

## Phase transformation of metastable products in Mg-Si systems

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Transuranic (TRU) waste, which is one of the radioactive waste, is supposed to be surrounded by engineered barrier made up of bentonite and cement at the geological disposal sites. It is necessary to consider the influence of groundwater when we assess safety of the barrier. Since candidate disposal sites are thought to be the coast in Japan nowadays, we have to consider that groundwater flows from seawater. Magnesium might be derived from bentonite and groundwater, and silica might be supplied from cement and cement. Thus, we need to understand the interaction between the barrier materials and groundwater in Mg-Si systems. According to some previous studies, it is suggested that magnesium silicate hydrates (M-S-H) are formed as groundwater dissolves cement or pore fluids from cement alter bentonite. Since TRU waste needs isolation for at least next few million years, M-S-H, which are metastable quasicrystals, should be transformed into stable minerals. However, phase transformation behavior of M-S-H is still not clear. Therefore, this study tried to identify a mineral that is transformed from M-S-H. M-S-H were synthesized by mixing magnesium oxide powder (MgO) and silica fume (SiO<sub>2</sub>) in a deionized water with different MgO/SiO<sub>2</sub> (M/S) ratios (0.8, 1.3, and 1.7) and water/solid (w/s) ratios (45 and 500) at ambient temperature. Then, the mixtures were aged at 25 and 50°C for up to 6 months, or at 90, 120, and 180°C for up to 3 months. The XRD profiles of the all the run products were consistent with the formation of M-S-H, as identified by a previous study (Roosz et al., 2015). For those mixed with higher M/S ratios, brucite was also identified as time elapsed. At 25°C and 50°C, samples after 0.5, 1, 3, and 6 months were compared, but these seem to have no visible change in crystallization based on FWHM of the peaks. Then, XRD profiles of the samples at different temperatures after the same reaction time were compared, and peaks of serpentine were also observed at 180°C under a condition of M/S 1.3 and w/s 45. Since rising temperature is proportional to increasing reaction rate, this result suggests that a part of M-S-H is transformed into serpentine. Moreover, to investigate the sample which contains serpentine further, TG-DTA, FE-SEM observation, and TEM observation were carried out. From TG-DTA, dehydration reactions (i.e., endothermic reactions) was observed around 90°C, 380°C, and 600°C, and an exothermic reaction was observed around 870°C. The dehydration reactions around 90°C and 380°C are caused by M-S-H and brucite, respectively. The dehydration reaction around 600°C and exothermic reaction around 870°C is assigned to thermal behavior of chrysotile, which is a member of serpentine group. This finding are also supported by electron microscope observation of the samples, showing tubal aggregates like chrysotile. Additionally, IR spectra were measured to observe bonding state of atoms. As with XRD analysis, samples at different temperatures after the same reaction time were compared. The bands in the range from 950 to 1100 cm<sup>-1</sup> indicate Si-O-Si stretching vibrations of Q<sup>3</sup> tetrahedra, and there were no big changes of absorbance. The bands around 896 cm<sup>-1</sup> indicate Si-O-Si stretching vibrations of Q<sup>2</sup> tetrahedra, and the absorbance of these bands is decreasing with raising the temperature. Therefore, as reaction temperature is rising, Q<sup>3</sup>/Q<sup>2</sup> is getting high. This means a trend of layer silicate formation. To summarize these analyses, these results suggest that a part of M-S-H is transformed into layer silicate, in this case, especially, chrysotile.

Keywords: Magnesium Silicate Hydrates, serpentine, Transmission Electron Microscope