SCM dissolution – probing the impact of solution chemistry

R. Snellings

LMC, EPFL

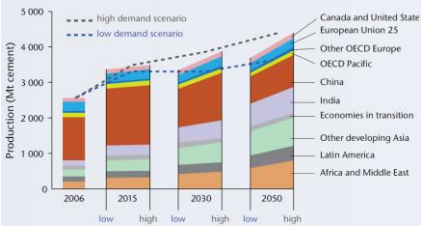
Gems workshop 2014
Dübendorf, 8th of May 2014

SCMs - some figures

- Global cement production ± **3.7 Gton** (USGS, 2012)
- Global clinker factor **0.77** (2010)

± 520 Mton of SCMs/fillers p.a.

- **BFS**
  - **290 Mt** produced (USGS, 2013)
  - Fully used
- **FA**
  - **670 Mt** produced (WCA, 2013)
  - ± 1/3 used
- **AC/P**
  - Activated clays, pozzolans
  - Large deposits, widespread
- **LL**
  - Limestone ternary blended cements
  - **4%** of earth crust



(WBCSD, 2009)

SCMs - outstanding questions

Small improvements have large impacts

- SCM replacement is limited by reactivity
- Supplies of highly reactive SCMs are limited

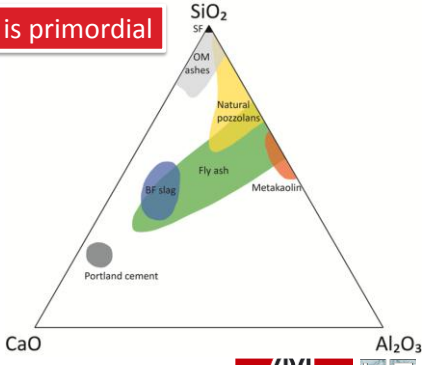
SCM reactivity enhancement is primordial

Beneficiation

- Upgrade SCM properties
- Grinding, separation,…

Activation

- Optimise reaction environment
- OPC, synergies, admixtures,…



ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

SCMs - outstanding questions

Outstanding research questions

1. Link SCM properties and reactivity

- SCM composition
- SCM particle properties (fineness, surface area)

2. Link reaction environment and SCM reactivity

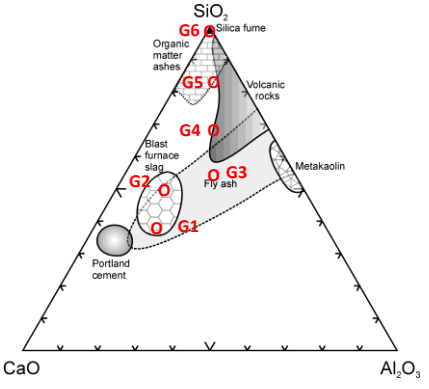
- Pore solution composition (pH, inhibitors, accelerators)
- Hydration products (type, growth rate)

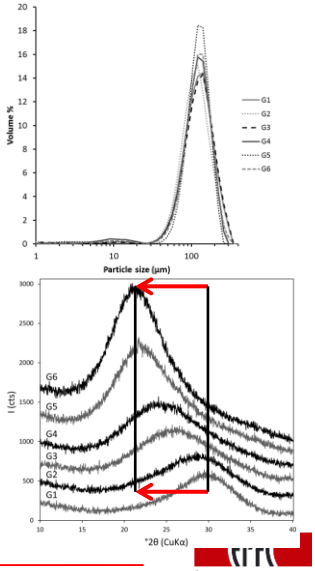
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Solution thermodynamics in the analysis of SCM dissolution experiments

1. Experimental: material synthesis and characterisation

- Synthetic glasses (CaO-SiO_2-Al_2O_3)

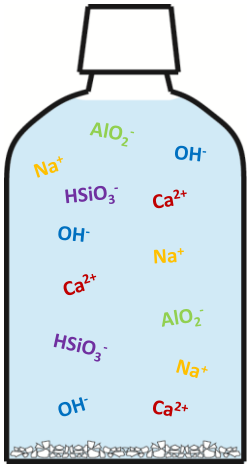




- SCM-types: BFS, FA, natural pozzolans, SF

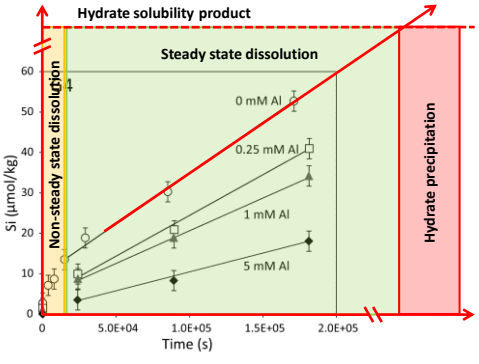
2. Experimental setup

- Batch reactor: closed system
  - Fixed T (20 C)
  - Glass SA to solution volume: SA/V = 0.1-1 cm^{-1}
  - Extended time before hydrate precipitation
  - Sampling at selected time intervals
  - Variable solution concentrations (pH, solutes,…)
- Solution preparation
  - Ultrapure H_2O, reagent grade solutes
  - Boiling and N_2 purging of H_2O to remove CO_2
  - pH 13 + variable concentrations of Al, Ca, Si, SO_4,…



2. Experimental setup

- ICP-OES measurement of release of glass components
  - Matrix matched standards, concentrations down to 2-3 µM measurable
- Dissolution rate calculation



- Glass dissolution rates calculated from linear increase in indicator element concentration (X) over time (t) during steady state regime
- $r_{+,X} = \frac{d(X)}{\Delta t} / (\nu_X m\, A\, V_{soln})$
- ν_X is the mole fraction of the indicator element in the glass

2. Thermodynamic calculations: hydrate saturation

- Saturation index (SI):
  - e.g. Portlandite ($Ca(OH)_2$): $Ca(OH)_2 \leftrightarrow Ca^{2+} + 2(OH)^-$

$$SI = log\left(\frac{IAP}{K_{eq}}\right) = log\left(\frac{[Ca^{2+}][OH^-]^2}{K_{eq}}\right)$$

Calculated activity from measured concentrations

Solubility product

Ion Activity Product

SI > 1: phase supersaturated in solution: might precipitate

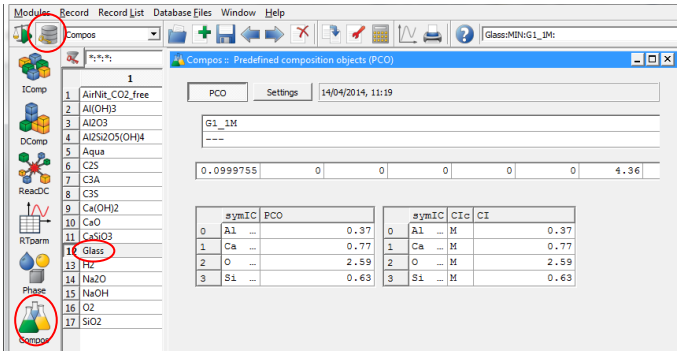
SI < 1: phase undersaturated in solution: phase dissolves

2. Thermodynamic calculations: hydrate saturation

- Dissolution of Glass G1 at pH 13 (NaOH)
  - Enter G1 component

wt%	G1
CaO	43
Al_2O_3	19
SiO_2	38

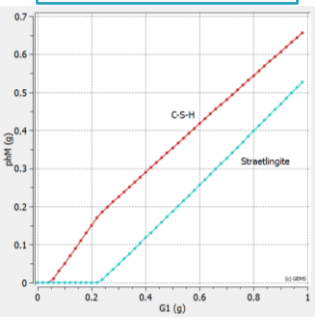
mol/100g	G1
Ca	0.77
Al	0.37
Si	0.63
O	2.59



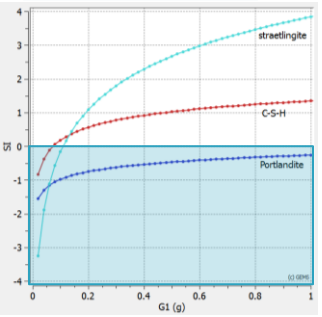
2. Thermodynamic calculations: hydrate saturation

- Dissolution of Glass G1 at pH 13 (NaOH)
  - Recipe: 1 g G1 in 1000 g H_2O, pH 13 (NaOH)
  - Process simulator: variable G1 addition

Hydrate precipitation (g)



Hydrate saturation (g)

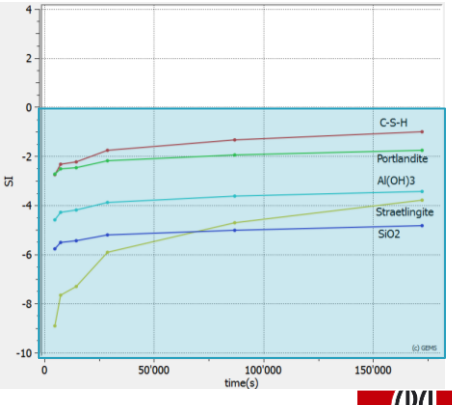


2. Thermodynamic calculations: hydrate saturation

- Dissolution of Glass G1 at pH 13 (NaOH)
  - Check of solution saturation during experiment
  - Dissolution experiment running over 2 days

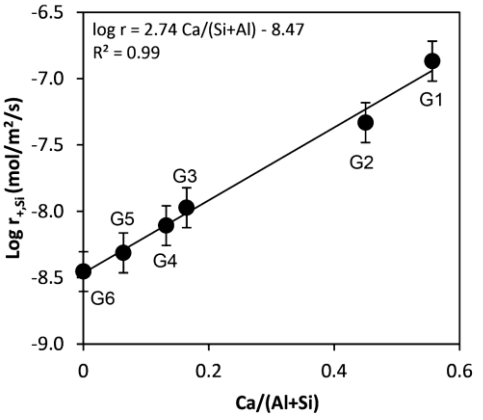
Time (s)	Ca (µM)	Al (µM)	Si (µM)
4680	9.7	4.4	9.8
7440	16.2	8.2	18.4
14520	17.5	9.9	20.7
28800	35.2	19.7	37.0
86760	64.1	36.3	61.6
172260	102.8	55.2	97.9

Solutions remain undersaturated during dissolution experiment



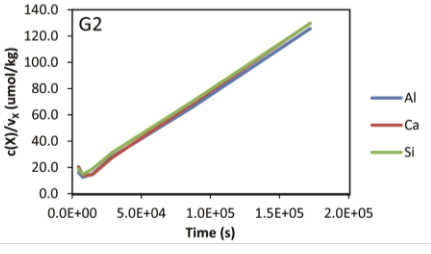
3. Results: Glass composition

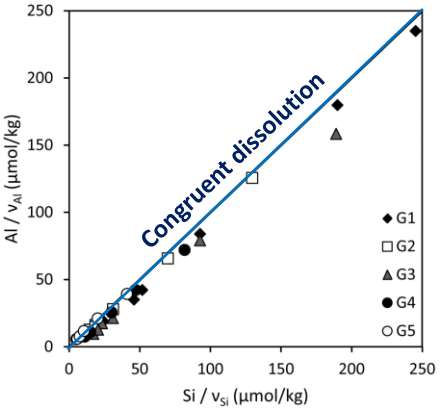
- Dependence of dissolution rates on glass composition



3. Results: Incongruent or congruent dissolution?

- **Steady state dissolution** of the glasses is **congruent at pH 13**, no indication of preferential leaching of glass components





3. Dissolution kinetics and solution saturation

- The dissolution rate of a phase *r* is described by *(constant pH, T)* (TST)*:*

$$r = r_{+,T,pH}\left(1 - exp(\Delta G_{diss}/RT)\right)$$

- The driving force ΔG_{diss} depends on the solution undersaturation

$$\Delta G_{diss} = RT \ln\left(\frac{IAP}{K_{eq}}\right) = \Delta G_{0,diss} + RT \ln IAP$$

Equilibrium constant for the dissolution reaction?

3. Dissolution kinetics and solution saturation

- Glass is thermodynamically unstable in an aqueous solution

  ⇨ determination of K_{eq}?

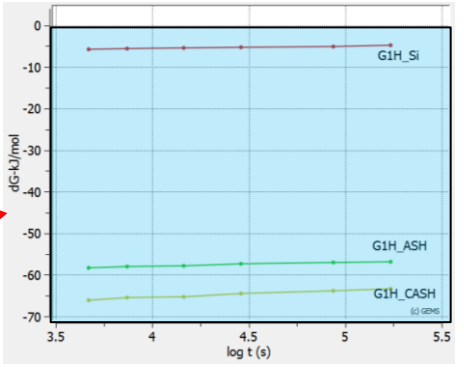
- Dissolution occurs through a hydrated surface layer – which composition?
  - $Ca_{1.21}Al_{0.59}SiO_2(OH)_{4.19} \rightarrow 1.21Ca^{2+} + HSiO_3^- + 0.59Al(OH)_4^- + 0.83(OH)^-$
  - Amorphous silica layer?
  - Aluminosilicate layer?
  - Ca-aluminosilicate layer?

$K_{eq}/\Delta G^0_R$ can be calculated from a combination of $K_{eq}/\Delta G^0_R$ of amorphous SiO_2, amorphous $Al(OH)_3$, and $Ca(OH)_2$

3. Calculation of glass saturation degree

- Calculation of glass saturation degree using GEMS
  - E.g. G1 dissolution experiment
    - G1H_silica: Keq = 1.51
    - G1H_ASH: Keq = 1.12
    - G1H_CASH: Keq = -5.19
  - Entered in DB (ReacDC)

Time (s)	Ca (µM)	Al (µM)	Si (µM)
4680	9.7	4.4	9.8
7440	16.2	8.2	18.4
14520	17.5	9.9	20.7
28800	35.2	19.7	37.0
86760	64.1	36.3	61.6
172260	102.8	55.2	97.9

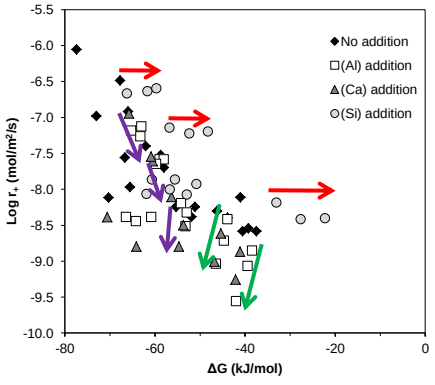


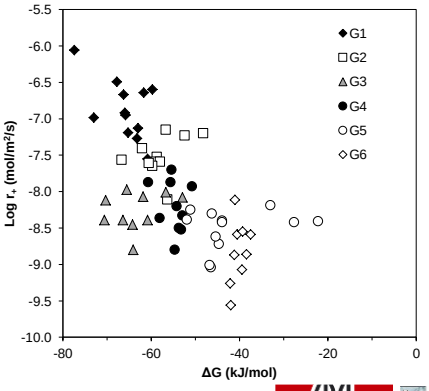
Calculation of K_{eq} of hydrated alumino silicate surface $Al_{0.59}SiO_2(OH)_{1.77}$

$$logK_{G1H\_ASH} = logK_{Al(OH)_{3,a}}.0.59 + logK_{SiO_{2,a}}.1 = 1.12$$

3. Calculation of glass saturation degree

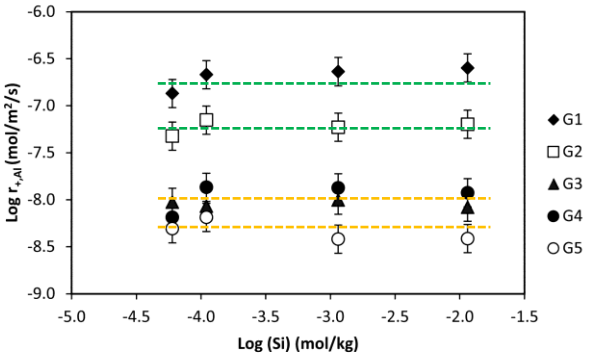
- Calculation of glass saturation degree using GEMS
  - Plot of *r* vs. dG_{diss} to check affinity effects
    - Different glasses, varying initial **(Al)**, **(Ca)**, **(Si)**





3. Dissolution kinetics and solution saturation

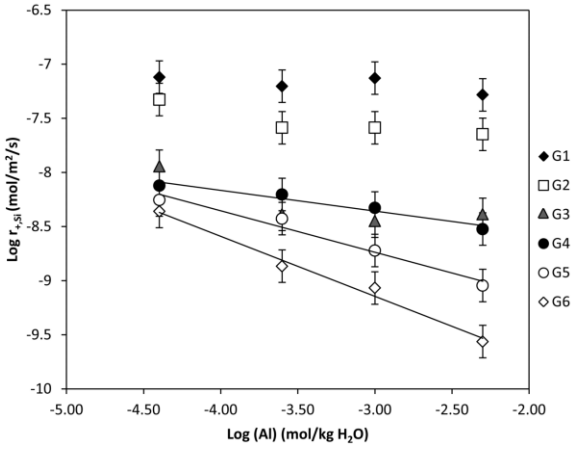
- Effect of solution saturation tested by (Si) addition (pH 13, NaOH)
  - No significant variation of dissolution rates
  - Supports far-from-equilibrium dissolution conditions



ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

3. Results: dissolution kinetics - inhibitors

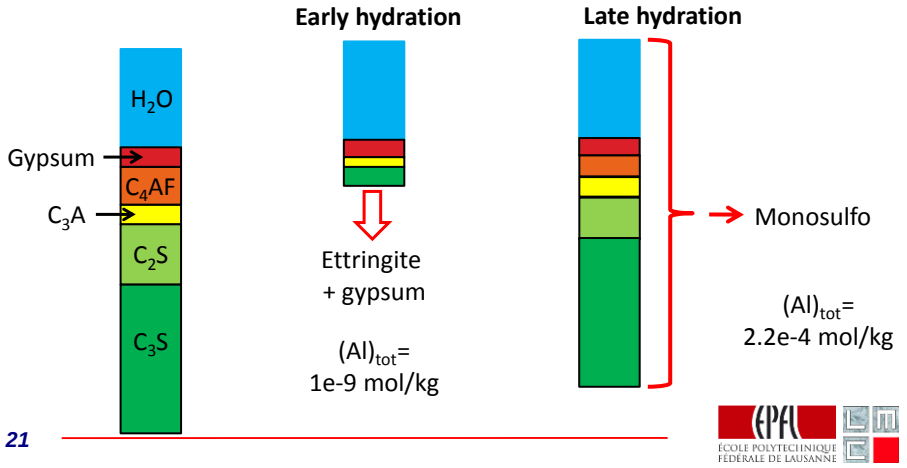
- Effect of (Al) on glass dissolution rates (pH 13, NaOH)



ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

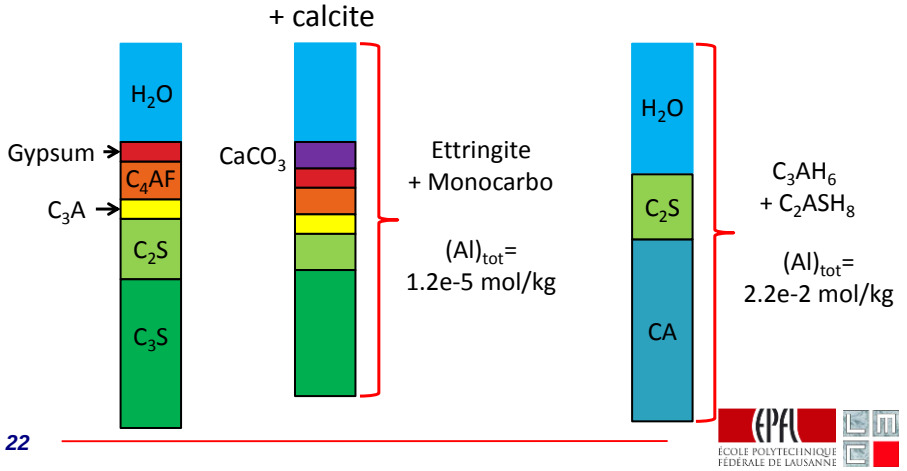
3. Calculation of $(Al)_{tot}$ in hydrated cements

- What $(Al)_{tot}$ can be expected in hydrated cements?
  - Depends strongly on hydration product assemblage!



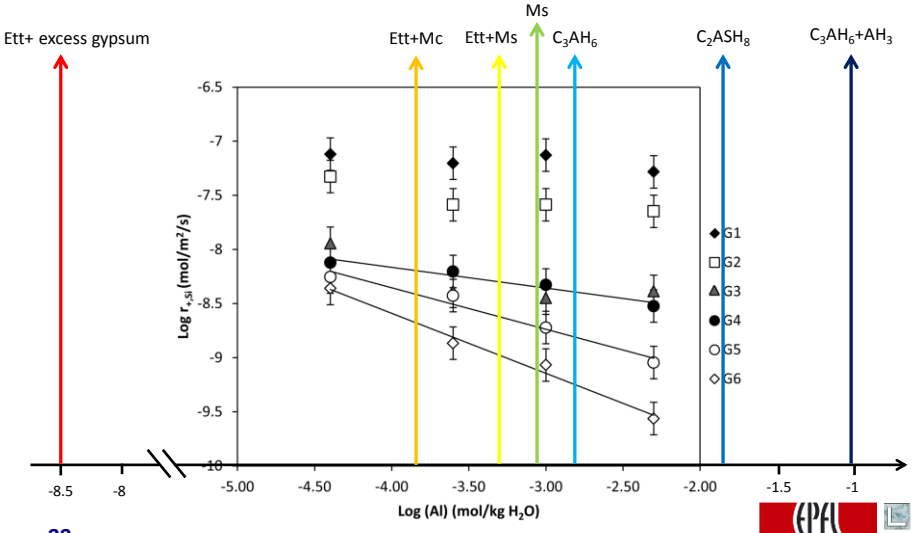
3. Calculation of $(Al)_{tot}$ in hydrated cements

- What $(Al)_{tot}$ can be expected in hydrated cements?
  - Depends strongly on hydration product assemblage!



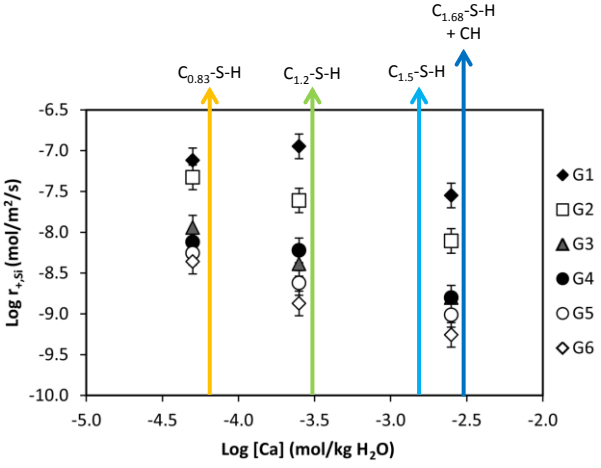
3. Results: dissolution kinetics - inhibitors

- Effect of Al on glass dissolution rates (pH 13, NaOH)



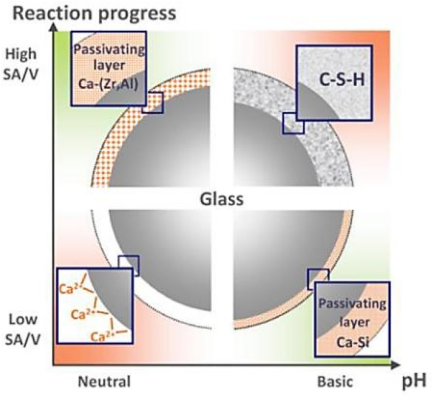
3. Results: dissolution kinetics - inhibitors

- Effect of Ca on glass dissolution rates (pH 13, NaOH)



Double effect of Ca on silicate dissolution

- **Effect of Ca is variable:**
  - **At high pH:**
    - **High dilution:** Passivating layer formation inhibiting effect
    - **Low dilution:** C-S-H formation Resumption of hydration



(Mercado-Depierre et al., 2014)

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Summary

- We used GEMS to calculate and support that
  - Hydrates were undersaturated during the dissolution experiments
  - The glasses were strongly undersaturated during the experiments - assuming various hydrated surface layers
  - Addition of Si to the solution did not affect dissolution rates – no clear affinity effect (at the studied concentrations)
  - Al and Ca concentrations in various cementitious systems, identifying the role of Al as an inhibitor

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE