

Nanoscale process in the alteration of bentonite-iron system under the hyper alkaline conditions

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Because of the use of cementitious materials in geological disposal repositories for high-level radioactive waste (HLW), hyper alkaline solutions derived from dissolution of the cementitious materials are likely to alter the bentonite buffer material, of which the major constituents are montmorillonite and quartz. The alteration potentially results in deterioration of its capability as an engineered barrier. Iron derived from degradation of steel overpack, which is in contact with the buffer material in the repositories, may affect the bentonite alteration.

Although bentonite alteration has been studied extensively, detailed mechanisms of the alteration phenomena at sub-micron scale still need to be understood to develop macro-scale models for bentonite alteration. For this purpose, we have demonstrated a laboratory experiment, in which compacted bentonite (ca. 1 MPa) was reacted with selected aqueous solutions; a solution saturated with $\text{Ca}(\text{OH})_2$, a 1 mol/l NaOH solution, a simulated groundwater saturated with $\text{Ca}(\text{OH})_2$, or a 1 mol/l FeCl_2 solution, for the period of 2, 7, 9 and 14 days at the temperature of 130 °C. The pHs of the solutions remained high in the range of 12.5 to 13.5, during the reaction. The pH of the FeCl_2 solution was kept almost constant within 4-5. The solid specimens were characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), focusing on the interface between the bentonite constituting minerals. The solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The solution analysis reveals a gradual increase in Na and K concentrations in the solutions saturated with $\text{Ca}(\text{OH})_2$ as a function of time, indicating that montmorillonite dissolved in the alkaline solution. Both Ca and Si concentrations are nearly constant for the period of reaction. The thermodynamic calculation using Geochemists Workbench reveals that the Ca concentration is constrained by the $\text{Ca}(\text{OH})_{2(s)}$ solubility and the Si concentration is supersaturated with respect to calcium-silicate-hydrate (CSH). The SEM images of the cleaved samples show the occurrence of montmorillonite, spherical silica particles, BaSO_4 that is initially included in bentonite and CSH within the interlayer of montmorillonite. Further, in the all bentonite specimens reacted with the FeCl_2 solution, numerous iron nanoparticles at the size of 5 to 20 nm occurred homogeneously in the bentonite, suggesting that Fe nanoparticles derived from overpack degradation become a mobile carrier of hazardous radionuclides and potentially enhance their migration.

Keywords: bentonite, iron, hyper alkaline, SEM, TEM