Geological disposal of silicon-rich vitrified ILW products in a cement-based engineered barrier system: addressing key uncertainties

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Geological disposal of new ILW wasteforms

Novel ILW treatment processes generate new wasteforms

- Differ in composition and properties from conventional cement-grouted ILW
  - e.g. many vitrified wasteforms are silicon-rich

One possible disposal option:

- Disposal alongside cement-grouted ILW in a cement-based engineered barrier system

Key uncertainties

Placing vitrified ILW in a highly alkaline environment raises two questions:

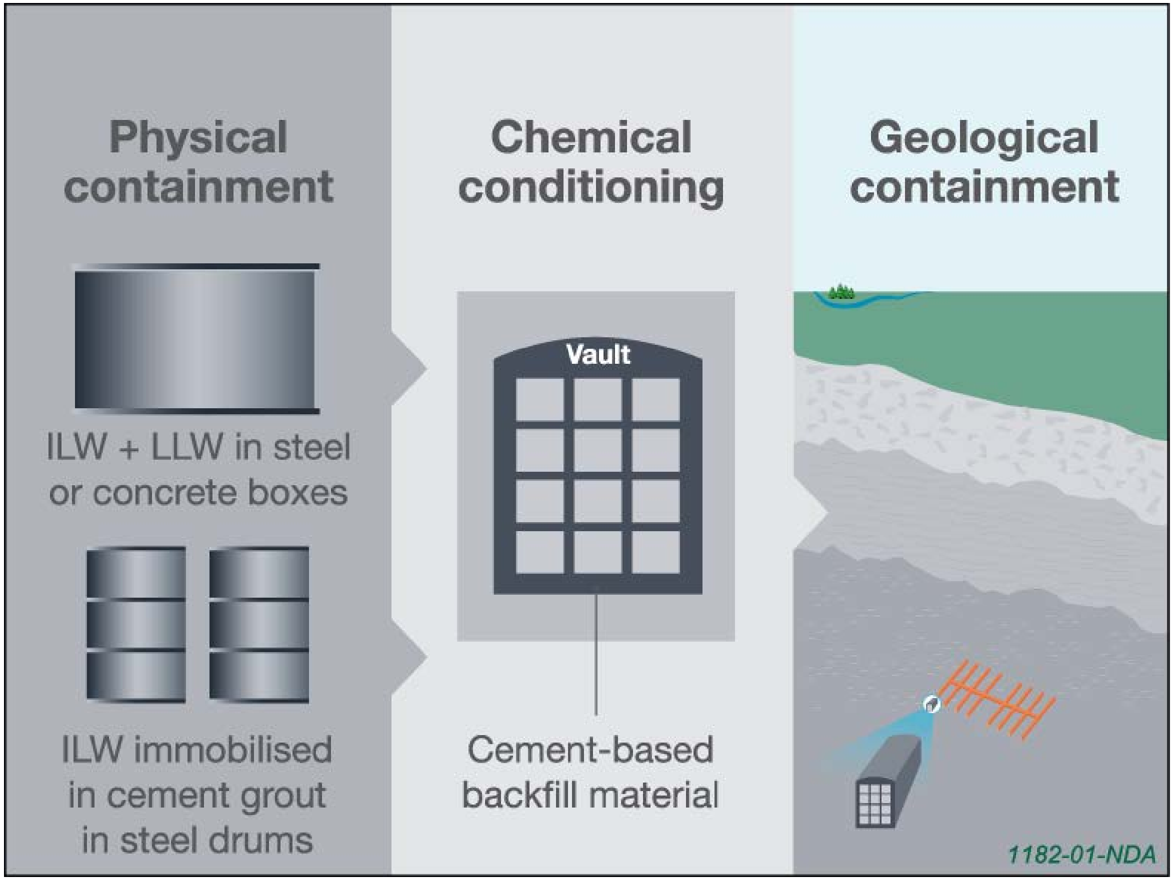
- How will the vitrified ILW behave?
- What impact would emplacement of vitrified ILW have on the properties and performance of the cementitious backfill?

Outline

- UK cement-based disposal concept
- Low Ca/Si ratio C-S-H gel leaching
- Illustrative vitrified ILW products
- Glass dissolution
- Assessment of impact of vitrified ILW on properties and performance of backfill
- Conclusions

Cement-based disposal concepts

Illustrative ILW concept for higher strength rock



Higher strength rock

Principle of ‘chemical containment’

One barrier to radionuclide migration in ILW disposal concept

- Establish alkaline conditions to minimise solubility and maximise sorption of key species

Vault backfill around waste packages plays key role

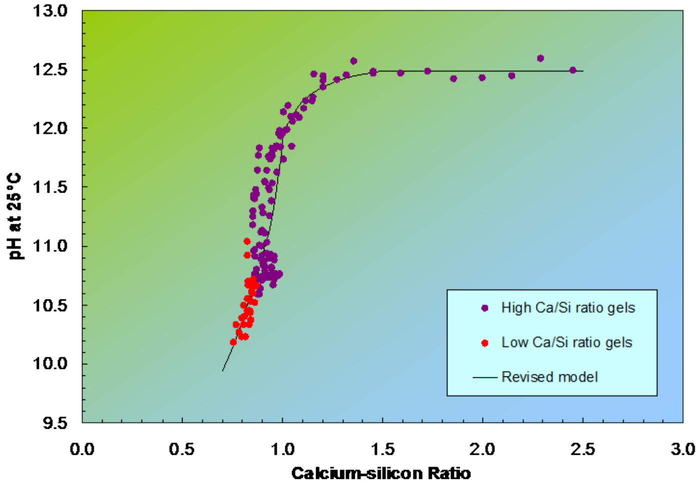
- compatible with wasteforms (mainly cementitious in the UK)
- capable of maintaining desirable properties over appropriate timescales
  - pH buffering to alkaline pH (≥ 9)
  - Sorption capacity
- have appropriate mass transport properties
  - sufficiently permeable to allow escape of gas with no over-pressurisation
- sufficient strength and dimensional stability to retain waste packages in required positions

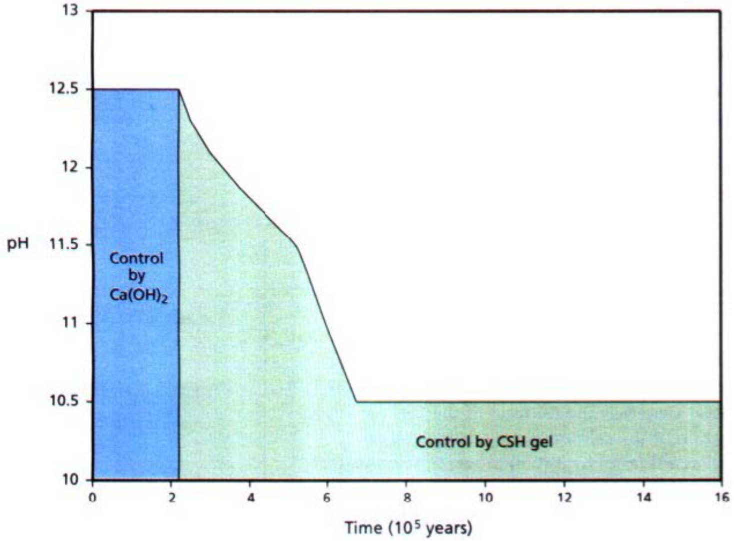
NRVB

- NRVB (Nirex Reference Vault Backfill) was developed in the UK as vault backfill for the illustrative UK ILW/LLW disposal concept in a higher-strength host rock
- The NRVB comprises ordinary Portland cement with a fine aggregate containing crushed limestone filler and hydrated lime (calcium hydroxide)

Leaching of cement backfills and C-S-H gels

- Calcium silicate hydrate (C-S-H) phases in cement important for
  - pH buffering
  - Sorption capacity
- Leaching data available for C-S-H gels and NRVB
  - Mainly in deionised water but also in sodium chloride solutions
- Understanding can be applied to estimation of pH performance of cement-based systems
  - Homogeneity assumed



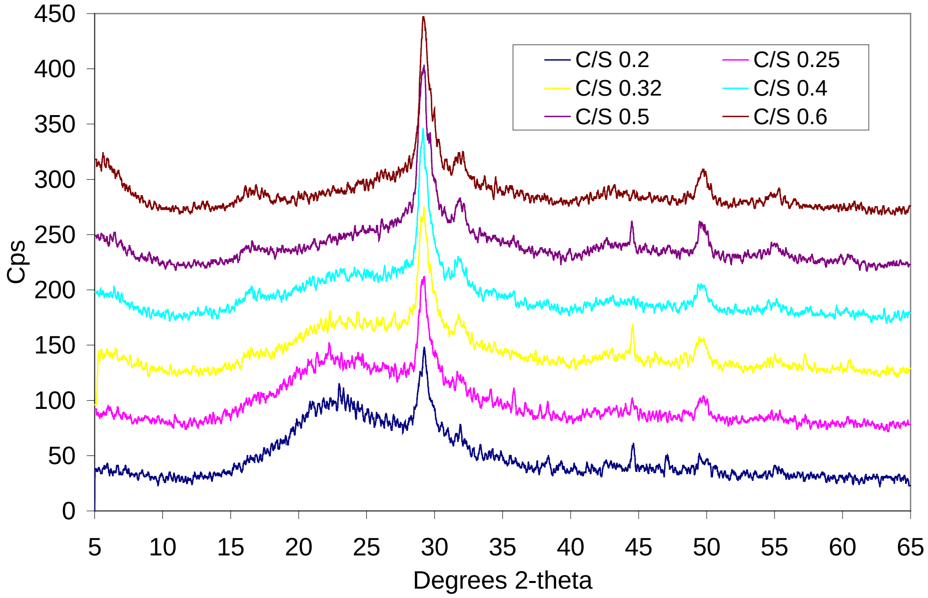


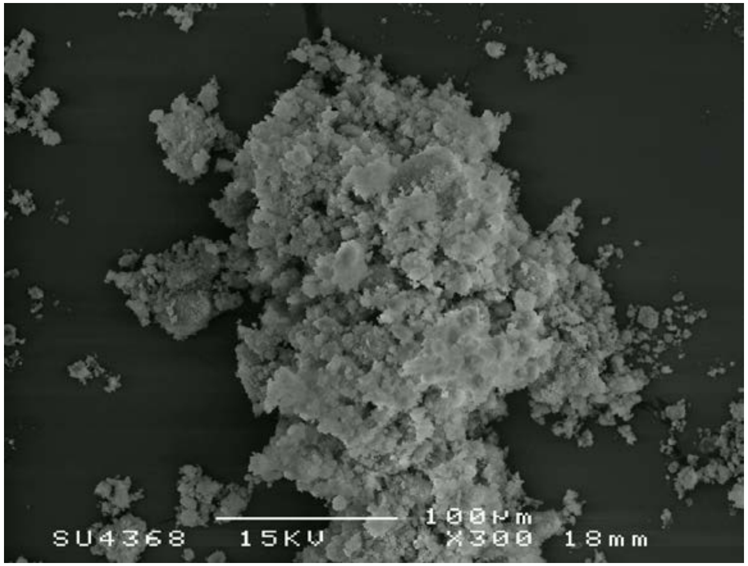
Low Ca/Si ratio C-S-H gel leaching studies

Low C/S C-S-H gels

Gels prepared by reacting CaO with colloidal silica for > 1 month

C/S = 0.2, 0.25, 0.32, 0.4, 0.5, 0.6





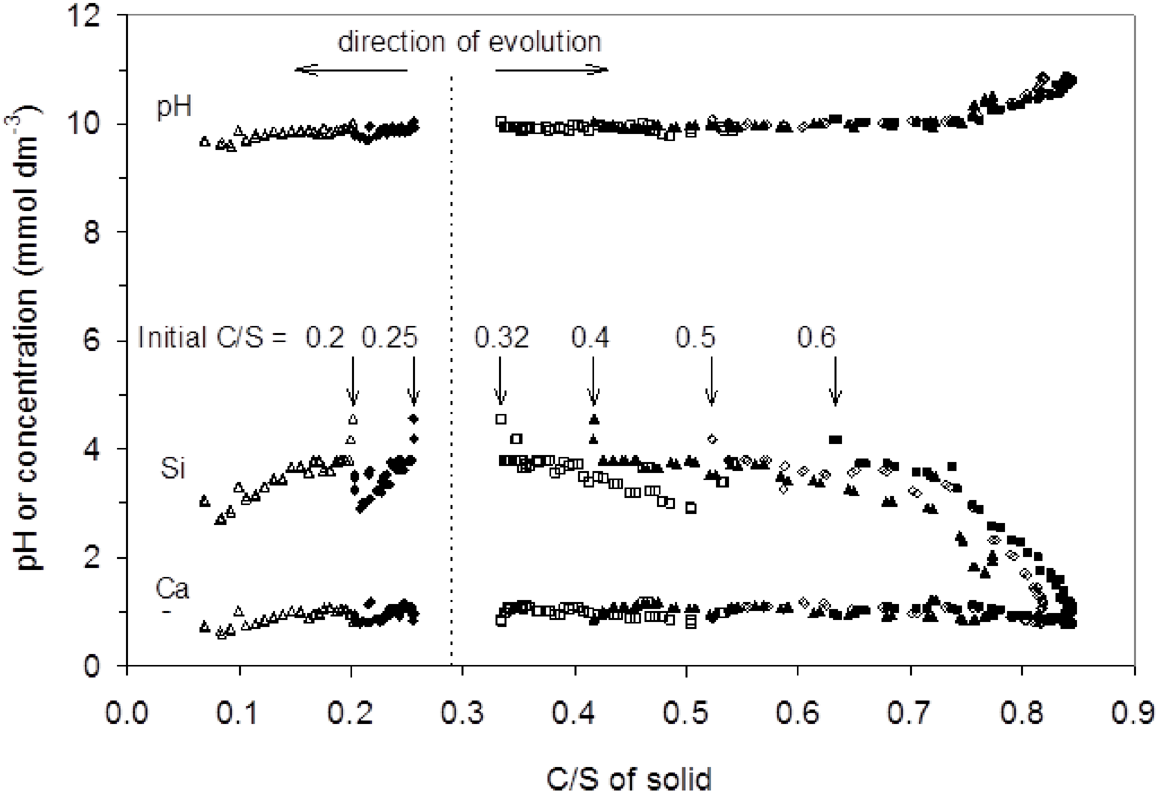
Gels are an intimate mixture of C-S-H (I) and $SiO_{2\ (am)}$

Dynamic leaching of C-S-H gels

- 4g C-S-H gel in 600 cm^3 N_2-sparged demineralised water
- Sealed, placed in water batch at 25 ± 1°C
- After typically 20 days, decanted 480-500 cm^3 solution in glovebox
    - Measured pH at 25 ± 1°C
    - Sample passed through 0.45µm filter, acidified for ICP-OES of Ca, Si
- Refilled with water and re-sealed.

- 17 exchanges in 1 year to achieve minimum leaching ratio 2 $m^3\,kg^{-1}$
- Then after a further 7-month equilibration,
    - 2 further exchanges each after 20 days
    - 2 further exchanges after 4 and 5 months respectively
- Measured final composition (C/S) of gel by quantitative EDX
- Changes in phases identified by XRD

Dynamic leaching of low C/S C-S-H gels



- For all gels, extended plateau with C/S(s) from 0.1-0.7 with pH 9.7 – 10.2
  - $C/S_{aq} = 0.29 \pm 0.03$
- For gels with C/S >0.3, C/S(s) increases towards congruently dissolving composition with C/S = 0.83

Implication

- If the C/S value of the pH-buffering C-S-H phases in the near field decreases below that of the congruent dissolution point (due to perturbations in the porewater chemistry), the natural tendency of the system is to restore congruent dissolution at a pH around 10.8

Illustrative vitrified ILW products

Illustrative vitrified ILW products

Clinoptilolite/sand glass (Clino)

- waste mix: clinoptilolite, sand, NaOH, $Mg(OH)_2$
- made by plasma vitrification in a cold crucible (Tetronics Limited)
- sodium (calcium) alumino-silicate type glass

Geomelt® high-metals waste trial product (HMW)

- waste mix: steels, Al, Mg, Misch metal
- made by in-can vitrification
- 2-phase product
  - metal - predominantly iron
  - iron-rich soda lime-based glassy slag

Products are <u>not</u> optimised

Illustrative vitrified ILW products

Glassy phases "homogeneous"

Clino glass amorphous in XRD

Geomelt HMW product

- Minor Ca(Fe,Mg) Si_2O_6, $MgLaAlSiO_6$ phases
- Of surrogate radioelements
  - Sr, Cs, Eu retained in glass
  - Ru, Rh retained in metal
- Of metal wastes
  - Mg, La, Ce, Al primarily in glass

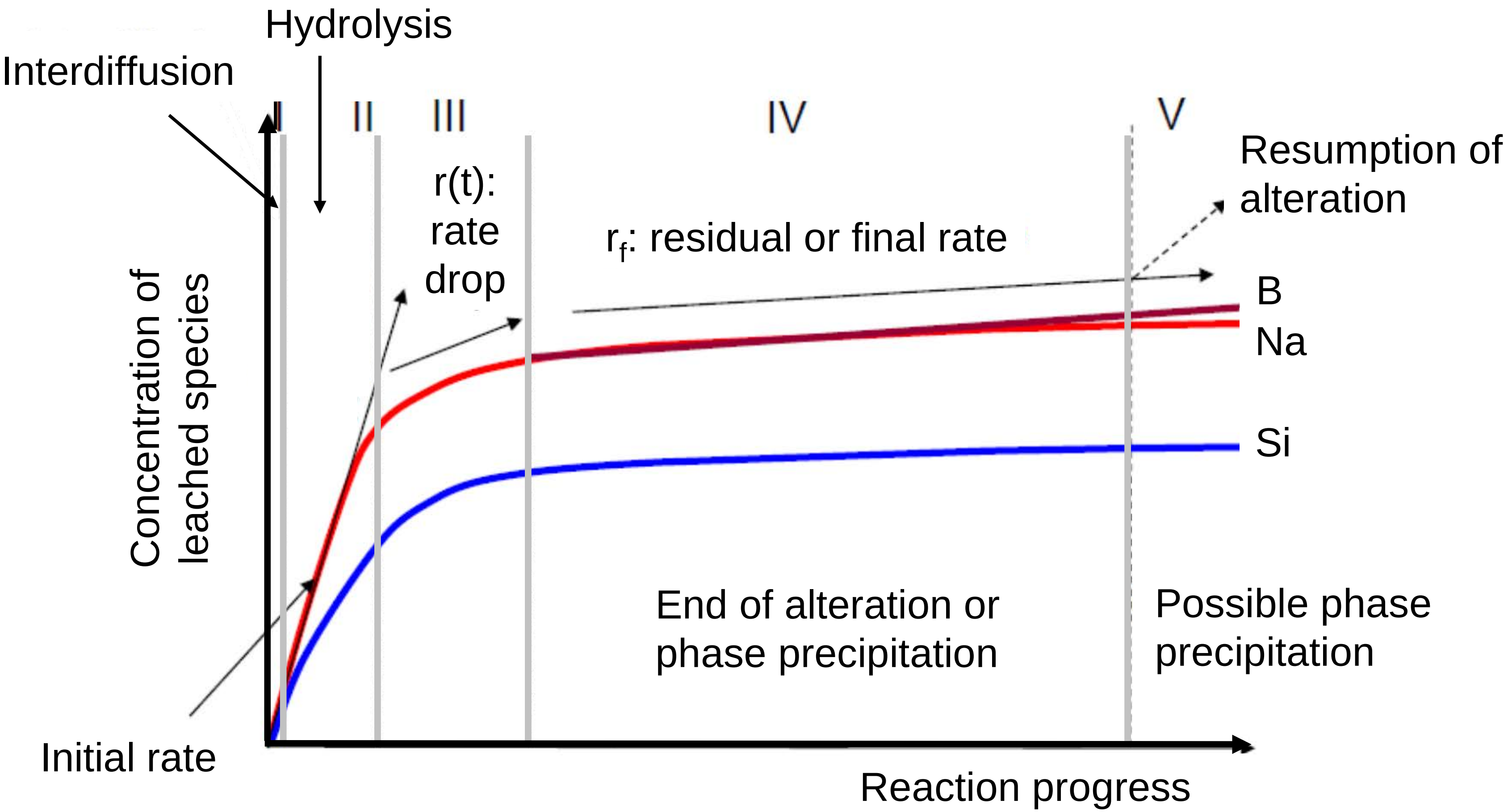
- Note: lack of soluble tracers (e.g. B, Li, Cs, Mo) in glassy products

Composition wt%

Component oxide	Clino glass	HMW slag
SiO_2	66.0	46.0
Na_2O	14.6	6.7
B_2O_3	-	-
MgO	5.5	4.8
Al_2O_3	9.1	8.4
Fe_2O_3	0.8	10.6
Li_2O	-	-
CaO	1.7	5.7
CeO_2	-	11.9
La_2O_3	-	5.4
K_2O	1.1	0.4
Others	1.2	0.1

Glass dissolution studies

Glass dissolution behaviour



Hydrolysis

Interdiffusion

r(t): rate drop

r_f: residual or final rate

Resumption of alteration

End of alteration or phase precipitation

Possible phase precipitation

Concentration of leached species

Initial rate

Reaction progress

Product Consistency Test type B (PCT-B)

Leaching of crushed glass

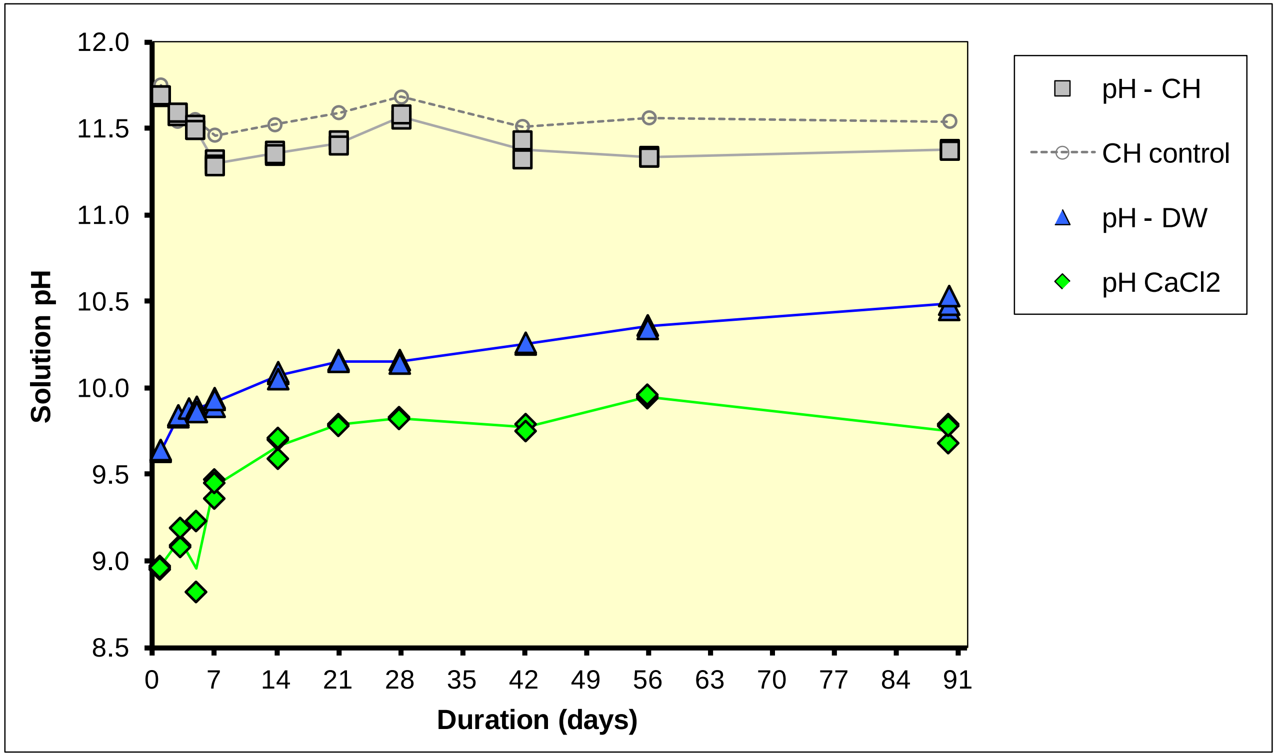
- 75-150µm size fraction
- SA/V ~ 1200 m^{-1}
- 50°C
- Triplicate tubes + 1 or 2 controls stopped periodically up to 90 days

Solutions used

- DW – demineralised water
- CH – near-saturated $Ca(OH)_2$ solution
  - [Ca] = 0.0186M, pH 11.7 at 50°C
- $CaCl_2$ – 0.0186M $CaCl_2$ solution

- Tests in CH solution performed in N_2 atmosphere
- Tests in DW, $CaCl_2$ solution performed in air

HMW slag in DW, $CaCl_2$ and CH – pH at 50°C

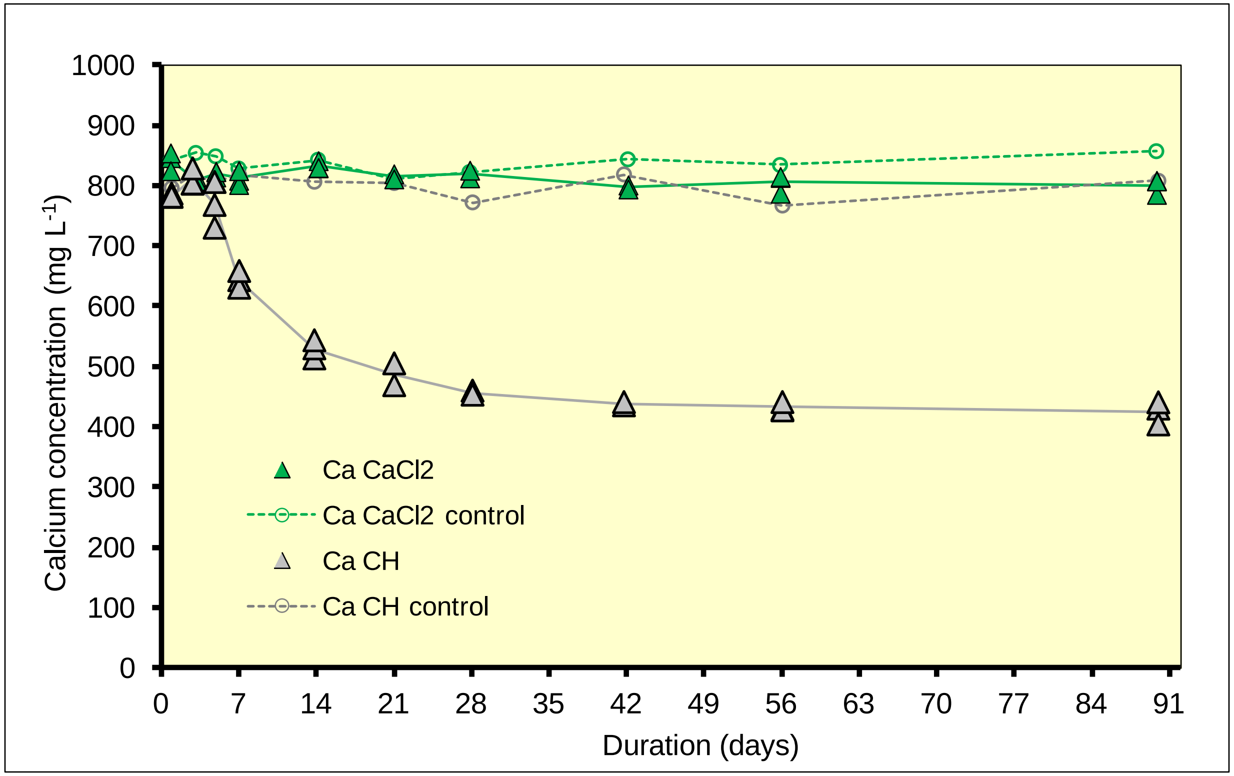


- DW and $CaCl_2$ in air
- CH in N_2 atmosphere

- Slag is alkaline (n.b. Na_2O is 6.7wt%, CaO 5.7wt%)
  - in DW results in pH rising to ~10.4 in 90 days
  - pH rise reduced in $CaCl_2$ solution
- Possible pH reduction in CH solution

HMW slag in $CaCl_2$ and CH solutions

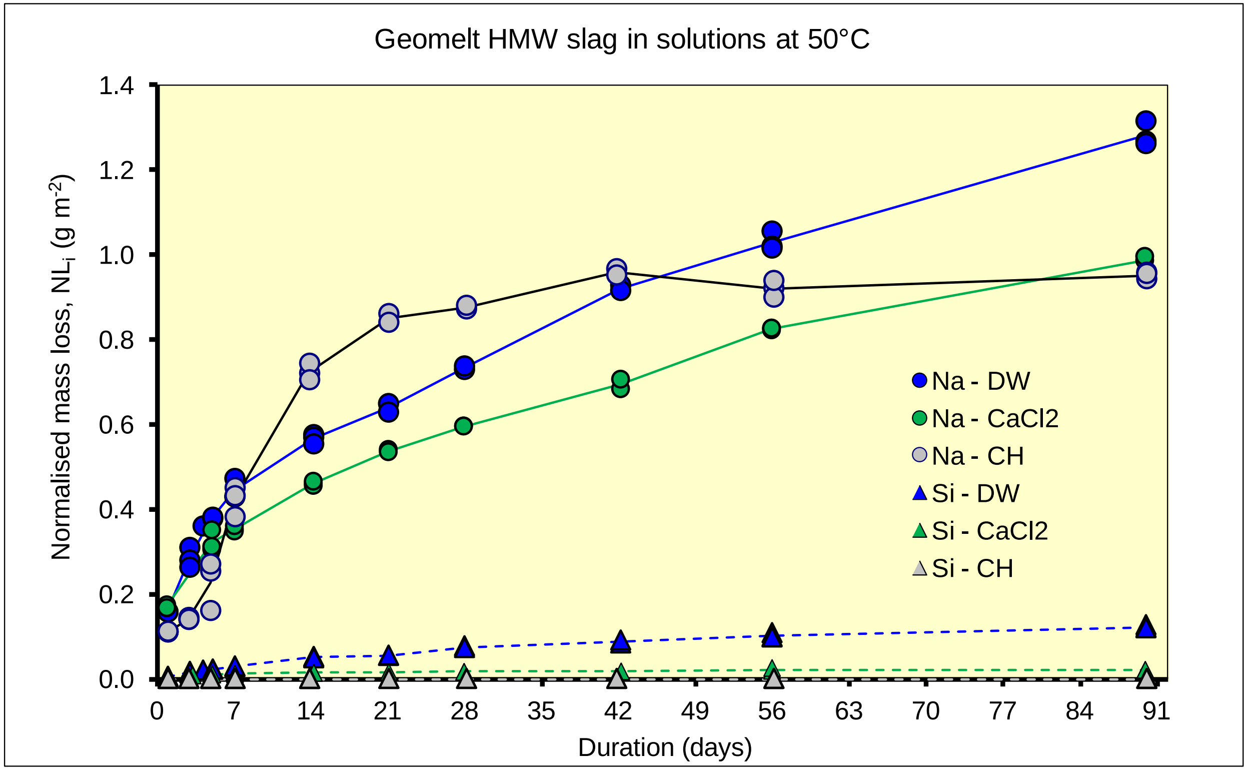
Calcium concentration



- In CH solution, Ca interacts with surface
  - ~50% removed from solution over 90 days
- Possible (?) removal of Ca from $CaCl_2$ solution

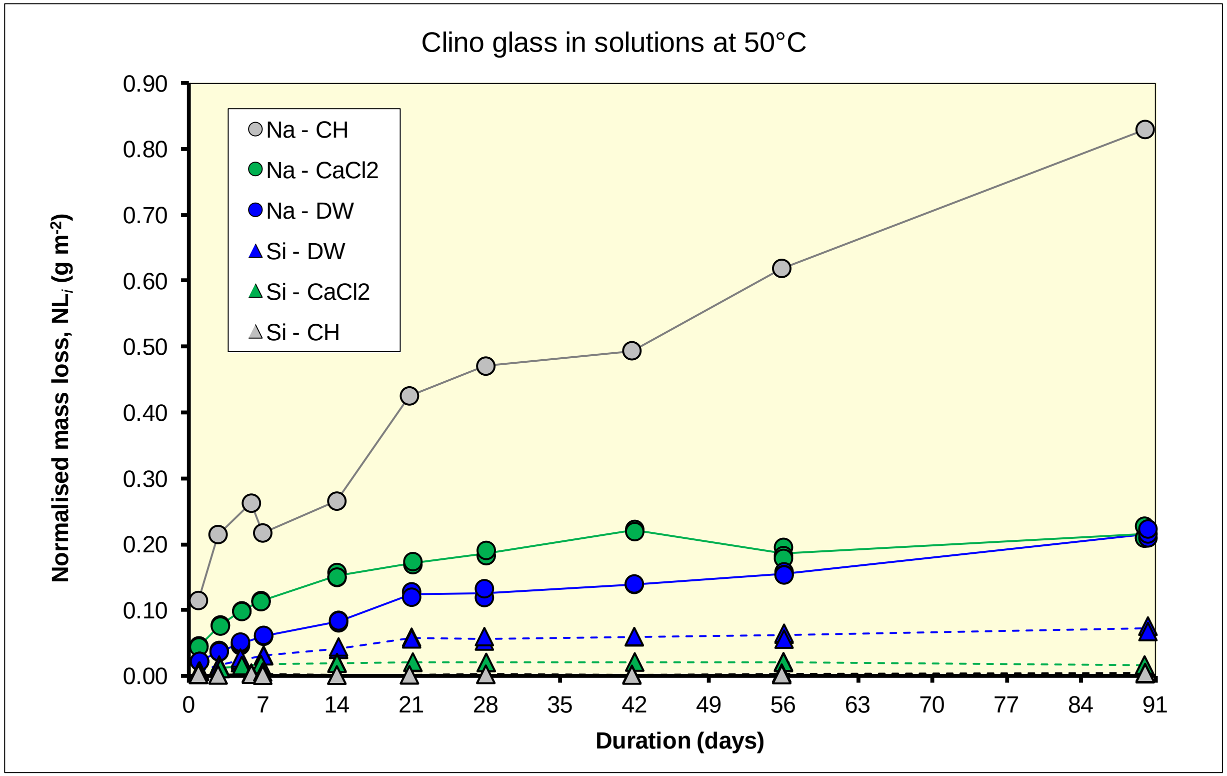
HMW slag in DW, $CaCl_2$ and CH solutions

Normalised mass loss



- ► Initially, dissolution rate (based on Na) in CH similar to that in DW and $CaCl_2$ solution despite higher pH (~11.6)
- ► High retention of Si and other major elements (Al, Mg, Ce, La) in alteration layer, including Ca in DW

Clino glass in DW and CH solutions

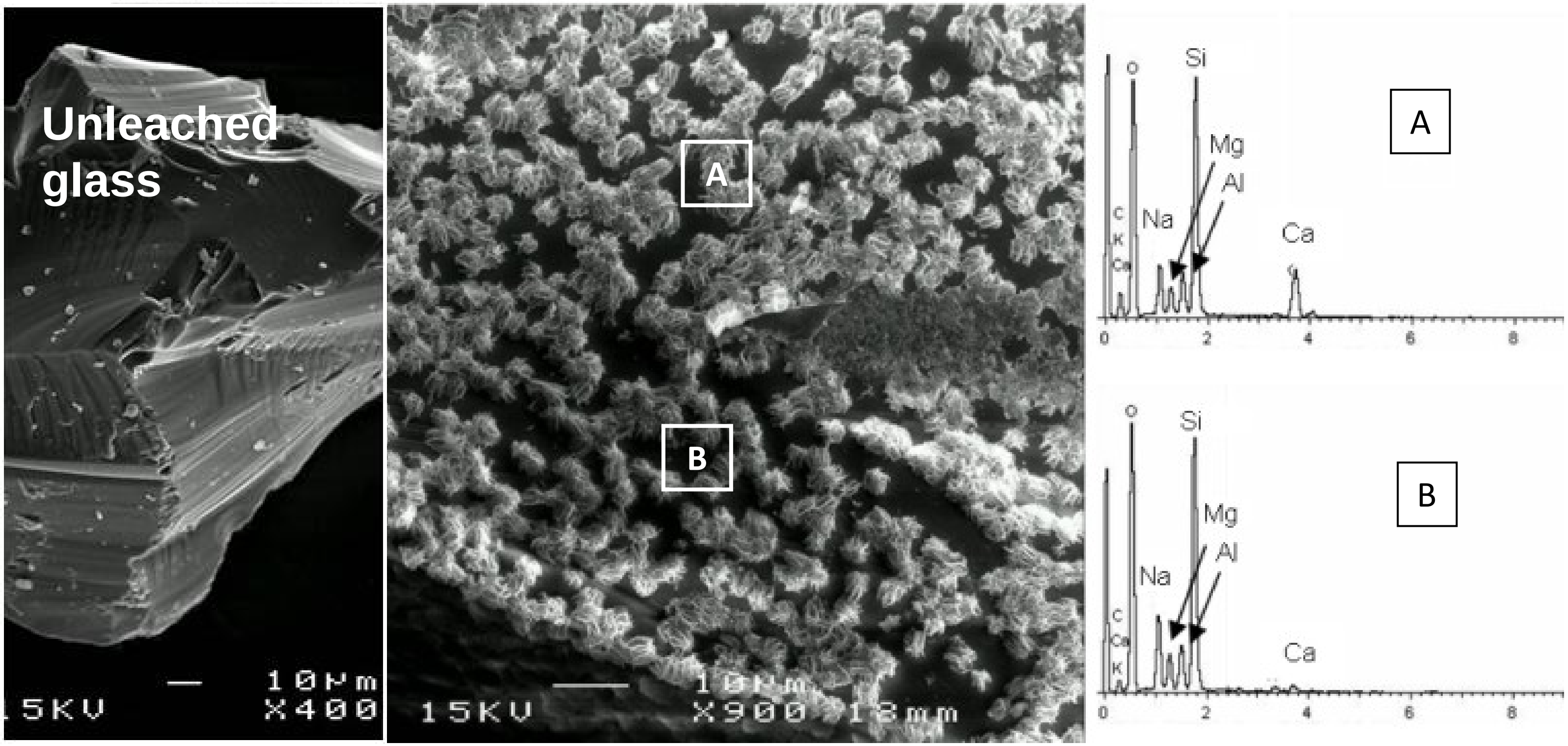


CH	**pH 11.7**
DW	**pH 9.7**
$CaCl_2$	**pH 9.0**

In CH solution, alteration rate higher than in DW

- initial rate (1-5 days) higher by factor of 5
- Alteration continuing at longer times

SEM/EDX – Clino glass surface



Clinoptilolite glass after 42 days in saturated $Ca(OH)_2$ solution at 50°C

► calcium-rich precipitates on surface

C. Utton *et al* J. Nuclear Materials 435, 112-122, 2013

Findings

$Ca(OH)_2$ solution (representative of cement-based near-field)

- lower dissolution rates than expected under high imposed pH (12.0 – 12.6) compared to Na/KOH systems
- presence of calcium is important
  - all glasses react with calcium
  - observe formation of C-S-H secondary products on glass surface

Assessment of impact of ILW products on cementitious backfill

Assessment methodology

- Define initial compositions for
  - backfill (NRVB)
  - vitrified wastes – Clino glass and Geomelt High Metals Waste product
- Calculate the elemental releases from corrosion of vitrified waste with time
- Use thermodynamic modelling to calculate composition of backfill mixed with corrosion products at 1000, 10,000 and 100,000 years
  - PHREEQC
  - Solid phases from Nagra PSI TDB, CEMDATA, GW/EQ36
- Evaluate effects of changes in mineralogy on porewater pH, backfill sorption, porosity and volume changes
  - Closed system
  - Pseudo-open system with groundwater leaching of Na, K

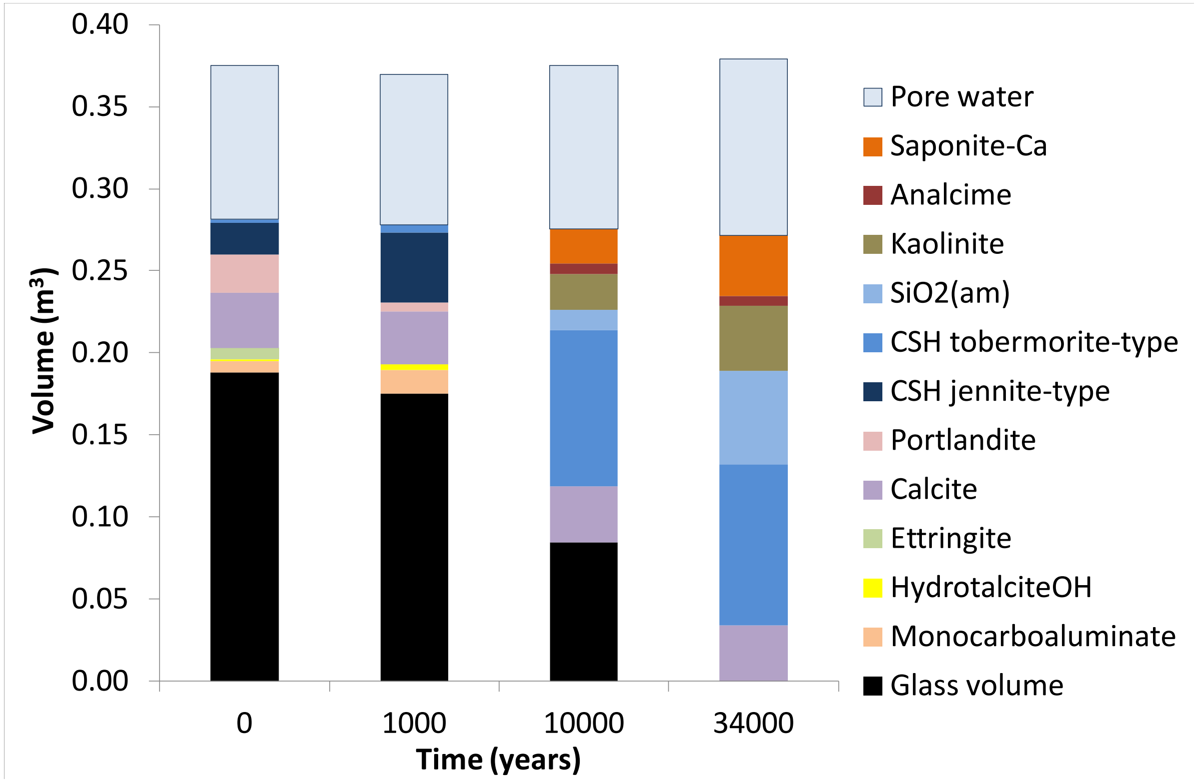
Assumptions

- Vitrification canisters ignored
- Dissolution of vitrified products congruent and rates constant
  - Clino – initial rate 0.042 g m^{-2} day^{-1}
  - Geomelt HMW – illustrative residual rate 0.006 g m^{-2} day^{-1}
  - Cracking of glass monolith ignored
- 1:1 volume ratio of wasteform to backfill
  - System fully re-saturated from time = 0
- Only bulk reactions of the full backfill volume considered
  - Thermodynamic equilibrium of backfill plus corrosion products
- Groundwater flow (for pseudo-open system)
  - Treated as simple pore water exchange for Na, K removal
  - Full interactions of groundwater with backfill and wasteform not considered

NRVB / Clino glass interactions

Changes in mineralogy

- Low C/S C-S-H, amorphous silica. Sodium minerals analcime and saponite-Na only
- Increase in reactive surface area
- pH reduced, at longer times

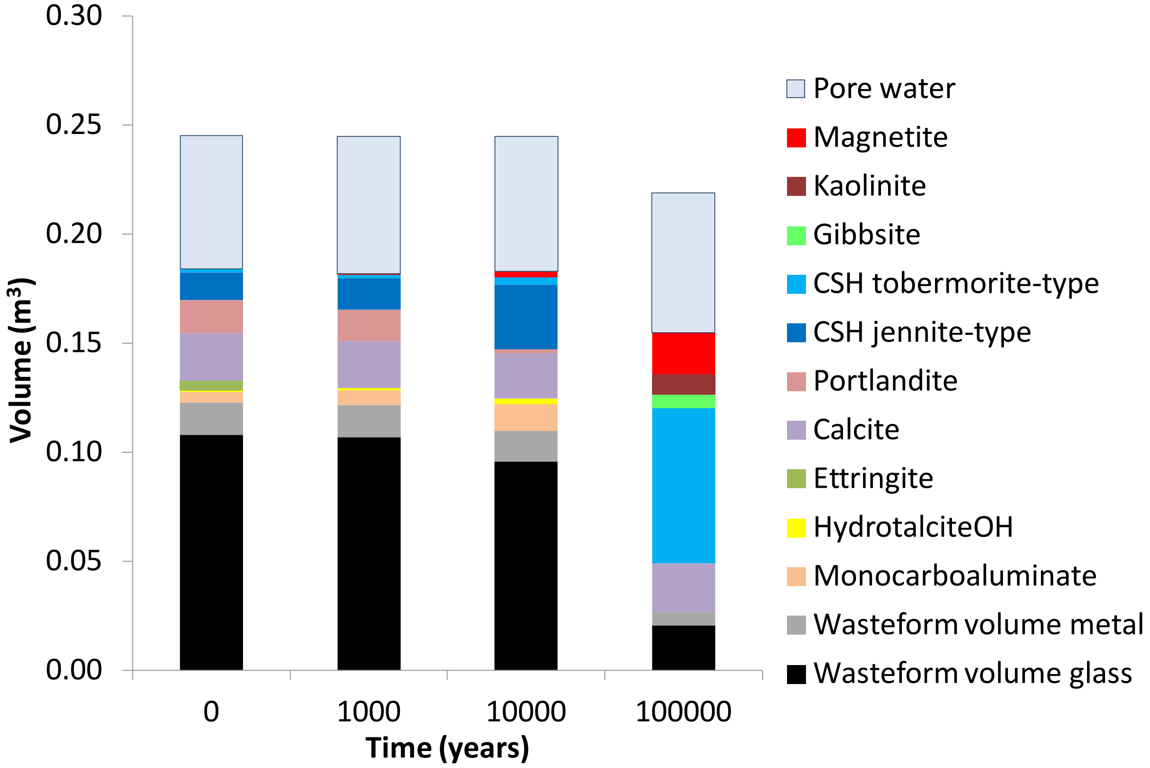


Years	0	1,000	10,000	34,000
Pore Fluid pH	13.1	13.4	9.3	9.0
Total surface area of backfill and mineral phases (m^2)	35,000	56,000	200,000	290,000

NRVB / Geomelt HMW product interaction

Changes in mineralogy

- Low Ca/Si C-S-H formed
- Decrease in volume of solid phases (Na removal)
- Possible increase in void space
- pH reduced
- Increase in reactive surface area



Years	0	1,000	10,000	34,000
Pore Fluid pH	13.1	12.8	12.8	9.8
Total surface area of backfill and mineral phases (m^2)	35,000	38,000	61,000	130,000

Summary of NRVB interactions with vitrified waste

- Significant silicon content in glass. Potentially reduces C/S ratio of backfill, thus buffering to lower pH (9 to 10 if Na and K removed)
- Some reduction in pore volume if we assume Na can build to concentrations where Na minerals can precipitate.
  - (Groundwater interactions may have other effects of pore volume, but not considered here)
- The sorption capacity of the NRVB is predicted to increase
  - Mainly due to incorporation of the Si from glass into C-S-H
  - Sorption coefficients for lower C/S C-S-H are similar those for higher C/S ratios

Conclusions

- Vitrified ILW products may display relatively low dissolution rates in a cementitious environment
- C-S-H gel systems are resilient in their capacity to buffer pH to alkaline values even at low calcium to silicon ratios that might result from the interactions of silicon-rich materials with a cement backfill
- The overall pH-buffering capacity of the backfill is not expected to be reduced by such interactions; rather the buffering will be at a lower pH, but for an extended period
- In addition, the overall sorption capacity of the backfill is predicted to increase due to the larger quantity of C-S-H phases
- These findings support the view that placing vitrified ILW alongside cemented ILW would be a potentially viable disposal option

Acknowledgements

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Thank you for your attention

Any questions?