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Supplement of

Dissolution of simplified nuclear waste glass and formation of secondary phases

Felix Brandt et al.

Correspondence to: Felix Brandt (f.brandt@fz-juelich.de)

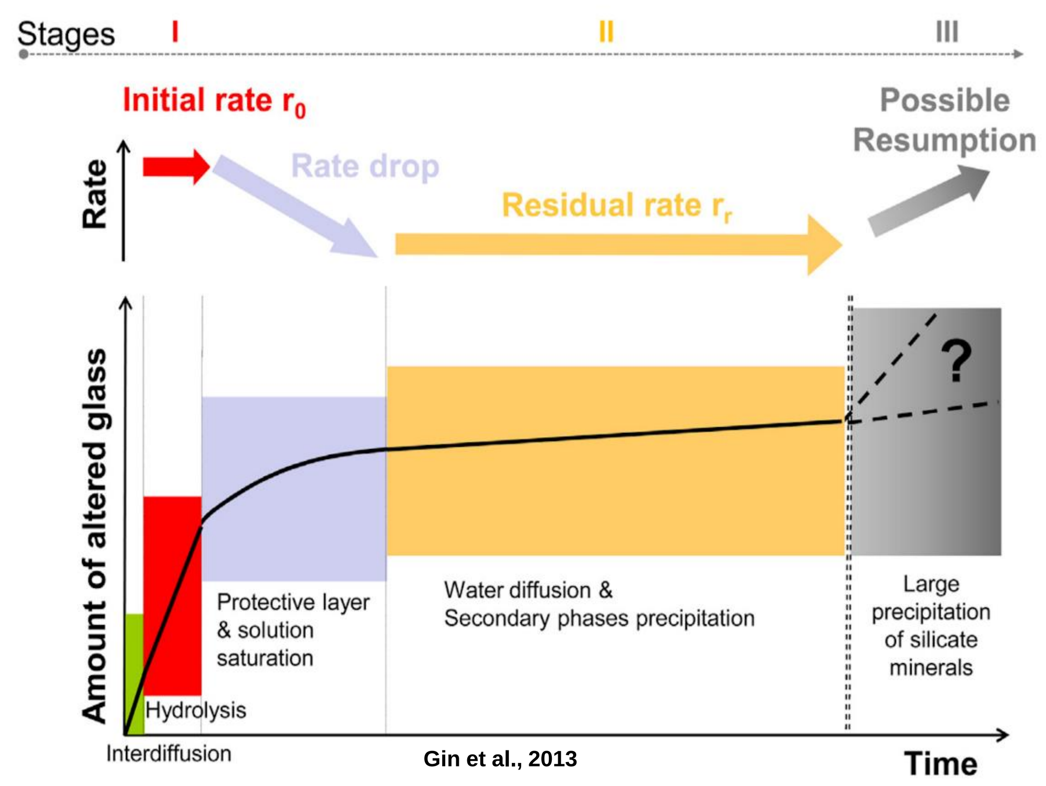
Dissolution of simplified nuclear waste glass (ISG) and formation of secondary phases

Felix Brandt[1], Martina Klinkenberg[1] , Sébastien Caes[2], Jenna Poonoosamy[1], Wouter Van Renterghem[3], Juri Barthel [4], Karel Lemmens[2], Dirk Bosbach[1], Karine Ferrand[2]
[1]Institute of Energy and Climate Research (IEK-6), Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany; f.brandt@fz-juelich.de
[2]Institute for Environment, Health and Safety, SCK CEN, B-2400 Mol, Belgium; [3]Institute for Microstructural and Non-Destructive Analysis, SCK CEN, B-2400 Mol, Belgium
[4]Ernst Ruska-Centre (ER-C 2), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Introduction & Objectives:

Leaching mechanism = selective removal of cations

- Still state-of-the art for waste management agencies **but under debate in the scientific community**



Models based on the proposed leaching mechanism are mainly based on macroscopic experiments at low surface area to volume (SA/V) ratio (e.g. Frugier et al., 2018)

- Details of surface alteration layer (SAL) formation?
- Formation of new phases and incorporation of RN?
- Relevant experimental conditions e.g. high pH, low T due to the presence of concrete and cement?

➔ The microscopic view

Effect of high pH

- Morphology and properties of altered phase?
- Type of newly formed secondary phases?

Lower temperature

- More difficult to form crystalline secondary phases?
- Slower dissolution of the glass?

Higher SA/V

- More secondary phase formation?

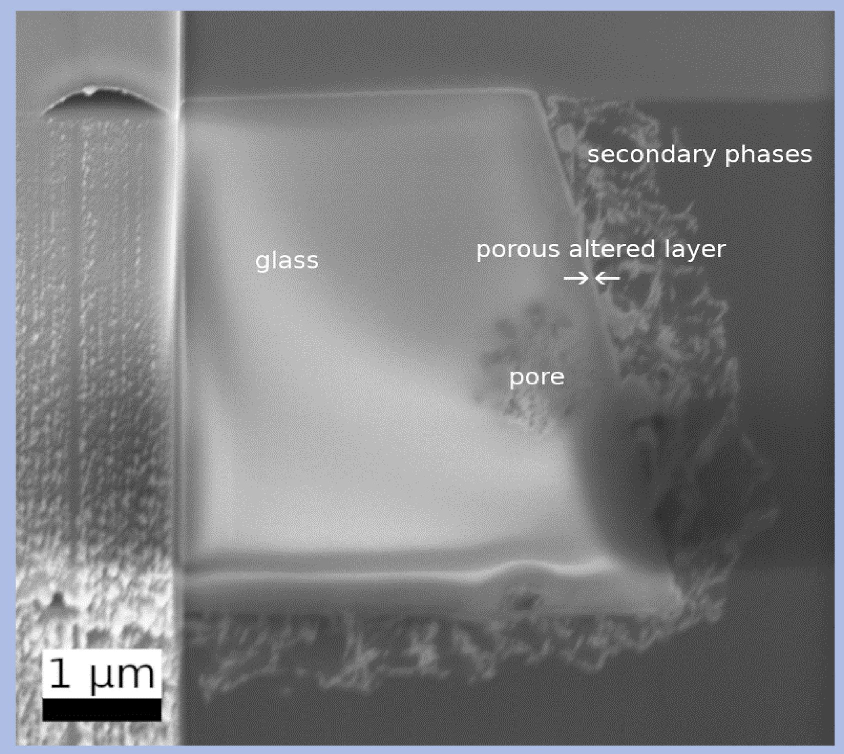
Results:

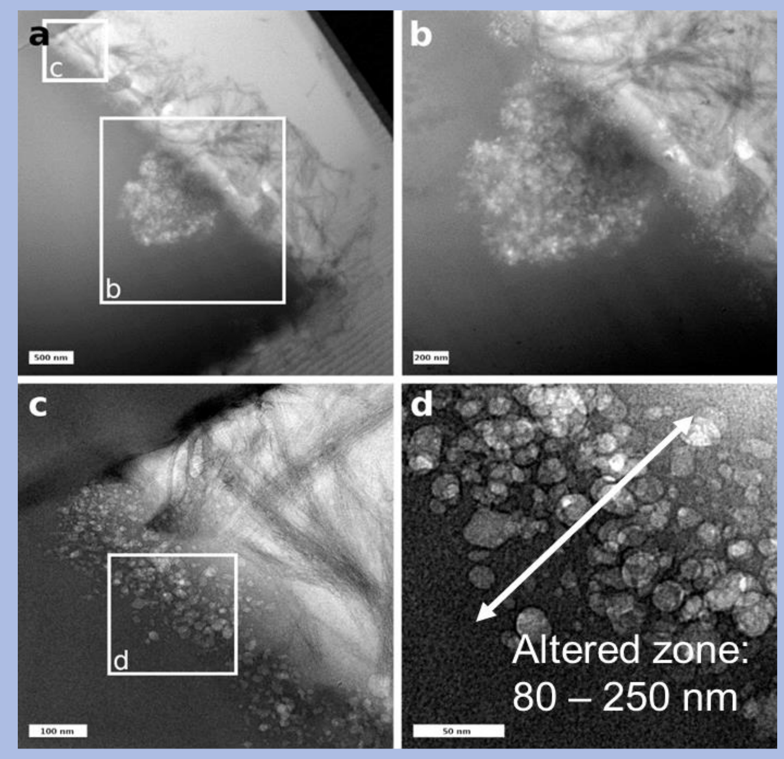
Identification of secondary phases (XRD + SEM)

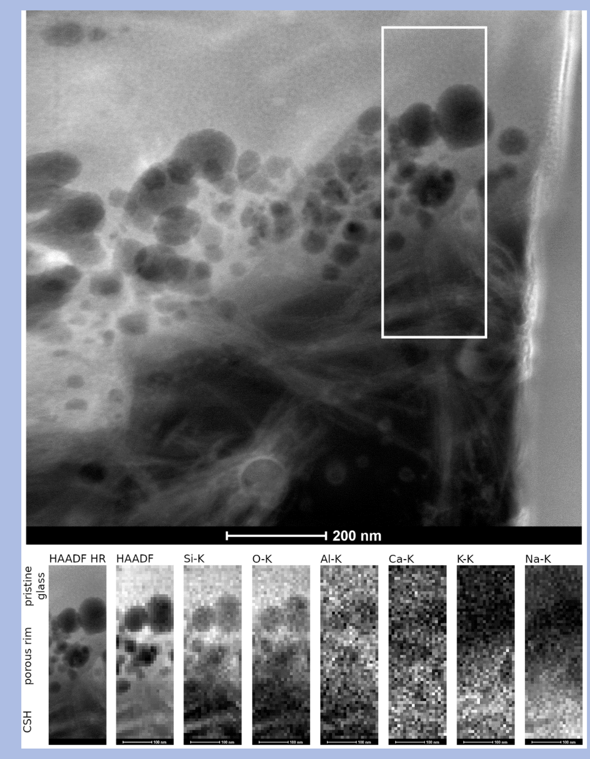
– Zeolites (Na and K zeolite)
– Calcium silicate hydrate phases (CSH)

Microscopic perspective, residual stage:
the glass/SAL interface (TEM), SA/V = 264000 m^{-1}

- Very thin porous altered layer, **no colloids Structure resembles a bubble foam**
- Fibrous secondary phases relationship with the cavities of the porous layer?

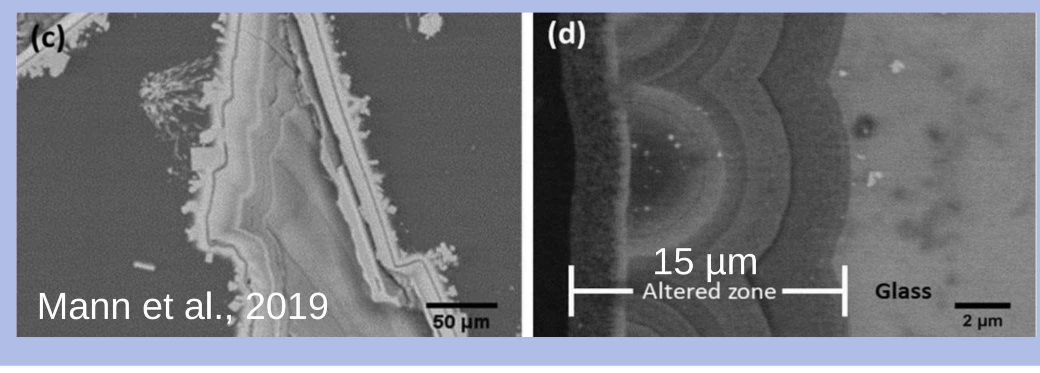






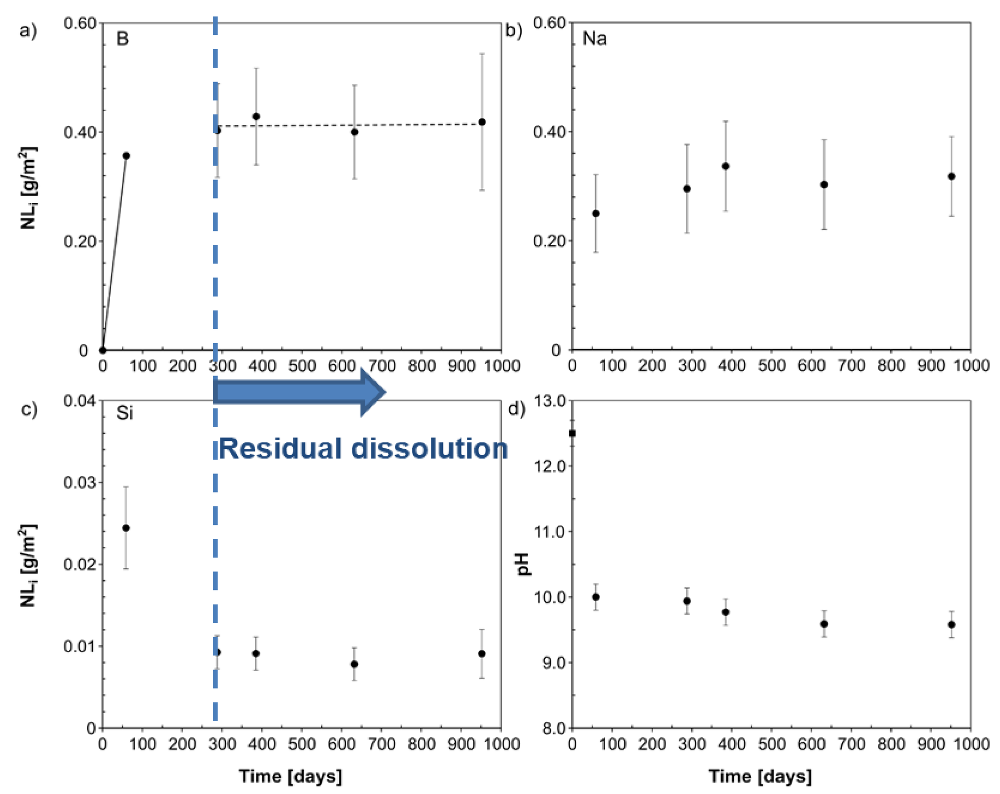
SA/V = 8300 m^{-1}
Mann et al., 2019, ISG glass in YCWCa @70 °C

- Gel layer of multiple **colloidal bands**
- Sharp boundaries between layers
- Crystalline phases formed around the outer edge



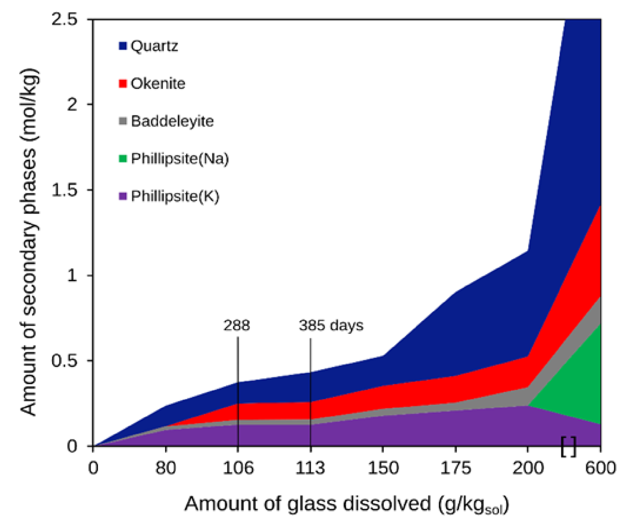
Macroscopic perspective

Normalized element release NL_i = amount of glass (g/m²) dissolved at a given time calculated from the element release. NL_i and residual rateof 6 x 10^{-6} g/m²d in the usual range



Thermodynamic equilibrium calculation based on mass balance of dissolved elements (NL_i)

Blind prediction: All cations released end up in secondary phases, if they are supersaturated.



	Calculated (113 g glass dissolved)	Experiment (385 days)
Na (mg/L)	13856	12807
Al (mg/L)	< 0.01	0.12
Ca (mg/L)	0.34	7.83
K (mg/L)	8911	4549
Si (mg/L)	1164	723.75
Zr (mg/L)	0.00	0.0006
B (mg/L)	6356	6969
SO_4 (mg/L)	196	188
$pH_{(70\ °C)}$	10.1	9.6

Predicted and observed

- Zeolite
- CSH (Okenite)

Not observed due to kinetics

- Quartz
- Baddeleyite

Summary and Conclusions:

SA/V ratio is a key parameter for the dissolution rate and the formation of the altered glass surface and secondary phases at high pH conditons.

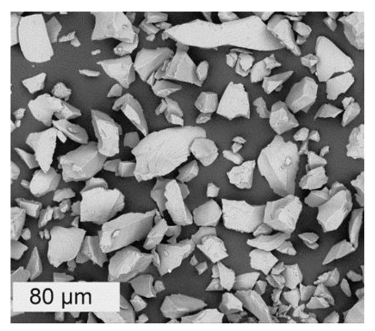
- **Macroscopic** element release NL_i and residual dissolution rate of 6 x 10^{-6} g/m²d **in a usual range**
- **No resumption** although secondary phases are formed
- **Thermodynamic blind predictions** can predict the observed secondary phases, some phases are missing due to kinetic reasons
- CSH phases and zeolites confirmed by SEM, XRD or TEM. Stable phases such as K-zeolite present as well as metastable Na-zeolite and CSH of a kinetically controlled composition.
- The **unusual microstructure:** very thin, porous layer from which CSH phases appeared to have grown

➔ Competition between dissolution/re-precipitation of secondary phases and formation of a leached layer

Materials and Methods:

ISG

Element	Wt%	Mol%
Si	26.3	18.0
B	5.4	9.6
Na	9.0	7.6
Al	3.2	2.3
Ca	3.6	1.7
Zr	2.4	0.5
O	50.1	60.3



YCWCa

Element	Concentration (mg/kg)
Al	0.06 ± 0.04
B	< 1
Ca	17.8 ± 1.8
Na	3120 ± 310
K	12400 ± 1200
Si	0.48 ± 0.21

Batch experiments at high pH and high SA/V

Parameter	Setting
Temperature (°C)	70
Particle fraction (µm)	20 – 25
Mass of glass powder (g)	3 ± 0.005
Specific surface area of glass powder by BET (m²/g)	0.440 ± 0.002
Solution composition	YCWCa, pH(70 °C) = 12.5 ± 0.2
Weight of solution (g)	5 ± 0.005
SA/V (m^{-1})	264 000
Duration (days)	59, 288, 385, 632, 952

Modelling of thermodynamic equilibria (GEMS-PSI)

– Estimation of secondary phase equilibrium assuming congruent dissolution and precipitation

Characterization of the solid

– Separation of crystalline secondary phases
– XRD of separated grain size fractions
– Electron microscopy: SEM, FIB, TEM

Sample taken from day 385

- Sample embedded in resin
- Polished to obtain a cross-section
- FIB section prepared perpendicular to the polished surface

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Frugier, P. et al 2008. J. Nucl. Mater. 380, 8–21. DOI: 10.1016/j.jnucmat.2008.06.044
Gin, S. et al. 2013. Mater. Today 16, 243–248. DOI: 10.1016/j.mattod.2013.06.008
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