The kinetics and mechanisms of schwertmannite transformation to goethite and hematite under alkaline conditions

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ABSTRACT

The transformation of schwertmannite to goethite and/or hematite in high pH solutions was studied between 60 and 240 °C using synchrotron-based, in-situ energy-dispersive X-ray diffraction (EDXRD). Powder diffraction and electron microscopy indicate that the crystallization of hematite and goethite occurred via intermediate ferrihydrite. At temperatures ≤80 °C goethite was the only crystallization product, while at temperatures >80 °C goethite and hematite crystallized almost simultaneously. At temperatures ≥150 °C a secondary crystallization stage was observed in which goethite transformed to hematite. The activation energies of nucleation for goethite and hematite are 27 ± 1 and 25 ± 1 kJ/mol, respectively, while the activation energies of crystallization are 33 ± 1 and 28 ± 1 kJ/mol. Most of the sulfate was released from the schwertmannite during the early stages of crystallization with <5% of the sulfate remaining associated with the solid phase after crystallization was complete. Sulfate from the initial schwertmannite retarded the dissolution of ferrihydrite, which inhibited the nucleation and the early stages of goethite formation, but did not significantly affect the later stages of goethite crystallization. At high temperatures the presence of sulfate favored the crystallization of hematite over goethite. The activation energy of crystallization for the secondary transformation of goethite to hematite is 103 ± 3 kJ/mol.

Keywords: Schwertmannite, ferrihydrite, goethite, hematite, sulfate, time-resolved, energy-dispersive X-ray diffraction

INTRODUCTION

Schwertmannite, with an idealized formula Fe₈O₉(OH)₆SO₄, commonly forms in acid mine drainage (AMD) environments as a poorly crystalline and nanoparticulate mineral phase (e.g., Bigham et al. 1990, 1996; Childs et al. 1998; Yu et al. 1999; Jönsson et al. 2005). The oxidation of pyrite in these systems releases large amounts of ferrous iron, sulfate, and acidity into associated ground and surface water. The oxidation of ferrous to ferric iron when the waters come into contact with the atmosphere leads to the precipitation of various Fe³⁺ (oxy)hydroxides and (oxy)hydroxy-sulfate minerals. At circum-neutral pH values ferrihydrite is the dominant phase formed, schwertmannite is the most common direct precipitate from AMD waters in the pH range 2–4, and jarosite is the prevalent phase at pH <2 (Brown 1971; Cravotta et al. 1999).

Characterization of natural and synthetic samples using electron microscopy has shown that schwertmannite forms spherical aggregates of up to 2 μm in size that consist of radially oriented, acicular crystals, ca. 100 nm in length and 10 nm wide (e.g., Bigham et al. 1990, 1996; Loan et al. 2004; Regenspurg et al. 2004). Based on data from both synthetic and natural samples, Bigham et al. (1990) suggested that schwertmannite has a structure similar to akaganéite (β-FeOOH) with double corner-sharing chains of FeO₆ (OH)₆ octahedra that produce square tunnels parallel to the c axis. These tunnels are stabilized by the presence of sulfate oxyanions, which form bidentate bridging complexes with Fe³⁺ in the structure. Studies also indicate that the individual schwertmannite particles are elongated along the c axis of the schwertmannite structure (Bigham et al. 1990; Bigham and Nordstrom 2000). However, Loan et al. (2004) showed that the individual schwertmannite particles have a maghemite-like structure, similar to that described by Janney et al. (2001) for ferrihydrite, although within the particles there was also evidence of more disordered and amorphous regions.

Natural and synthetic schwertmannite have variable iron, sulfate, and water contents (e.g., Bigham et al. 1990, 1996; Childs et al. 1998; Yu et al. 2001, 2002) leading to a general formula that can be expressed as Fe₇O₉(OH)₆₋₂(SO₄)₂₋ₓH₂O, where 1 ≤ x ≤ 1.75 (Bigham et al. 1994). In addition to the highly variable sulfate content, sulfate can be substituted by a range of (toxic) anions, such as arsenate (e.g., Carlson et al. 2002; Fukushima et al. 2003a, 2003b, 2004), selenate (Waychunas et al. 1995), and chromate (Regenspurg and Peiffer 2005). Schwertmannite has a high surface area (e.g., 240–320 m²/g for synthetic and 125–225 m²/g for natural samples; Bigham et al. 1990) and reactivity that results in a high sorption capacity for a wide variety of dissolved trace elements and contaminants (Webster et al. 1998; Jambor and Dutrizac 1998). For example, schwertmannite has been shown to effectively remove arsenic (e.g., Carlson et al. 2002; Fukushima et al. 2004), chromium (Regenspurg et al. 2005), selenium (Waychunas et al. 1995), copper, and zinc (Swedlund and Webster 2001) from solution. This efficient contaminant sequestration shows that schwertmannite can exert a significant...