Kinetics of Fe\textsuperscript{3+} mineral crystallization from ferrihydrite in the presence of Si at alkaline conditions and implications for nuclear waste disposal

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**ABSTRACT**

Fe\textsuperscript{3+} 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 Fe\textsuperscript{3+} 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

**INTRODUCTION**

Fe\textsuperscript{3+} hydroxide and oxide phases such as goethite (α-Fe\textsubscript{2}O\textsubscript{3}) and hematite (α-Fe\textsubscript{2}O\textsubscript{3}) are widely distributed in different natural (e.g., soils, sediments) and engineered environments (e.g., geological waste disposal, water treatment technologies). Due to their high surface areas and surface reactivity, these phases have excellent sorption capacities for anions (e.g., sulfate, phosphate, arsenate, etc.) and metals (e.g., Pb, Cu, Ni), as well as organic compounds, exerting significant controls on the transport and availability of these substances (Cornell and Schwertmann 2003).

In engineered environments such as deep geological repositories for high-level nuclear wastes, initially reducing conditions may eventually give way to more oxidizing conditions in the long term due to influx of oxygenated groundwater. In such cases, poorly ordered Fe(II,III) hydroxysalts, ferrihydrite, goethite, and hematite are among a suite of corrosion products expected to form during aqueous corrosion of important steel components of the repository, such as the steel overpack (Refait et al. 2003; Kwon et al. 2007; Hazan et al. 2013). In Japanese disposal concepts, the use of cement as structural liners for tunnels, as mechanical support for the backfill and as grouting material for fractures arising from the country’s active geologic setting (NUMO 2004b) is expected to generate alkaline fluids around the repository. A breach in the canister, coupled with the presence of alkaline fluids, could result in the dissolution of vitrified waste and the release of high-yield radionuclides (e.g., U, Se, Tc) into the wider environment. Formation of Fe\textsuperscript{3+} phases from steel corrosion, however, may provide a sink for these elements, which exist as oxyanions, via adsorption and/or co-precipitation (e.g., Bargar et al. 1999; Rovira et al. 2008; Marshall et al. 2014). In particular, ferrihydrite, a poorly ordered Fe-oxyhydroxide that forms by the hydrolysis of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} ions (Cudennec and Lecerf 2006; Dyer et al. 2010), has exhibited superior sorption properties for these elements due to its high specific surface area (Das et al. 2013). In aqueous systems, oxide phases such as goethite and hematite typically crystallize via the transformation of the metastable and poorly ordered intermediate phase ferri-