

Formation of magnesium silicates and its geochemical modeling at high alkaline conditions

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In geological disposal of waste generated from reprocessing of spent fuel, a large amount of cement material is used for vitrified waste and grout, and the disposal site is predicted to be a high alkaline environment over time. Therefore, it is urgent to understand radionuclides migration and alteration of the barrier materials under high alkaline environment. In general, most mineral surfaces are negatively charged under high alkaline conditions. Therefore, negatively charged anions are poorly adsorbed to the mineral surface. Although the nuclide is considered to be poorly adsorbed in the safety assessment, the nuclide would be delayed by the dynamic processes such as precipitation and solid solution formation without adsorption. For example, layered double hydroxides (LDH), calcium silicate hydrate (C-S-H) and magnesium silicate hydrate (M-S-H) with positively charged surface and a high anion exchange capacity even at a high alkaline environment (Goh, Lim, and Dong 2008)(Evans 2008). In this context, the objective in this study is to clarify the Mg-bearing phases produced by mixing the interstitial water of cement (high alkaline) and the groundwater of Mg-HCO₃ system in the geological disposal environment. For formation of LDHs, 50 mM of each of Mg ion solution (Mg(NO₃)₂ · 6H₂O), Al or Fe ion solution (Al(NO₃)₃ · 9H₂O or Fe(NO₃)₃ · 9H₂O), and silicate anion solution (Na₂SiO₃) as an initial solution was mixed with different ratios. After the mixing, these mixed solutions were adjusted to pH 9 or pH 12 and left at 25 °C for 24 hours. The reason for paying attention to silicate ions is that they are concerned about dissolution from cement materials and vitrified bodies used in waste disposal and considered to be analogues of ⁷⁹Se and ⁹⁹Tc.

In Mg-Al system, at pH 9, in the case of adding above 15 mM silicate ions, M-S-H and amorphous aluminium (with Al ion), or M-S-H and smectite (without Al ion) were precipitated. On the other hand, in the case of below 15 mM silicate ions, LDH (Mg/Al 0.5) and gibbsite or boehmite (Mg/Al 0.5) were precipitated. At pH 12, in the case without Al ion and with Mg ion, brucite was confirmed. Moreover, M-S-H (Mg/Al 0.1) or LDH (Mg/Al 0.3) instead of gibbsite and boehmite were generated. In other systems, no change was observed with the precipitates at pH 9.

In Mg-Fe system, formation of LDH was confirmed in a system containing less silicate ion and much Mg ion, but ferrihydrite or M-S-H was precipitated in other systems containing Fe ion.

In order to investigate these results thermodynamically, by calculating and incorporating M-S-H and LDH database based on previous study (Hase et al. 2017), we could represent thermodynamically precipitated mineral species.

Keywords: magnesium silicate, layered double hydroxide