Modelling of low-pH cement degradation in a KBS-3 HLNW repository

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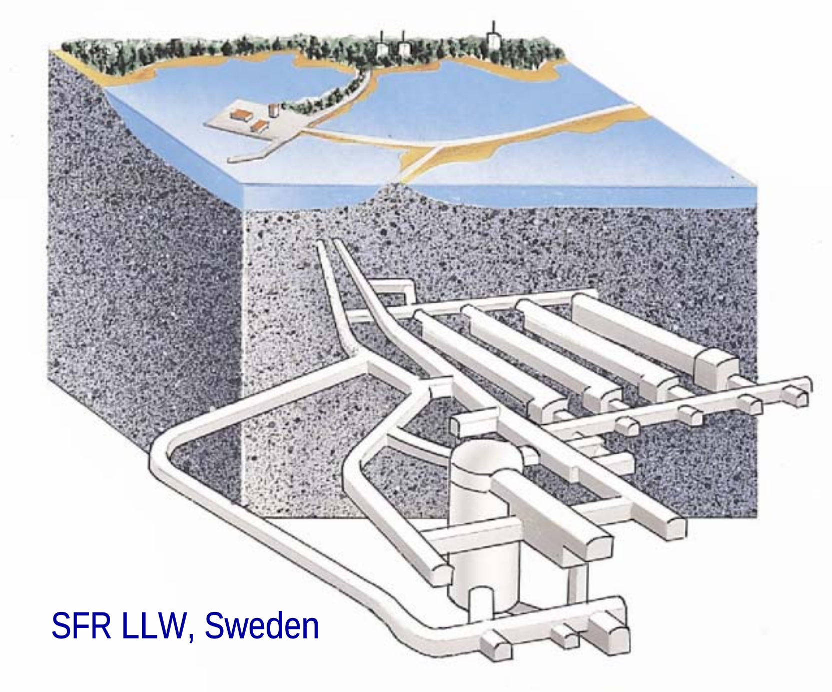
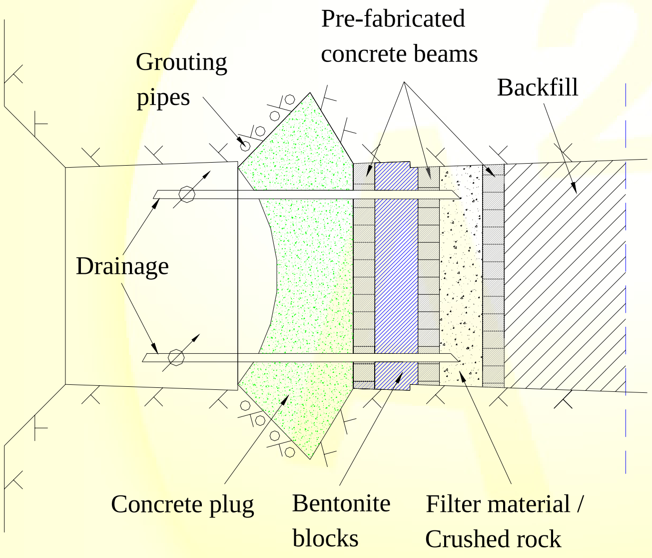
AMPHOS XXI Consulting

Motivation

- Low-pH cements.
  - Why to use low-pH cements in radioactive waste repositories:
    - Aqueous speciation of silicon at pH>10 enhances solubility of clay barrier.
    - Low-pH cements may supply 50% less hydroxyls than conventional OPC.



SFR LLW, Sweden



Tunnel plugs in HLNW repository, Sweden

Conceptual and data uncertainties

Modelling cement degradation.

- Predictive modelling of the cement (CSH gels) dissolution is required to evaluate the pH evolution of porewater.

Open issues

Treatment of CSH → Pure phases vs. Solid solutions

Kinetics of CSH → Rates of precipitation/dissolution of intermediate phases

Diffusion coefficients in cement porewater

Secondary precipitates → Ettringite, calcite, silica, …

CSH behaviour approaches

CSH dissolution/precipitation approaches.

- A number of approaches have been developed to implement the incongruent dissolution of cements in reactive transport codes.

- Local equilibrium approach 1. Thermodynamic equilibrium with pure solid phases.
  - Dissolution (sometimes using kinetic laws) of CSH-like crystalline phases (tobermorite, jennite, …) and precipitation of secondary phases.
  - *Flaws:* inability to model incongruent dissolution.

CSH behaviour approaches

CSH dissolution approaches

- Local equilibrium approach 2. Thermodynamic equilibrium with solid solutions.
  - Dissolution of CSH phases with initial specified Ca/Si ratio. Arbitrary end members, not necessarily present in the system. Formation of new CSH with different Ca/Si ratio. Ability to reproduce incongruent dissolution using non-ideal SS.
  - *Flaws:* Instantaneous re-equilibration of the SS with the fluid (Nernst-Berthelot approach).

CSH behaviour approaches

CSH dissolution approaches

- Kinetic precipitation/dissolution of CSH solid solutions (Lichtner and Carey, 2007).
  - Implementation of the solid solution theory but using a discrete number of intermediate solids. Dissolution/precipitation is governed by (irreversible) kinetics (Doerner and Hoskins approach). Incongruent dissolution using non-ideality terms.
  - *Flaws:* Lack of kinetic data for many CSH phases.

CSH behaviour approaches

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- Examples: CSH dissolution using non-ideal solid solutions.
  - A classic example of this kind of approach is found in Berner (1988, 1990 and 1992).

Dependence of K on solid composition

C/S range Model solid	Apparent solubility product
C/S=0 SiO_2	$\log K' = -2.70$
0<C/S≤1 SiO_2 CaH_2SiO_4	$\log K' = -2.04 + (0.792/(C/S-1.2))$ $\log K' = -8.16 - ((1-C/S)/C/S \cdot (0.78 + (0.792/(C/S-1.2))))$
1<C/S≤2.5 Ca(OH)2 CaH_2SiO_4	$\log K' = -4.945 - (0.338/(C/S-0.85))$ $\log K' = -8.16$
C/S>2.5 $Ca(OH)_2$ CaH_2SiO_4	$\log K' = -5.15$ $\log K' = -8.16$

Reactions:

$SiO_2 + 2\,H_2O \Leftrightarrow H_4SiO_4(aq)$

$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2\,OH^-$

$CaH_2SiO_4 \Leftrightarrow Ca^{2+} + H_2SiO_4^{2-}$

End members

CSH behaviour approaches

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- Examples: CSH dissolution using non-ideal solid solutions.

  - Variable end members depending on Ca/Si ratios in CSH.
  - For Ca/Si>1.5, portlandite diss. controls the chemistry.
  - For Ca/Si>1, portlandite and CaH_2SiO_4 have commonly been selected as end members of solid solution (Berner, 1990; Börjesson et al., 1997).
  - For Ca/Si<1, different SS models have been proposed with different end member: CaH_2SiO_4 – SiO_2 (Berner, 1992).
  - For Ca/Si>1.5 to <1, $Ca(OH)_2$-SiO_2 (Sugiyama & Fujita, 2006 and Carey & Litchner, 2007).

Low-pH cements

CSH approach comparison

- Implementation of CSH dissolution using non-ideal solid solutions in reactive transport codes.

  - Models covering the whole Ca/Si

    → Test the low-pH cement alteration

    → Solid solution end-members: $Ca(OH)_2$ and SiO_2

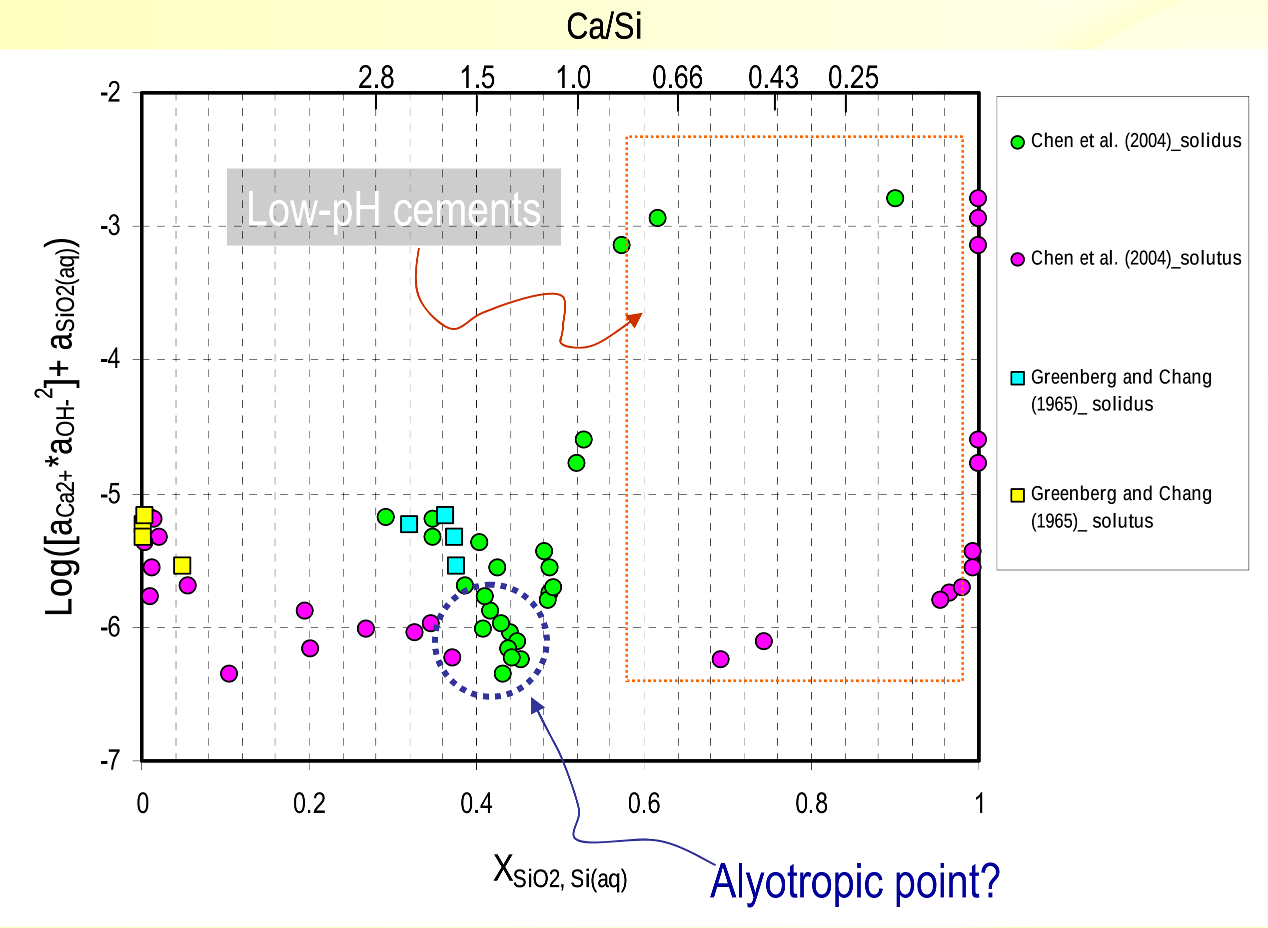
$$Ca(OH)_2, [Ca(OH)_2]_x \cdot [SiO_2]_{1-x}, \ldots, [SiO_2]$$

    - Model of Sugiyama & Fujita (2006)

    - Model of Carey & Lichtner (2007)

CSH approach comparison

- Data from Greenberg & Chang (1965) and Chen et al. (2004) in a Lippmann diagram.



CSH approach comparison

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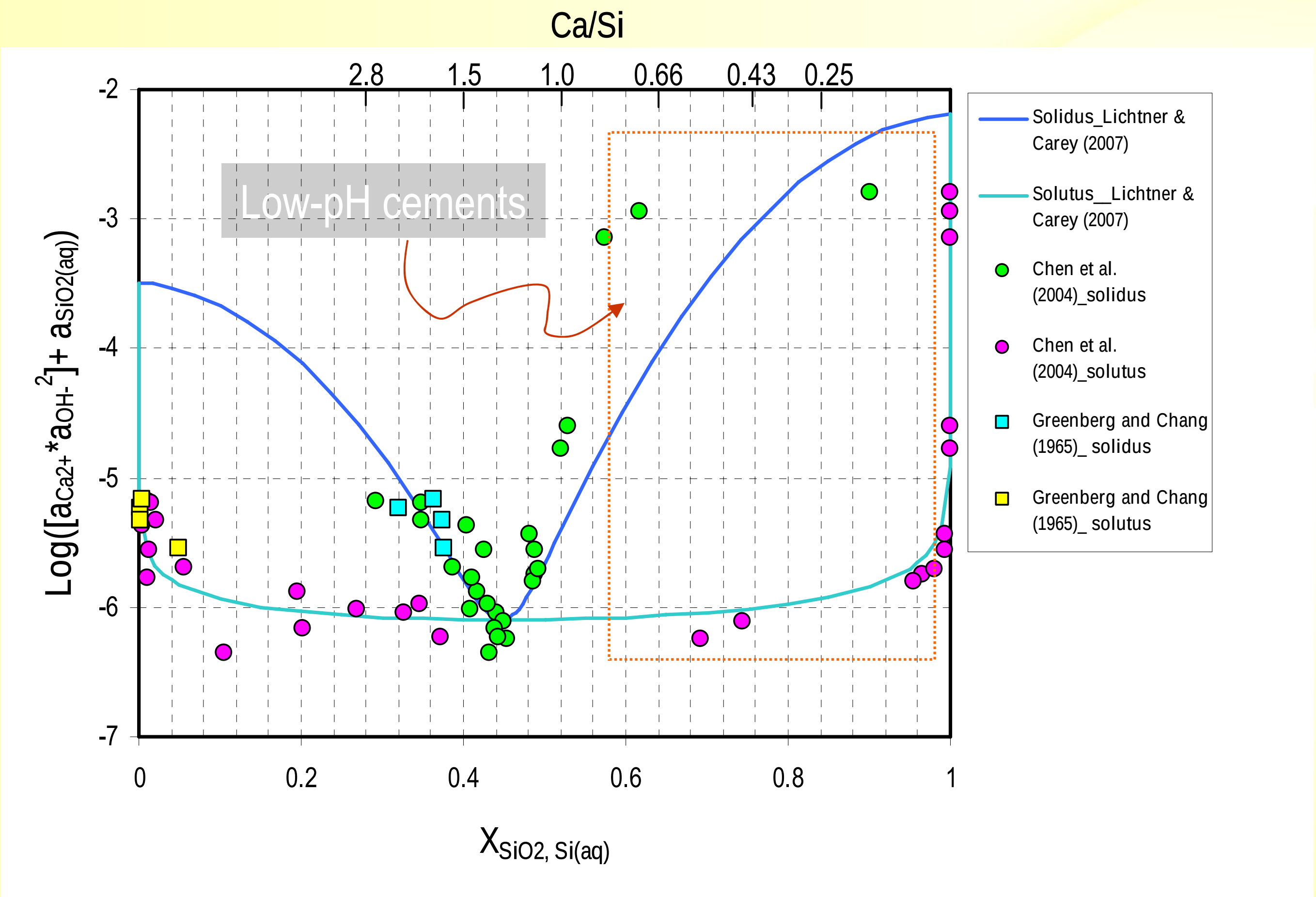
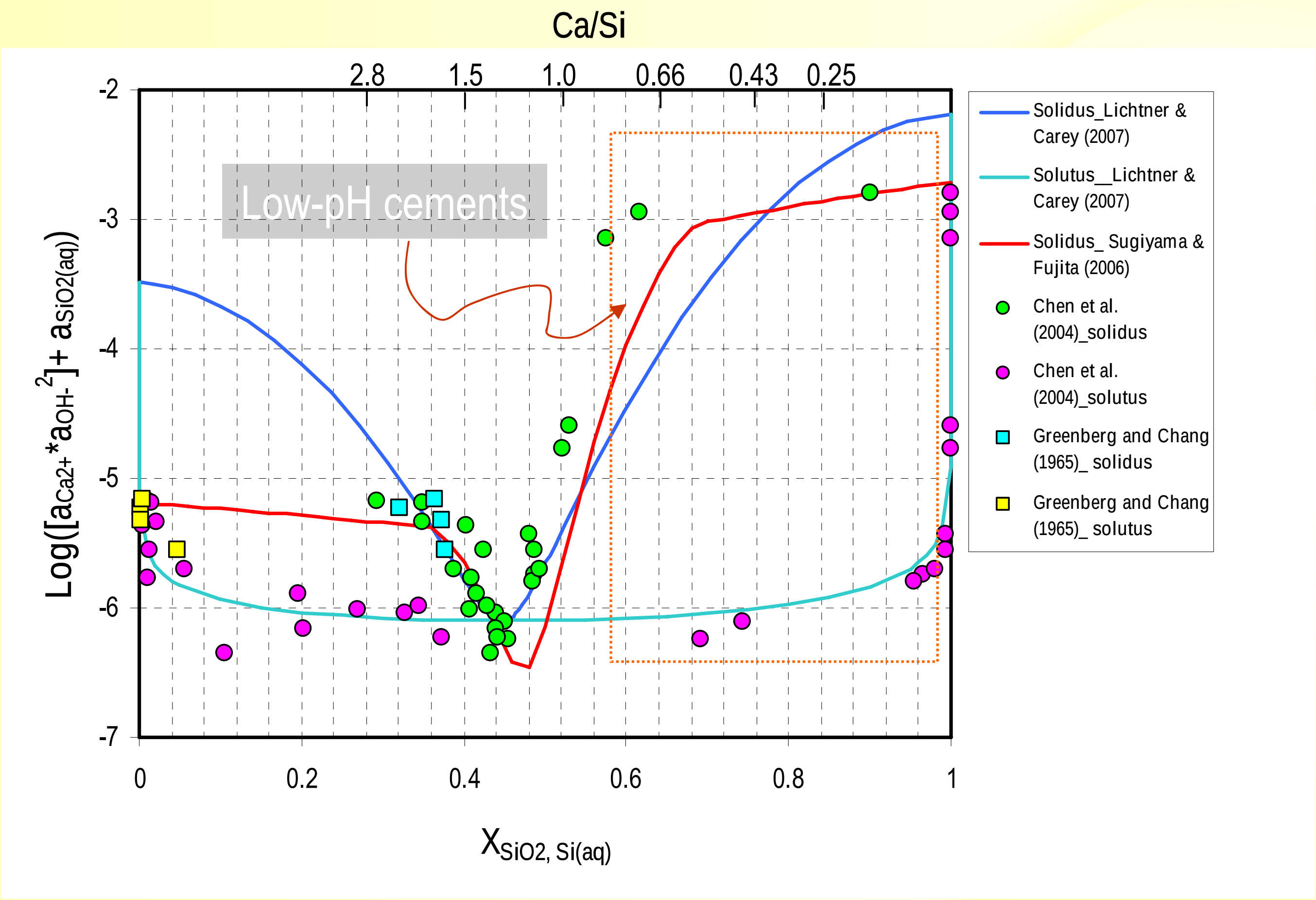
- **Non-ideal SS. Carey & Lichtner (2007).** Non-ideality parametres: a_0= -29.67, a_1= 0.28, a_2= -0.0032



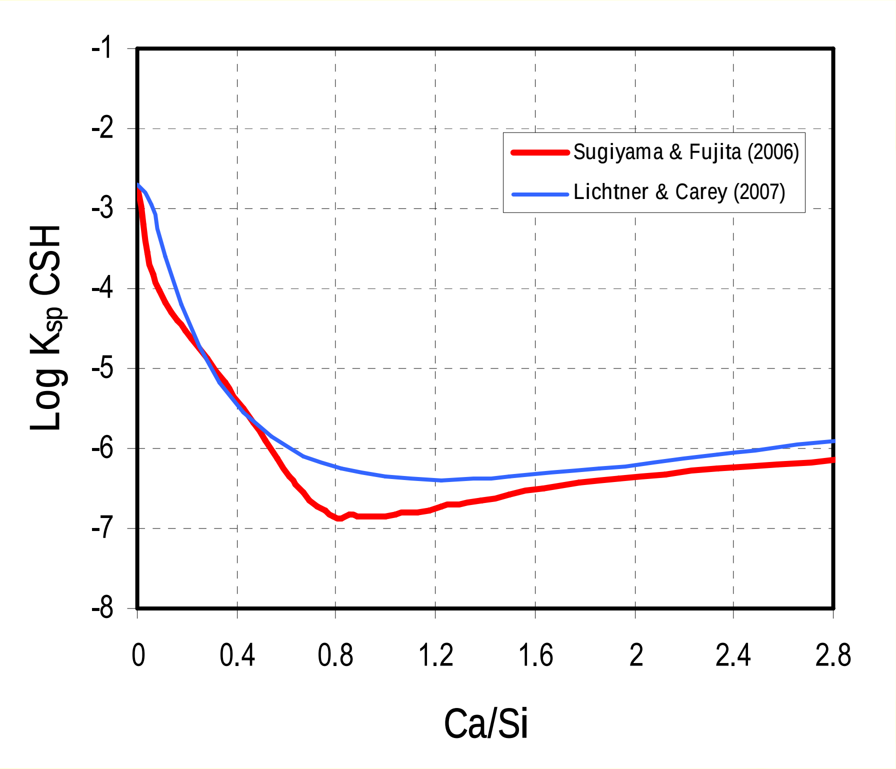
CSH approach comparison

- Non-ideal SS. Sugiyama & Fujita (2006). Conditional solubility constants



CSH approach comparison

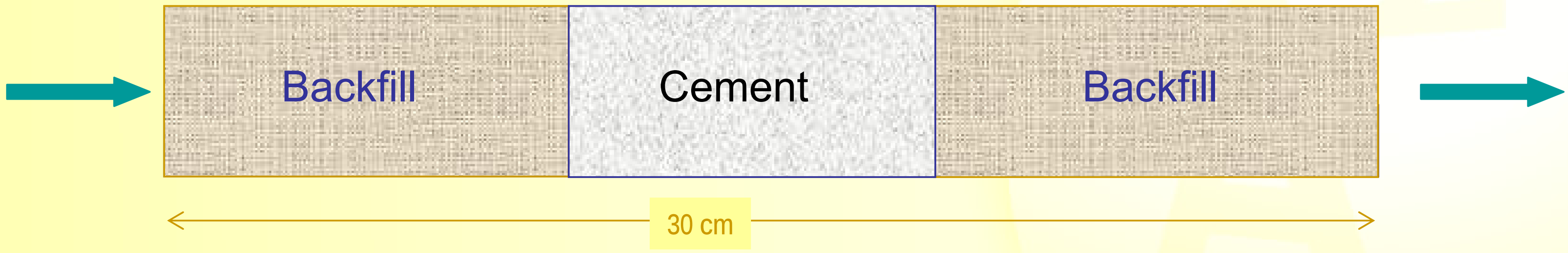
- Calculated logK:



Cement degradation model: The system

CSH degradation: Reactive transport modelling

- 1D
- Granitic, diluted water (pH=7.9; $I=2.6\times10^{-2}M$)
- Non-reactive backfill
- Initial CSH composition: 50% volume, Ca/Si=2.85
- Molar volume: 160 cm^3/mol
- Porosity: 12.5%



Cement degradation model: The code

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- Numerical tool

  - **RCB** (Saaltink et al., 2005) → RETRASO + CodeBright

    Multiphase flow and thermomechanics (CodeBright)

    Reactive transport of solutes (RETRASO)

- Main capabilities:
- Multiphase flow modelling (liquid and/or gas).
- Heat flow modelling.
- Simulation of solute transport by advection, dispersion and diffusion in gas and liquid phase.
- **Simulation of chemical reactions, <u>including solid solutions</u>**.
- Simulation of the effects of precipitation and dissolution of mineral phases on porosity and permeability.

Cement degradation model: The code

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- Numerical tool
  - **RETACO** (Saaltink et al., 2005) → RETRASO + CodeBright
- Mineral dissolution/precipitation is treated following kinetic laws.

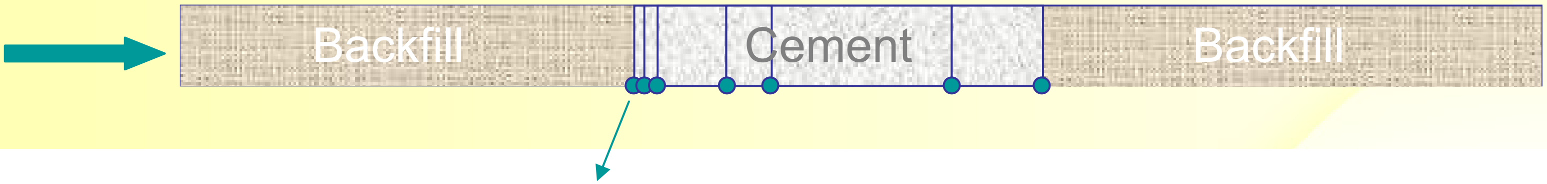
reactive area — activation energy — IAP/K

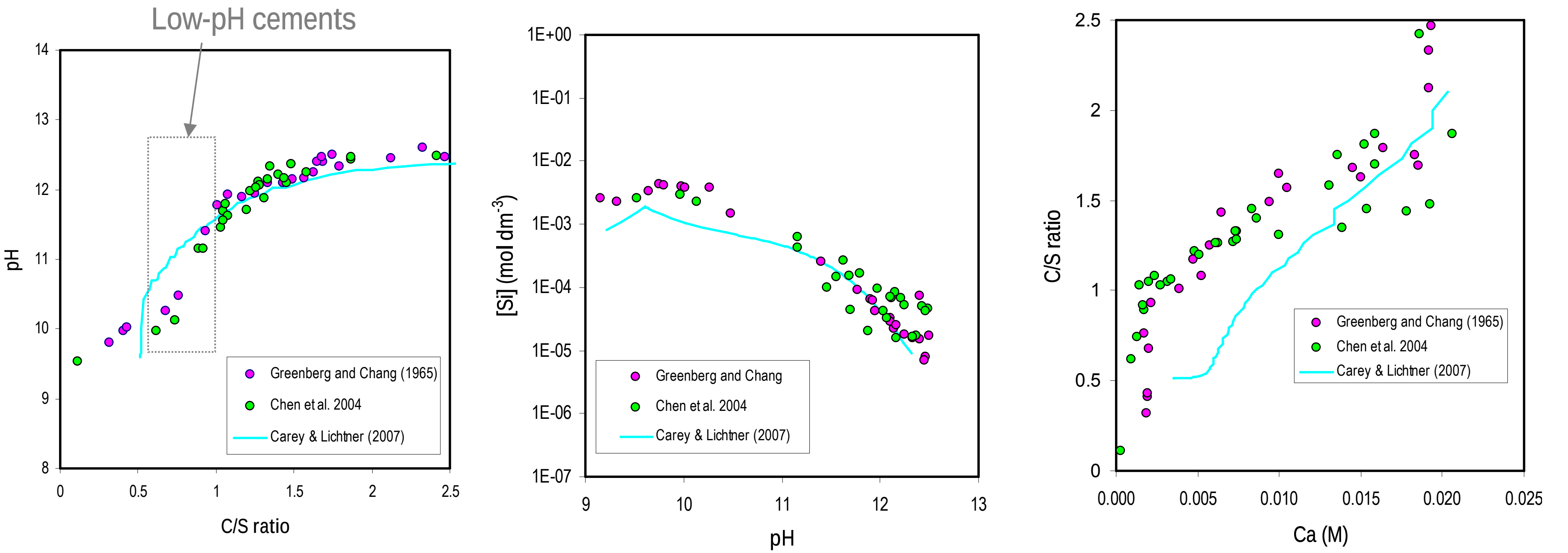
$$r_m = \sigma_m \zeta_m \exp\left(\frac{E_{a,m}}{RT}\right) \sum_{k=1}^{N_k} k_{mk} \prod_{i=1}^{N_s} a_i^{P_{mki}} \left(\Omega_m^{\theta_{mk}} - 1\right)^{\eta_{mk}}$$

- Uncertainties: dissolution/precipitation rates for CSH, molar volumes for intermediate solid solutions, diffusion coefficients, ...

Cement degradation model: Comparison

- CSH degradation: Carey & Lichtner (2007). Results





Experimental data from Chen et al. (2004) and Greenberg and Chang (1965)

Cement degradation model: Comparison

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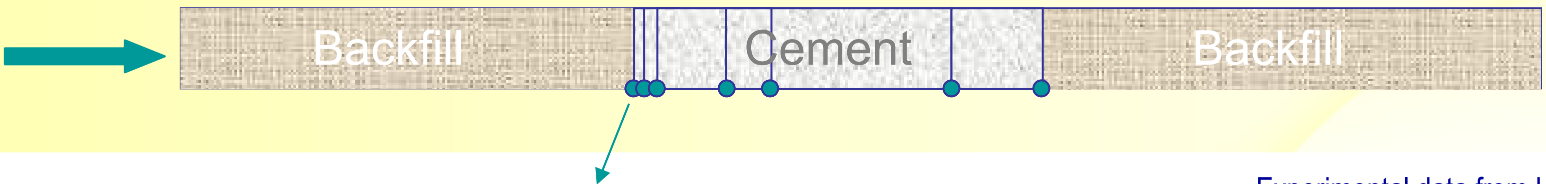
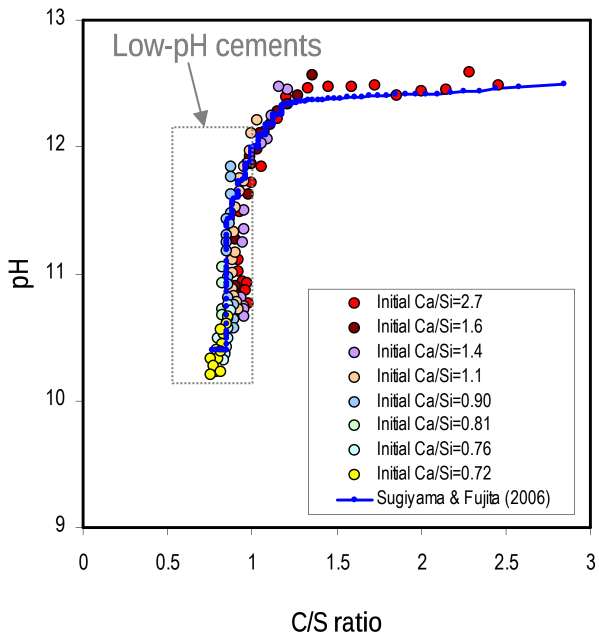
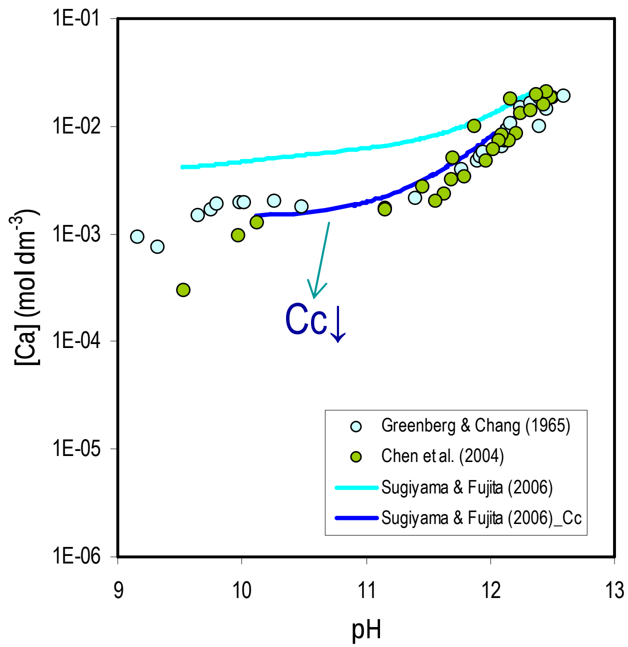
- CSH degradation: Sugita & Fujiyama (2006). Results



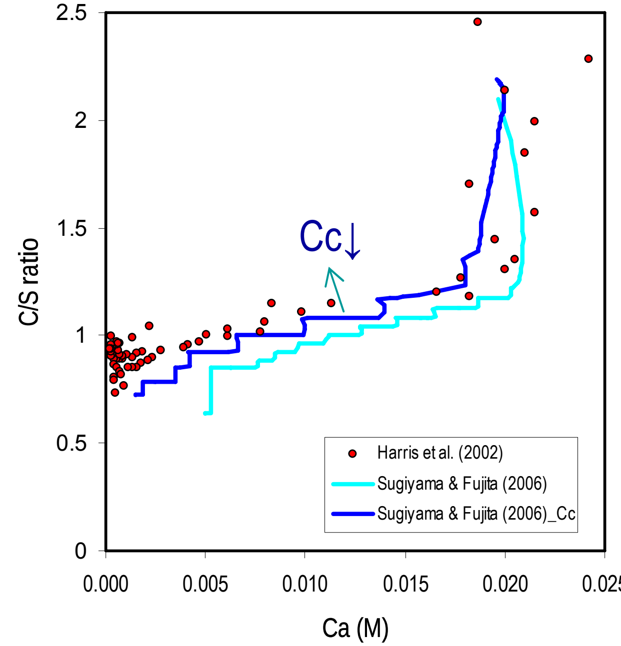
Experimental data from Harris et al. (2002)





Experimental data from Chen et al. (2004) and from Greenberg and Chan (1965)

Experimental data from Harris et al. (2002)



Cement degradation model: Comparison

CSH degradation: Carey & Lichtner (2007). Results

- The Carey & Lichtner approach reproduces well the degradation of CSH in the **Ca/Si range from 3 to 1**.
- At lower ratios, the model does not fit much with experimental data, as already suggested by the Lippmann diagrams.

CSH degradation: Sugiyama & Fujita (2006). Results

- The Sugiyama and Fujita (2006) approach reproduces well the changes in **CSH composition in the range of Ca/Si<1**, which are characteristic of low pH cements.
- Aqueous calcium seems to be overpredicted in the simulations compared with experimental data. Including **precipitation of calcite**, the fit is better. However, it is not clear the precipitation of this mineral during the experiments.

Cement degradation model: Implementation

- CSH degradation: Carey & Lichtner (2007). Effect of porosity changes on hydraulic properties.

  - Uncertainties:

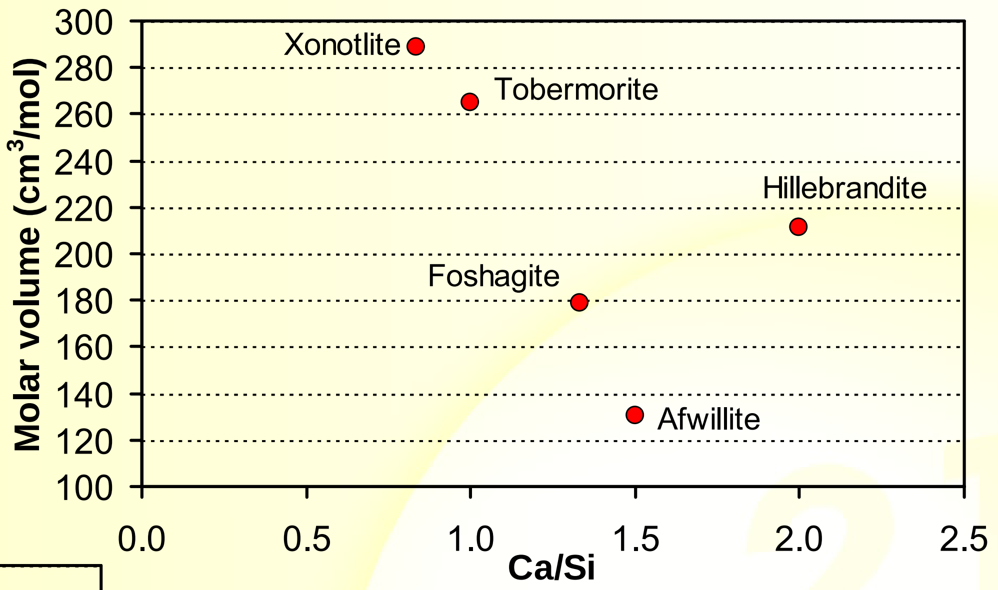
    → Which are the molar volumes of the intermediate CSH phases?

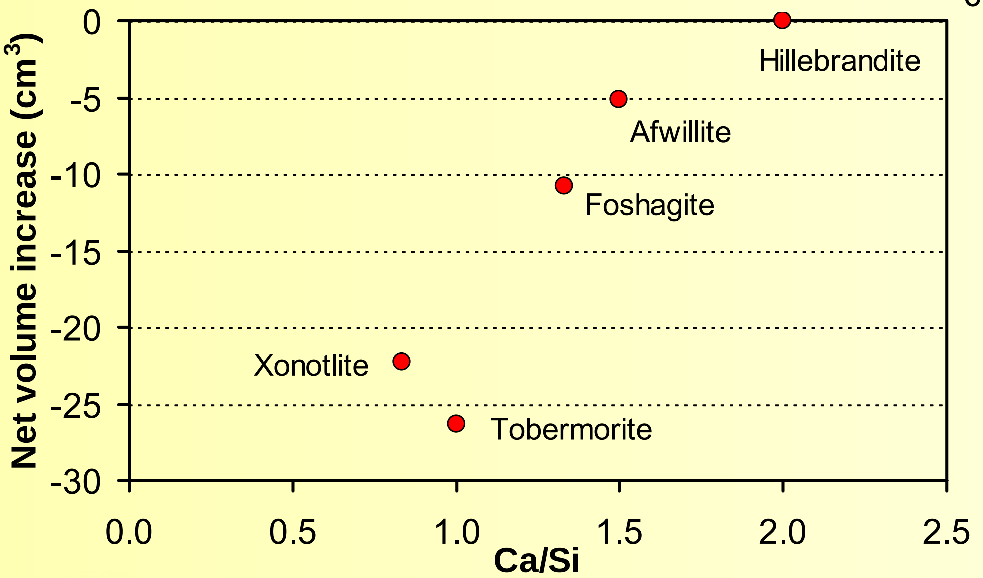
    → And the reactive areas?

    The final results from modelling are strongly dependent on these parameters.

CSH molar volumes

Decreasing Ca/Si ratio lead to increasing molar volumes. Is this meaning that CSH degradation lead to reducing porosity?





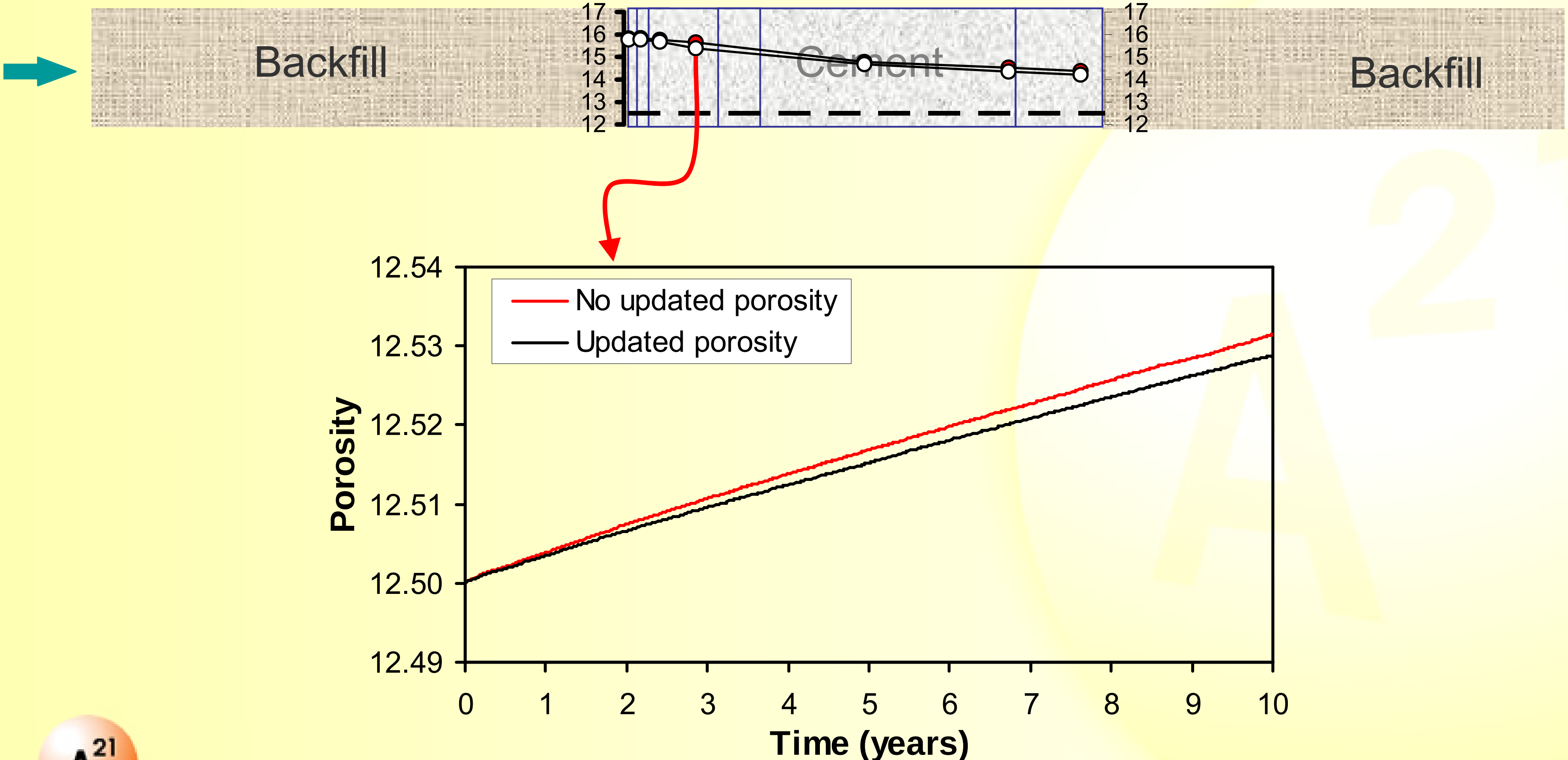
Ca leaching let to a a decrease of net volume in the reaction!!!

But there is still an unknown on the behaviour of CSH gels.

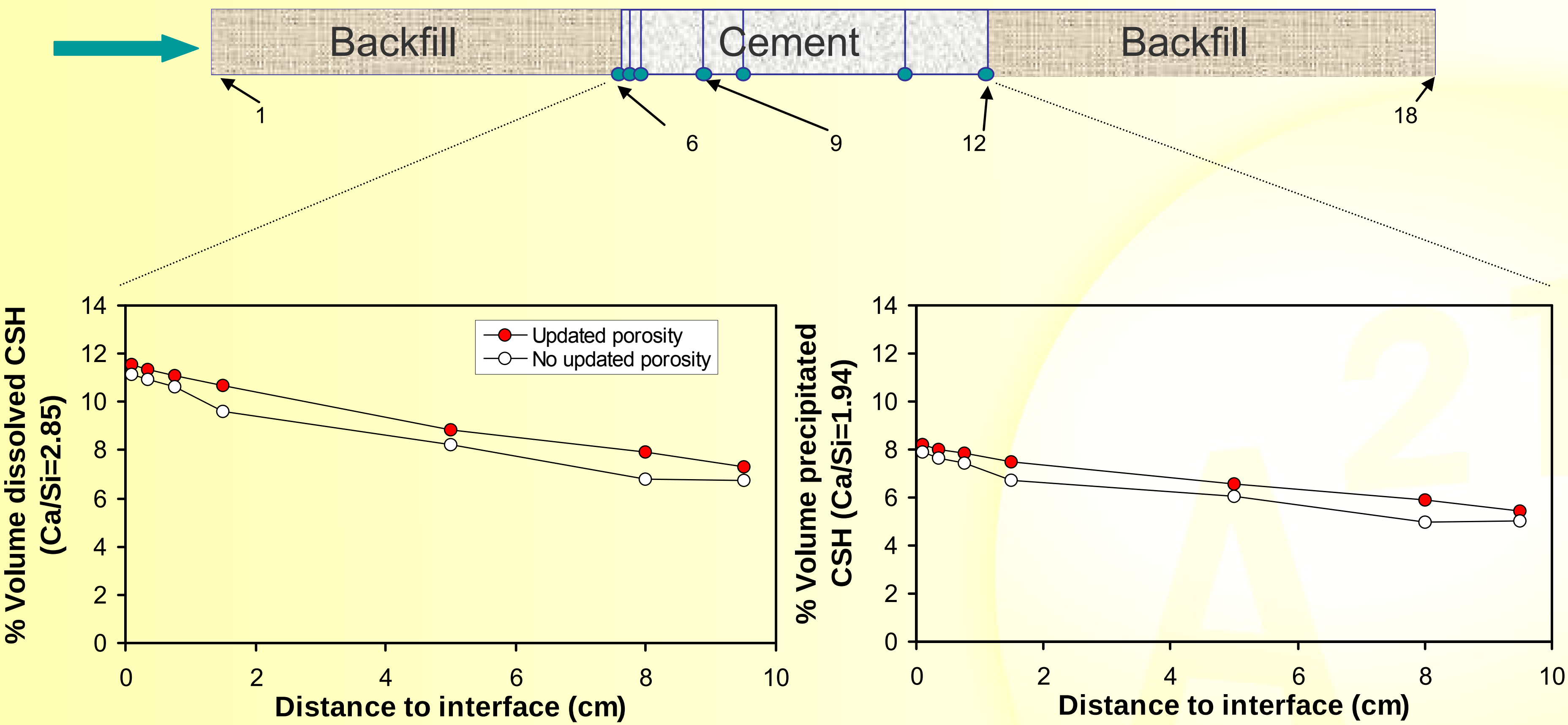
We are considering a single value for the molar volume of different CSH phases: 160 cm^3/mol

Cement degradation: porosity changes

- CSH degradation: Carey & Lichtner (2007). Effect of porosity changes on hydraulic properties.



Cement degradation: CSH behaviour



The net CSH pool results in a larger dissolution when porosity has not been updates in transport processes

Preliminary conclusions

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Final remarks

- Among the CSH dissolution/precipitation approaches, the ones from Sugiyama & Fujita (2006) and Carey & Litchner (2007) are the most consistent from thermodynamic and experimental point of view.
- The approach from Sugiyama & Fujita (2006) seems to better reproduce experimental data for low-pH cement.
- Porosity updates in reactive transport models is very relevant and can result in substantial errors if not considered, despite the large uncertainty in CSH properties (molar volumes and reactive surface).
- Further work is envisaged to consider the long term evolution of low-pH cements in the KBS-3 repository by considering the presented approach.