Hot Isostatic Pressing of glass and ceramic wasteforms for UK higher activity wastes

Neil Hyatt.

The University of Sheffield, UK.

n.c.hyatt@sheffield.ac.uk

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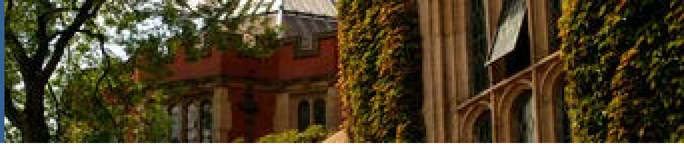
Novel thermal treatments for HAW



Why do we need alternative waste treatment options?

UK context: complex clean up and decommissioning programme

Baseline technologies: super-compaction, cement encapsulation

- Estimate 287,000 m^3 higher activity waste (ILW, ex. HLW)
- Project 378,000 m^3 conditioned higher activity waste
- Project 488,000 m^3 packaged higher activity waste
- Cost of >£110 Bn, timescale of 100 years (ex. GDF)

Potential advantages of thermal treatment of HAW

- Passive safety: eliminate gas evolution, non-dispersible product
- Minimise volume: eliminate voids, water, combustibles
- Storage: lower unit cost, improved safety, reduced monitoring
- GDF operations: transport, emplacement, environmental impact
- GDF closure: package longevity, no organics, far field uncertainty
- Security: fissile materials

Some key barriers

- Technical maturity and cost uncertainties
- Officialdom and industry mind-set
- Market drivers
- Uncertain compatibility with GDF concepts

WIPP release 14.02.2014

- Exothermic reaction involving mixture of organic materials and nitrate salts.
- Activity release on and off site, worker exposure.
- Recovery program: minimum 2y at cost of $242M.
- Completely avoidable with a passively safe waste package

Image credit: http://www.wipp.energy.gov/

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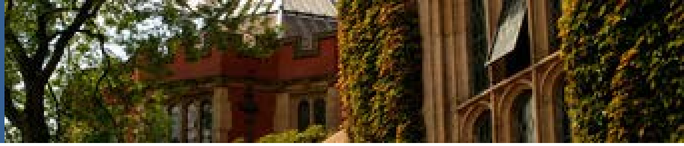
Early UK thermal treatment studies



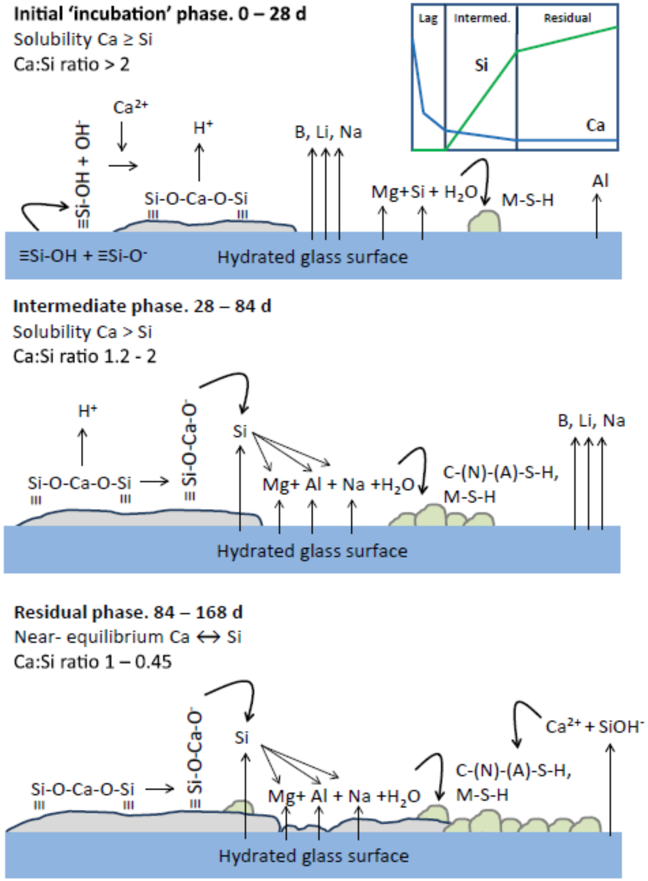
Hinkley Point A vitrification project ca. 2008

- University of Sheffield with Magnox South Sites Ltd
- Materials informatics approach to glass design
- 88 compositions → 33 selected → 6 candidates
- Screening / optimisation: 2 compositions for 4 waste types
- Exceeded all specification requirements
- First compatibility studies for cementitious GDF

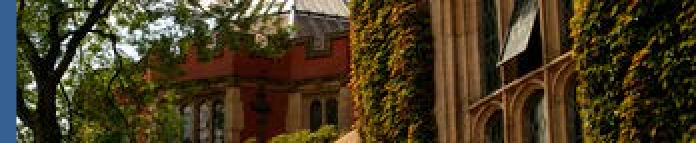
Disposability of vitrified product in cementitious GDF

- Are vitrified products compatible with cement GDF?
- Reaction of dissolved Si with Ca released from cement
- Formation of surface CSH and MSH layers
- Under some conditions may passivate glass surface
- Provided first comfort on disposability

See: N.C. Hyatt & M. James, Nuclear Engineering International, March 2013.



Need for a tool-box approach



Attribute	Joule Heated Melter	In Container Vitrification	Induction Melter	Plasma system	HIP
Compatability with organic waste feed	Moderate	High	Moderate	High	Low
Compatability with inorganic waste feed	High	High	High	High	High
Compatability with metallic waste feed	Low	High	Low	Moderate	Moderate
Capability of producing heterogeneous wastefom	Low	High	Moderate	High	High
Waste feed characterisation requirements	High	Low	Moderate	Low	Moderate
Tolerance to waste variation	Low	High	Moderate	Low	Moderate
Containment of volatiles	Moderate	Moderate	Moderate	Low	High
Control of product quality	High	Moderate	High	Moderate	High
Potential volume reduction	Moderate	Moderate	Moderate	Moderate	High
Technical maturity	High	Moderate	High	High	Moderate

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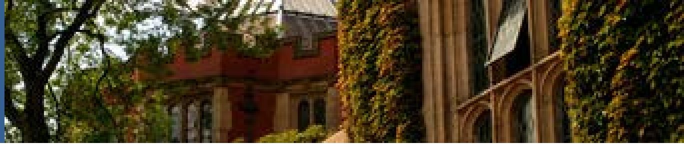

NDA Strategic Business Case (2013-14)

- Collaborative project funded by NDA Strategy Directorate
  - Galson Sciences Ltd, NNL, UoS
- Developed a strategic Business Case for a thermal treatment demonstration facility for radioactive wastes
  - Supported NDA's strategic commitment to consider thermal treatment as a viable alternative to cement encapsulation
  - Focused on treatment of ILW

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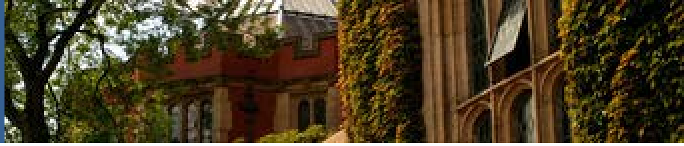
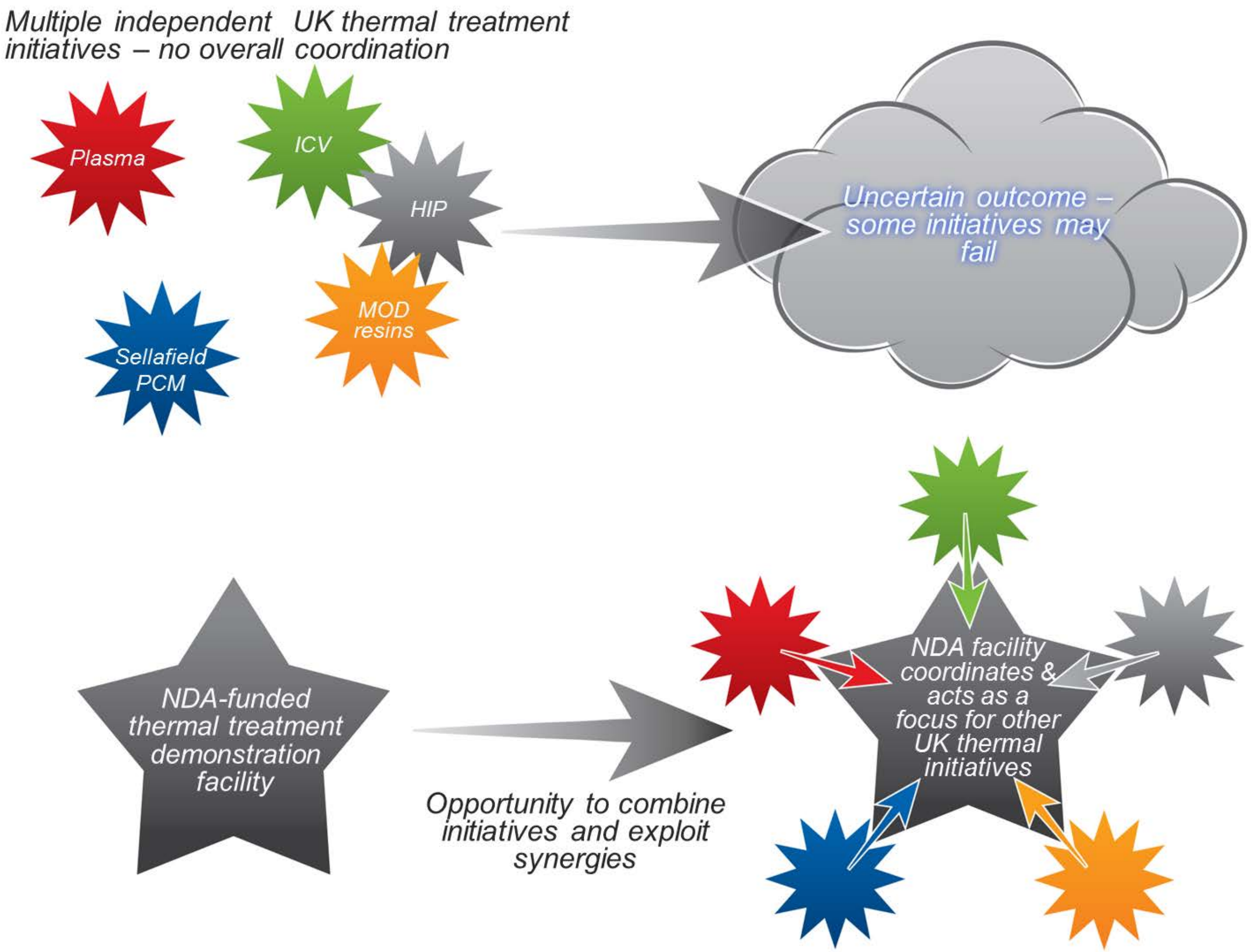
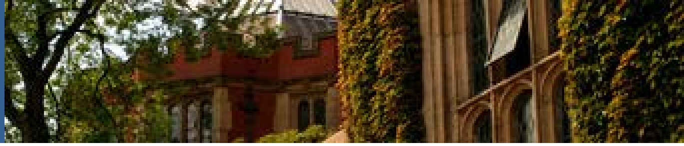


Case for Change

- Current thermal treatment initiatives are fragmented, different organisations, differing requirements – no coordination
- Existing UK initiatives mostly at Proof of Concept stage (TRL ~3)
  - But initiatives in other countries more advanced
- Advantage not being taken of potential synergies between waste producers
- Opportunity to influence treatment of some UK waste streams may soon be lost
- Financial risk to suppliers is a major barrier to progress
- A thermal treatment demonstration facility could help coordinate existing work

UK Thermal Treatment Demonstrator

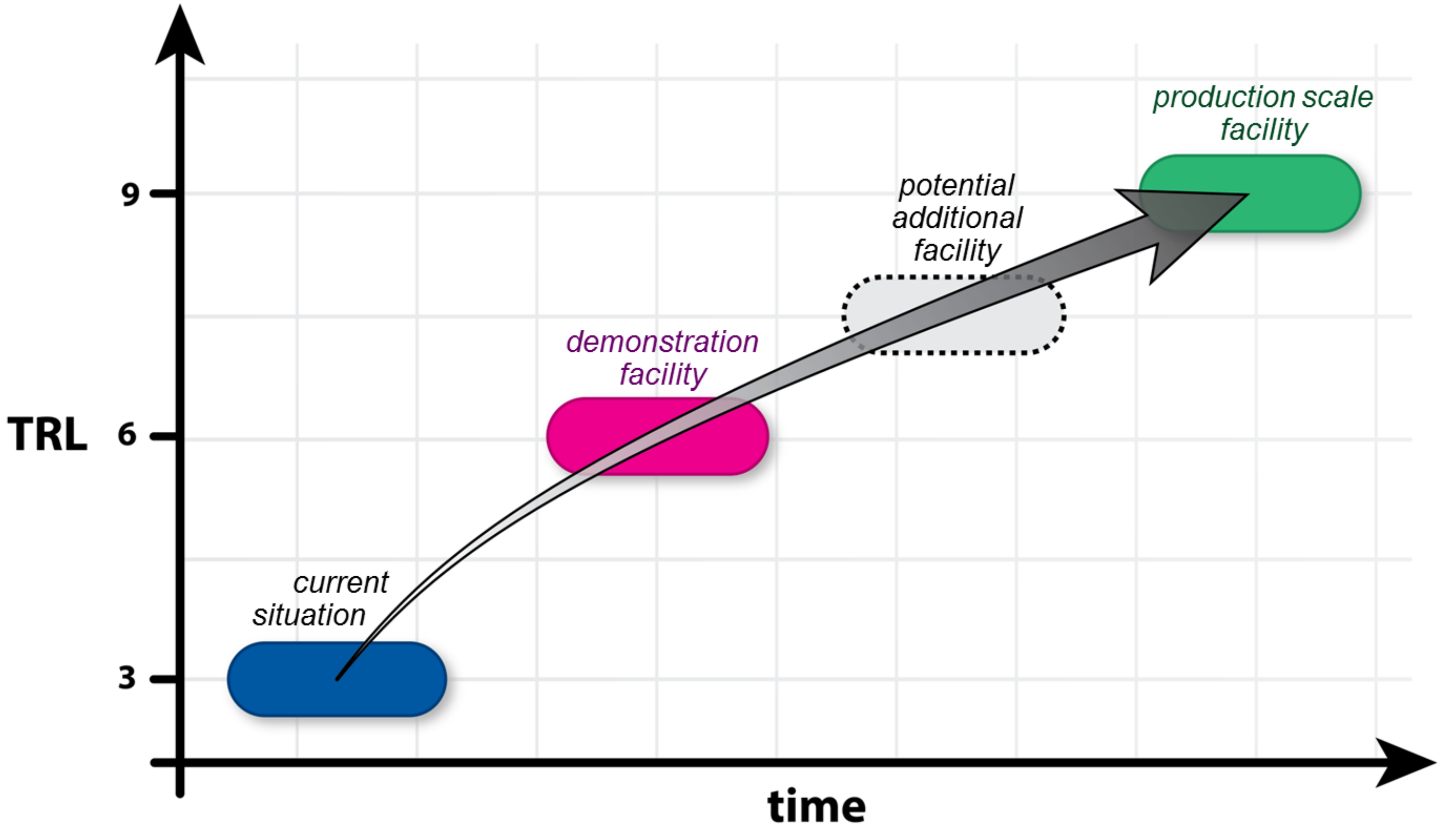




Outcomes and Benefits

- Raise the TRL level above the current UK ceiling of around 3
- Develop treatments to reduce waste volume, destroy reactive components
- Stepping stone to a future integrated waste management programme
- Direct operational experience of thermal treatment
- De-risk programme by removing barriers
- Confirm Volume Reduction Factors (VRFs) and promote disposability assessment of thermally treated wasteforms
- Provide an alternative option to grout encapsulation
- Further develop expertise within the supply chain and academia, and facilitate engagement with regulators

UK Thermal Treatment Demonstrator



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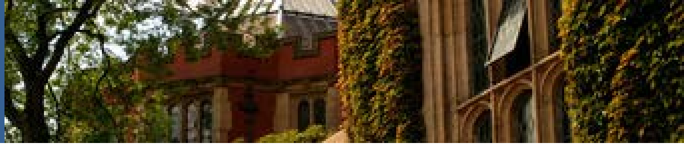

Way Forward

- Thermal treatment business case delivered to NDA in early 2014
- Building on this business case, NDA launched an Integrated Project Team on thermal treatment of radioactive waste
- Opportunity now exists to build a European initiative to coordinate and promote thermal treatment R&D
- Key goals and objectives
  - Reduce packaged waste volume – storage and disposal cost savings
  - Destroy chemical reactivity, reduce voidage – facilitate operational and post-closure safety case development
  - Consistent application of Waste Hierarchy

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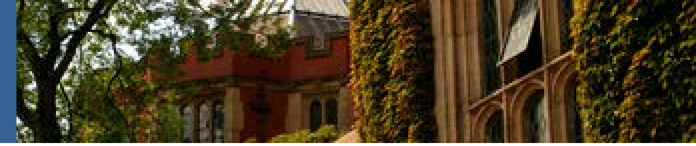
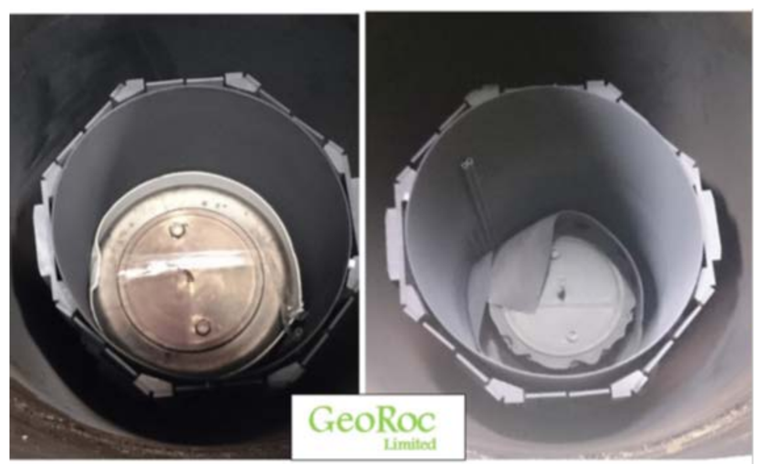


Waste applications

- Pu residues (NNL & UoS)
- Magnox sludge wastes (Georoc & UoS)
- Fuel element debris (UoS)
- Inorganic ion exchange materials (UoS)
- Glass encapsulated TRISO fuel particles (UoS)
- HLW glass ceramics (UoS, USW, PNNL)
- Advanced ceramic wasteforms (UoS, POSTEC)

Product wasteforms

- Glass, ceramic, glass-ceramic
- Glass encapsulated composite
- Metal encapsulated composite



100 L HIP can trial

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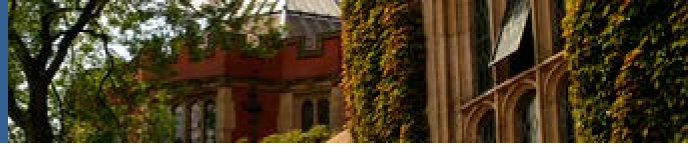


<u>Mature technology:</u> exploited on industrial scale

- Biomedical implants, turbine blades
- e.g. 5m^3 HIP for aerospace alloys, Camas, WA.

<u>Principle:</u> apply pressure and temperature to consolidate, bond or densify materials.

Defined as the reference treatment method for:

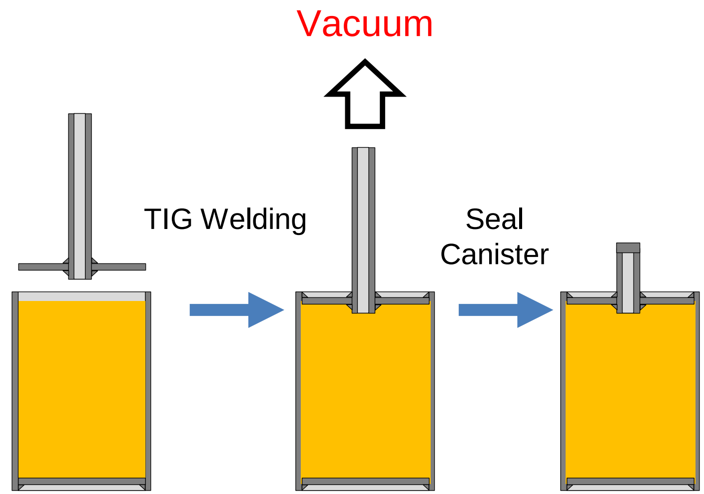
- Idaho HLW calcines (US)
- Pu residues (UK)
- ^{99}Mo production wastes (Australia)

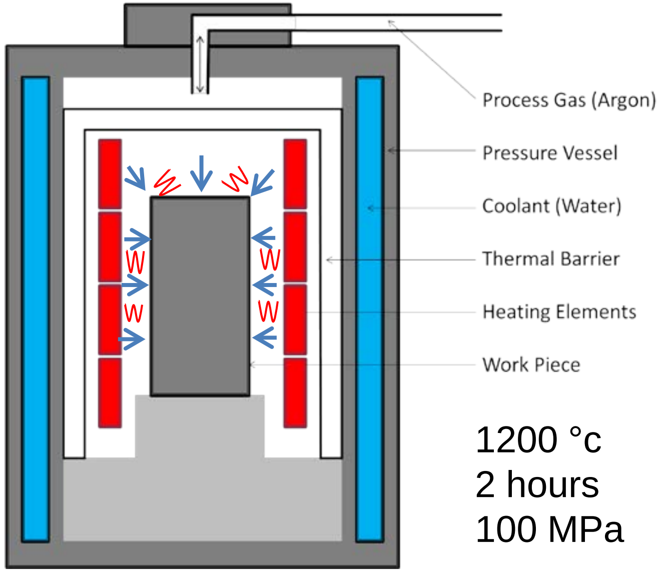
<u>Basic process</u>

1. Waste material / matrix formers added to HIP can
2. Lid and evacuation tube (with filter) welded on
3. Bake out step, crimp and seal evacuation tube
4. HIP processing cycle
5. Can is primary containment for waste package

<u>Advantages of HIP technology</u>

- No volatile off gas during process
- Process diverse wastes in single facility
- Waste loading of 100% feasible
- Packaged waste volume minimised





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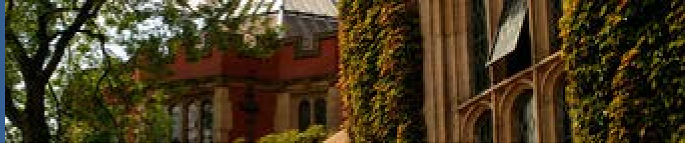
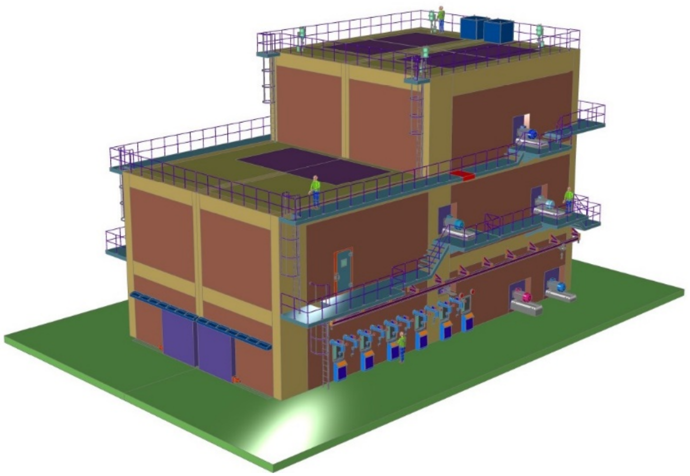


Technical maturity: TRL 4-5

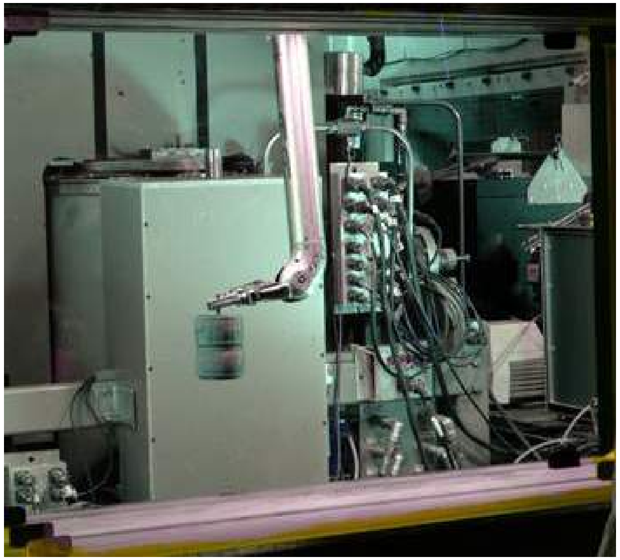
- HIP and front-end unit operations are mature on an industrial scale.
- HIP and front-end unit operations have been nuclearised.
- Nuclearised HIP waste treatment plant concept designs exist for, ILW, HLW, and actinide wastes:
- Active research HIP facilities safely operated in Australia and USA.

HIP Technology R&D needs

- Waste stream specific R&D – waste processing envelope and safety case, product disposability.
- Integration of individual process units at full scale operation.
- Pilot plant construction and operations for processing of wastes.



GeoRoc Magnox sludge concept plant



Hot-Cell HIP at INL - Courtesy of INL

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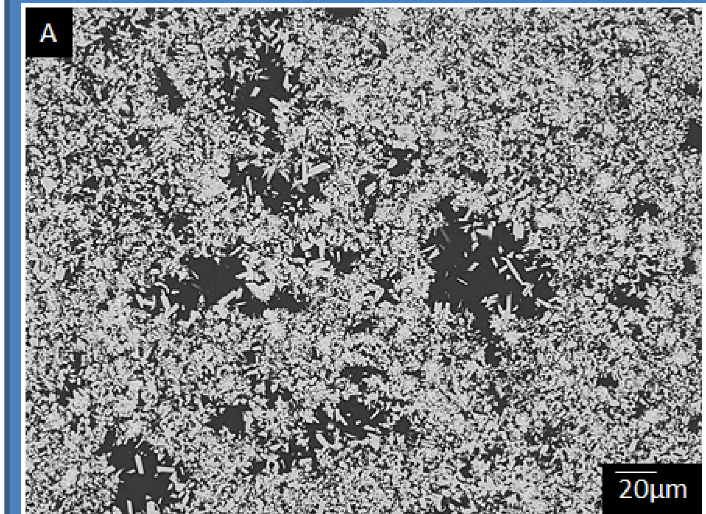
Glass ceramics for Pu residues

Waste stream characteristics

- Variable waste inventory: sludges, pellets and fuel pins, plus metallic composite fuels.
- Fissile materials vary from PuO_2, UO_2 and MOX powders, to highly impure scrap material.
- Pu recovery is uneconomic so material requires conditioning as a waste.

Proposed waste treatment process

- Residues to be conditioned as a glass-ceramic wasteform by Hot Isostatic Pressing
- Partition Pu into ceramic zirconolite host phase, impurities are partitioned into albite glass phase.
- Pilot plant construction and operations for processing of wastes.
- Concept proposed and developed by NNL & ANSTO, with scientific underpinning by UoS.



Ceramic phase: $CaZrTi_2O_7$
Glass phase: $Na_2(Al,B)_2Si_6O_{16}$
70% ceramic / 30% glass

Key R&D issues:

Phase assemblage dependence on

- Glass composition
- Ceramic / glass fraction

Need optimisation of processing route and throughput

Mechanism of PuO_2 digestion in melt and Pu partitioning – role of CaF_2

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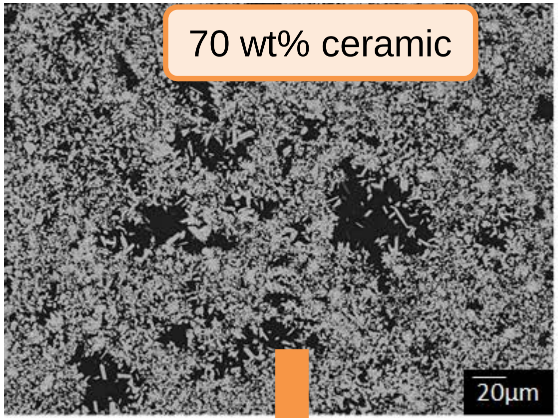
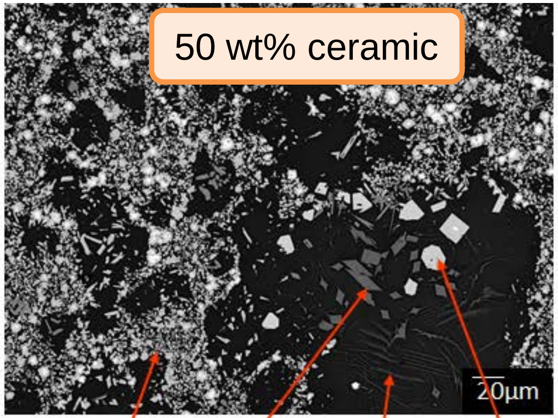
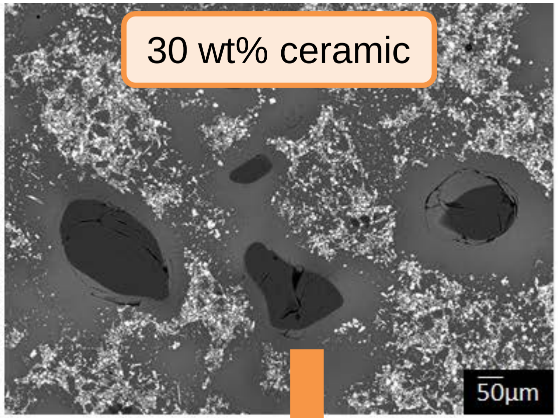
Glass ceramics for Pu residues

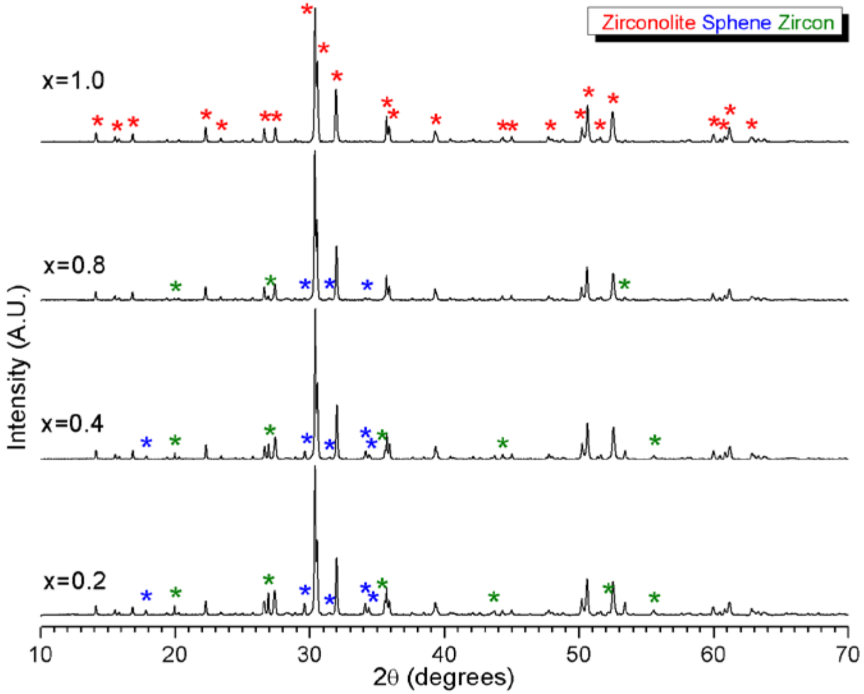
Full Al_2O_3 glass (x =1)

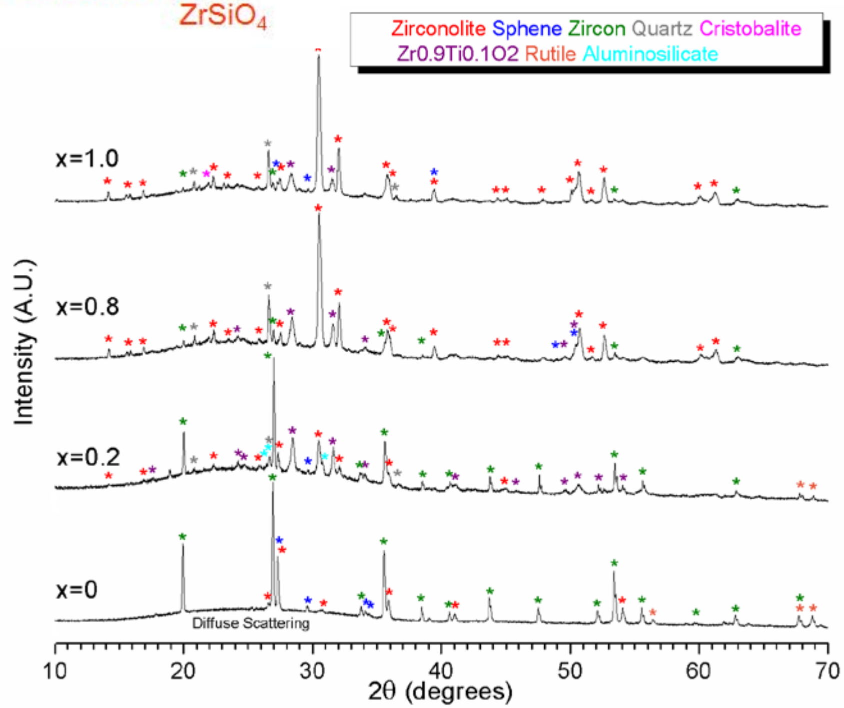


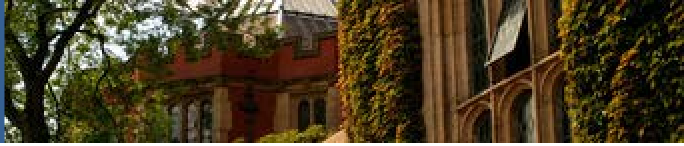




Increasing Al_2O_3







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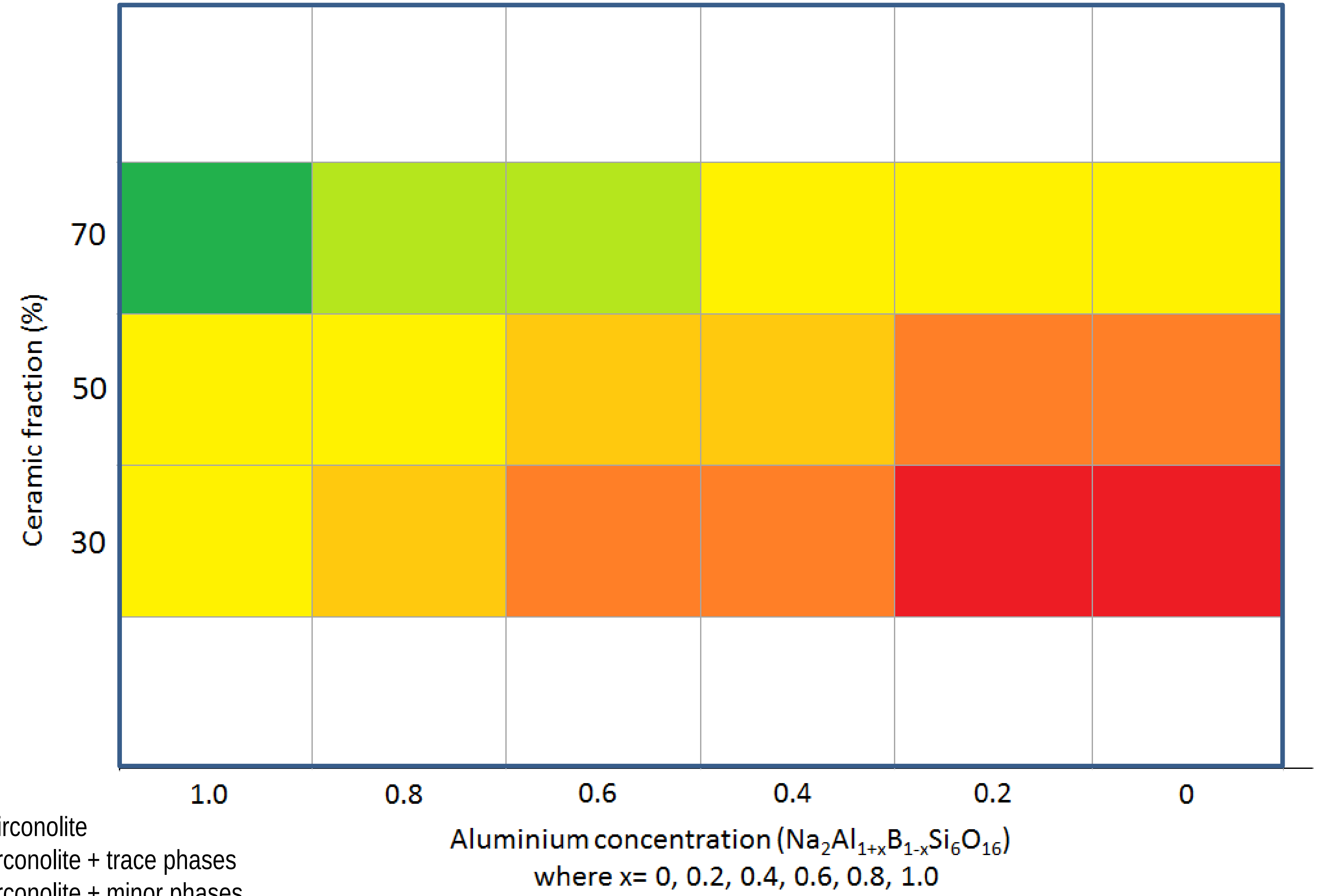
Glass ceramics for Pu residues



Key
- Single phase zirconolite
- Major phase zirconolite + trace phases
- Major phase zirconolite + minor phases
- Mix of multiple phases, inc. zirconolite
- Zircon major phase + minor zirconolite
- Zircon major phase + trace zirconolite

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Glass ceramics for Pu residues

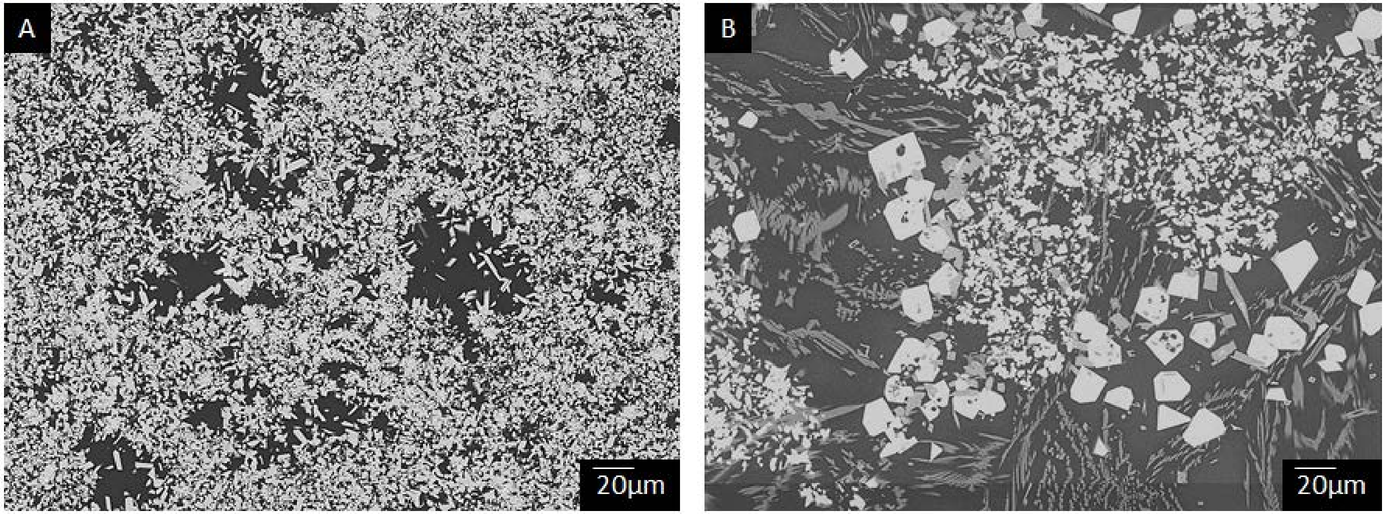
Formation of the zirconolite depends on two competing reactions, where $[SiO_2]$ represents silica in the glass phase:

$$CaO + ZrO_2 + TiO_2 + SiO_2 \rightarrow CaTiSiO_5 + ZrSiO_4 + TiO_2$$

$$CaO + ZrO_2 + TiO_2 + SiO_2 \rightarrow CaZrTi_2O_7 + 2[SiO_2]$$

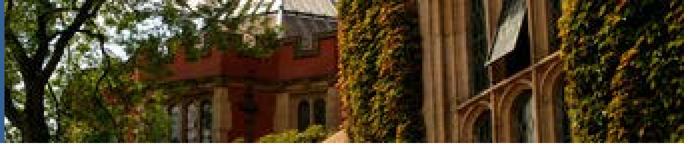
$$\mathbf{CaTiSiO_5 + ZrSiO_4 + TiO_2 \rightleftharpoons CaZrTi_2O_7 + 2[SiO_2]}$$

The zirconolite phase is favoured by:
* Low glass fraction where silica is consumed to form the glass network
* High Al_2O_3 content glass – requires silica to be stabilised



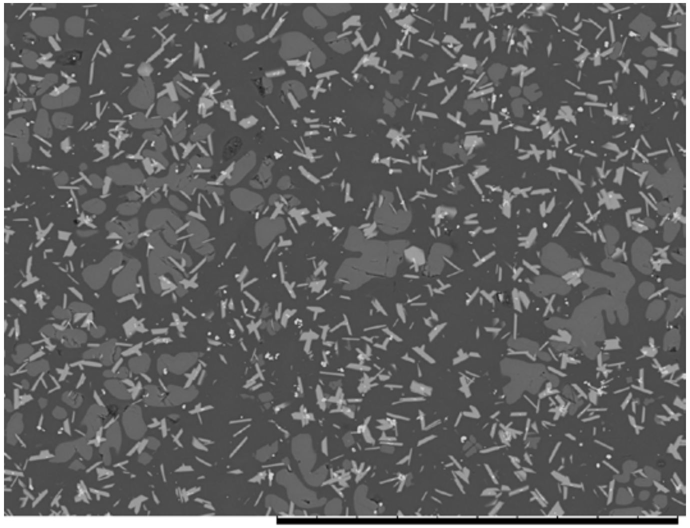
Published in Journal of Nuclear Materials "The influence of glass composition on crystalline phase stability in glass-ceramic wasteforms." Ewan Maddrell, Stephanie Thornber & Neil C. Hyatt, 2014.

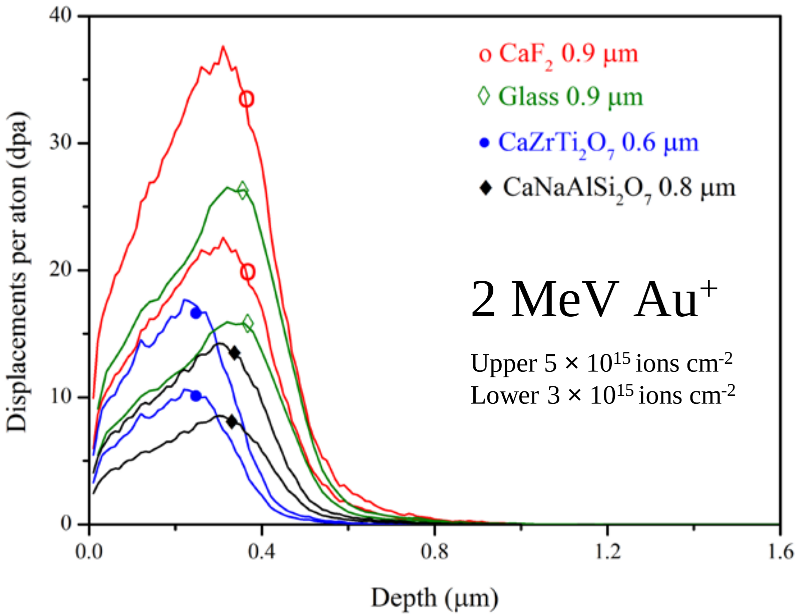
Glass ceramics for Pu residues

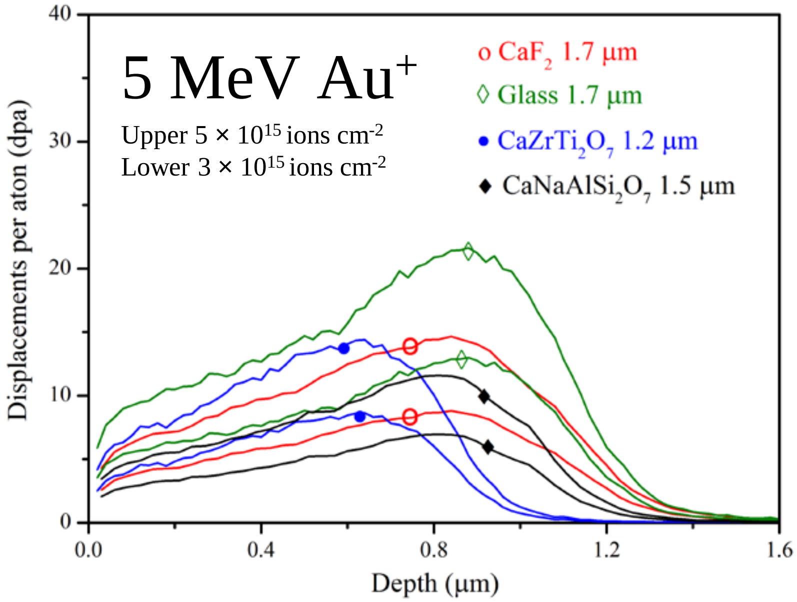


Radiation damage effects

- Expect crystalline to amorphous phase transition in zirconolite at <2 dpa (ca. 10^4 y at 10 wt% Pu; lifetime dose ca. 10 dpa)
- Use fast heavy ions as a proxy for alpha recoil damage.
- Note: both crystalline and amorphous phases are irradiated







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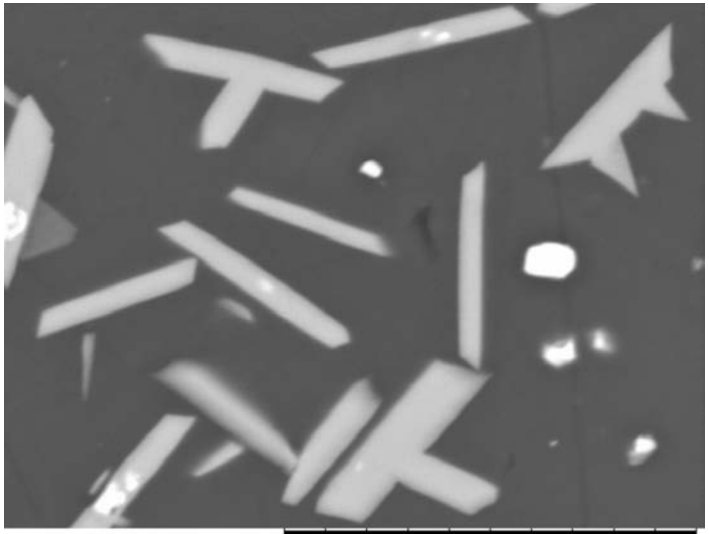
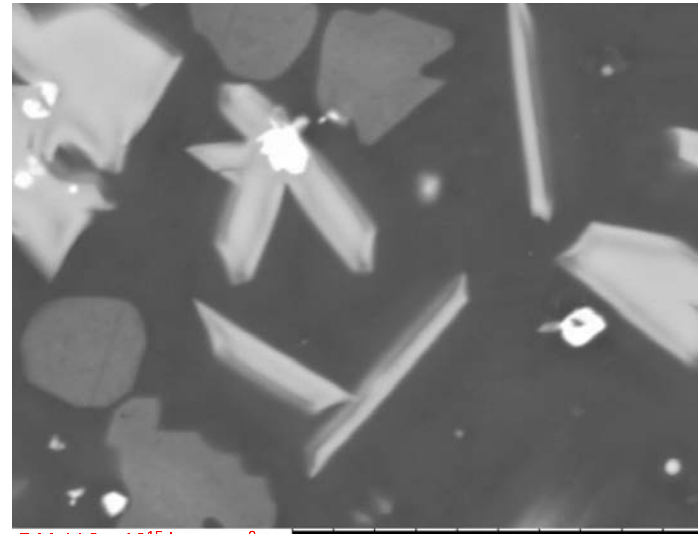
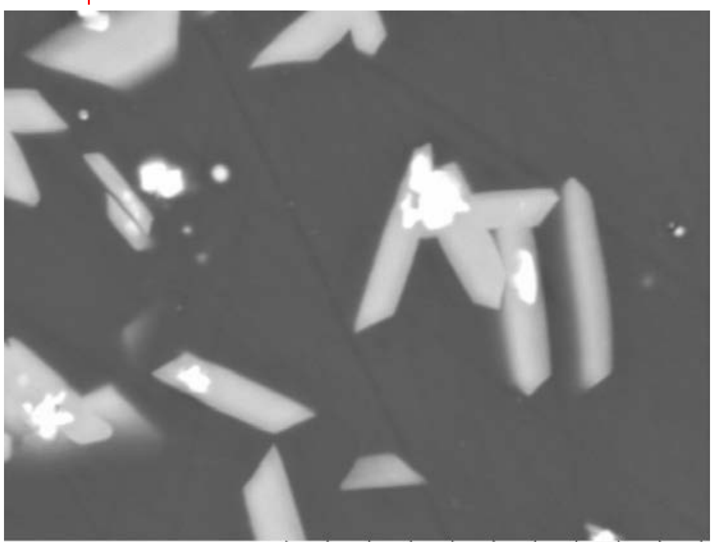


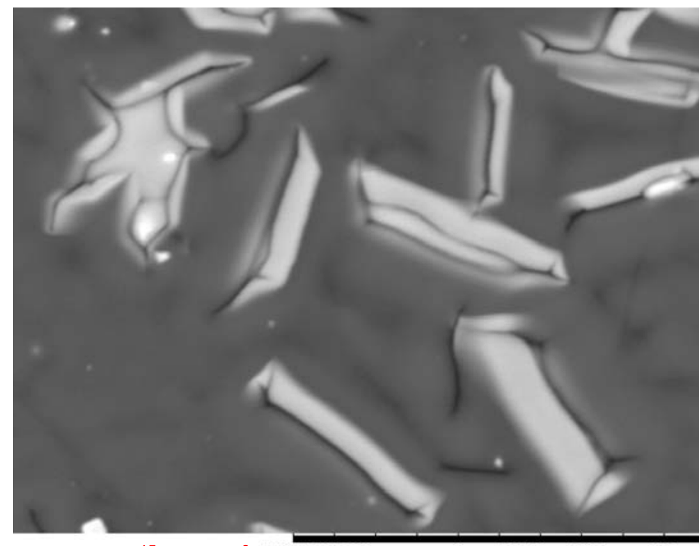
2 MeV 3 x 10^{15} ions cm^{-2}
Max 9 dpa



5 MeV 3 x 10^{15} ions cm^{-2}
Max 7 dpa



2 MeV 5 x 10^{15} ions cm^{-2}
Max 17 dpa



5 MeV 5 x 10^{15} ions cm^{-2}
Max 14 dpa

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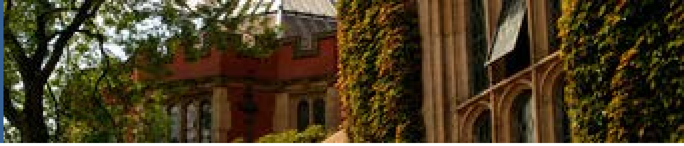
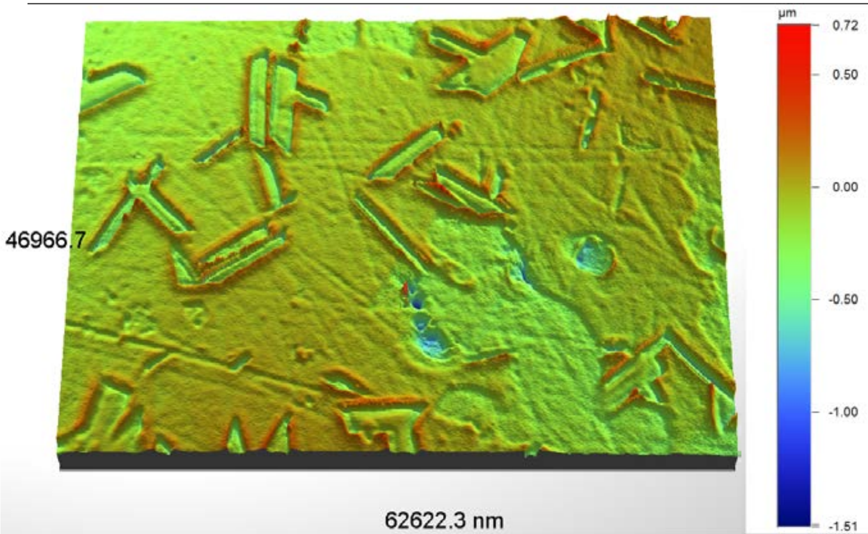
Glass ceramics for Pu residues





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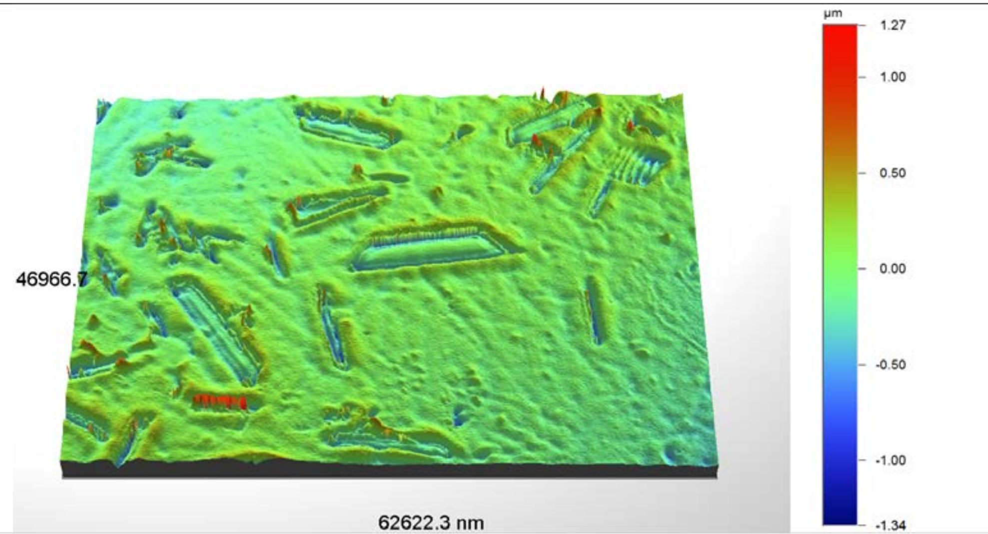

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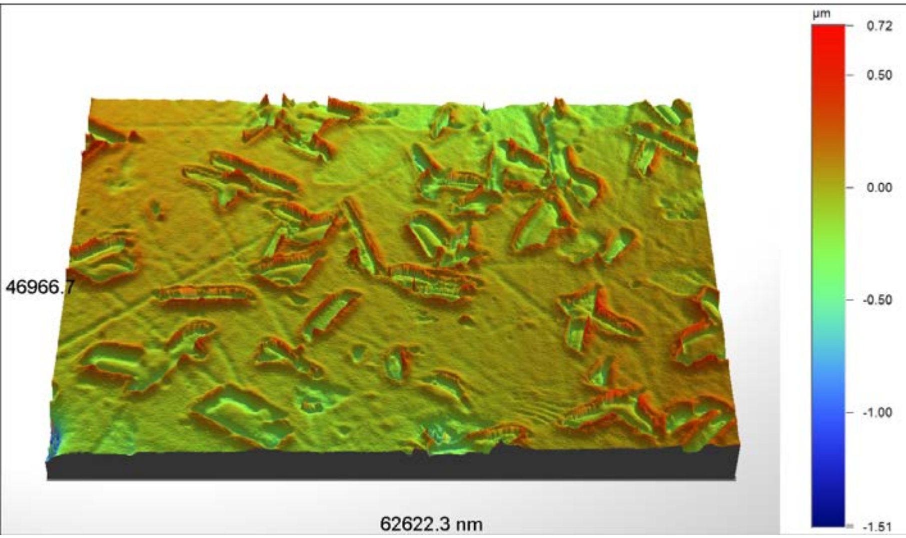
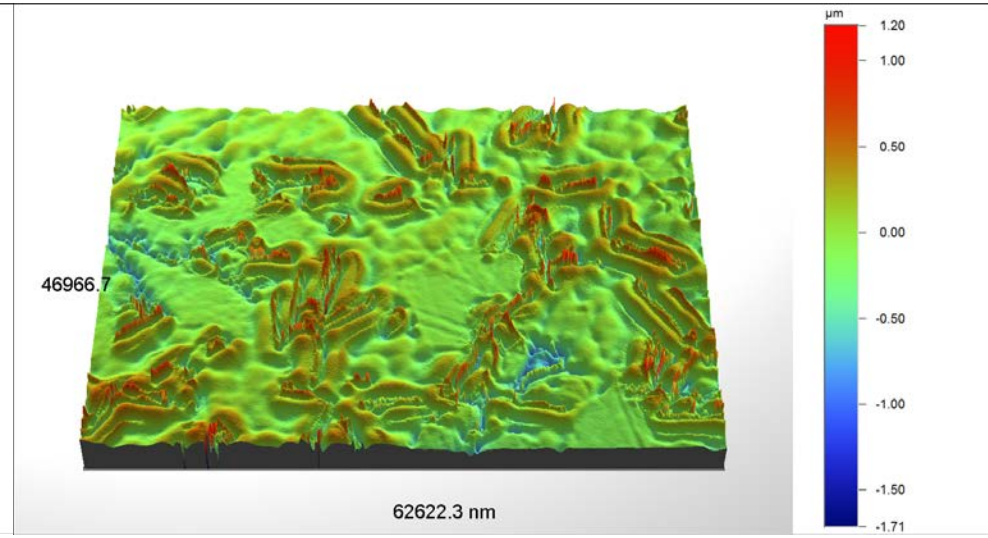
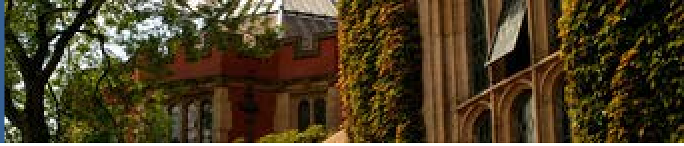


2MeV 5 x 10^{15} ions cm^{-2}
Max 17 dpa



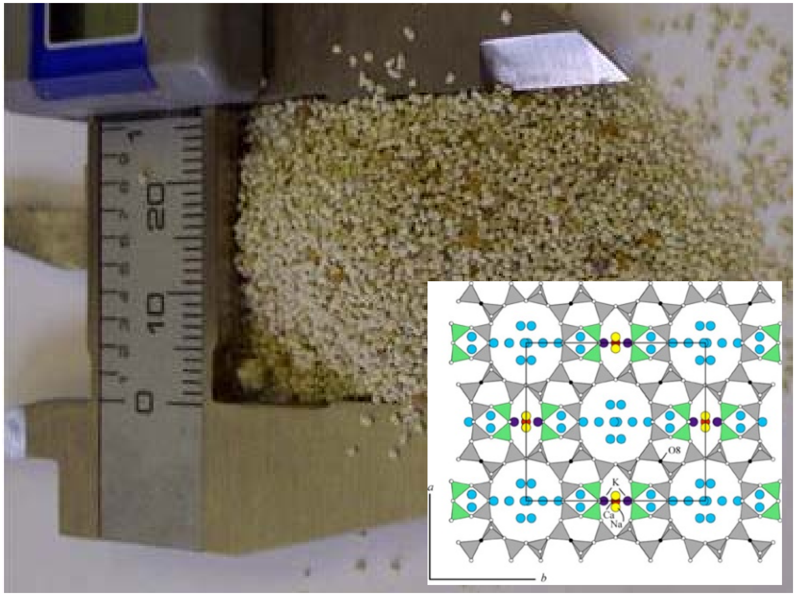
5MeV 5 x 10^{15} ions cm^{-2}
Max 14 dpa



HIP of clinoptilolite – sand ILW

Clinoptilolite waste

- ❖ Mineral zeolite $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot12H_2O$
- ❖ Filter beds 90 wt% clinoptilolite / 10 wt% sand
- ❖ Highly selective ion exchange for Cs (and Sr)
- ❖ Activity: >50 $TBqm^{-3}$ b,g and 0.2 $TBqm^{-3}$ a
- ❖ Waste inventory: 2400 m^3
- ❖ Fraction of ILW inventory: 1% volume, 4% activity
- ➢ Pozzolanic reaction in cement: Cs release



Formulation of wasteform

- ❖ Ion exchange: target 1wt% Cs_2O and 0.5 wt% S
- ❖ Addition of 5 wt% $NaAlO_2$ or $Na_2B_4O_7$
- ❖ Bake-out 700 ^oC for 2h at 25 mTorr
- ❖ HIP cycle: 1200 ^oC for 2h, 100 MPa, 10 ^oC / min
- ➢ Full retention of Cs inventory (cf. JHCM)
- ➢ 75% volume reduction

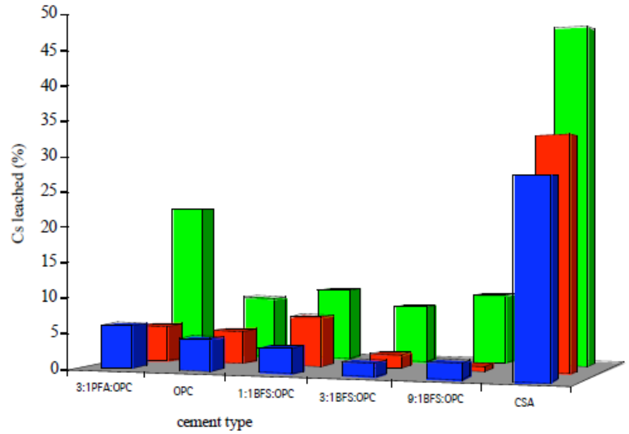


Figure 7. Cs leaching for all cement systems containing 20% Cs exchanged clinoptilolite following 3 (front), 28 (middle) and 90 (back) days of hydration at 20°C (unground clinoptilolite median particle diameter: 627.7μm) by soxhlet extraction.

L.E. Gordon *et al.*, MRS Symp. Proc., 1107 (2008).

Neil Hyatt
Department of Materials Science & Engineering

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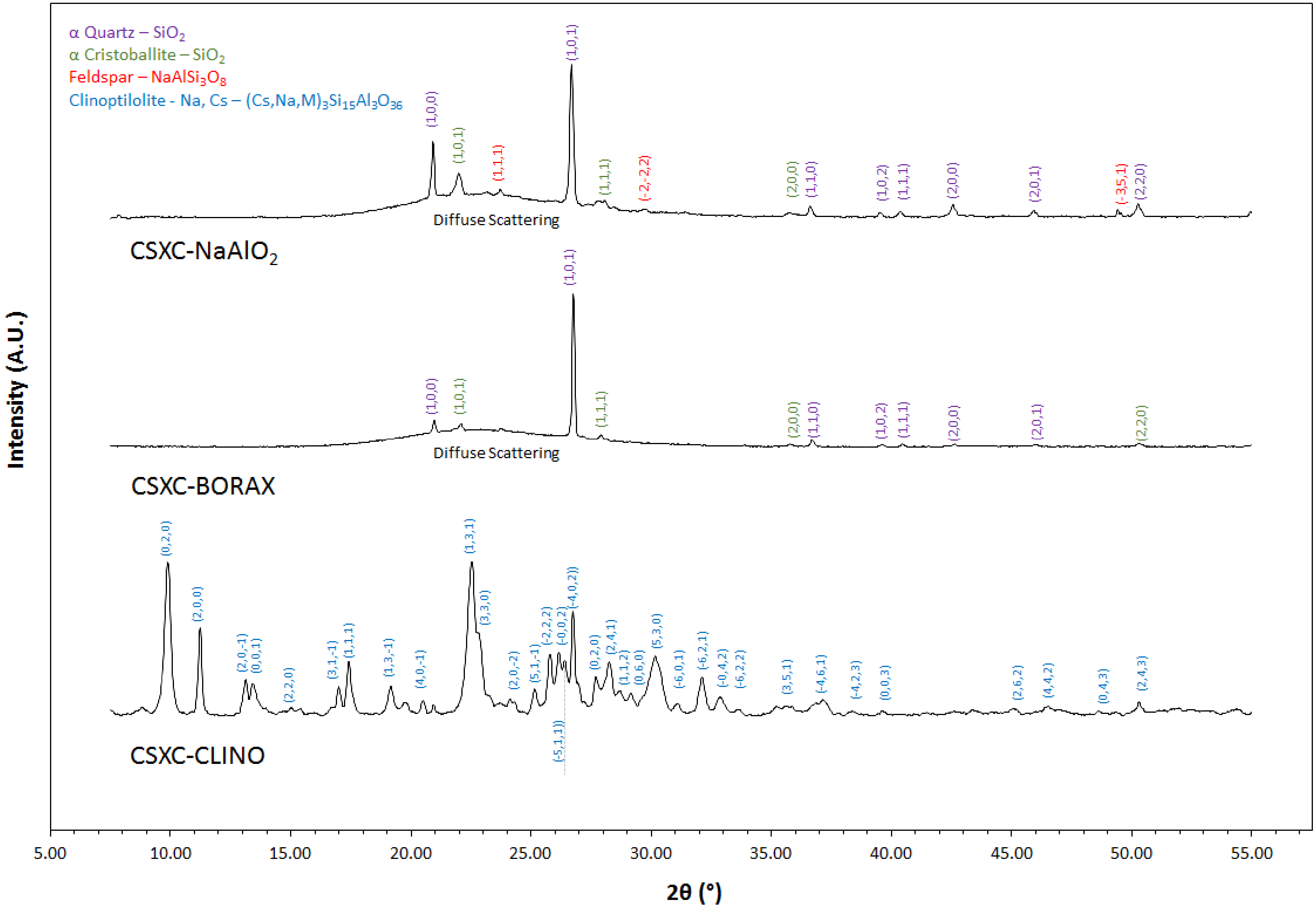

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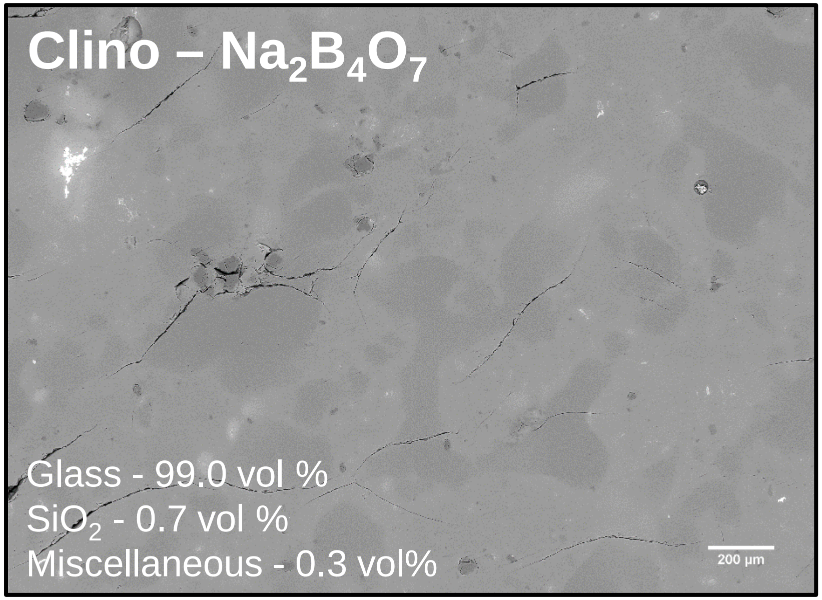
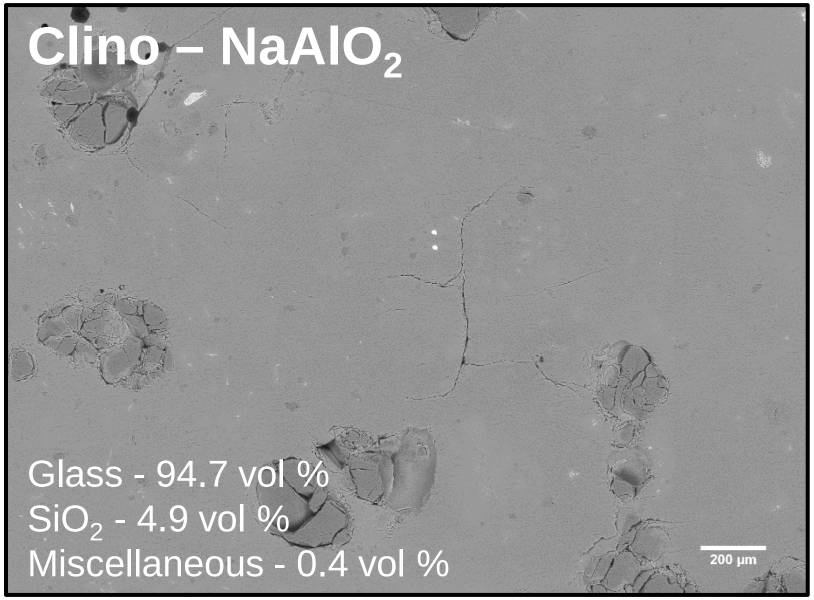
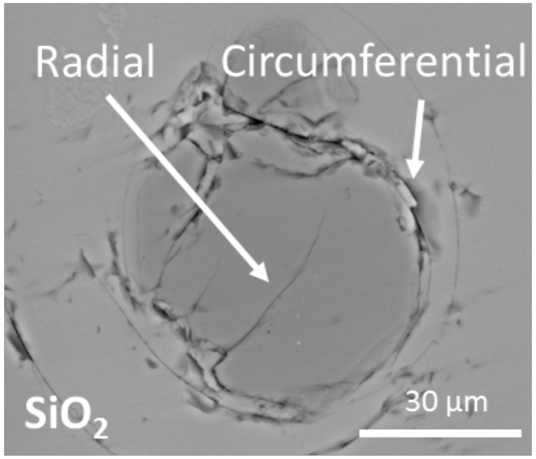
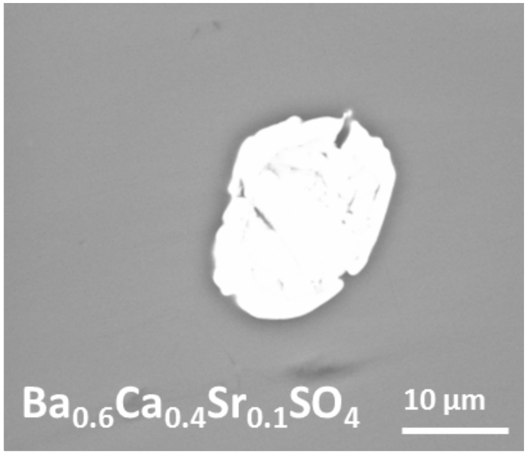
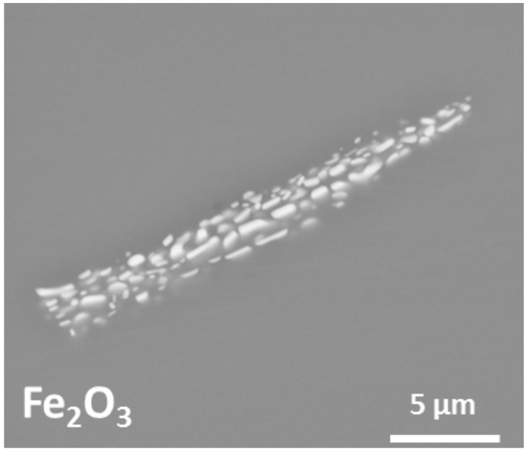
HIP of clinoptilolite – sand ILW











The University Of Sheffield.
Neil Hyatt
Department of Materials Science & Engineering

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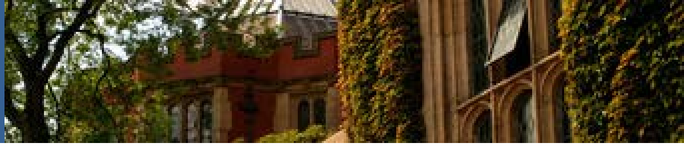


The kinetics of glass dissolution are modelled using Transition State Theory:

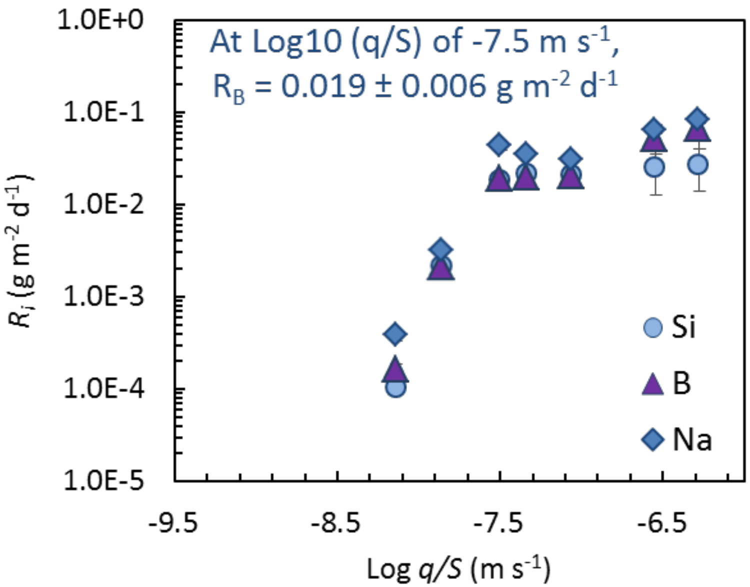
$$R_i = k_0 v_i e^{-E_a/RT} a_{H^+}^{n} \left[1 - \left(\frac{Q}{K}\right)^{\sigma}\right]$$

- Rate: R_i
- Intrinsic rate constant: k_0
- Stoichiometric coefficient: v_i
- Activation energy: E_a
- H^+ activity and reaction order w.r.t. a_{H+}: $a_{H^+}^{n}$
- Activity product of rate limiting reaction / equilibrium constant: Q/K
- Overall reaction order: σ

Each paramegter can be determined through systematic variation by keeping Q/K at near zero, i.e. in the forward rate. regime

Single-pass flow-through (SPFT) methodology

Varying the q/S ratio can influence the chemical potential between the glass and a solution.



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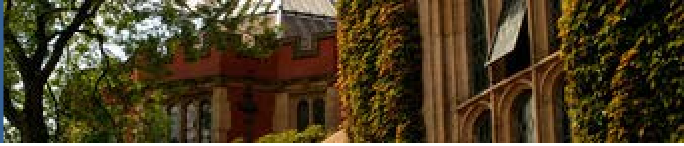
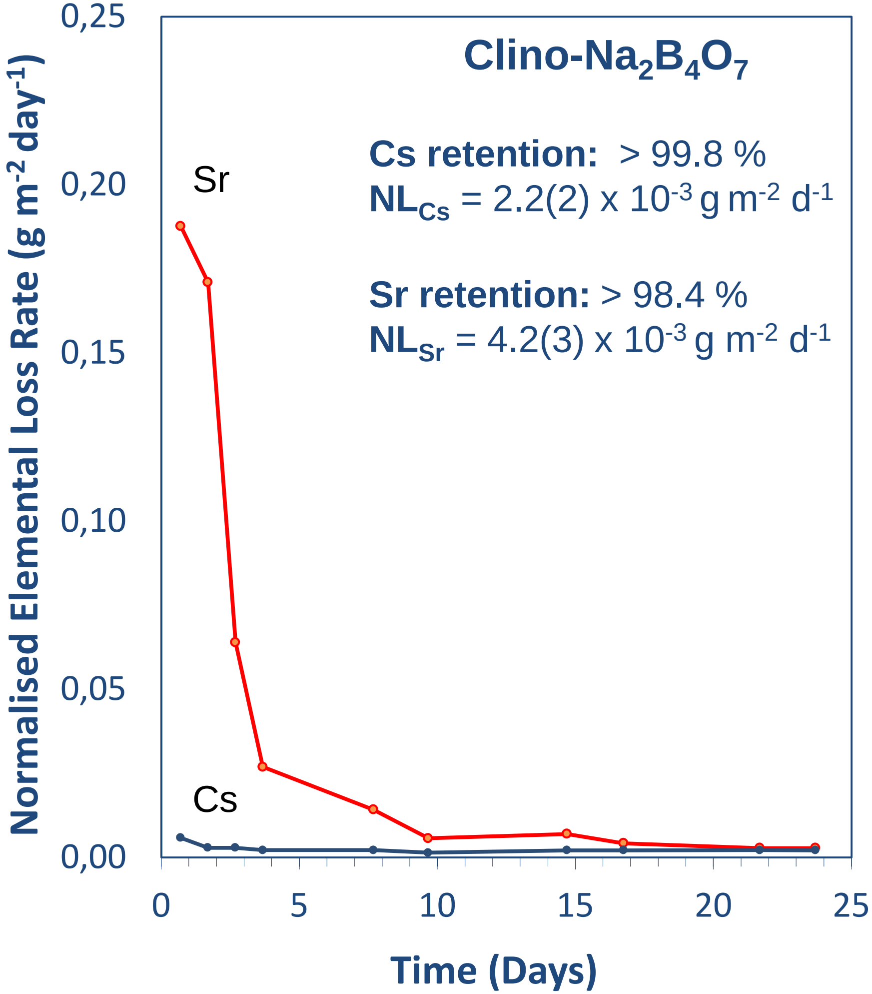
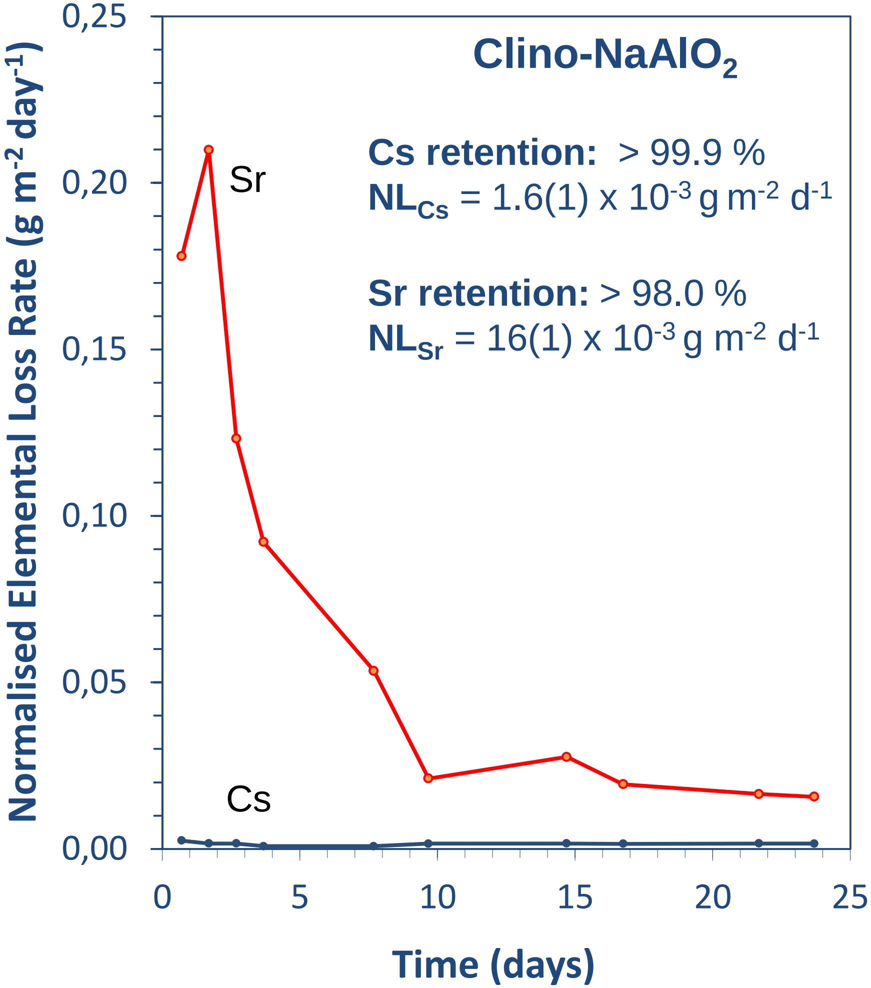


SPFT Testing - pH 4 (HNO_3), log Q/S = -7.0, 90 °C (also pH 2, 6, 9, 11 in progress)





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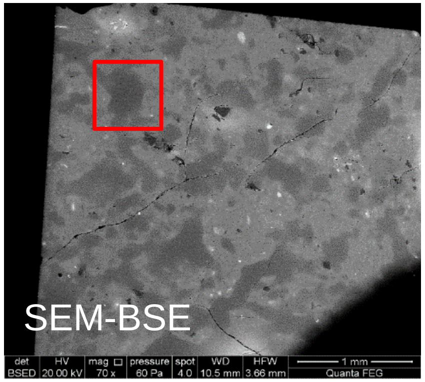
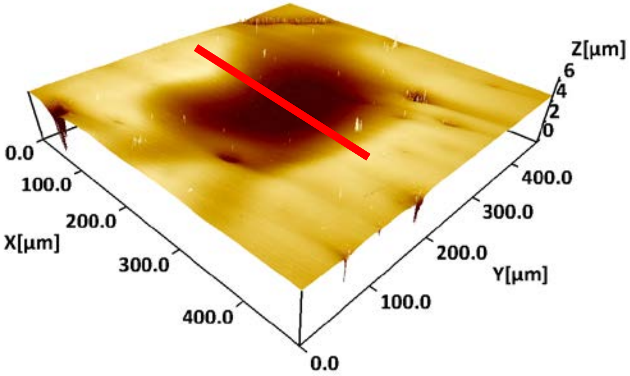
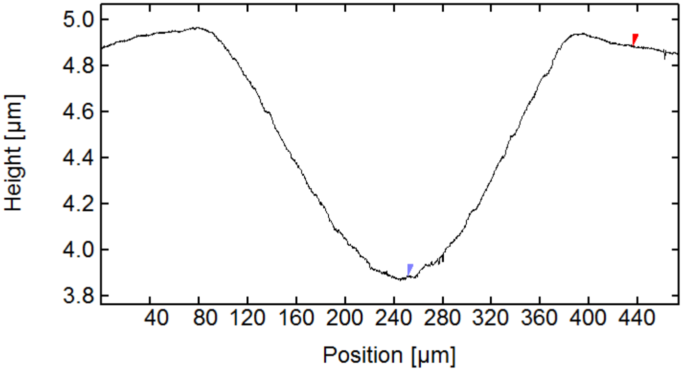
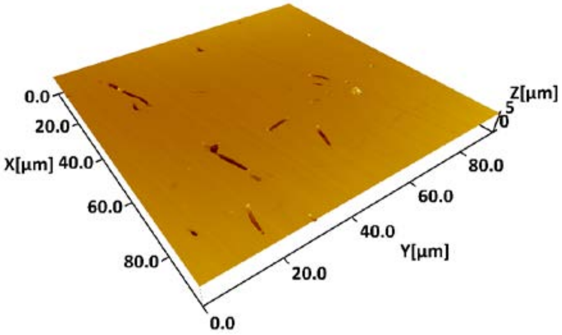
VSI experiments show different behaviour for the different glass compositions
1. Silicon rich glass – retreat rate < 0.2 nm day^{-1}
2. Boron rich glass – retreat rate ~1 μm day^{-1} and presence of pitting

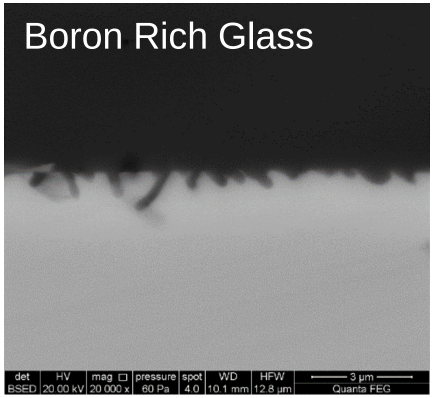


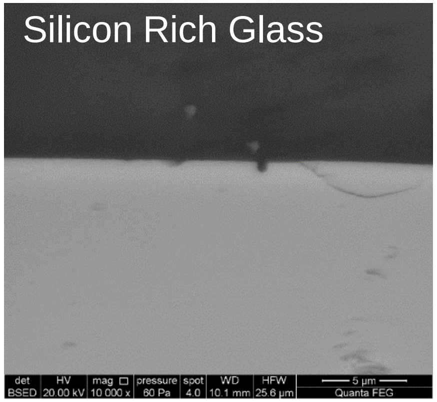




Boron Rich Glass







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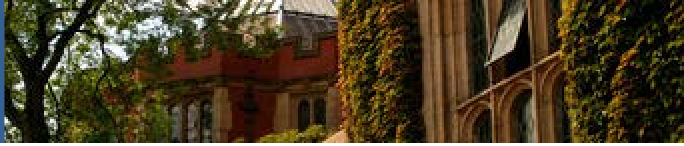
Volume / cost	HIP	Cement	Saving
Waste volume	630 m^3	9230 m^3	3 Vaults
Disposal (£M)	6	95	88
Storage (£M)	16	158	142
Packaging (£M)	6	112	106
Transport (£M)	1	5	4
Total (£M)	**29**	**370**	**341**

Conclusions



- EU decommissioning programmes are likely to require novel thermal waste treatment strategies to minimise volume and increase passive safety of complex wastes.
- Thermal products will be significantly different from existing wasteforms, long term behaviour of is a knowledge gap and may challenge international disposal concepts.
- Conversely, thermal products may allow variation and optimisation of current disposal concepts to give more credit to robust wasteforms.
- There is currently a window for a integrated approach to increase the technical maturity of thermal technologies, innovate and optimise wasteforms, and demonstrate disposability.
- Good opportunity for collaborative endevaour: minimise cost and duplication of effort, whilst maximising knowledge exchange, to address common aims for mutual benefit.

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