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Inducing the Resumption of Alteration in Simulant UK Radioactive Waste Glasses

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Plan for Today

1) Background
2) Methodology
3) Results
4) Discussion/Conclusions

"If you are a romantic, you can say we are all literally stardust…

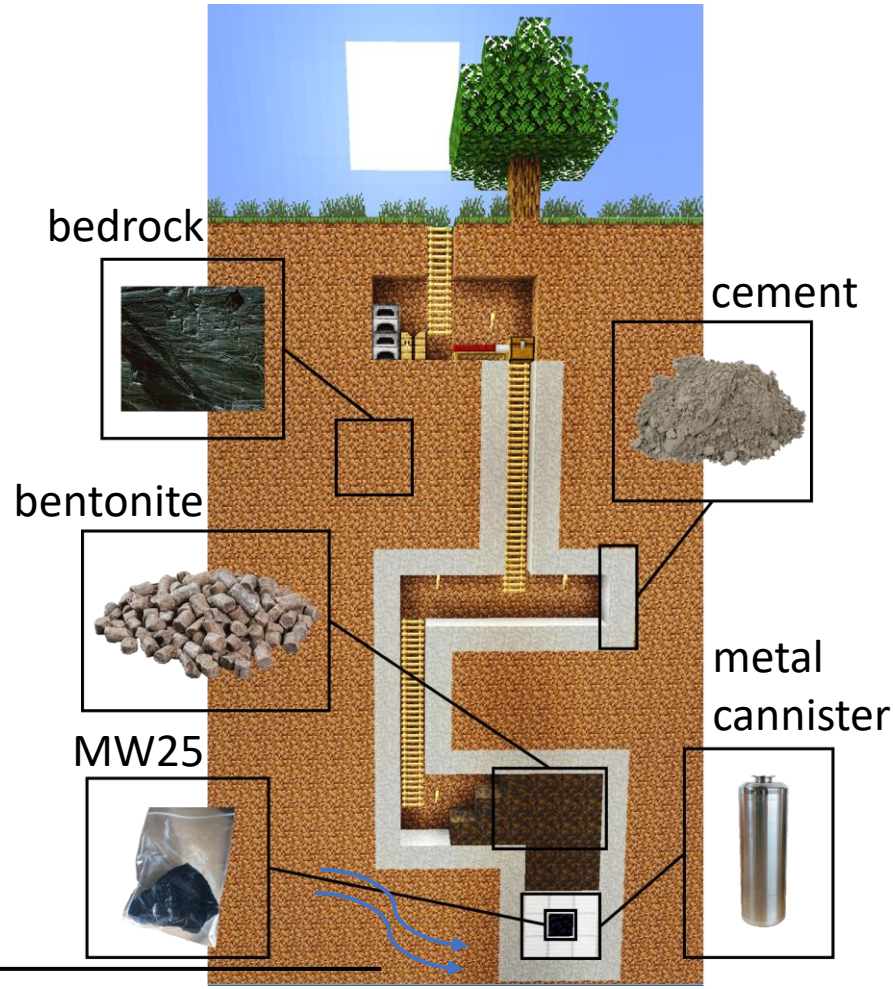
If you are less romantic, you can instead say that we are the nuclear waste from the fuel that makes stars shine."

– Lord Martin Rees

A bit of background – why is this important?

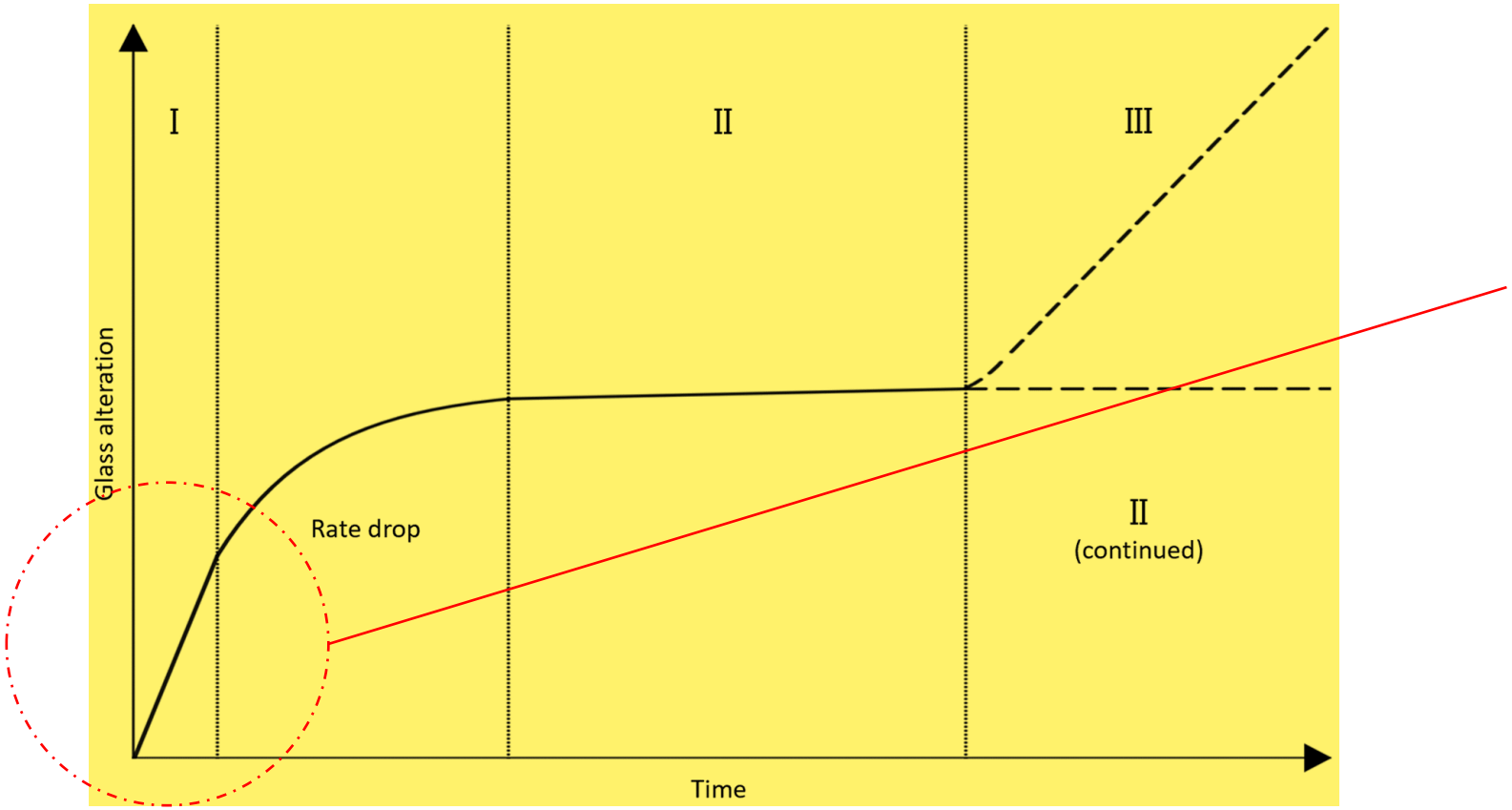
‘Mixture Windscale’ 25 wt% magnesium non-oxidising (Magnox) waste loaded boro-alumino-silicate glass (MW25) – Nuclear Waste Services

The UK’s proposed deep geological disposal facility ‘GDF’ ->



Current Understanding – Stage I

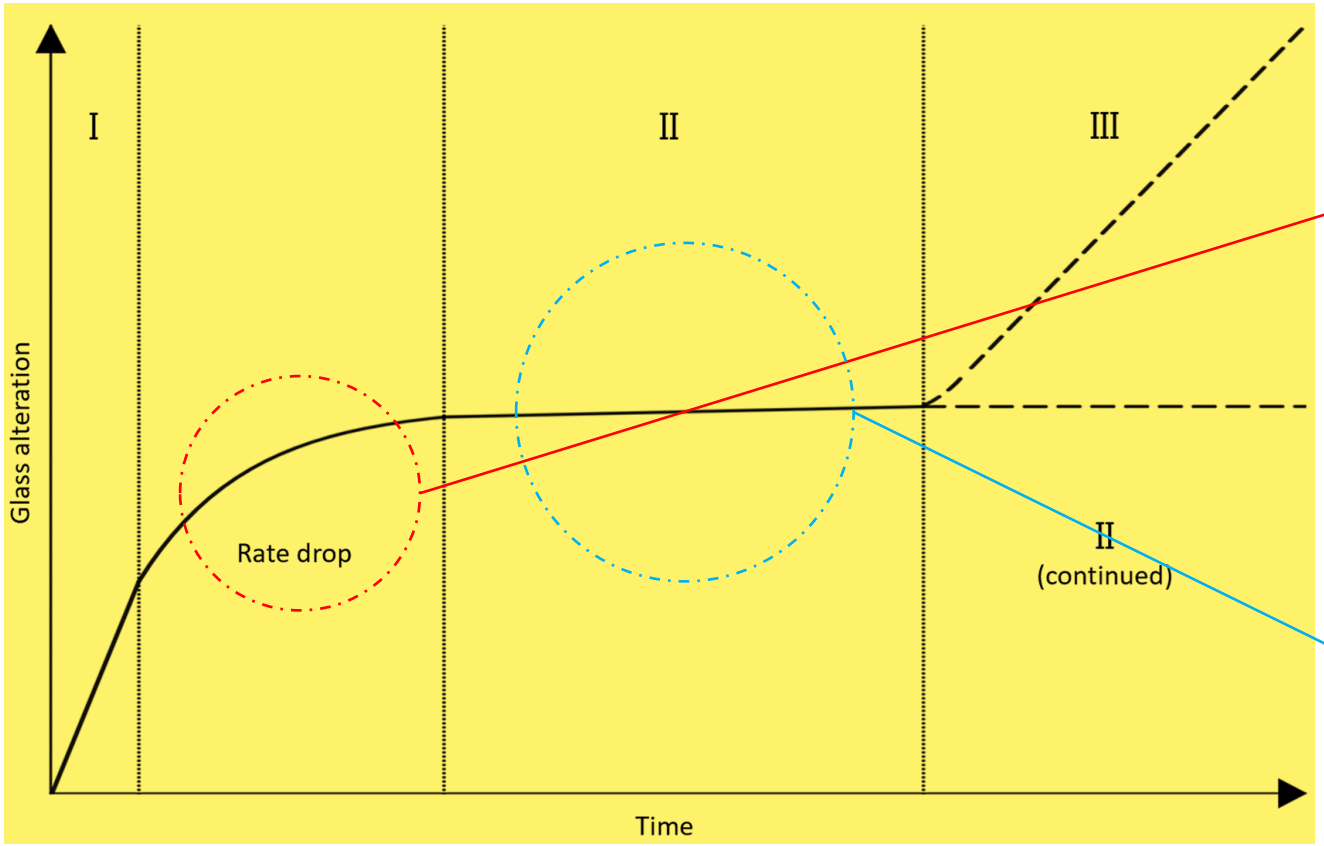
Glass alteration with time



- Interdiffusion (hydration/ion-exchange) occurs rapidly at surface.
- This exposes covalently bonded silicate network.
- The ‘initial rate’ of alteration in Stage I is limited by the slower hydrolysis of this network.

Current Understanding – Stage II

Glass alteration with time

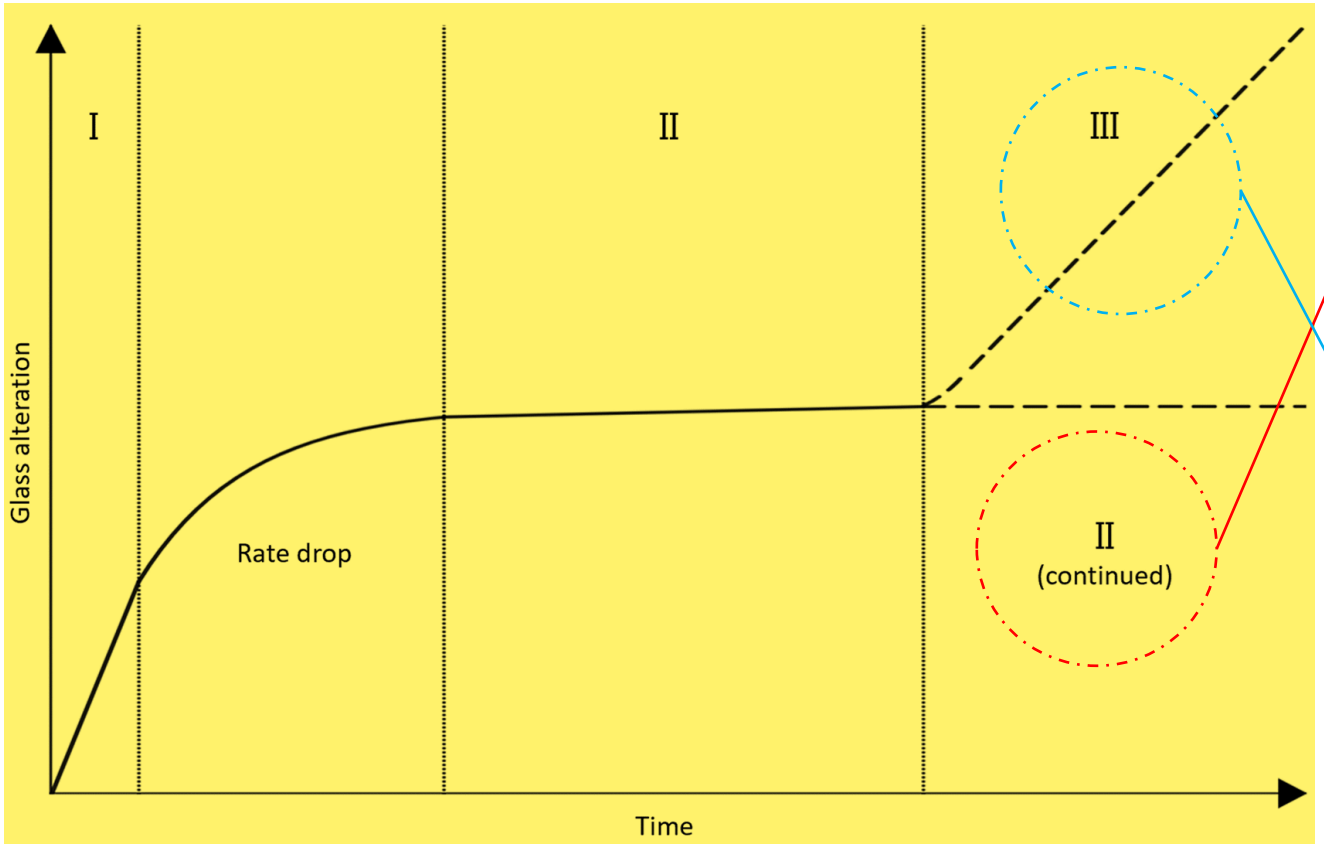


- Certain elemental solubility limits begin to be approached.
- The thermodynamic force driving dissolution is reduced.
- The rate of alteration begins to drop.
- Formation of amorphous, porous, hydrated aluminosilicate gel ‘alteration layer’.
- Acts as a protective barrier against water diffusion, ion-exchange, and hydrolysis.

- Over a certain time period, the rate will drop by a factor of one thousand and plateau.
- This is the ‘residual rate’ of Stage II behaviour.

Current Understanding – Stage III

Glass alteration with time



- It was thought and hoped that this residual rate would continue indefinitely.
- Instead, after hundreds to thousands of days, the nucleation of zeolites at the glass surface has occasionally been observed internationally.

- The loss of aluminium eliminates the passivating properties of the alteration layer.
- The desaturation of silicon in solution reintroduces the thermodynamic force driving a ‘resumption of alteration’.
- This can occur at close to initial rates.
- This process is self-perpetuating, and its rate defines ‘Stage III’.

Current Understanding – UK

- International glasses are compositionally different to UK glasses preventing a direct comparison.
- Predominantly due to the high magnesium content in UK glasses arising from the use of magnesium cladding.
- In France and the US, resumption has been induced by artificially adding zeolites from outside the system to simulate their formation.
- This occurred at high temperatures (≥ 90 °C) and high, artificially increased $pH_{(25°C)}$ (≥ 10).
- Repeatable with UK glasses.

Selection of Analcime

B. Y. Zhen-Wu et al. 2021

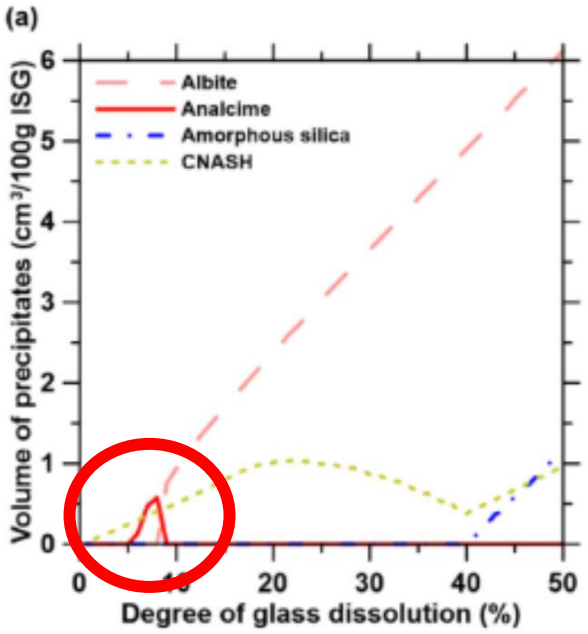
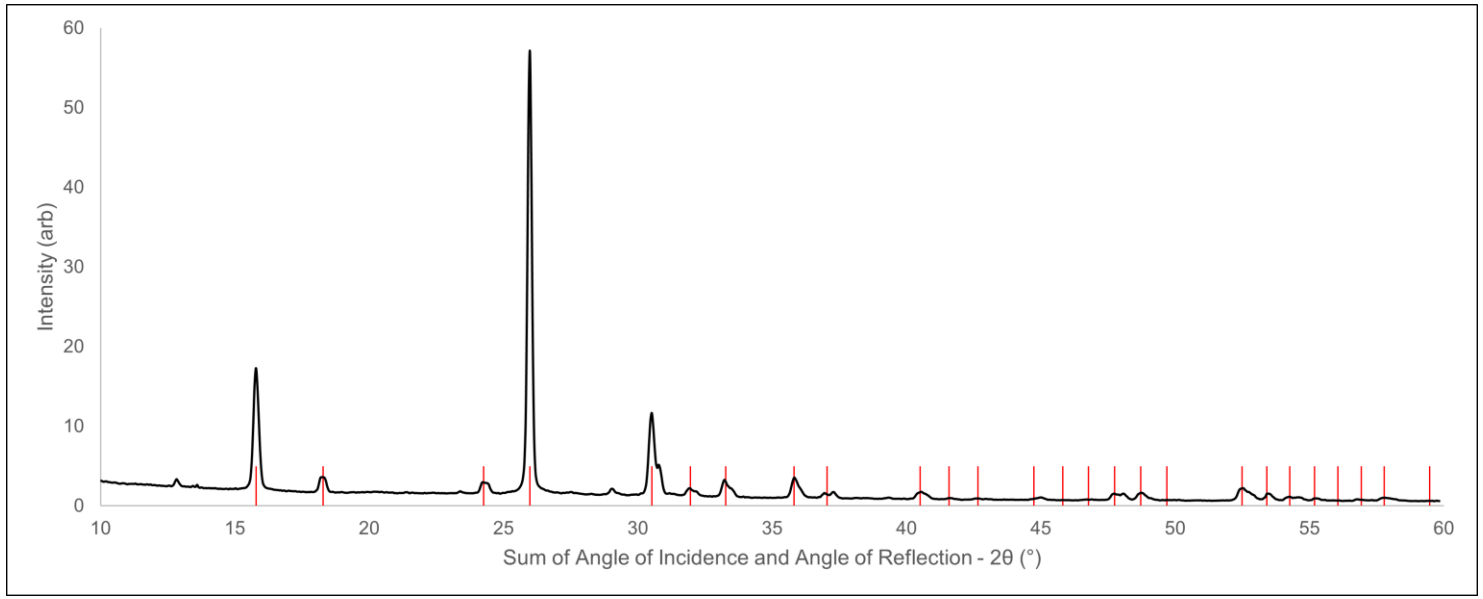


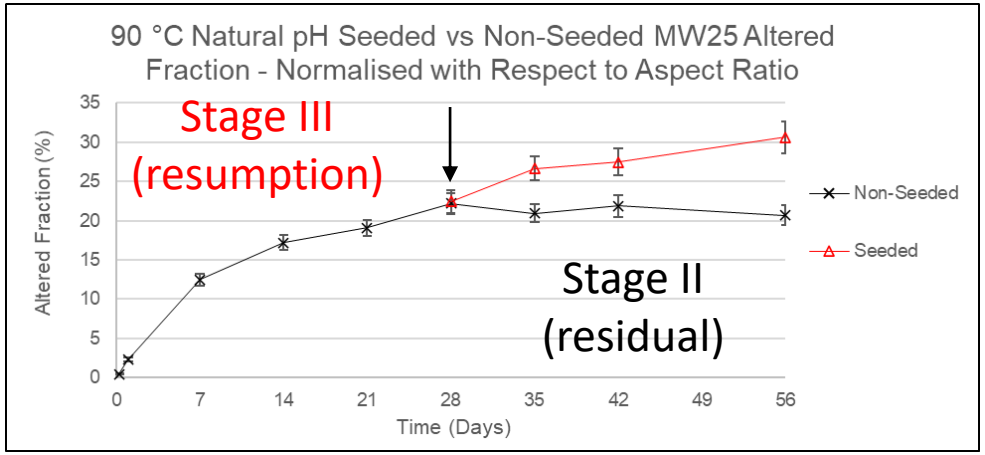
Fig. 2. (a) Simulated volume of the secondary phases forming upon the dissolution of the International Simple Glass (ISG) at 90 °C and for an initial KOH concentration of 0.05 mol·L⁻¹ as a function of glass dissolution (in mass%). (b) Calculated log activities of the Ca, Na and B aqueous species within the simulation. The yellow area indicates the range of degrees of glass dissolution wherein analcime is predicted to precipitate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

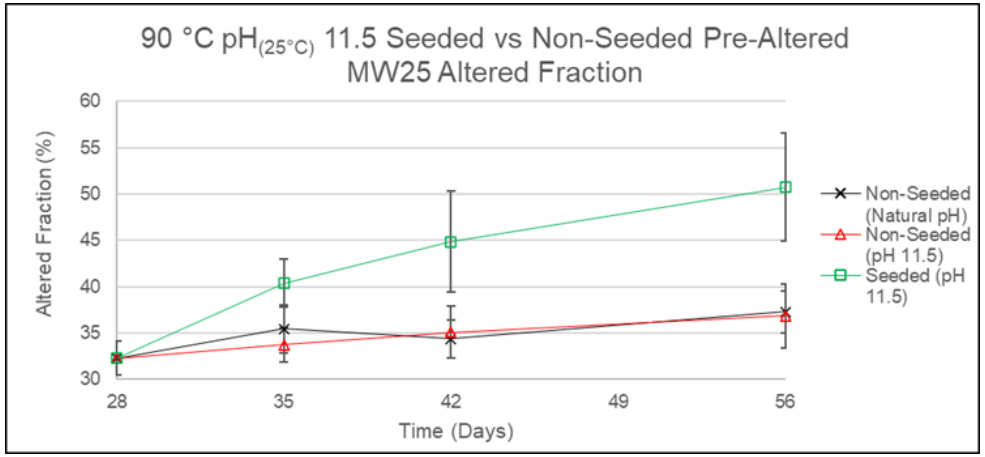
XRD spectra of analcime sample obtained – red lines indicate agreement with peaks from literature



Summary of Results to Date

- Resumption was not observed in any non-seeded runs.
- Resumption was not observed at 40 °C, however the experimental runtime was not sufficient to rule out this eventuality.
- The induction of resumption was observed at 90 °C over 56 days following seeding with variation in
  - the time of seeding (0, 7, 28 days),
  - the amount of seed used (S_G : S_Z ratio of 1:1, 2:1, 4:1), and
  - the solution $pH_{(25°C)}$ at time of seeding (natural 9.7 – 12.5).
- Significantly, resumption was induced at natural pH for the first time in any glass.
- This led to very large percentages of still ongoing glass alteration over time (> 55 %).





Methodology

ASTM Method B [1]

77 days at 90 °C

All carried out in triplicate

60 mL

MW25 75 – 150 µm (also CaZn MW28 and IS)

S_G / V_S ratio of ~ 2000 m^{-1}

Analcime, clinoptilolite, natrolite, zeolites X and Y
38 – 75 µm

S_G / S_Z ratio of 2:1 and 40:1 after 28 days

Natural $pH_{(25\ °C)}$ of 9.7
(MW25 & CaZn)

CaZn leachant pre-saturated with SiO_2 dissolved in KOH

Artificial $pH_{(25\ °C)}$ of 12.5 (IS)

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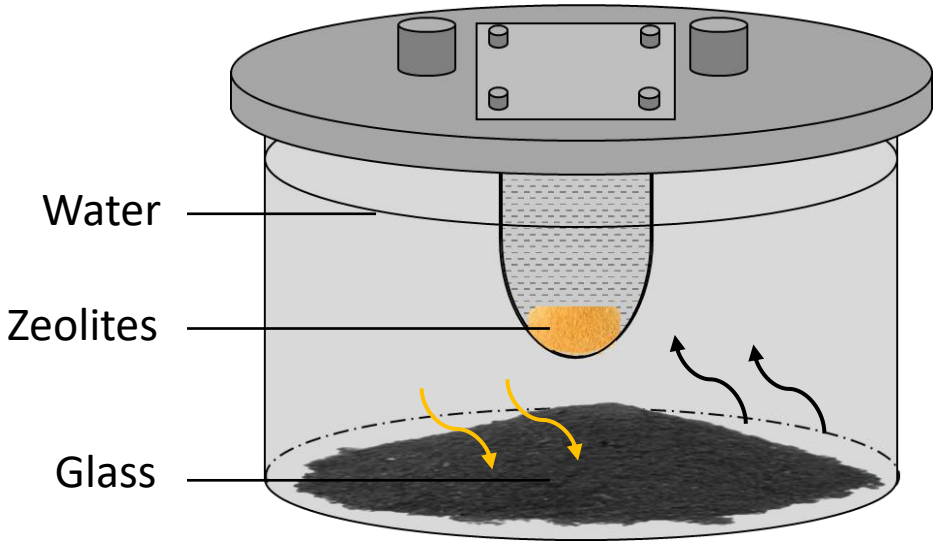
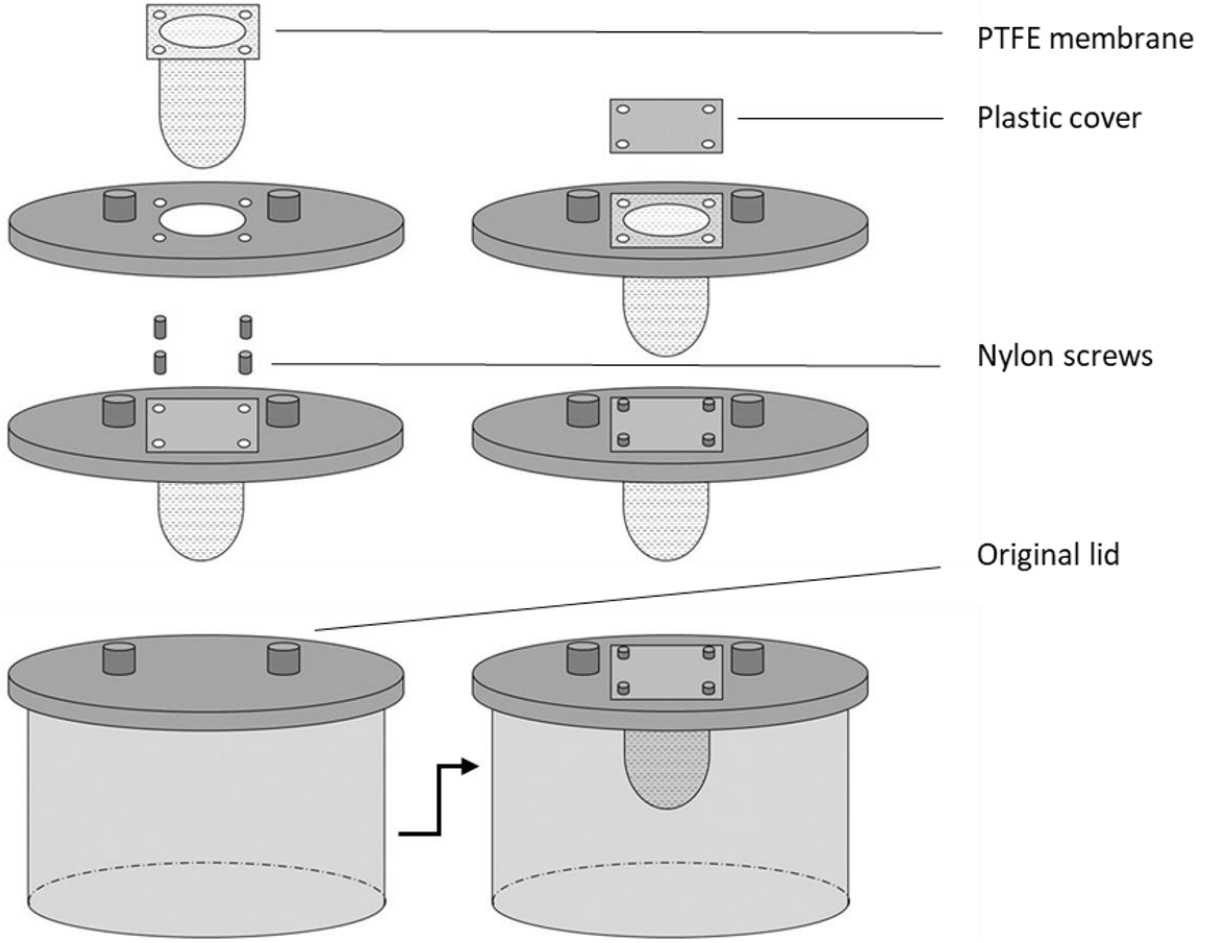
[1] **American Society for Testing Materials**, *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)*, **2005**.

Affinity Modifications

- Some pots were modified to physically separate the glass and zeolites.
- Allows for a comparison between surface chemical interactions and a pure affinity effect.





Pre-Saturation of CaZn with SiO_2 in KOH

M. Harrison et al. 2018

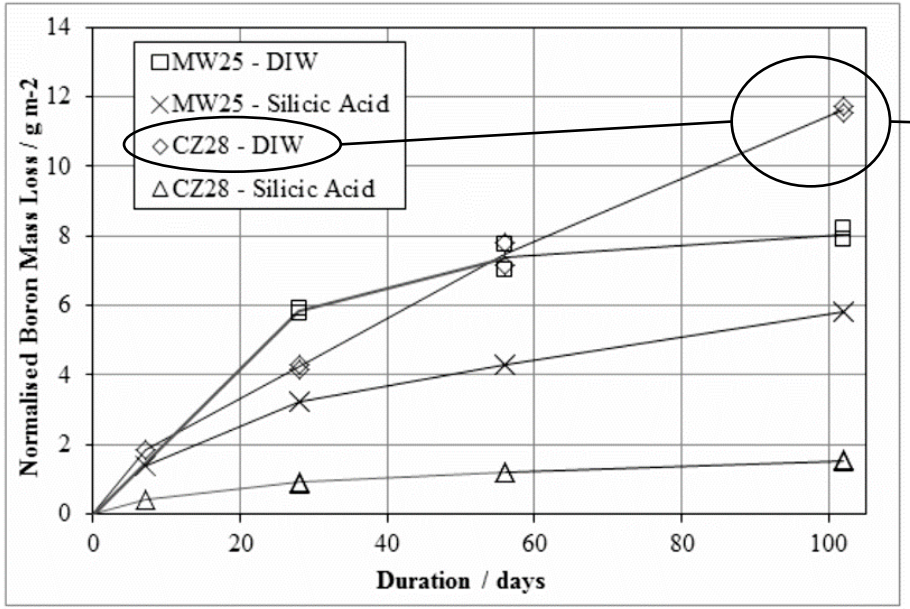
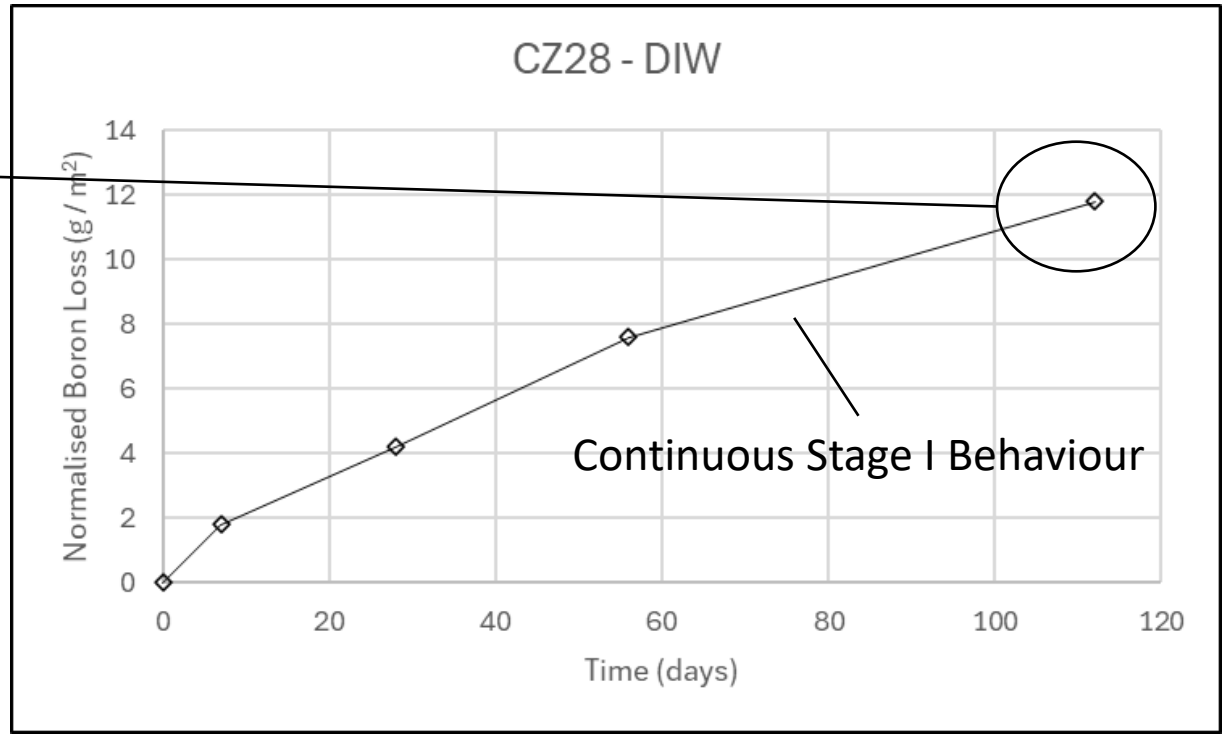
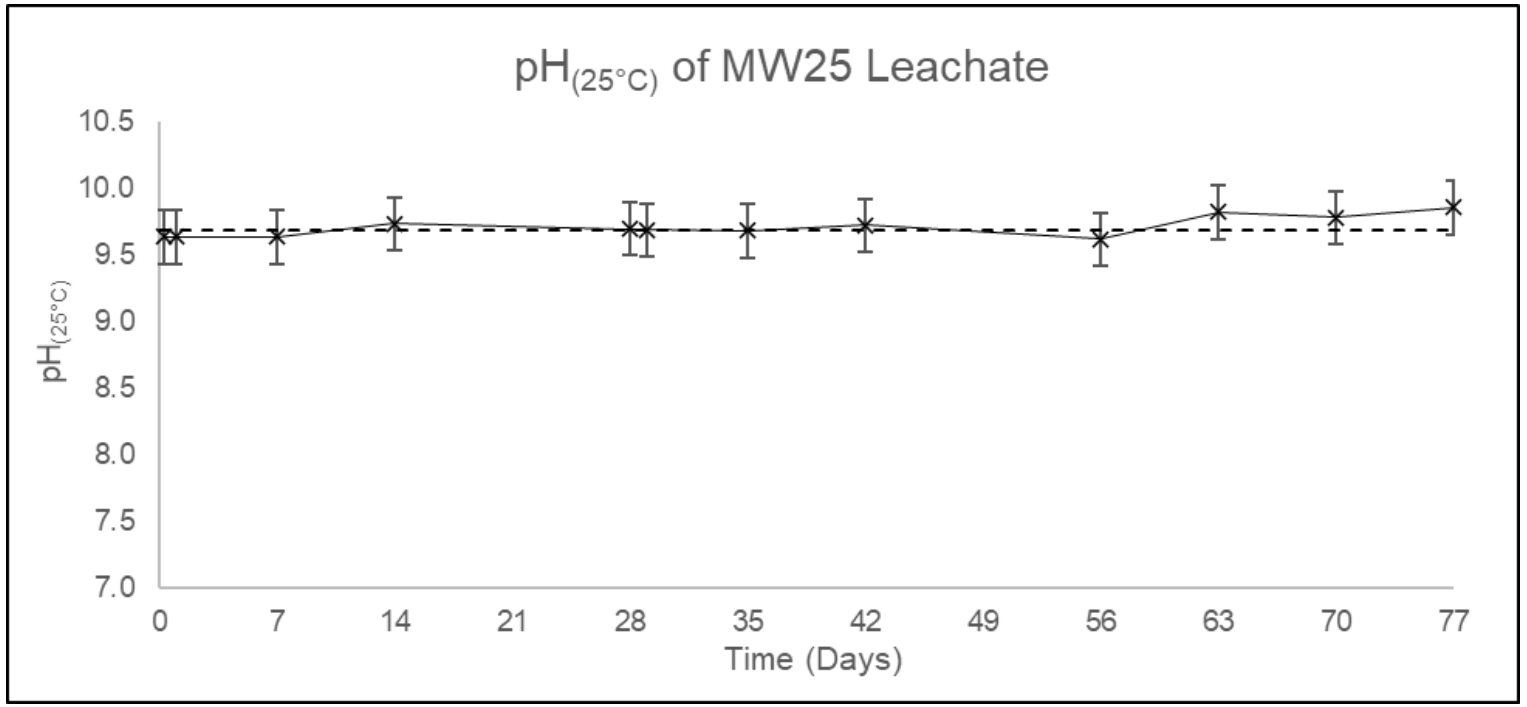


Fig. 1. Normalised boron mass loss, NL(B), in g m^{-2} for MW25 and CZ28 glasses in DIW and silicic acid solution (the symbols show the duplicate test results with the lines joining the average values).



Natural pH (Seeded and Non-Seeded, MW25 and CaZn)



Artificially Increased pH

M. Fournier et al. 2017

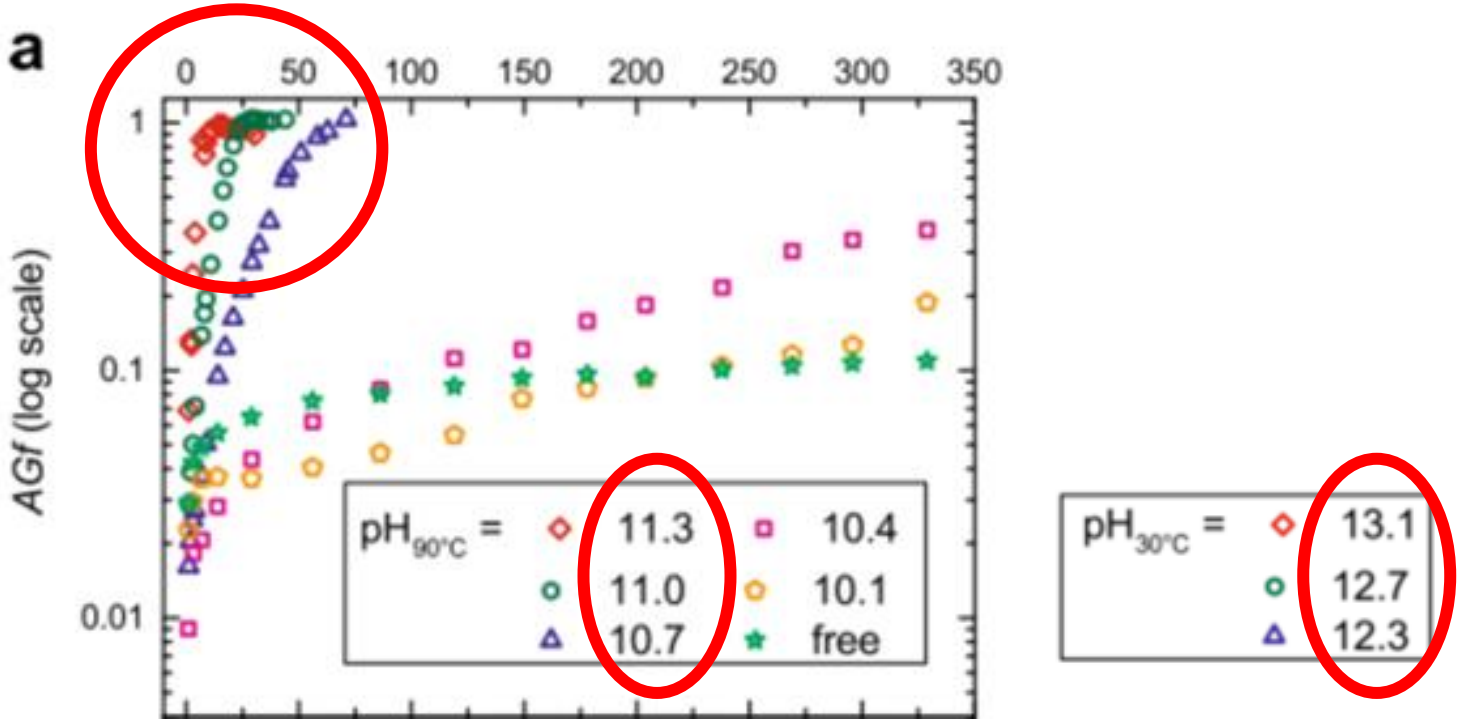
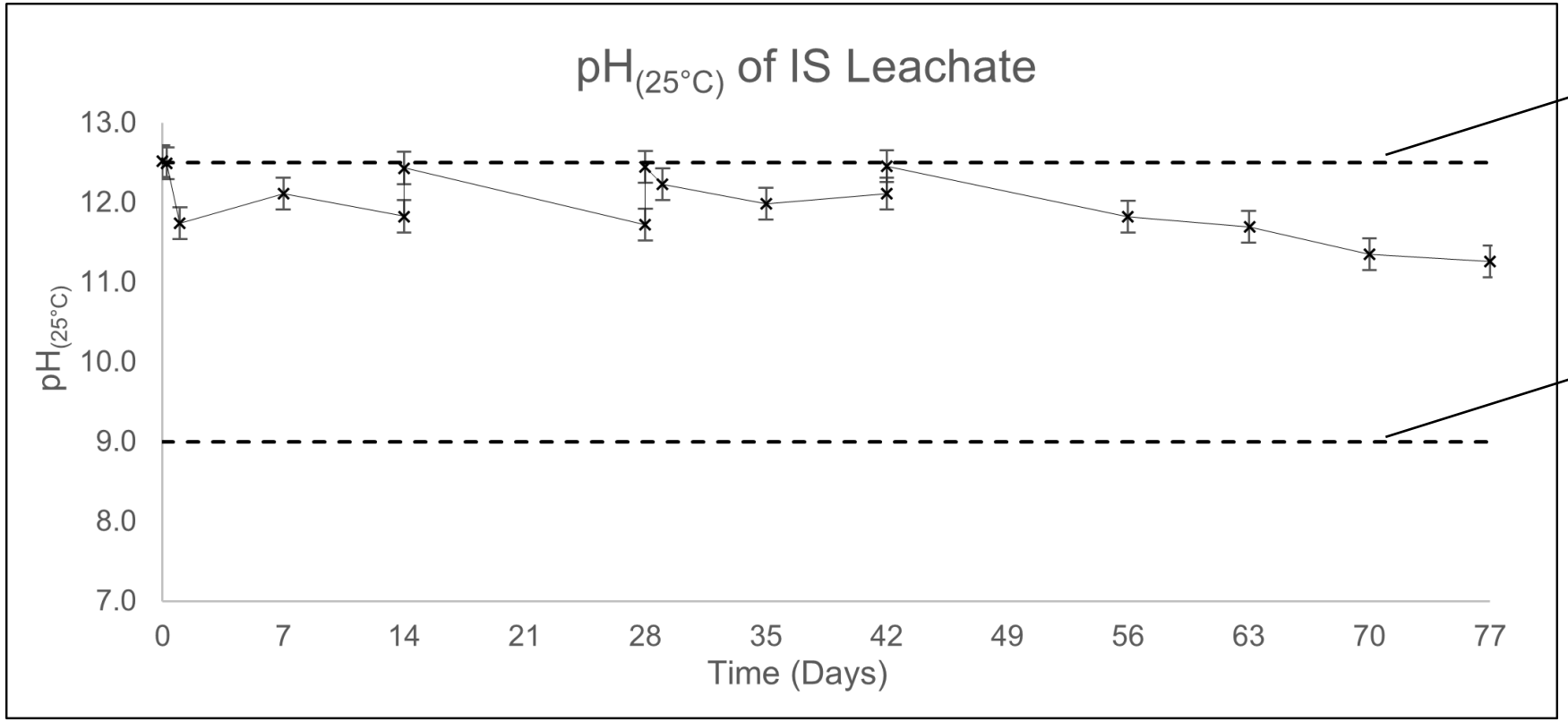
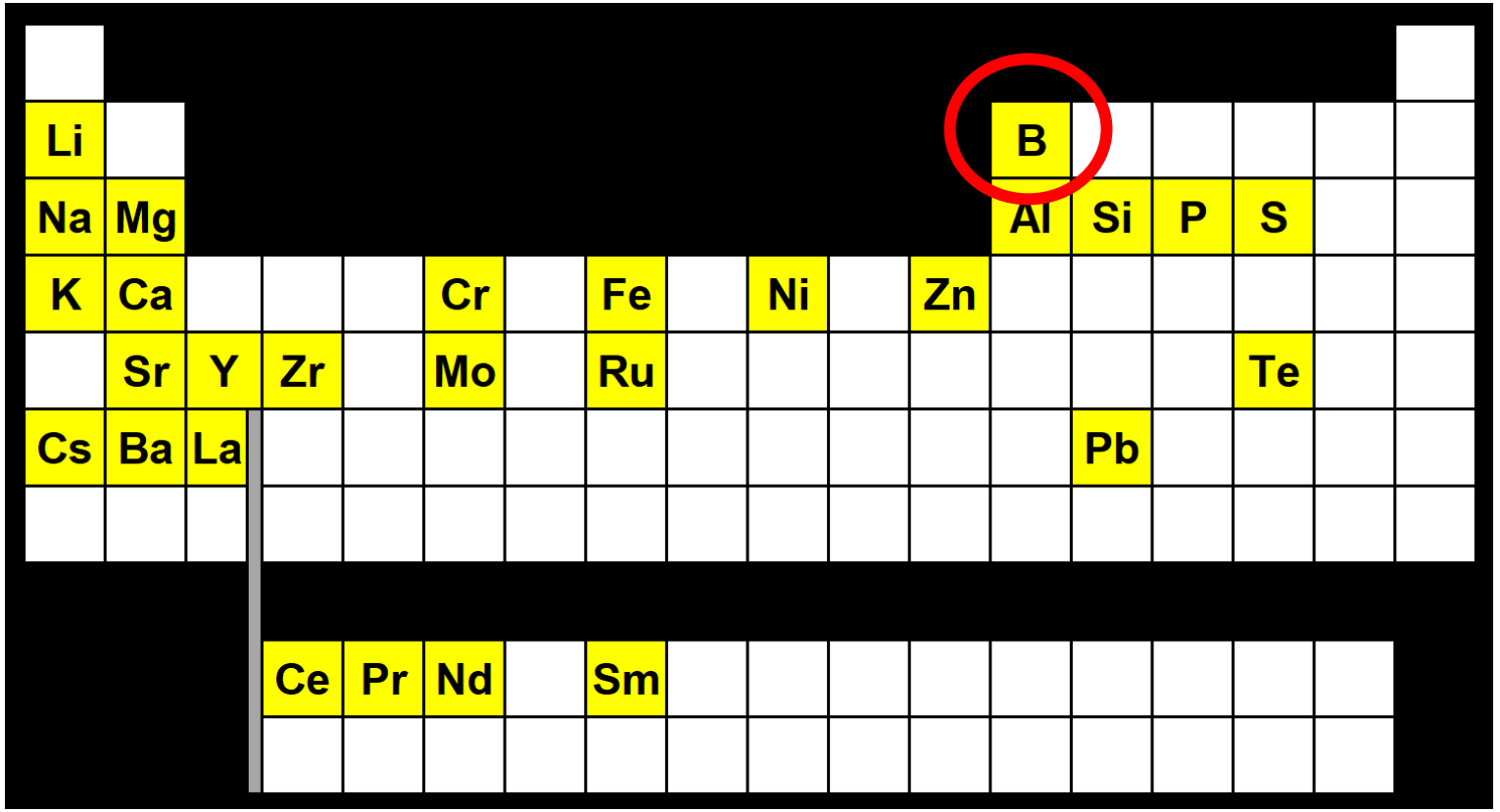


Fig. 3 Seeded leaching tests results: at **a** 90 °C (S-1770 test series) and **b** 30 °C (s-1770 test series) with an *S/V* ratio of 1770 m^{-1}. Graphs show the evolution of the altered glass fraction AGf and the aluminum concentration. Figure to compare with Fig. 1 for unseeded tests

pH (Seeded and Non-Seeded, IS)

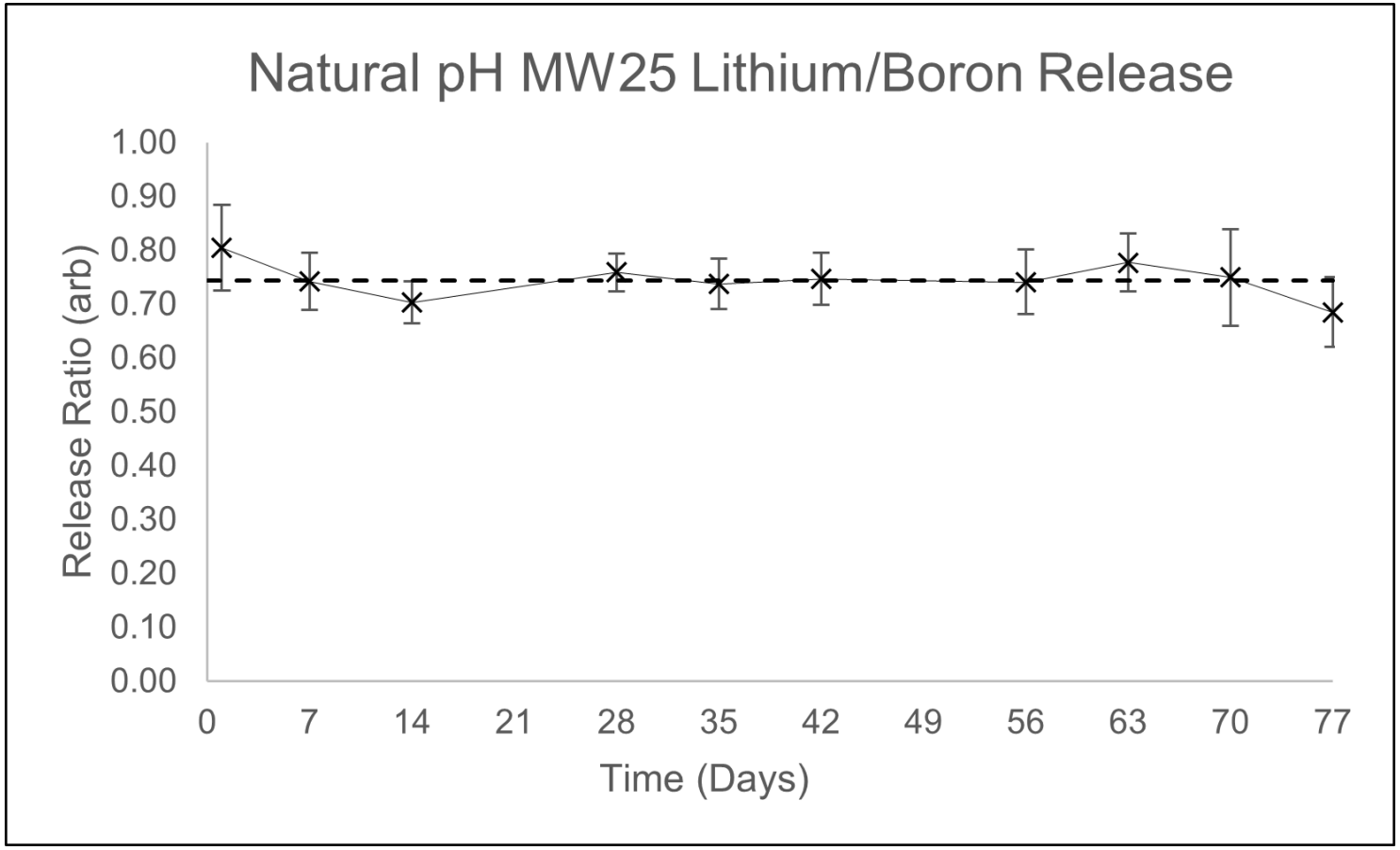


Elemental Release ICP-MS



- Glass network former.
- Relatively high wt% in the glass.
- Does not precipitate out in secondary phases.

Boron as a Tracer



Elemental Release Results (MW25)

Release relative to boron (arb units)

Element	MW25
Li/B	0.66 ± 0.04
Na/B	0.56 ± 0.03
Si/B	0.022 ± 0.002
Cr/B	0.022 ± 0.002
Sr/B	0.004 ± 0.001
Mo/B	0.72 ± 0.06
Te/B	0.12 ± 0.01
Cs/B	0.036 ± 0.005
Ba/B	0.0008 ± 0.0001

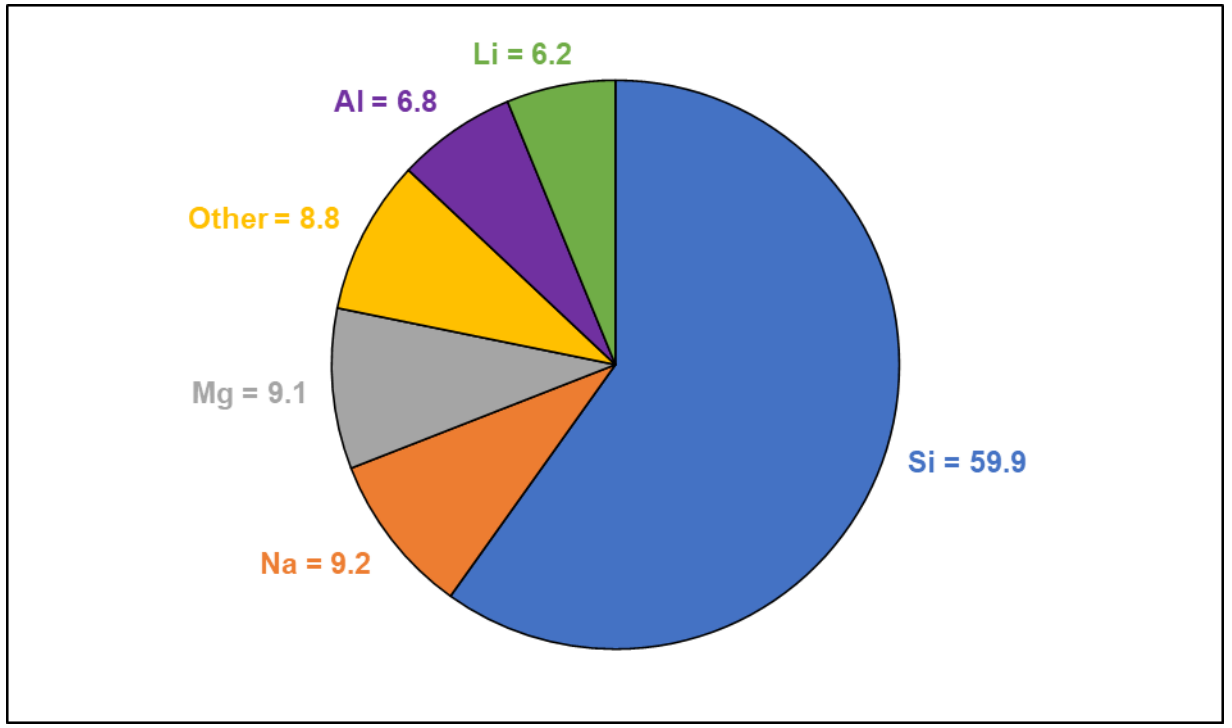
Mass fraction retained within secondary phases

Element	Al, Mg, P, S, Fe, Ni, Y, Zr, Ru, La, Ce, Pr, Nd, Sm	Ba	Sr	Cr	Si	Cs	Te	Na	Li	Mo	B
Retained (wt%)	100	99.9	99.6	97.7	97.7	95.5	85.9	42.9	28.6	1.9	0

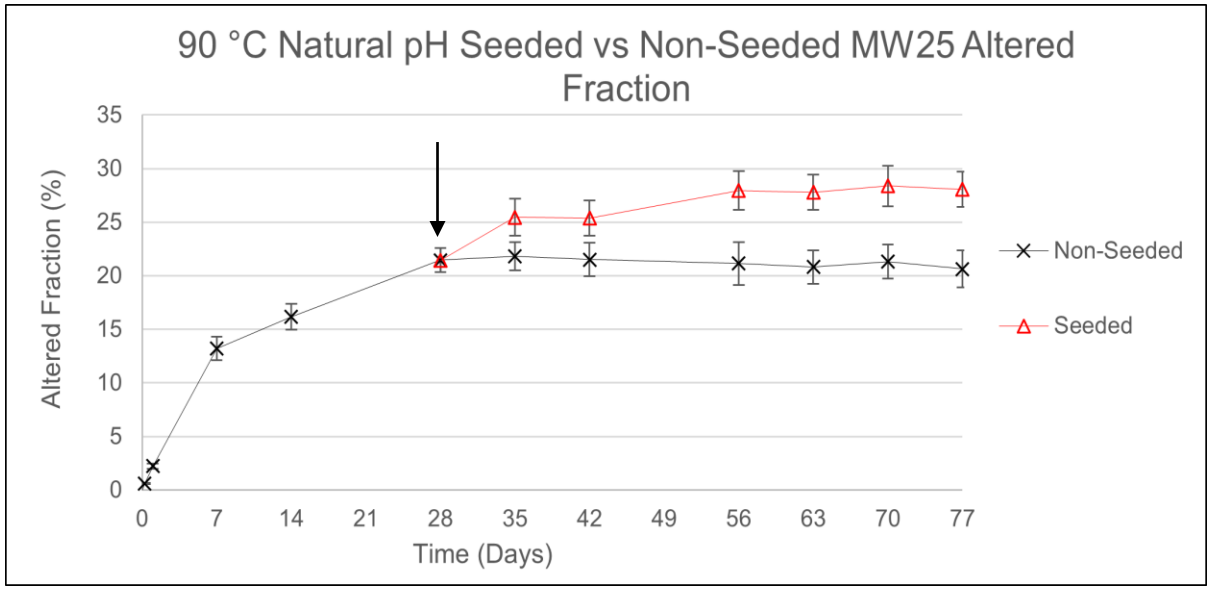
Ca present in CaZn leachate, and Al present in IS leachate

Elemental mol.% of Secondary Phases

- Silicon, sodium, magnesium, aluminium, and lithium dominate the secondary phase compositions
- Notably, aluminium is absent from the leachate, as is magnesium which may explain disparate behaviour between British and international glasses



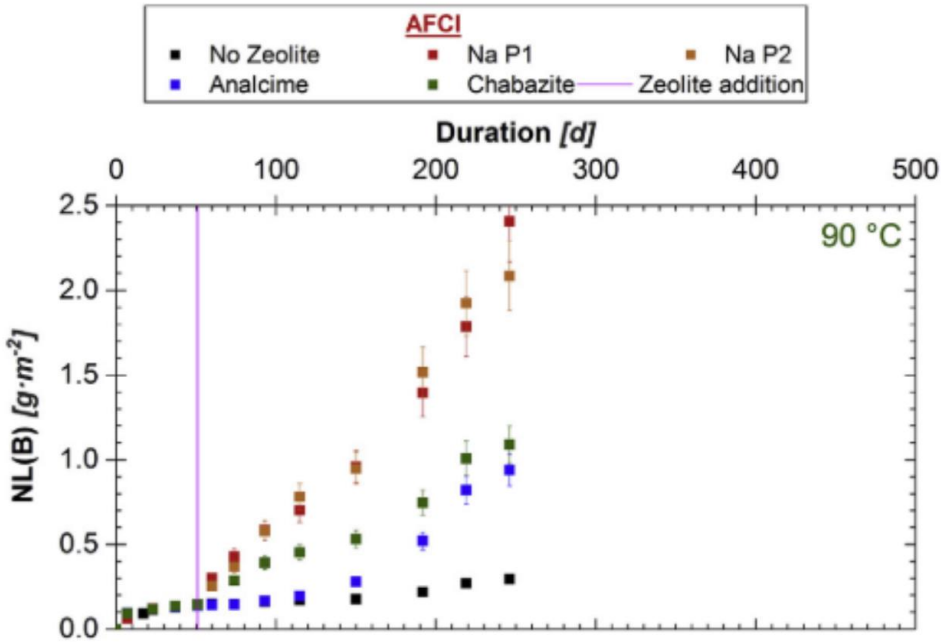
Key Results (MW25)

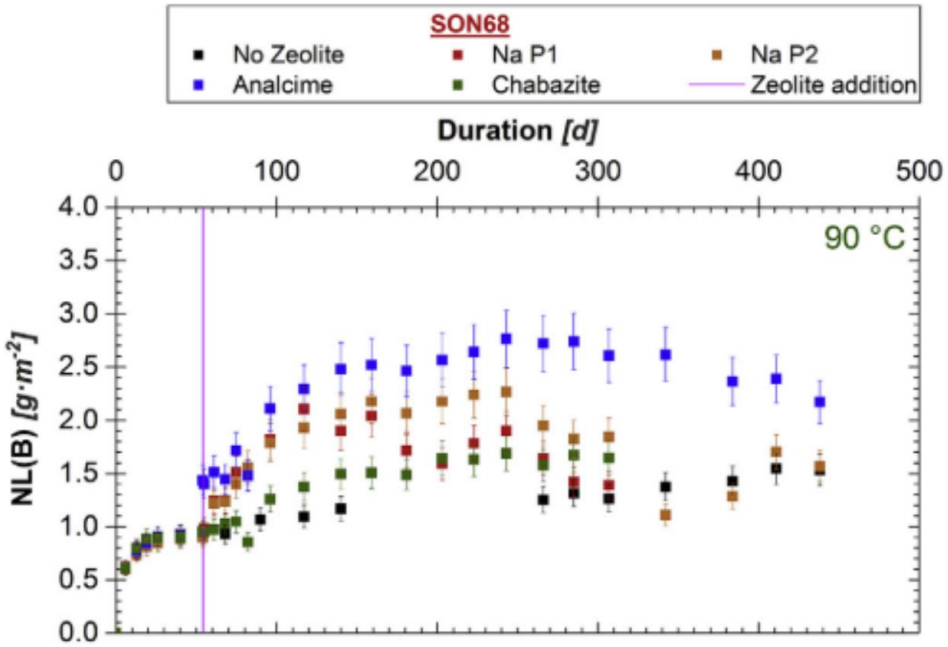


- Resumption was not observed in any non-seeded experiments with MW25.
- Resumption was observed in every seeded experiment.
- Rates did not vary across 5 zeolite types.
- Rates did not vary with S_G / S_Z ratio (2:1 vs 40:1).
- Rates did not vary when utilising the affinity setup.
- A residual rate was returned to by the seeded runs.

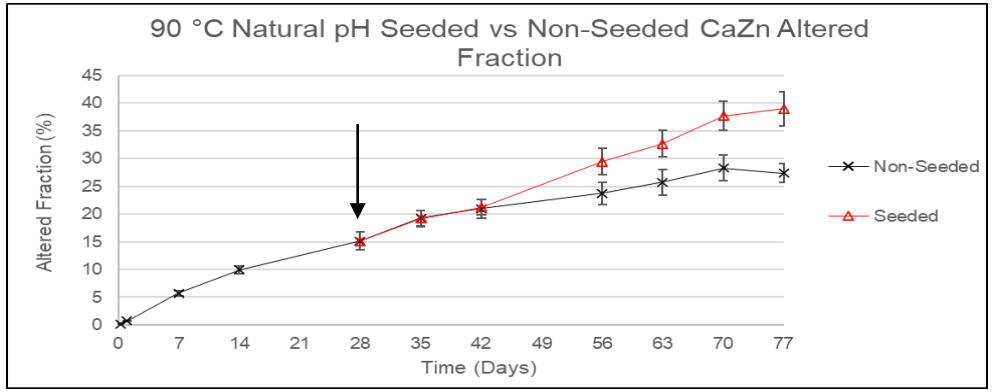
Variation of Zeolites

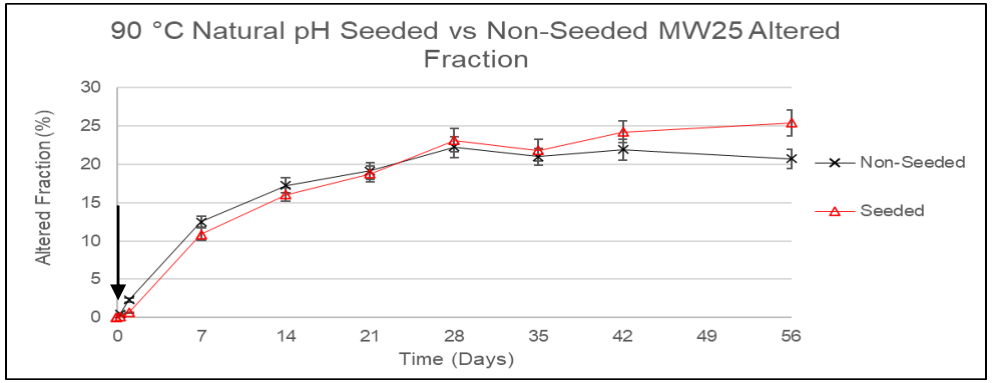
B. Parruzot et al. 2019





CaZn

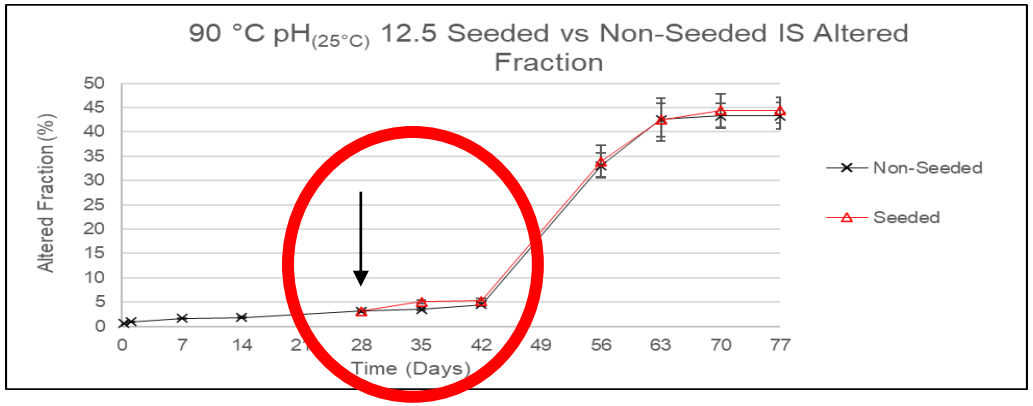


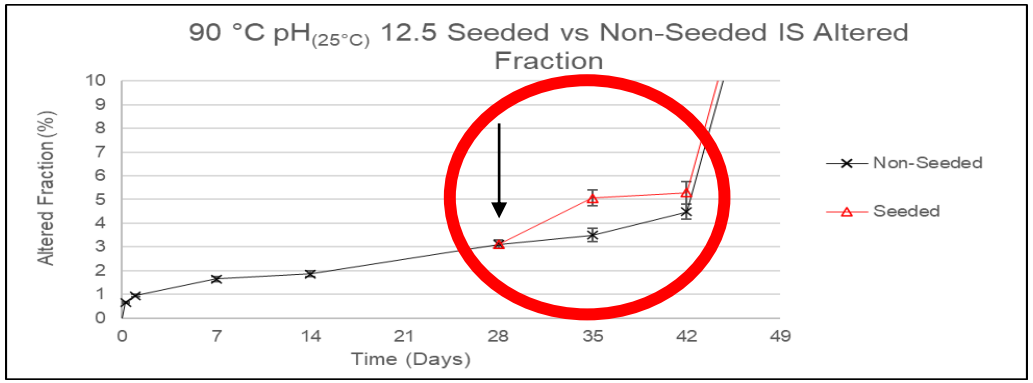


Delayed response – not unprecedented as residual rate must be reached for differentiation

IS

- Effect seen before natural resumption occurred
- Loss of Al from leachate





Summary and Conclusions

- The resumption of alteration has been successfully induced for the first time in MW25.
- The results have demonstrated the potential for resumption to be induced by any zeolite forming in any amount at any time anywhere in the system at a range of pHs including natural pH for the first time in any waste glass.
- The affinity effect has been revealed as the primary cause of resumption, with no clear protective alteration layer benefit.
- These results have been supported by preliminary geochemical modelling on PHREEQC.
- SEM/EDS, XRD, and NMR analyses are planned/ongoing to confirm composition of secondary phases.
- CaZn and IS results support these conclusions and may contribute towards a mechanistic understanding.

- Further experiments and modelling are required to determine the probability of these events occurring naturally and therefore the significance of these results to a GDF safety case.

Thank you for listening!

Further results will be available soon…

“Delay is life.” – Lord Salisbury