

The Thermal Behaviors of Ferrihydrite and Schwertmannite in Acid Mine Drainage

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Introduction

Fourier transform infrared spectroscopy (FT-IR), thermal analysis and X-ray diffraction patterns were used to analyze the ferrihydrite and schwertmannite. This study is undertaken to evaluate the thermal behavior of the minerals using X-ray diffraction, Fourier transform infrared spectroscopy and thermal analysis.

Ferrihydrite is a common iron oxide mineral in low temperature surface environments such as soils, lake and drainage bottom, and hot spring deposits (Schwertmann and Fischer, 1993; Schwertmann and Taylor, 1989). Because of its small grain size and large surface area, even small amounts of ferrihydrite can have important consequences for many soil properties (Cornell and Schwertmann, 1996; Jambor and Dutrizac, 1998). Ferrihydrite is important in environmental geology because of its common occurrence in mine-waste environments and its demonstrated ability to adsorb or form coprecipitates with organic compounds and ions of a wide variety of elements (Jambor and Dutrizac, 1998; Jambor, 1994). Natural ferrihydrite is difficult to isolate and characteristically contains impurities, even a few mole percent of which may have significant effects of its structure and phase transition behavior (Parfitt et al., 1992; Paige et al., 1997; Cornell and Schwertmann, 1996).

The mineral, schwertmannite, is poorly crystalline with a tunnel structure to resemble that of akaganite nominally β -FeOOH (Bigham et al., 1996). It occurs there, and elsewhere, as an ochreous precipitate from acid, sulphate-rich waters. A high specific surface area in the range of 100 to 200 m²/g and broad X-ray diffraction lines are consistent with its poorly crystalline character (Bigham et al., 1994). Its ideal formula is Fe₈O₈(OH)₆SO₄ but may range to Fe₈O₈(OH)_{4.5}(SO₄)_{1.75} depending upon the degree to which tunnel and surface sites are saturated with sulfate (Bigham et al., 1996).

Materials and Methods

Materials

The solid samples used in this study were collected from the top 0.5-1cm of bed sediment or pebble coated materials. Bed sediment was bright yellowish-orange and reddish brown in color and very fine, and probably contained detrital materials.

Analytical Methods

X-ray Diffraction Analysis

For identification of mineral constituents of precipitates, X-ray diffraction analyses were conducted using CoK α radiation with automatic horizontal goniometer equipped with a

scintillation counter and graphite monochromator and a 1° divergence slit. All specimens were step scanned from 3° to $70^\circ 2\theta$ in step size $0.05^\circ 2\theta$ and with 20 sec scanning time.

Fourier Transform Infrared spectroscopy(FT-IR)

Infrared absorption spectra were recorded with Bomem DA 8.16 FT-IR spectrometer from 400cm^{-1} to 4000cm^{-1} using KBr pellets(0.1% sample) and a scan speed of $150\text{cm}^{-1}/\text{min}$.

Thermal Analysis

Differential thermal analysis(DTA) and thermogravimetry(TG) of representative ferrihydrite and schwertmannite were run on samples using Setaram LABTGA at a heating rate of $10^\circ\text{C}/\text{min}$. Weight loss was determined of 20-35mg samples in alumina crucibles at temperatures ranging from ambient 1200°C .

Results and Discussion

Ferrihydrite

Thermal decomposition of the ferrihydrite from acid mine drainage precipitates produces a low-temperature endotherm in 123°C (Fig. 1). The endothermic reaction is associated with a weight loss of approximately 18.89% that probably derives from the vaporization of a layer of chemisorbed H_2O as well as structural $\text{OH}/\text{H}_2\text{O}$. After vaporization of structural $\text{OH}/\text{H}_2\text{O}$, ferrihydrite is completely convert to hematite at approximately 400°C . A final weight loss of approximately 21.18% in 850°C can be attributed to decomposition of ferrihydrite to yield hematite. Saleh and Jones(1984) and Eggleton and Fitzpatrick(1988) found a weight loss of 22.4% for a synthetic 6-line ferrihydrite and of 19.65% for 6- and 2-line ferrihydrite, respectively.

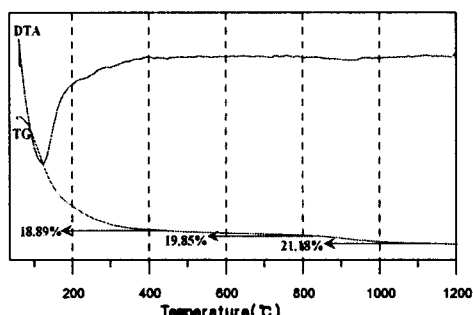


Fig. 1. Differential thermal(DTA) and Thermogravimetric(TG) patterns of ferrihydrite.
(Total initial sample weight=26.49mg)

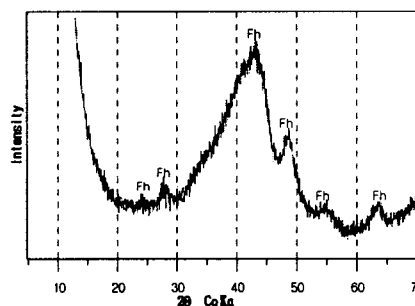


Fig. 2. X-ray diffraction patterns of ferrihydrite.

X-ray diffraction pattern of ferrihydrite(Fig. 2) consist of six broad diffraction bands. In all case, the diffraction bands are broad, but consistent character of the diffraction indicates a material is poorly crystallized but certainly not X-ray amorphous. X-ray diffraction analyses of ferrihydrite samples taken after cooling of the thermal reaction at 400°C indicate partially converted to poorly crystallized hematite.

FT-IR spectrum of ferrihydrite is dominated by broad, OH -stretching band at 3390cm^{-1} and another prominent absorption feature related to H_2O deformation is expressed at 1629cm^{-1} .

Schwertmannite

Thermal decomposition of schwertmannite the stream bottom sediments produces a low-temperature endotherm in approximately 150°C followed by an exotherm at 540°C. A second endothermic reaction peak appears at approximately 650°C. The initial endothermic reaction is associated with a weight loss of approximately 20% that probably derives from the vaporization of a monolayer of chemisorbed H₂O(Schwertmann et al., 1985) as well as structural OH. The final endotherm at 650°C can be attributed to SO₃ with Fe that volatilization produces a weight loss of 5 to 10%.

FT-IR spectrum of schwertmannite is dominated by broad, OH-stretching band at 3300cm⁻¹(Fig. 3). Another prominent absorption feature related to H₂O deformation is expressed at 1631cm⁻¹. Intense bands at 1128, and 1052cm⁻¹ reflect a strong splitting of the ν_3 (SO₄) fundamental due to the formation of a bidentate bridging complex between SO₄ and Fe(Bigham et al., 1990). This complex may result from the replacement of OH groups by SO₄ at th mineral surface through ligand exchange or by the formation of linkages within the structure during nucleation and subsequent growth of the crystal(Bigham et al., 1990). Related features due to the presence of structural SO₄ include bands at 986 and 482cm⁻¹ are attributed to Fe-O stretch. Lazaroff et al.(1982) studied in detail the IR properties of ochreous precipitates produced by bacterial oxidation of acid ferrous sulfate solutions in the laboratory. In their analyses, Lazaroff et al.,(1982) describe a single, broad ν_3 (SO₄) absorption band at 1110-1120cm⁻¹ with a shoulder at 1170 to 1180cm⁻¹ due to "additional sulfate IR activity." Band at 970 to 980 and at 1045cm⁻¹ were assigned to ν_1 (SO₄) and δ (OH), respectively.

The X-ray powder diffraction pattern of schwertmannite consists of eight broad diffraction bands(Fig. 4). X-ray diffraction analyses of samples taken after cooling at room temperature of the thermal reaction at 400°C, this material is at least partially convert to poorly crystallized hematite(Fig. 4). The extent of hematite transformation appears to be negatively related to the SO₄ content(Bigham, et al., 1990).

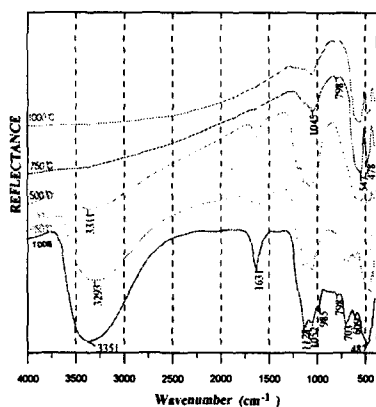


Fig. 3. FT-IR patterns of schwertmannite heated at given temperatures for 1 hour.

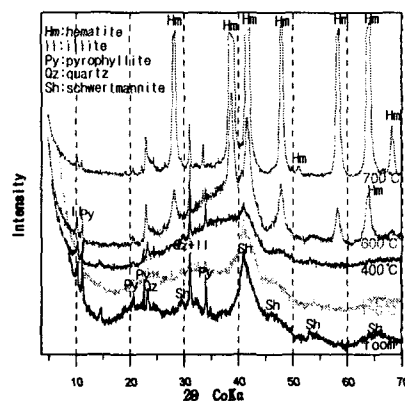


Fig. 4. XRD patterns of schwertmannite heated at given temperatures for 3 hours.

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