Properties of precipitates in alkaline Fe^{2+}-SiO_2-H_2O systems

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Understanding the alteration of the constituent materials of multi-barrier system is crucial for long-term safety assessments of high-level radioactive waste disposal. Whereas previous studies have aimed to understand respective properties and alteration of materials such as stainless steel and glass, few studies have focused on the interaction between these materials due to the difficulty of the experiments under anoxic condition. If secondary phases formed between these materials consume both of dissolved Fe^{2+} from the steel and dissolved silica from the glass, the secondary phases should be considered in addition to kinetics of glass dissolution and native iron magnetization. Hence, this study focuses on the interface and aim to understand properties of precipitates in Fe^{2+}-SiO_2-H_2O systems.
Laboratory experiments with different conditions (Fe^{2+}/Si(initial molar concentration) = 0.4, 0.7, 1.0, 1.3, 1.5 and pH = 7, 10, 12) were conducted in a N_2 or Ar gas filled globe box to maintain reducing environment. After mixing of Fe^{2+}- and silica-bearing solution under all experimental condition, light greenish materials formed. X-ray diffraction (XRD) and infrared (IR) spectroscopy revealed the formation of Fe-bearing hydrated silicate which has similar XRD and IR spectra with those of magnesium silicate hydrate (M-S-H) under all experimental conditions. Therefore, the precipitate may be ferrous silicate hydrate (F-S-H) in Fe^{2+}- SiO_2-H_2O system. Furthermore, the XRD results showed formation of ferrous hydroxides at high Fe/Si condition (Fe/Si ≧1.3) whereas the results showed formation of amorphous silica at low Fe/Si condition (Fe/Si=0.4, pH=10). This suggests that F-S-H has preferable range of Fe/Si like M-S-H. Consequently, ferrous hydroxides or amorphous silica prefer to be formed when Fe^{2+} or silica is excessively dissolved in the system, respectively. Solution chemistry after precipitation under alkaline conditions (pH = 10, 12) indicated that both Fe^{2+} and Si were almost entirely consumed for precipitation of F-S-H. On the other hand, under the condition with pH7, F-S-H precipitated but Fe^{2+} and Si are still present in solution. This reveals that alkaline condition is absolutely essential for formation of F-S-H.
This study implies that F-S-H can form at glass-steel interfaces when disposal environment is alkaline condition. If so, kinetics of F-S-H formation and alteration of F-S-H should be considered to understand evolution of the barrier interface between glass and steel and positive and negative impacts of F-S-H phases.

Keywords: Nuclear waste disposal, Ferrous silicate hydrate , Ferrous iron

