Interaction of HLW glass with cement or cement waters

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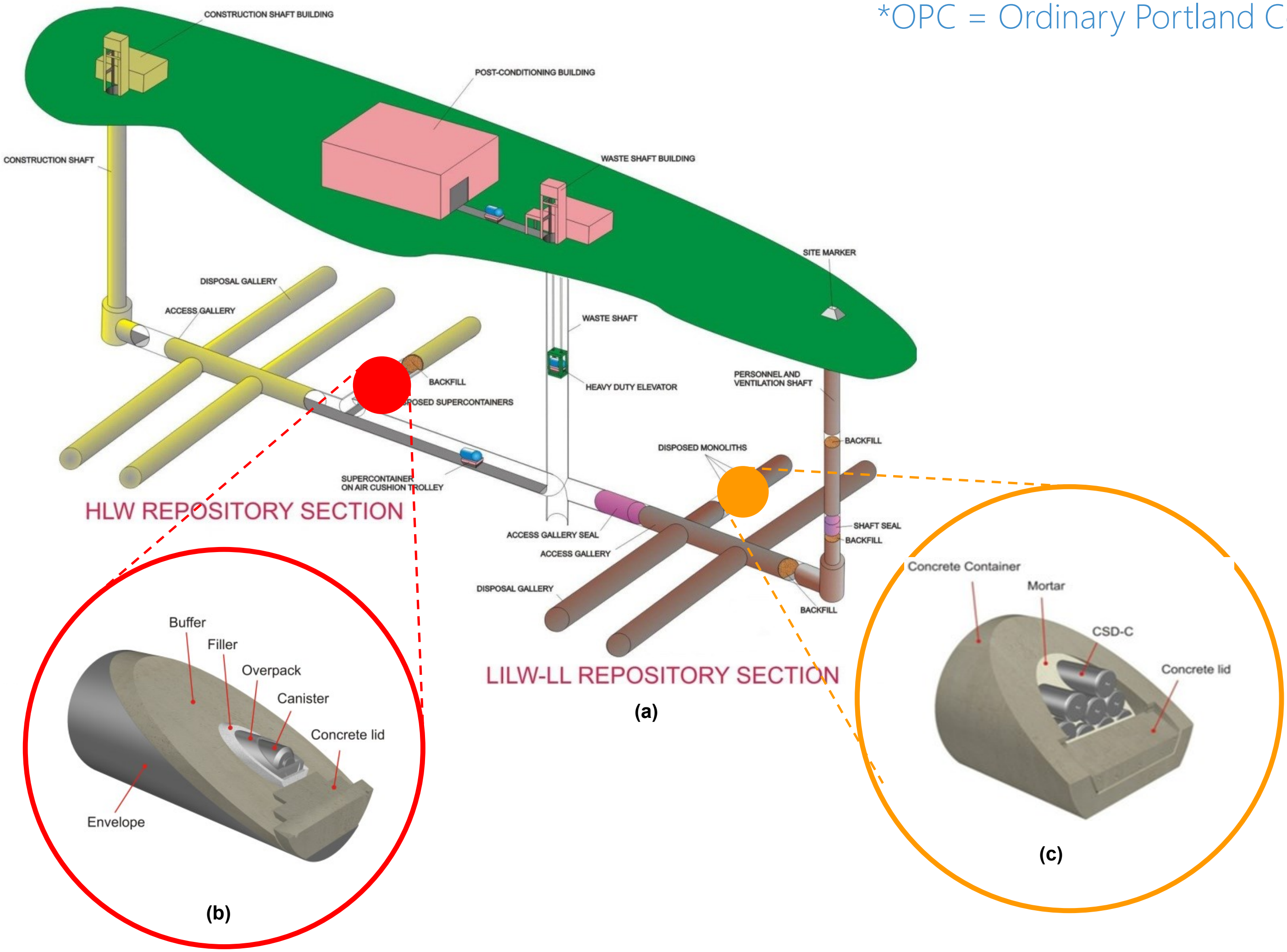
Reference Belgian geological disposal design for vitrified HLW foresees a concrete buffer with OPC*

*OPC = Ordinary Portland Cement



Why study interaction of HLW glass with cement ?

- Most countries consider geological disposal of vitrified nuclear waste and/or spent nuclear fuel
- Host rock and disposal design vary between countries
- Concrete can be present in near field as backfill material, as a construction material, as container material, or HLW can be close to ILW repository, and affected by an alkaline plume .
- Study of high pH conditions to better understand the mechanisms of secondary phase formation

Content

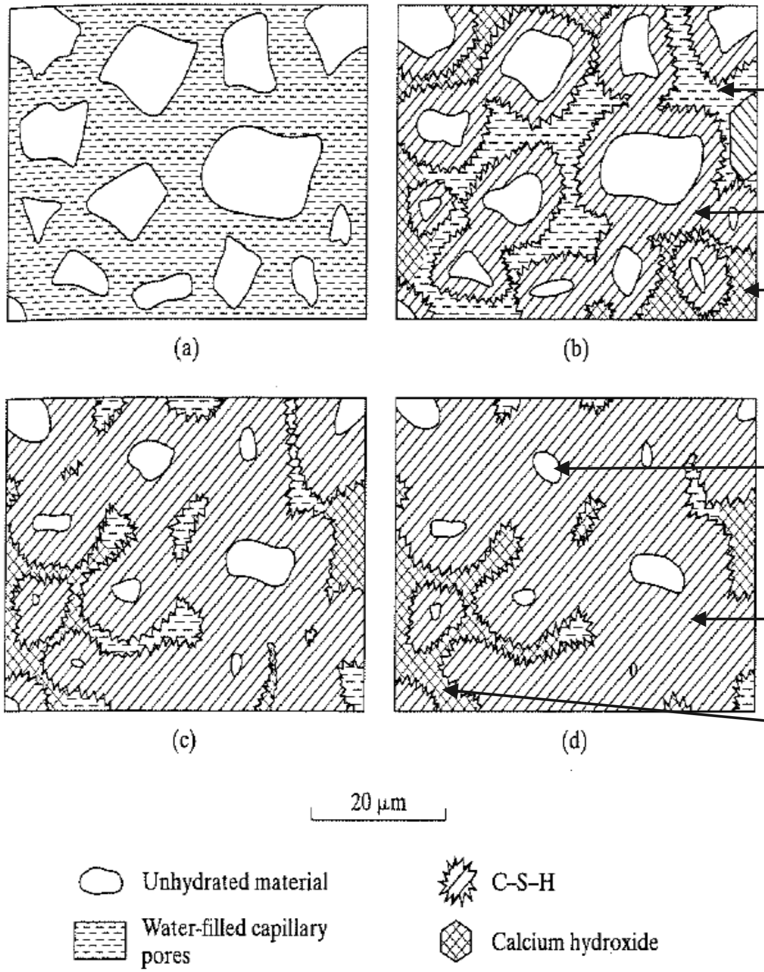
- Why study interaction of HLW glass with cement ?
- Main types of cement considered in (geological) disposal
- Effects of cement on HLW glass dissolution mechanisms
- Effect of cementitious environment on glass dissolution rate
- Possible causes of pH decrease by reactions with the glass
- Dissolution kinetics
- Summary
- Literature list

Content

Types of cement considered in (geological) disposal

- Concrete made with Ordinary Portland Cement (OPC)
  - Clinker phases ($3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $CaSO_4 \cdot 2H_2O$, K_2O, Na_2O)
  - Cement pore water has pH 13.5
- Low pH cement (addition of pozzolanic materials)
  - Cement pore water has pH ≤ 11
- Minerals in the hardened OPC paste:
  - **Calcium Silicate Hydrates (C-S-H**) (= low Ca/Si for low pH cement)
  - **Portlandite $Ca(OH)_2$** (= low for low pH cement)
  - Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O$
  - Hydrogarnet $Ca_3Al_2(OH)_{12}$
  - Hydrotalcite $Mg_4Al_2(OH)_{14}{:}3H_2O$
  - Hematite Fe_2O_3
  - **K_2O, Na_2O**

Microstructure of Portland cement paste



Water-filled pores

C-S-H

Portlandite

Unhydrated material

C-S-H

Portlandite in C-S-H matrix

FIGURE 4.7

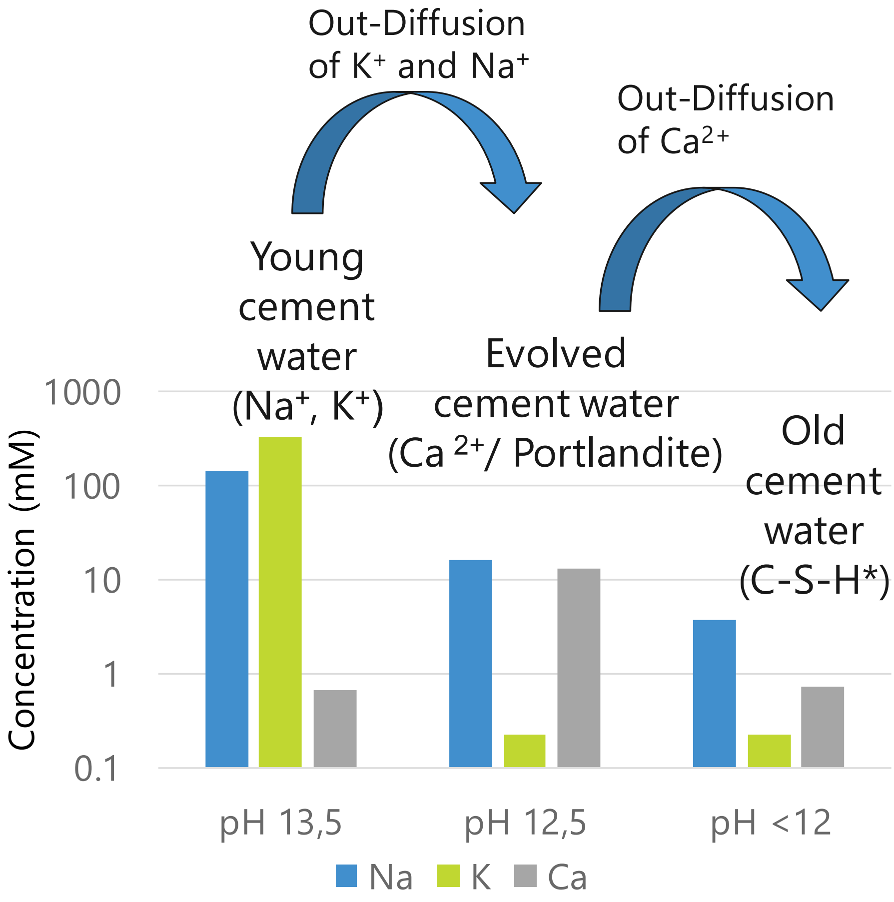
Schematic outline of microstructural development in portland cement pastes: (a) initial mix; (b) 7 days; (c) 28 days; and (d) 90 days. (Calcium sulfoaluminates are included as part of C–S–H for simplification, although they crystallize as separate phases.)

Picture taken from text book (Concrete, Mindess et al.)

Ordinary Portland Cement induces high pH

Example of evolution in contact with Boom Clay

- OPC Concrete (Cem I) : pH evolution from 13.5 → <12



Out-Diffusion of K^+ and Na^+

Out-Diffusion of Ca^{2+}

Young cement water (Na^+, K^+)

Evolved cement water (Ca^{2+}/ Portlandite)

Old cement water (C-S-H*)

*C-S-H = Calcium Silicate Hydrates

Low pH cement induces moderately alkaline pH

- Low pH concrete : addition of pozzolanic compounds
  - Siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (e.g. silica fume)
- Effect of pozzolanic compounds:
  - portlandite consumption : portlandite + silicate → C-S-H
  - OPC dilution (less portlandite per unit of volume)
  - decrease of the Ca/Si ratio of the C-S-H, which decreases their equilibrium pH and enhances their sorption capacity of alkalis
- Target pH ≤11

Content

- Why study interaction of HLW glass with cement ?
- Main types of cement considered in (geological) disposal
- Effects of cement on HLW glass dissolution mechanisms
  - Effect of high pH of pore water
    - On ion exchange
    - On Si network hydrolysis and gel formation
    - On secondary phase formation
  - Effect of cement phases on glass alteration
- Effect of cementitious environment on glass dissolution rate
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Main glass dissolution mechanisms

- $\equiv Si\text{-}O\text{-}A + H_3O^+ \rightarrow Si\text{-}OH + A^+ + H_2O$ (ion exchange)
  $\equiv Si\text{-}O\text{-}A + H_2O \rightarrow Si\text{-}OH + A^+ + OH^-$
- $\equiv Si\text{-}O\text{-}Si\equiv + H_2O \rightarrow 2 \equiv Si\text{-}OH$ (hydrolysis)
  $\equiv Si\text{-}O\text{-}Si(OH)_3 + H_2O \rightarrow \equiv Si\text{-}OH + H_4SiO_4$
- $\equiv Si\text{-}OH + \equiv Si\text{-}OH \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$ (condensation)

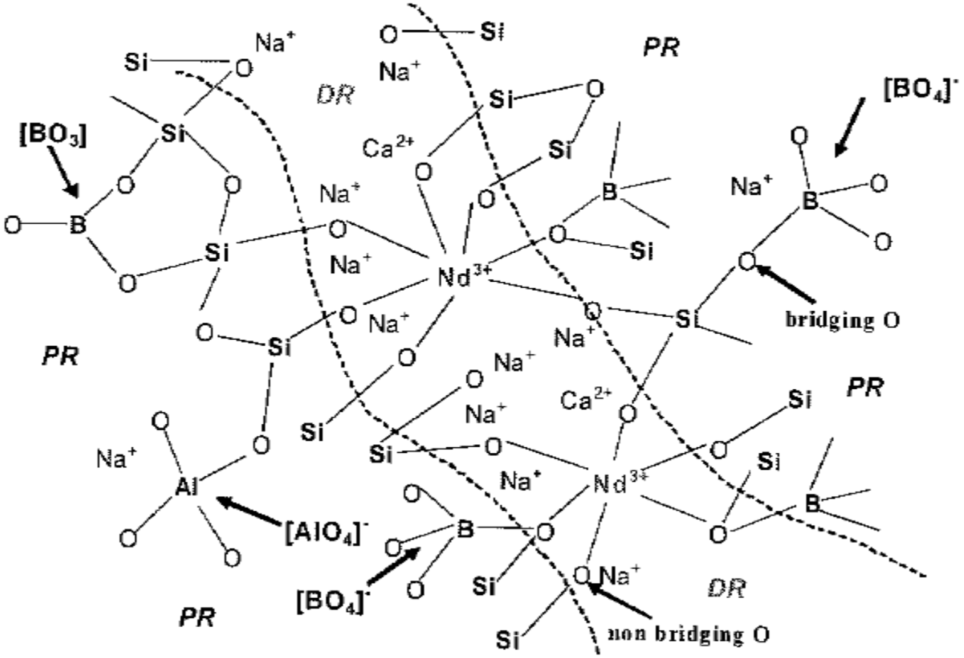


Illustration from Caurant et al. 2009

Ion exchange rate decreases at high pH

- $\equiv$Si-O-A + H_3O^+ → Si-OH + A^+ + H_2O (ion exchange)

- The interdiffusion coefficient for H_3O^+ and cations and the release rate by interdiffusion decreases with pH (Ojovan et al., 2007).

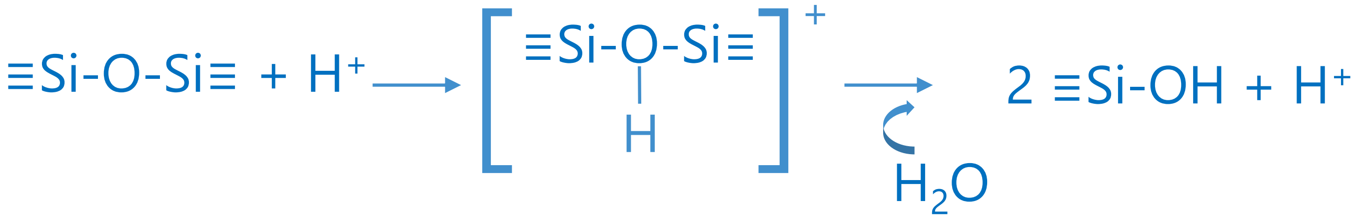
$$D_{iH} \approx \alpha_i D_H 10^{-pH}$$

$$rx_i = \rho f_i\left(\frac{\alpha_i D_{0H}}{\pi t}\right)^{0,5} 10^{-0.5pH} \exp\left(\frac{-E_{di}}{2RT}\right)$$

- Ion exchange only relevant below pH 10
  - → At higher pH, most Na or Li are released by matrix dissolution
- Local network reorganization causes dissolution and out-diffusion of boron → diffusion coefficient of boron in SON68 decreases for increasing pH between pH 8 and 10 (30 – 50 – 90°C) (Chave et al., 2007).

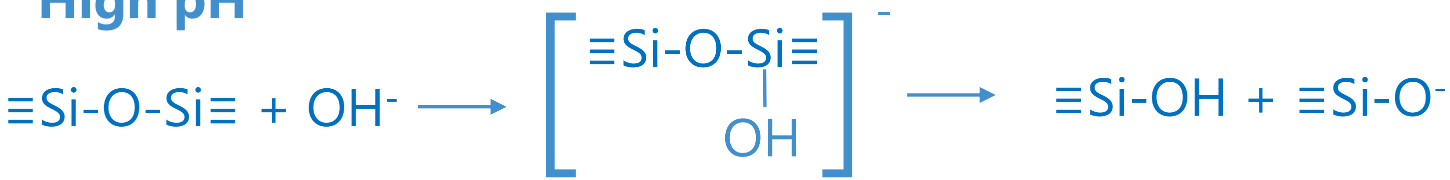
Hydrolysis of silica network catalyzed by H^+ and OH^-

Low pH



$$\equiv Si\text{-}O\text{-}Si\equiv \ + \ H^+ \longrightarrow \left[\ \equiv Si\text{-}\underset{\underset{H}{|}}{O}\text{-}Si\equiv\ \right]^+ \xrightarrow[H_2O]{} 2 \ \equiv Si\text{-}OH \ + \ H^+$$

High pH



$$\equiv Si\text{-}O\text{-}Si\equiv \ + \ OH^- \longrightarrow \left[\ \equiv Si\text{-}O\text{-}\underset{\underset{OH}{|}}{Si}\equiv\ \right]^- \longrightarrow \ \equiv Si\text{-}OH \ + \ \equiv Si\text{-}O^-$$

High pH of cement water accelerates hydrolysis

Equation for SON68 in range 25 – 100 °C and pH 6 - 10

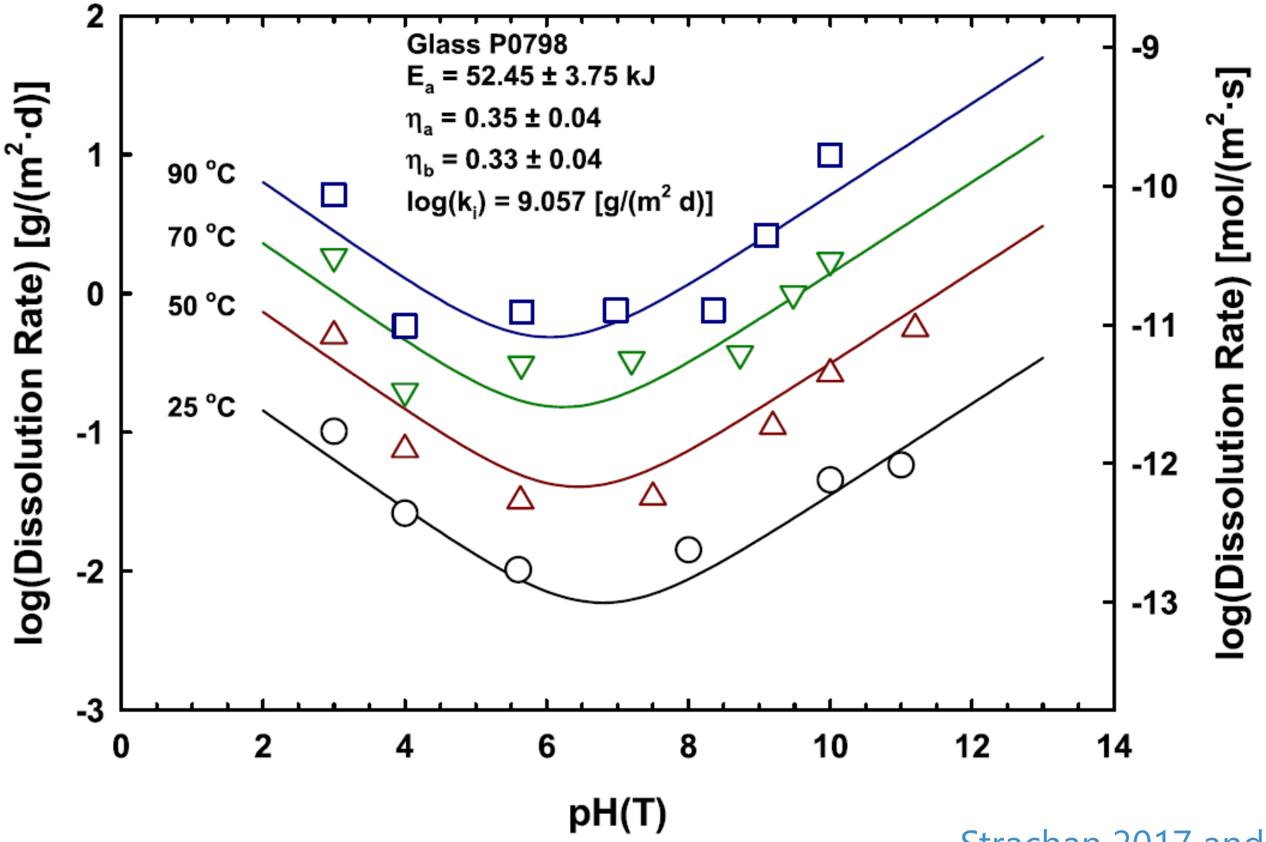
$$\mathbf{r_0\ (T,\ pH) = k_+\ [H^+]^n\ e^{-Ea/RT}}$$

r_0 = forward rate ($g \cdot m^{-2} \cdot d^{-1}$); $k_+ = 1.2 \times 10^8$ ($g \cdot m^{-2} \cdot d^{-1}$); $n = -0.4$; $E_a = 76\ kJ \cdot mol^{-1}$;
$R = 8.31 \times 10^{-3}\ kJ \cdot mol^{-1} \cdot K^{-1}$

(source: Frugier, 2008)

Hydrolysis catalyzed by H^+ and OH^-

Illustration for glass PO798



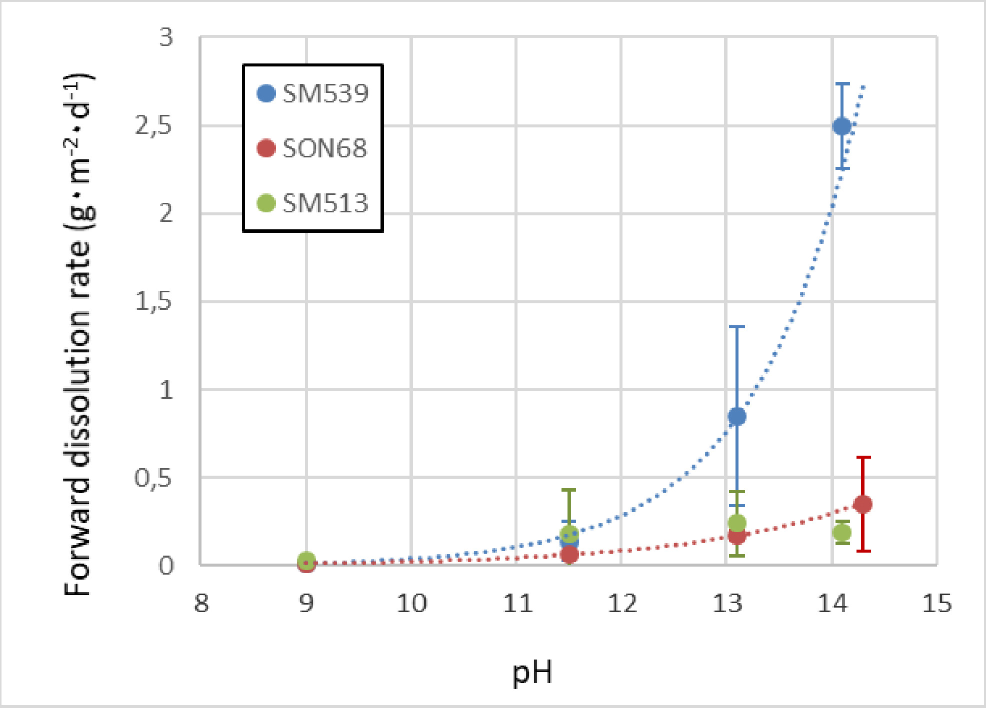
Strachan 2017 and Inagaki 2006

Effect of high pH on forward dissolution rate (~on hydrolysis) depends on glass composition

- Stronger pH effect for Al-rich glass SM539
- Weaker pH effect for Si-rich glass SM513

(wt%)	SON68	SM539	SM513
SiO_2	45.48	35.28	52.15
Al_2O_3	4.91	19.83	3.61
Na_2O	9.86	9.21	9.12
CaO	4.04	5.05	5.54
B_2O_3	14.02	25.58	13.08
Others	21.69	5.05	16.50

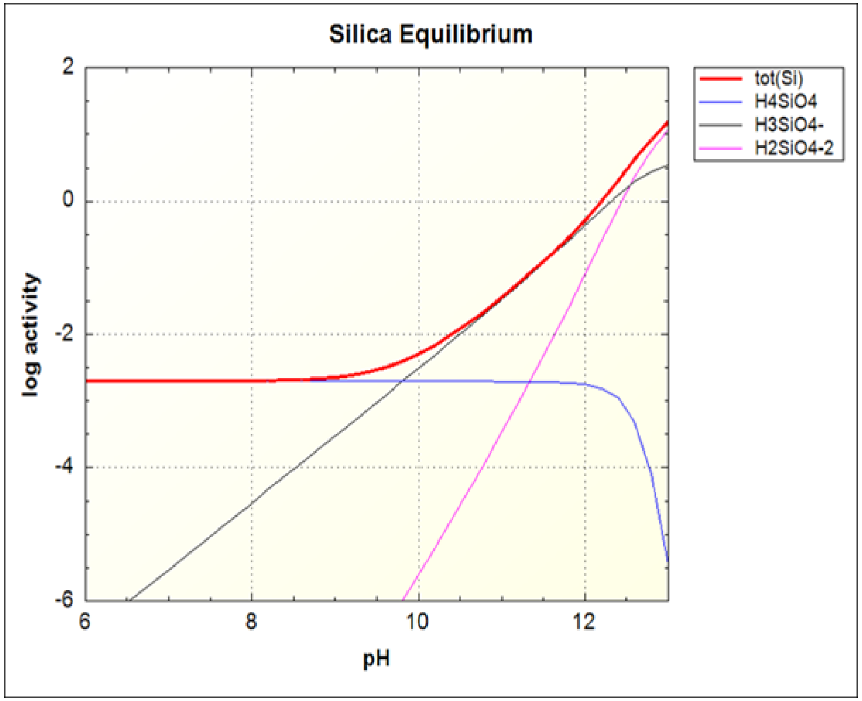
Tests at 30°C



Gel formation (condensation) decreases at high pH

$\equiv Si\text{-}OH + \equiv Si\text{-}OH \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$

- Increase of SiO_2 solubility with increasing pH
- $\equiv Si\text{-}O\text{-}Si(OH)_3 + H_2O \rightarrow \equiv Si\text{-}OH + H_4SiO_4$

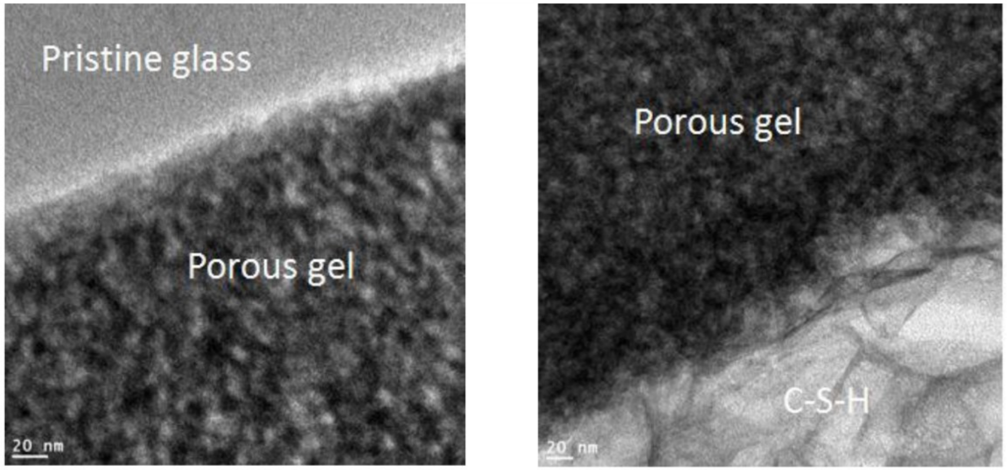


Solubility of amorphous silica as a function of pH at 25 °C

- Less Si retention, porous gel with little protective properties

Example of porous alteration gel with little protective properties

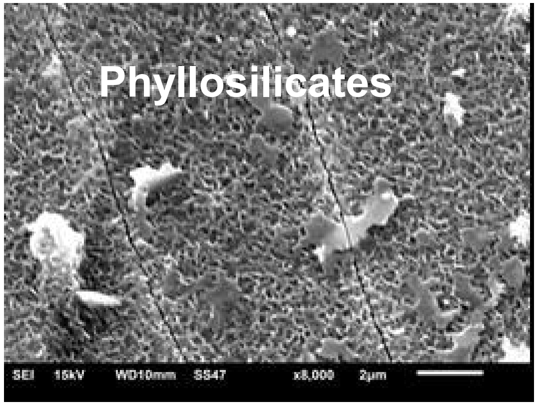
- Pores around 10 nm, 2-5 times larger than in gels formed at neutral pH
- Homogeneously distributed and interconnected
- Fast transport of water molecules through the gel

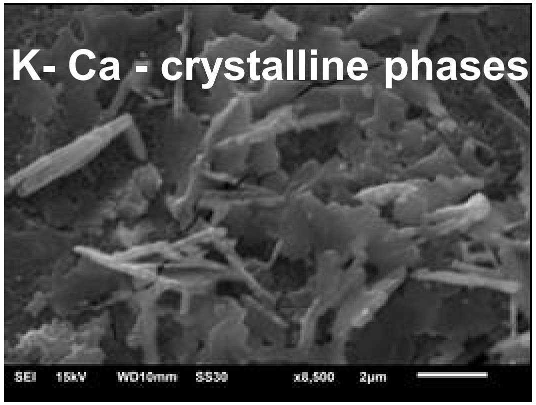


HRTEM micrographs of SON68 glass powder in contact with hardened OPC paste powder after 713 days at 30°C. (left) pristine glass/gel interface, (right) the glass gel/C-S-H interface (Ferrand et al., 2013)

Effect of high pH on secondary phase formation

- pH < 10 : (crystalline) secondary minerals of the phyllosilicate type and calcium and rare-earth phosphates (for SON68)
  - Low residual dissolution rate
- pH > 10 : zeolites and C-S-H phases are observed on top of the phyllosilicate layer for SON68
  - → Alteration resumption
- More amorphous phases at low temp.
- Precipitation accelerated at high temp.
- Precipitation accelerated at higher pH

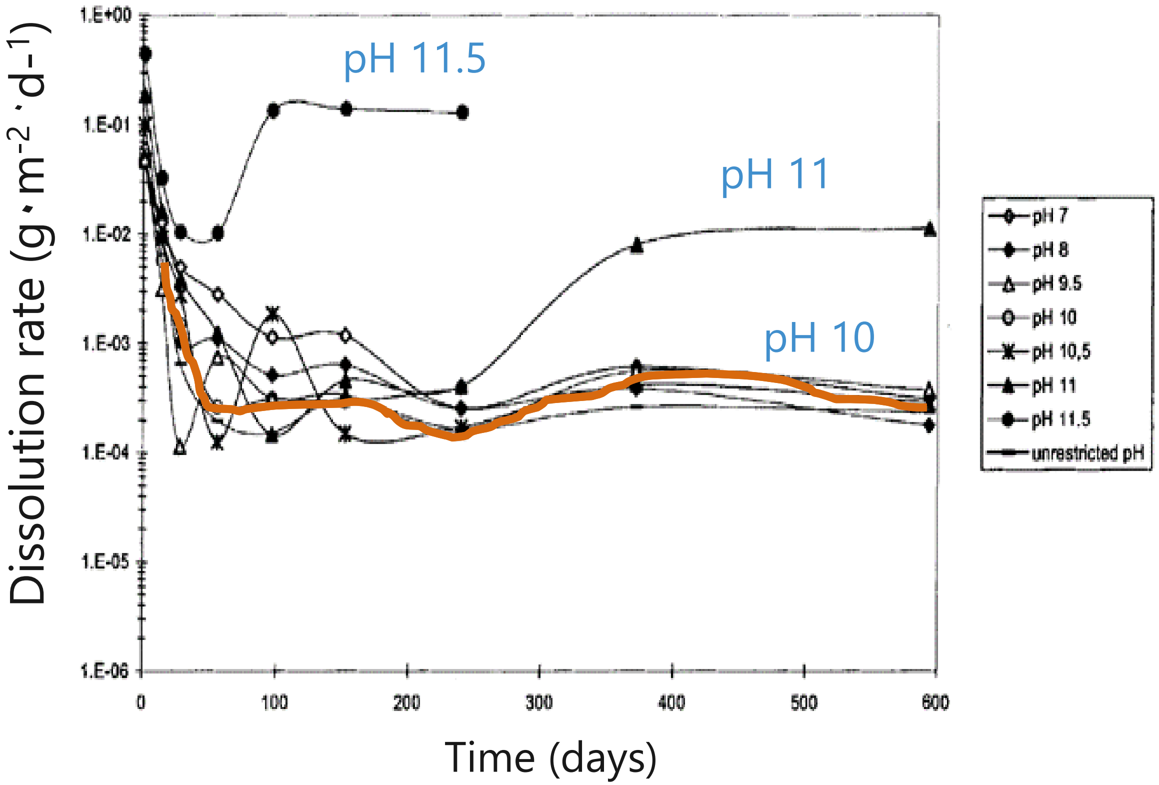




Overview in Fournier, M., Gin, S. and Frugier, P. (2014) Resumption of nuclear glass alteration : State of the art, Journal of Nuclear Materials 448, pp. 348-363.

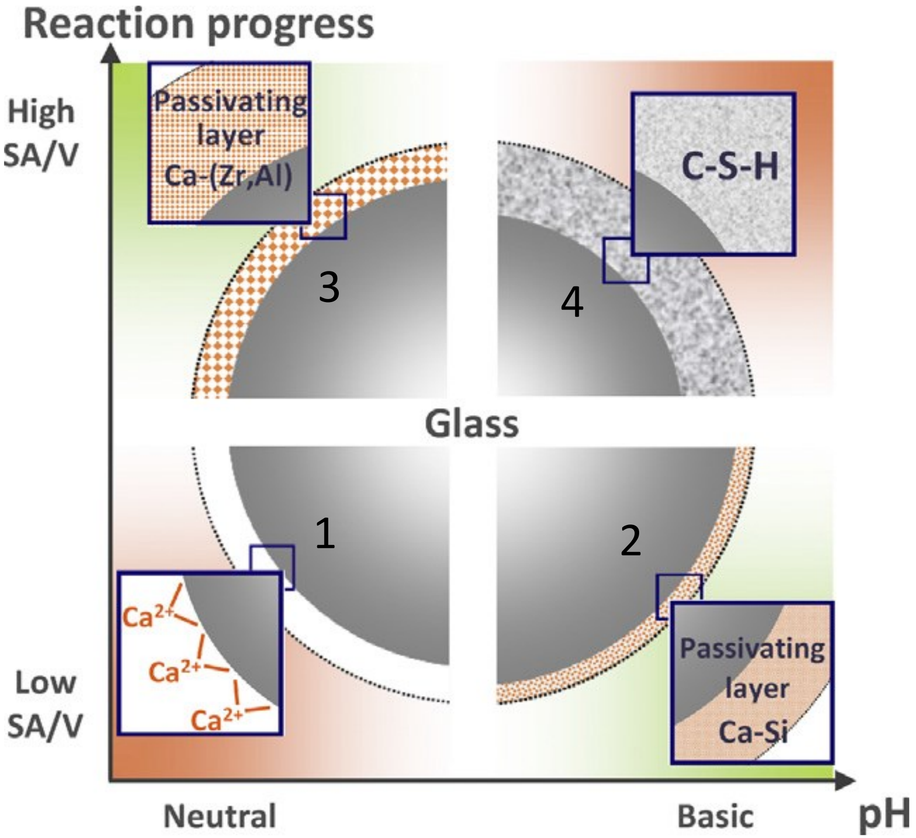
Effect of high pH on secondary phase formation

- pH > 10.5 : alteration resumption for SON68 at 90°C



SON68 dissolution rate as a function of time in buffered KOH of pH 7 – 11.5 at 90 °C (Gin and Mestre, 2001)

Effect of Ca on the HLW glass alteration



Schematic presentation of the four main glass alteration mechanisms in presence of Ca, depending on the alteration conditions, i.e. pH and reaction progress. Green and red shading symbolize the dissolution rate decreasing and increasing effects of Ca on glass alteration, respectively. Picture taken from Mercado-Depierre et al. (2013).

Summary of effects of high pH

- Ion exchange rate becomes low
- Hydrolysis rate increases
- Condensation in gel decreases
- Secondary phase formation is promoted

→ Overall dissolution rate increasing effect

→ Ca may favor or slow down hydrolysis

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- Effects of cement on HLW glass dissolution mechanisms
  - Effect of high pH of pore water
  - Effect of Ca on HLW glass alteration
  - Effect of cement phases on glass alteration
    - C-(A)-S-H formation, Si enrichment of C-S-H, Alkali-Silica Reaction
    - Alteration layers at glass / concrete interface
- Effect of cementitious environment on glass dissolution rate
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Effect of cement phases on glass dissolution
Formation of typical phases

- C-S-H and C-A-S-H formation

$1.6\ Ca(OH)_2 + H_4SiO_4 = Ca_{1.6}\ SiO_{3.6} : 2.58\ H_2O + 1.02\ H_2O$

$1.4\ Ca^{2+} + Ca_{1.6}\ SiO_{3.6} : 2.58\ H_2O + 2\ Al^{3+} + 8\ H_2O = Ca_3Al_2(SiO_4)(OH)_8 + 8.8\ H^+ + 2.18\ H_2O$

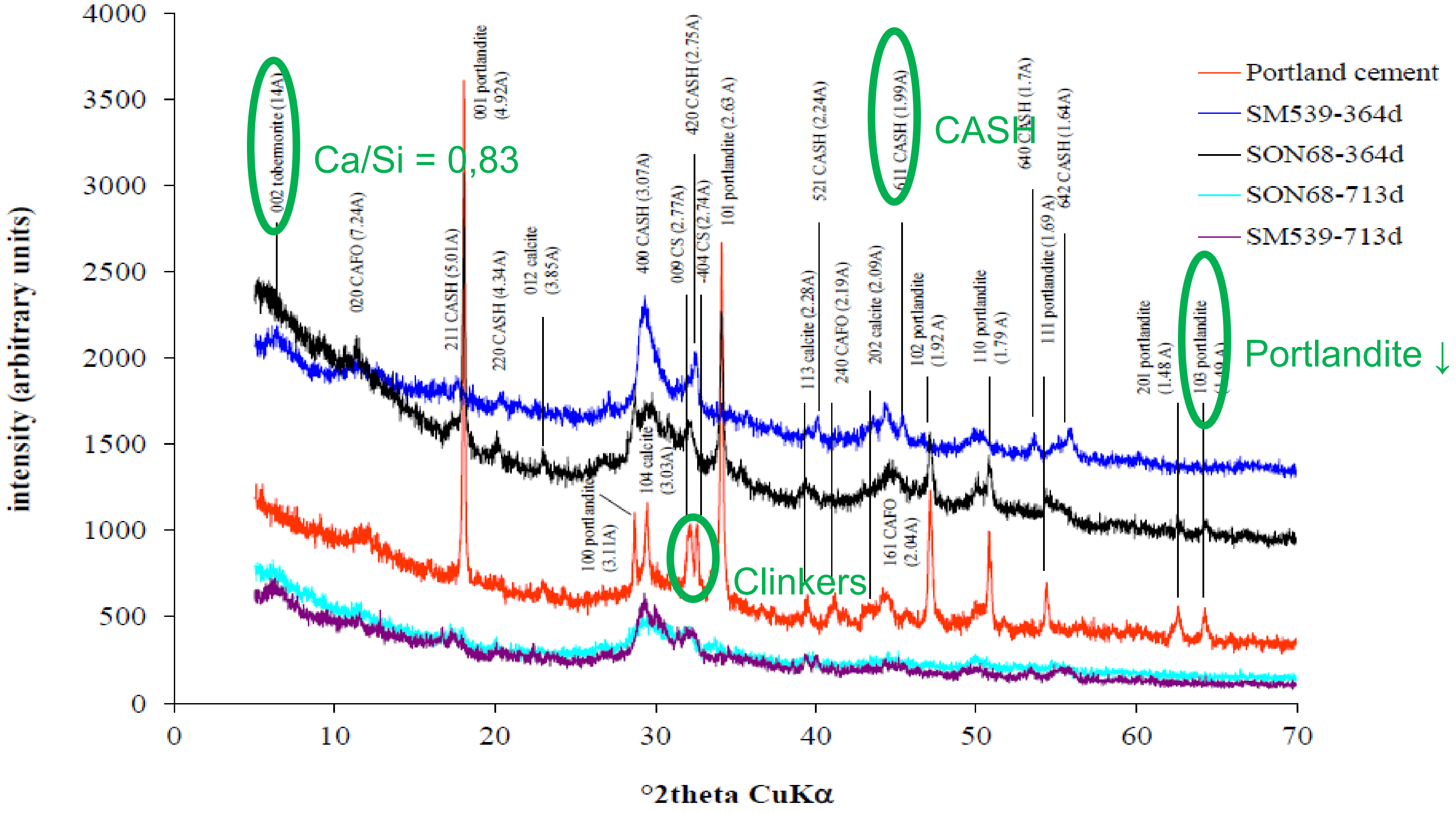
(katoite)

- Si-enrichment of C-S-H phases
  - Ca/Si ratio in OPC cement 1.2 - 2 (Si-poor)
  - By enrichment with glass Si: Si-poor C-S-H → Si-rich C-S-H (low Ca/Si)

- Formation of alkali-silica-reaction (ASR) gel
  - Advanced hydrolysis of Si-O-Si linkages
  - ≡Si-O$^-$ balanced by Na$^+$ and K$^+$
  - Swelling by water absorption

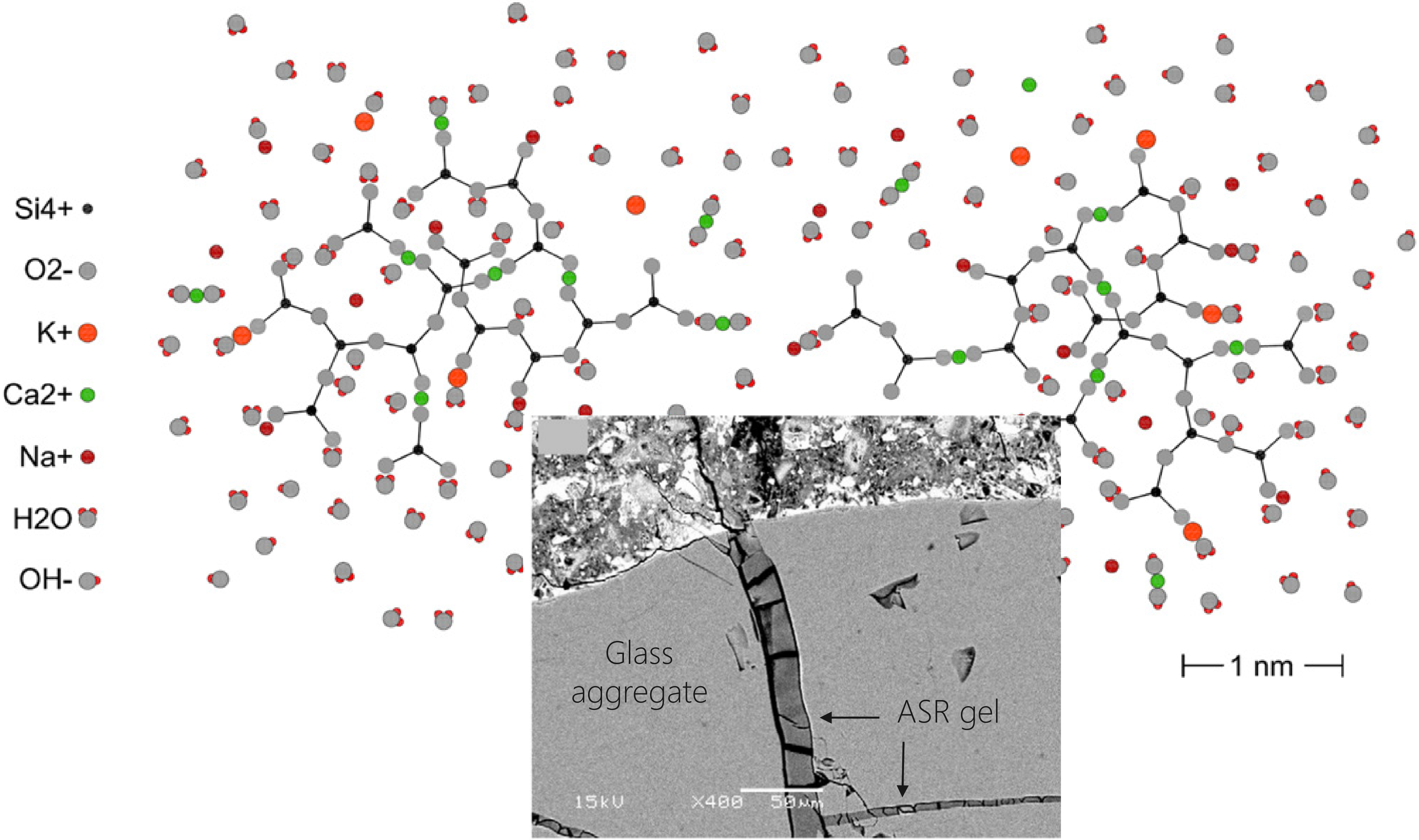
Results from experiments of glass with cement:

XRD patterns of altered glass/cement powder mixtures (30°C)



Structure of ASR gel

(from Rajabipour, 2015)



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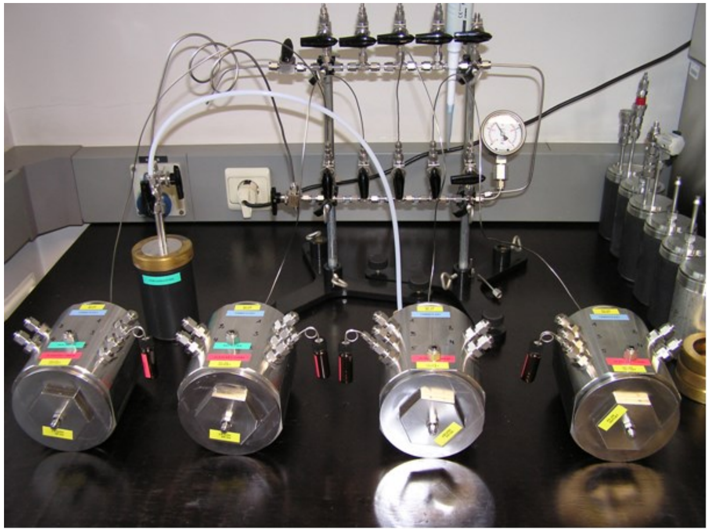
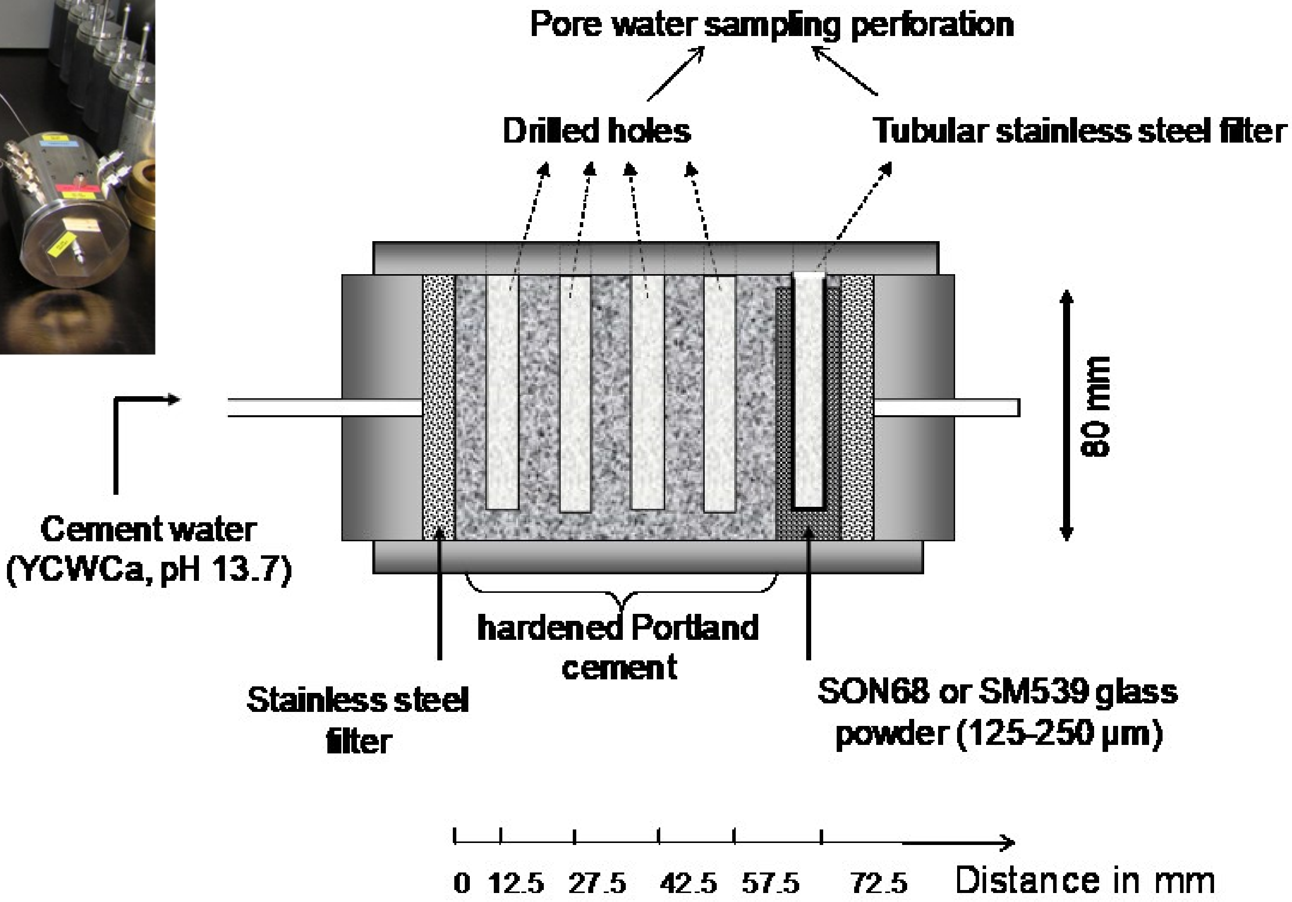
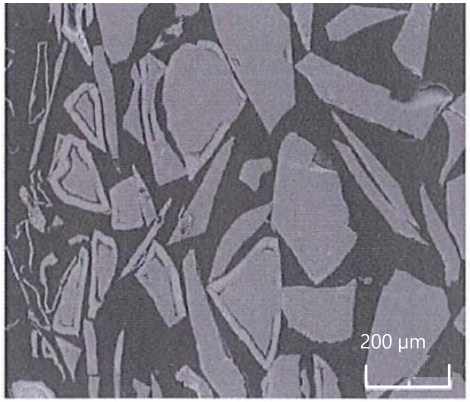
Mock-up test to study glass/concrete interface

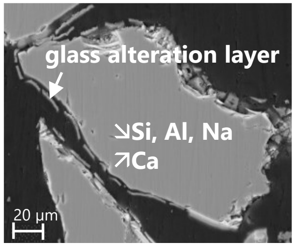


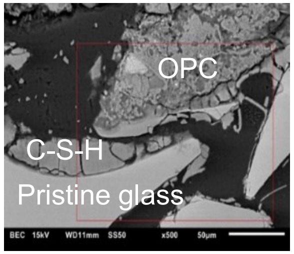


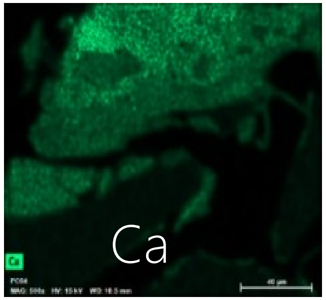
Dissolution behavior of the glass

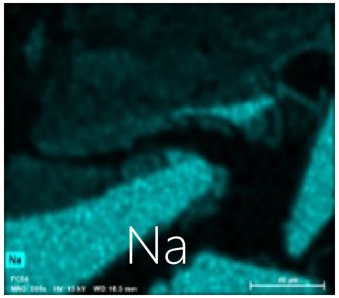
- After 30 months, glass particles are much more altered within 300 - 400 µm from interface with cement following K evolution

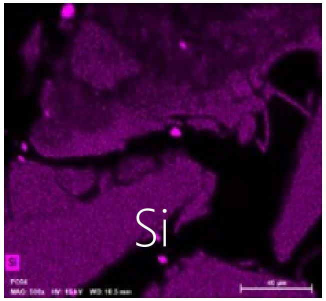


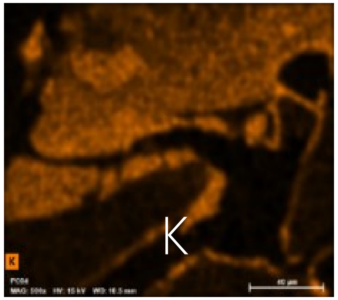












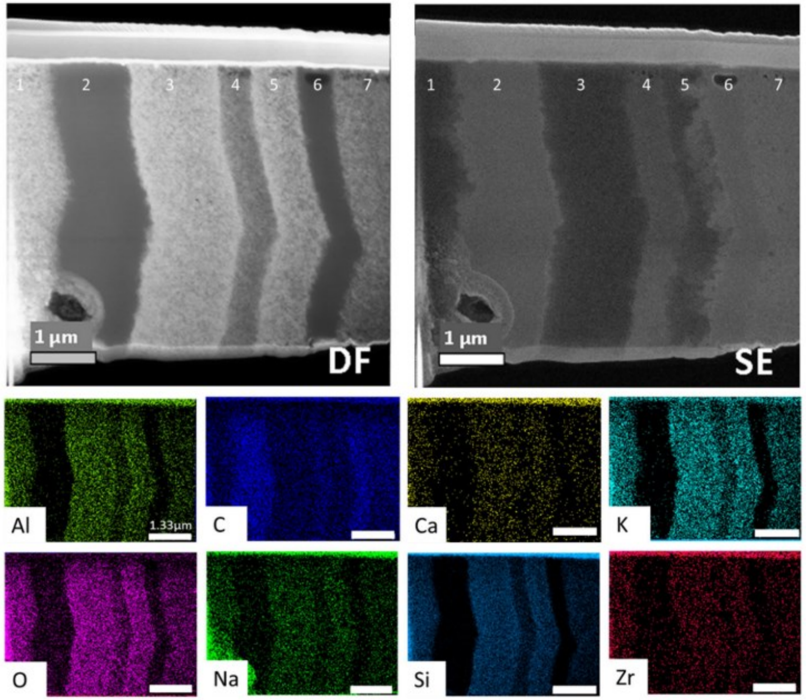
- Thin alteration layer (< 2 µm)
- C-(A)-S-H phases incorporating alkali

Dissolution behavior of the glass

- For Al rich glass SM539: lamellar layers
- Similar observations with ISG in Young Cement Water at 70°C
- Compatible with alternative, dissolution/precipitation model

SM539

International Simplified Glass



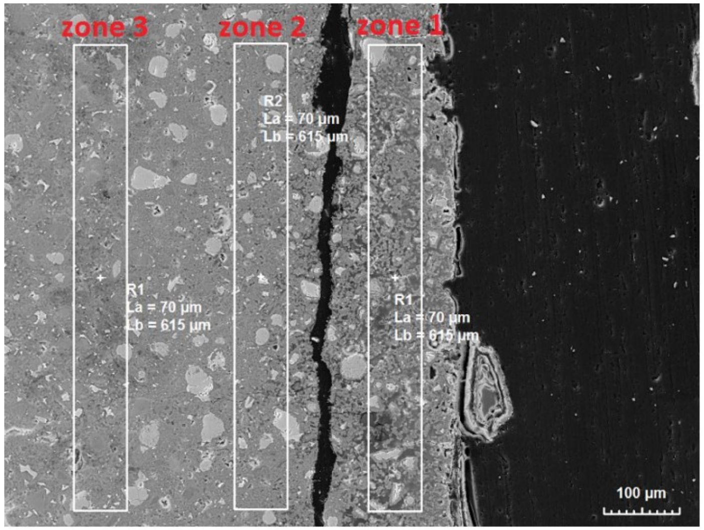
Scanning Transmission Electron Microscopy analyses

Mann et al., 2019

Observation on the concrete side

- Changes in composition and microstructure on a few hundred micrometers

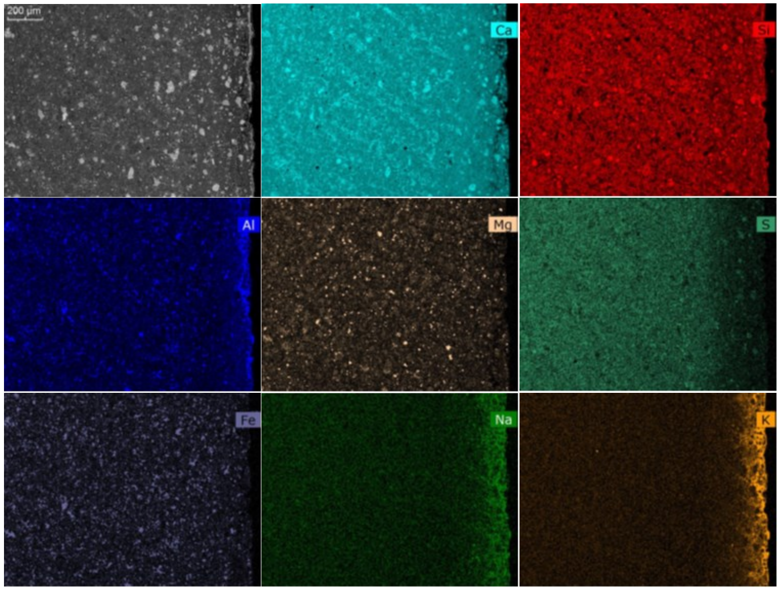
OPC paste in contact with SM539



Typical features reported in cement chemistry

- ➢ Opening of the cement porosity
  - ❑ portlandite and C-S-H dissolution

OPC paste in contact with SM539

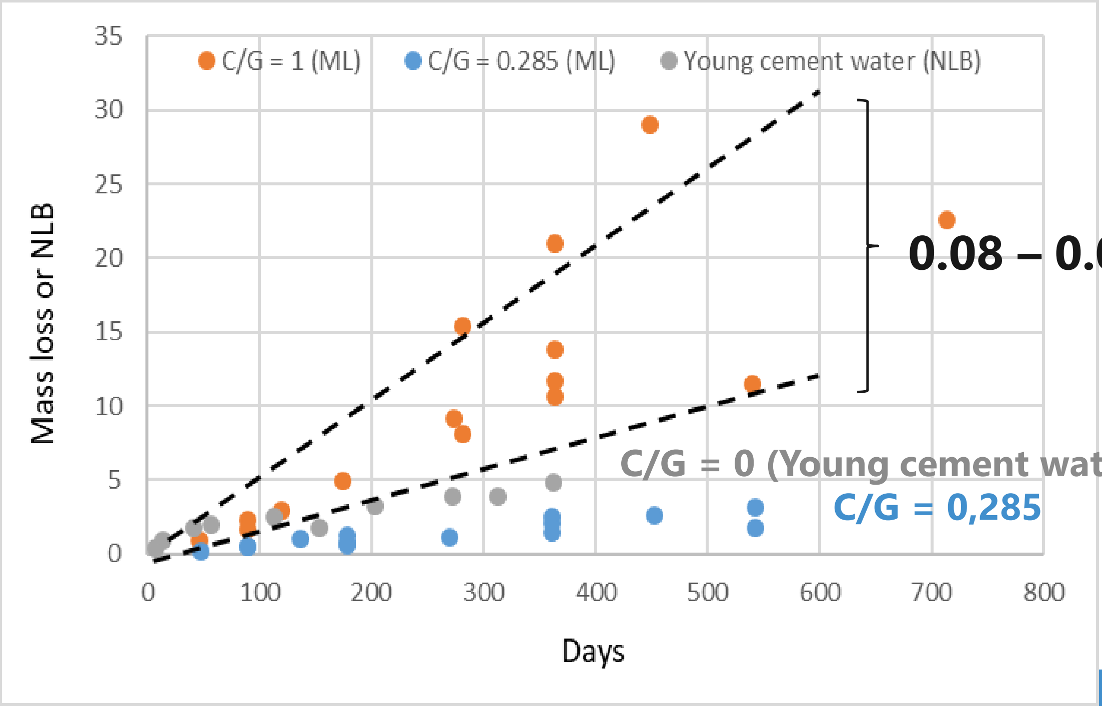


- ➢ Enrichment in Si, (Al), K and Na and depletion in Ca, Mg and S
  - ❑ Dissolution of Calcium Aluminate mono or tri-sulfate (ettringite)
  - ❑ C-S-H and C-A-S-H formation
  - ❑ Alkalis (and Al) binding by C-S-H phases

Content

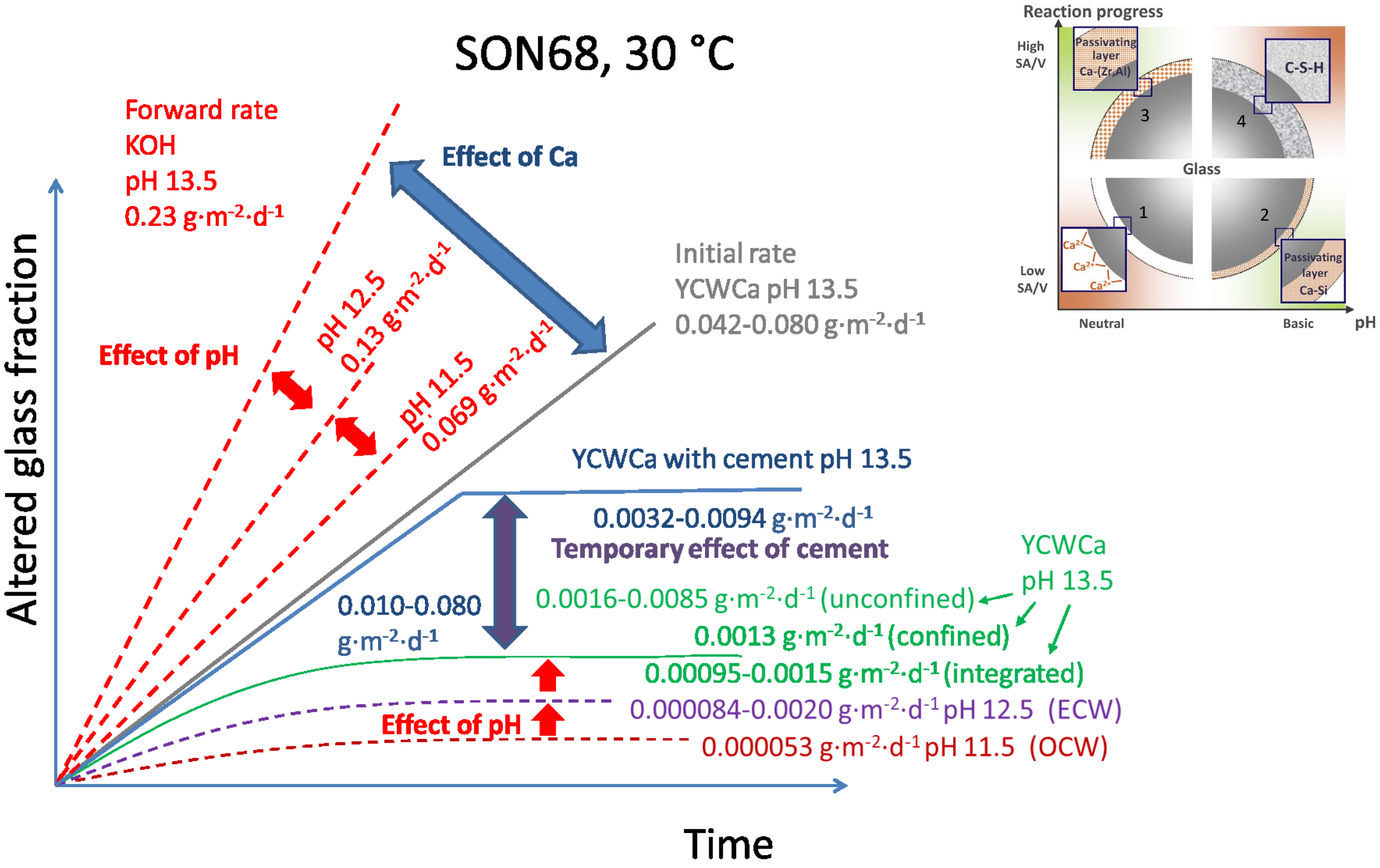
Portlandite reacts with glass matrix and triggers further glass dissolution

- SON68 powder in contact with hardened OPC paste powder in young cement water (pH 13.5)
  - Dissolution rate increases when cement/glass ratio increases
  - It approaches maximum rate of hydrolysis (0.02 – 0.08 g·m^{-2}·d^{-1}) when cement/glass ratio increases to 1/1
  - Dissolution rate low cement/glass ratio ≈ young cement water without cement



0.08 – 0.02 g·m^{-2}·d^{-1}

Summary of SON68 dissolution rates in cementitious conditions



(Lemmens and Ferrand, 2019)

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Possible causes of pH decrease by reactions with the glass

- Consumption of OH^- by hydrolysis of borosilicate network

$$\equiv Si\text{-}O\text{-}Si\equiv \ + \ 2\,OH^- \rightarrow 2\,\equiv Si\text{-}O^- + H_2O$$

$$\equiv Si\text{-}O^- + 3\,(OH^-)_{aq} \leftrightarrow (H_3SiO_4^-)_{aq}$$

$$(=B\text{-}OH)_s + 2\,(OH^-)_{aq} \leftrightarrow (B(OH)_3)_{aq}$$

(dissolving species leave Si-O^- groups on the solid surface to charge balance, not shown in the equation)

- Dissociation of the $H_3SiO_4^-$ and H_3BO_3

$$H_3SiO_4^- \leftrightarrow H_2SiO_4^{2-} + H^+$$

$$H_3BO_3 \leftrightarrow H_2BO_3^- + H^+$$

- Formation of secondary phases consuming OH^- and Na^+, K^+ or Ca^{2+}

$5\,Ca^{2+} + 6\,HSiO_3^- + 4\,OH^- + 5.5\,H_2O \dashrightarrow Ca_5Si_6H_{21}O_{27.5}$ (Tobermorite)

- Reactions with opposite effect (pH increase):

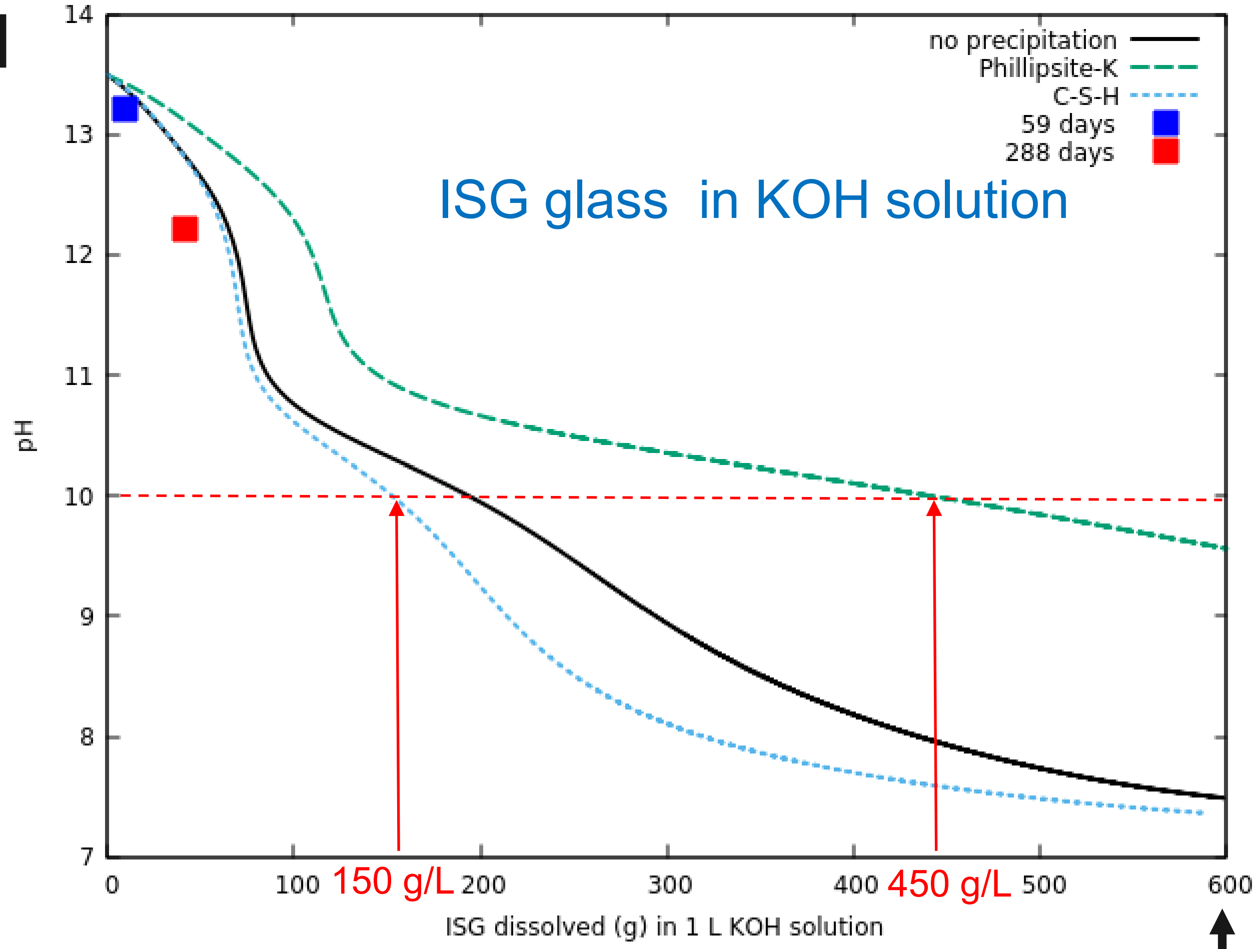
Ion exchange: $\equiv Si\text{-}O\text{-}Na + H_2O \leftrightarrow Si\text{-}O\text{-}H + Na^+ + OH^-$

Zeolite precipitation : $K^+ + Al(OH)_4^- + 3\,H_2SiO_4^{2-} \rightarrow KAlSi_3O_8 + 6\,OH^- + 2\,H_2O$

(phillipsite)

Calculations with PHREEQC (Thermochimie database, 30°C)

pH

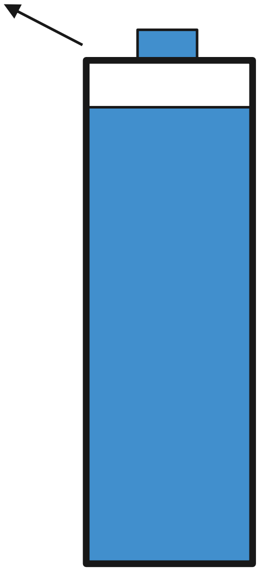


Reaction progress

Complete dissolution

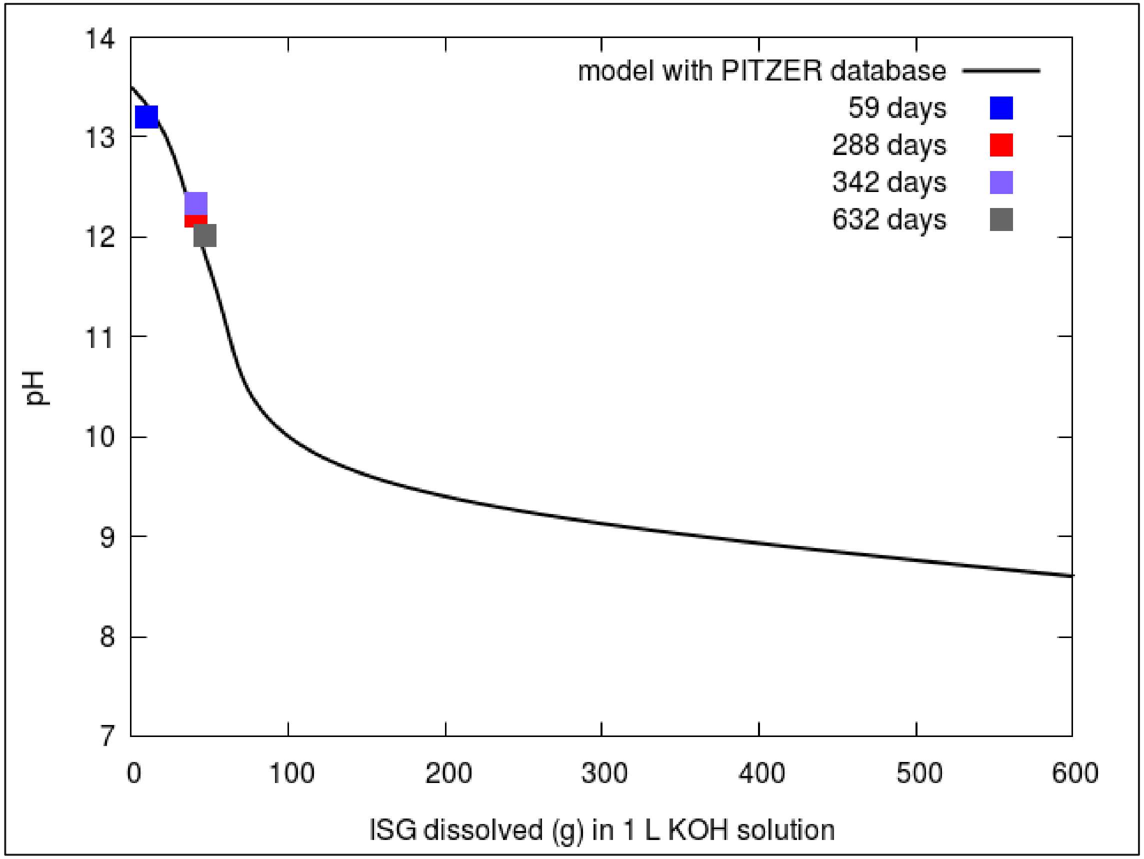
450 g/L x 25 L space in waste container
= 11,25 kg glass
= 3% of glass block

Total volume 175 L
Useful volume 150 L



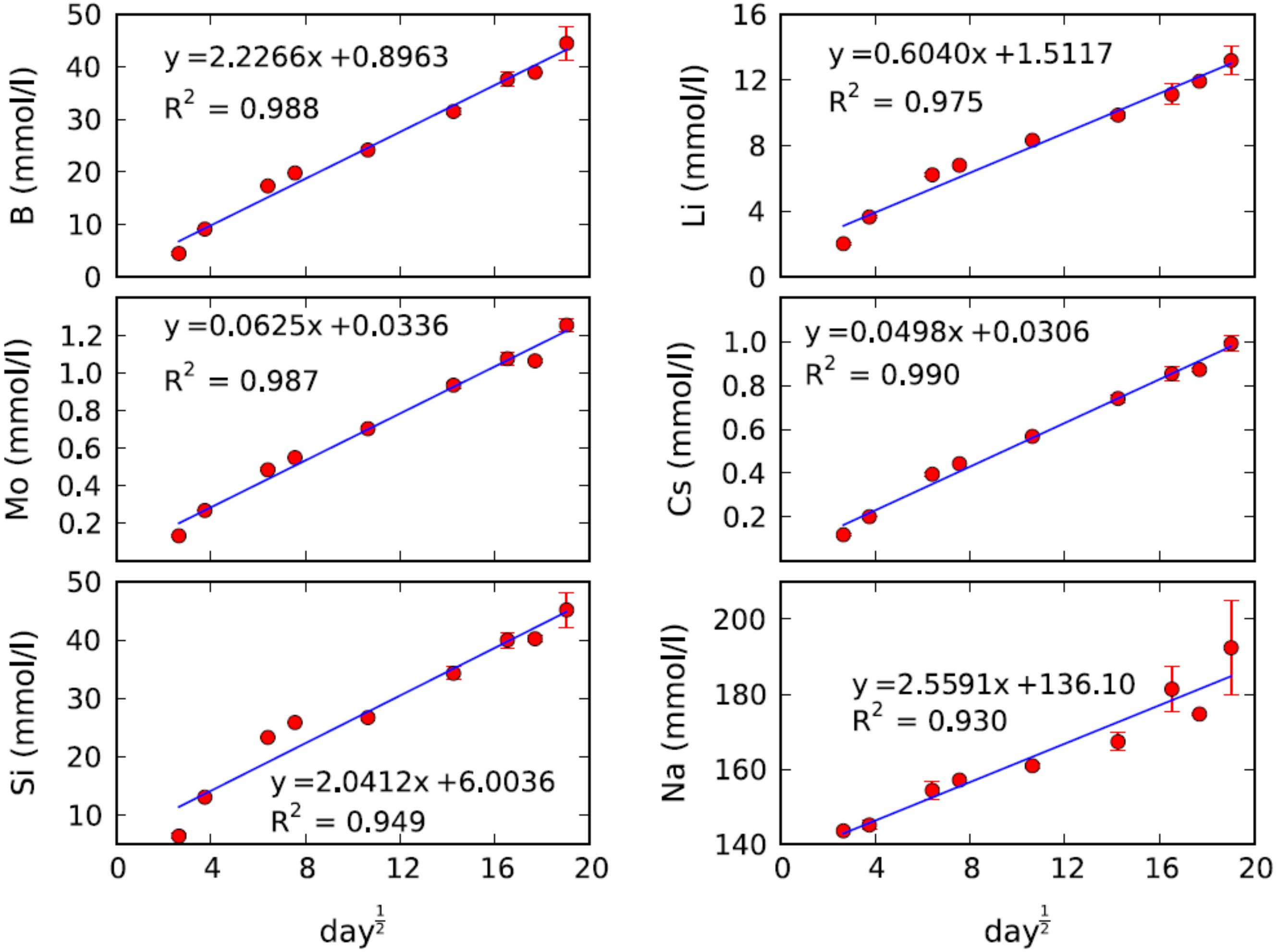
Latest calculation can explain pH decrease without precipitation

- ISG glass in KOH solution (Ca-borate precipitation ?)



Content

Dissolution in cement water at pH 13.5 could be explained by diffusion law

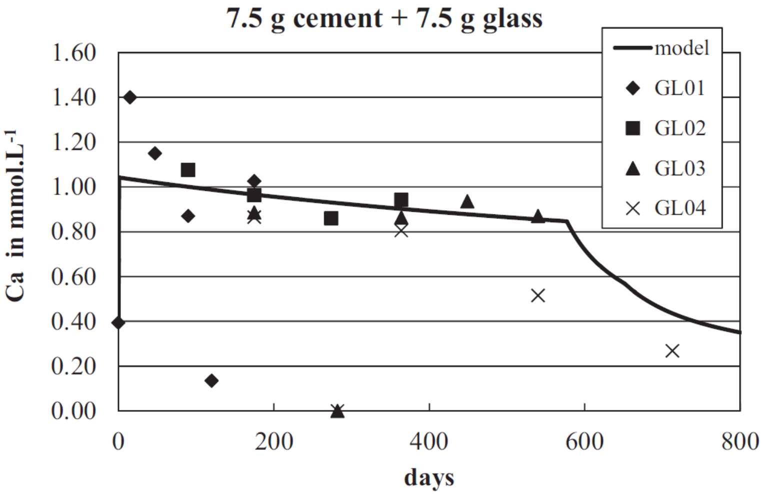


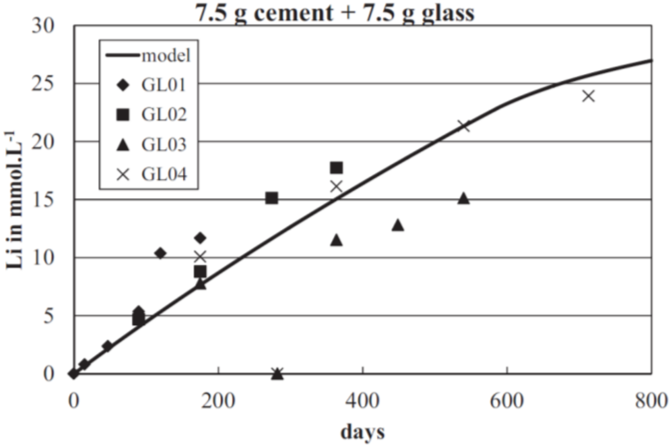
$$\frac{dC_i}{dt} = \frac{A\rho}{VM_i} x_i \sqrt{\frac{D_i}{\pi t}}$$

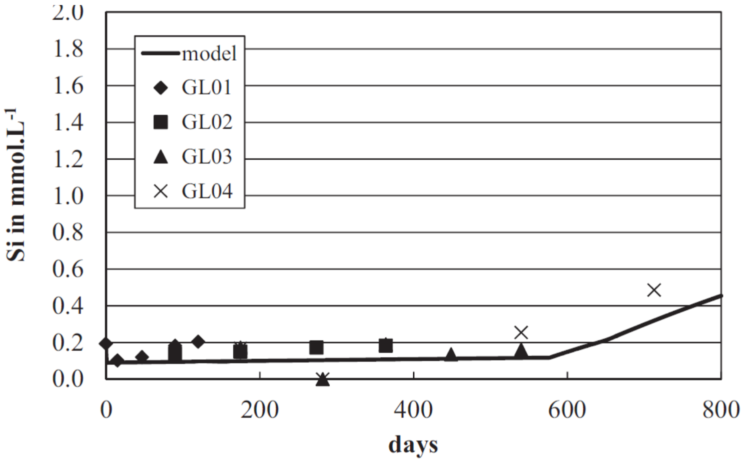
Elemental concentrations vs square root of time at 30 °C for tests with SON68 in YCWCa at SA/V = 2412 m^{-1}. The good fit with the straight line suggests that the release is diffusion controlled (Liu et al., 2015).

Dissolution in cement water with cement at pH 13.5 could be explained by Ca triggered congruent dissolution

$$\frac{dM}{dt} = -r_0 \frac{A_0}{V}\left(\frac{m}{m_0}\right)^{2/3}\frac{[Ca^{2+}]}{[Ca^{2+}_{portlandite}]}\left(1-\frac{Si}{Si_{sat}}\right)$$







- [Ca] initially imposed by portlandite (1.4 mM)
- [Ca] decrease due to C-S-H formation
- [Si] controlled by C-S-H
- Gradual portlandite consumption
- Threshold [Ca] = 0.4 mM

Ferrand 2013

Congruent dissolution of SON68
Alteration layers of few nm to 3 µm

364 days, 30°C, cement

540 days, 30°C, cement,
local precipitation layer

Summary

- Cementitious conditions (high pH, cement phases) tend to increase glass dissolution rate
- Dissolution rate decreases with time in the parametrical experiments, and is expected to decrease in more realistic conditions
- Dissolution rate decreases due to
  - Diffusion limited kinetics (protective alteration layers ?)
  - pH decrease (at high SA/V)
  - Consumption of portlandite by C-S-H formation
  - Decrease of porosity of concrete by C-S-H formation (?)
- Formation of porous alteration layers and C-S-H on the glass
- Sometimes multilayer formation on glass
- Dissolution processes are highly coupled (dissolution/precipitation/diffusion)
- Low dissolution rates possible if pH decreases to 11.5 at 30°C (10.5 at 90°C)
- Risk of alteration resumption

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Thank you for your attention

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