

Kinetics of Fe³⁺ mineral crystallization from ferrihydrite in the presence of Si at alkaline conditions and implications for nuclear waste disposal

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ABSTRACT

Fe³⁺ minerals are ubiquitous in diverse near-surface environments, where they exert important controls on trace species transport. In alkaline environments such as the glass-steel interface in geological high-level radioactive waste disposal sites that use cement for plugging and grouting, Fe minerals are closely associated with Si that may affect their crystallization behavior as well as their capacities to regulate hazardous element cycling. While it is well known that Si retards Fe mineral crystallization, there is currently an overall lack of quantitative information on the rates of crystallization of stable Fe minerals in the presence of Si at alkaline conditions. Crystallization of Fe³⁺ minerals goethite and hematite from ferrihydrite co-precipitated with different amounts of Si was studied at pH 10 and at temperatures ranging from 50 to 80 °C using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mineral abundances evaluated from Rietveld refinement of XRD data show that the proportion of goethite in the final assemblage decreases relative to hematite with increasing Si. TEM observation of goethite and hematite crystals formed in the presence of Si show significant morphological differences compared to those formed in the absence of Si. Rate constants for crystallization derived from fitting of time-dependent changes in mineral abundances with the Avrami equation show a decreasing trend with increasing Si for both goethite and hematite. Apparent activation energies for crystallization for both minerals increase with increasing Si, with that of goethite increasing more drastically compared to hematite, indicating the inhibitive effect of Si on the crystallization of both minerals. The overall inhibition of crystallization may be explained in terms of the effects of Si on the surface properties of the ferrihydrite precursor. The rate constants and apparent activation energies reported in this study may be useful in estimating the crystallization behavior and timescales of Fe minerals in both natural and engineered environments. This information may eventually be helpful in predicting the fate of hazardous elements in such environments.

Keywords: Ferrihydrite, goethite, hematite, silica, crystallization kinetics, activation energy