

INFLUENCE OF SULFATE ON Fe-OXIDE FORMATION: COMPARISONS WITH A STREAM RECEIVING ACID MINE DRAINAGE¹

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Abstract—An ochreous precipitate isolated from a stream receiving acid-sulfate mine drainage was found to consist primarily of goethite and lesser amounts of ferrihydrite-like materials. The Fe-oxide fraction, including goethite, was almost totally soluble in acid ammonium oxalate. Similar materials were produced in the laboratory by hydrolysis of ferric nitrate solutions containing 250 to 2000 $\mu\text{g/ml}$ sulfate as Na_2SO_4 . Initial precipitates of natrojarosite transformed to Fe-oxides upon aging for 30 days at pH 6.0. The proportion of goethite in the final products decreased with increasing sulfate ($\text{SO}_4/\text{Fe} = 0.2$ to 1.8) in the initial hydrolysis solutions; only ferrihydrite-like materials were produced at SO_4/Fe ratios > 1.5 . Variations in SO_4/Fe solution ratios also produced systematic changes in the color (10R to 7.5YR) and surface areas (49 to 310 m^2/g) of the dried precipitates, even though total S contents were relatively constant at 2.5 to 4.0%.

Key words—Acid mine drainage, Feroxyhite, Ferrihydrite, Goethite, Iron, Natrojarosite, Sulfate.

INTRODUCTION

Acid mine drainage (AMD) commonly arises by the exposure and subsequent oxidation of the iron sulfides found in many coals and associated rocks. The general process can be described by the following sequence of reactions generating sulfuric acid and ferrous iron (Vuorinen *et al.*, 1983):

- (1) $\text{FeS}_2 + 3.5 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{H}^+ + 2 \text{SO}_4^{2-}$,
- (2) $\text{Fe}^{2+} + 0.25 \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.5 \text{H}_2\text{O}$,
- (3) $\text{FeS}_2 + 2 \text{Fe}^{3+} \rightarrow 3 \text{Fe}^{2+} + 2 \text{S}$,
- (4) $\text{S} + 1.5 \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{H}^+ + \text{SO}_4^{2-}$, and
- (5) $\text{Fe}^{2+} + 2.5 \text{H}_2\text{O} + 0.25 \text{O}_2 \rightarrow \text{Fe}(\text{OH})_{3(s)} + 2 \text{H}^+$.

Reaction (2) is considered to be the rate-determining step in the dissolution of iron sulfide because the abiotic oxidation of Fe^{2+} is very slow at pHs typical of AMD (Singer and Stumm, 1970). In the presence of acidophilic iron oxidizing thiobacilli, however, the oxidation rate is accelerated five to six times over that achieved under abiotic conditions (Nordstrom, 1982).

Much attention has been paid to the generation of acidity by sulfide oxidation, but the fate of iron released in this process has not been well documented. Upon entering a stream system, Fe^{2+} is thought to oxidize and undergo hydrolysis as described by Reaction (5). A voluminous yellow precipitate, known colloquially as "yellow boy," forms almost immediately when AMD comes in contact with fresh water. The formation of this precipitate generates additional acidity and con-

tributes a highly reactive sediment to the stream (Robinson, 1981).

Most technical sources (e.g., Stumm and Morgan, 1981) have identified this colloidal precipitate as simply "amorphous" ferric hydroxide; however, ferrihydrite has been isolated from ochreous precipitates found near sulfide mines (Chukhrov *et al.*, 1973; Carlson and Schwertmann, 1981) where, in at least one case, its formation was related to rapid oxidation of Fe^{2+} by acidophilic bacteria (Chukhrov *et al.*, 1973). Using Mössbauer spectroscopy, Crosby *et al.* (1983) identified feroxyhite (δ' - FeOOH) as the dominant iron compound in a mine stream sediment from Great Britain. Other researchers (Chukhrov *et al.*, 1977; Carlson and Schwertmann, 1980) also noted that feroxyhite is precipitated by rapid oxidation of Fe^{2+} in solution but contended that the pH must be alkaline to slightly acid for optimum crystallization. The pH of most AMD is less than 3.5, and Nordstrom (1982) hypothesized that the fresh "yellow boy" found in AMD may in fact be jarosite which gradually decomposes to ferrihydrite or goethite upon exposure to more dilute waters. Lazaroff *et al.* (1982) reported that an "amorphous" ferric hydroxysulfate was the primary iron compound produced by bacterial oxidation of FeSO_4 in acid laboratory solutions. The precipitates examined had a reddish brown color and a variable Fe/SO_4 ratio (3.5–5) compared to the distinctive canary yellow color of jarosites with Fe/SO_4 ratios of about 1.5. Lazaroff (1963) also reported that high concentrations of sulfate are required for the bacterial oxidation of Fe^{2+} and the subsequent precipitation of ferric compounds in acidic environments. Relative to nitrate or chloride systems, the sulfate ion appears to promote the nucleation and growth of ferric

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oxides and to destabilize the colloidal phase causing flocculation at low pH (Dousma *et al.*, 1979).

Because of the uncertainty associated with the nature and formation of ferric compounds in acidic, high sulfate media, the primary objectives of the present study were: (1) to isolate, identify, and characterize a representative sample of colloidal precipitate formed in a stream receiving acid mine drainage, and (2) to examine the role of sulfate in the formation of ferric precipitates under laboratory conditions.

MATERIALS AND METHODS

Collection of field samples

About 60 liters of water containing a voluminous, yellow precipitate was collected during a period of low discharge from a stream affected by AMD in south-eastern Ohio. The precipitate was allowed to settle in the laboratory, and the supernatant liquid was decanted. The solid phase was then concentrated by centrifugation, washed by dialysis, quick-frozen, and freeze-dried. Separate water samples were collected from the acidic mine effluent and from the receiving stream at one site above and several locations below the point of acid discharge. These samples were placed in foil-wrapped, polyurethane bottles (Heaney and Davison, 1977) and transported under ice to the laboratory where they were immediately analyzed for pH, Eh, dissolved oxygen (DO), sulfate, Fe^{2+} , and total dissolved iron using procedures detailed elsewhere (Brady, 1982).

Preparation of laboratory specimens

To avoid introducing oxidation rate as a variable, laboratory specimens were prepared by initially hydrolyzing a series of 0.02 M $\text{Fe}(\text{NO}_3)_3$ solutions containing 0, 250, 500, 1000, 1500, and 2000 $\mu\text{g}/\text{ml}$ sulfate (as Na_2SO_4) for 12 min at 60°C. These concentrations yielded SO_4/Fe solution ratios of 0–1.8 and bracketed the range of sulfate encountered in the receiving stream examined in this study (Brady, 1982). Two aging procedures were used in specimen preparation. One set of precipitates was dialyzed against solutions containing the same concentrations of sulfate introduced at the time of initial hydrolysis. To mimic the constant introduction of fresh water in a receiving stream, a second set of precipitates was dialyzed against distilled water following the initial hydrolysis reaction. In both experiments, the dialysis solutions were changed daily and were adjusted to pH 6.0 to approximate the pH of reference stream waters. Because settleable precipitates formed almost immediately in those solutions containing sulfate, subsamples were removed for analysis after 36 hr of dialysis. The remaining precipitates were dialyzed for 30 days to approximate the maximum residence time of "yellow boy" in local streams. Following dialysis, all precipitates were freeze-dried and stored in a closed desiccator.

Analytical methods

Mineral samples were analyzed for total sulfur using a Leco induction furnace and semi-automatic titrator employing KIO_3 as a titrant. Oxalate-extractable Fe (Fe_o) was determined after Schwertmann (1964) and dithionite-citrate-bicarbonate extractable Fe (Fe_d) after Mehra and Jackson (1960). Iron in the extracts was measured using a Varian AA-6 atomic adsorption spectrophotometer. Dry colors of all materials were described using Munsell color charts under natural sunlight. Specific surface areas of samples dried over P_2O_5 were measured by the BET triple-point method using a Quantachrome Quantasorb instrument with N_2 as the adsorption gas.

X-ray diffraction (XRD) analyses of random powder mounts were conducted using $\text{CuK}\alpha$ radiation (35 kV, 20 mA) on a Philips PW 1316/90 wide-range goniometer fitted with a theta-compensating slit, a 0.2-mm receiving slit, and an AMR diffracted-beam graphite monochromator. Samples were step scanned from 10° to $65^\circ 2\theta$ at $0.05^\circ 2\theta$ increments using a counting time of 40 s/increment. The digital data were stored on floppy discs using an IBM personal computer, re-formatted for compatibility with the Lotus 1-2-3 graphics package, and plotted using an IBM XY 749 plotter. A differential X-ray diffraction (DXRD) pattern was obtained from the stream precipitate by subtracting X-ray diffraction data acquired following oxalate extraction from that collected before partial dissolution of the natural specimen (Schulze, 1981).

Infrared (IR) adsorption spectra were recorded with a Beckman IR-4250 spectrometer using both KBr pellets (0.2% sample) and oriented films on AgCl windows. The latter were deposited from aqueous suspension to yield a final concentration of 0.6 mg/cm^2 (Russell, 1979) and then dried over P_2O_5 for at least 24 hr prior to analysis. Thermal scans were made from 50° to 600°C using a DuPont 990 Thermal Analyzer, a differential scanning calorimeter (DSC) cell, 20-mg samples, N_2 atmosphere, and a heating rate of $10^\circ\text{C}/\text{min}$. Transmission electron micrographs were obtained using a Zeiss 9-S electron microscope. Samples were prepared for observation by dispersing 1 mg of precipitate in 50 ml of water with an ultrasonic probe and subsequently transferring one drop of suspension to a Formvar film mounted on a 200-mesh copper grid.

RESULTS AND DISCUSSION

Water quality

Selected water quality data from the field study area are summarized in Table 1; additional site and dissolved metal data are available elsewhere (Brady, 1982). Stream water from the reference site above the point of acid discharge exhibited a neutral reaction and contained low background levels of dissolved iron and sulfate. Both the Eh and DO content of the reference

Table 1. Selected water quality data.

	Eh (mV)	pH	DO ($\mu\text{g}/\text{ml}$)	SO ₄ ($\mu\text{g}/\text{ml}$)	Fe ⁽²⁺⁾ ($\mu\text{g}/\text{ml}$)	TDI ¹ ($\mu\text{g}/\text{ml}$)
Reference water	314	7.3	4.5	310	0	<1
Acid mine effluent	584	2.9	5.0	4543	1118	1172
Receiving stream ²	659	3.1	5.1	1020	82	138

¹ Total Dissolved Iron (TDI) = total iron passing a 0.1- μm filter.

² About 1 km below point of acid discharge.

water were lower than those of the acid mine effluent and the polluted segment of the receiving stream. These differences can be attributed to pH effects and to the fact that AMD inhibits the activity of most aquatic organisms, thereby keeping biological oxygen demand at a minimum.

The pH of the acid discharge was within the range of 2.0–3.5 normally reported for AMD (Fenchel and Blackburn, 1979). The pH rose at downstream locations through dilution; however, increases were modest because surface and ground waters in the area are weakly buffered. Associated with the low pH of the mine effluent were high levels of dissolved Fe²⁺ and sulfate. The concentrations of both species decreased markedly in the receiving stream due to dilution and/or precipitation effects. The 10-fold reduction in total dissolved iron over a linear distance of only 1 km was especially pronounced, and the related decrease in the proportion of Fe²⁺ confirmed that rapid oxidation, hydrolysis, and precipitation of iron had occurred in the natural, acid-sulfate environment.

Chemical data

The natural stream precipitate collected in this study was almost 90% reductant soluble indicating a large oxidic Fe component. Most of this component was also solubilized by a 2-hr treatment in the dark with pH 3.0 ammonium oxalate ($\text{Fe}_o/\text{Fe}_d = 0.99$, Table 2). High oxalate solubility is normally associated with extremely poor crystallinity (Schwertmann, 1964), and ferrihydrite, with observed Fe_o/Fe_d ratios between 0.80 and 0.97, is the only common Fe-oxide for which such high oxalate solubilities have been reported (Schwertmann and Fischer, 1973; Carlson and Schwertmann, 1981).

All the aged laboratory products were completely soluble in dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960); hence, the reported Fe_d values (Table 2) can be equated to their total iron contents. Specimens prepared in the presence of sulfate uniformly contained almost 10% less Fe_d than that formed by hydrolysis in distilled water. This result suggests that sulfate and/or additional water was retained by the Fe-oxide structure which, in turn, implies reduced crystallinity. Reduced crystallinity was supported by higher Fe_o/Fe_d ratios for all sulfate-treated samples. For water-

Table 2. Properties of stream precipitate and laboratory specimens.

Sulfate treatment ($\mu\text{g}/\text{ml}$)	Munsell color	Specific surface (m^2/g)	S _t ¹ (%)	Fe _o ¹ (%)	Fe _d ¹ (%)	Fe _o /Fe _d
Natural precipitate from acid mine drainage						
—	10YR 6/8	97	3.0	29.6	29.9	0.99
Water-dialyzed specimens ²						
0	10R 3/4	119	0.0	39.4	55.6	0.71
250	5YR 4/8	159	2.7	36.7	47.7	0.77
500	5YR 4/8	183	2.5	34.3	47.2	0.72
1000	8YR 5/8	232	2.7	38.8	44.9	0.86
1500	7.5YR 5/8	99	3.0	40.2	46.4	0.87
2000	7YR 5/8	49	2.7	42.0	46.1	0.91
Sulfate-dialyzed specimens ²						
250	5YR 4/8	217	3.4	36.0	46.3	0.78
500	5YR 4/8	228	3.7	40.3	46.2	0.87
1000	5YR 4/6	310	3.3	38.5	46.3	0.83
1500	7.5YR 5/8	172	4.0	38.5	46.3	0.83
2000	6.5YR 5/8	82	4.0	38.4	46.2	0.83

¹ S_t = total sulfur; Fe_o = oxalate-extractable iron; Fe_d = dithionite-citrate-bicarbonate-extractable iron.

² Aged for 30 days.

dialyzed materials, Fe_o/Fe_d generally increased with increasing sulfate in the initial hydrolysis solution. A similar trend was not apparent for those precipitates aged in the continued presence of sulfate.

The total sulfur (S_t) contents of the natural stream precipitate and the laboratory products formed in the presence of sulfate ranged from 2.5 to 4.0% by weight. For the latter, these levels of S_t translate to Fe/SO₄ ratios of 3.8–6.3 and are comparable to those obtained in precipitates from microbially oxidized FeSO₄ solutions by Lazaroff *et al.* (1982). Although sulfate dialysis resulted in slightly higher S_t contents (Table 2), uniform levels of sulfur were incorporated into the precipitates subjected to each dialysis treatment despite graded levels of sulfate in the initial hydrolysis and/or wash solutions. This result suggests that the precipitates formed under the conditions of this study could accommodate only a limited amount of structural and/or specifically adsorbed sulfate.

X-ray powder diffraction

XRD analysis of the untreated stream precipitate (Figure 1a) yielded reflections due primarily to goethite and quartz plus a broad peak between 30 and 37°2 θ indicating the presence of another poorly crystallized Fe-oxide. Given the high oxalate solubility of this sample (Table 2), the presence of goethite is surprising inasmuch as this mineral has been reported to be relatively insoluble in acid ammonium oxalate for reaction times of as long as 4 hr (Schwertmann *et al.*, 1982). To evaluate the presence of goethite further, a sample of the stream precipitate was subjected to a rapid, 15-min oxalate extraction in the dark. This procedure re-

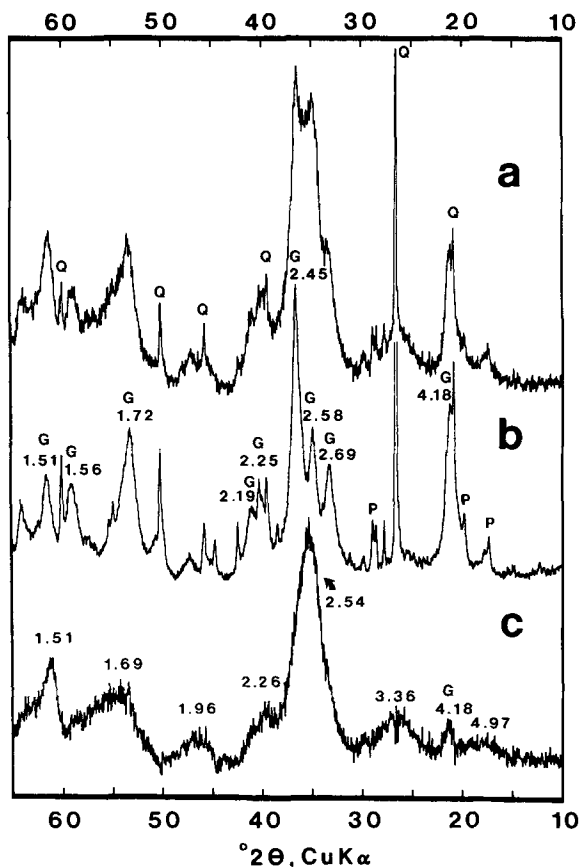


Figure 1. X-ray powder patterns from the natural stream precipitate: (a) untreated, (b) following 15-min oxalate extraction, (c) following spectral subtraction of (b) from (a) (DXRD). G = goethite, Q = quartz, P = phyllosilicate. Full scale \approx 300 counts. $\text{CuK}\alpha$ radiation. "d" values in Å.

removed 78% of the total reductant-soluble Fe (Fe_d) and left an Fe-oxide residue that consisted almost entirely of goethite (Figure 1b). Treatment of the sample with DCB or acid ammonium oxalate for 2 hr left a residue of detrital quartz and phyllosilicates. The reason for the high oxalate solubility of the goethite in this sample is not known but may be related to the presence of occluded or surface-adsorbed sulfate. Ferrous iron has also been reported to catalyze the dissolution of Fe-oxides in acid ammonium oxalate (Fischer, 1972); however, the stream precipitate was found to contain less than 0.2% Fe^{2+} . The spectral contributions of the material dissolved by rapid extraction with oxalate were evaluated by subtracting the data in Figure 1b from that in Figure 1a using the technique of Schulze (1981). The resulting DXRD pattern (Figure 1c) displays many of the diffraction effects normally associated with poorly ordered Fe-oxides, such as ferrihydrite and feroxyhite. The nature of these effects can be systematically addressed by comparing them with those obtained from analyses of the laboratory precipitates.

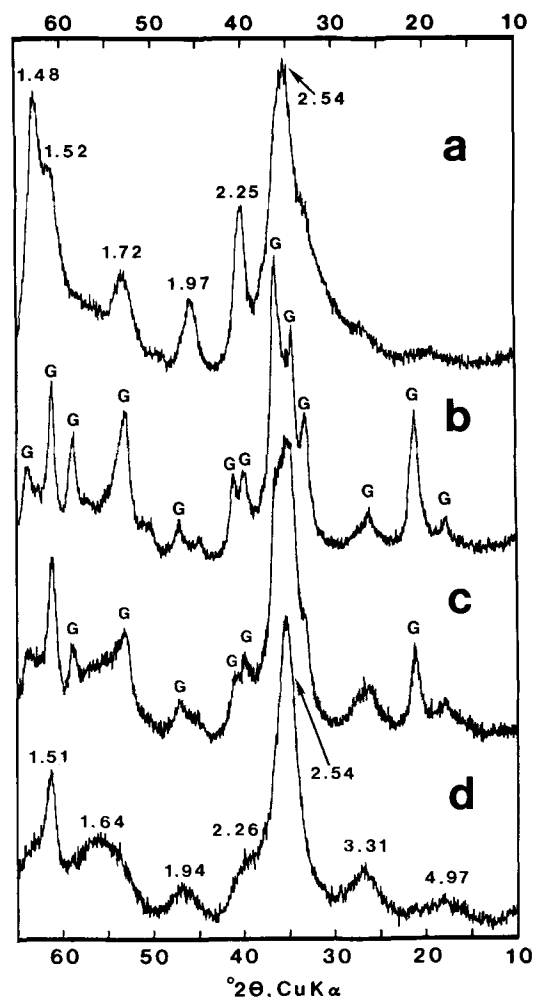


Figure 2. X-ray powder patterns from water-dialyzed laboratory specimens initially hydrolyzed in the presence of (a) 0 $\mu\text{g/ml}$ SO_4 , (b) 500 $\mu\text{g/ml}$ SO_4 , (c) 1000 $\mu\text{g/ml}$ SO_4 , and (d) 2000 $\mu\text{g/ml}$ SO_4 . G = goethite. Full scale \approx 300 counts. $\text{CuK}\alpha$ radiation. "d" values in Å.

Representative XRD traces of the water-dialyzed laboratory samples are presented in Figure 2. When sulfate was excluded from the hydrolysis and wash solutions, a precipitate was obtained that yielded the six diagnostic lines of well-crystallized ferrihydrite, including the intense but asymmetric 110 line at 2.54 Å and the normally unresolved doublet centered at 1.50 Å (Towe and Bradley, 1967) (Figure 2a). In contrast, the precipitates hydrolyzed in the presence of 250 or 500 $\mu\text{g/ml}$ sulfate (Figure 2b) yielded most of the diagnostic lines for goethite and a high background in the 2.5- and 1.7–1.5-Å regions indicating the presence of another poorly crystallized Fe-oxide. Here again, the Fe_d/Fe_a ratios for these samples (Table 2) were high considering their substantial goethite content.

With increasing sulfate, the diagnostic goethite lines became broader, weaker in intensity (Figure 2c), and eventually disappeared. In Figure 2d they are com-

pletely replaced by a series of reflections, including relatively intense lines at 2.5 and 1.5 Å, that are characteristic of poorly ordered Fe-oxides, such as ferrihydrite and ferroxihite. The spectrum in Figure 2d compares favorably with that obtained by DXRD analysis of the natural stream precipitate (Figure 1c); however, a comparison of these spectra and the ferrihydrite pattern in Figure 2a reveals several noteworthy differences. Specifically, the 2.25- and 1.47-Å lines are much weaker in the former, the reflections at 1.97 and especially 1.72 Å have broadened and shifted to lower spacings, and those at 2.5 and 1.5 Å have become sharper and more symmetrical. Pronounced differential line broadening like that expressed in Figures 1c and 2d indicates anisotropic crystal growth and probably also reflects lower crystallinity. Ferrihydrite and ferroxihite have similar structures and differ primarily in the z-periodicity of their octahedral sheets. In practice, the two minerals are distinguished by the presence of a diagnostic 1.97-Å ferrihydrite line and by a slight difference in spacing for the 114 ferrihydrite and 102 ferroxihite reflections at 1.72 and 1.69 Å, respectively (Chukhrov *et al.*, 1977). The presence of a 1.94-Å line in Figures 1c and 2d supports the presence of ferrihydrite; however, the reflection at 1.64–1.69 Å and the enhanced symmetry of the 2.54- and 1.51-Å reflections appear to be more characteristic of ferroxihite. These results suggest that both phases may be present. Although few detailed analyses of similar systems are available, Carlson and Schwertmann (1980) and Crosby *et al.* (1983) also reported the possible co-occurrence of ferrihydrite and ferroxihite in natural specimens.

A 3.3-Å line was observed in XRD spectra from all specimens synthesized in the presence of sulfate and in the DXRD pattern of the natural stream precipitate. In some spectra (e.g., Figure 2b), this line can be equated with the 201 reflection of goethite. In others (e.g., Figures 2c and 2d), it is disproportionately intense, and is not related to goethite. Although this reflection cannot fully be accounted for, it is interesting to note that a 3.3-Å reflection (partially obscured by subtracted quartz) is reported for many recently published DXRD spectra from natural ferrihydrites (Schwertmann *et al.*, 1982; Campbell and Schwertmann, 1984) and was recorded as a broad reflection from the synthetic ferrihydrite originally prepared by Towe and Bradley (1967). Chukhrov *et al.* (1977) also obtained weak reflections at 3.1 and 4.5 Å from laboratory preparations of δ -FeOOH. A final possibility is that this reflection indicates the presence of poorly crystallized akaganéite (β -FeOOH). The most intense diffraction line of akaganéite is at 3.32 Å, and other reflections coincide closely with those produced by ferrihydrite and ferroxihite. On the other hand, akaganéite has rarely been observed in nature, and its formation in the laboratory appears to require the presence of chloride or fluoride (Brown, 1980). In addition, the strong 110 line of akaganéite

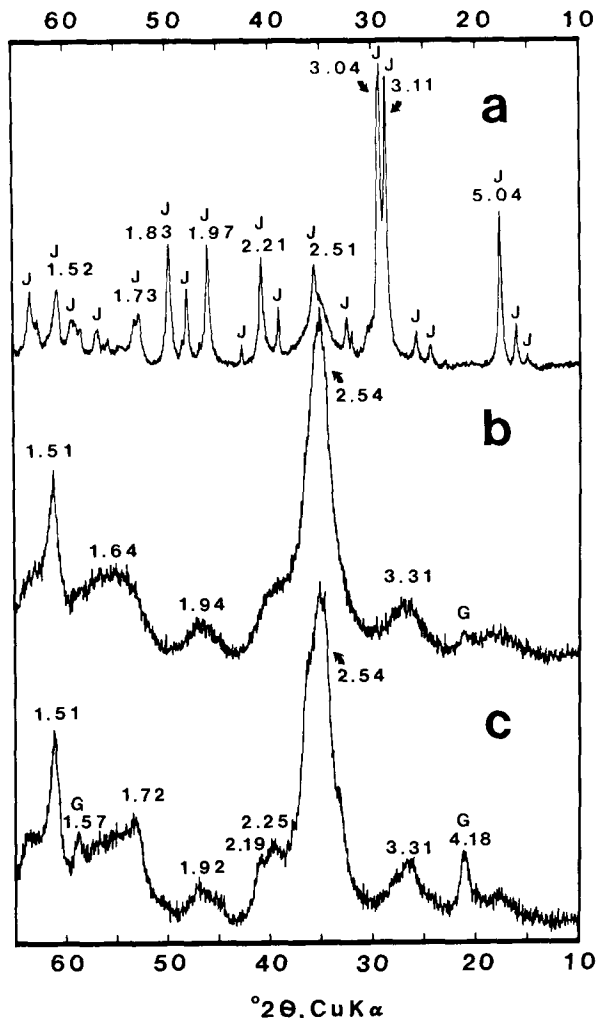


Figure 3. X-ray powder patterns from laboratory specimens initially hydrolyzed in the presence of 1500 $\mu\text{g/ml}$ SO_4 (a) after 36-hr water dialysis, (b) after 30-days water dialysis, and (c) after 30-days dialysis in 1500 $\mu\text{g/ml}$ SO_4 solution. J = natrojarosite, G = goethite. Full scale \approx 300 counts. $\text{CuK}\alpha$ radiation. "d" values in Å.

at 7.4 Å was not observed in any of the spectra examined in this study.

XRD results from the sulfate-dialyzed preparations were similar to those described for the H_2O -washed specimens except that aging in the presence of sulfate tended to preserve the goethite component. This effect is demonstrated in Figure 3 for samples initially hydrolyzed in the presence of 1500 $\mu\text{g/ml}$ sulfate. Also presented in Figure 3a is a scan from a corresponding 36-hr dialyze. In all experiments in which $\text{Fe}(\text{NO}_3)_3$ was initially hydrolyzed in the presence of sulfate, natrojarosite was the primary compound formed after aging for 36 hr. This result is consistent with the hypothesis that jarosite may commonly be the initial mineral phase produced in streams receiving AMD (Nords-trom, 1982).

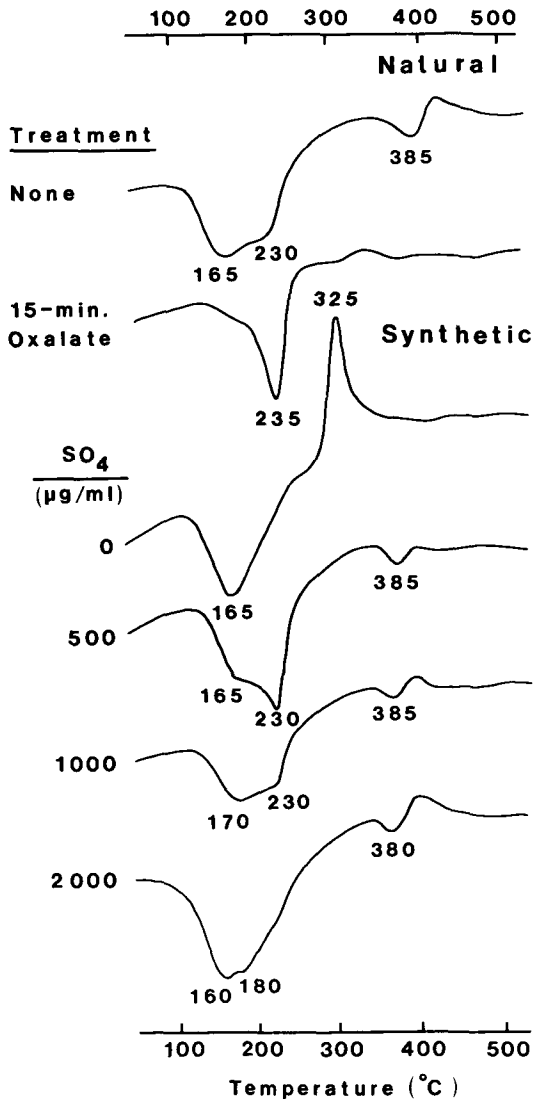


Figure 4. Differential scanning calorimeter traces from natural and synthetic specimens.

Thermal behavior

Thermograms of the natural stream precipitate and the water-dialyzed laboratory specimens are presented in Figure 4. The natural precipitate exhibited two poorly resolved endotherms between 150° and 250°C and a third endotherm at 385°C. Treatment of the sample with ammonium oxalate for 15 min eliminated both the low- and high-temperature features, leaving a well-defined goethite endotherm at 235°C. This temperature of decomposition is much lower than those normally reported for goethite and is consistent with the high oxalate solubility (low crystallinity) of this specimen. The pattern obtained from the natural sample compared favorably with that acquired from the laboratory product initially hydrolyzed in the presence of 1000 µg/ml sulfate. Those samples prepared at lower sulfate levels exhibited more pronounced goethite endo-

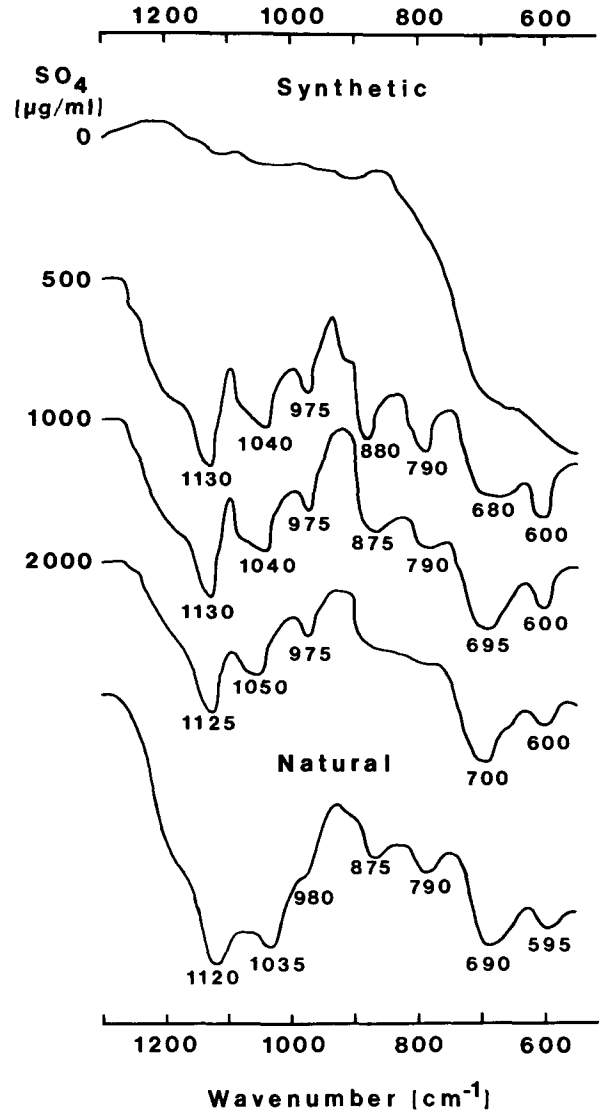


Figure 5. Infrared spectrograms from natural and synthetic specimens.

therms, whereas those synthesized at the highest sulfate concentrations (i.e., 2000 µg/ml) showed no evidence of goethite. Thermograms from the latter consisted of double endothermic peaks between 150° and 200°C followed by a weak endotherm at 375°–400°C. Carlson and Schwertmann (1980) described similar thermal behavior for a well-crystallized natural specimen of ferrihydrite. Only the specimen synthesized in the absence of sulfate yielded the single, strong exothermic peak between 300° and 350°C that has been reported to be characteristic of synthetic ferrihydrite (Chukhrov *et al.*, 1973; Carlson and Schwertmann, 1981).

Infrared characteristics

All samples exhibited IR characteristics typical of poorly crystallized Fe-oxides; these included major absorption features related to OH-stretching at 3400 cm⁻¹,

HOH-deformation at 1620 cm^{-1} , and $[\text{FeO}_6]$ octahedral vibrations from 430 to 470 cm^{-1} (data not shown). In addition to these general characteristics, several variable features were observed in the 600 – 1200-cm^{-1} range (Figure 5). The spectrum from the synthetic material prepared in the absence of sulfate was relatively featureless in this region. In contrast, all other specimens, including the stream precipitate, produced several IR bands that can be attributed to sulfate vibrational modes. These bands include the ν_1 fundamental at 975 cm^{-1} (poorly resolved in the stream sample) and bands at 1040 and 1125 cm^{-1} with a shoulder at 1180 cm^{-1} that are probably due to the ν_3 fundamental of SO_4 . In analyses of bacterially induced precipitates from acid sulfate media, Lazaroff *et al.* (1982) considered the absorbance at 1125 cm^{-1} to be diagnostic of material they identified as "amorphous" ferric hydroxysulfate, whereas features at 1180 and 1070 cm^{-1} were attributed primarily to the ν_3 (SO_4) fundamental of jarosite. In contrast, Harrison and Berkheiser (1982) observed a splitting of the ν_3 (SO_4) fundamental into the three designated bands as a result of specific adsorption of sulfate on the surface of hydrous iron oxide. The results of the present study also suggest that sulfate was present primarily in outer sphere coordination with iron atoms at the oxide surface.

In addition to SO_4 resonance features, the two OH-bending vibrations of goethite at 790 and 880 cm^{-1} were clearly present in IR spectra of the stream precipitate and of most of the synthetic specimens hydrolyzed in the presence of sulfate. In a manner consistent with XRD and thermal results, these bands decreased in intensity with increasing sulfate and eventually disappeared at the highest sulfate level (Figure 5). Additional bands were present at 600 and 700 cm^{-1} in spectra from all specimens except that prepared without sulfate. Lazaroff *et al.* (1982) observed similar features and attributed the latter to the hindered rotation of coordinated water molecules. The absorbance at 600 cm^{-1} remains unassigned.

Physical properties

The color of the stream precipitate (Table 2) was much yellower than those commonly observed for natural samples enriched with poorly crystallized Fe-oxides (e.g., Carlson and Schwertmann, 1980, 1981). It was also yellower than the synthetic materials produced in this study; however, the latter showed a distinct trend toward yellower colors with increasing levels of sulfate at the time of initial hydrolysis. At the highest sulfate concentrations, a slight reddening effect was apparent. Initial decreases in redness of the laboratory products were apparently related to the formation of goethite, which typically displays colors with hues of 10YR to 7.5YR. Reddening at the higher sulfate levels in turn reflected a lower content of goethite relative to more poorly crystallized Fe-oxides.

Sulfate also had a marked influence on the specific surface areas of the synthetic specimens. For comparable levels of initial sulfate, the products that were subsequently aged in sulfate solutions consistently displayed higher surface areas than their water-dialyzed counterparts. For both products, however, surface areas increased with increasing sulfate to levels of $1000\text{ }\mu\text{g/ml}$ in solution and then diminished in magnitude. The surface area of the natural precipitate was comparable to those obtained at the highest sulfate levels, and all were within the range of values reported by Crosby *et al.* (1983) for poorly crystallized Fe-oxides, including one specimen of acid mine stream sediment.

Variations in the measured surface areas also correlated well with the morphological characteristics of the samples as determined by transmission electron microscopy (Figure 6). The ferrihydrite particles synthesized in the absence of sulfate (Figure 6A) were very small (40 – $50\text{ }\text{\AA}$ diameter) and highly aggregated. The high degree of aggregation apparently led to an underestimation of surface area inasmuch as values greater than $119\text{ m}^2/\text{g}$ would be expected for particles of this size. A much larger proportion of independent, lath-shaped particles was present in specimens prepared in the presence of 250 – $1000\text{ }\mu\text{g/ml}$ sulfate (Figure 6B); these particles were presumably finely divided goethite. Above $1000\text{ }\mu\text{g/ml}$ sulfate, larger particles having electron dense interiors and numerous finger-like projections from the surface were produced (Figure 6C). These particles were similar in morphology to those formed in the stream environment (Figure 6D) and to the natural ferrihydrite particles described by Chukhrov *et al.* (1977).

CONCLUSIONS

Poorly crystallized, iron-rich precipitates are commonly produced by the oxidation of pyritic compounds in soils, sediments, coal, and metallic ore deposits (Nordstrom, 1982). The acid waters draining such materials generally contain high quantities of sulfate; however, the effect of sulfate on iron precipitation has not been rigorously evaluated. Analyses performed in this study demonstrated that goethite and ferrihydrite-like compounds were the dominant mineral phases comprising a fresh, voluminous precipitate collected from a stream receiving acid mine drainage in southeastern Ohio. Similar products were obtained by hydrolysis of Fe^{3+} solutions containing sulfate in concentrations comparable to those of natural AMD-affected streams.

Under both field and laboratory conditions, specific adsorption of the sulfate anion caused rapid destabilization of the colloidal sols produced by Fe^{3+} hydrolysis. Jarosite was the initial mineral phase produced in the laboratory; however, it transformed rapidly to oxyhydroxides with dilution and increase in pH of the surrounding solutions. The concentration of sulfate in the initial hydrolysis solutions also had a marked influence on both the type and proportion of final oxide

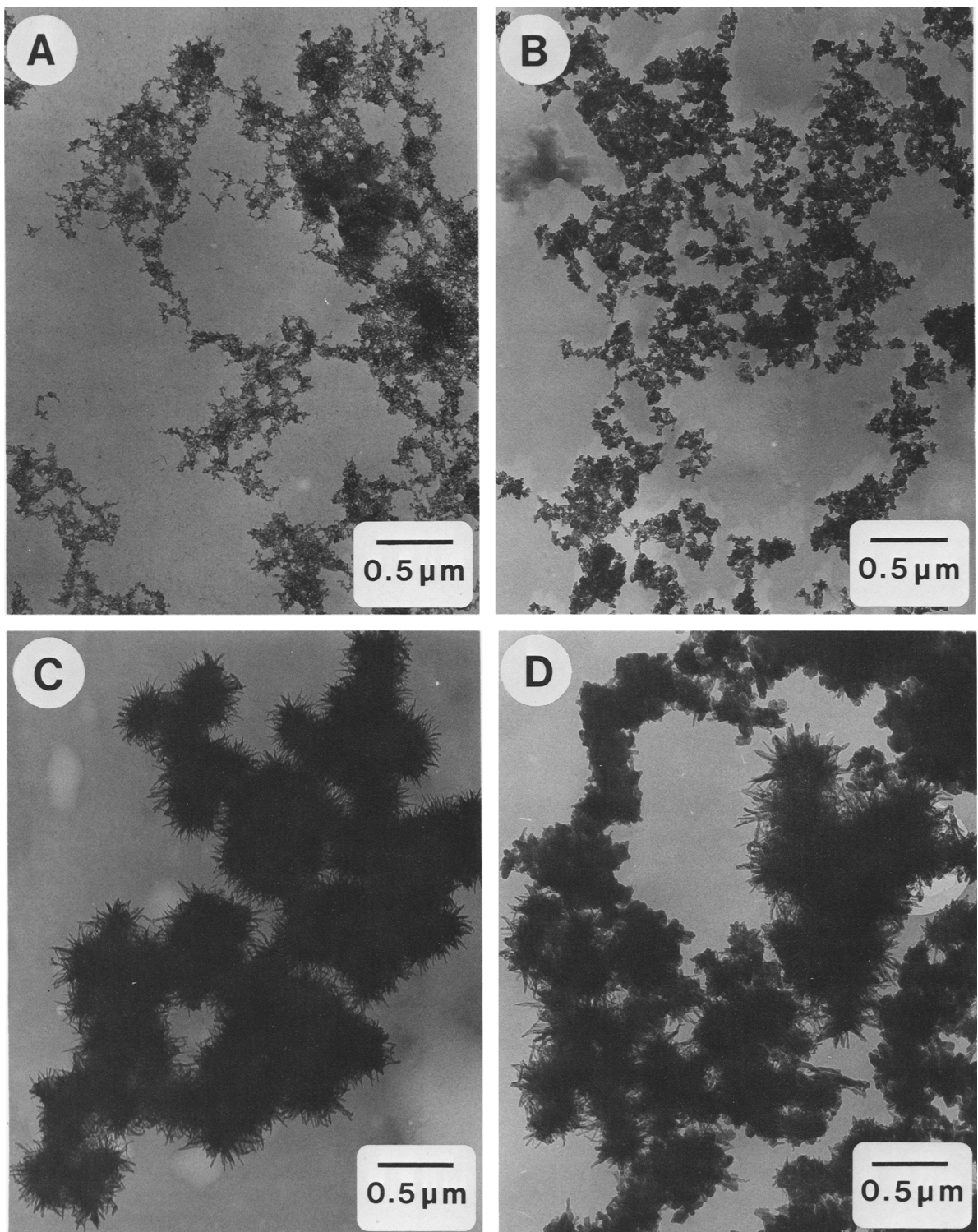


Figure 6. Transmission electron micrographs of water-dialyzed specimens (A) 0 $\mu\text{g/ml SO}_4$, (B) 500 $\mu\text{g/ml SO}_4$, (C) 1500 $\mu\text{g/ml SO}_4$, and (D) the natural stream precipitate.

phases produced. Specifically, ferrihydrite was obtained by rapid hydrolysis of Fe^{3+} in the absence of sulfate. The addition of sulfate at SO_4/Fe solution ratios <0.5 enhanced the formation of goethite relative to ferrihydrite; however, the proportion of goethite decreased with further increases in sulfate. At solution ratios >1.5 , goethite formation was completely inhibited, and the aged precipitates displayed characteristics of both ferrihydrite and ferrioxyhyte. Minor XRD peaks suggested that other phases, such as poorly crystallized akaganéite, may also have been present. In any case, DXRD analyses of the stream precipitate confirmed that a similar poorly crystallized oxide had formed under natural conditions. The exact mechanism by which sulfate influences oxide speciation could not be elucidated; however, the disappearance of goethite at high SO_4/Fe solution ratios suggests that sulfate anions can successfully compete with hydroxyls for surface adsorption sites and thereby inhibit the oxidation and oxalation reactions (Stumm and Morgan, 1981) that result in the formation and growth of goethite crystals from monomeric Fe^{3+} species in solution.

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