INSIGHTS INTO LONG-TERM ALTERATION OF BENTONITE-CEMENT SYSTEM BASED ON COUPLED MASS-TRANSPORT/CHEMICAL REACTION ANALYSIS

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INTRODUCTION
Montmorillonite is the main constituent of bentonite buffer materials in radioactive waste repositories. Highly alkaline environments induced by cementitious materials are likely to alter montmorillonite, and are likely to deteriorate the physical and/or chemical properties of the buffer materials. The deterioration causes variation in hydraulic conductivity of compacted sand-bentonite mixture, a candidate material of the buffer, and induces major uncertainties in the radionuclide migration analysis. The variation has not been quantitatively understood. We focus our experimental efforts on predicting long-term variations in hydraulic conductivity of compacted sand-bentonite mixture. The prediction requires mathematical models and a number of input parameters. In our previous study (Nakayama et al., 2004; Yamaguchi et al., 2007), the dissolution rate of montmorillonite in the, diffusivity of hydroxide ions in, and the hydraulic conductivity of compacted sand-bentonite mixtures were experimentally determined and formulated; a PHREEQC-based, coupled mass-transport / chemical-reaction code (MC-BENT) was developed for predicting hydraulic conductivity of the bentonite buffer.

In order to provide reliability to the long-term prediction of bentonite buffer performance under disposal conditions, we intended

- to understand alteration behavior of cementitious material as the source of alkaline plume,
- to verify the models and the code by comparing with experimental observations, and
- to calculate the long-term alteration and look closely into the results to identify key issues.

EXPERIMENTAL
Hardened cement pastes were prepared with water-to-cement ratio of 0.45 and pulverized into 0.25-0.09 mm. The pulverized materials were sealed in polyethylene bottles with artificial seawater or deionized water at the liquid/solid ratio of 10 dm⁻³ kg⁻¹ under argon. Then the solid and the aqueous phases were separated by filtration and the aqueous phase was replaced by fresh one. The procedure was repeated until planned cumulative liquid/solid ratios that represent an index of progress of the alteration. The aqueous phase was analyzed for pH and concentrations of Ca, Si, Al and Mg. The solid phase was identified by X-ray powder diffraction (XRD). The quantity of portlandite in the solid phase was measured by differential thermal analysis and thermogravimetry (DTA/TG).

MODELLING, CODING AND VERIFICATION
In order to predict the alteration of cement based materials and accompanying leaching of cement constituents, a secondary mineral formation model was developed based on available knowledge. The model includes brucite, Mg(OH)₂; gypsum, CaSO₄·2H₂O; Friedel’s salt, 3CaO·Al₂O₃·CaCl₂·10H₂O;
ettringite, 3CaO·3CaSO₄·32H₂O; calcite, CaCO₃; 4MgO·SiO₂·8H₂O; sepiolite, Mg₂Si₄O₁₀(OH)₂·6H₂O; hydrocalcite, Mg₂Al₃CO₃(OH)₆; monosulphate, 3CaO·Al₂O₃·3CaSO₄·12H₂O; hydrogarnet, 3CaO·Al₂O₃·6H₂O; katoite; Ca₆Al₅(Si₉O₂₄)(OH)₄; gibbsite, Al(OH)₃; chalcedony, SiO₂ and C-S-H. The mineral model was incorporated into the MC-BENT and verified by reproducing evolution of liquid phase composition and changes in mineralogy of solid phase observed in the leaching experiment of hardened cement pastes, as exemplified in Figure 1.

In order to estimate the hydraulic conductivity of bentonite materials under the temperature of deep underground, the hydraulic conductivity model (Yamaguchi et al., 2007) was supplemented with temperature dependent viscosity factor

\[ K = 1.2 \times 10^7 \, l \cdot s^{-1} \times 10^{4.2 \rho_{\text{mol}}} \times (9.0 \times 10^{-5} \, T^{2.3} - 2.8 \times 10^{-2} \, T + 1.5) \]

where \( K \) is the hydraulic conductivity (m s⁻¹), \( I \) the ionic strength of the permeant solution (mol dm⁻³), \( \rho_{\text{mol}} \) the effective montmorillonite dry density (Mg m⁻³) and \( T \) the temperature (K). The model was incorporated into the MC-BENT and was able to reproduce results of a hydraulic conductivity test for sand-bentonite mixture with a 6\times10⁻³ M Ca(OH)₂ solution at 80 °C (RWMC, 2002), being an indication of verification of the model.

**LONG-TERM ALTERATION ANALYSIS AND DISCUSSION**

We calculated changes in mineralogy of bentonite buffer materials and accompanying changes in the hydraulic conductivity over 10,000 y. We identified the temperature as an important factor dominating the alteration of the buffer. We also identified that the alteration is limited by slow kinetics of the dissolution of montmorillonite and by the diffusive mass transfer. Figure 2 shows that the mineralogical change proceeds rather fast during the initial 1,000 y and slows down afterwards. Salinity of the groundwater has both positive and negative effects on the hydraulic conductivity.

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