

# REACTIVE TRANSPORT CALCULATIONS ON THE GEOCHEMICAL EVOLUTION OF CEMENT/CLAY INTERFACES

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In Switzerland the deep geological disposal in clay-rich rocks is foreseen not only for high-level radioactive waste but also for intermediate-level and low-level radioactive waste as well. Typically, intermediate- and low-level radioactive waste repositories contain huge quantities of cementitious materials used for waste conditioning, confinement and as backfill for the emplacement caverns. We are investigating the interactions of such a repository with the surrounding clay rocks and with other clay materials such as sand/bentonite mixtures, potential materials for backfilling the access tunnels. With the help of a numerical reactive transport model we are comparing the evolution of cement/clay interfaces for different geochemical and transport conditions.

In this work, the reactive transport of chemical components is simulated with the multi-component reactive transport code OpenGeoSys-GEM. It employs the sequential non-iterative approach to couple the mass transport code OpenGeoSys (<http://www.ufz.de/index.php?en=18345>) with the code GEMIPM2K (<http://gems.web.psi.ch/>) for thermodynamic modeling of aquatic geochemical systems with the Gibbs Energy Minimization (GEM) method. For each time step, the advection-dispersion equation is first solved for all dissolved species, and then the changed composition of the phase assemblage is passed to the chemical solver which calculates the local equilibrium on each grid node. The concentrations of dissolved chemical species are then taken as the result for this time step, and used as an initial condition for the next transport step. Details regarding code development and verification can be found in Shao *et al.* (2009).

The mineral composition and the pore solution of a CEM I 52.5 N HTS hydrated cement as described by Lothenbach & Wieland (2006) are used as a starting point for the cement compartment. The setup is based on the most recent CEMDATA07 thermodynamic database including several ideal solid solutions for hydrated cement minerals in conjunction with the Nagra/PSI thermodynamic database 01/1.

The bentonite model, representing MX-80 bentonite, was calibrated based on the data of Bradbury & Baeyens (2002). The definition of montmorillonite, the main ingredient of bentonite, includes cation exchange processes and amphoteric  $\equiv\text{SOH}$  sites as described in Bradbury & Baeyens (2002). In other reactive transport codes based on the Law of Mass Action (LMA) for solving geochemical equilibria, cation exchange processes are usually calculated assuming that the clay mineral is represented by a  $X$ -“ligand” initially occupied with  $\text{Na}^+$ . We implemented a more chemically plausible solid solution model of ion exchange in clay. For such a model it is more convenient to formulate each end member with exactly one negative charge per formula unit “*Mont*”, according to the following exchange reaction



The corresponding equilibrium constant  $K_G$  (expressed in the Gapon convention in mole fractions) for the ideal mixing is

$$K_G = \frac{x_{M_{0.5}\text{Mont}}}{x_{\text{NaMont}}} \cdot \frac{a_{\text{Na}^+,aq}}{a_{M^{2+},aq}^{0.5}} \quad (2)$$

It is numerically the same as a Gaines-Thomas selectivity coefficient  $K_{GT}^c$  or Vanselow (1932) selectivity coefficient  $K_V^c$  for mono-to-monovalent exchange. For mono-to-divalent exchange the following relation exists

$$K_G = K_V^{0.5} = \left( K_{GT,M}^c \cdot \frac{n}{2zn} \right)^{0.5}. \quad (3)$$

Here  $\Sigma n$  is the sum of the mole amounts and  $\Sigma zn$  is the sum of equivalents of ions present on the exchanger.

As a first application we will present the results of calculations on the interaction between a cement compartment and sand/bentonite mixtures under different transport conditions.

**References:**

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