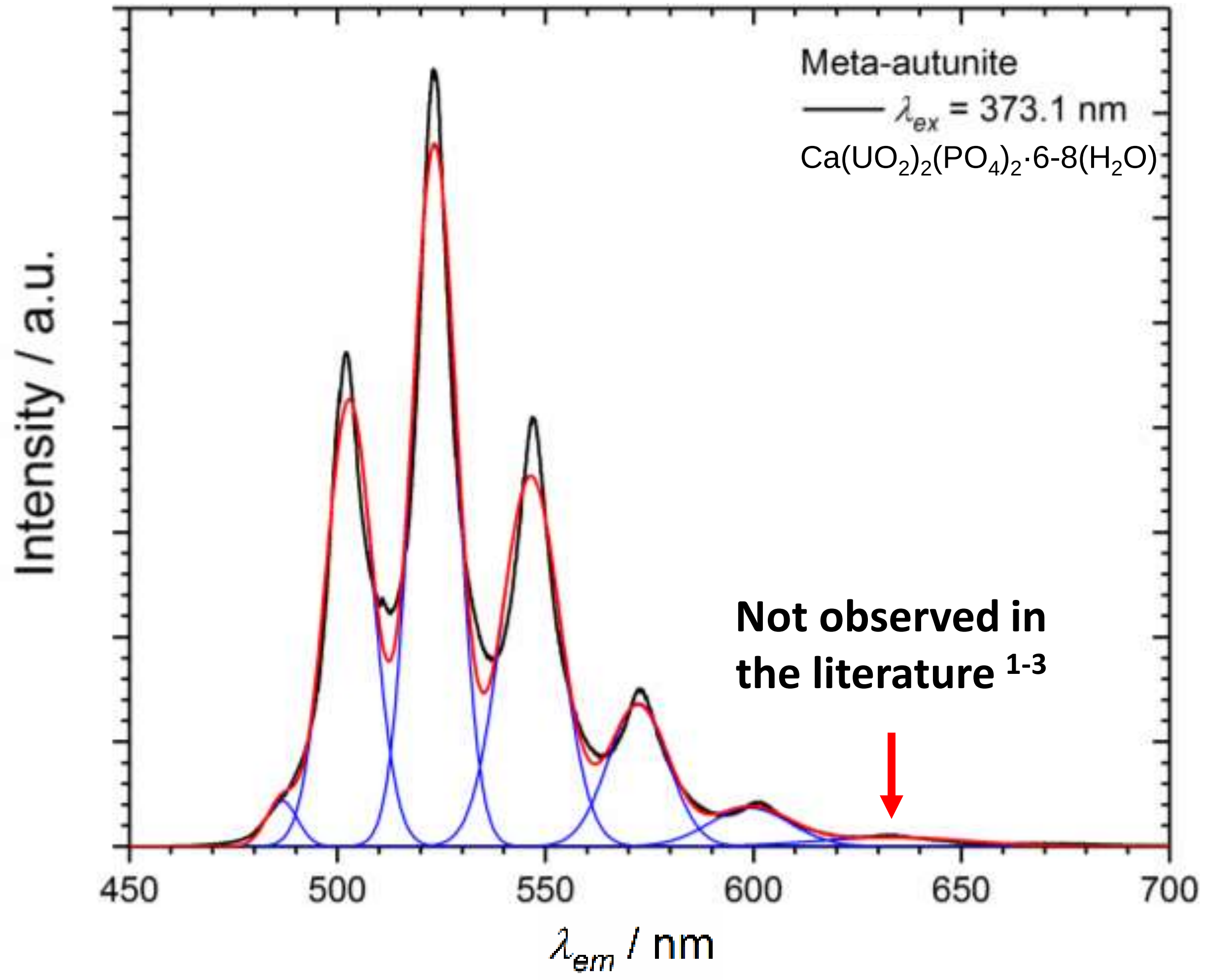
1) Frost, *et al.*, (2006)
2) Driscoll, *et al.*, (2014)
3) Bonales, *et al.*, (2015)

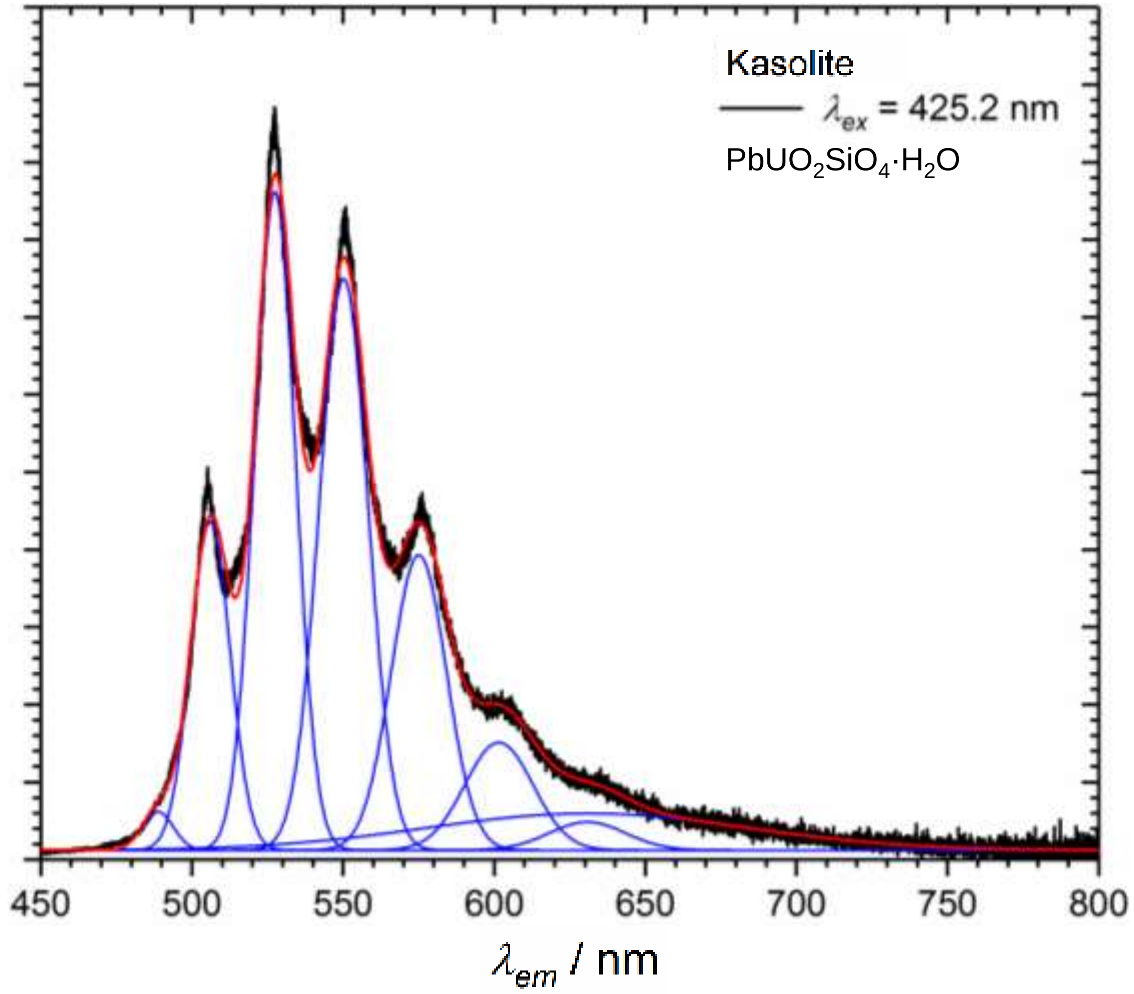
Fluorescence Excitation Spectra



λ_{ex} = 354.1, 363.9, 373.5, 397.8, 404.3, 414.2, 425.6, 438.4, 456.5, 472.6 and 486.1 nm

Fluorescence Emission Spectra



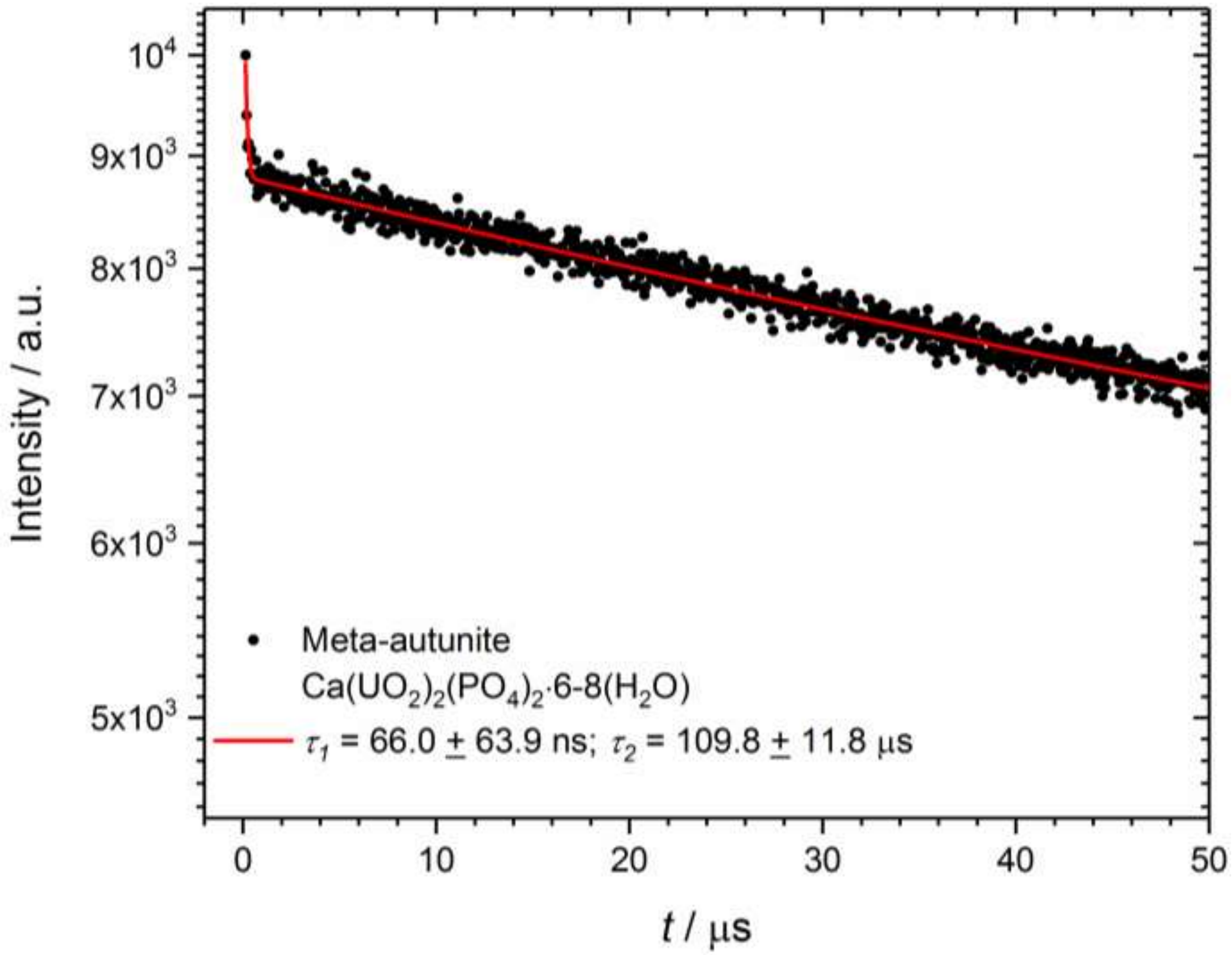


λ_{em} = 486.7, 502.8, 523.3, 546.5, 572.3, 599.1 and 633.5 nm (literature agreement [1-3])

λ_{em} = 488.8, 506.1, 527.4, 550.2, 575.1, 601.6 and 630.9 nm (literature agreement [4])

1) Geipel, *et al.*, (2000); 2) Baumann, *et al.,* (2006); 3) Baumann, *et al.,* (2008); 4) Wang, *et al.*, (2005)

Fluorescence Decay: Meta-autunite

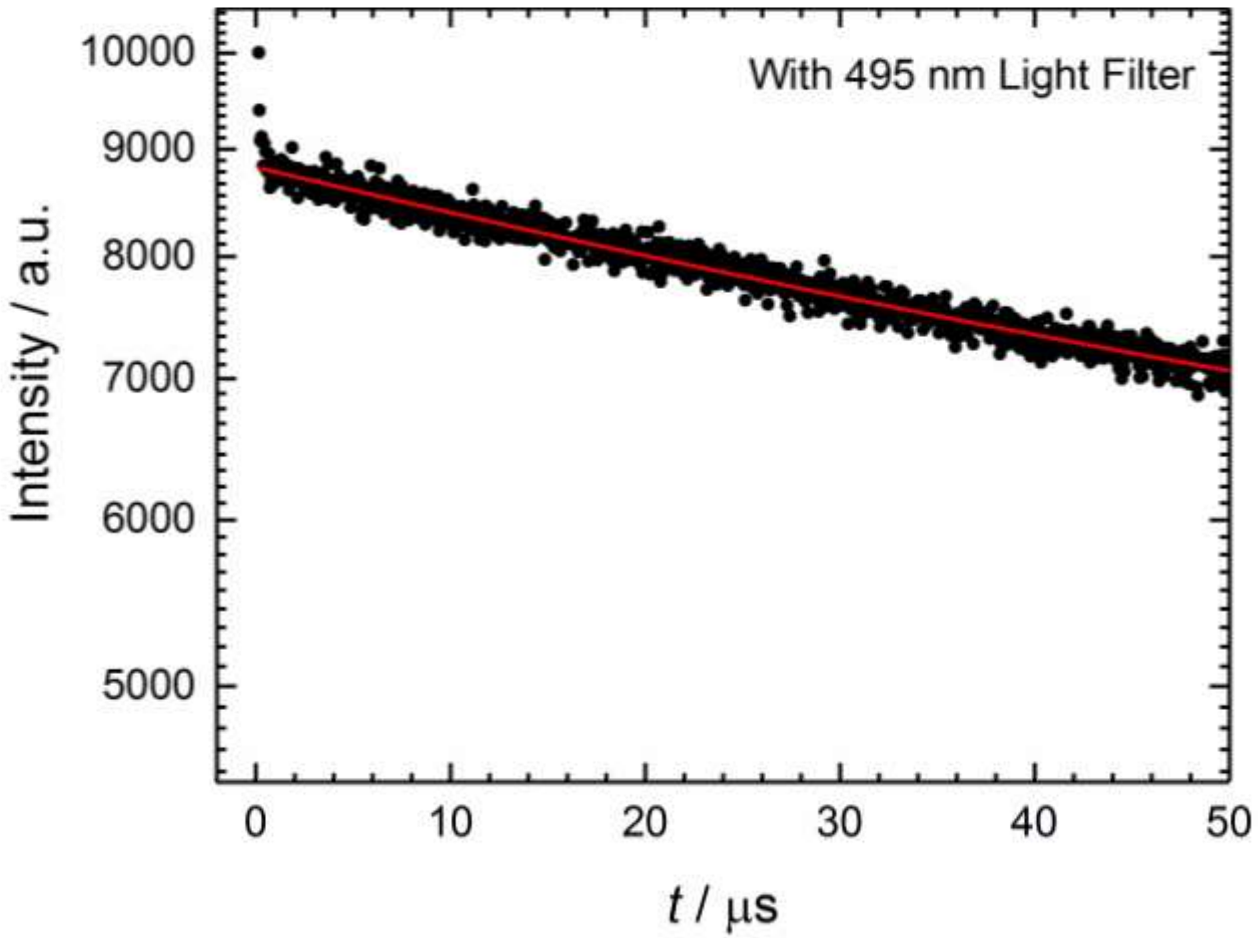


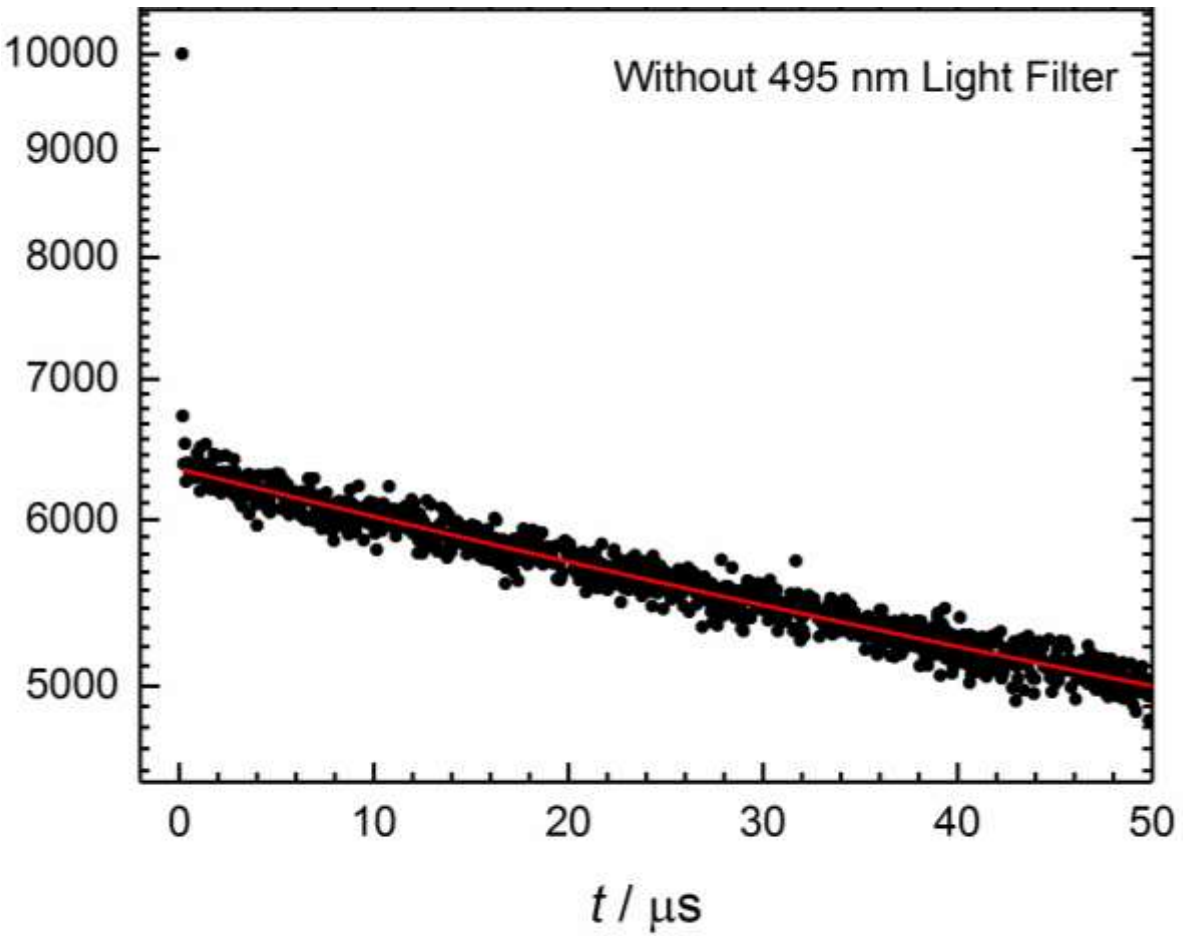
λ_{ex} = 357.6 nm
λ_{em} = 522.8 nm

	τ / μs
This Study	100.2 ± 9.4 OR 0.101 ± 0.146 0.912 ± 0.828 137.4 ± 22.1
[1]	0.740 ± 0.100
[2]	0.043 ± 0.004 0.740 ± 0.100
[3]	0.410 ± 0.015 3.300 ± 0.310

1) Geipel, *et al.,* (2000); 2) Baumann, *et al.*, (2006); 3) Baumann, *et al.*, (2008)

Fluorescence Decay: Meta-autunite





Future Work

- TRLFS and Raman spectroscopy + XRD, SEM/EDX
  - Analytical grade U compounds
  - Minerals from: - British Geological Survey
    - National Museum of Wales
    - Natural History Museum

  ⇨ Reference Collection Database

- TRLFS and Raman spectroscopy of solutions

- Real time simulation of U corrosion

- Assess feasibility of remote environmental measurements

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SEM-EDX David Jones
TRLFS Craig Graham (Edinburgh Instruments)

Loan of minerals Kay Green (British Geological Survey)
Tom Cotterell (National Museum of Wales)
Mike Rumsey (Natural History Museum)

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Thank you all for listening

Paper 18132, Session 100

The DISTINCTIVE University Consortium: Theme 2: PuO_2 and Fuel Residues

L.Boast[a], L.Jones[b], D.Laventine[c], N.Palmer[d], R.Sawar[c], S.Sutherland-Harper[b], S.K.Sun[a], B.Tegner[b], S.Thornber[a], J.Wellington[e], **C. Boxall[c]**, P.Cook[f], C.L.Corkhill[a], J.W.Hobbs[f], N.C.Hyatt[a], M.J.Joyce[c], N.Kaltsoyannis[b], A.Kerridge[c], F.R.Livens[b], R.Orr[g], S.M.Pimblott[b], M.Read[d], H.Steele[f], M.C.Stennett[a], R.J.Taylor[g], D.Woodhead[g]

[a]Dept. of Materials Science & Engineering, University of Sheffield, Sheffield S1 3JD, UK; [b]School of Chemistry, University of Manchester, Manchester M13 9PL, UK; [c]Dept. of Engineering / Dept. of Chemistry, Lancaster University, Lancaster LA1 4YR, UK; [d]School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK; [e]Dept. of Chemistry, University College London, London WC1H 0AJ, UK; [f]Sellafield Ltd, Sellafield Site, Seascale, Cumbria CA20 1PG UK UK; [g]National Nuclear Laboratory, Central Laboratory, Seascale, Cumbria CA20 1PG UK

MANCHESTER 1824 The University of Manchester

Lancaster University

UCL

The University Of Sheffield.

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- 10 Universities
- 3 Industrial partners: NNL, NDA, and Sellafield Ltd
- 53 research projects

- Theme 1 - AGR, Magnox and Exotic Spent Fuels
- **Theme 2 - PuO_2 and Fuel Residues**
- Theme 3 - Silo Ponds and Legacy Wastes
- Theme 4 - Structural Integrity

Theme 2 – Introduction, Aims & Objectives

- The UK has a civil inventory of an eventual 140 tonnes of separated Pu from the reprocessing of Magnox and AGR spent fuels.
- UK HMG's preferred option is re-use as MOX or Pu-rich metallic fuel
- ~5% of stockpile is not suitable for reuse and is recommended for direct disposal.
- Will take >15 years to implement re-use, requiring UK Pu is kept in its current state for that period *i.e.* as PuO_2 powder in interim storage cans at Sellafield.

Aim. To provide technical underpinning to the ongoing development of options for the UK's stockpile of separated plutonium

Work Packages & Objectives.

- **WP1 Interim Storage:** To understand how structure & properties of PuO_2 change with time in the presence of H_2O, and the roles these processes play in gaseous product evolution from PuO_2 in storage
- **WP2 Disposition:** To understand radiation induced amorphisation & dissolution kinetics of Pu wasteforms
- **WP3 Characterisation**: To develop novel, fast neutron based radiometric methods for the quantification, isotopic composition assessment & remote imaging of Pu-bearing materials.

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WP1: PuO_2 during Interim Storage

Interim storage of PuO_2 involves sealing in inert steel containers. Under certain circumstances, these cans may pressurise; must be avoided in practice.

"worker performing general housekeeping and relocating storage cans in the interim storage vault noticed plutonium bearing storage can was ***bulging on both ends*** " – Lawrence Livermore National Laboratory 1994

5 routes to gas production have been suggested:

(i) Helium accumulation from α decay;

(ii) Decomposition of polymeric packing material;

(iii) H_2O desorption (steam) from hygroscopic PuO_2;

(iv) Radiolysis of adsorbed water;

(v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

Last 3 all involve PuO_2/H_2O interactions and are complex, inter-connected and poorly understood. Investigate by modelling and experiment

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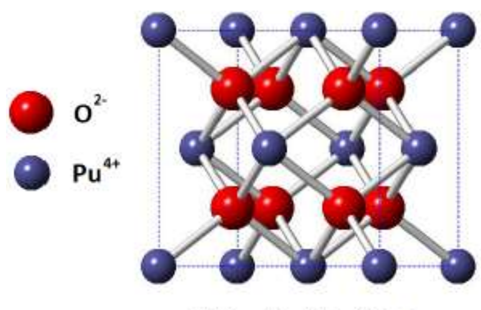
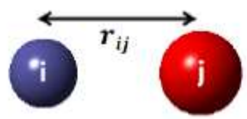
WP1: Modelling water adsorption on UO_2 & PuO_2

- **First approach** – static, free energy and molecular dynamic simulation techniques employing pair potentials refined and developed by **Mark Read – Birmingham**
- Potentials derived empirically by fitting to crystal structure and basic mechanical & optical properties
- Then used to predict other properties of material by energy minimisation of bulk structure & surfaces



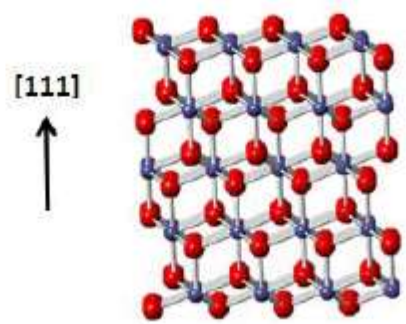
Unit cell of Pu(IV) O_2



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

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

- Implementation by **Nathan Palmer – Birmingham** indicates that stability of most common crystal faces runs
- (111) > (110) > (100)



Surface	E_{Surf}^{Rel} (Jm^{-2})
(100)	549.24
(110)	2.07, 1.539[a]
(111)	1.32, 1.069[a], 1.33[b]
(210)	3.06, 3.35[b]
(211)	2.30
(221)	1.63, 1.65[b]
(310)	3.09, 3.30[b]
(311)	2.62, 2.94[b]
(331)	1.74, 1.76[b]

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

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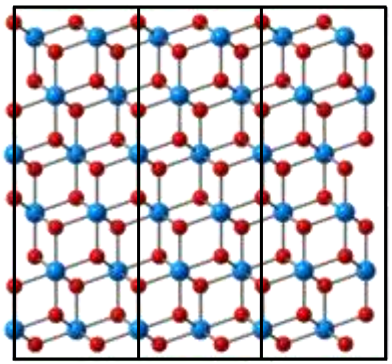
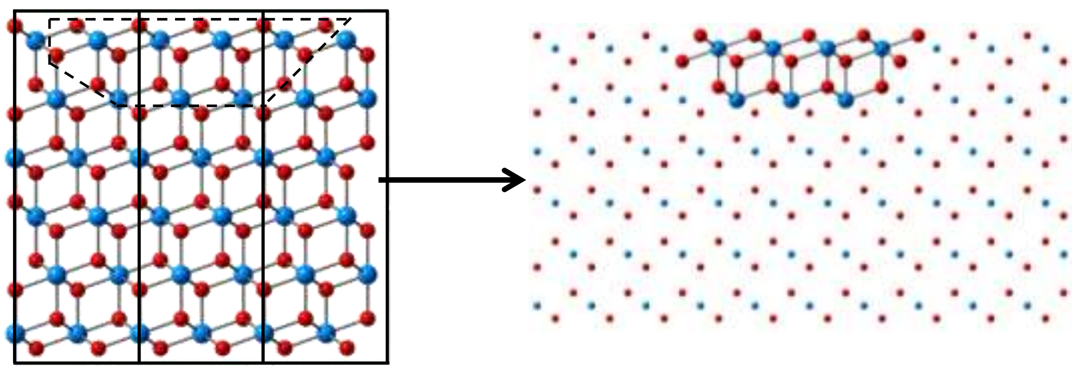
WP1: Modelling water adsorption on UO_2 & PuO_2

Second approach: The interaction of water with the low index {111}, {110} and {100} surfaces of UO_2 and PuO_2 are modelled quantum mechanically using density functional theory at the embedded cluster (**Joe Wellington – UCL**) and periodic boundary condition (**Bengt Tegner – Manchester**) levels.



- Density functional theory (DFT) with periodic boundary conditions (PBC); use a repeating unit cell to represent the bulk solid or surface
- Problem: Best flavours of DFT are computationally very demanding

- Periodic Electrostatic Embedded Cluster Method (PEECM)
- Define a cluster to be treated quantum mechanically with hybrid DFT (PBE0)

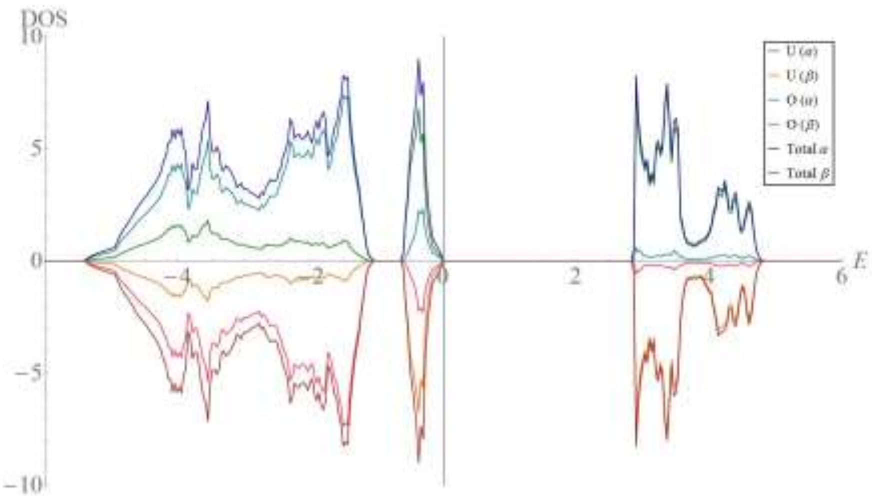


- Embed the cluster in an infinite array of point charges
- Point charges recreate the long-range Coulombic interactions and reproduce the Madelung potential in the cluster

WP1: Modelling water adsorption on UO_2 & PuO_2

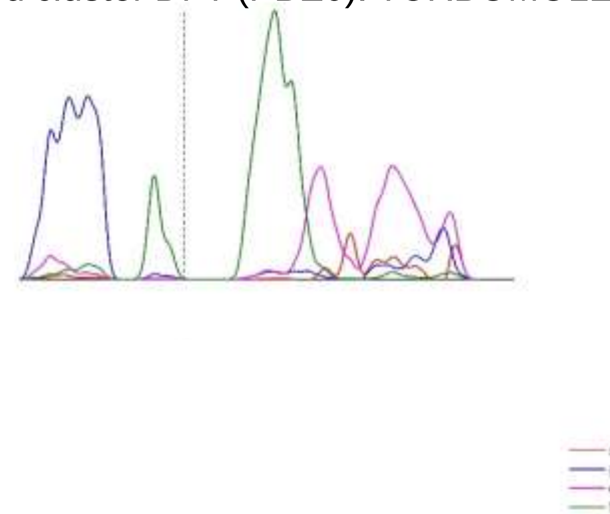
Benchmarking the bulk: density of states for AnO_2 (An = U, Np, Pu)

Periodic DFT (PBE+*U*, *U* = 4 eV). VASP.



Embedded cluster DFT (PBE0). TURBOMOLE.

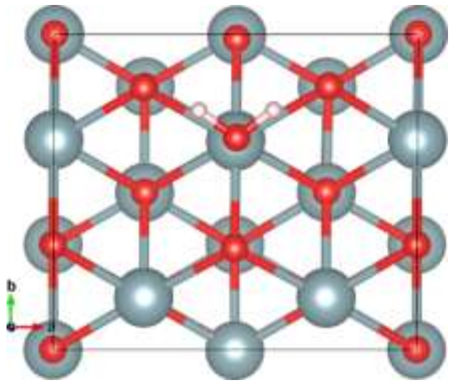
UO_2:
Mott-Hubbard
insulator



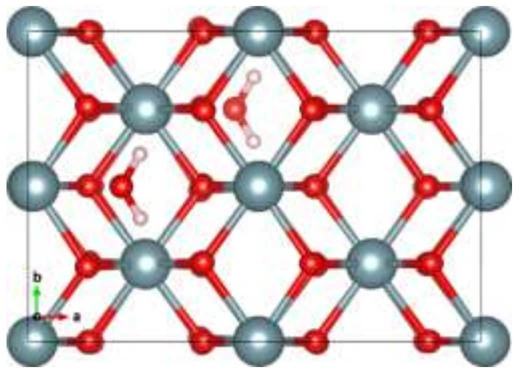
WP1: Modelling water adsorption on UO_2 & PuO_2

Three types of surface modelled for each actinide oxide:

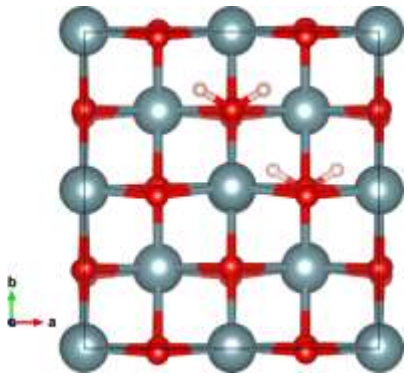
(111)



(110)



(100)



Five types of adsorption modelled at each surface:

Purely Molecular:	4 x (H_2O)
Mixed Molecular / Dissociative:	3 x (H_2O) and 1 x (H + OH)
Mixed Molecular / Dissociative:	2 x (H_2O) and 2 x (H + OH)
Mixed Molecular / Dissociative:	1 x (H_2O) and 3 x (H + OH)
Purely Dissociative:	4 x (H + OH)

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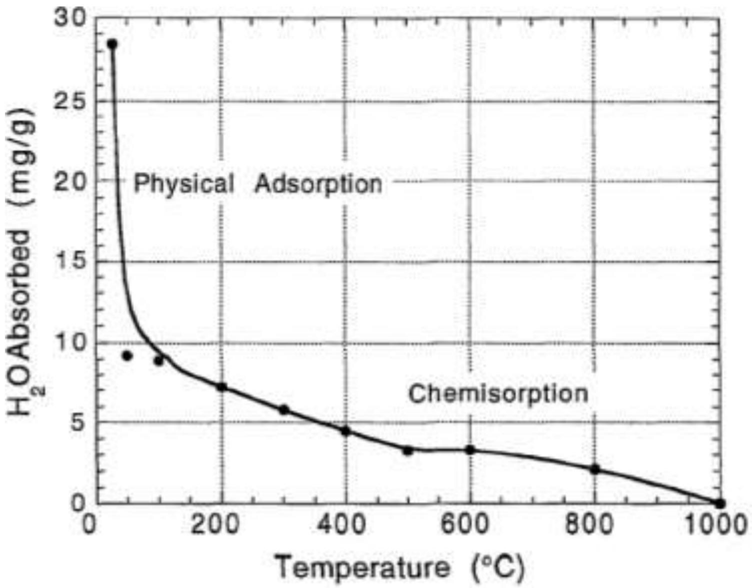
WP1: Modelling water adsorption on UO_2 & PuO_2

Modelled desorption temperatures

	{111} + $2H_2O$ + 2(OH + H)		{110} + 4(OH + H)		{100}	
p	UO_2	PuO_2	UO_2	PuO_2	UO_2 + H_2O + 3(OH + H)	PuO_2 + 4(OH + H)
10^{-13}	138	120	228	208	271	302
10^{-7}	186	162	301	276	356	396
1	300	265	472	434	555	615
3	313	277	490	452	577	638
5	319	282	499	460	587	650



Desorption temperatures from {111} are low ⇒ no water on PuO_2 {111} in the storage cans

Stakebake[1] found (experimentally) two distinct temperature ranges for water desorption from PuO_2, interpreted as
373-423 K: weakly bound second layer (or above) waters
573-623 K: waters bound directly to the PuO_2 surface

Could the lower temperature range be due to desorption from the {110} surface monolayer and the higher to {100}?

[1] J.L. Stakebake *J. Phys. Chem.* **77** (1973) 581-586

Outputs:

J.P.W. Wellington, A. Kerridge, J.P. Austin and **N. Kaltsoyannis** *J. Nucl. Mat.* **482**, 2016, 124 (DOI: 10.1016/j.jnucmat.2016.10.005).
B.E. Tegner, M. Molinari, A. Kerridge, S.C. Parker and **N. Kaltsoyannis** *J. Phys. Chem. C* 2017 (DOI: 10.1021/acs.jpcc.6b10986).
Highlighted in ‘Nuclear power in the 21st century’ by **N. Kaltsoyannis** and S.T. Liddle. *Chem* **1,** 2016, 652–662. Invited *Catalyst* article – see also reaction pieces by Dame Sue Ion and Dr Robin Taylor.
Chosen as a case study in the annual report to EPSRC of the Materials Chemistry High Performance Computing Consortium.

WP1: Measuring water adsorption on UO_2 & ThO_2

- The **Quartz Crystal** Nanobalance (QCN) measures in-situ mass changes at the surface of a piezoelectrode. Changes in mass, due to oxide formation or dissolution at the electrode surface or adsorption / desorption of gases, result in resonant frequency changes of the quartz crystal.
- Changes in frequency can be related to changes in mass through the Sauerbrey equation:

$$\Delta f = -\left(\frac{n f_0^{\,2}}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

- Knowing the surface area of the metal oxide layer and the mass of water absorbed allows the number of layers to be accurately calculated.
- The differences in temperature at which water absorption/desorption occurs allows the thermodynamics to be determined, indicating which layers are chemi- or physio-sorbed.
- Studies of water adsorption at the surfaces of UO_2, ThO_2 and CeO_2 layers as PuO_2 surrogates being conducted by **Dom Laventine** – Lancaster
- Work about to move to Central Lab for studies on real PuO_2 samples

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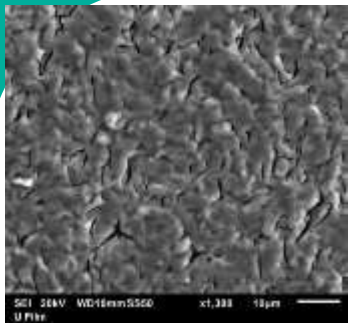
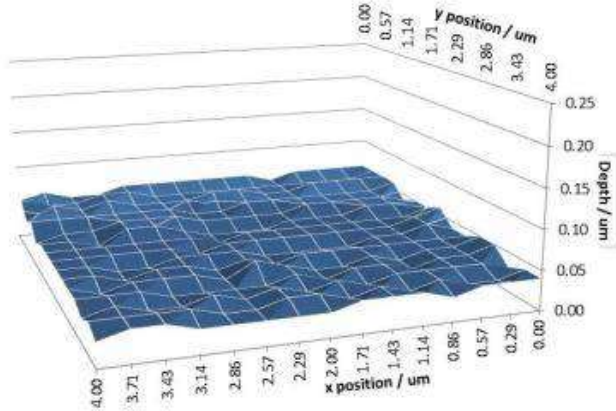
WP1: Measuring water adsorption on UO_2 & ThO_2

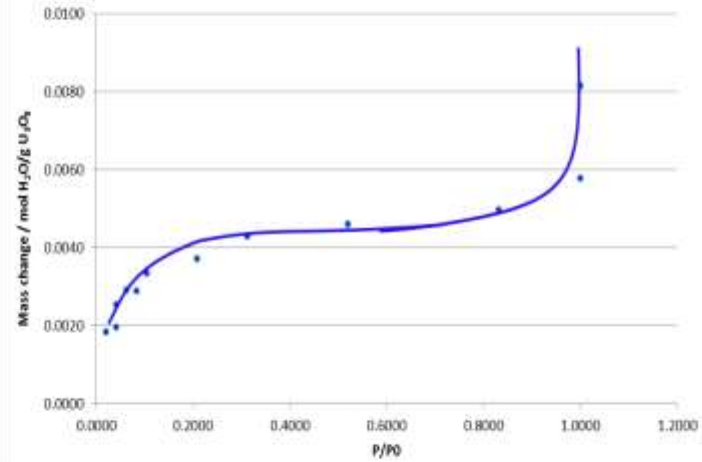


25 ug $U(NO_3)_3$
Calcine.: 1000°C
18 ug U_3O_8 (QCM)
42 nm (XRF)

Calcine.: 500°C
$V_m = 3.10 \times 10^{-12}\ m^3$
$\Delta H_{abs} = 54.1\ kJmol^{-1}$

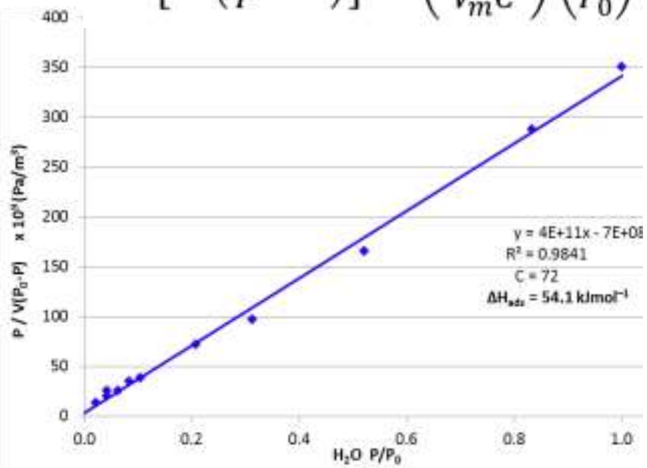
Calcine: 1000°C
$V_m = 1.50 \times 10^{-12}\ m^3$
$\Delta H_{abs} = 48.1\ kJmol^{-1}$

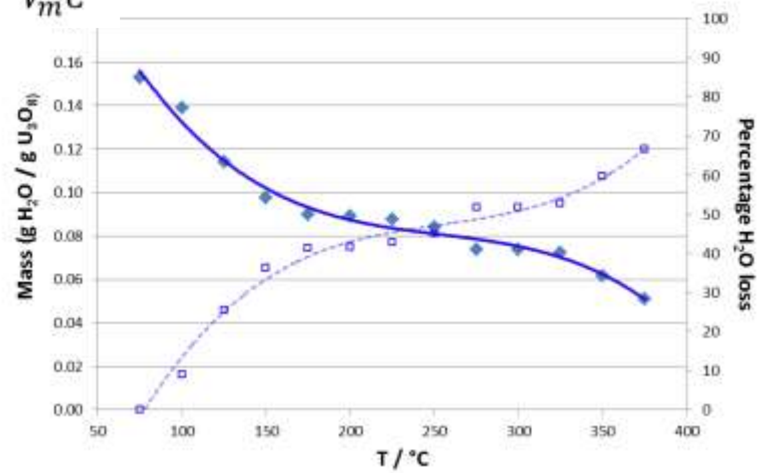




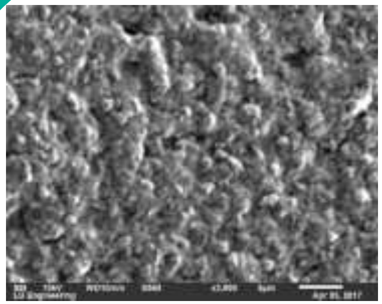
$$1/\left[V_a\left(\frac{P_0}{P}-1\right)\right] = \left(\frac{C-1}{V_m C}\right)\left(\frac{P}{P_0}\right) + \frac{1}{V_m C}$$

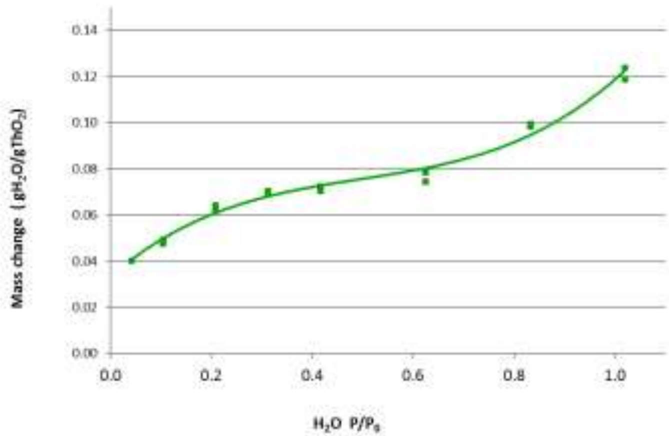
$$C = e^{(\Delta H_{ads} - \Delta H_{liq}/RT)}.$$

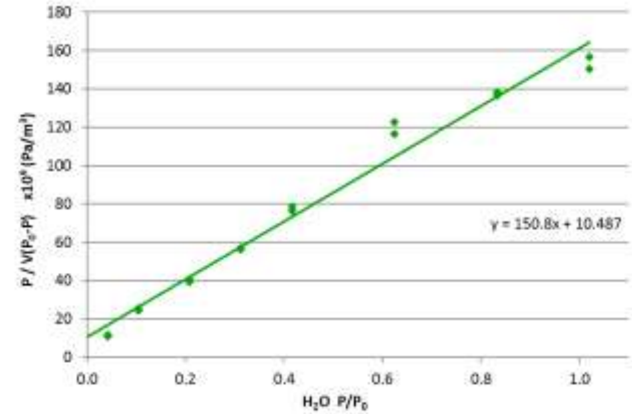




WP1: Measuring water adsorption on UO_2 & ThO_2



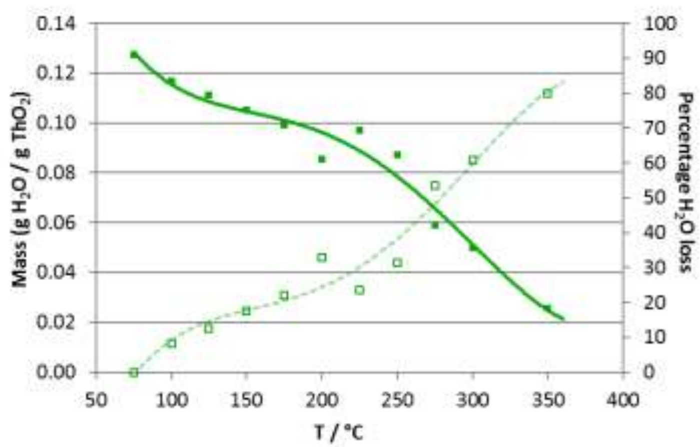


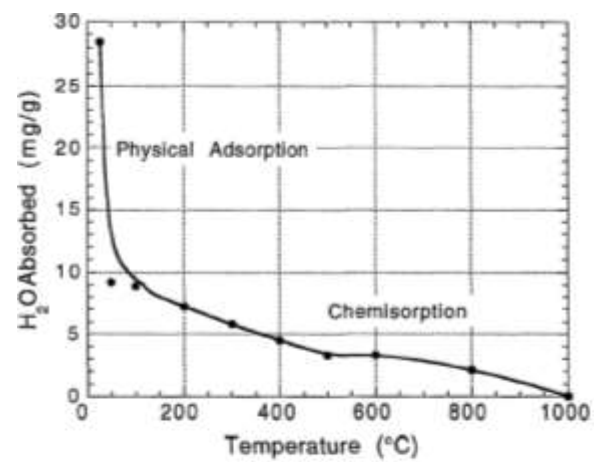


50 ug $Th(oxal)_2$
Calcine.: 1000°C
34 ug ThO_2 (QCM)

$V_m = 1.88 \times 10^{-12}\ m^3$
$SA = 142\ m^2g^{-1}$
$\Delta H_{abs} = 54.6\ kJmol^{-1}$

Close to Paffet range of 44 to 51 $kJmol^{-1}$

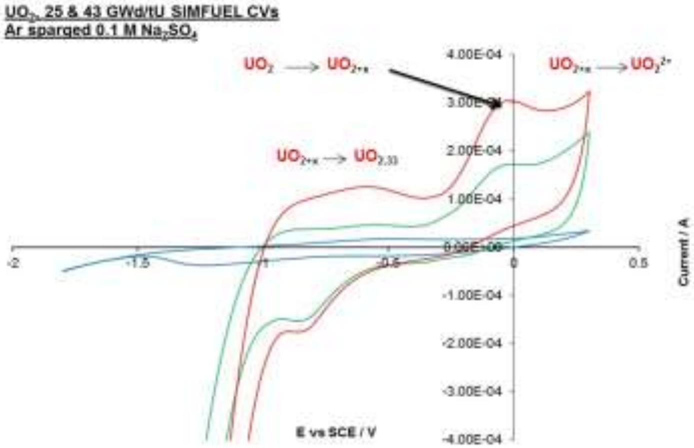


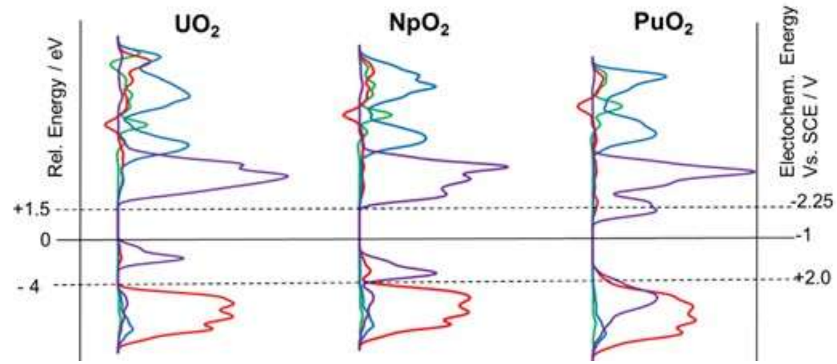


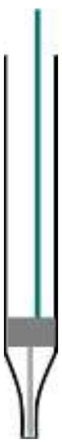
Outputs

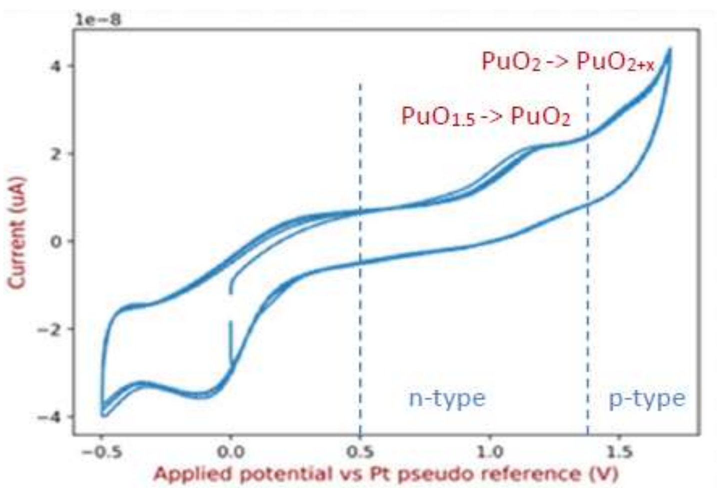
- "Direct mass analysis of water absorption onto ceria thin films", D.Laventine, C.Boxall in "The Scientific Basis of Nuclear Waste Management", N.C.Hyatt, R.Ewing, Y.Inagaki, C.Jantzen (Eds), Cambridge University Press, Cambridge UK, MRS Advances., 6 pages (2017) DOI: 10.1557/adv.2016.671
- "Direct Mass Analysis of Water Absorption onto Ceria Thin Films" D.Laventine, C.Boxall, IChemE Sustainable Nuclear Energy Conference (SNEC) 2016, East Midlands Conference Centre, University of Nottingham, 12th–14th Apr 2016.
- "Direct mass analysis of water absorption onto ceria thin films" D.Laventine, C.Boxall, ATALANTE 2016, Le Courm, Montpelier, France, 5th–10th Jun 2016.

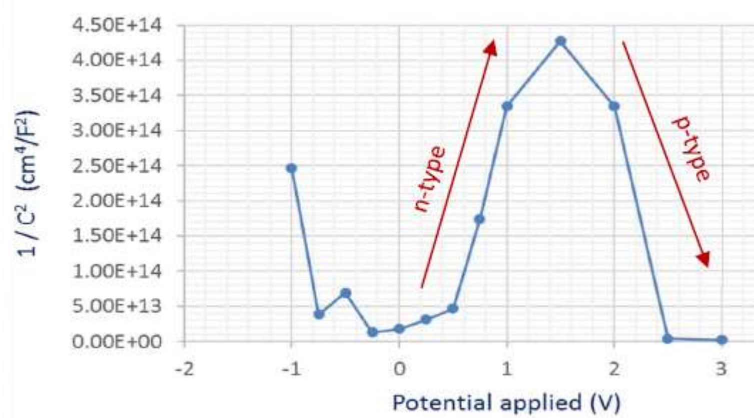
WP1: Electrochemical Study of PuO_{2+x}









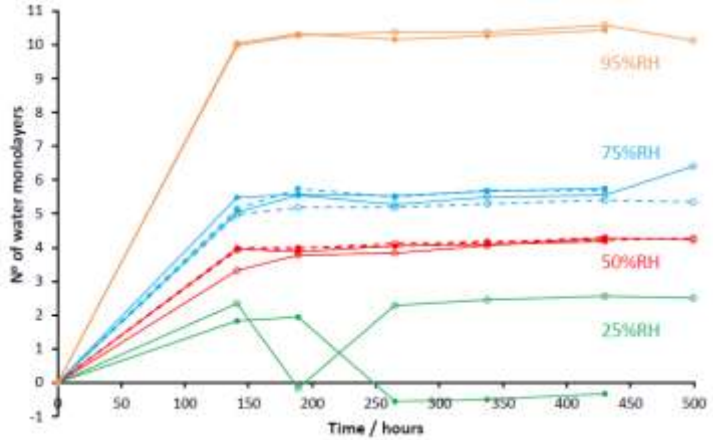


WP1: H_2 generation from PuO_2 surface-sorbed H_2O

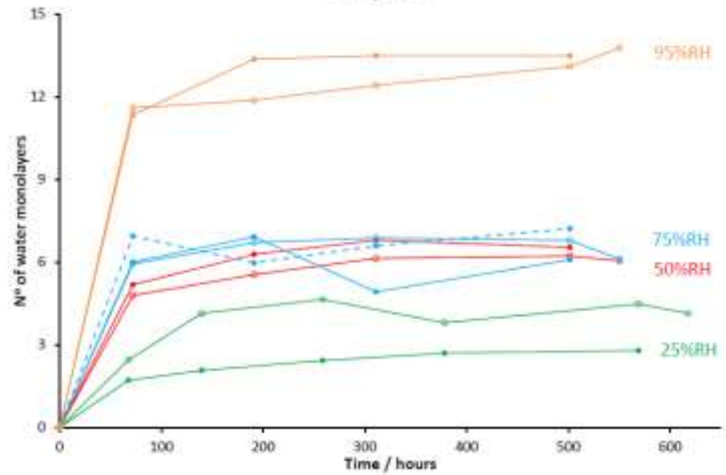
- Measure H_2 evolution from H_2O on Magnox & THORP PuO_2 as a function of number of monolayers of H_2O sorbed and atmospheric composition - N_2, Ar
- PuO_2 properties:

Sample	SSA ($m^2\,g^{-1}$)	Specific activity (Bq-α g^{-1} Pu)
Magnox	8.9 ± 1.1	5.5×10^9
Thorp	6.1 ± 1.0	1.8×10^{10}

Isotope fraction	Magnox	Thorp
Pu-238	0.0025	0.0217
Pu-239	0.7119	0.5379
Pu-240	0.2341	0.2862
Pu-241	0.0373	0.0745
Pu-242	0.0119	0.077
Am-241	0.0023	0.0026



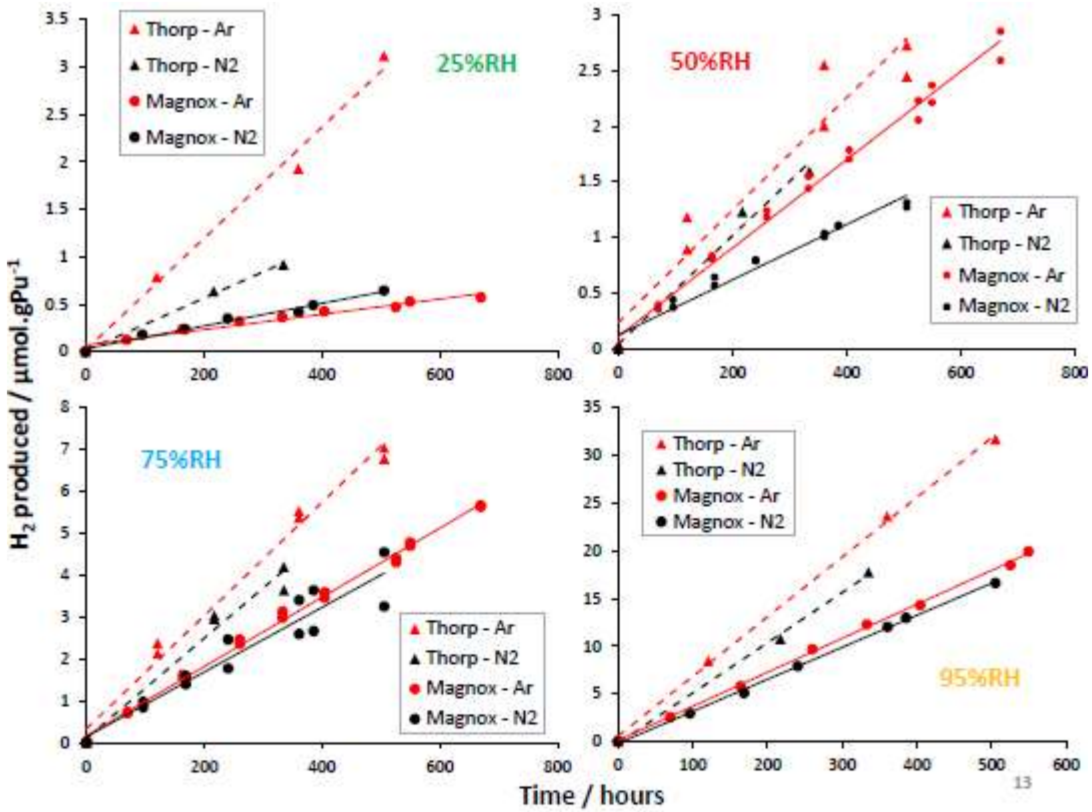
Magnox Humidification



THORP Humidification

WP1: H_2 generation from PuO_2 surface-sorbed H_2O

- Measure H_2 evolution from H_2O on Magnox & THORP PuO_2 as a function of number of monolayers of H_2O sorbed and atmospheric composition - N_2, Ar



Conclusions

- Linear H_2 production with no steady state
- Increasing H_2 with increasing number of monolayers
- THORP generates more H_2 than Magnox across all %RH
- Magnox – little difference between N_2 and Ar
- THORP – more H_2 produced in Ar than in N_2 **– Pu 241 isotopics**?

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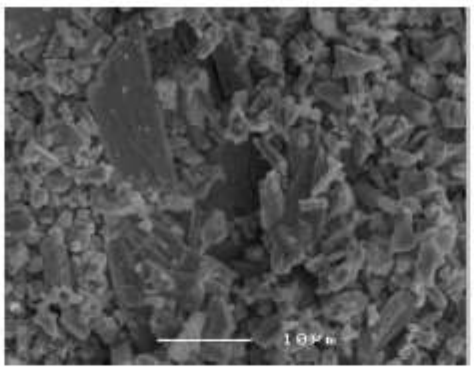
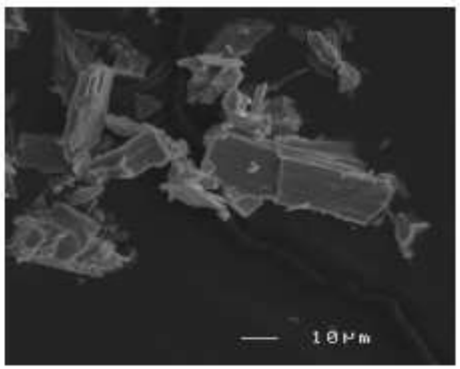
WP1: Effect of oxide surface on gas phase chemistry

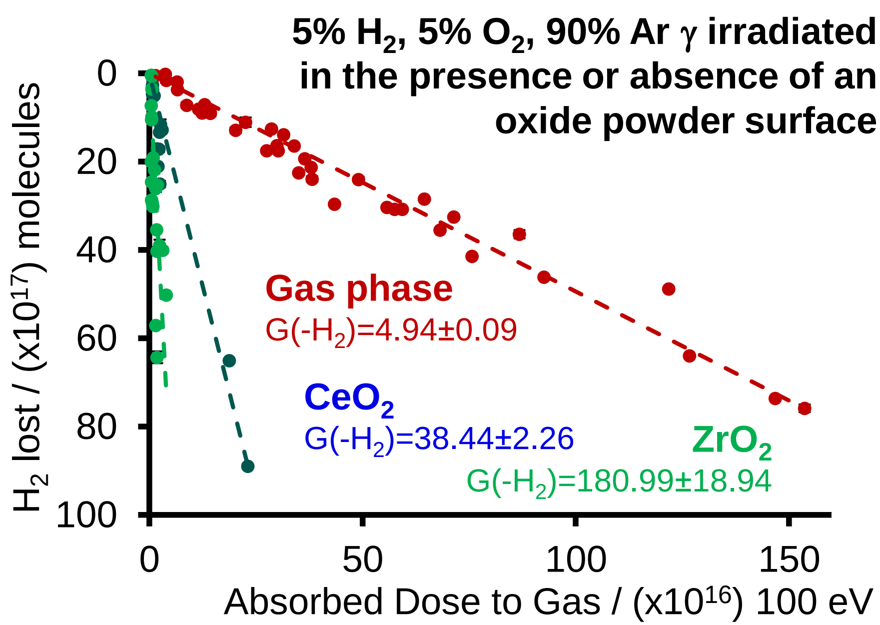
- Studies of gas phase & surface chemistry of surrogates using He^{2+} ion or ^{60}Co γ-irradiation.
- Atmosphere and moisture content controlled.; Analysis using gas chromatography.
- ^{60}Co γ-irradiation indicate H_2 depleted from headspace in presence and absence of CeO_2 and ZrO_2 surrogates and, in all cases, rate is zero order / independent of $[H_2]$
- Same results with He^{2+} ions in indicating no LET effect
- Reaction faster with surrogate; suggests oxide surface acts as O_2/H_2 recombination catalyst



CeO_2
2.52 ± 0.02 $m^2 g^{-1}$



ZrO_2
9.23 ± 0.03 $m^2 g^{-1}$



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WP2: Pu Disposition – UK Policy

UK plutonium management policy states: *any remaining plutonium which is not converted into MOX fuel, or otherwise reused, will be immobilised and treated as waste for disposal*

Is MOX as technically mature as assumed?

US MOX fuel fabrication facility (MFFF) is projected to be at least $6 billion over budget and 15 years late

UK MOX scenario utilises same MELOX reference design as MFFF and could be vulnerable to similar difficulties

•Additional need for plutonium pre-treatment

•Unrealistic design assumptions; inadequate review / challenge

•Substantive design variation during build

•Inadequate supply chain capability

Conclusion: UK Strategy would be significantly de-risked if stockpile immobilisation option developed in parallel

Analysis presented at House of Commons, All Party Parliamentary Group on Nuclear Energy.

Publication: N.C. Hyatt, Energy Policy, 101, 303-309, 2017.

The University Of Sheffield.

Image: Shaw Areva MOX Services

Energy Policy

Plutonium management policy in the United Kingdom: The need for a dual track strategy

Neil C. Hyatt

Research Councils UK Energy For a Low Carbon Future

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WP2: Pu Disposition – Ceramics

Betafite $CaUTi_2O_7$ is a candidate ceramic for Pu disposition

Synthesis is difficult, yield <80%, and requires average U oxidation state >U^{5+}, e.g. by Ca excess $Ca_{1+x}U_{1-x}Ti_2O_7$

This is undesirable for geological disposal due to higher solubility of U^{5+}/U^{6+}

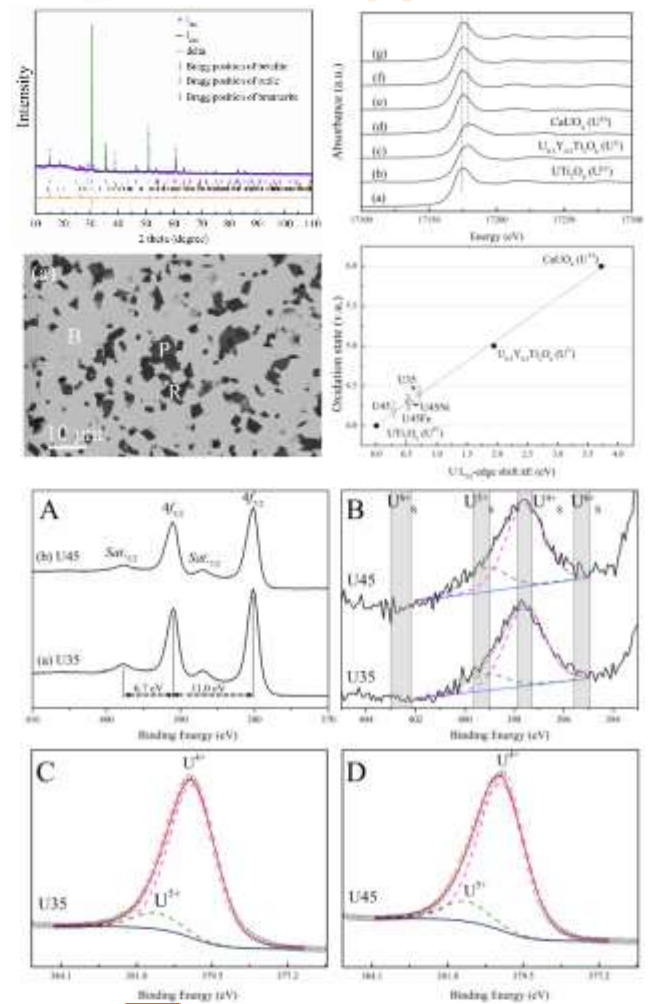
New approach, stabilisation of structure by ZrO_2 solid solution, with average U oxidation state close to 4+

- $Ca_{0.96}U_{0.48}Zr_{0.18}Ti_{2.20}O_7$ – yield 85%, av. $U^{4.3+}$
- $Ca_{0.87}U_{0.67}Zr_{0.16}Ti_{2.01}O_7$ – yield 96%, av. $U^{4.2+}$

Average U oxidation state determined by UL_3 XANES at NSLS and Photon Factory

Contribution of U^{4+}/U^{5+} solved uniquely by U 4f XPS studies at ITU Karlsrhue – possibility of U^{6+} definitively *excluded*

This research has optimised a leading Pu ceramic wasteform for disposal by control of U oxidation state



Publication: S. Sun *et al.*, *RSC Advances*, in submission, 2017

WP2: Pu Disposition – Glass & Ceramics

1: Hot isostatically pressed glass-ceramics for plutonium disposition; Steph Thornber

New formulation development – eliminated CaF_2 addition due to concerns regarding α,n reaction on ^{19}F

Optimised phase assemblage in favour of zirconolite $CaZrTi_2O_7$, through ceramic / glass ratio

Determined mechanisms of Ce / U partitioning between ceramic / glass phase; NDA funding to undertake Pu studies at ANSTO

Publications: J. Nuclear Mater., 485 (2017) 253; 456 (2015) 461.

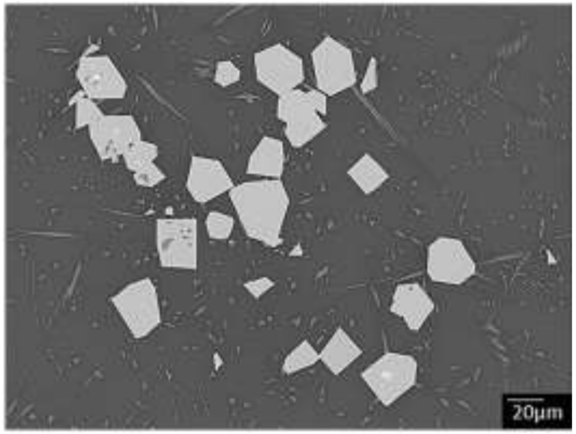
2: Processing and performance of vitrified higher activity wastes; Luke Boast

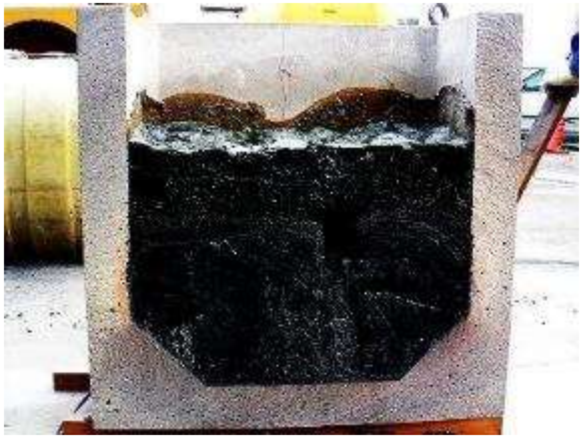
Successful vitrification of plutonium contaminated materials using recycled bottle glass

Vitrified products show very slow dissolution kinetics in simplified hyperalkaline fluid of cementitious disposal facility

Pilot scale vitrification studies performed at NNL in collaboration with Kurion using Geomelt system

The University Of Sheffield. ansto KURION





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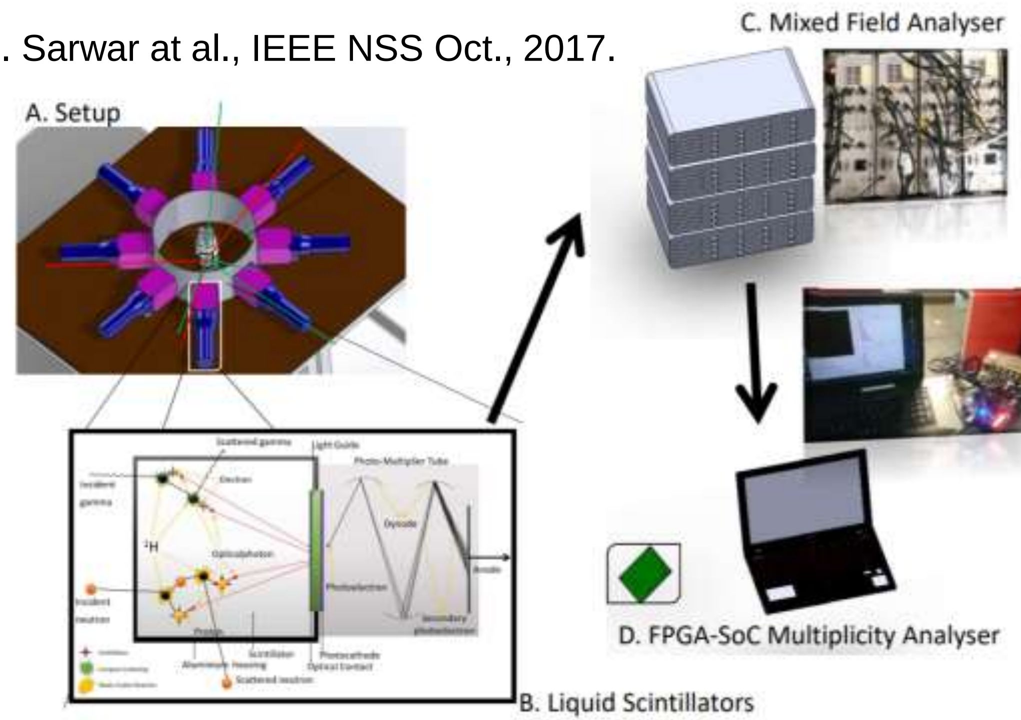
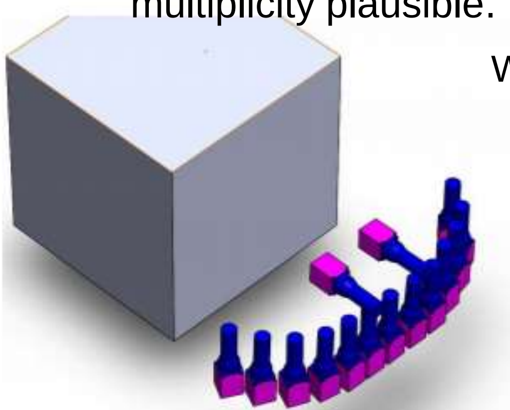
WP3 Characterisation: Isotope measurement by multiplicity detection – Cf-252 studies

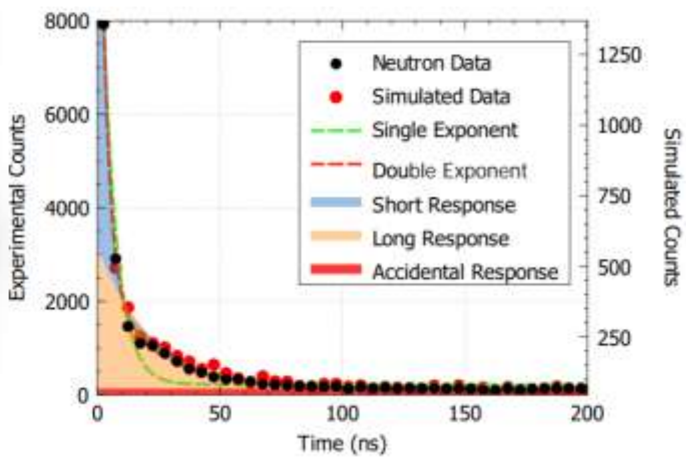
- Seeking to measure Pu-238, 240 & 242 and Cm-244 from multiplicity
- Measurement of neutrons from fission, known to decay with time
- Hard to measure without shifting n bandwidth which widens time over which burst is measured – giving false positives in multiplicity
- Using fast neutron system, have measured closer to the true burst – the **Rossi-α Distribution**
- So fewer stray events detected
- Thus better ageing measurement by multiplicity plausible.

R. Sarwar at al., IEEE NSS Oct., 2017.

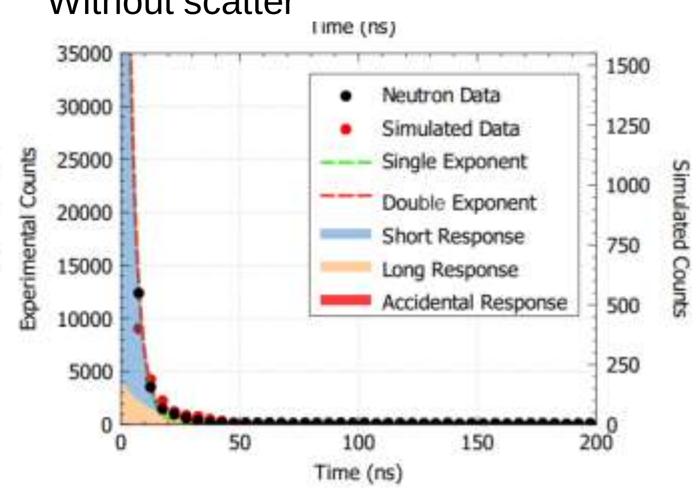




With scatter



Without scatter



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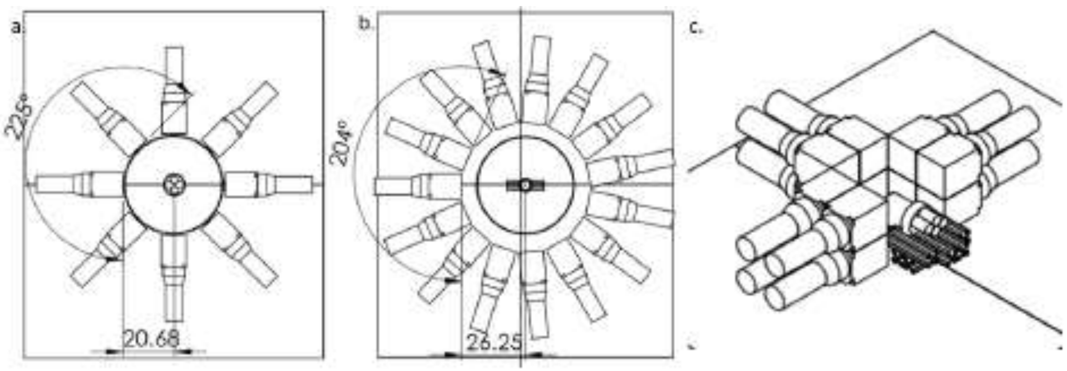
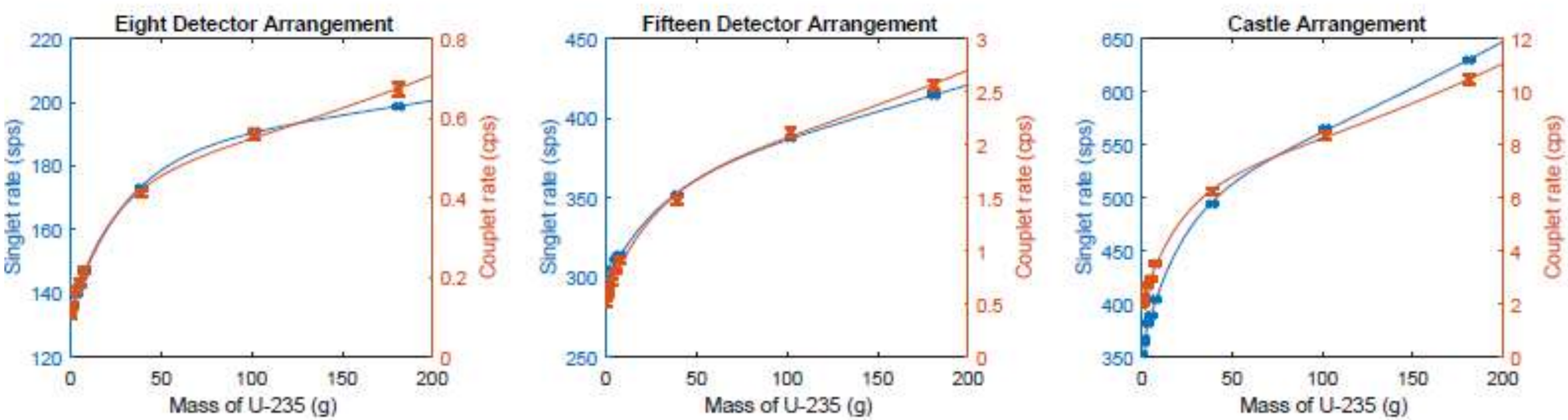
WP3 Characterisation: Isotope measurement by fast neutron assay – U-235 up to 93.25 wt% of UO_2

- Explored range of assay arrangements for ageing measurements, at ORNL
- Easy for low enrichment but more difficult for 'interesting' enrichments
- This shows can use these systems for samples of the scale that ageing would be needed for: next step: real samples with known histories

Lancaster University

Oak Ridge National Laboratory





R. Sarwar et al., submitted NIM A, January 2018

Summary

WP1 – Interim Storage

- Of the surfaces, {111} is the most stable, {100} the least stable
- Water is present as adsorbed hydroxyl groups on the {110} and {100} surfaces even at elevated temperatures and pressures, conditions likely to be found in the UK's PuO_2 storage canisters
- Experimentally determined water desorption temperature ranges for PuO_2 *could be* due to desorption from the hydroxylated {110} and {100} surface monolayers – but beware stability of {100}

- Measured absorption of water onto CeO_2, UO_2 & ThO_2 films by direct mass analysis at a range of RH.
- Calculated surface area of the films, and the volume of water monolayer and ΔH of absorption @75°C.
- Varied the temperature of the Ce/U/ThO_2-H_2O systems, showing desorprtion of water up to ~400°C.
- Preliminary electrochemical experiments indicate possibility of generating PuO_{2+x} - peroxide?

- From water sorbed on PuO_2 surface, we see linear H_2 production with no steady state
- Increasing the monolayer coverage increases the H_2 production rate
- THORP generates more H_2 than Magnox across all %RH
- H_2 depletes upon He^{2+}, γ irradiation, accelerated by Ce/ZrO_2 surrogates. H_2/O_2 recombination catalysis?

WP2 - Disposition

- Optimised leading Pu ceramic wasteform betafite, $CaUTi_2O_7$, for disposal by U oxidation state control
- Developed new HIPed glass-ceramic for Pu disposition, eliminating CaF_2 addition and optimising in favour of zirconolite.
- UK Strategy would be de-risked if Pu immobilisation option developed in parallel to MOX option.

WP3 - Characterisation

- Characterisation of scatter component of Rossi-a Distribution, allowing for implementation of real-time system for fast neutron multiplicity and spectroscopy using scintillation detectors…
- …deployable on (UO_2) samples of high (U-235) enrichment.

Next Steps – TRANSCEND

Aim. To provide technical underpinning to the ongoing development of options for the UK's stockpile of separated plutonium

Objectives.

- **Interim Storage:** Understand how surface structure & properties of pristine and radiation damaged PuO_2 change with time in the absence and presence of water and chloride contaminants
- **Disposition:** To understand the mechanisms of incorporation of Pu into ceramic and glass-ceramic wasteforms, and to understand the effect of self-induced radiation damage on such wasteforms
- **Characterisation**: Use on real samples and deployment for characterisation of sub-surface contamination

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Acknowledgements

Sellafield Ltd

NATIONAL NUCLEAR LABORATORY

NDA
Nuclear Decommissioning Authority

OAK RIDGE National Laboratory

PF

KIT
Karlsruhe Institute of Technology

ansto

KURION

UTGARD LABORATORY

midas

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EPSRC

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Understanding [U,Pu,Tc]-cement mineral interactions for radioactive waste management

Antonia Yorkshire, Claire Corkhill & John Provis
University of Sheffield

11/09/2018
York

Introduction – ILW in cements

[1] N.C. Hyatt et. al., Thermal treatment of simulant plutonium contaminated materials from the Sellafield site by vitrification in a blast-furnace slag, *J. Nucl. Mater.* **444**, 186-199, 2014.
[2] Department of Energy and Climate Change, Implementing Geological Disposal, 14D/235, 1-54, 2014.

Theme Two - Where do I fit in?

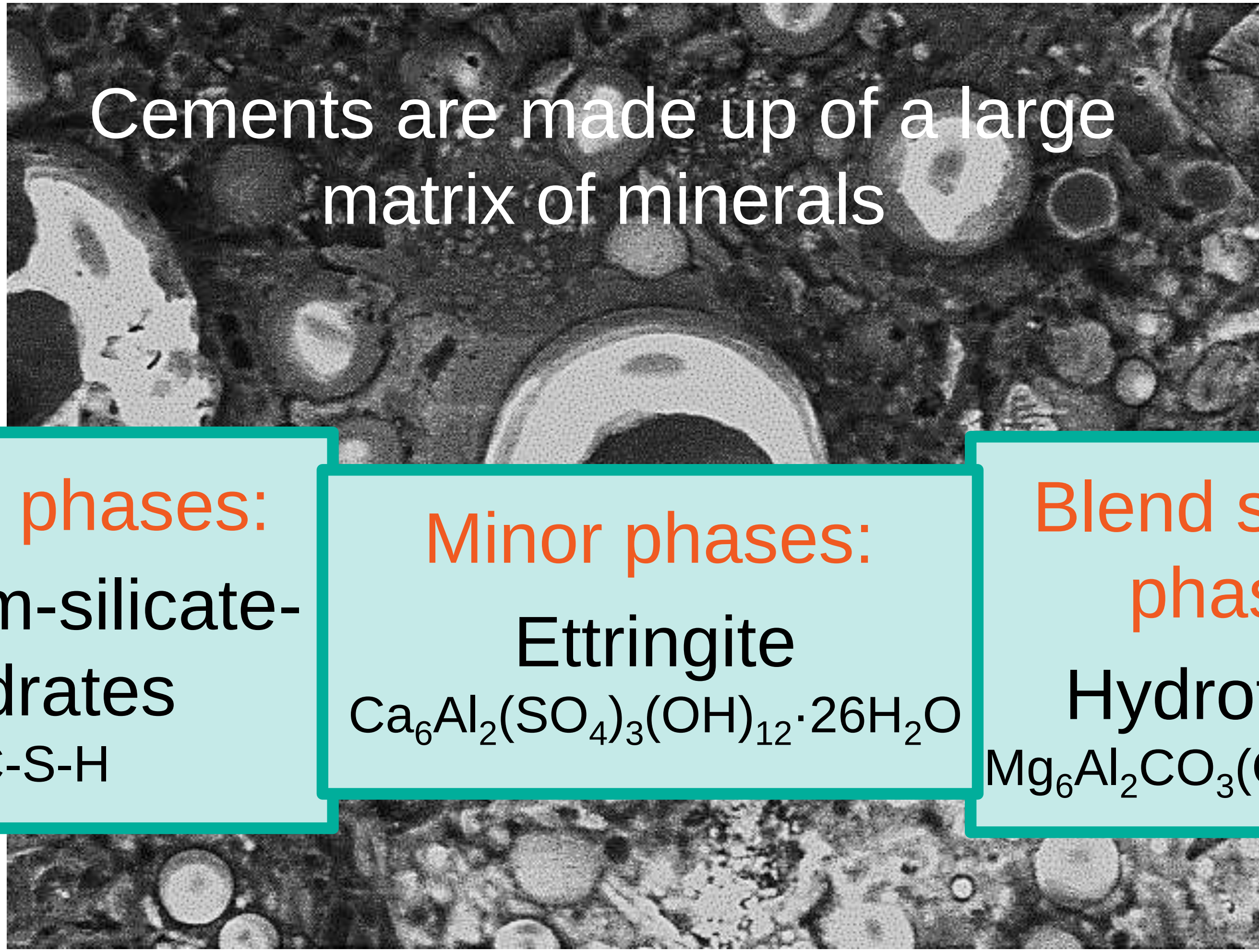
PuO_2 & Fuel Residues

- Interested in cement interactions with:

U Pu Tc

- Common interest in how waste residues interact with the materials that are currently being used to store them

Project objectives



Cements are made up of a large matrix of minerals

Major phases:

Calcium-silicate-hydrates

C-S-H

Minor phases:

Ettringite

$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$

Blend specific phases:

Hydrotalcite

$Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$

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Analysis

- Inductively coupled plasma – optical emission spectroscopy (ICP-OES)
- Liquid scintillation counting (LSC)
- X-ray diffraction (XRD)
- X-ray absorption spectroscopy (XAFS)
- Solid-state nuclear magnetic resonance (SSNMR) spectroscopy

Analysis

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Solid state characterisation

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Uranium interactions with C-S-H

- Conventionally studied at trace concentrations[1][2][3]
- Uranyl nitrate, $(UO_2)_2(NO_3)_2$ (aq), added to C-S-H(0.6) → Ca/Si = 0.6
- A range of concentrations studied here:

Effect of pH on the C-S-H structure in the presence of U

Conditions imposed by a local concentration of the radionuclide

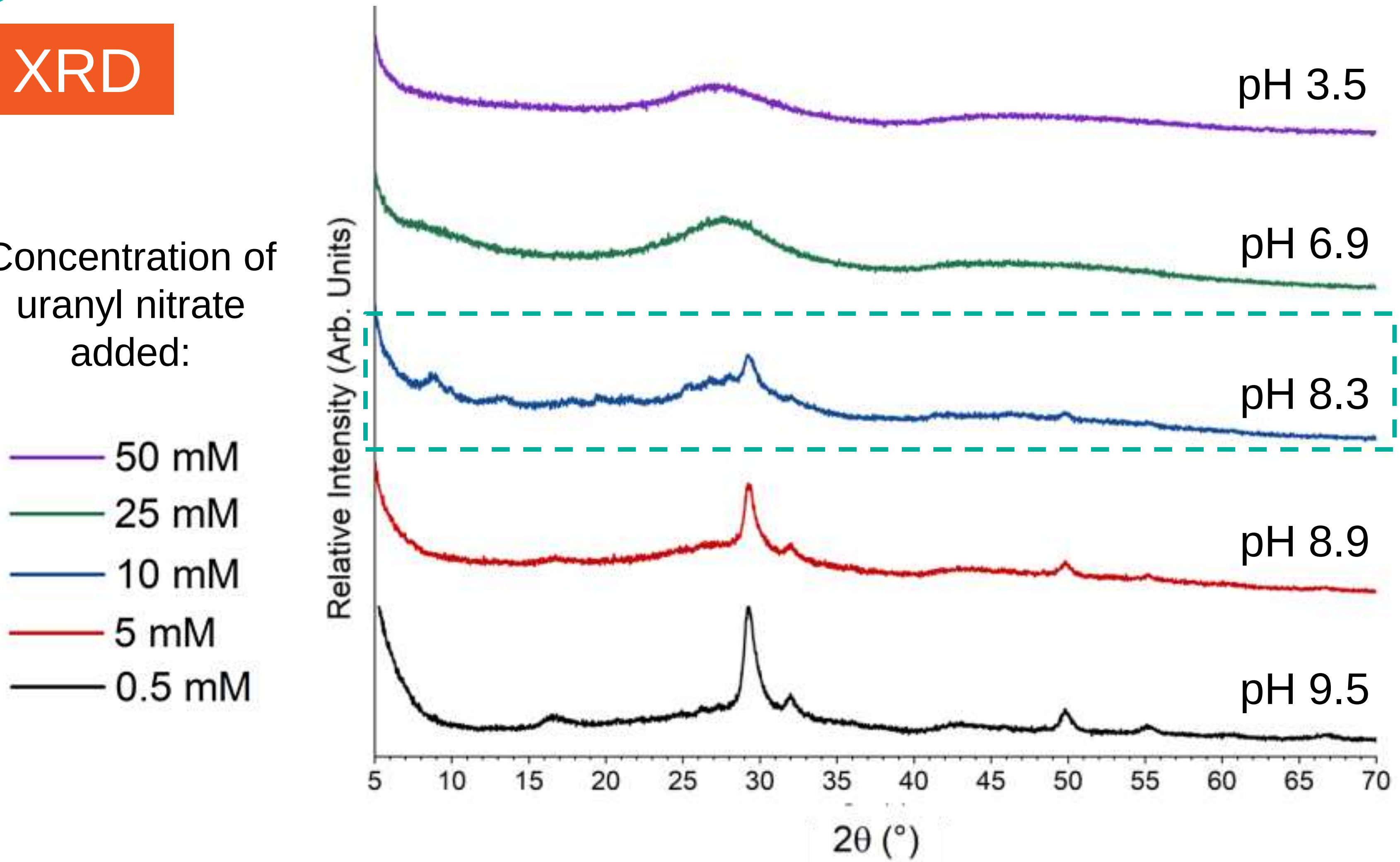
Changing mineralogy as a result

[1] Harfouche et. al. 2006
[2] Wieland et. al. 2010
[3]Mace et. al. 2013

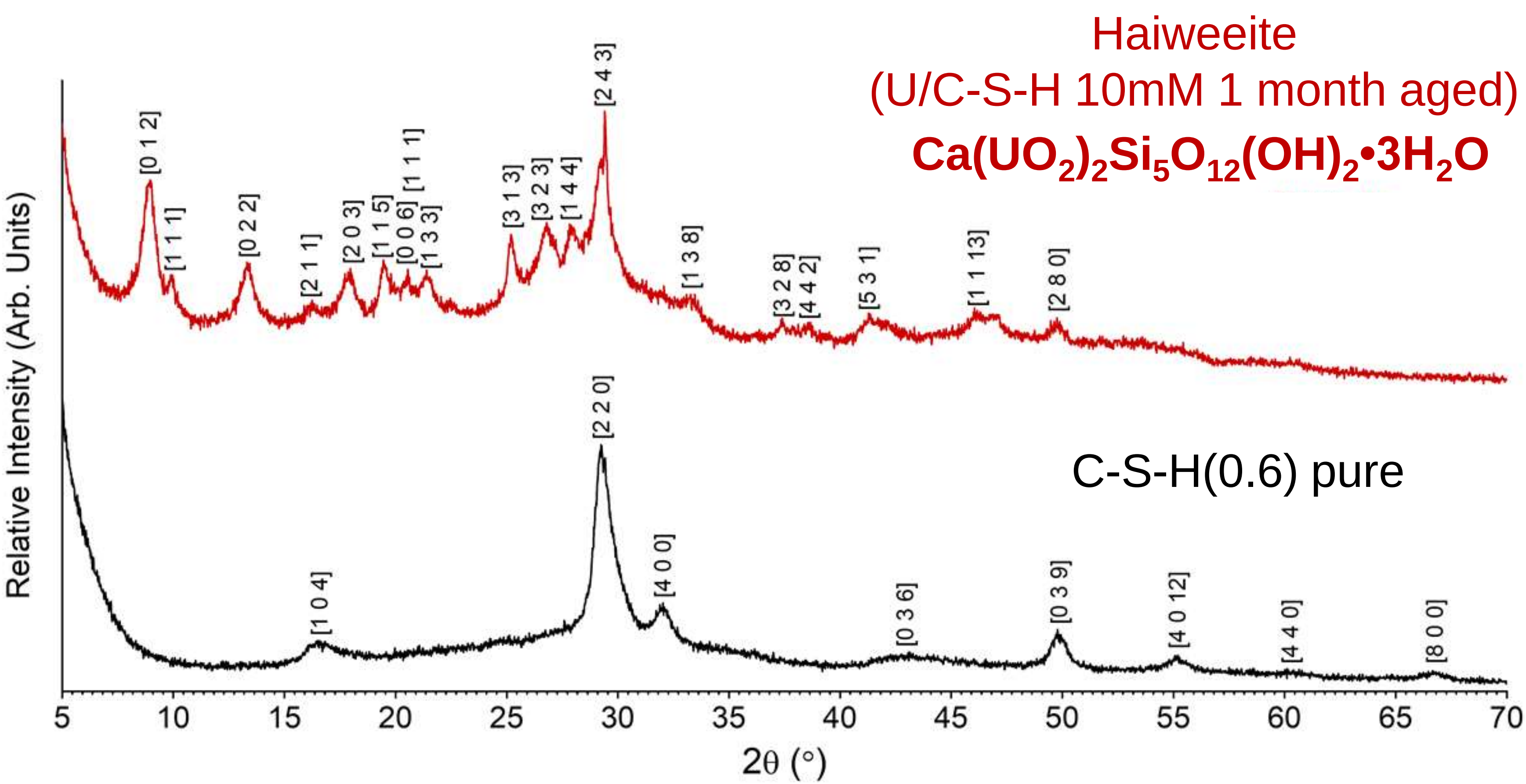
Uranium interactions with C-S-H

XRD

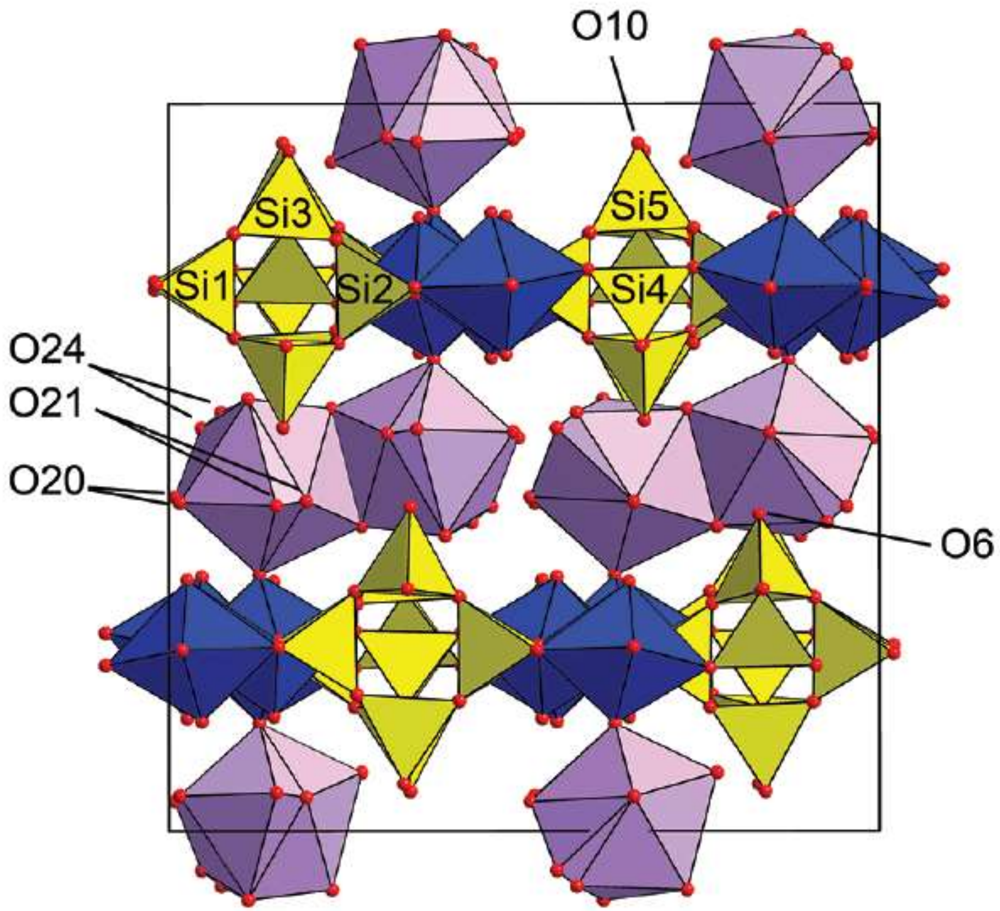
Concentration of uranyl nitrate added:



Uranium interactions with C-S-H



Uranium interactions with C-S-H



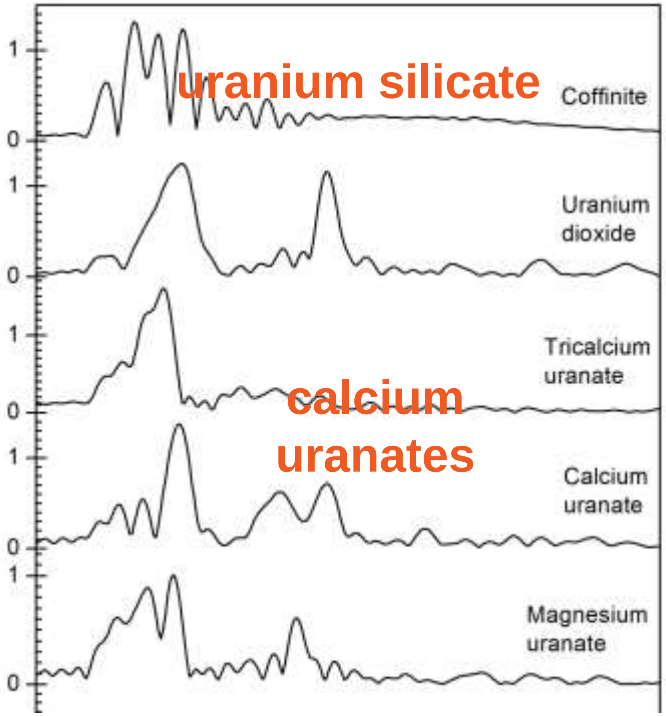
Plasil, J., Fejfarova, K., Cejka, J., Dusek, M., Skoda, R. & Sejkora, J., "Revision of the crystal structure and chemical formula of haiweeite, Ca(UO2)2(Si5O12)(OH)2·6H2O." *Am. Mineral.* **98,** 718–723 (2013)

- A uranyl sheet silicate with dimers of calcium polyhedra.
- Formation of which shows evidence that uranium can incorporate into cementitious materials by precipitation of new mineral phases

Uranium interactions with C-S-H

XAFS

L_{III}-edge = 17.166 keV



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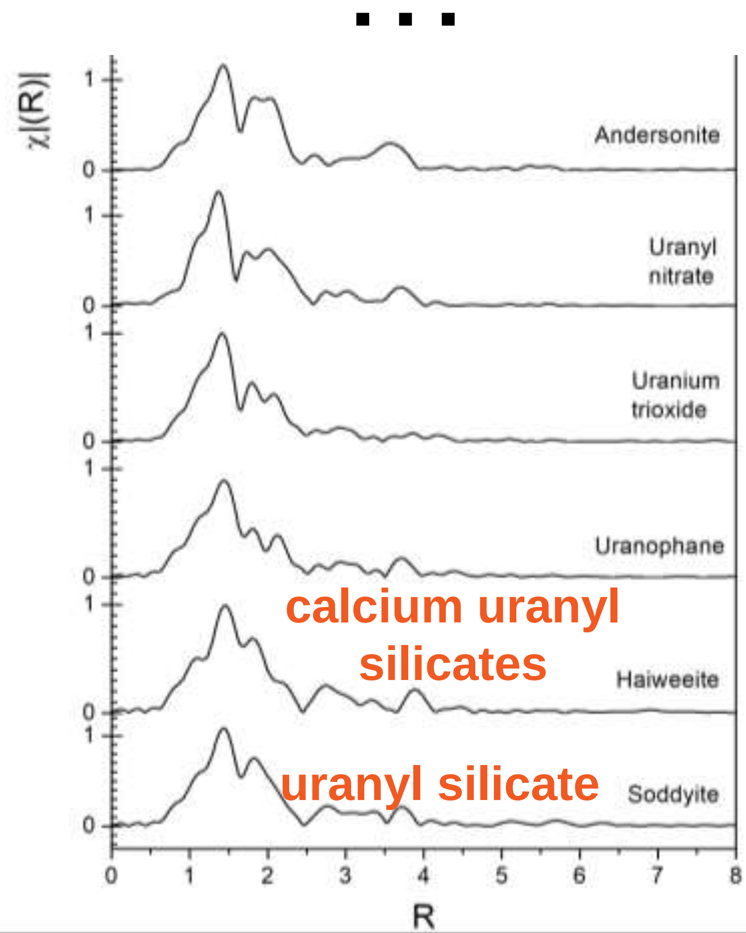

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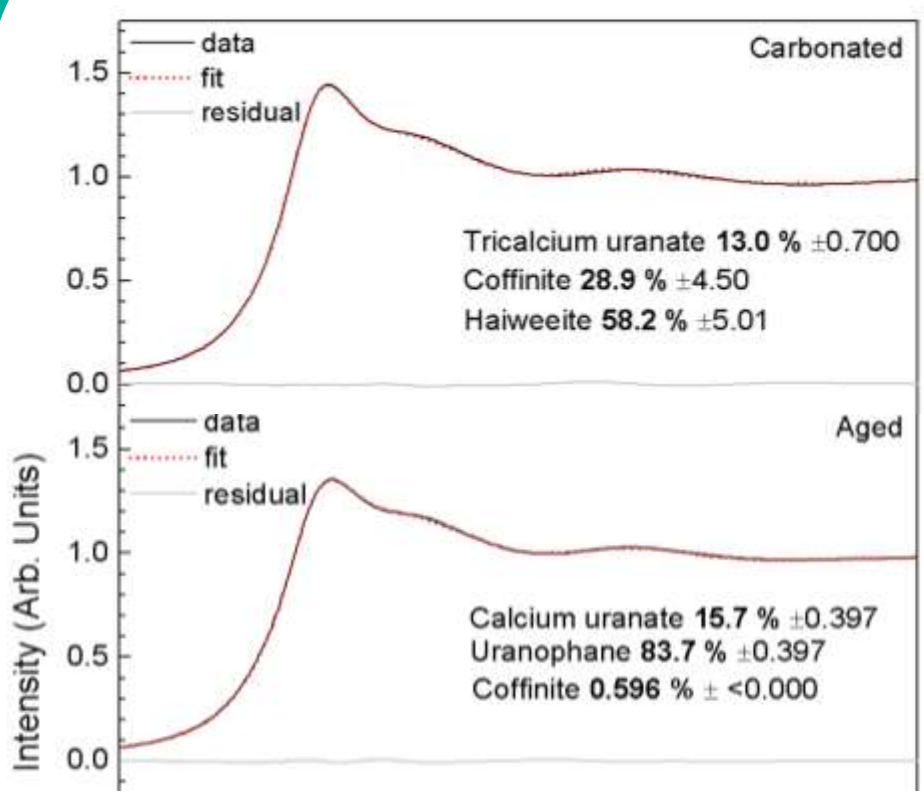
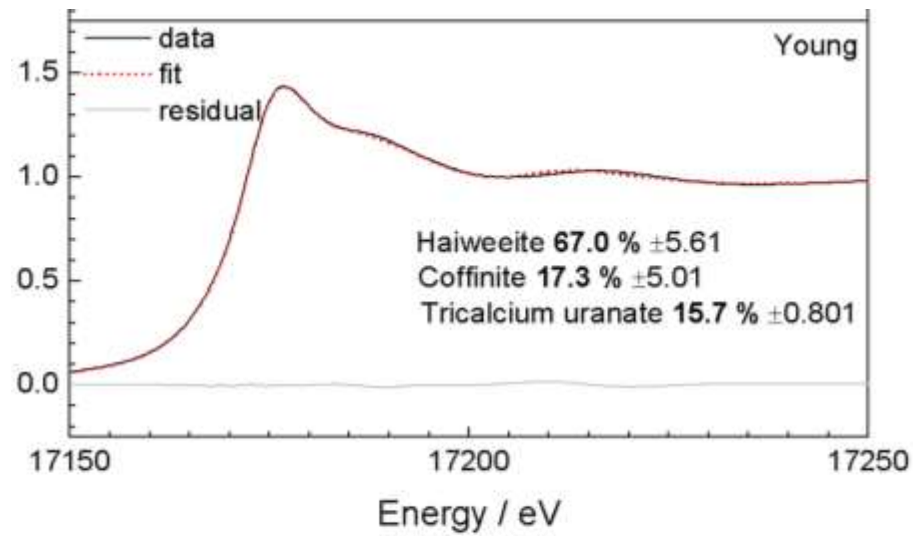
Uranium interactions with C-S-H





	R-factor (%)
Young	0.02645
Aged	0.01041
Carbonated	0.02245

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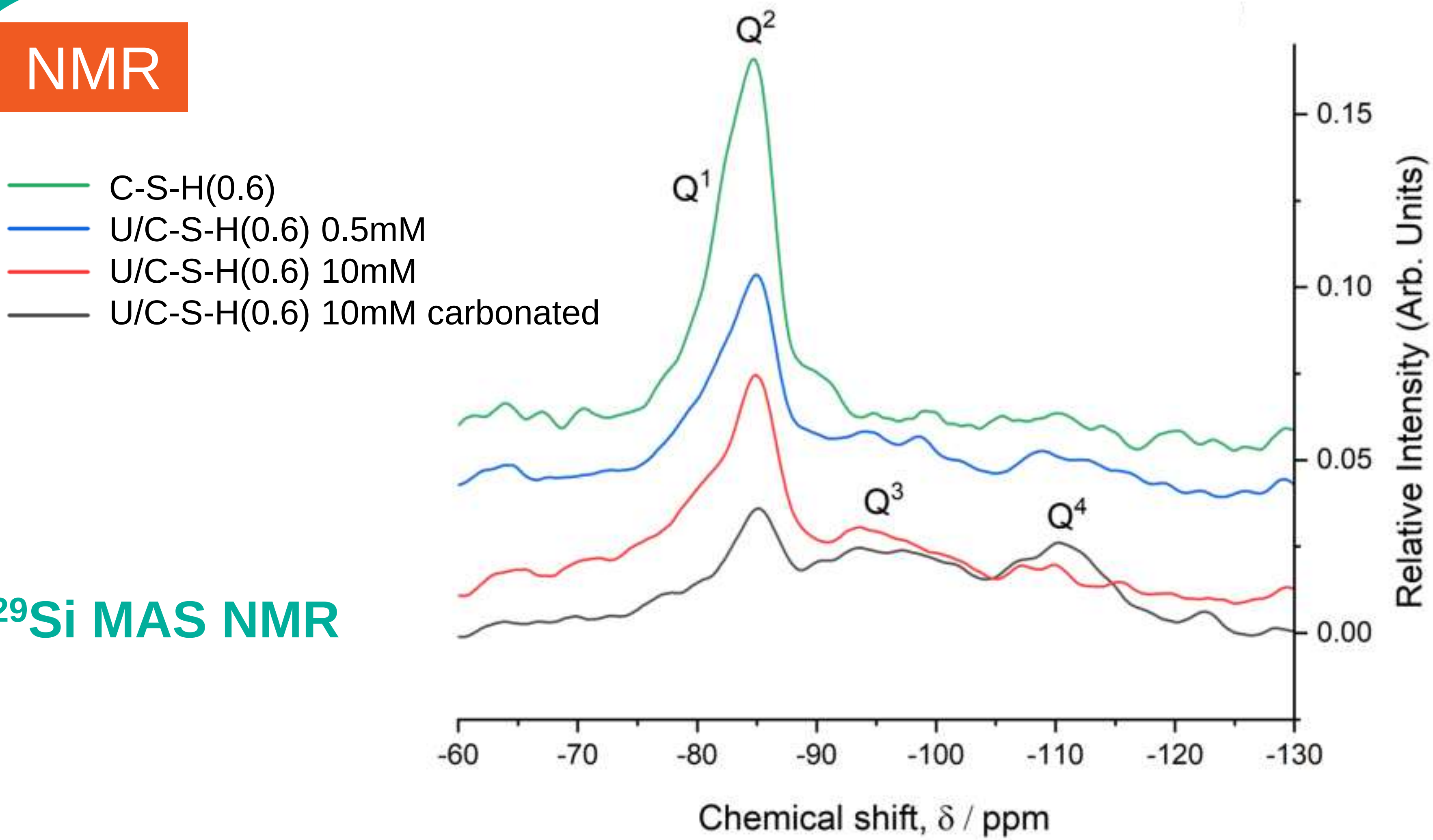
Uranium interactions with C-S-H

NMR



^{29}Si MAS NMR

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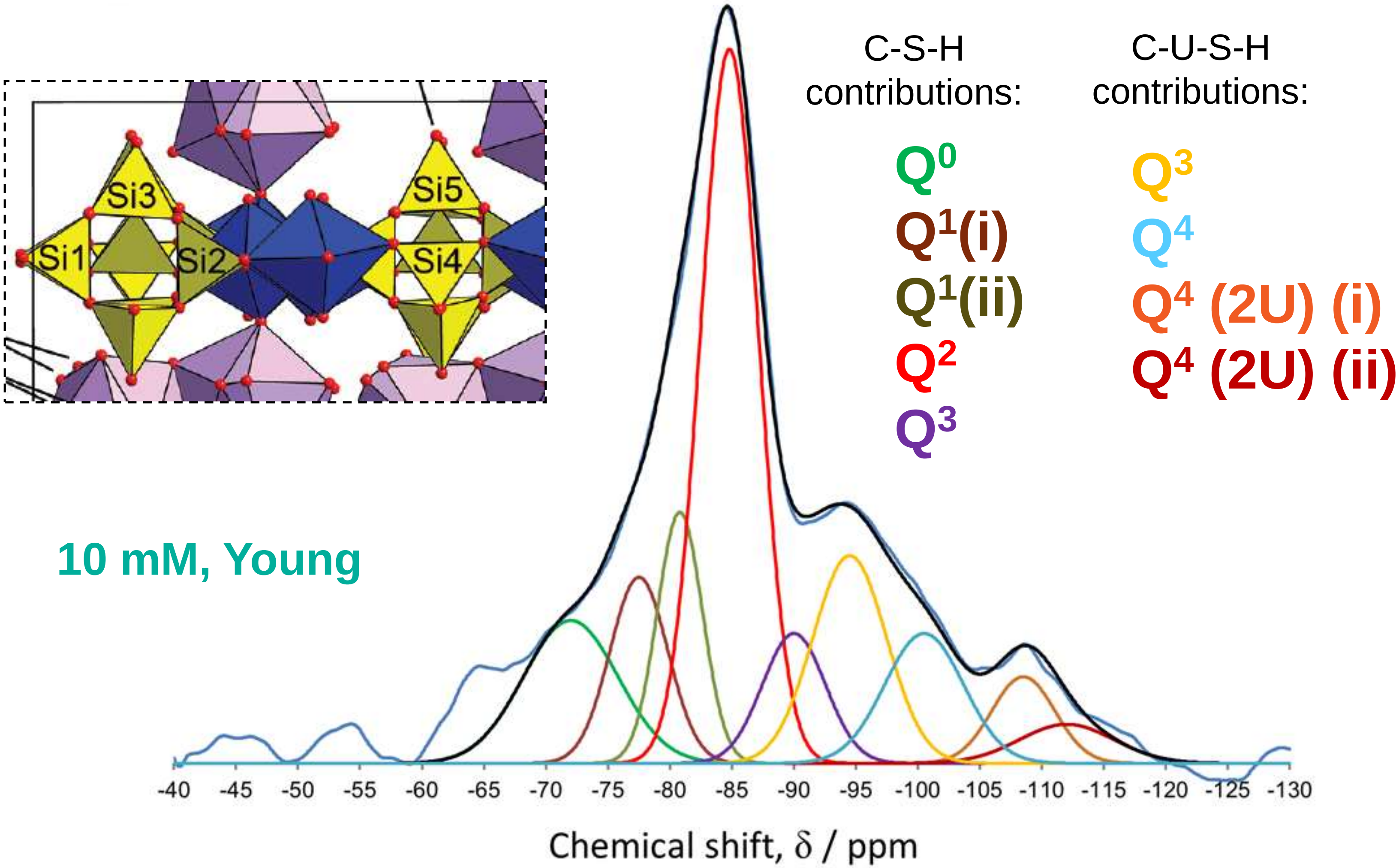
Uranium interactions with C-S-H



10 mM, Young

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Conclusions

- C-S-H is an important cement phase for uranium retention in ILW
- Evidence to show that uranium can be incorporated into cements due to the formation of **haiweeite** and **uranophane** type phases
- **No definitive technique to tell us what's going on – all the data form pieces of a puzzle**
- Shows the importance for small-scale sorption studies for ILW storage, but also the need to look at these mineral systems on a larger scale for geological disposal

Ongoing work

- NMR at the actinide user facility in September 2018

Institute for Transuranium Elements

EUROPEAN COMMISSION

^{29}Si MAS NMR measured on C-S-H phases contacted with plutonium

- Data sets for all radionuclides U, Pu, Tc/Re and cement phases C-S-H, ettringite, hydrotalcite

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

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Acknowledgements

Supervisors:
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Neil Hyatt, Brant Walkley, Sandra van Meurs

Others:
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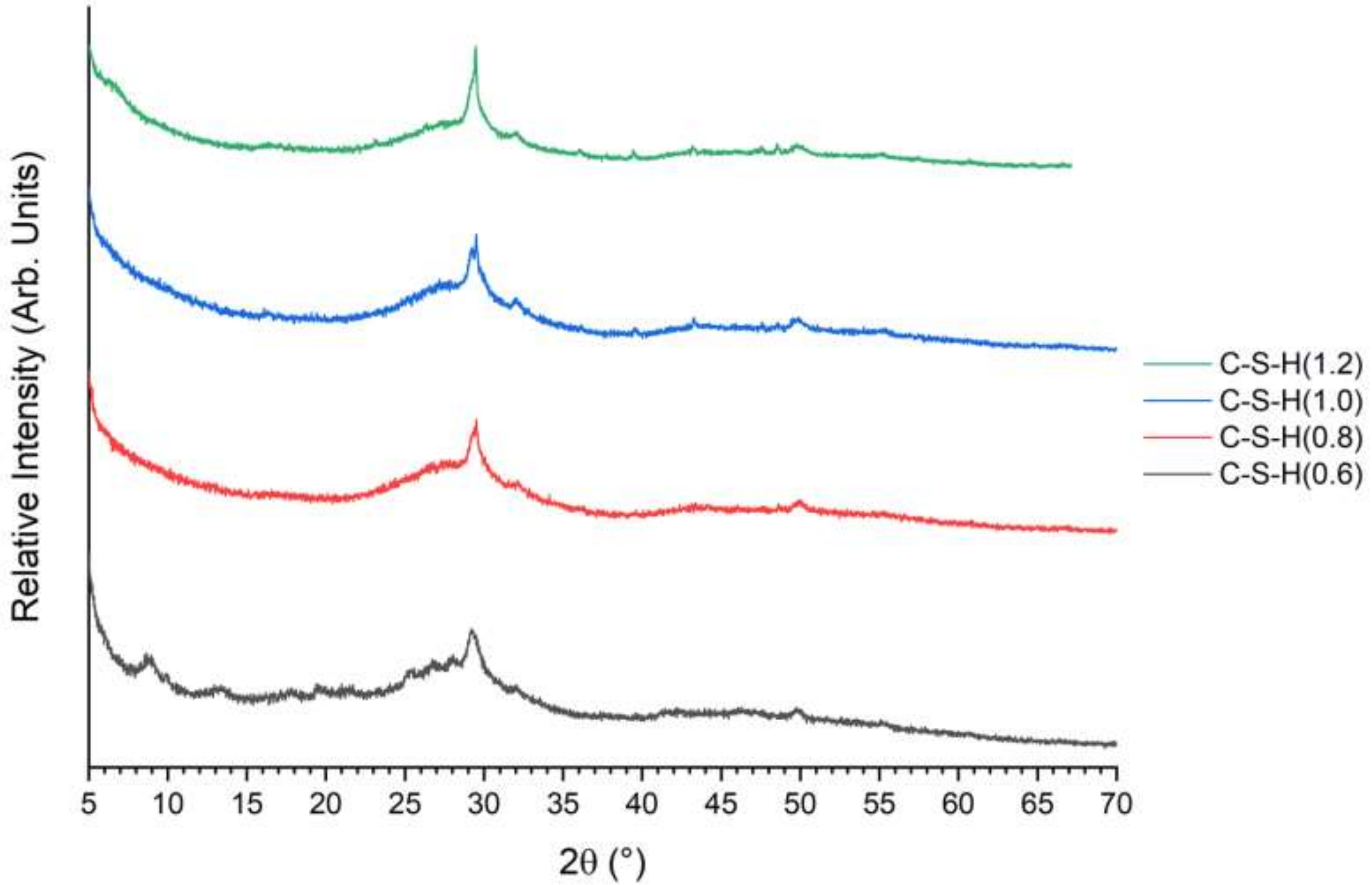
This research was conducted in part at the **MIDAS** facility at the University of Sheffield, which was established with support from the DECC.
Thanks go to the NDA for sponsorship and to NNL for industrial supervision.



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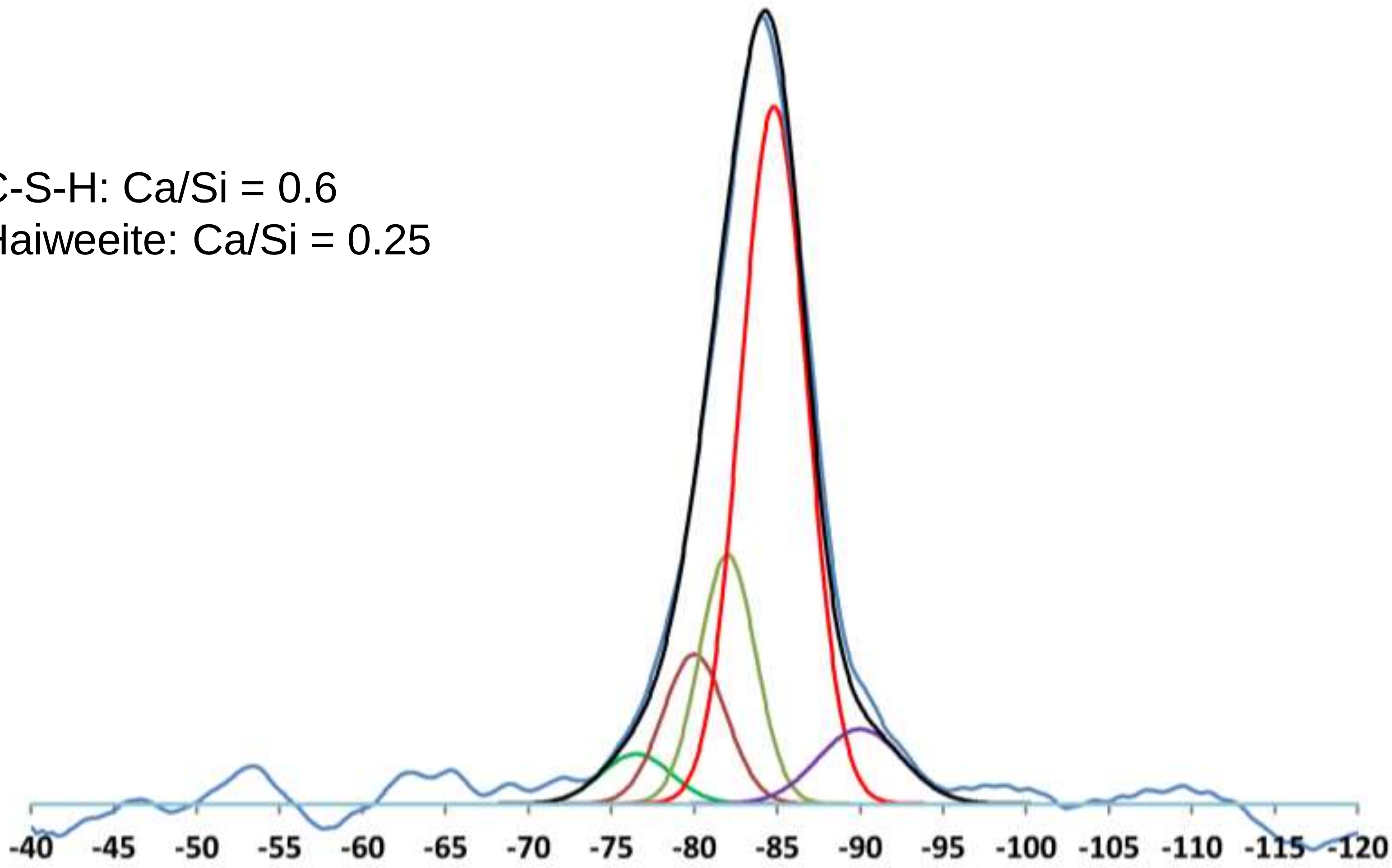
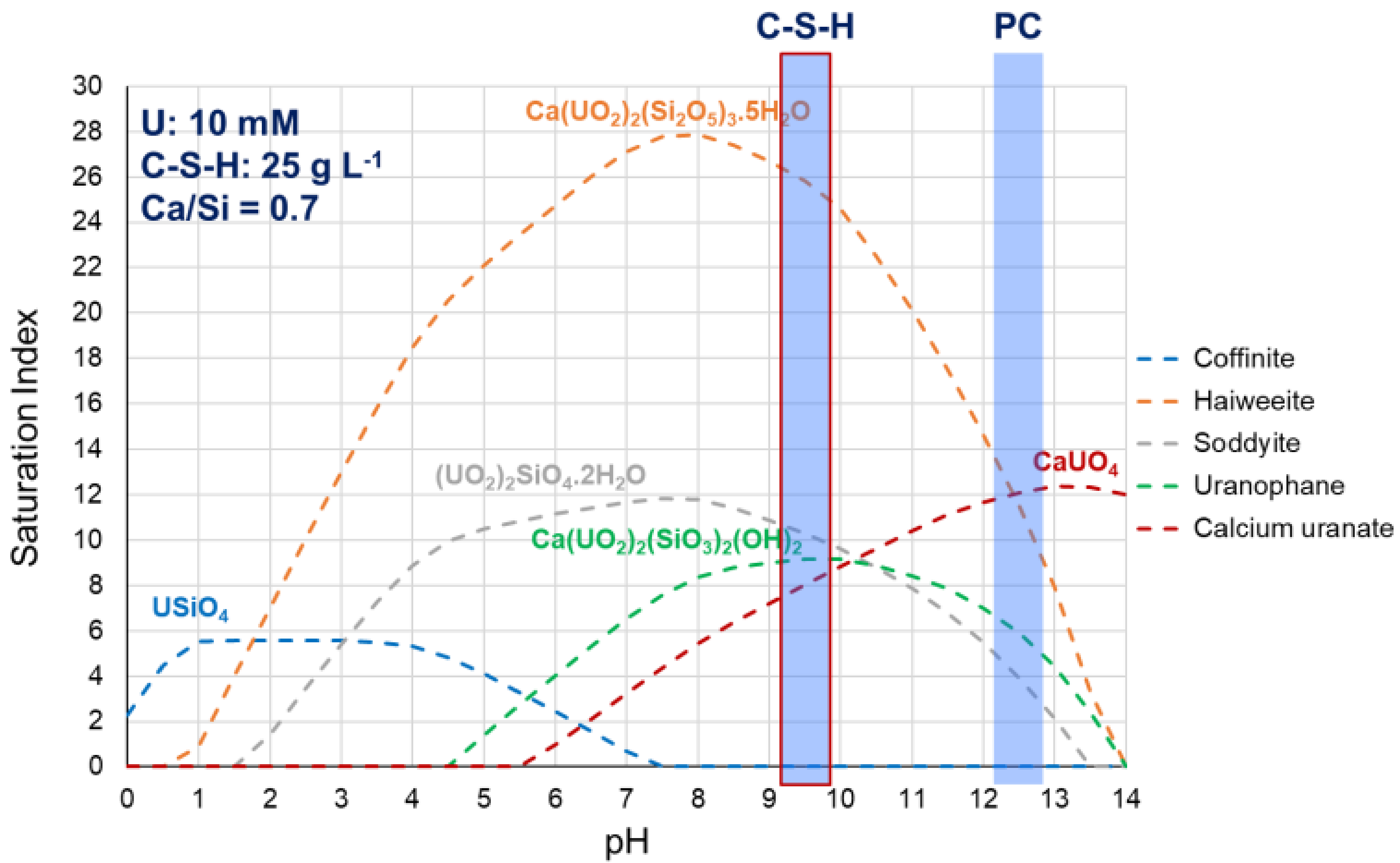
C-S-H: Ca/Si = 0.6
Haiweeite: Ca/Si = 0.25




C-S-H
PC
U: 10 mM
C-S-H: 25 g L-1
Ca/Si = 0.7
Ca(UO2)2(Si2O5)3.5H2O
(UO2)2SiO4.2H2O
Ca(UO2)2(SiO3)2(OH)2
USiO4
CaUO4
Saturation Index
pH
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Coffinite
Haiweeite
Soddyite
Uranophane
Calcium uranate

The DISTINCTIVE University Consortium: Legacy Ponds and Silo Wastes (an overview)

Joe Hriljac

School of Chemistry
University of Birmingham, UK

Pile Fuel storage Pond

1st Generation Magnox Fuel Pond

Magnox Swarf Storage Silo

Pile Fuel Cladding Silo

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Aims and Work Packages

Aim: To develop innovative technical approaches to help clean up UK legacy wastes by undertaking basic science and engineering research that could provide sound technical advances to underpin the efforts to decommission the LP&S.

Work Package 1 – Wasteforms and Wasteform Durability (6 projects)

Objective: To understand the durability of heterogeneous intermediate level waste glass-ceramic wasteforms from LP&S waste streams.

Work Package 2 – Effluent Treatment & Analysis (4 projects)

Objective 1: To develop improved ways to remove radionuclides from solution, using both novel inorganic ion exchange solids and tailored binding superparamagnetic nanoparticles, to treat complex and variable effluents.

Objective 2: To develop new micro- and ultra-filtration methods for use with sludges.

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Aims and Work Packages

Work Package 3 – Pond & Silo Sludges (12 projects)

Objective 1: To provide three-dimensional modelling and simulation for sludge disturbance, mobilisation and transport, with supportive experimental studies, and manipulation planning for removing corroding nuclear materials.

Objective 2: To develop a better understanding of gas hold-up in sludges.

Objective 3: To develop improved techniques for remote monitoring of sludges and heterogeneous wastes.

.

Academic Leads

Tom Scott, John Day (Bristol)

Bill Lee, Mary Ryan, Luc Vandeperre (Imperial)

Andrew Kerridge (Lancaster)

Mike Fairweather, Tim Hunter, David Harbottle (Leeds)

Nick Evans, Richard Holdich (Loughborough)

Nik Kaltsoyannis, Barry Lennox (Manchester)

Fred Currell (Queen’s University Belfast)

Neil Hyatt (Sheffield)

David Read (Surrey)

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Industry Leads

- SL: Martyn Barnes, Simon Kellet, Sean Morgan, Geoff Randall, Bill Rogerson

- NNL: Jonathan Austin, Anthony Banford, Matthew Barker, Bob Bowen, Tom Carey, Steve Graham, Mike Harrison, Luke O'Brien, Scott Owens, Divyesh Trivedi

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- Birmingham: Tzu-Yu Chen, George Day*, Ryan George*, Paul Martin
- Bristol: Antonis Banos*, Charilaos Paraskevoulakos*, Kate Wyness
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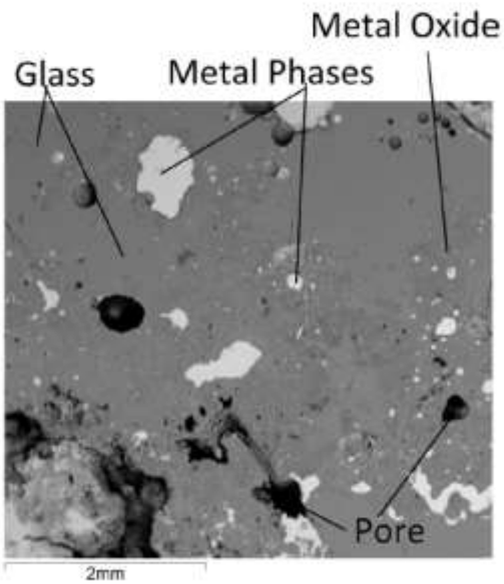
- Manchester: Olusola Ayoola
- Loughborough: Keith Schou
- QUB: Conrad Johnston*, Mel O'Leary*
- Sheffield: Luke Boast*
- UCL: Eszter Makkos*

Work Package 1 – Wasteforms

- **Glass-ceramic wasteforms (2 projects)**
  - In ***Microstructures and Corrosion of Intermediate Level Wasteforms Fabricated Using Novel Thermal Techniques*** Joule and plasma furnace heating were investigated as means to produce wasteforms from 3 Sellafield simulant ILW mixtures (plutonium contaminated material, site ion exchange plant waste, high metal content waste, Magnox sludge, asbestos, or pile fuel cladding). Several of the wasteforms made via Joule heating were suitably durable for safe disposal, showing protective corrosion layers or durable crystalline components. (Charles Hutchison / Bill Lee, Imperial)



SEM image of as-received plasma furnace high metal surrogate sample showing Al,Mg alloy metal in glass and ceramic matrix.

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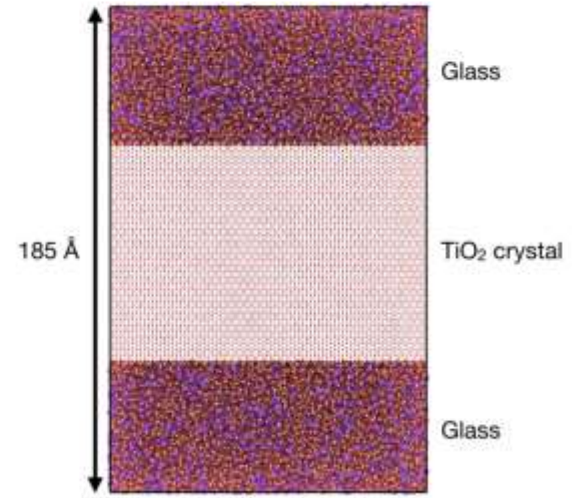
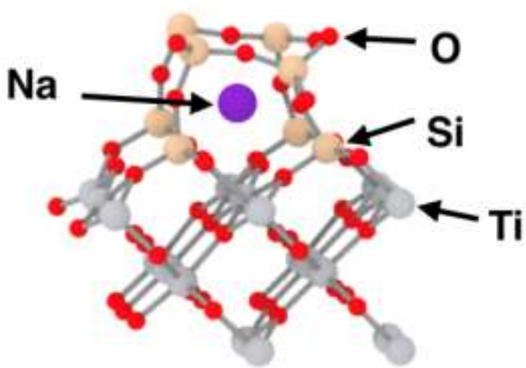
Work Package 1 – Wasteforms

- In ***Durability of Heterogeneous ILW Glass/Ceramic Wasteforms from Complex Wastestreams,*** Molecular Dynamics techniques are used to study a simplified glass/crystal composite material where rutile TiO_2 is sandwiched between glassy $(Na_2O)_x(SiO_2)_{1-x}$ layers. A key finding is the presence of partially ordered glass layers close to some of the interfaces, with preferential orientations for SiO_4 tetrahedra. In particular, the first silicate layer in contact with the crystal tends to be highly-structured, with Si ions occupying well-defined positions that depend on interface orientation, and showing 2-dimensional ordering depending on glass composition. Sodium ions reside in pores formed at the interface. (Paul Fossati / Bill Lee, Imperial)





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Work Package 1 – Wasteforms

- **Development of new glass wasteforms (1 project)**

  - In ***Thermal Treatment of Pu Contaminated Material (PCM) Waste*** a soda lime silica glass cullet was used as the glass forming additive for surrogate (Ce) Pu waste. The Ce was found as trivalent species, providing confidence that the slag component of the wasteforms developed here could incorporate Pu at the concentrations expected from treatment of PCM wastes. The materials produced here are broadly comparable, in terms of durability, to other simulant UK ILW glass products considered potentially suitable for geological disposal. (Luke Boast / Neil Hyatt, Sheffield)

Work Package 1 – Wasteforms

- **Wasteform package assessment (1 project)**

  - The project ***Assessment of the Behaviour of Metallic Uranium During Encapsulated Product Evolution*** was the first study dealing with the problem of the durability of UK ILW packages since the actual problem in the industry was spotted some years ago. The mechanical degradation of the packages was investigated in conjunction with the magnitude of the internal corrosion of the metallic ILW using experimental and modelling techniques. Grout, which is supposed to offer a monolithic bonding with the encapsulated waste and keep it fully constrained, has been observed to fail at very primary corrosion stages. The steel liner was found suitable to accommodate the volume expansion without failing thanks to its hardening behaviour. (Charilaos Paraskevoulakos / Tom Scott, Bristol)

Work Package 1 – Wasteforms

- **Thermal conversion of spent inorganic ion exchange materials into wasteforms (2 projects)**

  - In ***Glass composite materials for Fukushima ILW immobilisation*** two systems have been develop for used zeolite adsorbents. The first is a lead borosilicate (PBS) system that sinters fully at 500 ºC and the second is based on lead borate (PB) that sinters fully at 400 ºC. Full encapsulation of the model waste was achieved for waste loadings up to 50 wt.% in PBS and 40wt.% in PB, with both systems showing dense microstructures. (Dimitri Pletser / Bill Lee, Imperial)
  - In ***Novel Ceramic Wasteforms for Cs and Sr Encapsulation***, follow-up experiments on the HIPing products of Sr- and Sr,Cs-loaded IONSIV gave mixed ceramic wasteforms with Sr partitioned into $(Na,Sr)NbO_3$, $SrNb_2O_6$, $SrTi_{11}Nb_4O_{33}$ and $SrTi_{13}Nb_4O_{37}$ and Cs into $Cs_2TiNb_6O_{18}$. Additional experimental and computation studies focussed on assessing Ba retention in $Cs_2TiNb_6O_{18}$ after transmutation. (George Day / Joe Hriljac, Birmingham)

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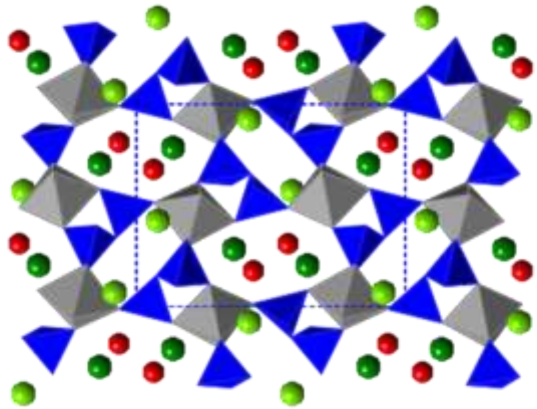
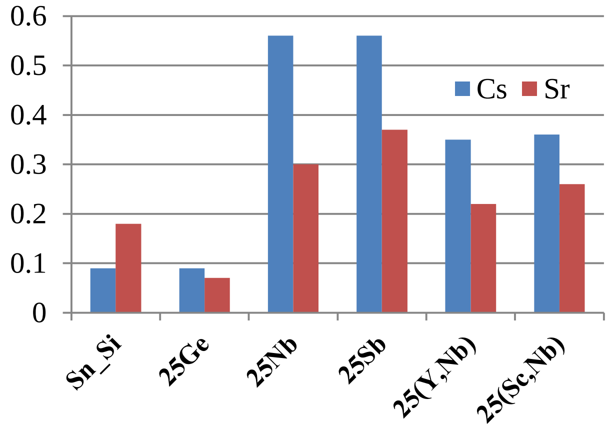
Work Package 2 – Effluent Treatment & Analysis

- **New materials for radionuclide removal from effluent (3 projects) & improved ultrafiltration (1 project)**
  - The aim of ***Novel Ion Exchange Materials*** was to systematically produce and test new silicates for selective Cs and Sr uptake with a design feature that they could be thermally converted directly into ceramic or glass-ceramic wasteforms after use. Metal-doped (Nb, Sb, Y, Sc) tin silicates were the primary focus of the work and show good promise. In parallel, work under ***New Ion Exchange Materials for Effluent Clean-up*** focussed on studies of related germanates. A noteable result in both cases is showing significantly improved uptake due to the doping which increases the ionic conductivity. (Tzu-Yu Chen / Ryan George / Joe Hriljac, Birmingham)





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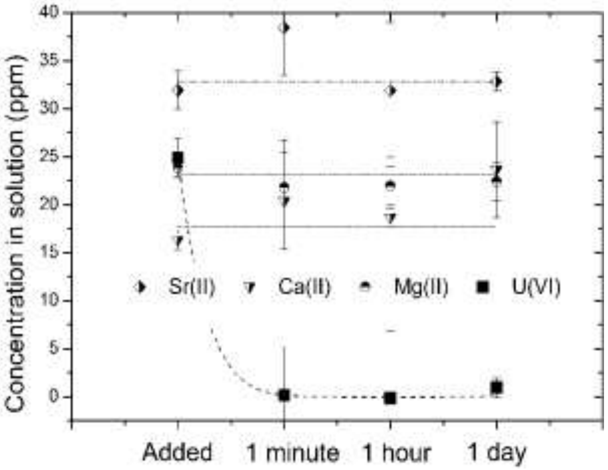
Work Package 2 – Effluent Treatment & Analysis

- In ***Magnetic Nanoparticles for Waste Separation or Sequestration*** superparamagnetic magnetite (Fe_3O_4) nanoparticles were functionalised with phosphate groups and showed fast and excellent removal of U even in competition with Ca, Mg and Sr. (Eleanori Cali / Mary Ryan / Luc Vandeperre, Imperial)



- In ***Enhanced Shear Micro- and Ultra-filtration Without Recycle Pumping*** it has been found that by oscillating the filter during filtration the pseudo steady state flux can be increased; for calcite an improvement of 2-3 times is common. Testing has demonstrated that this is linked to only the magnitude of the shear stress, and is independent on how that shear stress is applied. Ferric floc is used in the Enhanced Actinide Removal Plant (EARP) at Sellafield, and is the main interest for this project and the current focus of the work. (Keith Schou / Richard Holdich, Loughborough)

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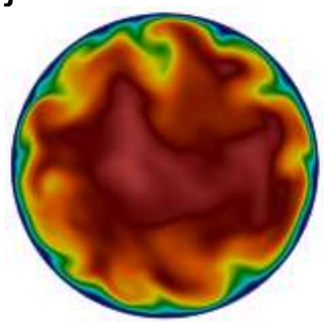
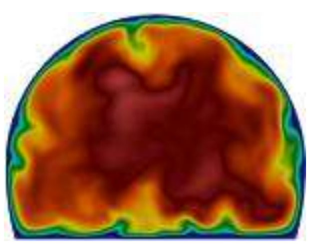
Work Package 3 – Pond & Silo Sludges

- **Sludge Modelling Studies (3 projects)**

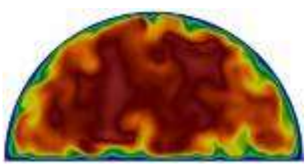
  - The aim of ***Measurement and Modelling of Sludge Mobilisation and Transport*** is to understand the influence of turbulence and gravity on particle agglomeration and breakup and how these phenomena affect the transport and deposition of radioactive particles suspended in the fluid phase. A large eddy simulation (LES) and distinct particle simulation technique based on a robust and efficient deterministic collision model, energy-balanced agglomeration model and shear-induced agglomerate breakup was developed. The computational fluid dynamics technique can handle correctly the interactions of particles with the carrier phase and with other complex boundaries (in terms of other particles and geometry walls). (Derrick Njobuenwu / Mike Fairweather, Leeds)



LES of full pipe flow
With Re = 53,000



LES of pipe flow with
a quarter bed height



LES of pipe flow with
a half bed height

DISTINCTIVE

Work Package 3 – Pond & Silo Sludges

- In ***Computational Investigation of the Interactions of Solvated Sr^{2+} Complexes with the Hydrated Brucite (0001) Surface*** DFT calculations were used to develop a computational model for the brucite surface and the solvated ions, which allow atomic scale insight into possible adsorption mechanisms between the two. During the course of the research an approach was developed and optimised to describe Sr complexes in water as well as in the vicinity of a hydrated brucite surface. (Eszter Makkos / Nik Kaltsoyannis, UCL)
- In ***Computational Simulations of Storage Pond Sludge Disturbance***, ab initio MD simulations were used to develop models of the Sr, Cs and U species that exist in alkaline aqueous conditions such as the SL legacy ponds. Current studies are modelling the interaction of these with CeO_2 (UO_2 analogue) surfaces. (Olivia Lynes / Andy Kerridge, Lancaster)

Work Package 3 – Pond & Silo Sludges

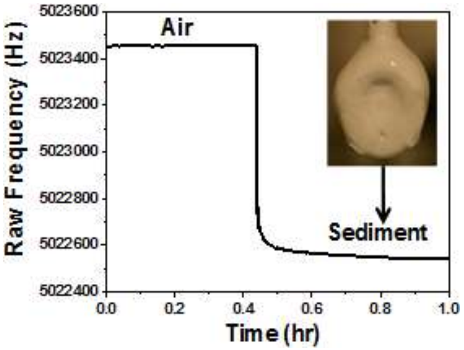
- **Sludge Characterisation Studies (5 studies)**

  - ***In-line Rheometry and Flow Characterisation of Dense Slurries in Pipe Flow Using Acoustic Methods*** (Hugh Rice / Mike Fairweather / Tim Hunter / David Harbottle, Leeds).

  - In ***Characterisation of Flocculated Waste Suspensions with Acoustic Backscatter*** the use and calibration of ultrasound was developed as a technique to measure suspended particle concentrations in solution. It has been successful in measuring intermediate particle concentrations up to 75 kg m^{-3} for non-cohesive, spherical glass particles and is now being applied to flocculated, cohesive sediments. (Alastair Tonge / Tim Hunter, Leeds)

Work Package 3 – Pond & Silo Sludges

- The project ***Quartz crystal microbalance (QCM) as a tool to measure complex suspension Rheology*** demonstrated the potential of QCM to determine the rheology of yield stress suspensions by monitoring the frequency and resistance responses of the QCM sensor in $Mg(OH)_2$ suspensions. (Andre Botha / David Harbottle / Tim Hunter, Leeds)



- The first phase of ***Development of Raman Spectroscopy Techniques for the Remote Analysis of Nuclear Wastes in Storage*** was to put together a spectral library of nuclear wet storage pond proxy materials and assess whether these are suitable for Raman Analysis. The next stage is to build a bespoke device suitable for deployment on a robot to take chemical analysis measurements in situ. (Kate Wyness / John Day, Bristol)

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Work Package 3 – Pond & Silo Sludges

- The aim of ***In-Situ Monitoring of the Legacy Ponds and Silos at Sellafield*** was to identify experimental factors that influence the quality of results of particle size distribution (PSD) mapping from sludge sampling and characterisation campaigns. The research has shown that in making inferences of sludge PSD characteristics at non-sampled locations, the use of deterministic methods such as the Triangular Delaunay Algorithm were more accurate than geostatistical methods in the absence of spatial auto-correlation and PSD maps with accuracies of 70% were achieved when samples from only 150 locations out of 200,000 possible locations in simulated sludge beds were analysed. (Olusola Ayoola / Barry Lennox, Manchester)

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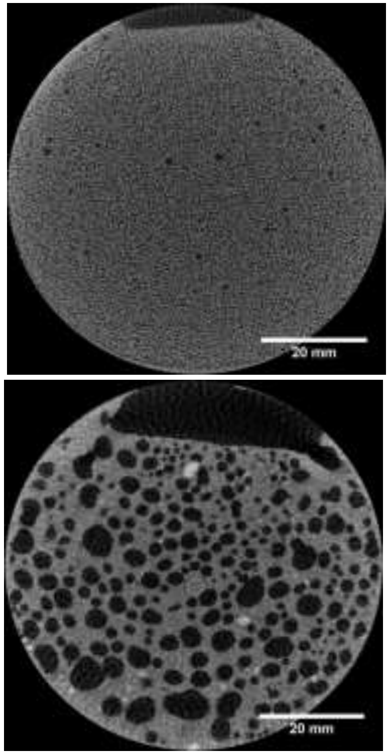
Work Package 3 – Pond & Silo Sludges

- **Gas Generation & Retention Studies (3 projects)**
  - The project ***Gas Retention and Release from Nuclear Legacy Waste*** has used clinical x-ray computed tomography to improve the understanding of how gas is transported through consolidated sludges and slurries found at various nuclear decommissioning sites in the UK and USA. Understanding the mechanisms for continuous, or chronic, gas release enables the identification of conditions where waste packages might be susceptible to large acute releases of flammable gas which could provide an avenue for the release of radionuclides. (Michael Johnson / David Harbottle / Tim Hunter, Leeds).



CT images of bubbles in commercial $Mg(OH)_2$ (top) and corroded Mg metal sediments (bottom)

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Work Package 3 – Pond & Silo Sludges

- The project ***Modelling Hydrogen Generation from Radioactive Sludges*** is using a computational approach to study two types of damage to the electronic structure (which determines the resulting chemistry) of brucite as an approximation to the ultimate effects of ionising radiation. Surprisingly, excess electrons are found to localise between the magnesium hydroxide layers in the bulk and MD simulations do not lead to any damage at room temperature. This may be due to the short timescales accessible to these types of simulations, ongoing work is examining surfaces with or without water coverage. (Conrad Johnston / Fred Currell, QUB)
- The aim of ***Irradiated Sludges, a Joint Theoretical/Experimental Study*** is to measure the rate of hydrogen production and diffusion in sludge simulants in order to understand if transport is strictly diffusion limited or if hydrogen movement can be slowed by ‘sticking’ to the sludge grains. (Mel O’Leary / Fred Currell, QUB)

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Selected Achievements to Date

- ~30 papers entered into Researchfish to date

- Joule heating has been shown to produce good wasteforms from mixed Sellafield ILW wastes via Joule heating.
- A soda lime silica glass cullet has been shown to be the basis of a new PCM waste with comparable durability to current UK ILW glass products considered suitable for geological disposal.
- The first study of the processes causing volume expansion in UK ILW canisters containing U metal in grout has shown that even though the grout fails at a very primary corrosion stage the steel liner will retain the product due to its hardening behaviour.
- New materials for removal of radionuclides, non-zeolite inorganic ion exchange materials and functionalised superparamagnetic iron oxide nanoparticles, have been developed and are currently being tested for clean-up of a series of mixed ion solutions as provided by SL.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Selected Achievements to Date

- Development of a non-intrusive acoustic backscatter measurement technique for monitoring suspended sediment particles is being installed on plant at Sellafield, allowing the improved design of waste processing options.
- Work on slurry transport and deposition has provided input to process design. According to Sellafield, the technology being developed could accelerate a 7 year hazard reduction programme (emptying of tanks) by more than 1 year, with multi-£M savings.
- Technical advice has been given regarding the design of a replacement for the Site Ion Exchange Effluent Plant (SIXEP) based on the slurry modelling and experimental work performed, with studies of gas hold-up in sludges informing operational planning at Sellafield for raw waste storage.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Acoustic in-line rheometry and friction factor modelling in low-Reynolds number non-Newtonian mineral slurries in pipe flow for continuous process monitoring and prediction

Hugh P. Rice
School of Chemical and Process Engineering
University of Leeds

DISTINCTIVE Conference, York, September 2018

Why nuclear and why acoustics?

- UK has large inventory of active legacy waste, stored in variety of vessels, awaiting transport, processing and disposal
- Challenges exist in characterising waste safely; acoustic methods are ideal as they are generally low-cost, easily deployed, non-hazardous and computationally undemanding

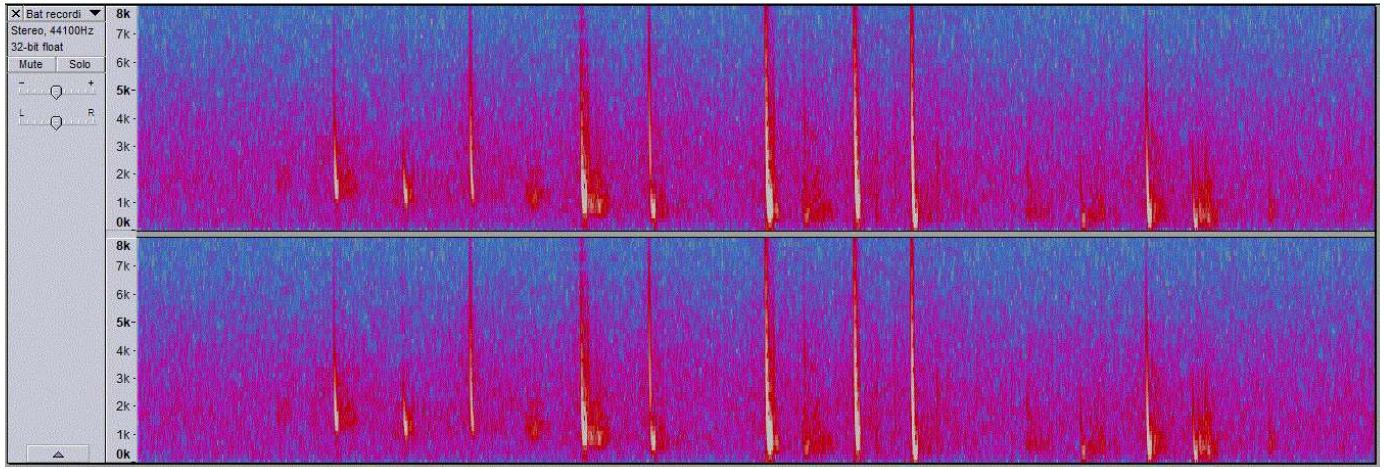


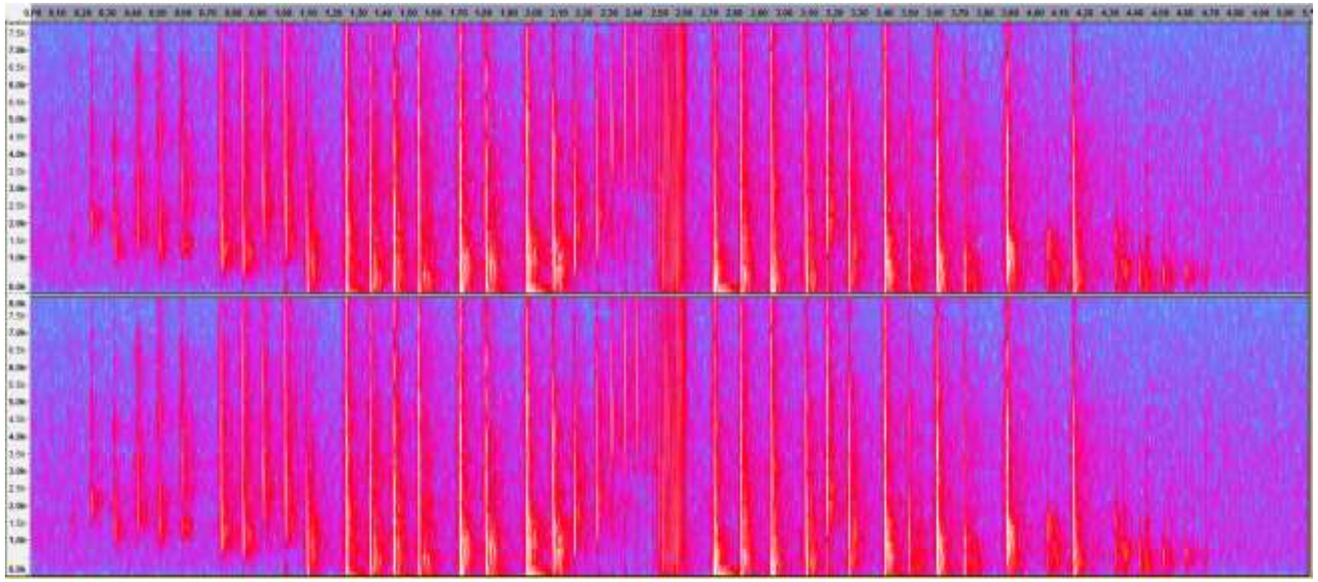

£67.5bn	£4.6bn	2120
is the provision for the cost of decommissioning and cleaning up Sellafield, before discounting future cash flows to their present values	is the estimated lifetime cost of the 14 major projects at Sellafield, before discounting future cash flows to their present values	is the target year for completing the clean-up of Sellafield

55	buildings at Sellafield have been decommissioned
1,400	buildings remain at Sellafield
£1.6 billion	spent on running and cleaning up Sellafield during 2011-12
£411 million	spent on major projects at Sellafield in 2011-12
£1.3 billion	is the estimated undiscounted lifetime cost of the largest project at Sellafield
9,231	permanent staff employed at the site on average by the site's operator (Sellafield Limited) during 2011-12
276	permanent full-time equivalent staff employed by the Nuclear Decommissioning Authority at 31 March 2012

Table: "Managing Risk Reduction at Sellafield", National Audit Office Report HC 630, 2012.

Acoustics in nature

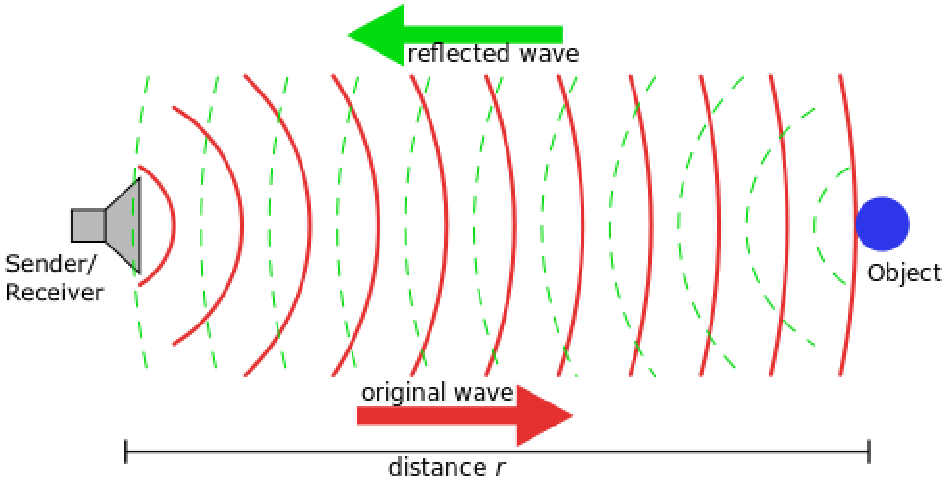


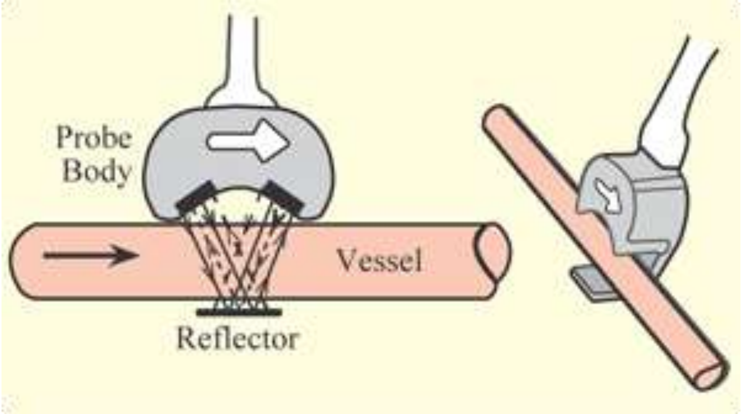


- *Wavelength @ 45 kHz ≈ 8 mm*
- *Wavelength @ 75 kHz ≈ 5 mm*

Upper: my garden, August 2018; lower: courtesy of Ian Rawes, London Sound Survey

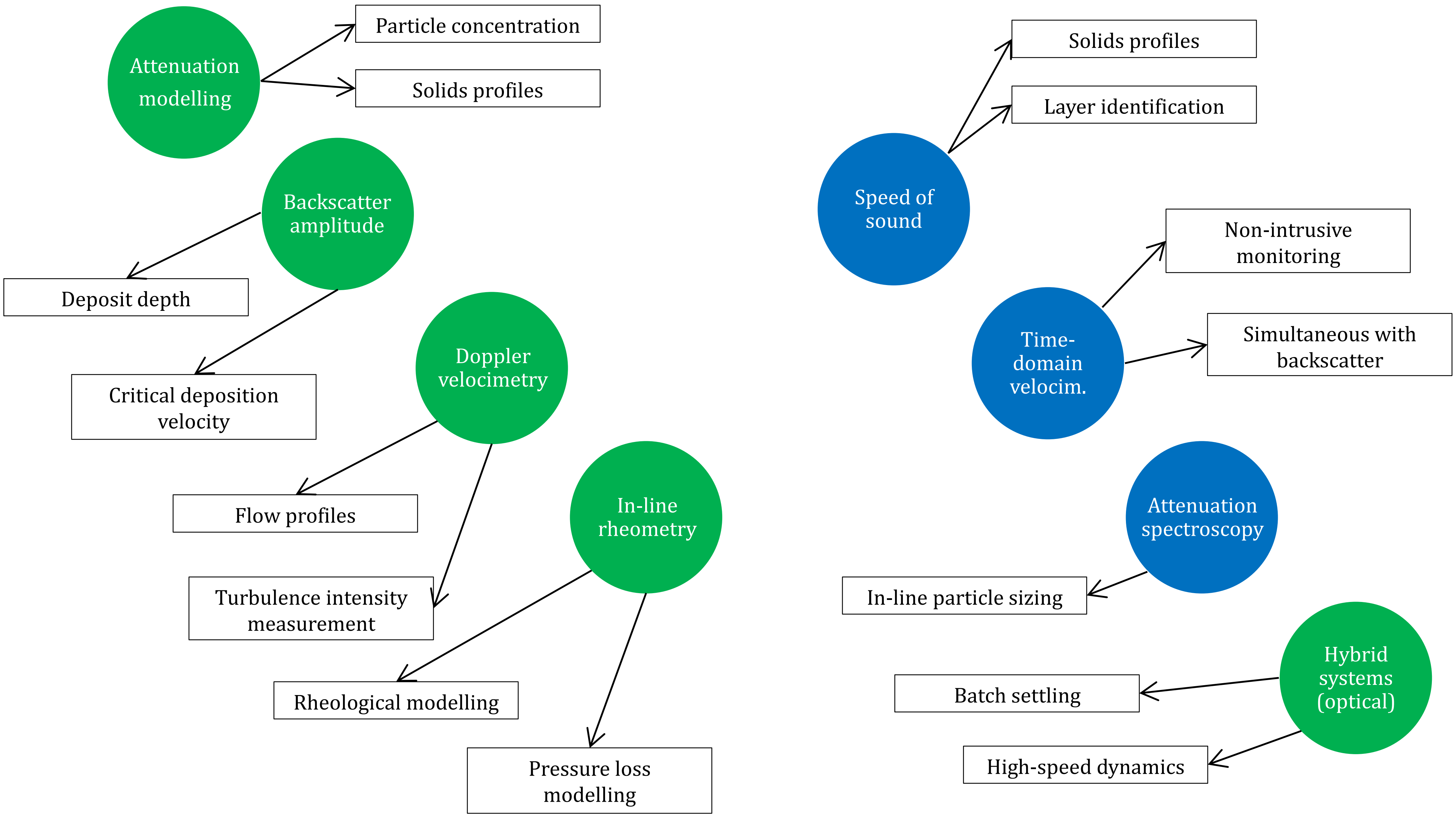
Acoustics in nature





- *Time of flight (speed of sound) + backscatter*
  - *Bats:* Range finding, “terminal buzz”
  - *Engineering:* Range finding, speed of sound
- *Doppler effect*
  - *Bats:* Velocimetry, sensitivity compensation
  - *Engineering:* Velocimetry
- *Frequency modulation*
  - *Bats:* “Chirp”, size / “texture” / “colour” of objects
  - *Engineering:* Size / shape / conc. of particles, etc.

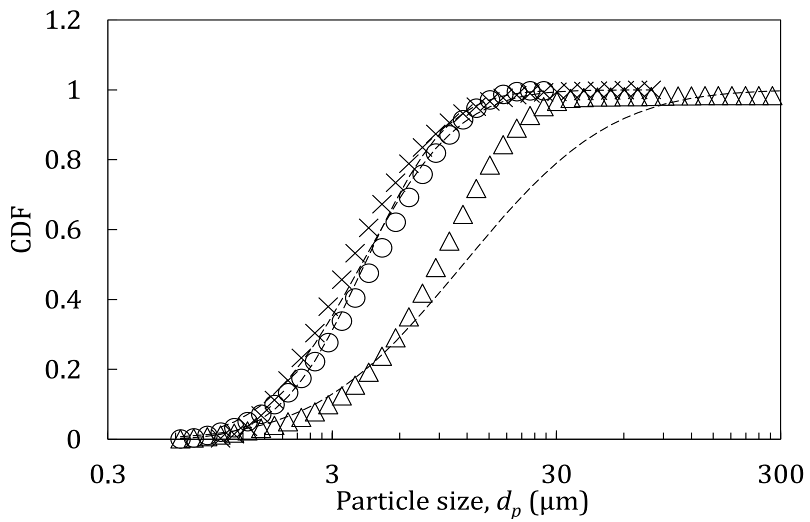
Nuclear Leeds acoustics roadmap



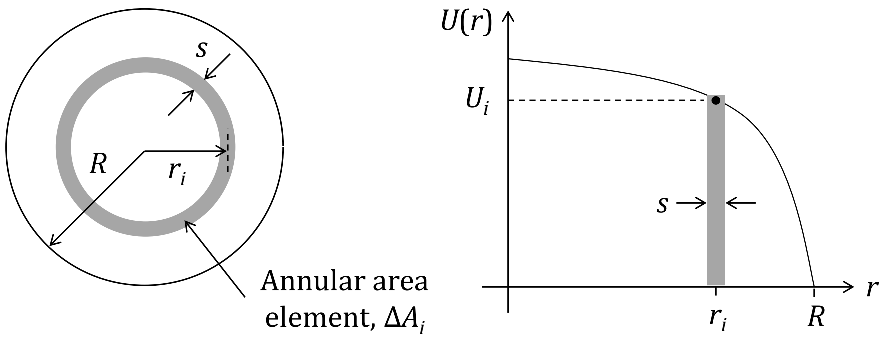
In-line rheometry of non-Newtonian flows (1/3)

- When hazards are present, in-line rheometry avoids need for sampling for off-line analysis
- In-line velocimetry-pressure drop rheometry method used to find viscosity, η, with $U(r)$ from velocimetry and ΔP from pressure sensors over length, L; flow rate Q from numerical integration of velocity profile

$$\eta(r) = \frac{\tau(r)}{\dot{\gamma}(r)};\dot{\gamma}(r) = -\frac{\mathrm{d}U(r)}{\mathrm{d}r};\tau(r) = \frac{\Delta P}{2L}r$$



Particle size distributions, crosses: $Mg(OH)_2$; circles: $CaCO_3$; triangles: $BaSO_4$ [2].



Numerical integration for flow rate measurement [2].

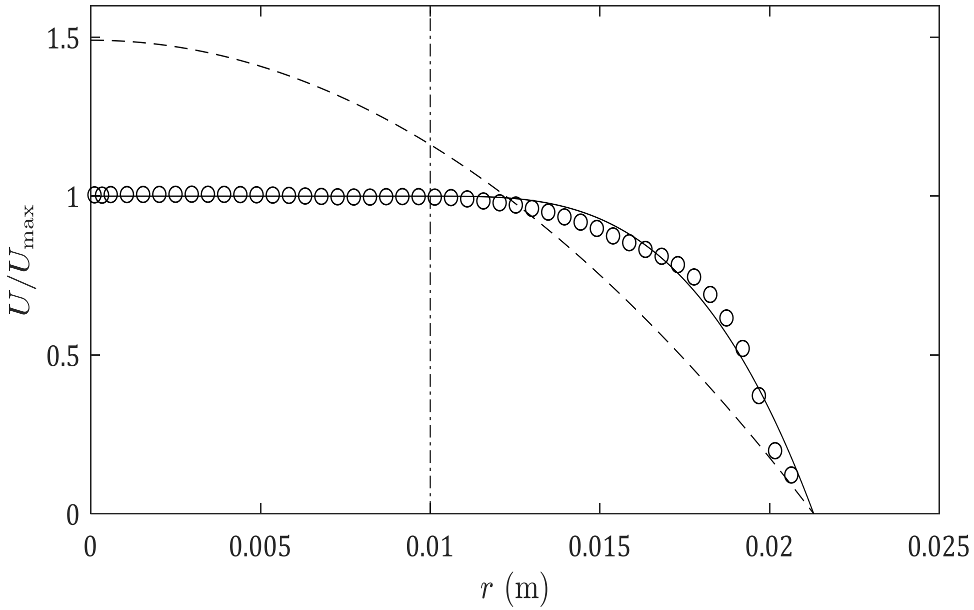
[1] Madlener K *et al*. (2009), Progr. Propulsion Phys. 1 237-250; [2] two papers in draft

In-line rheometry of non-Newtonian flows (2/3)

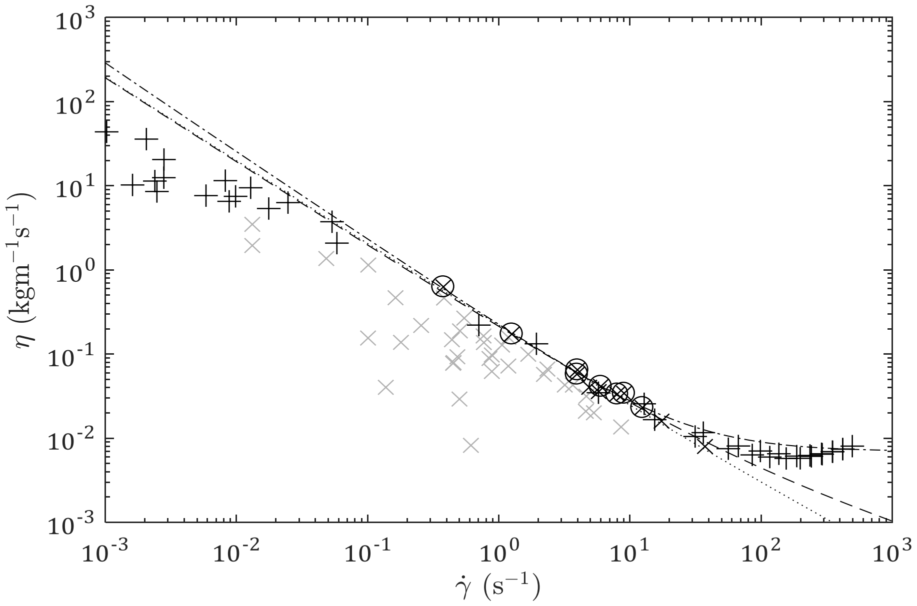
- Rheological parameters found for Herschel-Bulkley Extended (HBE) model for $CaCO_3$, $BaSO_4$, $Mg(OH)_2$ suspensions, where [1]:

$$\eta_{\mathrm{HBE}} = \tau_0 \dot{\gamma}^{-1} + K \dot{\gamma}^{n-1} + \eta_\infty$$

$$U(r) = \left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} \frac{R}{\left(\frac{1}{n}+1\right)} \left[\left(1-\frac{\tau_0}{\tau_w}\right)^{\frac{1}{n}+1} - \left(\frac{r}{R}-\frac{\tau_0}{\tau_w}\right)^{\frac{1}{n}+1}\right]$$



Measured (circles), fitted (solid line) and equivalent Newtonian (dashed line) velocity profiles, $BaSO_4$ at ϕ = 10%; vertical line: plug radius, r_p [2].

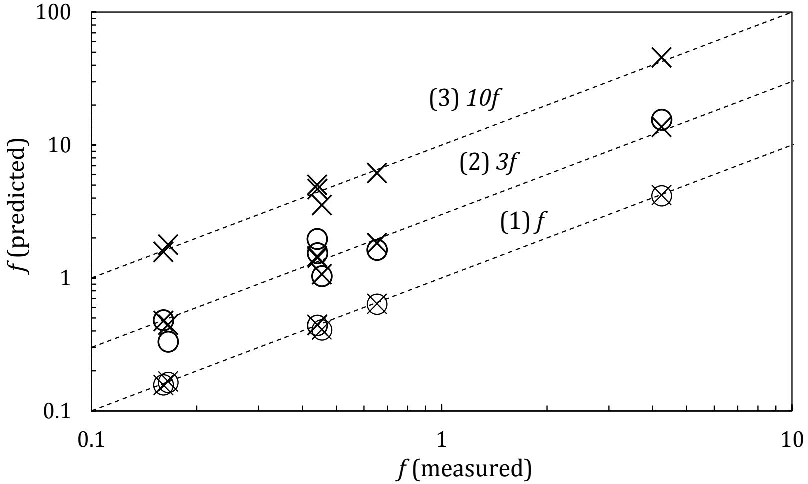


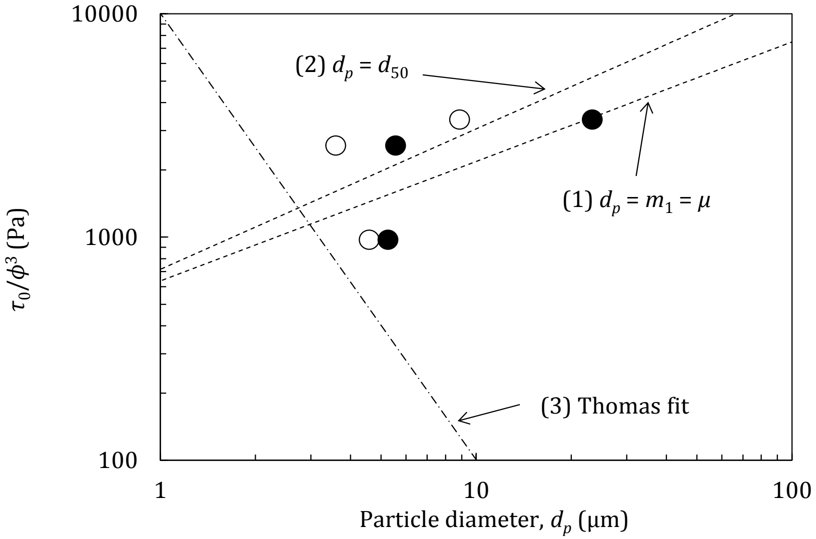
Rheological curves, $CaCO_3$ at ϕ = 10%. Lines: fits to rheometric and velocimetric data *via* two models. In-line data: crosses; off-line: pluses [2].

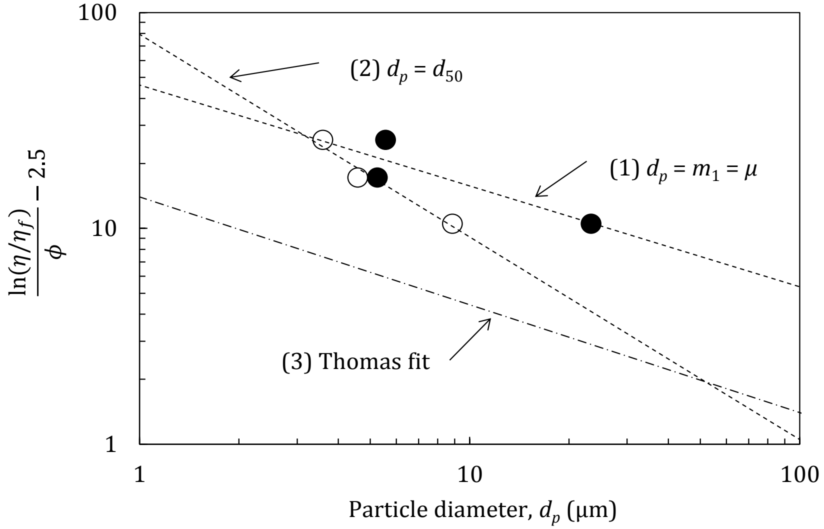
[1] Madlener K *et al*. (2009), Progr. Propulsion Phys. 1 237-250; [2] two paper in draft

In-line rheometry of non-Newtonian flows (3/3)

- Friction factor predictions for HBE model [1] tested and found to perform very well
- Yield stress and viscosity modelled and found to compare poorly to model [2] as cohesiveness and polydispersity (*i.e.* particle size distribution) not accounted for







$$f_{\text{Darcy}} = 8\left(\tau_0 + K\left(\frac{3m+1}{4m}\right)^n\left(\frac{8\bar{u}}{D}\right)^n + \eta_\infty\frac{3m+1}{4m}\frac{8\bar{u}}{D}\right)\Big/\left(\rho\bar{u}^2\right)$$

$$= 64\left(\frac{\tau_0}{8}\left(\frac{D}{\bar{u}}\right)^n + K\left(\frac{3m+1}{4m}\right)^n 8^{n-1} + \eta_\infty\frac{3m+1}{4m}\left(\frac{D}{\bar{u}}\right)^{n-1}\right)\Big/\left(\rho\bar{u}^{2-n}D^n\right)$$

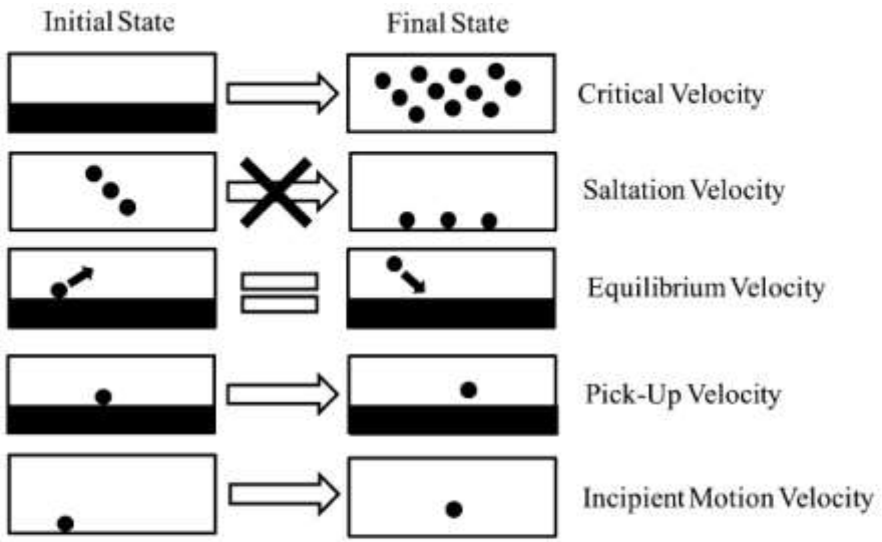
$$m = \frac{nK\left(8\bar{u}/D\right)^n + \eta_\infty\left(8\bar{u}/D\right)}{\tau_0 + K\left(8\bar{u}/D\right)^n + \eta_\infty\left(8\bar{u}/D\right)}$$

$$\tau_0 = a_1 d_p^{b_1}\phi^3$$

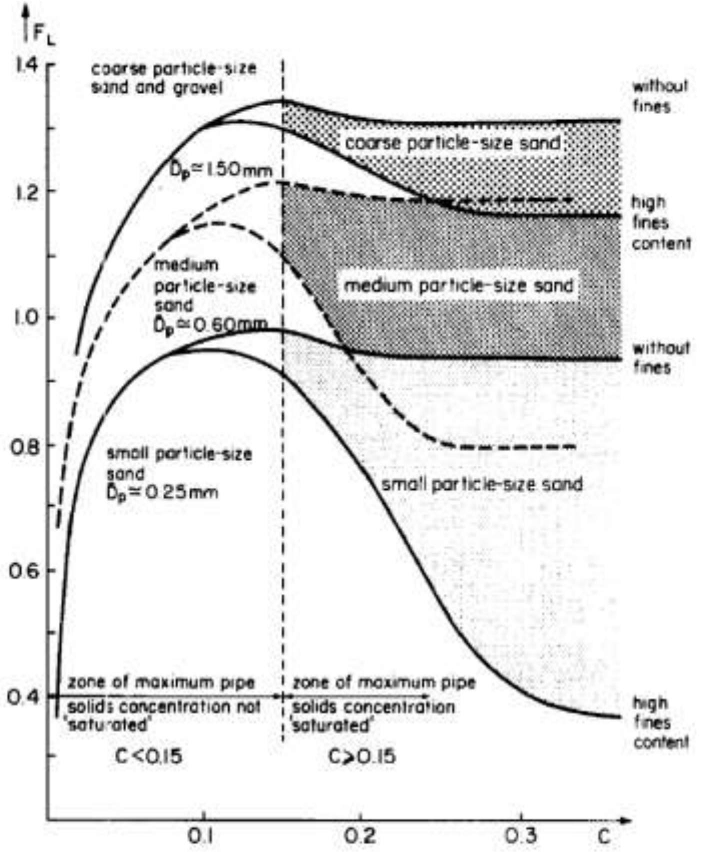
$$\eta_{\infty,r} = \exp\left[\left(2.5 + a_2 d_p^{b_2}\right)\phi\right]$$

[1] Madlener K *et al*. (2009), Progr. Propulsion Phys. 1 237-250; [2] Thomas DG (1961), AIChE J. 7 (3) 431-437.

Critical deposition velocity (1/3)



- U_c separates suspended and settling flows
- Measured U_c in pipe loop at several vol. fractions (ϕ = 0.5 to 10 %) by extrapolation of bed depth to zero *via* echo amplitude



- Based on limited available data, seek function of following form:

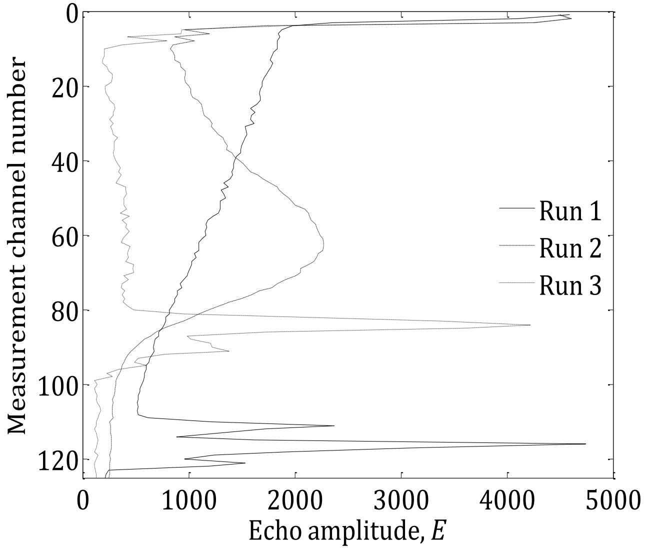
$$\mathrm{Re}_{pc} = a\mathrm{Ar}^b(\alpha\phi^{0.5} + 1) = U_c d/\nu$$

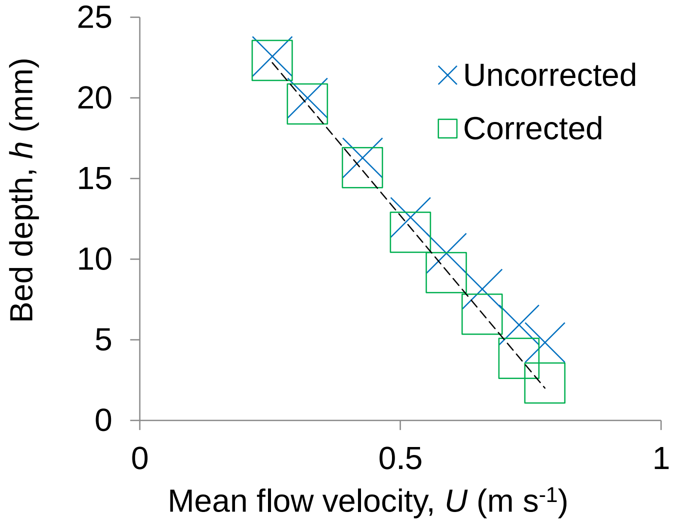
$$\mathrm{Ar} = gd^3(\rho/\rho_w - 1)/\nu^2$$

- Coefficients *a*, *b* and *α* found by fitting data in limit $\phi \to 0$ [1]

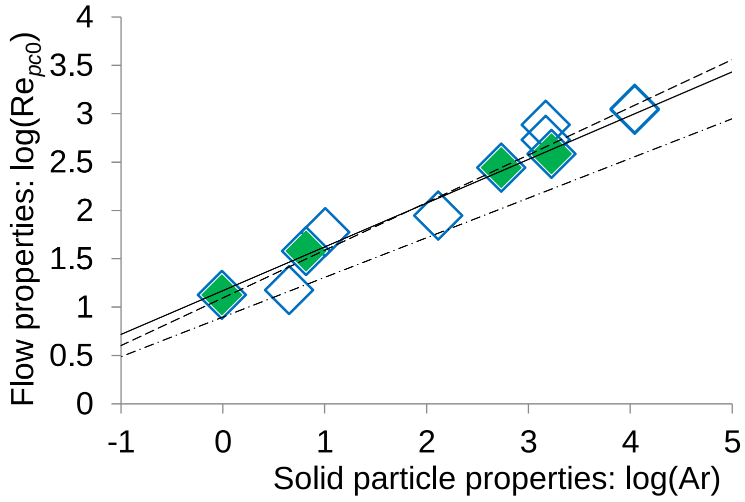
[1] Rice HP *et al.* (2015), Chem. Eng. Sci. 126 759-770; second paper in draft
Figures: top left: Soepyan FB *et al.* (2014), AIChE J. 60 (1) 76-122; bottom right: Parzonka W *et al.* (1981), Can. J. Chem. Eng. 59 291-296

Critical deposition velocity (2/3)





Left: Bed depth *via* echo amplitude, examples. Right: Bed depth *vs.* mean flow velocity, large glass particles at ϕ = 3 %, corrected for suspended sediment.



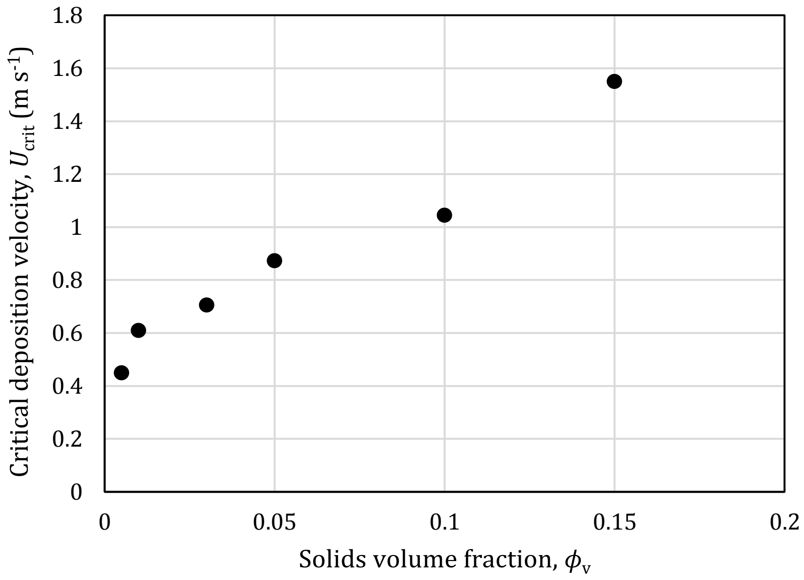
Critical particle Reynolds no. *vs*. Archimedes no. Open diamonds: literature; filled diamonds: new data [2]. Solid line: fit to all data; dashed-dotted and dashed: fit to literature.

- Found the following relationship by fitting [1]:

$$\mathrm{Re}_{pc} = 12.4\mathrm{Ar}^{0.493}(8.91\phi^{0.5} + 1) = U_c d/\nu$$

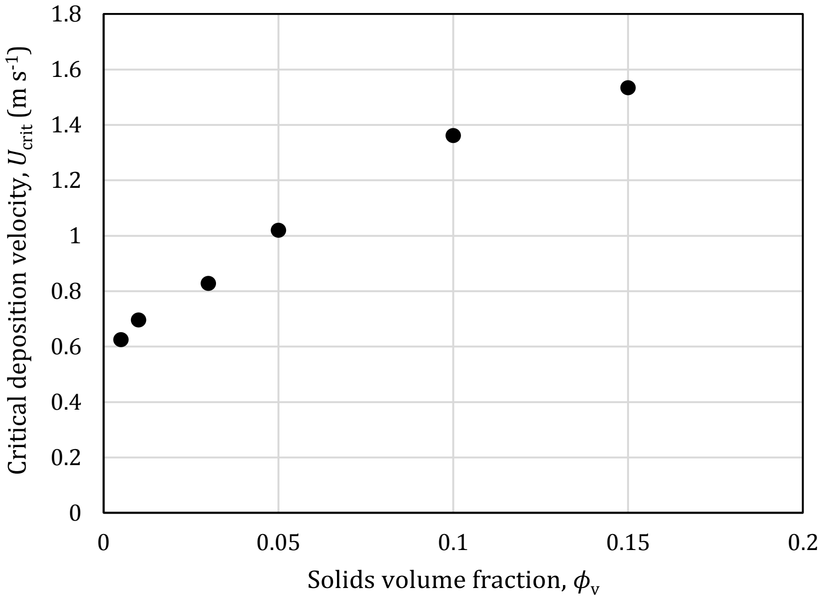
[1] Rice HP *et al.* (2015), Chem. Eng. Sci. 126 759-770

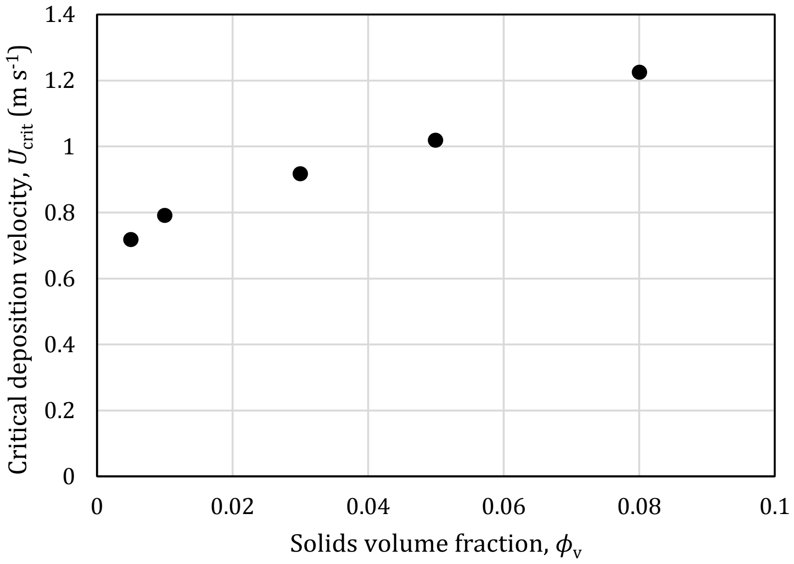
Critical deposition velocity (3/3)



Honite 22
(small glass)

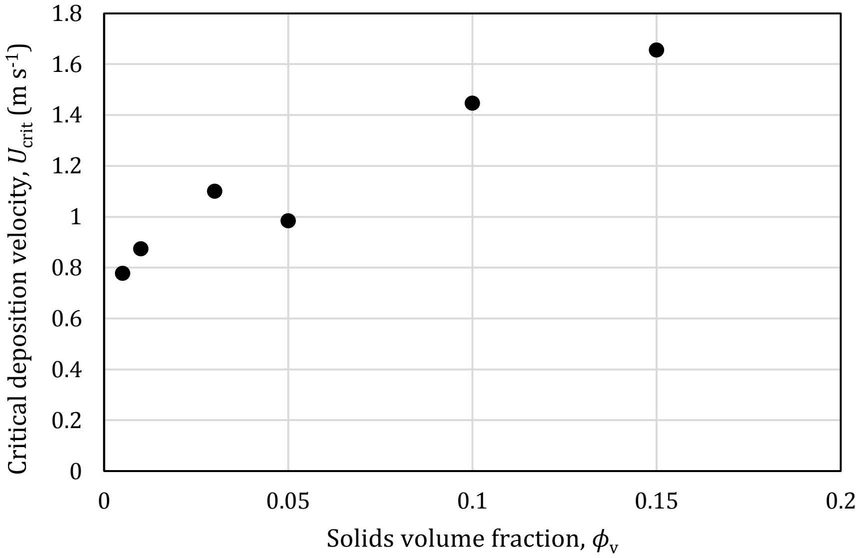
Honite 16
(large glass)





Guyblast 40/60
(small plastic)

Guyblast 30/40
(large plastic)



Paper in draft

Monitoring and modelling of batch settling

- Hybrid video-acoustic (speed of sound, backscatter and attenuation modelling) experimental system
- Aim to characterise settling in vessels of arbitrary shape with initial solids fraction ϕ_0

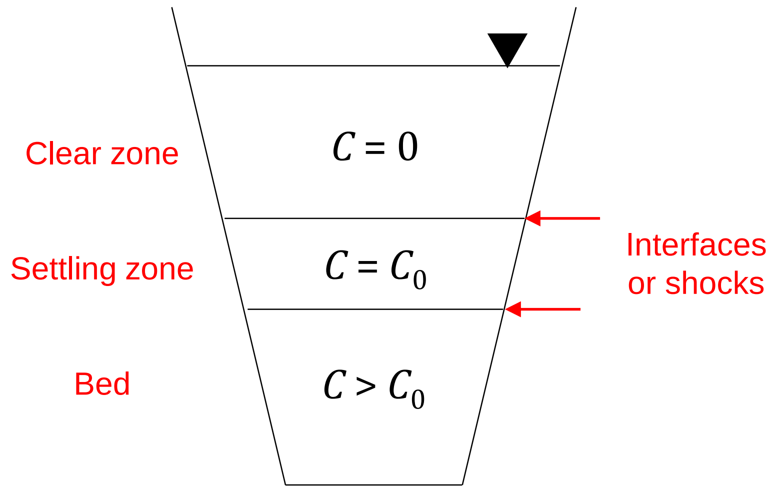
Mathematical/numerical problem

- Models become very complex when real properties accounted for:

1. Arbitrary cross-sectional area
2. Polydisperse solids fraction
3. Vessel size, wall friction, yield stress

- Aim to develop methods for finding constitutive relations from transient and equilibrium measurements [1]

$$A(x)\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(A(x)\left(f(C) + d(C)\frac{\partial C}{\partial x}\right)\right)$$



Experimental problem

- High-quality experimental data very scarce, but real nuclear systems may be difficult to access

1. Video used to track interface positions → settling velocity
2. Acoustic backscatter used to track interfaces → thickness of each zone
3. Speed of sound used to compute mean solids fraction in each zone → profiling in time, $\phi(z,t)$

$$t = \int_{s_1}^{s_2} \frac{\mathrm{d}s}{c(s)} \quad \text{where} \quad c(s) \leftrightarrow C(x)$$

[1] Burger R, Careaga J and Diehl S (2018), IMA J. Appl. Math. 83 526-552

Acknowledgements

Dr. Hugh P. Rice	SCAPE	h.p.rice@leeds.ac.uk

Supervisors (past and present):

Dr. Tim Hunter	SCAPE	t.n.hunter@leeds.ac.uk
Prof. Mike Fairweather	SCAPE	m.fairweather@leeds.ac.uk
Prof. Simon Biggs	Univ. Queensland	eait.dean@uq.edu.au
Prof. Jeff Peakall	Sch. Earth and Environment	j.peakall@leeds.ac.uk

Funding of projects shown in presentation:

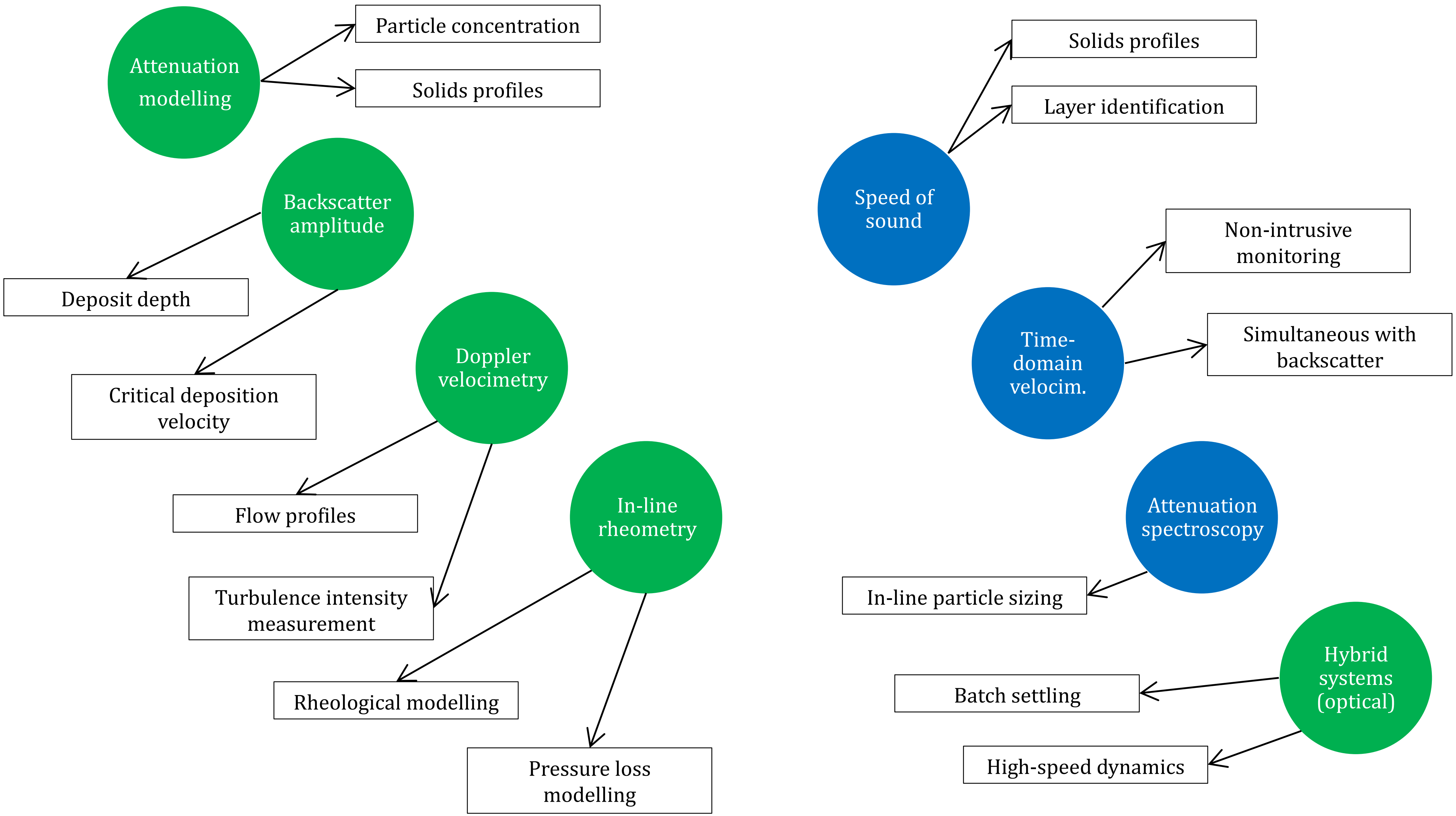
- EPSRC: EP/F055412/1, DIAMOND: Decommissioning, Immobilisation and Management of Nuclear Wastes for Disposal
- TSB/InnovateUK: Part of *Developing the civil nuclear power supply chain* call (Grant no. 101433), additional funding from NDA
- EPSRC: EP/L014041/1, DISTINCTIVE: Decommissioning, Immobilisation and Storage Solutions for Nuclear Waste Inventories
- EC: SPIRE-08-2015-680565, SPIRE programme: Sustainable Process Industry through Resource and Energy Efficiency
- Sellafield Ltd. (ongoing)

Nuclear Leeds website:
https://engineering.leeds.ac.uk/nuclear
Director: Prof. Bruce Hanson (b.c.hanson@leeds.ac.uk)

Member of the Leeds-Sellafield Ltd. Sludge Centre of Expertise

Sellafield Ltd

Nuclear Leeds acoustics roadmap



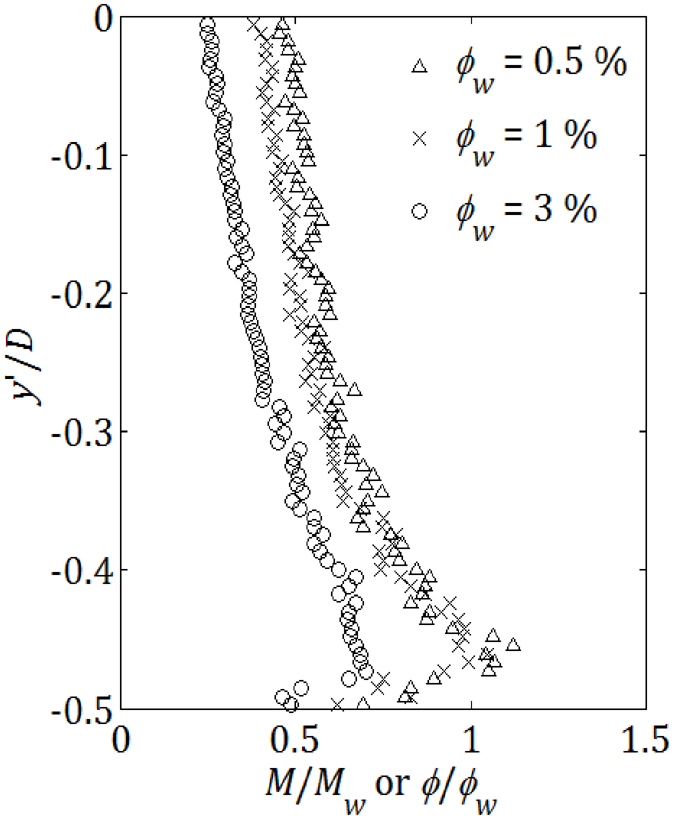
Measurement of suspended particle concentration

- Existing model [1] relating received voltage, V, to particle concentration, M, was extended [2] to allow acoustic coefficients (K_h and ξ_h) for arbitrary particle types to be measured directly
- Coefficients measured in homogeneous calibration mixing tank at frequencies f_1 and f_2
- Method applied to pipe flow over range of flow velocities and nominal concentrations

$$V = \frac{K}{\psi r} M^{1/2} e^{-2(\alpha_w + \alpha_s) r}$$

$$\alpha_s = \frac{1}{r} \int_0^r \xi(r')\, M(r') \mathrm{d}r' = \xi_h M$$

$$M = J_1^{(1-\xi_1/\xi_2)^{-1}} J_2^{(1-\xi_2/\xi_1)^{-1}};\ J = f(V)$$



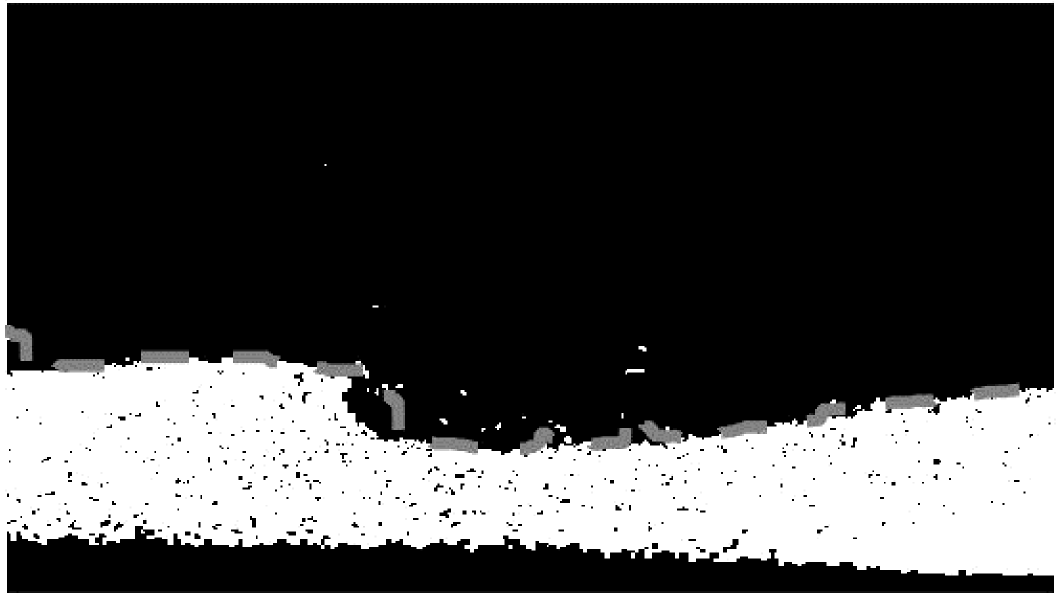
Normalised particle concentration *vs.* X-sectional distance in lower half of pipe flow with 77 µm glass beads [1].

- Method accurately predicts flow regime and M if attenuation is not strong
- Aim to compile database of acoustic properties for materials of interest; can be used to select optimal frequencies or maximum measurement domain

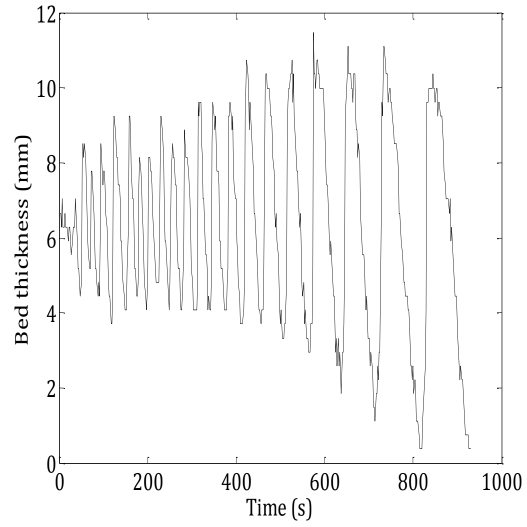
[1] Hurther D *et al.* (2011), Coast. Eng. 58 594-605; Thorne PD and Hurther D (2014), Cont. Shelf Res. 73 97-118
[2] Rice HP *et al.* (2014), J. Acoust. Soc. Am. 136 (1) 156-169; Chem. Eng. Sci. 126 745-758

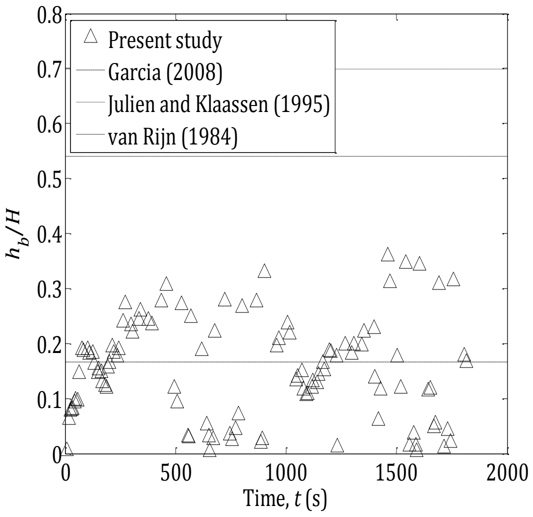
Time-varying bedforms (1/2)

- Time-dependent bedforms are common in nature, but have received less attention in industry, despite relevance to flow structure, mass transport and possible influence on plugging, *etc.*



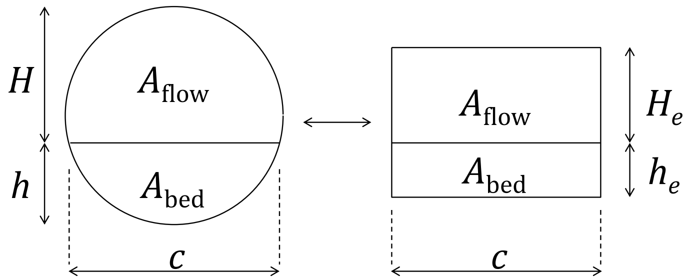
Time-varying bedforms (2/2)



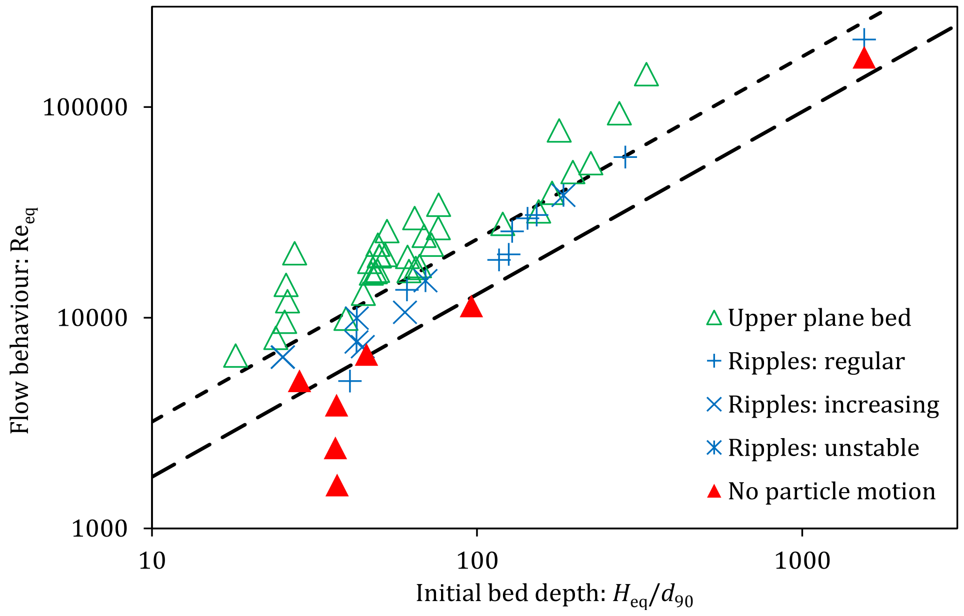


Left: Bed depth *vs.* time, example. Measured using same method as for critical transport velocity. Right: Relative bed depth *vs.* time, compared to several predictions. Both for small plastic particles.

- Suggestions made for universal scalings of natural and industrial bedform behaviour [1]:



- Initial bed depths and flow rates, Re_{flow}, of various bedform types give phase diagram for predictions (small plastic particles):

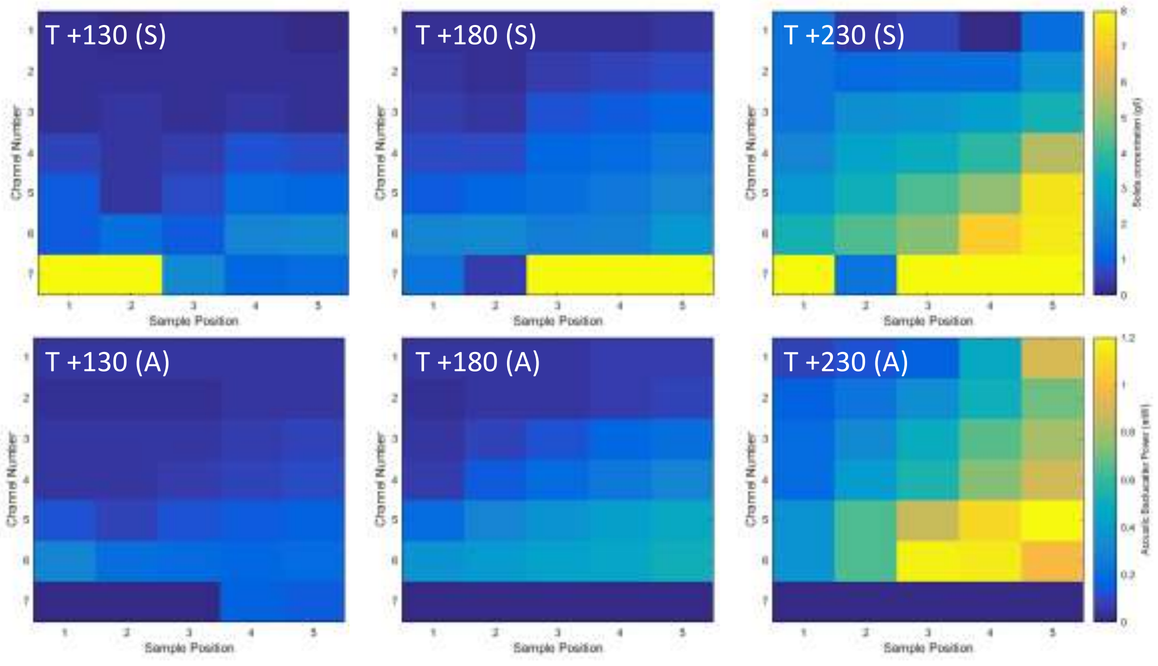


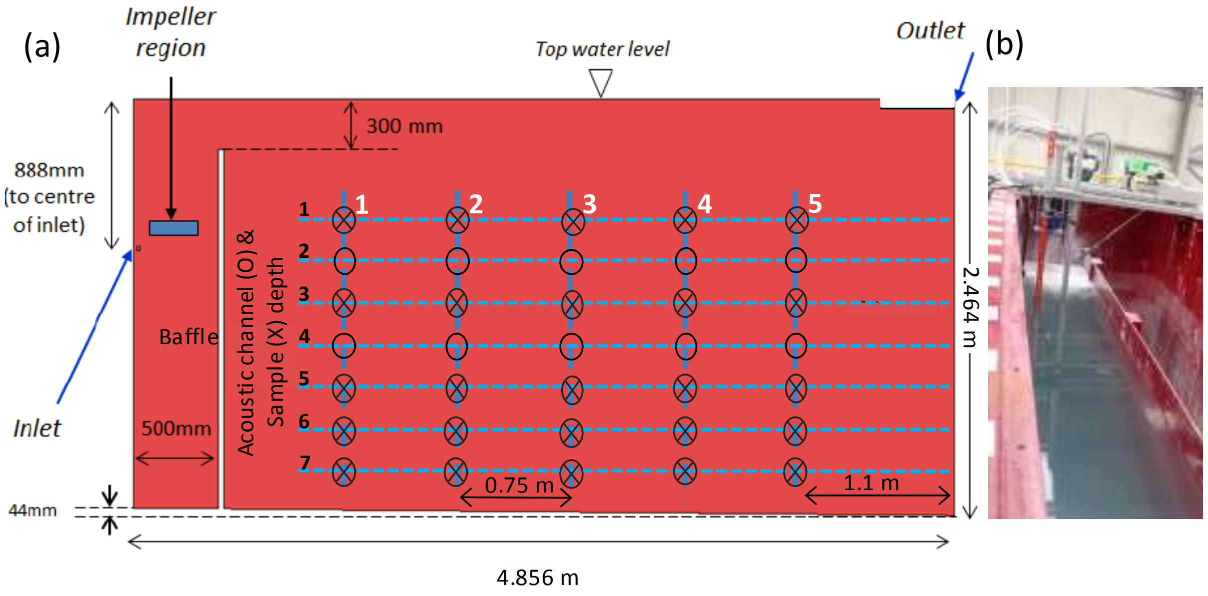
Phase diagram of bedform types, flow Reynolds no. vs. relative bed depth.

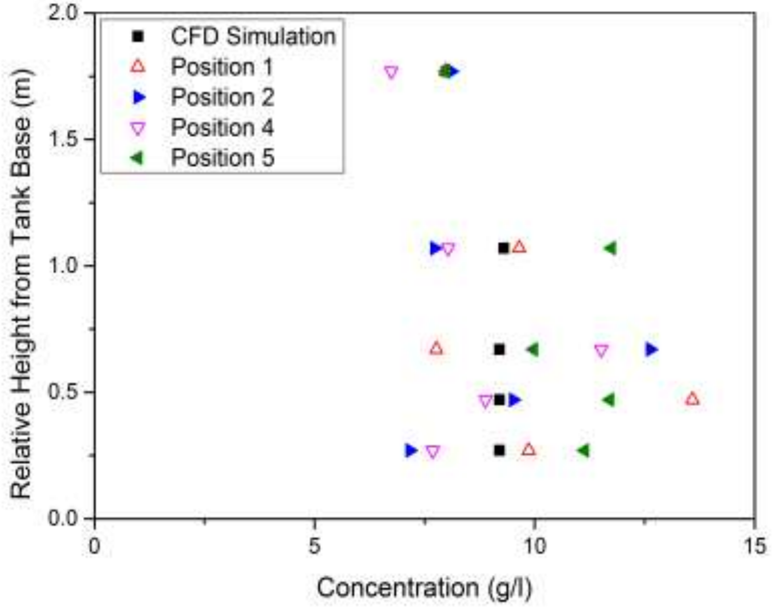
[1] Rice HP *et al.* (2017), Int. J. Multiph. Flow 93 1-16; THMT12 conference, Palermo, 2012

Application of acoustics to pilot-scale nuclear-type settling tank [1]

- Collaboration with MMI Engineering (numerical), NSG Ltd. (experimental hosting) and Sellafield Ltd. to characterise nuclear-type settler
- Acoustic results from custom-built, cutting-edge acoustic system (not shown) developed by colleagues in Sch. Electronic and Elec. Eng.

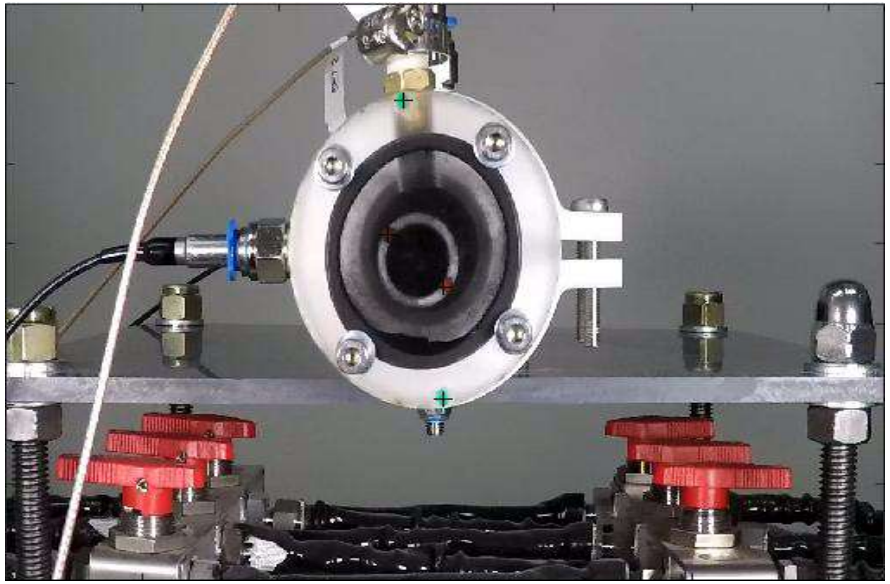


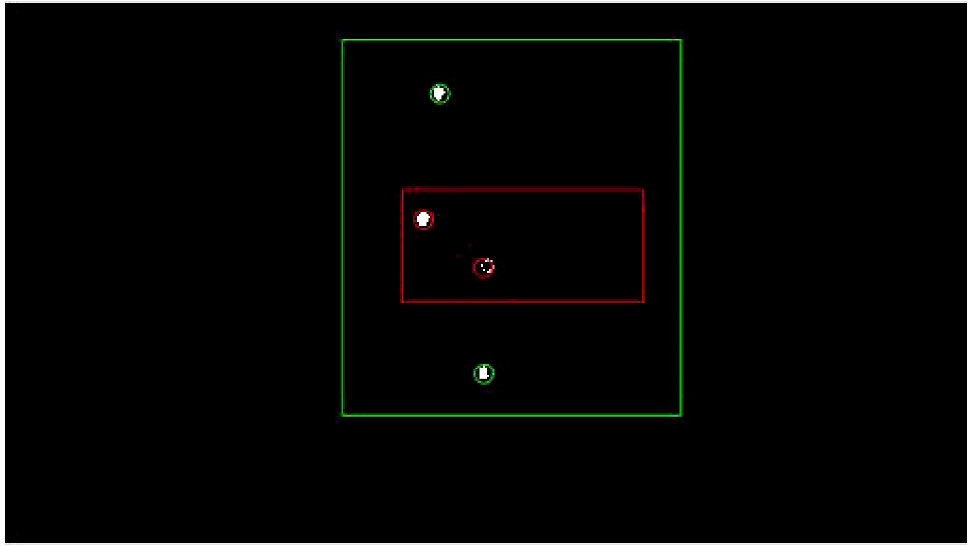




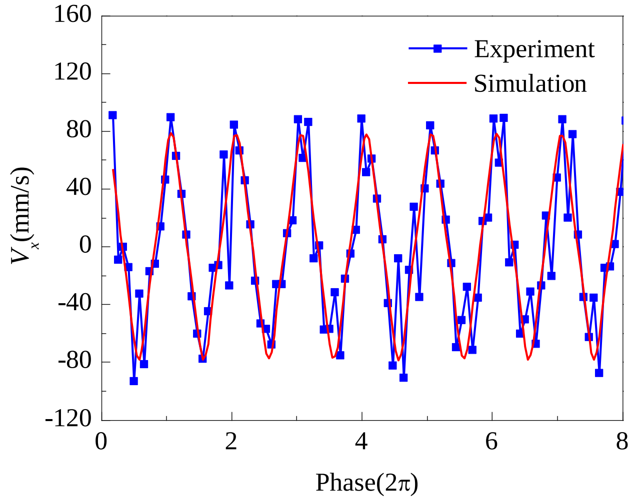
[1] IEEE International Ultrasonics Symposium 2015, Taipei, and 2016, Tours; Waste Management 2016, Phoenix; paper in draft

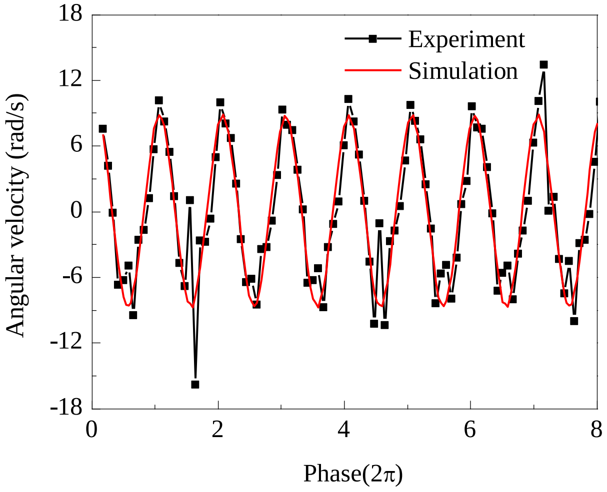
Acoustic-optical hybrid systems: agitated tube reactor [1]

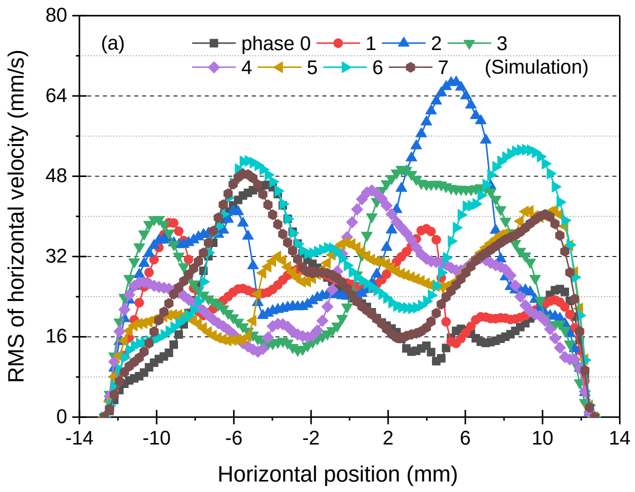


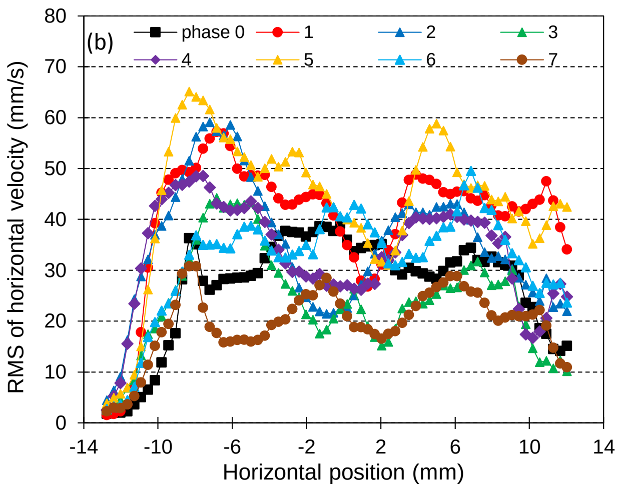


- Acoustic vs. numerical results









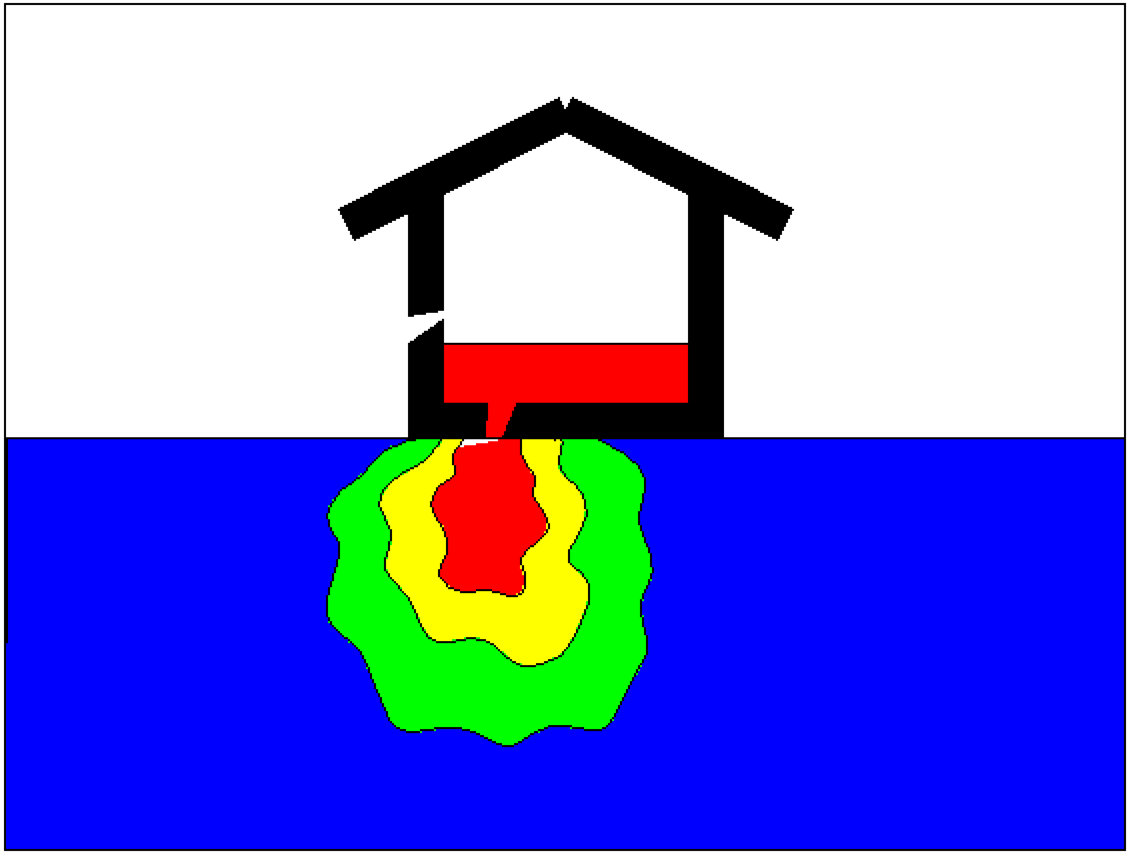
[1] Three papers in draft

The DISTINCTIVE University Consortium: Structural Integrity

Matteo Pedrotti and Pieter Bots
Department of Civil and Environmental Engineering, University of Strathclyde

C. Wong, G. El Mountassir, J. Renshaw, R. Maddelena,
A. Hamilton, R. J. Lunn

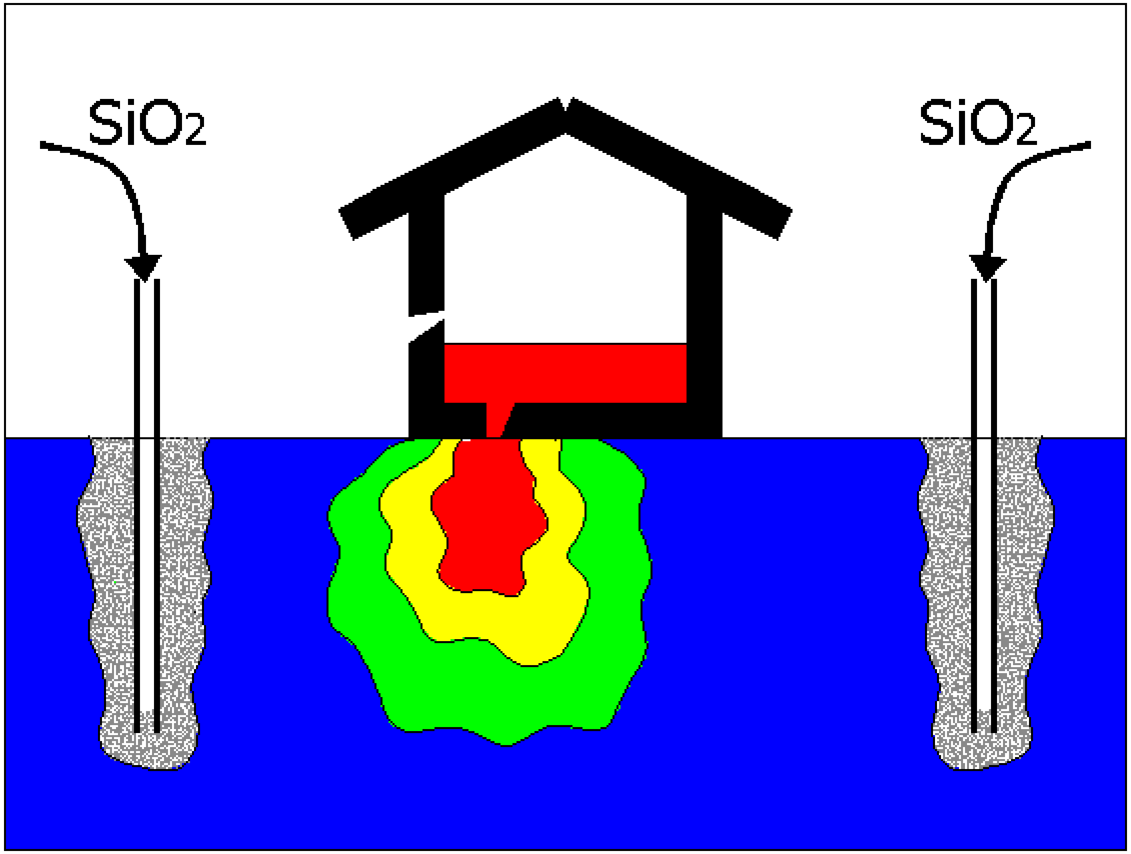
In-situ Ground Barriers



Contaminated site

SITE APPLICATIONS

Colloidal Silica Grout

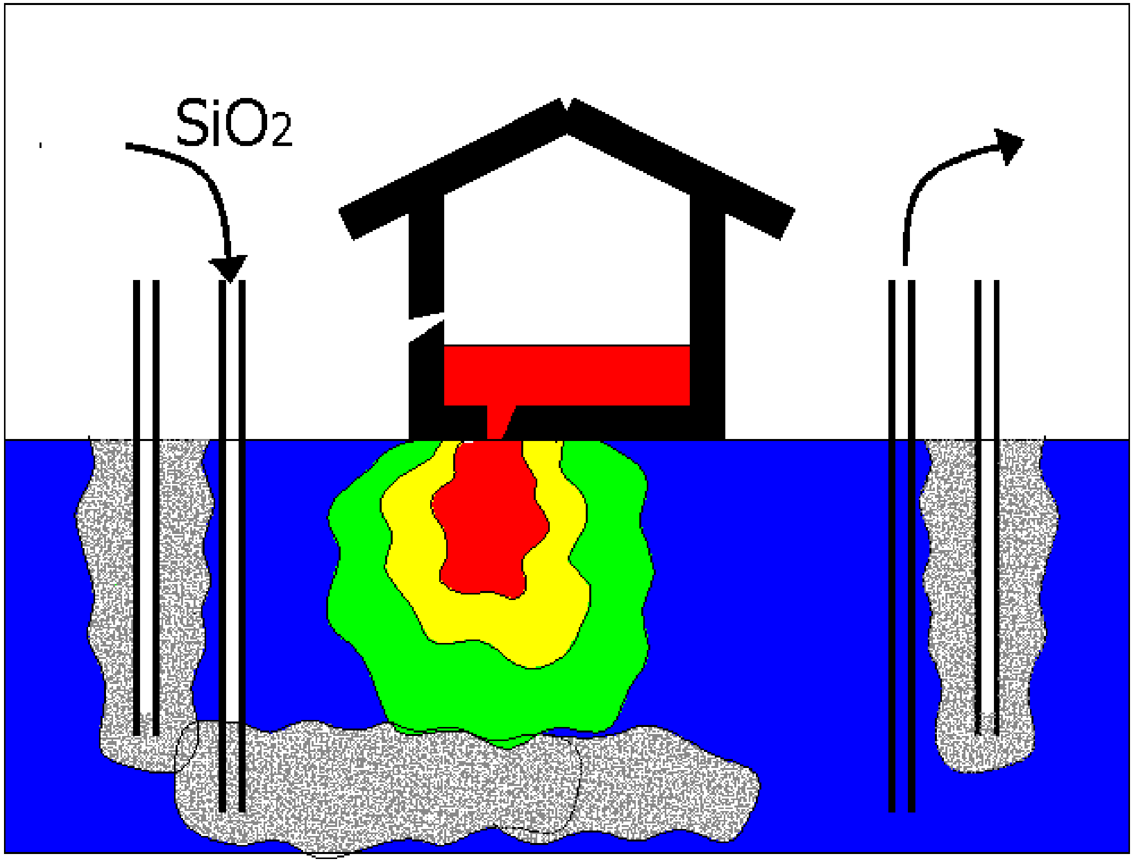


Contaminated site

SITE APPLICATIONS

- Vertical hydraulic barriers

Colloidal Silica Grout

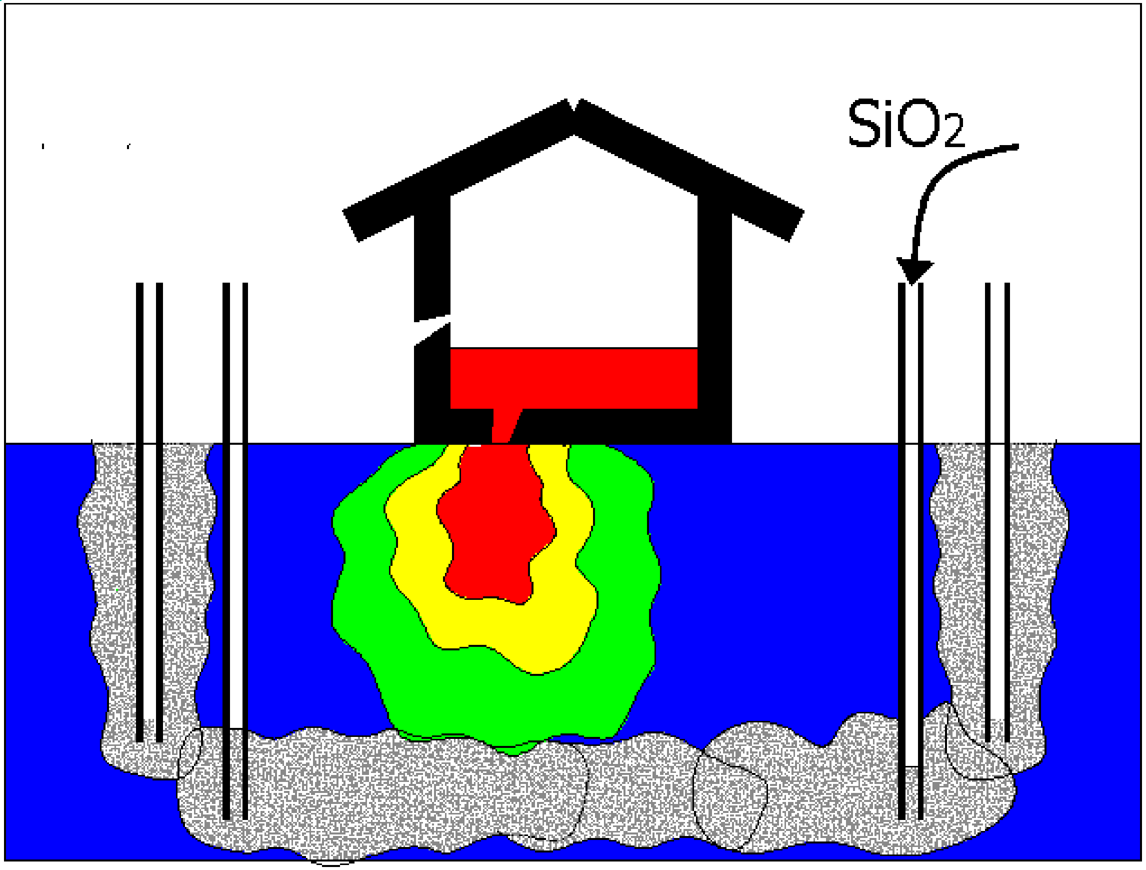


Contaminated site

SITE APPLICATIONS

- Vertical hydraulic barriers
- Horizontal hydraulic barriers

Colloidal Silica Grout

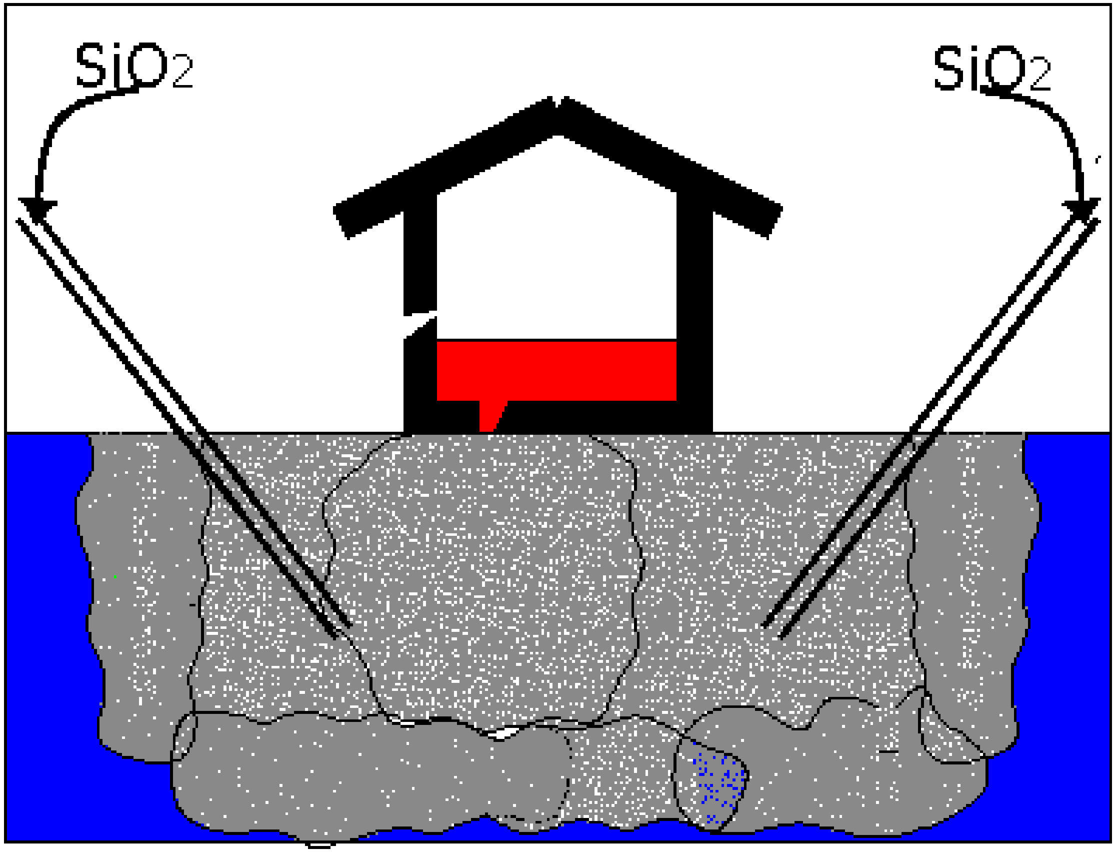


Contaminated site

SITE APPLICATIONS

- Vertical hydraulic barriers
- Horizontal hydraulic barriers

Colloidal Silica Grout

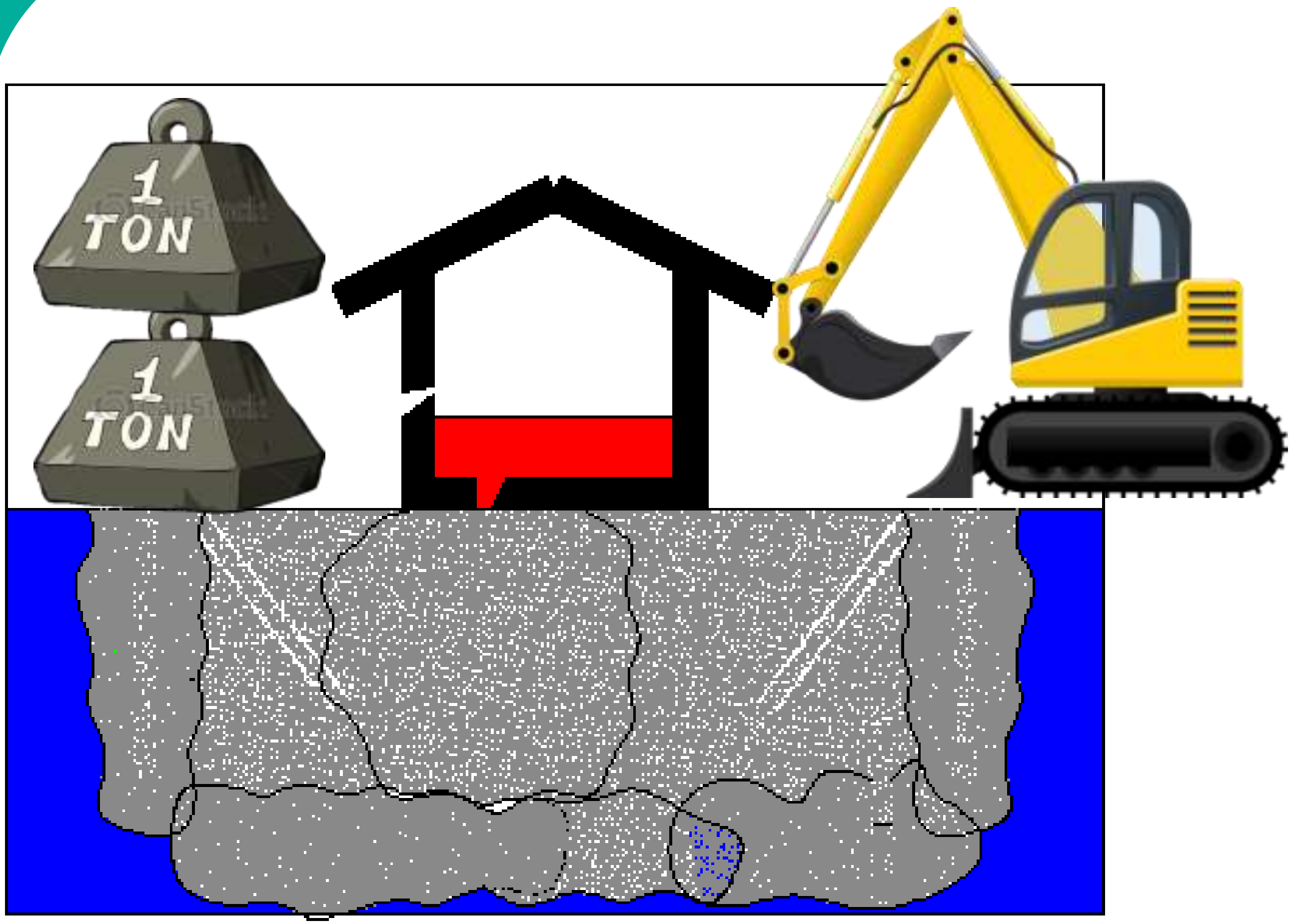


Contaminated site

SITE APPLICATIONS

- Vertical hydraulic barriers
- Horizontal hydraulic barriers
- Ground sealing

Colloidal Silica Grout



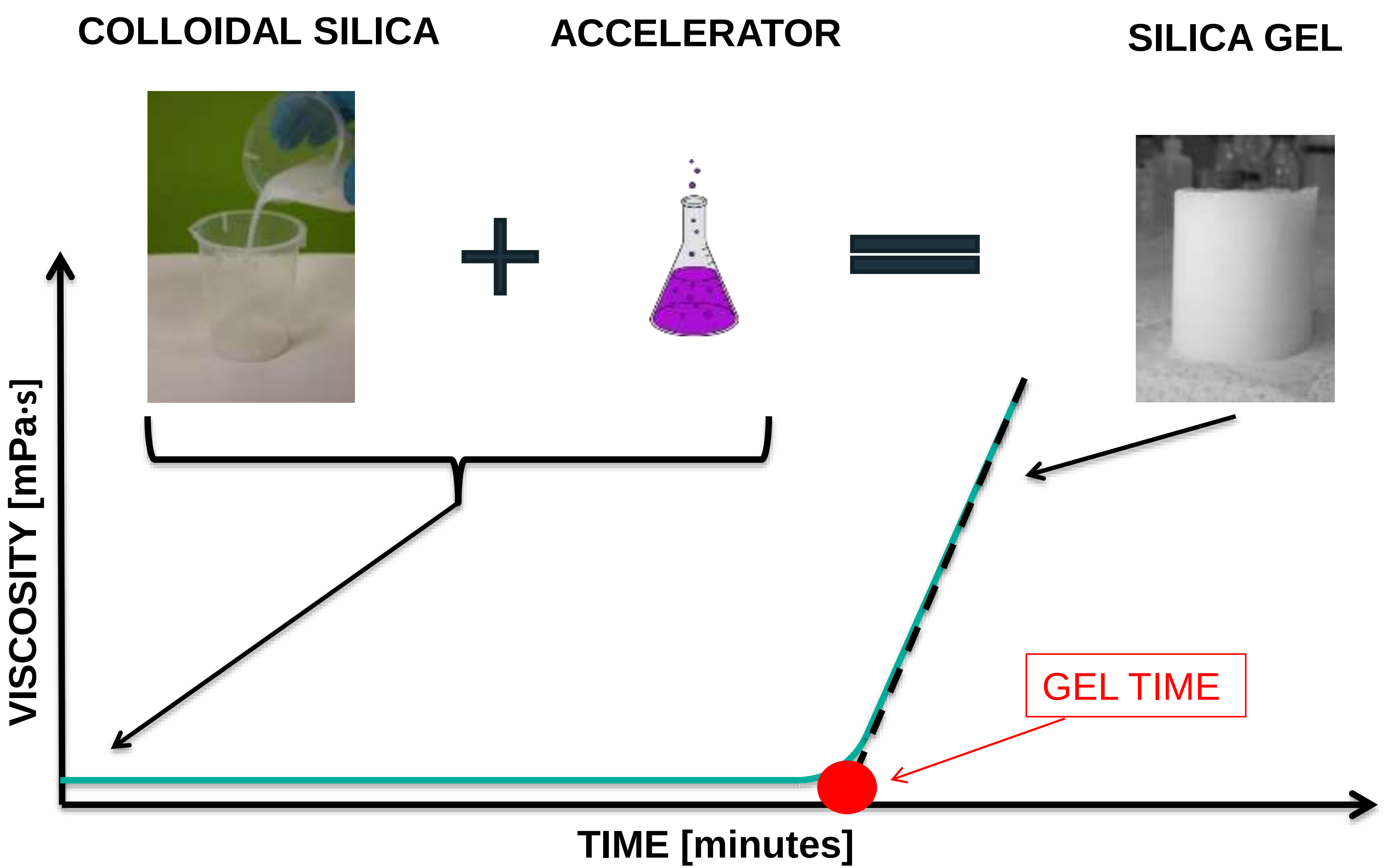
Contaminated site

SITE APPLICATIONS

- Vertical hydraulic barriers
- Horizontal hydraulic barriers
- Ground sealing
- Combined hydraulic & mechanical improvement

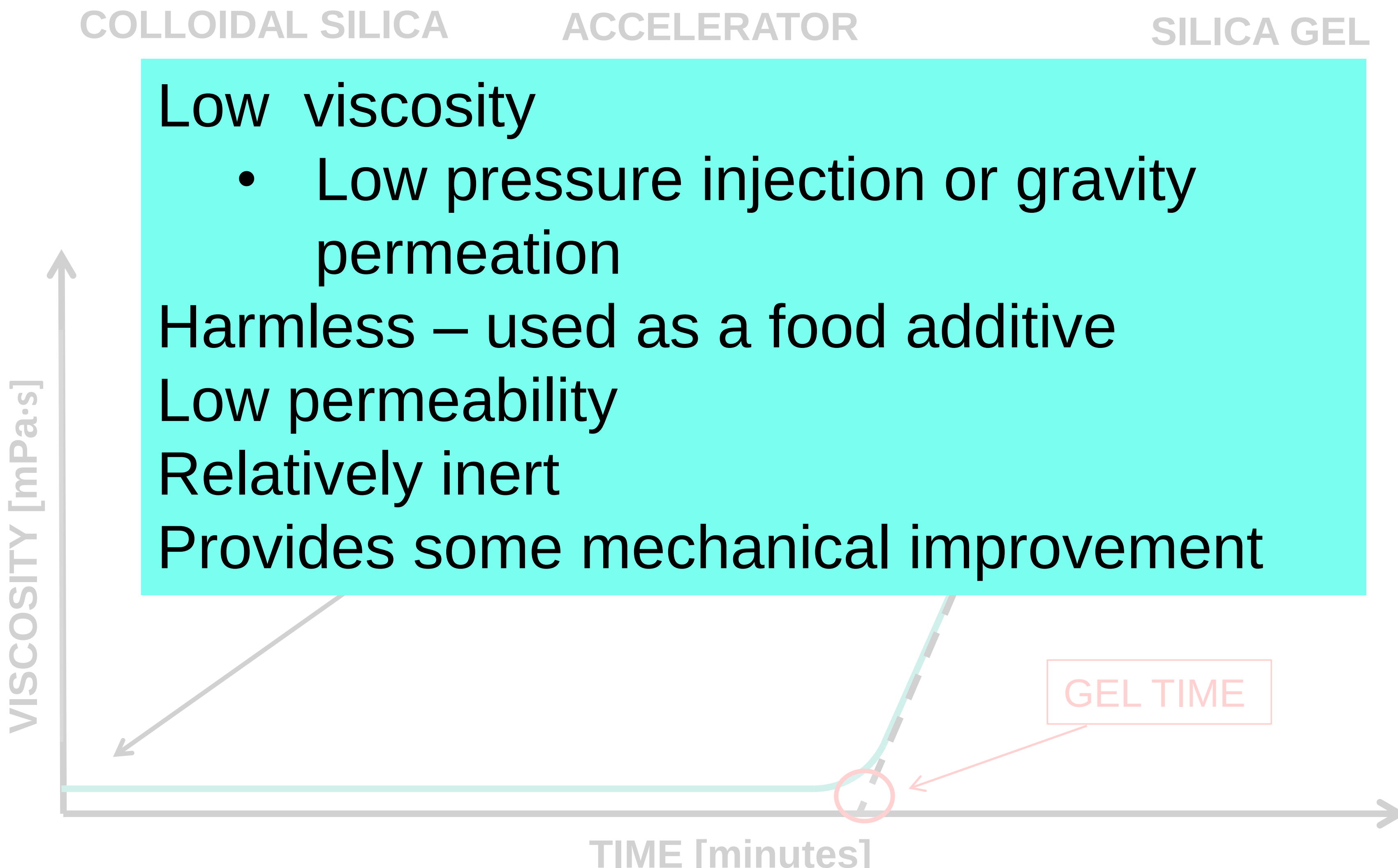
Grout Injectability

The Grout



COLLOIDAL SILICA
ACCELERATOR
SILICA GEL
VISCOSITY [mPa·s]
GEL TIME
TIME [minutes]

The Grout



Low viscosity
- Low pressure injection or gravity permeation

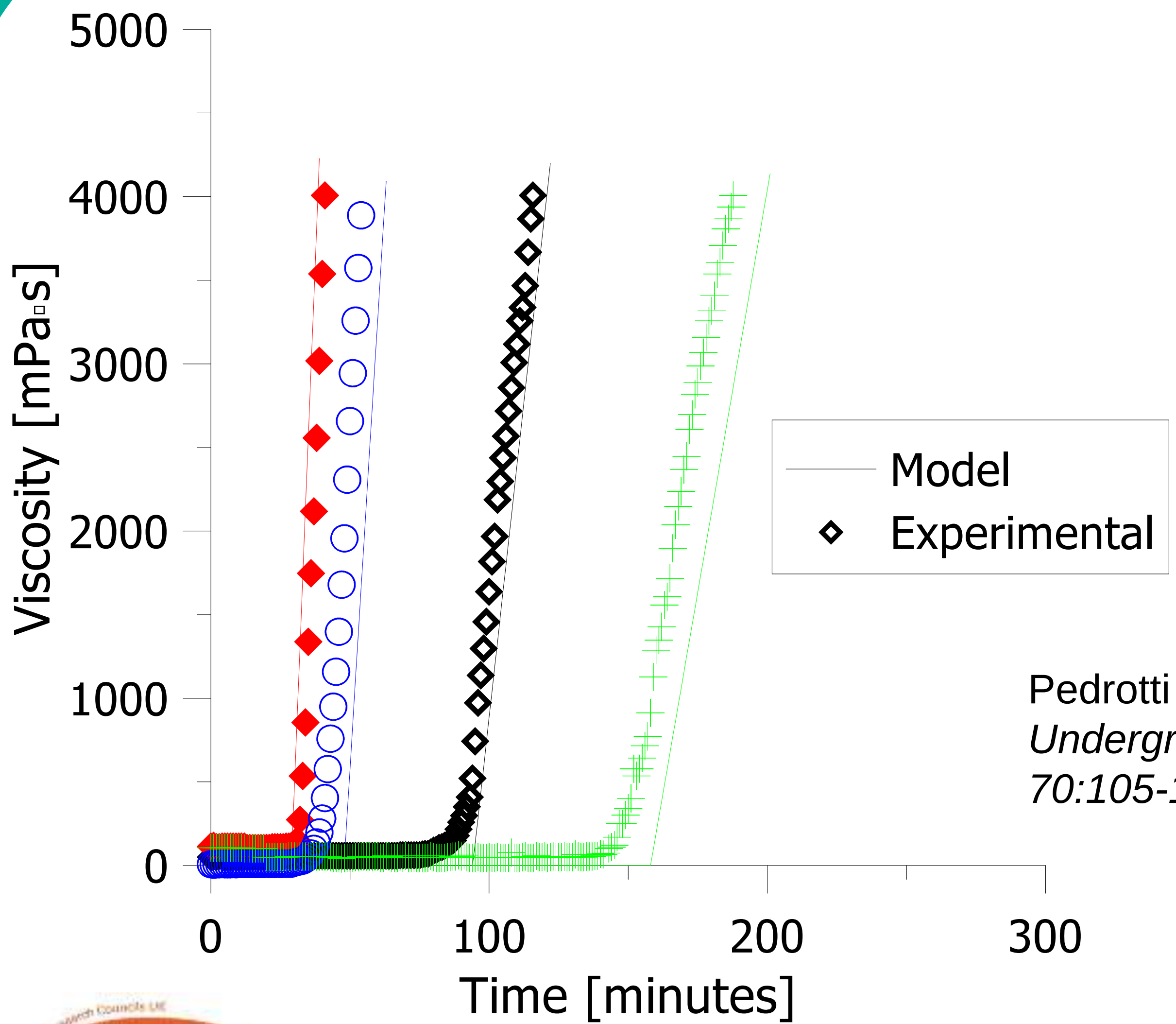
Harmless – used as a food additive

Low permeability

Relatively inert

Provides some mechanical improvement

Model Development

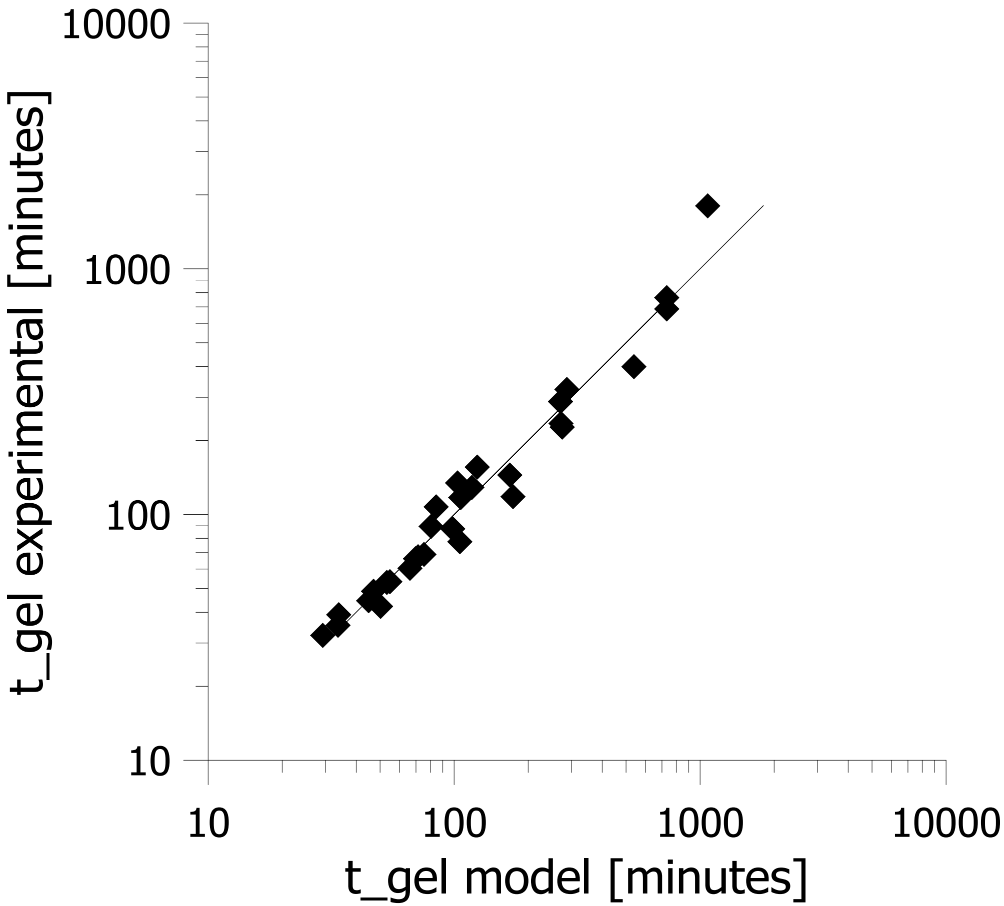


Gel time dependent on:

- pH
- Silica concentration
- Temperature
- Accelerator concentration
- Accelerator valency

Pedrotti et al. (2017) *Tunnelling and Underground Space Technology 70:105-1134*

Model Development



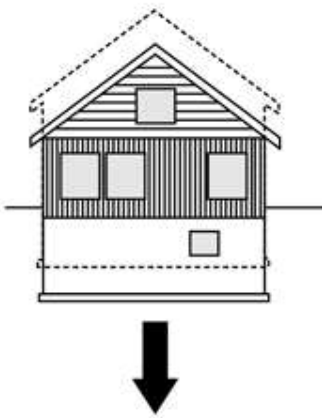
Gel time dependent on:

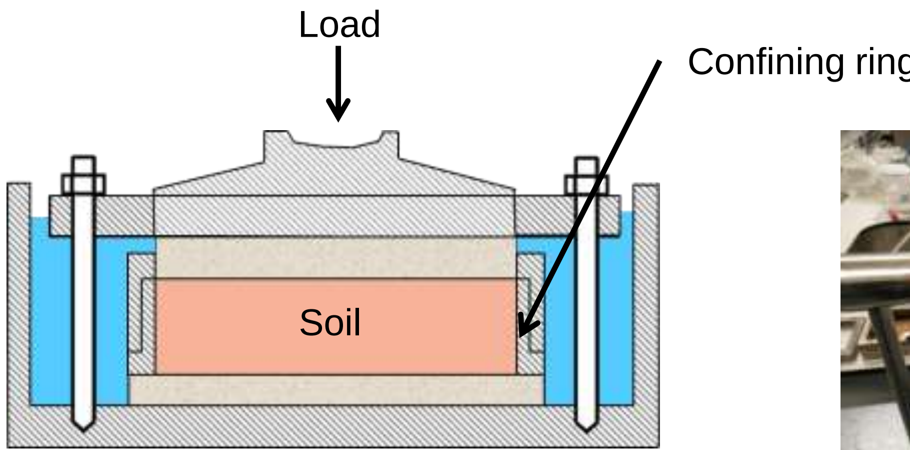
- pH
- Silica concentration
- Temperature
- Accelerator concentration
- Accelerator valency

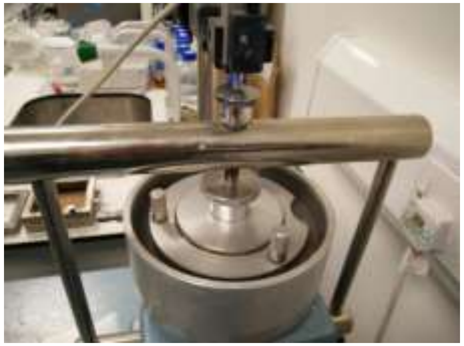
Pedrotti et al. (2017) *Tunnelling and Underground Space Technology 70:105-1134*

Geotechnical Grout Characterisation

Oedometer test



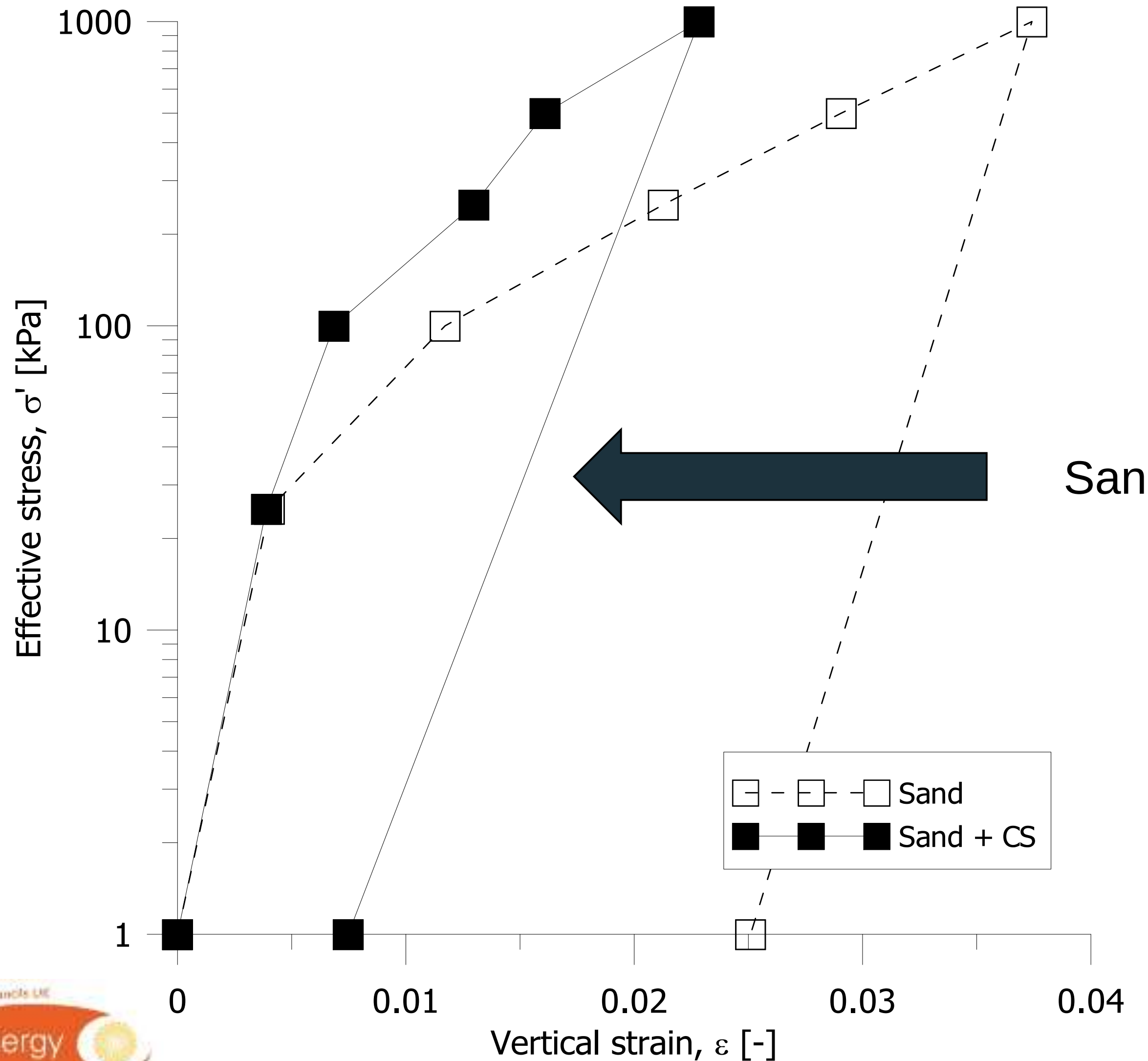




Loading frame

Experimental setup

Oedometer testing

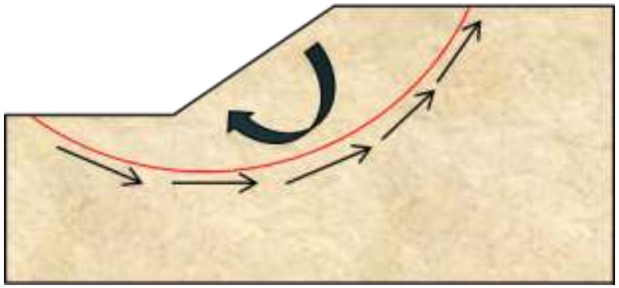


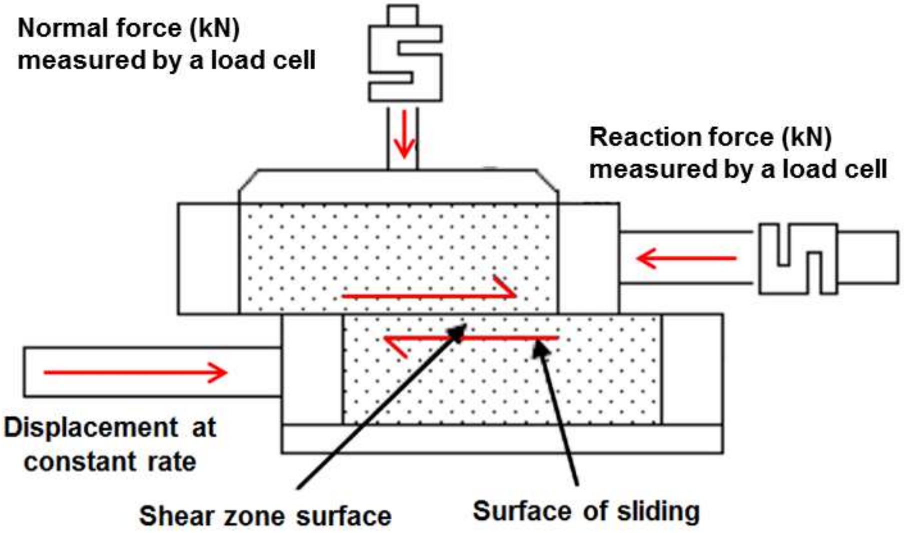
Sand/Colloidal silica

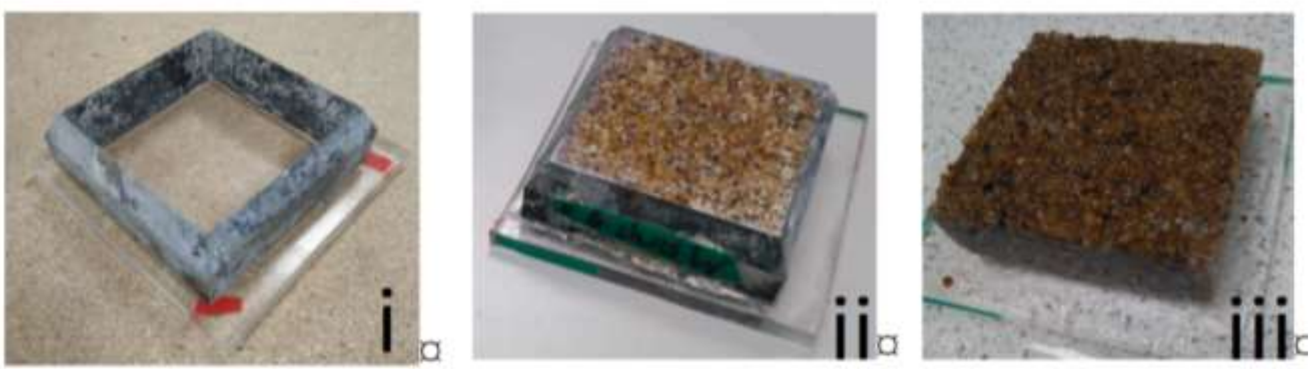
Wong, C., et al. (2018). Engineering Geology.

DISTINCTIVE

Direct Shear







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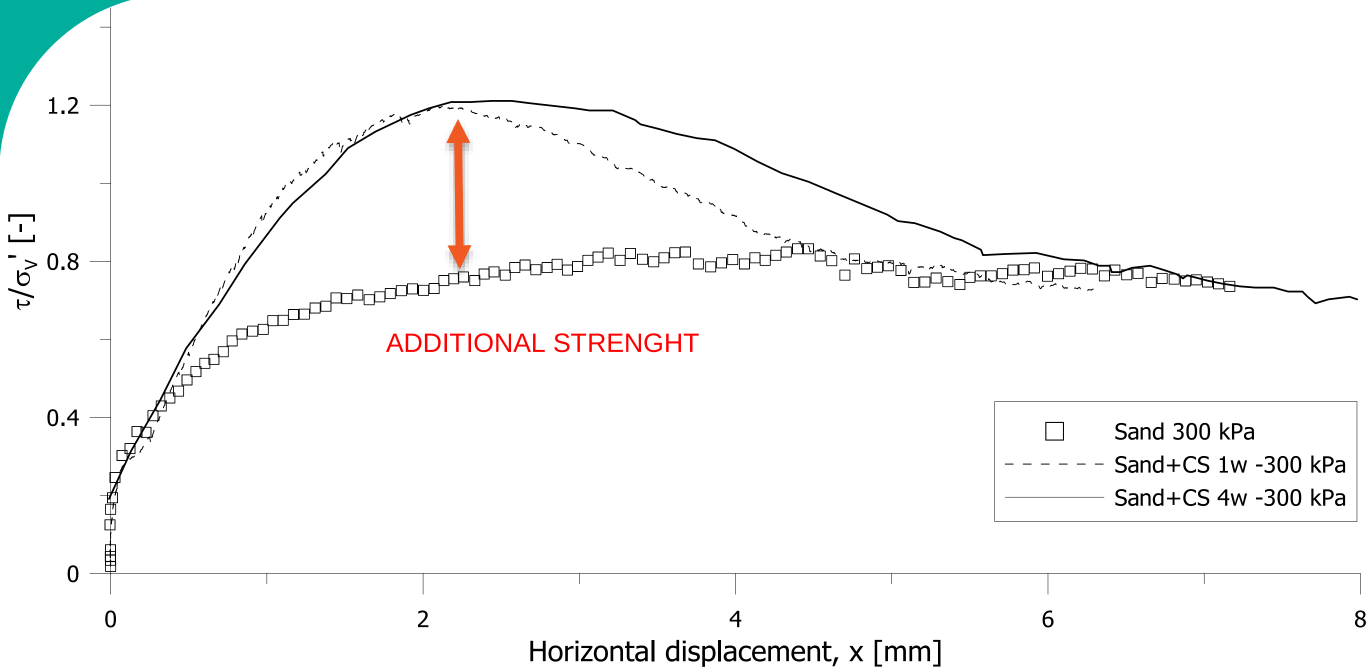
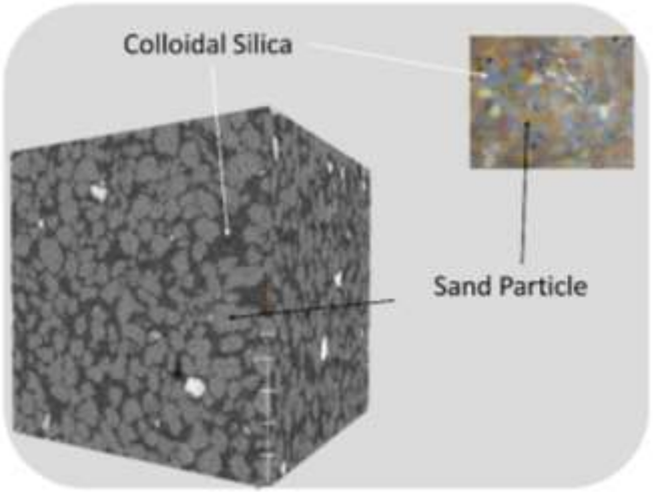
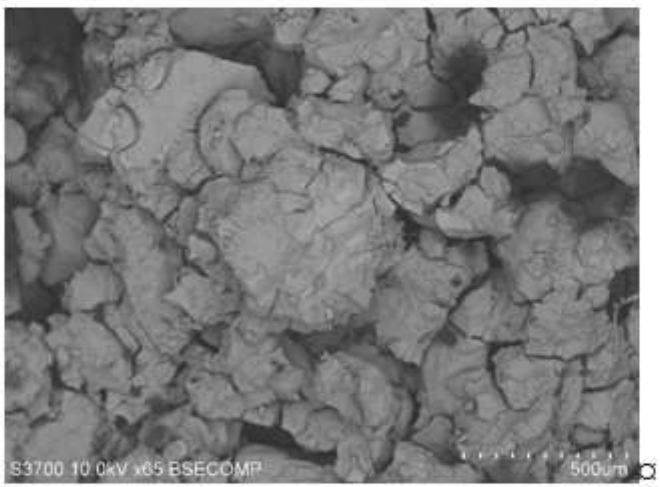
DISTINCTIVE

Direct Shear – Sand/CS



Wong, C., et al. (2018). Engineering Geology.



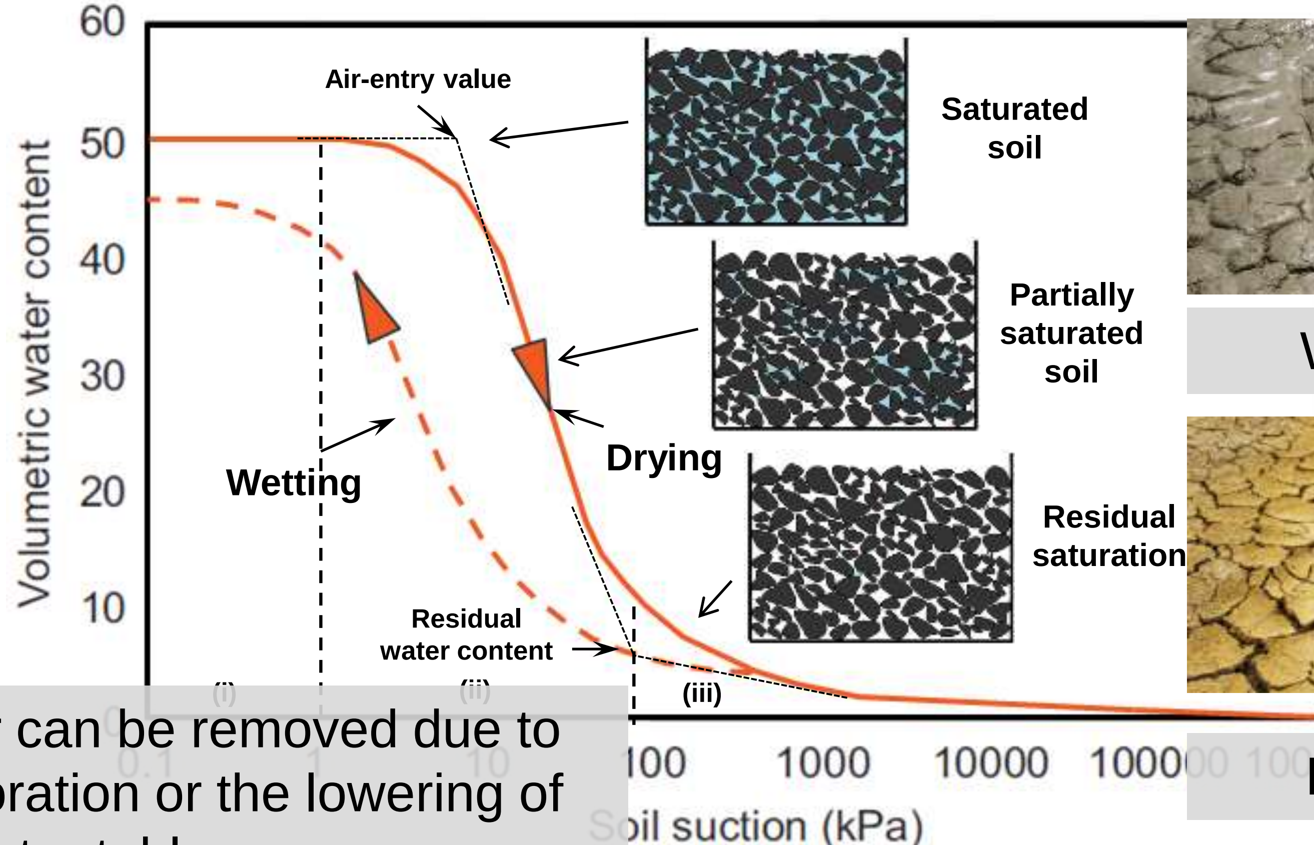


DISTINCTIVE

Hydraulic Characterisation

Soil Water Retention Curve

The soil-water retention curve defines the relationship between water content and soil suction (i.e. negative pore water pressure).

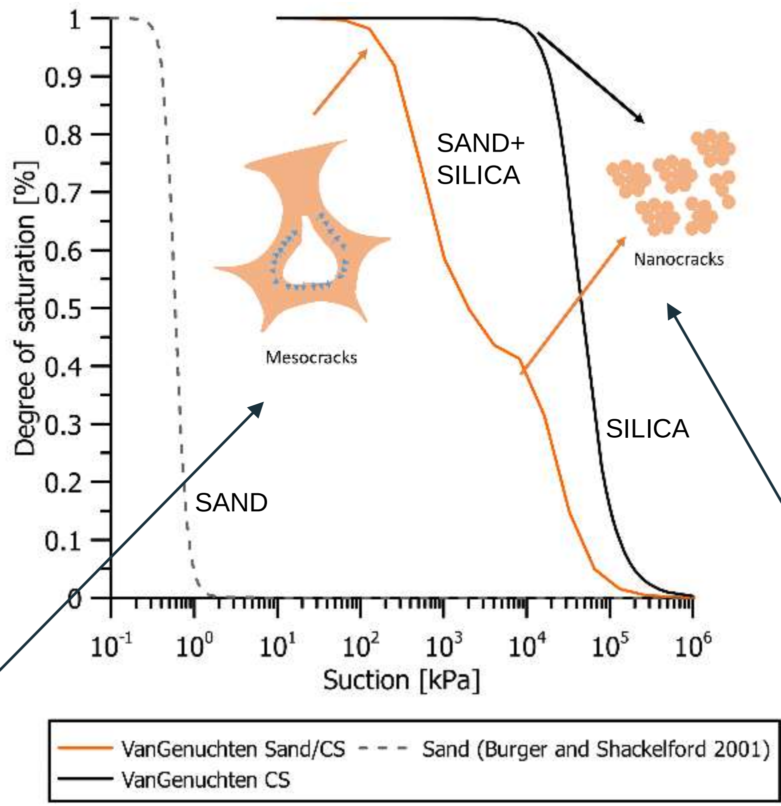


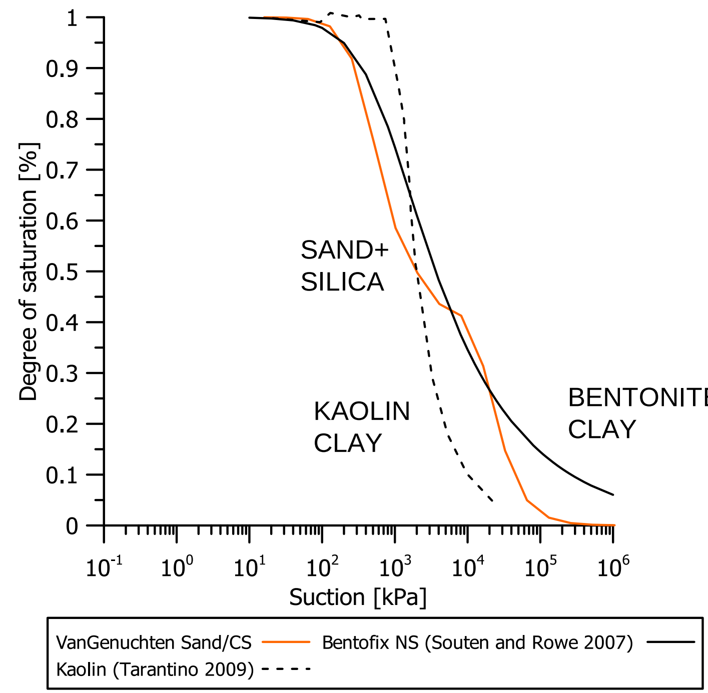
Wet soil

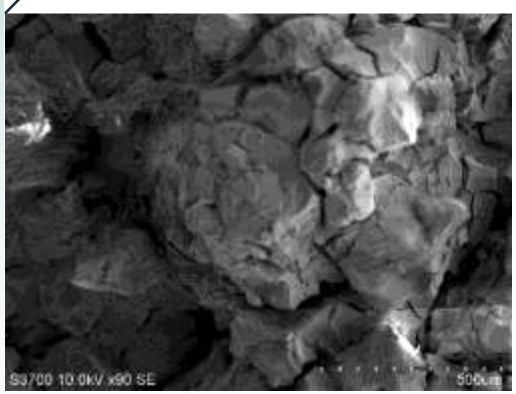
Dry soil

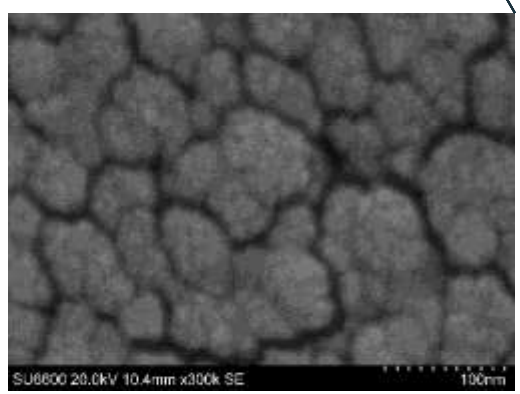
Water can be removed due to evaporation or the lowering of the water table.

Water retention curves







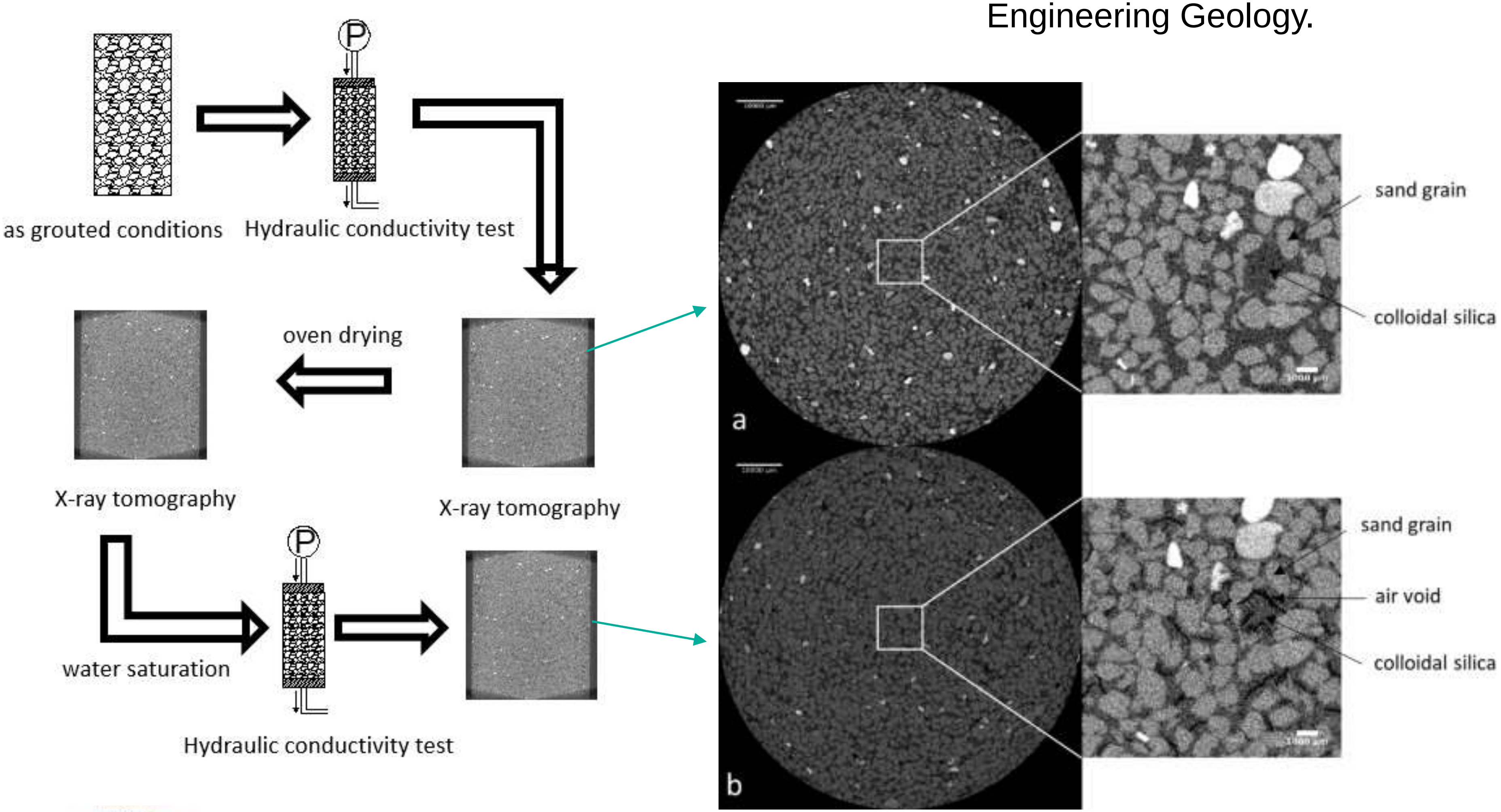


Pedrotti et al. (2019 - in revision). Engineering Geology.

DISTINCTIVE

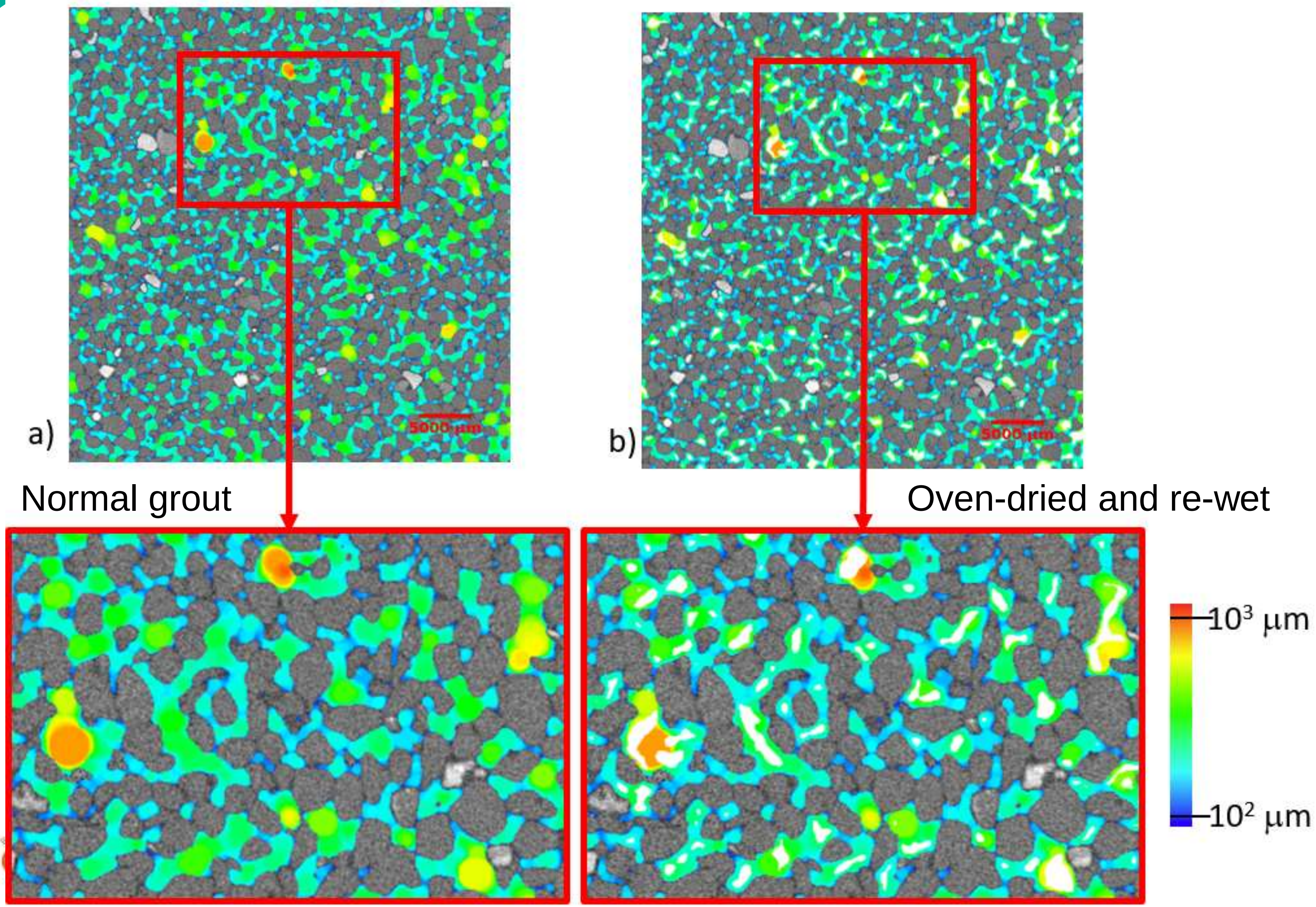
Durability: X-CT

Pedrotti et al. (2019 - in revision). Engineering Geology.

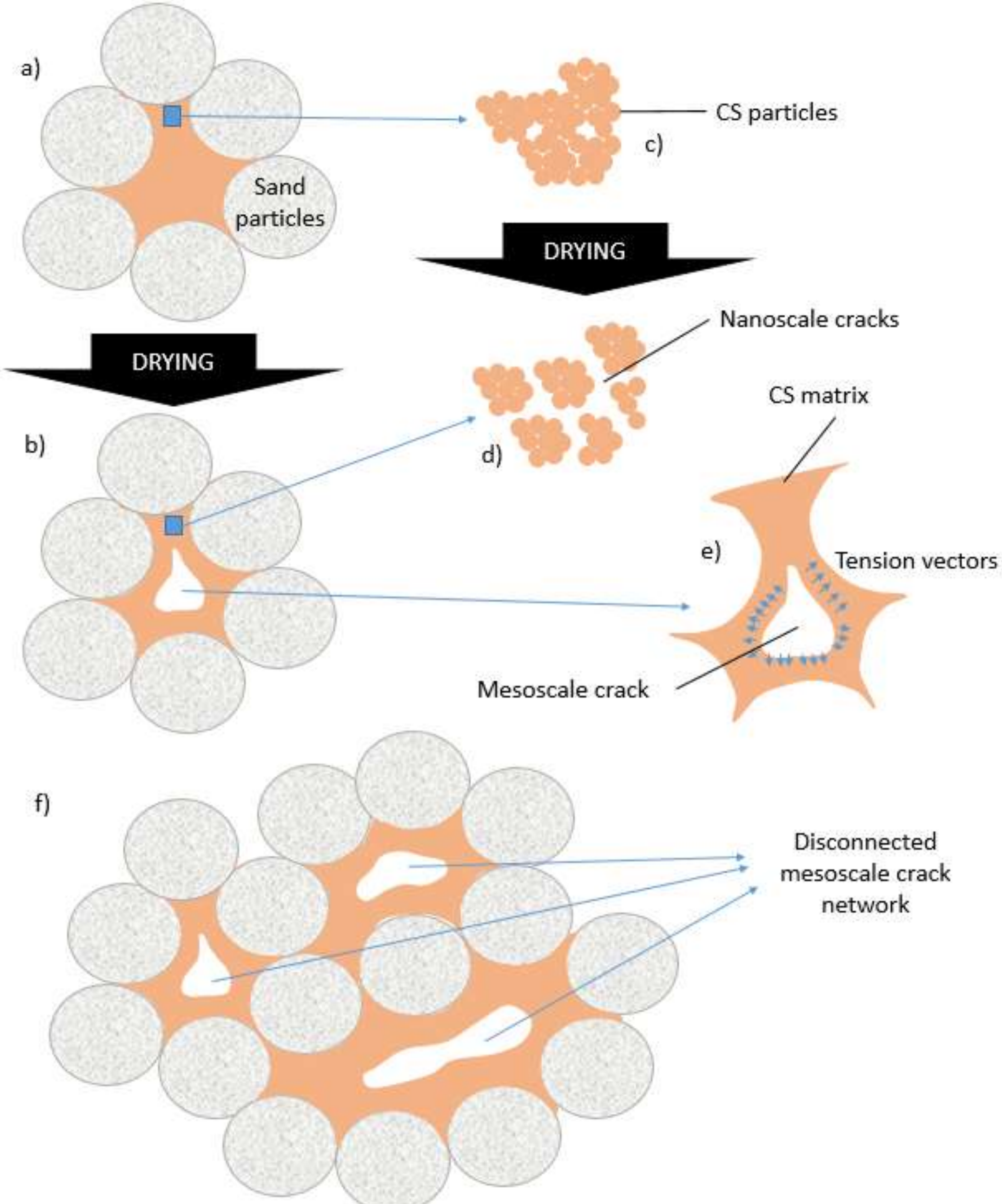


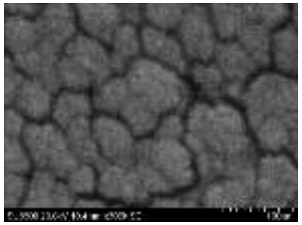
DISTINCTIVE

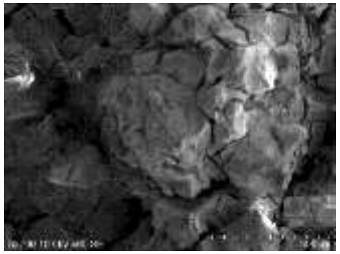
Durability over climate cycles



Cracking mechanism



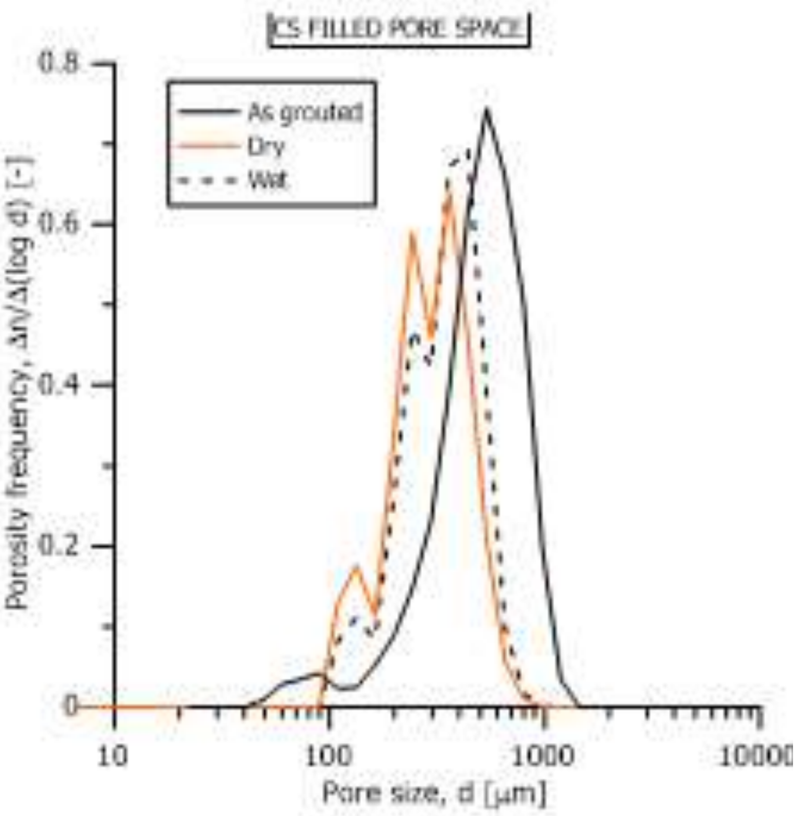




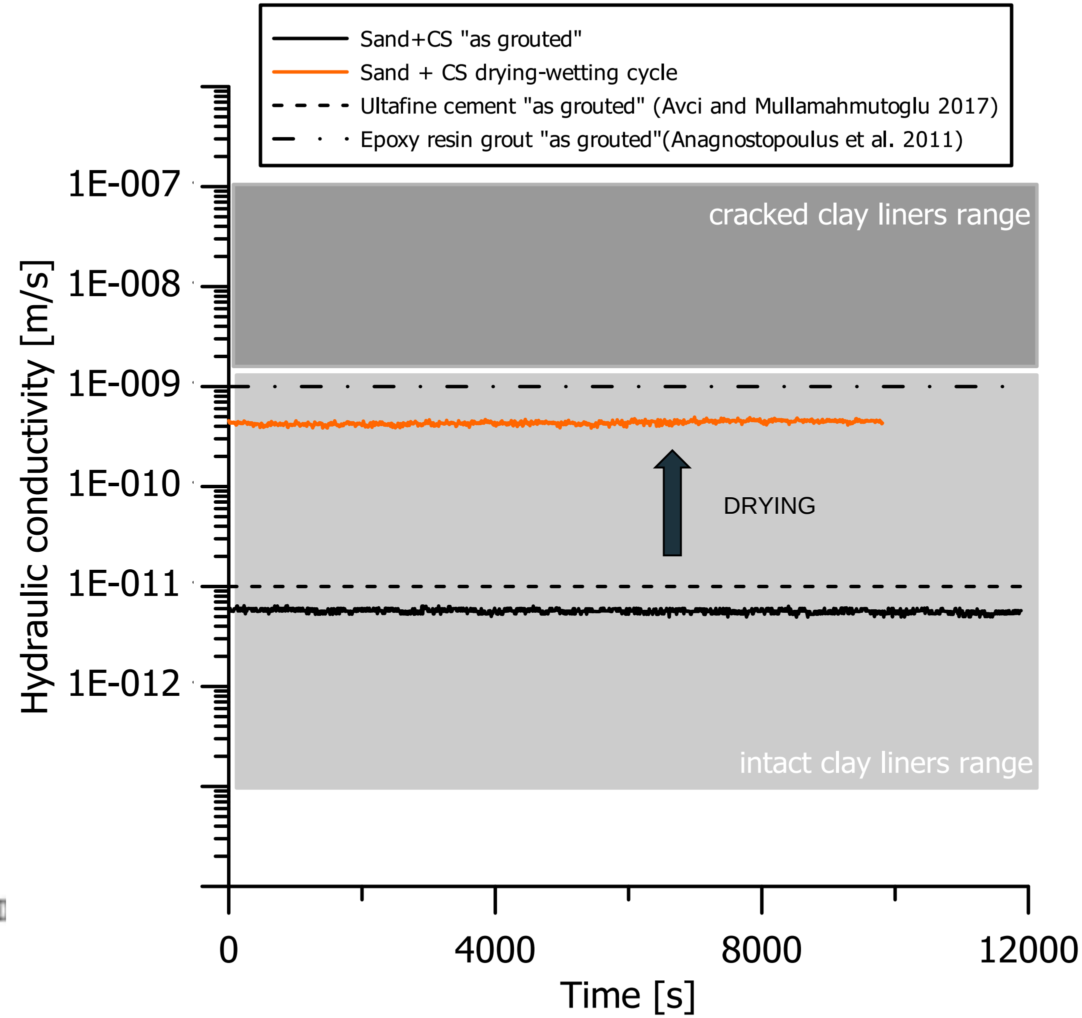
DISTINCTIVE

Pore size distribution

Pore size distribution before drying, oven dry and after re-wetting



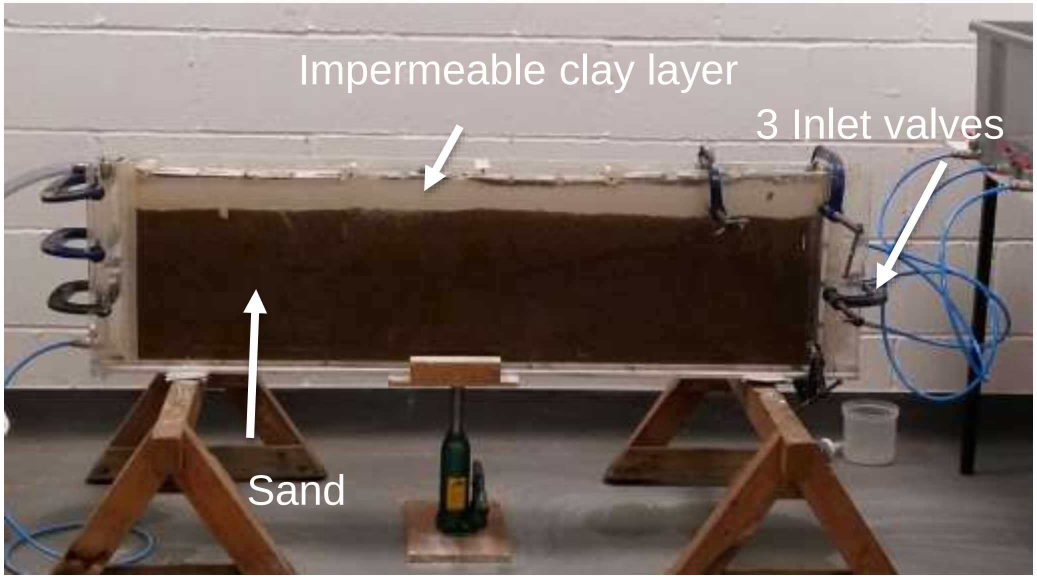
Corresponding hydraulic conductivity



Experiments
VS
Numerical models

Laboratory-scale Injection

Injection tank



Water sampling

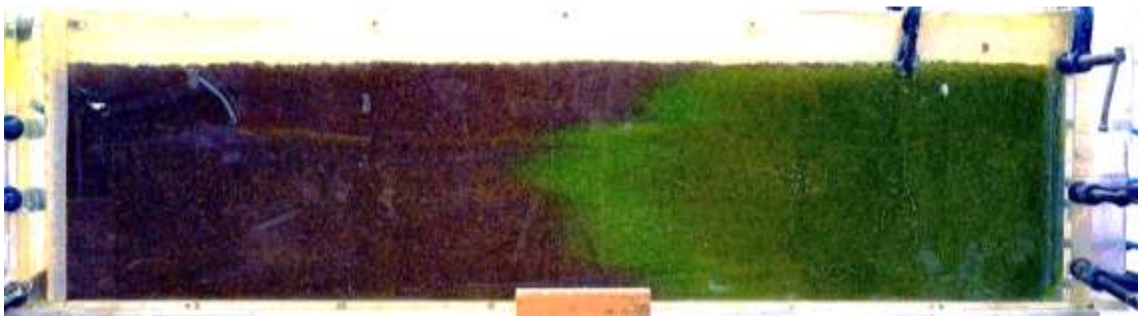
Sampling points to measure the electric conductivity

From the electric conductivity it is possible to calculate the silica concentration

Water samples were collected on the longitudinal axes 19 minutes after the injection started

Injection test

Δh=+5cm - flow~0.5 L/min 19 minutes after injection started

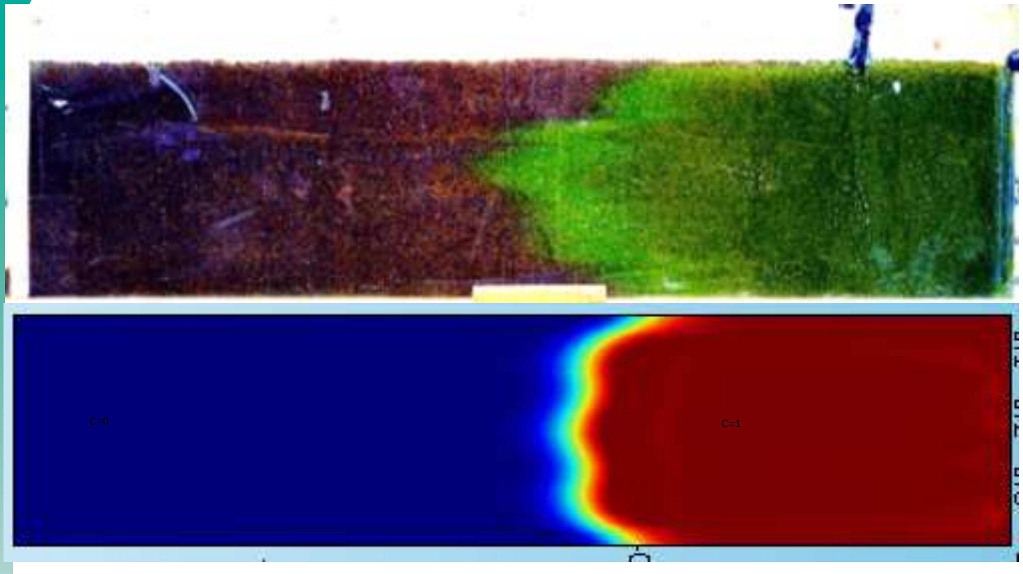


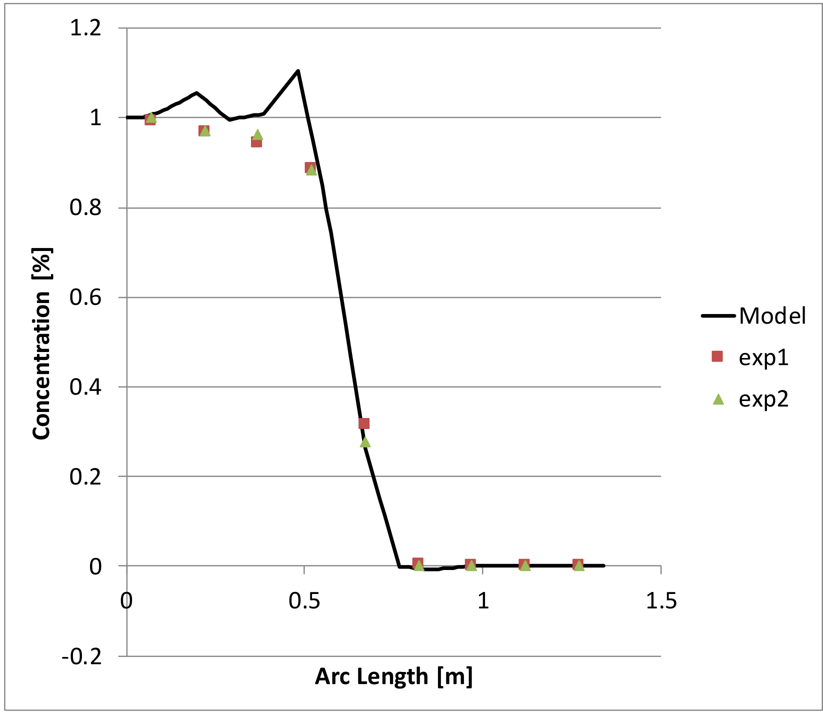
Fluorescein only
(constant density)

Colloidal silica
(no accelerator)
+
fluorescein

Colloidal silica GROUT
(accelerator)
+
fluorescein

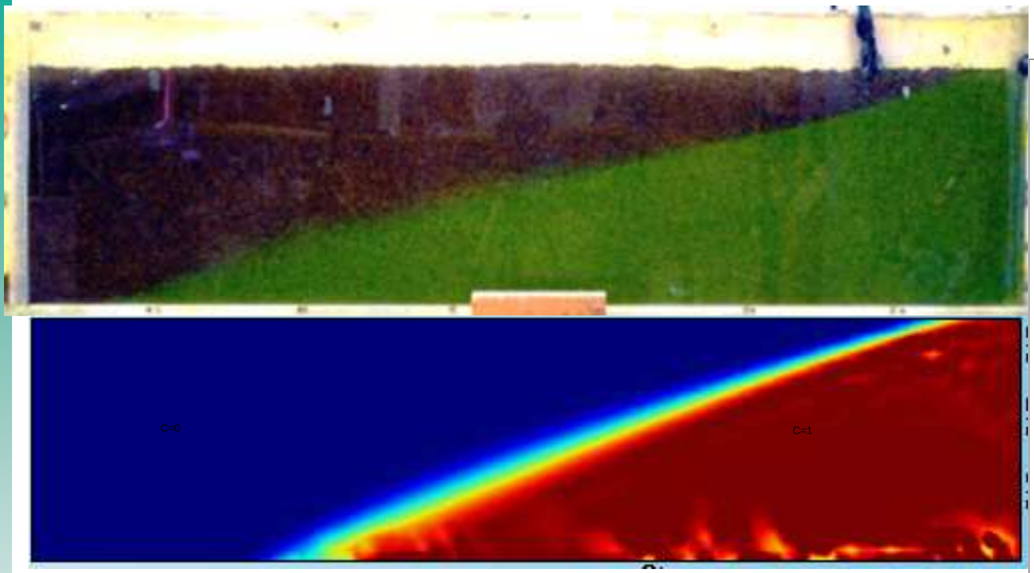
Results: Fluorescein

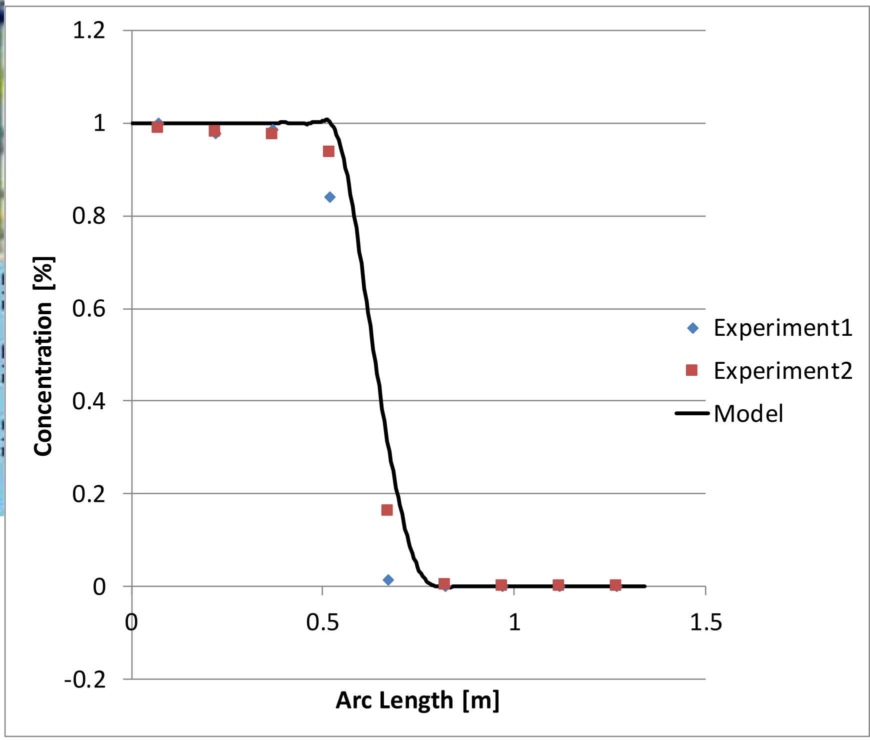




- Excessive transversal dispersion
- Numerical oscillations

Results: SiO2 (no accelerant)



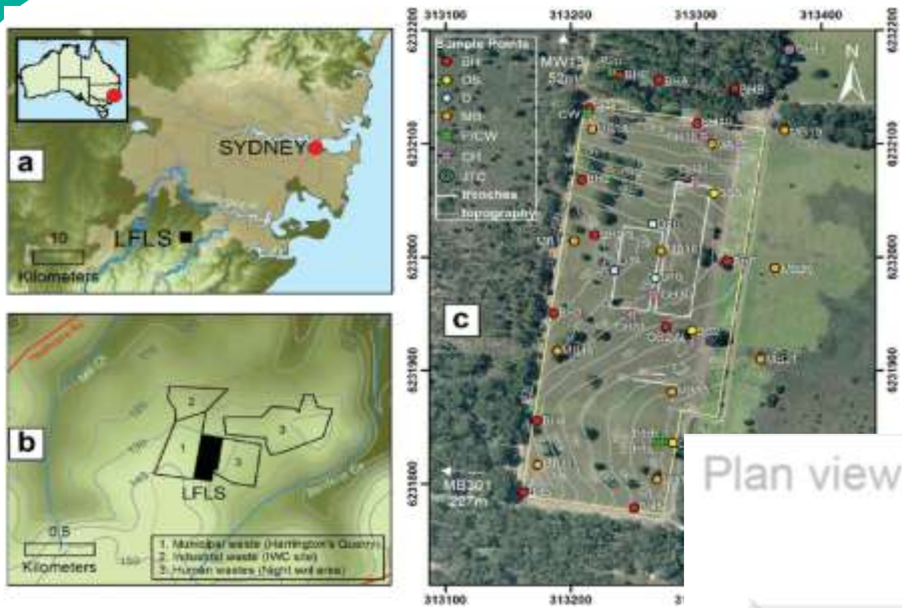


- Excessive transversal dispersion
- Less numerical oscillations
- Computation time= 40 hours

Results: Grout

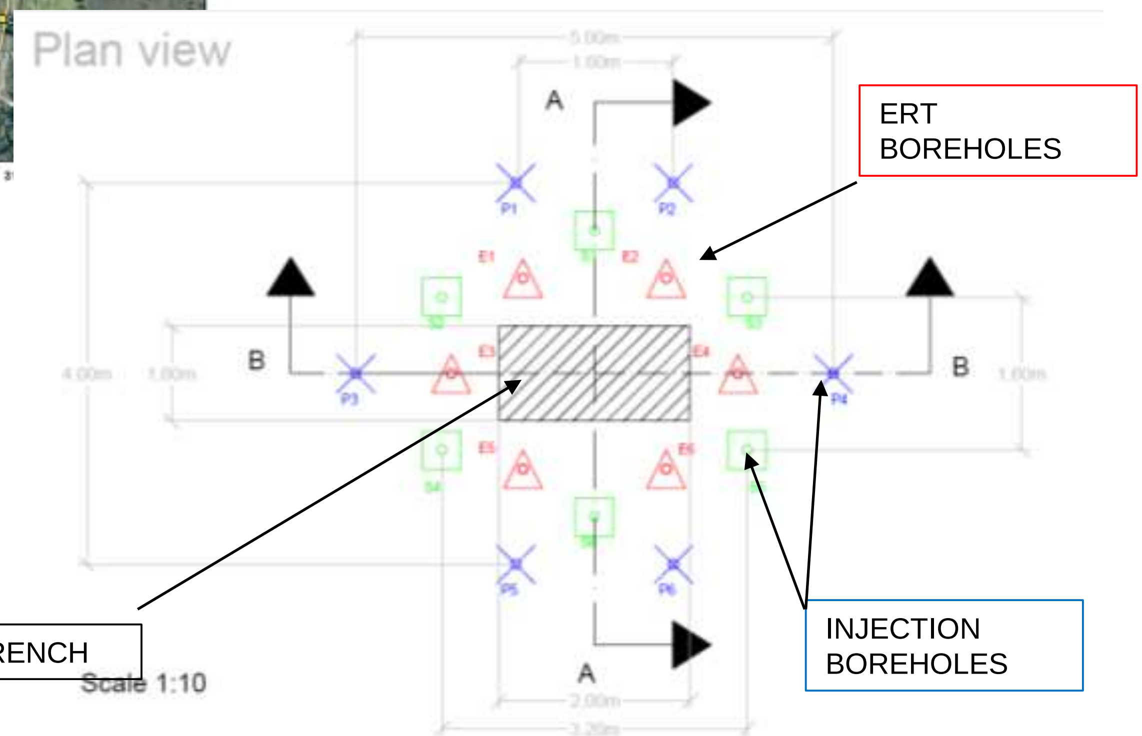
DISTINCTIVE

Injection monitoring



Immobilization of radioactive
wastes at the Little Forest Legacy Site

In collaboration with ANSTO



INJECTION MONITORING

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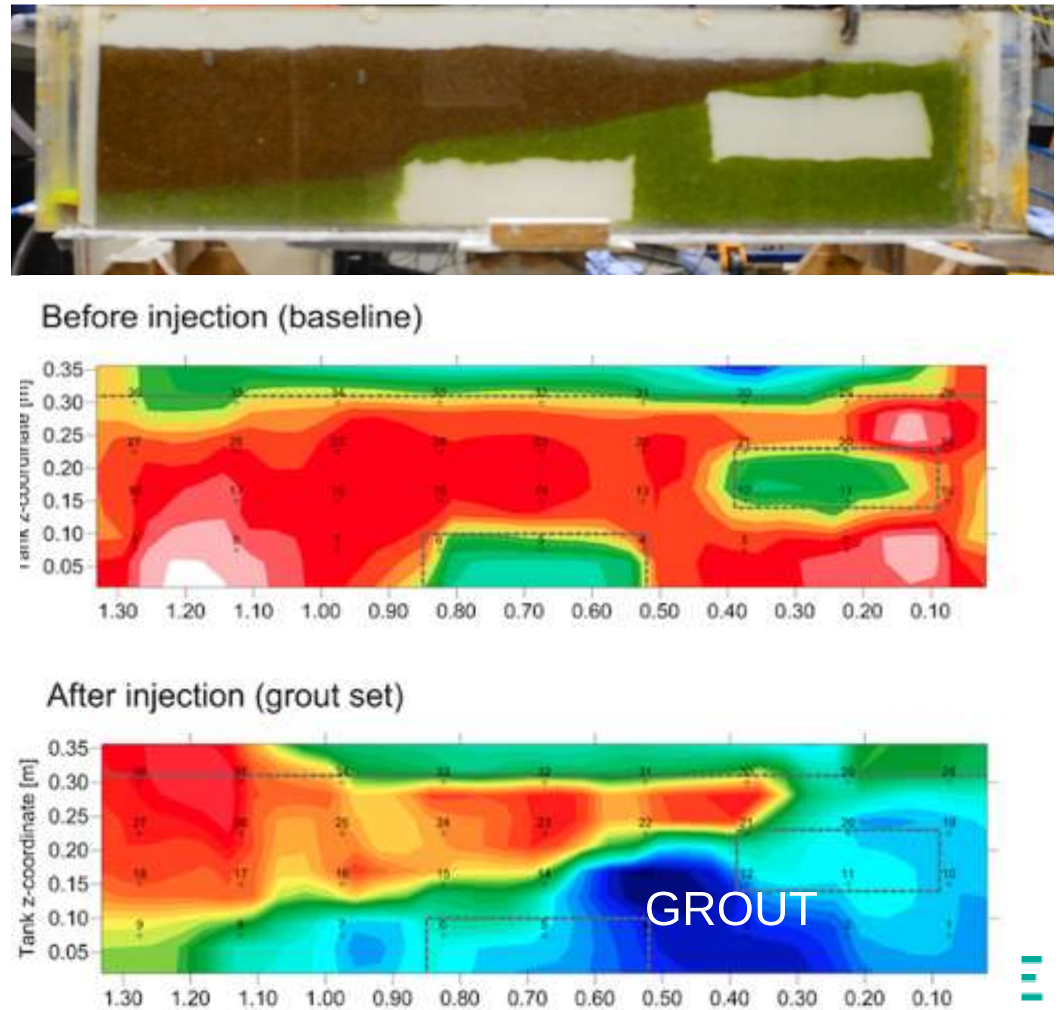
DISTINCTIVE

INJECTION MONITORING

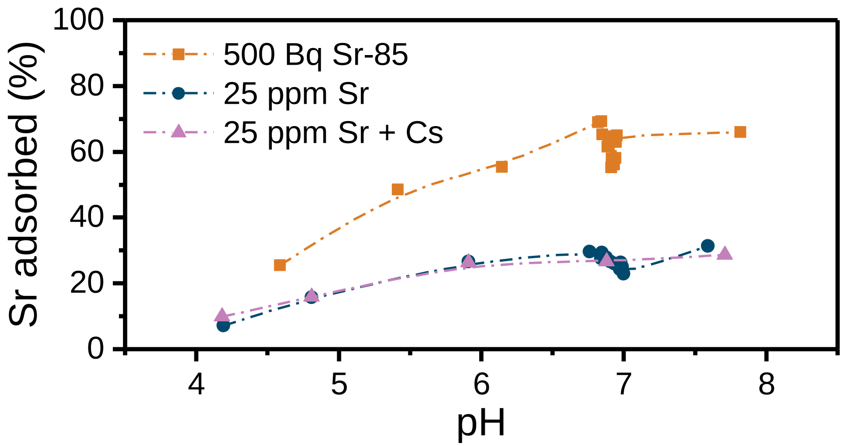
Collaboration with **BGS** for injection monitoring by means of **Electrical Resistivity Tomography (ERT) technique**.



Grout - Radionuclide Interactions

Effects of colloidal silica grouts on the mobility and speciation of Sr

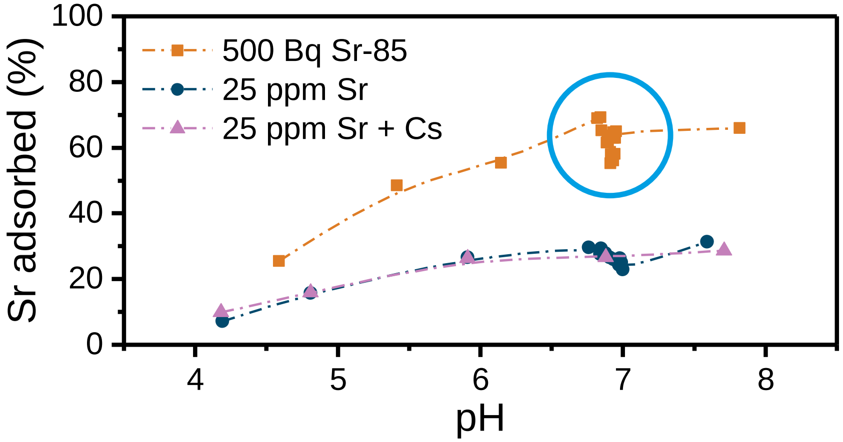
1. Adsorption experiments at pH 7 to a solid mixture to represent the soils and (corroded) wastes at the Little Forest Legacy Site.
   a. At low concentrations (500Bq)
   b. At elevated concentrations (25ppm)
2. Contaminated samples were grouted to:
   a. Perform leaching experiments with simulated groundwater (low concentrations)
   b. Perform detailed X-ray Absorption analyses at beamline B18 at Diamond Light Source



DISTINCTIVE

Leaching experiments methodology

- 0.25 g of simulated soil-waste mixtures were equilibrated with 25 ml of a solution with 500 Bq Cs-137 (~6 ppt) and Sr-85 (~23 ppq)
  [~90 and ~60% adsorption; Figure]
- Solids were separated from the solutions and grouted with:
  colloidal silica available in Europe (MP320) and Australasia (MP325)
  Na or Ca in the accelerant
- Leaching was performed with 20 ml of 10mM NaCl, and shaken at 90 rpm
- 10 ml sampled each day and replenished with 10mM NaCl
- Analysed with γ-spectroscopy



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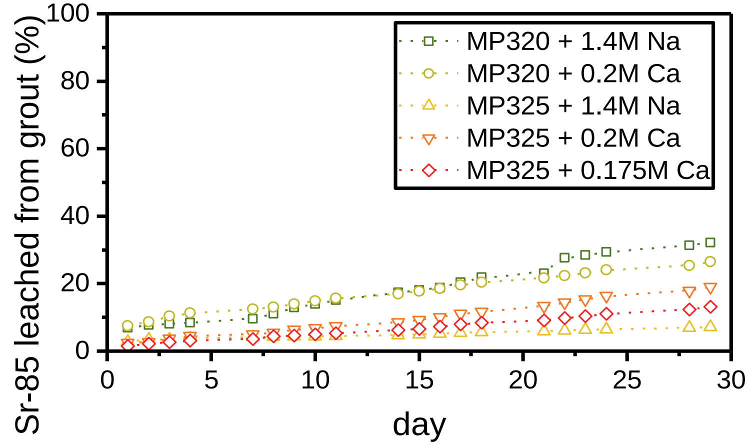
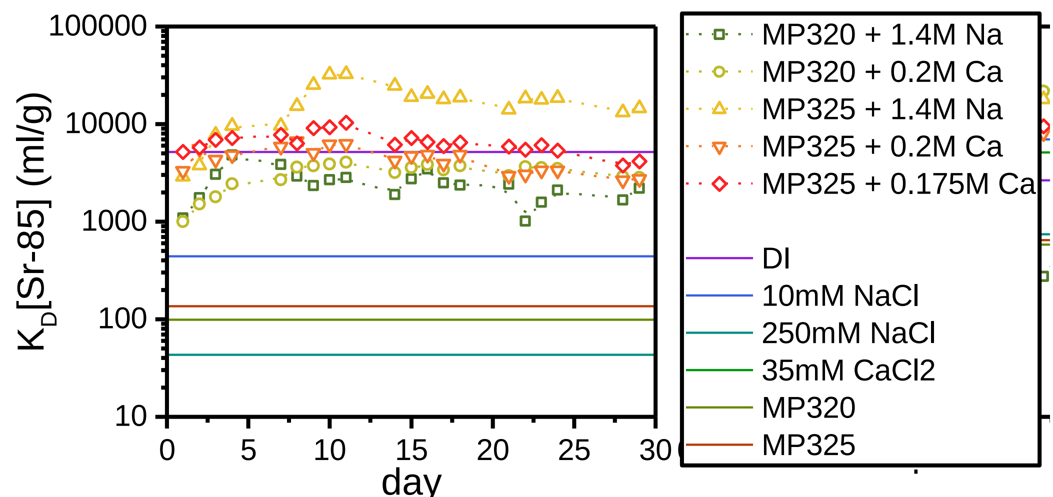
Leaching of Sr from grouted samples

- Sr leaching from samples
  - 5-20% was leached during sampling for 40 times
  - Calculated apparent K_D values showed higher fraction of Sr retained on the solid compared to desorption experiments from non-grouted samples (lines)
- No negative effects of grouting on mobility of Sr
- For both Cs and Sr, the Australasian grout MP325 with Na in the accelerant performed best (highest K_D)



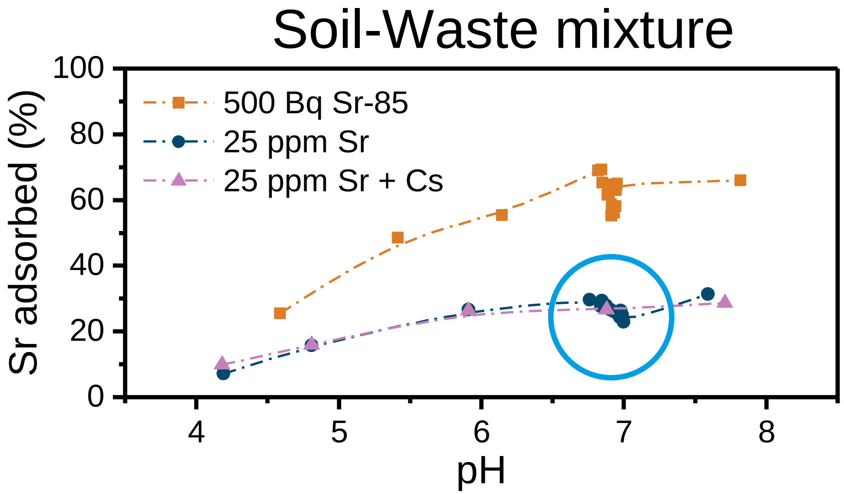


Energy

DISTINCTIVE

X-ray Absorption Spectroscopy analyses at Diamond Light Source

- 0.4 g of simulated soil or soil-waste mixtures were equilibrated with 40 ml of a solution with 25 ppm Cs or Sr, respectively
  [~40 and ~30% adsorption; Figure]
- Solids were separated from the solutions and grouted with:
  colloidal silica available in Europe (MP320) and Australasia (MP325)
  Na or Ca in the accelerant
- Half of the samples were leached (re-equilibrated) in 40 ml 10 mM NaCl
- Samples (incl. standards) were analysed for Cs and Sr XAS at Beamline B18 at Diamond Light Source



DISTINCTIVE

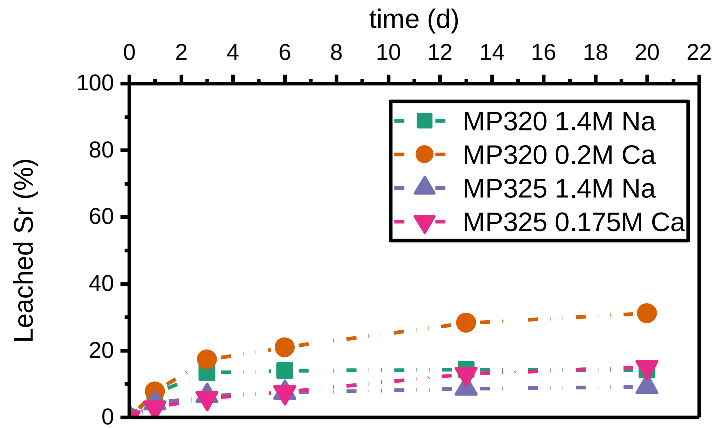
Effect of grouting on speciation of Sr

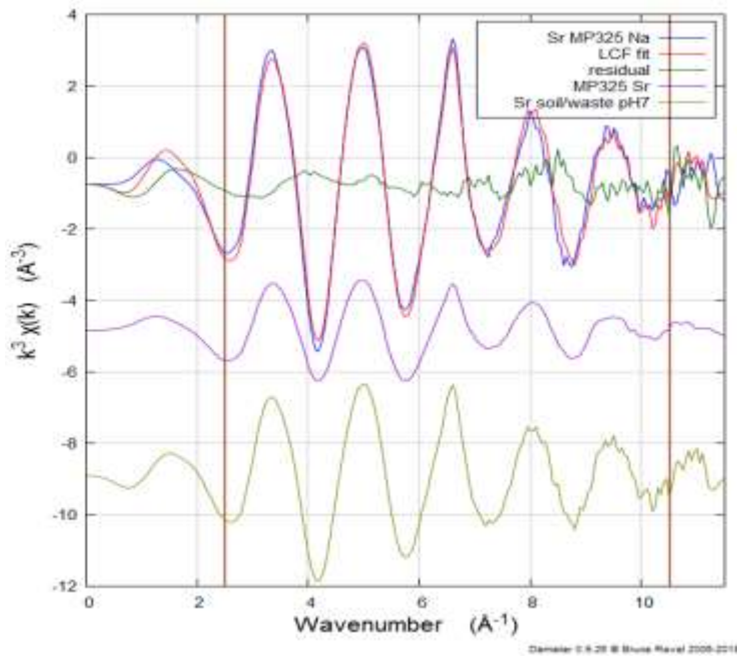
- Sr leaching from grout shows similar trends as the previous samples at 500Bq
- XAS data shows little variation in the spectra
- Preliminary analyses (through linear combination fitting) on the EXAFS:

Sample	Sr soil/waste	Sr grout
MP325 Na	67%	33%
MP325 Na leached	92%	8%
MP325 Ca	78%	22%
MP325 Ca leached	79%	21%
MP320 Na	81%	19%
MP320 Na leached	86%	14%
MP320 Ca	78%	22%
MP320 Ca leached	84%	16%

After grouting, Sr is dominantly complexed to soil/waste

Larger fraction of Sr affected by grout explains more Sr leaching than Cs

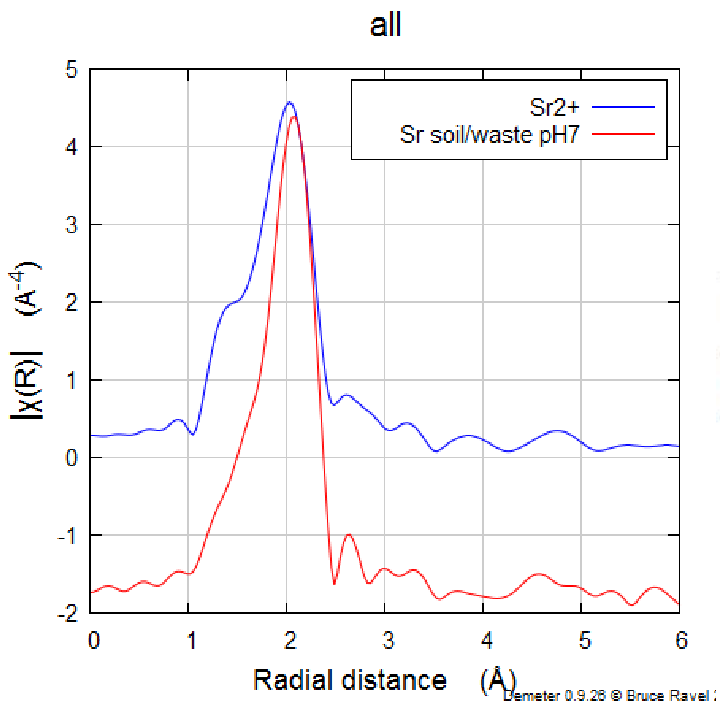


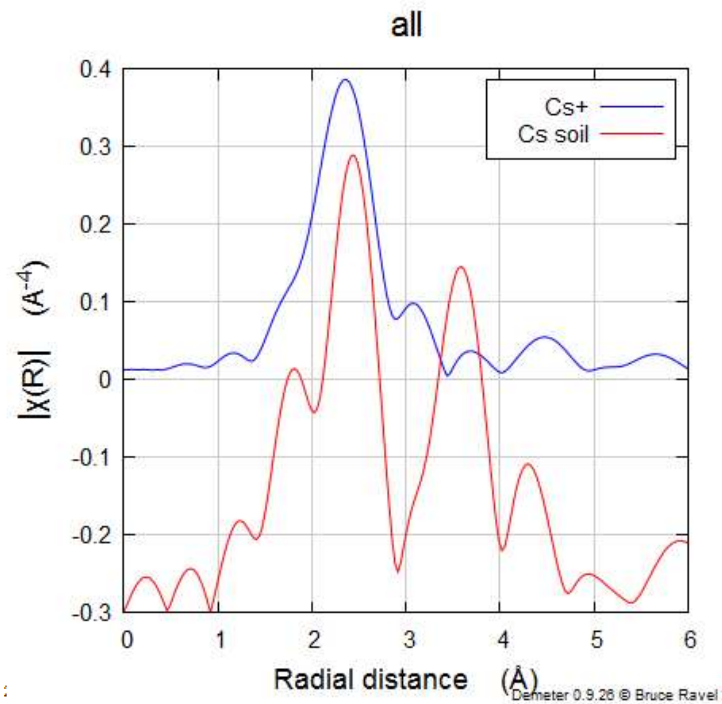


Further EXAFS interpretation ongoing

Observations and preliminary interpretations:

- The FT of the EXAFS shows the local coordination environment
- Sr: EXAFS is dominated by oxygen scatterers at ~2.6Å (e.g. from H_2O)
- Cs: EXAFS is heavily affected by oxygen at ~3Å (H_2O) and Si/Al at ~4.2Å (from mineral surfaces: illite and kaolinite)
- Indicates that Cs is more strongly bound to mineral surfaces compared to Sr





Energy

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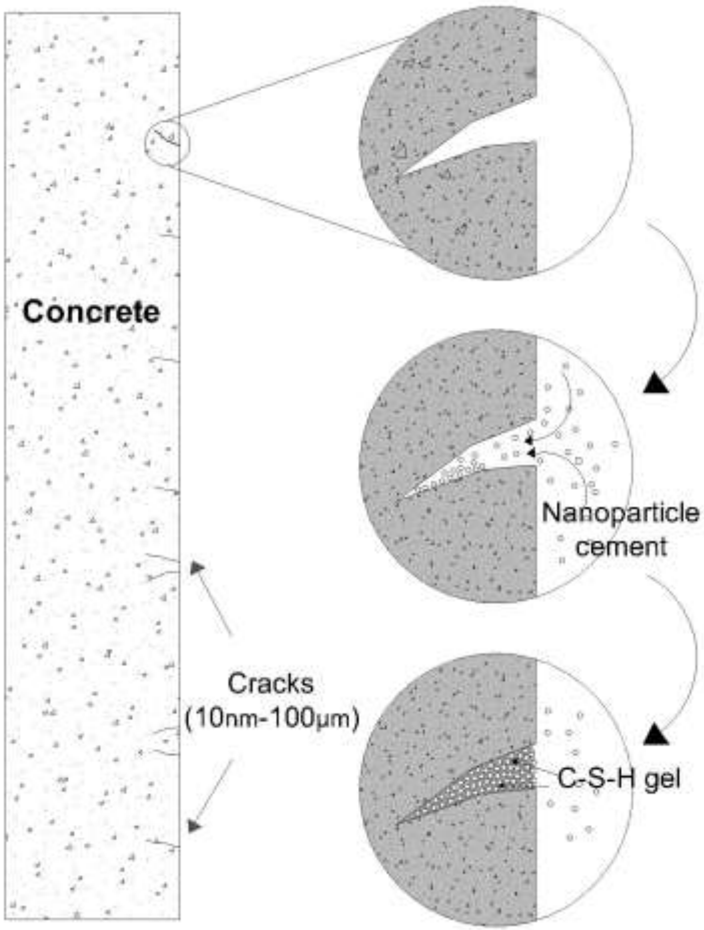
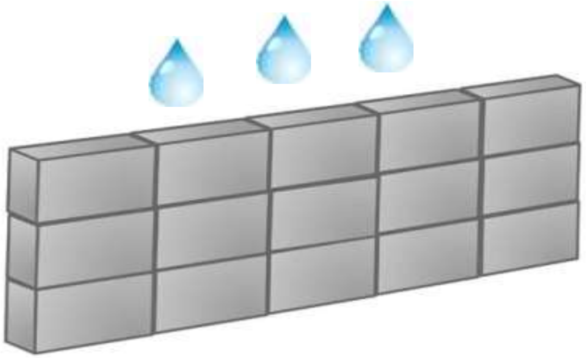
Low-pressure grouting of cracked cement

Silica injection



Aim: to investigate a novel non destructive and non invasive technique to seal nano-cracks.



Silica injection

$$SIO_2 + CA(OH)_2 + H_2O = C\text{-}S\text{-}H$$

Aim of the project is to investigate a novel non destructive and non invasive technique to seal nano-cracks, preventing deterioration and giving and adequate (controlled) impermeability to existing concrete structures

DISTINCTIVE

Materials

Portland cement

28 days curing

cement disc
h = 4mm
∅ = 35mm

Portland cement CEM II/A-L Strength class 42.5 MPa	
Components	%
Clinker	93
Gypsum added	7
Chemical composition (>0.2%)	
SiO_2	20.1
Al_2O_3	5.1
Fe_2O_3	3.4
CaO	63.0
MgO	2.6
SO_3	2.4
Na_2O	0.3
Density (g/cm^3)	3.2
Specific area (m^2/g)	0.38
Compressive strength, 28 days (MPa)	60

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DISTINCTIVE

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Nano-silica

Components	Nano-silica LUDOX T50©	Silica fume ELKEM©
State	Aqueous suspension	particles
Chemical composition (>0.2%)	%	%
SiO_2	50	99.9
Water	50	-
Particle size range (nm)	5-20	150-1000
Density (g/cm^3)	1.4	1.56
Specific area (m^2/g)	160	21.5

Silica fume

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Experimental Setup

Silica solution

Oven-drying the sample before and after the injection.

Record the weight of the sample before and after the injection.

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Experimental parameters

Particle size
of silica

Nano-silica (5-20 nm)

Silica fume (150-1000 nm)

Experimental parameters

Particle size
of silica

Nano-silica (5-20 nm)

Silica fume (150-1000 nm)

Concentration
of silica

10 % wt.

15 % wt.

20 % wt.

Energy

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Experimental parameters

Particle size of silica	Nano-silica (5-20 nm) Silica fume (150-1000 nm)
Concentration of silica	10 % wt. 15 % wt. 20 % wt.
Time of injection	7 days 14 days 28 day

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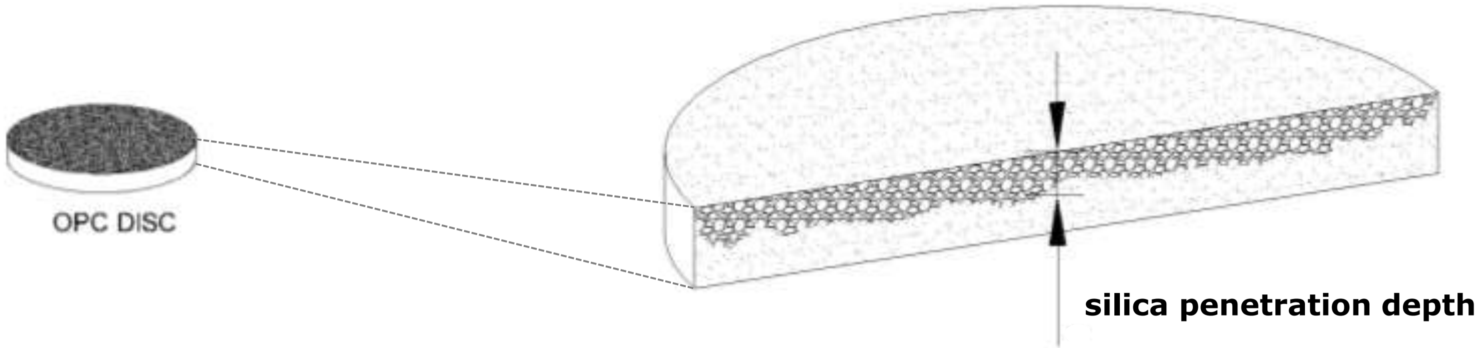
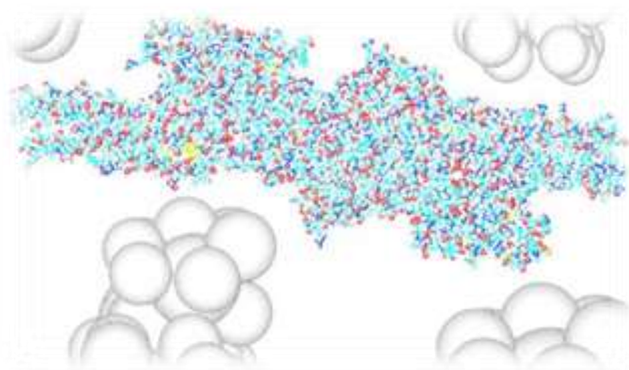
Microstructural analysis



After injection OPC sample was characterised by:

- **Porosity** measurements and weight change
- Thermo-gravimetric analysis (**TGA**)
- Powder X-Ray diffraction (**XRD**)
- Scanning Electron Microscopy (**SEM)** imaging



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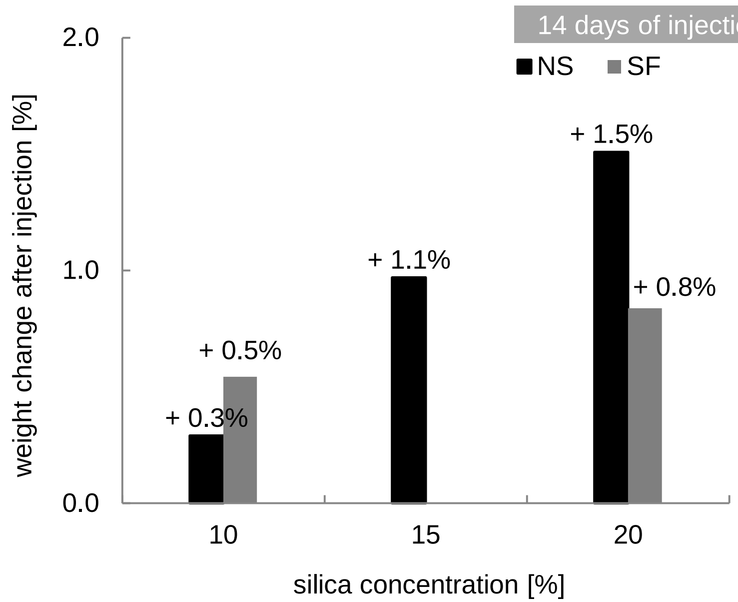
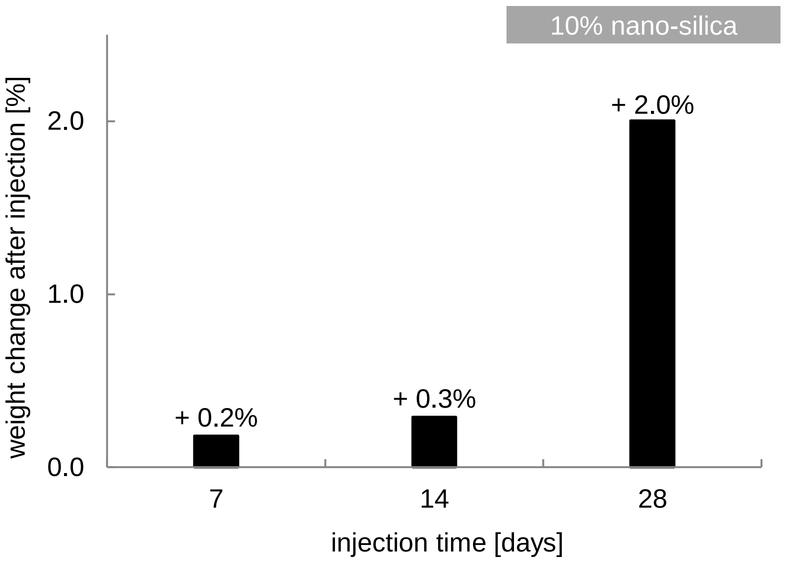
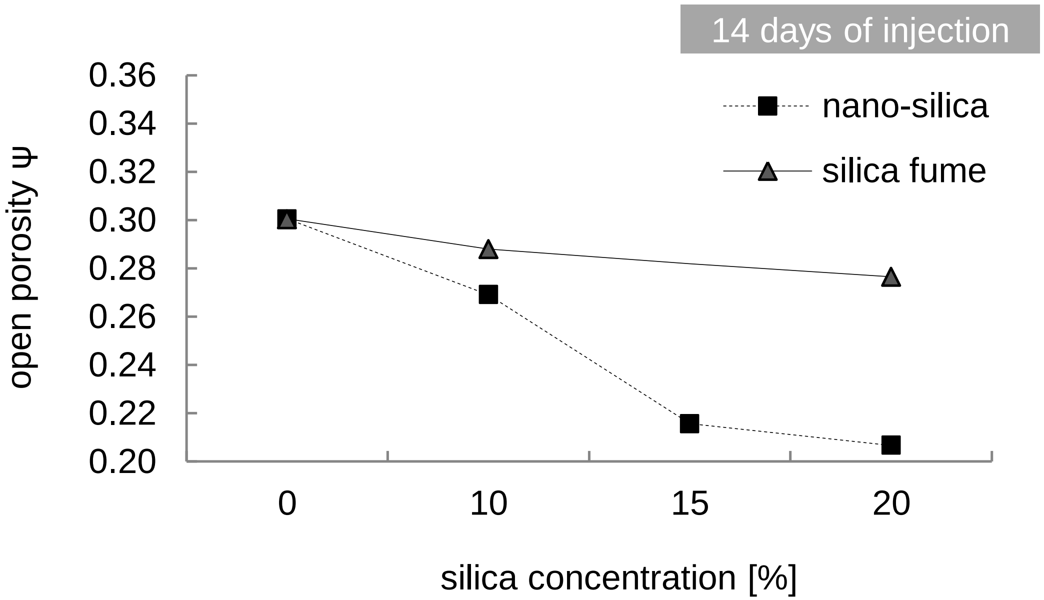
Weight change

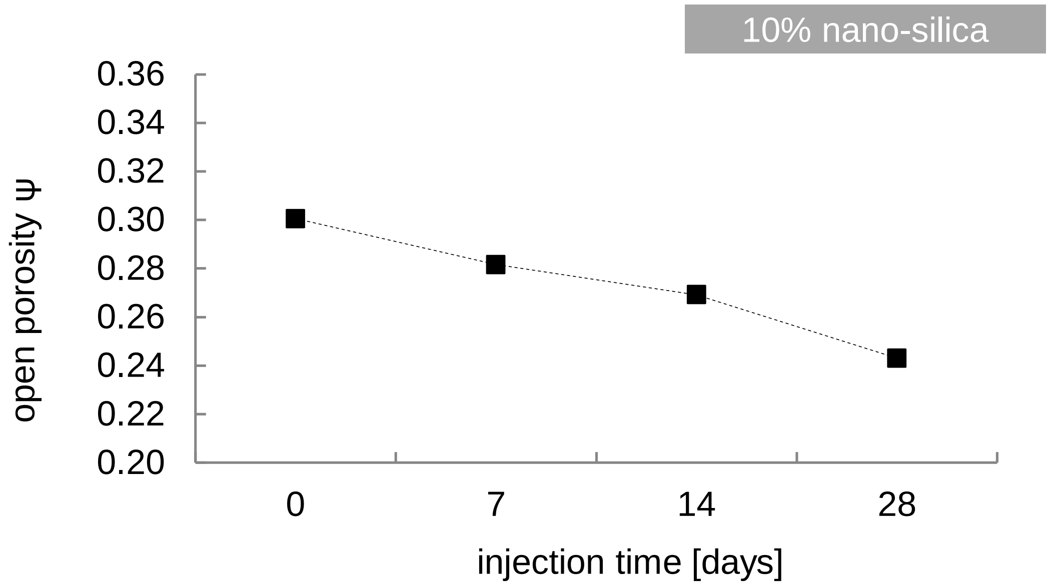
At the end of the injection period, the disc was removed and oven-dried at 60 °C for ca. 100 hours. The sample weight was recorded before and after injection to quantify the amount of silica in the pores.





Porosity





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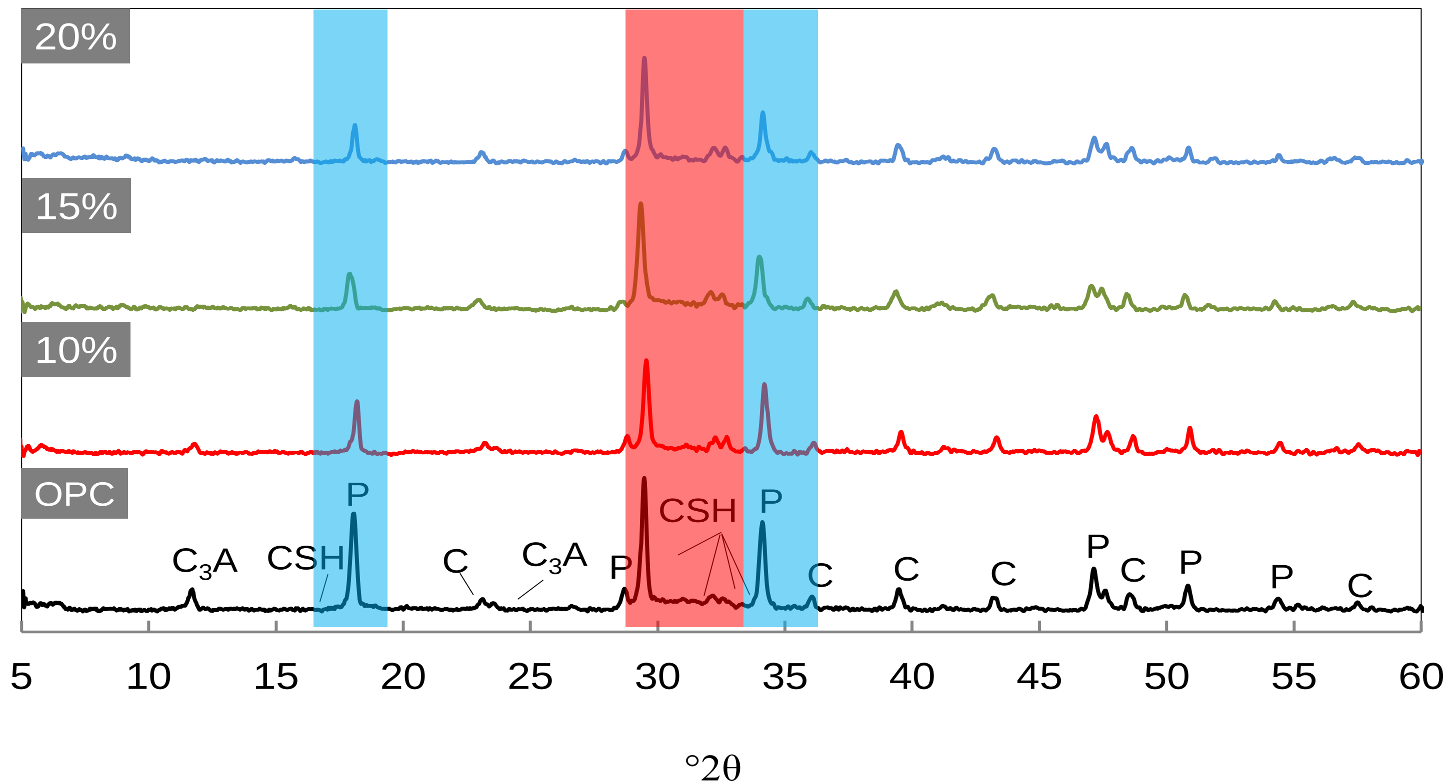
Powder X-Ray Diffraction

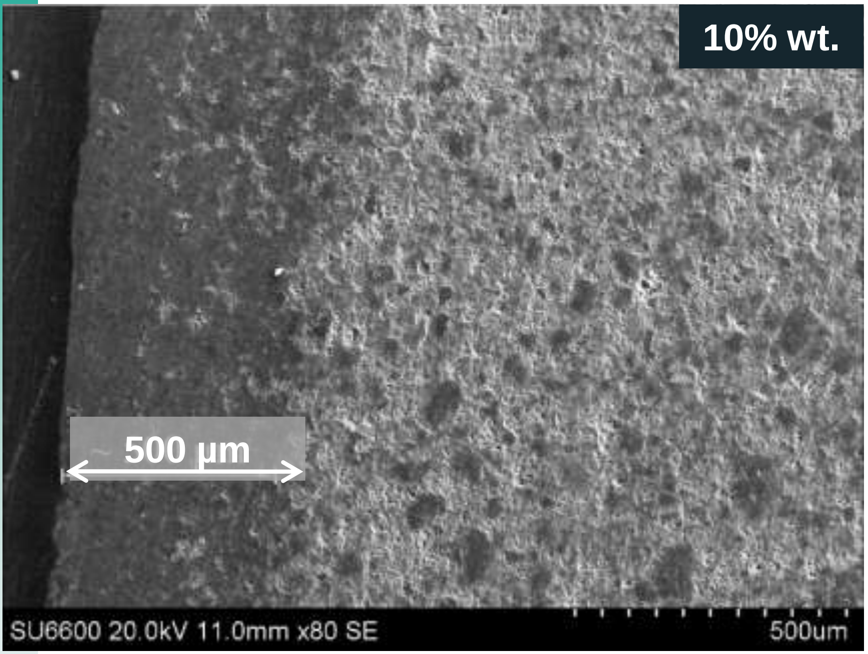
XRD analysis of the injected samples show a **progressive decrease in intensity of portlandite peaks and calcium aluminate phases reflection. Calcium aluminate phase**s (C_3A, peak at ca. 11.5 °2θ), present in the original clinker **reacted with nano-silica forming additional** C-S-H/C-A-S-H (calcium aluminate silicate hydrate), observed at ca. 15.5 °2θ.



XRD patterns for nano-silica injection samples at different concentration values for 14 days

SEM imaging

The silica concentration (10%, 15% and 20% wt.) influences the penetration depth, at a fixed injection time (14 days)



nano-silica injection

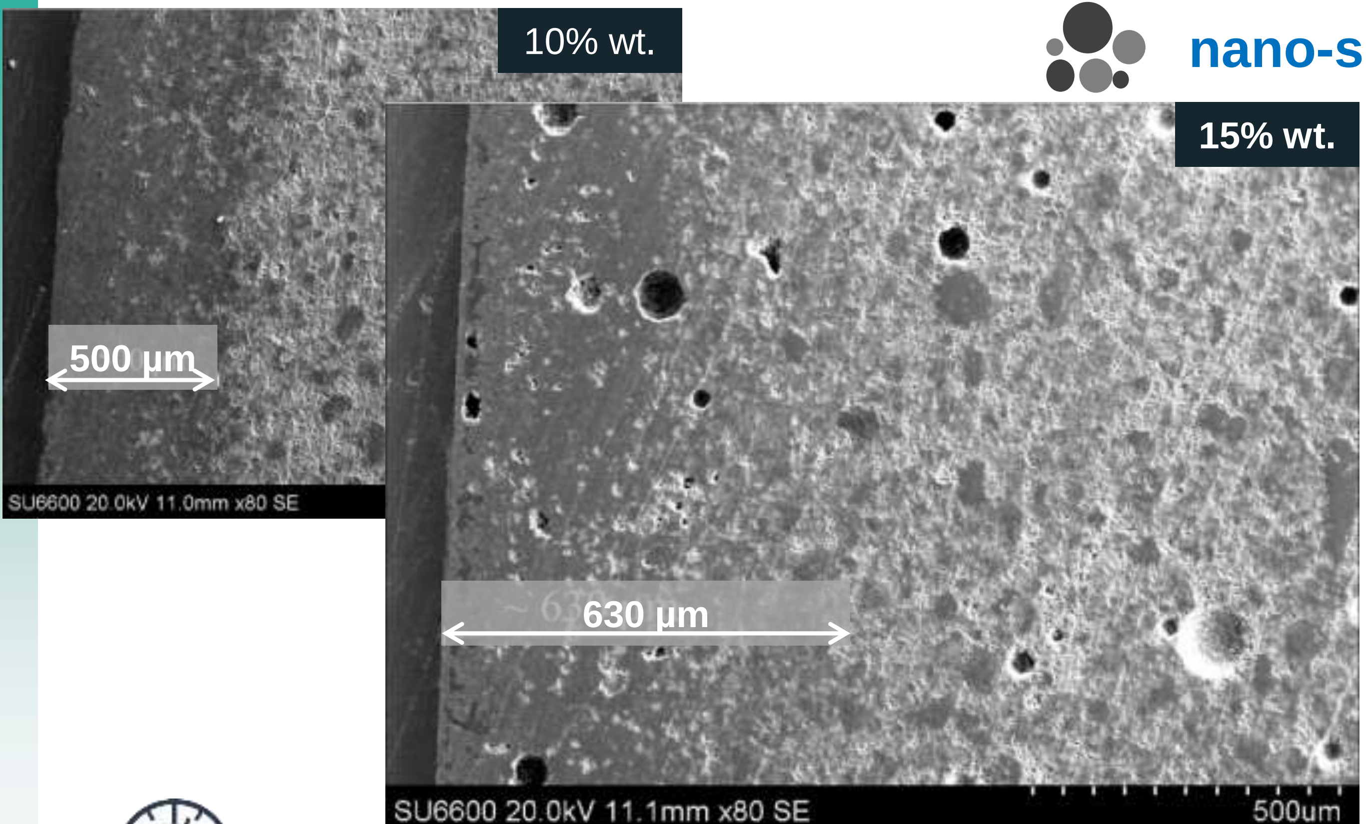
After 14 days of injection

DISTINCTIVE

SEM imaging

The silica concentration (10%, 15% and 20% wt.) influences the penetration depth, at a fixed injection time (14 days)

nano-silica injection



After 14 days of injection

DISTINCTIVE

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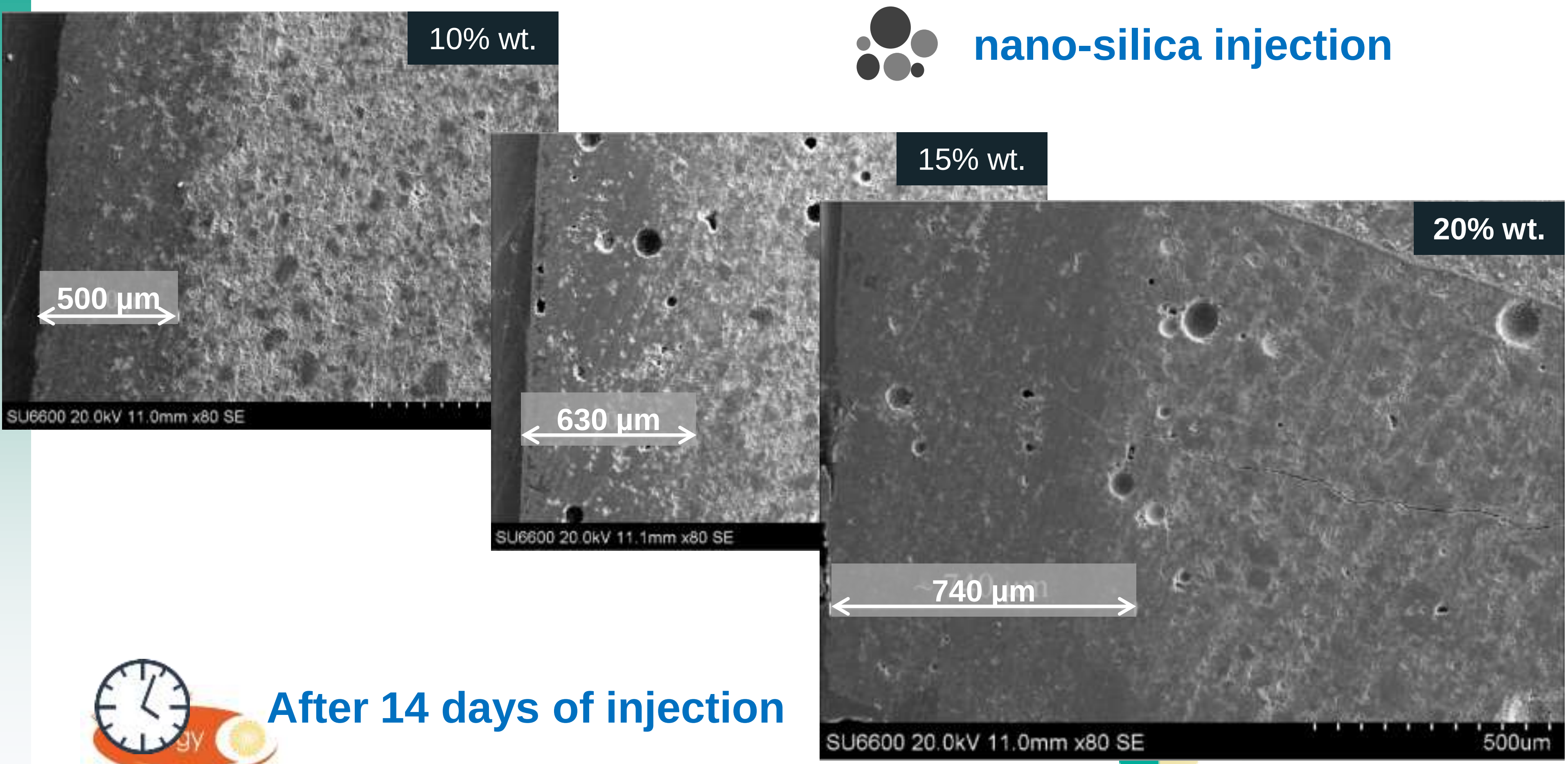
nano-silica injection



After 14 days of injection

Conclusions

Conclusions

Ground Barriers:

- **Numerical model** developed and validated for silica injection and gelling
- **ERT** for injection monitoring
- Grout provides **additional resistance** to ground consolidation and shear failure
- Hydraulic permeability of grout is similar to clay
  - **Suction due to drying** is higher than clay
  - Even when **aggressively dried and re-wet hydraulic conductivity remains in the clay range**

Conclusions

Un-grouted clay-rich soil (Little Forest Legacy Site)

- Sr and Cs are sorbed onto clays – predominantly illite
- most Cs is strongly bound
- the small amount of charge-bound Cs is displaced by the Sr during sorption

Grouted soil

- Desorption of Cs and Sr is lower within grouted soil
- XASF data show that most Cs is strongly bound in soil and no desorption occurs after the initial 10% loss which is probably the charge-bound fraction
- Sr is charge-bound, desorption occurs but K_d is one order of magnitude smaller in grouted soil

Conclusions

Gravity-driven cement repair

- Nano-particulate silica is more effective that silica fume
- Portlandite converted to C-S-H improving the durability and mechanical strength of degraded cement
- Permeability and porosity of surface layer is reduced increasing cement durability

THANKS

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A perspective from the industry funders

NATIONAL NUCLEAR LABORATORY

Sellafield Ltd

NDA
Nuclear Decommissioning Authority

What’s in it for us?

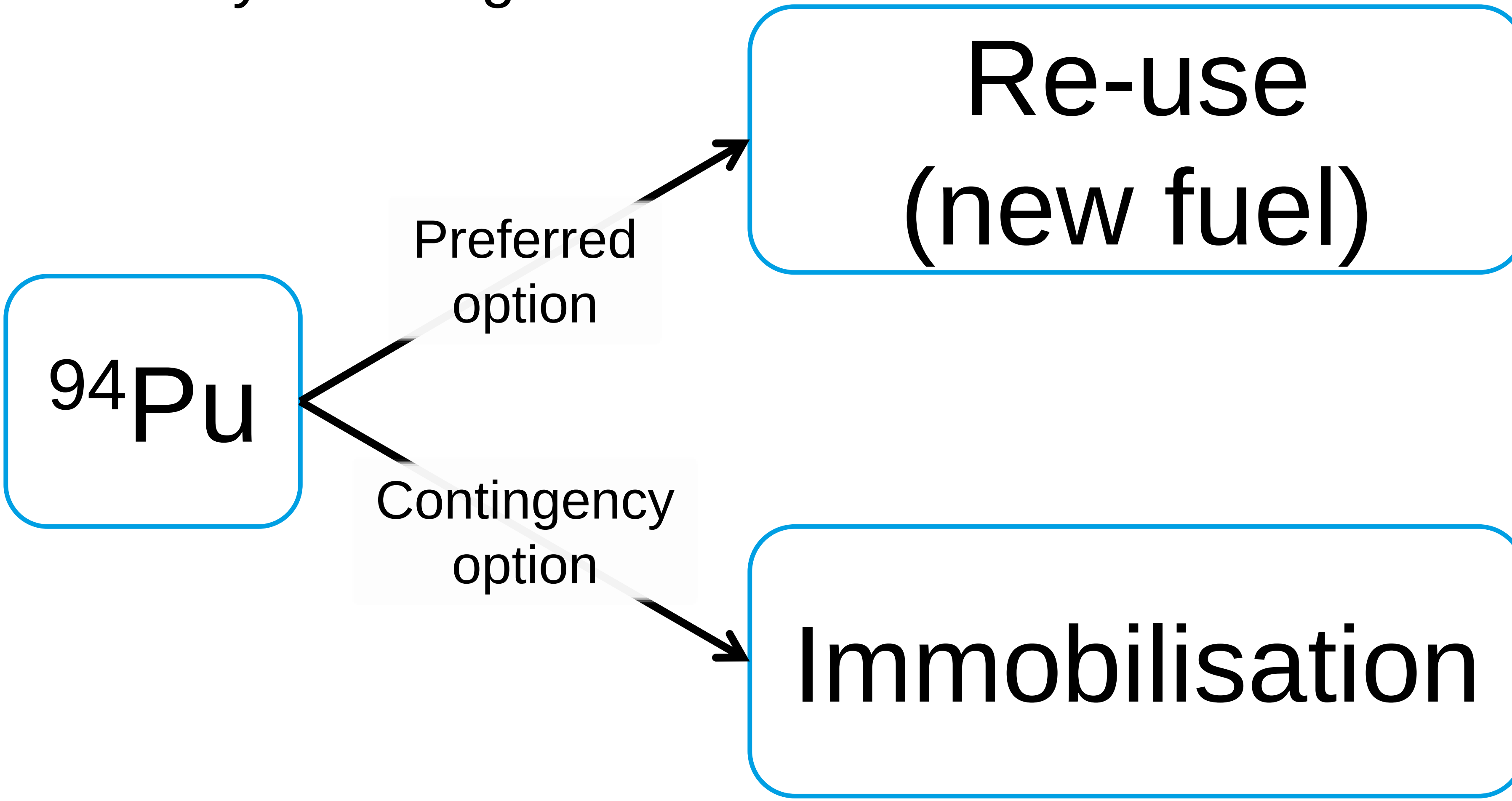
- Opportunity to steer fundamental R&D in decommissioning
- Access to the next generation of subject matter experts
- Maintain the academic skills base

Knowledge transfer

- Maintain the industry skills base

Case study – Pu HIP

Industry challenge:



Industry strategic option

Current front-running contingency option

Hot Isostatic Pressing (HIP)

HIP product cans from PuO_2 powder, interim stored then sent to GDF

DISTINCTIVE PhD project

The University Of Sheffield.

The University Of Sheffield.

The University Of Sheffield.

AIP
AMERICAN ISOSTATIC PRESSES, INC.

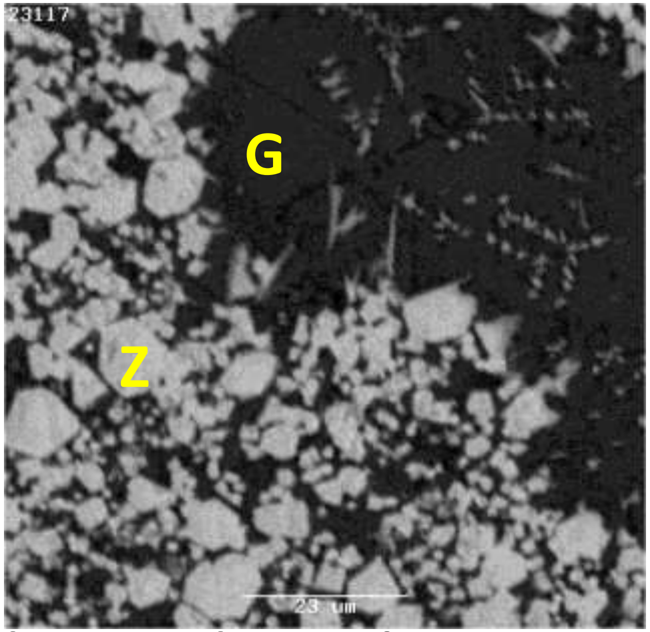
Australian Government
ansto

Australian Government
ansto

Australian Government
ansto

First ‘UK’ plutonium glass-ceramics

Sintered at 1250°C for 4hr.
Phase assemblage and microstructure were indicative of HIPed samples.
Full PuO_2 incorporation was achieved with preferential actinide partitioning into the ceramic.



EDX determined zirconolite composition:

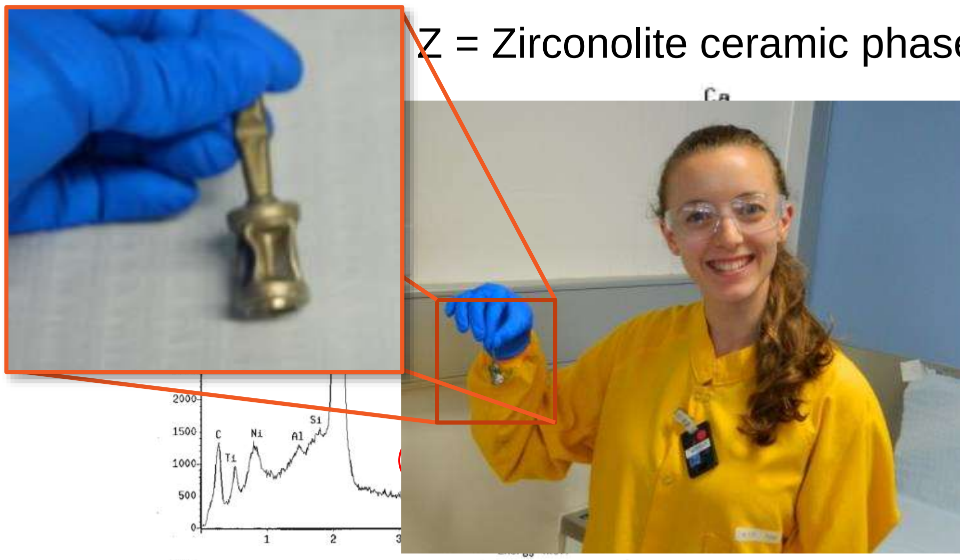
$$Ca_{0.83}Pu_{0.12}Na_{0.11}Zr_{1.14}Ti^{4+}_{1.31}Ti^{3+}_{0.64}Al_{0.05}O_7$$

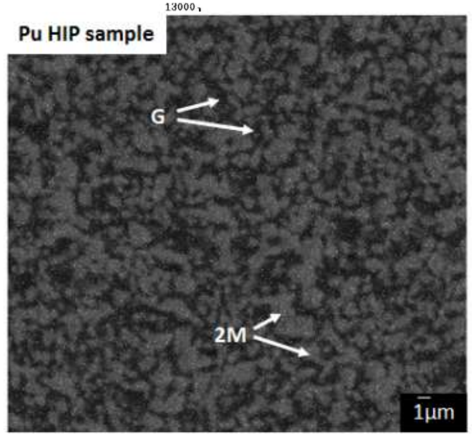
Approximate partitioning ratio (c:g)
Plutonium – 15:1

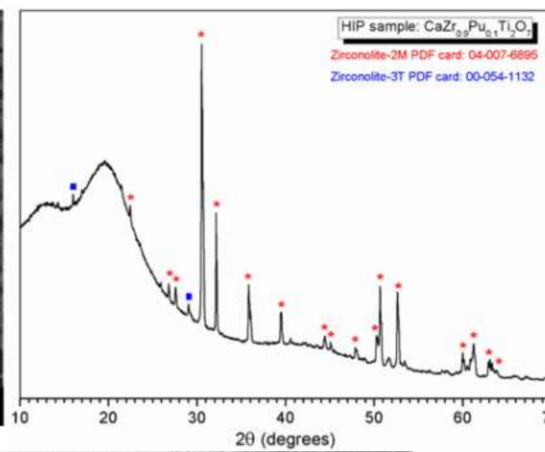
No undissolved PuO_2

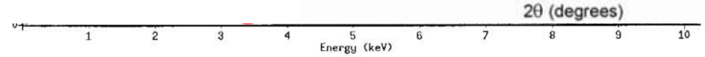
HIPed at 1250°C for 4hr.
Uniform microstructure of zirconolite distributed in glass matrix and full PuO_2 incorporation.

Z = Zirconolite ceramic phase









First ‘UK’ plutonium glass-ceramics

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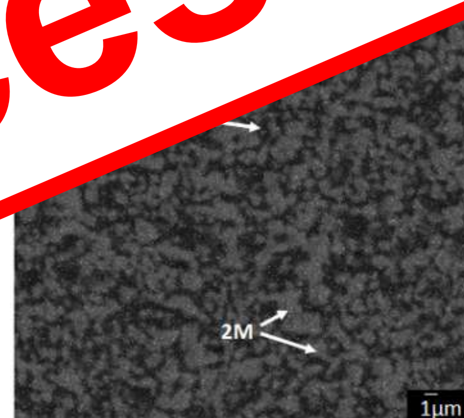
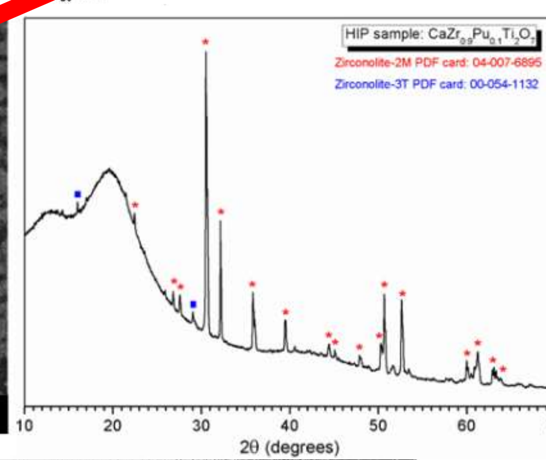
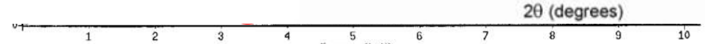
HIPed at 1250°C for 4hr.
Uniform microstructur… …ibuted in glass matrix and full P…

…mic phase

Academic success!







EDX deter…
$Ca_{0.83}Pu_{0.12}$…

Approxima… (c:g)
Plu… 15:1

No undissolved PuO_2

New recruit for industry

- Steph now employed by NNL
- Performing research on Pu HIP for NDA

New recruit for industry

Industrial success!

now
ved

ing
esearch on
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NDA

Conclusions

NATIONAL NUCLEAR LABORATORY

- Valuable contribution to delivery and continuing development of the NDA strategy
- Research themes aligned well with the industry science and technology needs
- Research output with potential to deliver impact to industry
- Building higher level skills to meet the future needs of the UK nuclear industry
- Important to build on this success in future

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