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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