

Reactive transport modeling of grout-rock interaction

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Grouting of water-conducting fractures with low-alkali cement is foreseen by Posiva (Finnish nuclear waste management agency) for the potential future repository for high-level nuclear waste in Finland. A possible consequence of the interaction between groundwater and grout is the formation of high-pH solutions which will be able to react with the host rock (gneisses) and alter its mineralogy and porosity.

A reactive transport modeling study of this possible alteration has been started following the recommendations from Posiva. First, the hydration of the low-alkali cement has been modeled, using results from the literature [1,2] as guide. The hydrated cement is characterized by the absence of portlandite and the presence of a C-S-H gel with a Ca/Si ratio about 0.8 after tens of years (Ca/Si is about 1.7 in Ordinary Portland Cement). Afterwards, a one-dimensional system simulating the contact between a grouted section of a fracture and the gneiss has been studied. The results from the simulations show a very fast (days to weeks) sealing of porosity at the rock-grout interface. The precipitation of C-S-H (tobermorite), and also ettringite in some cases, is responsible for this fast sealing of porosity. The mixing by diffusion of a Ca-rich solution from the grout and a Si-rich solution from the rock causes this precipitation.

New calculations have finally been started simulating the interaction between flowing water and grout and the alteration of the host rock as this water (high-pH plume) flows beyond the grouted section of a fracture.

[1] Lothenbach, B. & Wieland, E. (2009) *Chemical evolution of cementitious materials*. NEA Workshop, Brussels, Belgium. [2] Lothenbach, B. & Matschei, T. (2009) *Thermodynamic modelling: hydration modelling*. The Fred Glasser Cement Science Symp., Aberdeen, Scotland, UK.

C-S-H gel dissolution kinetics

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C-S-H gel, which constitutes at least 60% of the fully hydrated Portland cement paste, is the main responsible of the durability and barrier properties of cement. Although C-S-H solubility has been studied by many authors, the dissolution kinetics is not known. In this communication we present kinetic data based on the results obtained from flow-through experiments.

The C-S-H gel used in the experiments was obtained by hydration of synthesized C_3S ($3CaO \cdot SiO_2$), which results in the formation of C-S-H and portlandite. C-S-H was ground to a size fraction of $\sim 10 \mu m$ and the solid Ca/Si stoichiometric ratio was about 1.65 (electron microprobe analysis). The flow-through experiments were carried out at room temperature ($22 \pm 2^\circ C$) and under CO_2 -free N_2 atmosphere to avoid carbonation. Ca and Si concentrations and pH were monitored during the experiments. The flow rate was kept constant either at 0.05 or 0.13 mL min^{-1} .

The evolution of pH and Ca and Si concentrations showed three distinct stages during the experiments: (1) Ca concentration was much larger than Si at the start of the experiments, indicating preferential dissolution of portlandite ($Ca(OH)_2$) and slow close-to-equilibrium dissolution of C-S-H. (2) As the portlandite content diminished a gradual decrease in Ca and increase in Si was observed, indicating an increase in C-S-H gel dissolution. The aqueous Ca/Si ratio decreased to values below 10. pH also decreased. (3) Concentrations of Ca and Si and pH (9.7 – 11.4) reached steady state. At this stage the aqueous Ca/Si ratio remained constant at about 0.9 indicating that (i) the C-S-H gel was the main dissolving phase and (ii) the dissolution reaction was stoichiometric with respect to a phase with a Ca/Si ratio similar to that of tobermorite. Steady-state dissolution rates of the C-S-H gel normalized to the final BET specific surface area ranged from 10^{-11} to 10^{-10} mol $m^{-2} s^{-1}$.

Based on these results two main conclusions can be drawn:

1) The dissolution of the C-S-H gel is initially incongruent (preferential release of Ca) and evolves to the congruent dissolution of a phase with tobermorite stoichiometry (Ca/Si = 0.83), which is consistent with the solubility model presented by Kulik and Kersten [1].

2) The dissolution rate of this end-member is not especially fast, similar for instance to that of feldspars. These values highlight the necessity of considering C-S-H dissolution kinetics in cases where water flows by advection through mortar or concrete (fast transport; dissolution rate is the limiting factor in C-S-H dissolution).

[1] Kulik, D.A. & Kersten, M. (2001) *J. Am. Ceram. Soc.*, **84**, 3017-3026.