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A Fourier transform infrared study of the oxidation of pyrite

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Abstract

The oxidation of pyrite in an air atmosphere has been studied using Fourier transform infrared (FTIR) spectroscopy to identify phases present in the temperature range 430–680°C. Evidence of the formation of sulfate was obtained; the species was identified mainly as anhydrous iron(II) sulfate by comparison with the spectra of various iron sulfates and data from the literature. Iron(III) sulfate also formed as a minor phase. The FTIR analysis was supported by chemical analysis, both methods giving a maximum of iron(II) sulfate formed between 500 and 550°C. The FTIR method could be used to follow quantitatively the disappearance of pyrite as the oxidation progressed.

INTRODUCTION

The oxidation of pyrite has been extensively studied by thermal analysis and various reaction schemes for the oxidation process have been proposed. These include the direct oxidation of pyrite to hematite [1, 2]; the thermal decomposition of iron(III) sulfate to form hematite [1, 3]; the oxidation of iron(III) sulfate to produce $Fe_2(SO_4)_3 \cdot Fe_2O_3$ [3], and the formation of hematite either through thermal decomposition of the sulfate [3, 4] or through interaction between the sulfate and unreacted pyrite [5, 6]. Various techniques including X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used to analyze pyrite during the process of oxidation, but none of them has provided direct evidence of the sulfates formed. Quantitative XRD analysis of the phases formed

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at various temperatures during oxidation [7] indicated the presence of a significant proportion of an amorphous phase. Because of its low crystallinity, this phase could not be identified by XRD and was assumed to be iron(III) sulfate.

In this study, FTIR spectroscopy has been assessed as a means of identifying the phases formed during the oxidation of pyrite, with a special emphasis on the identification of the sulfate phases.

EXPERIMENTAL

Materials

The pyrite used in this study was a natural mineral, which was ground with an agate mortar and pestle and sieved through a 45 μm sieve. Analysis gave 47.6% iron and 52.8% sulfur, which accounted for 100.4% of the sample. Check analysis by electron probe microanalysis gave $Fe_{0.99}S_2$. An XRD pattern indicated that pyrite was the only detectable phase.

The quartz used in this study was a commercial product, about 98% pure, with a particle size of 50% less than 13.5 μm. The iron(III) oxide used was an ultrapure reagent (>99% pure) with a particle size of 50% less than 2 μm, supplied by Merck Chemical Company. The iron(II) sulfate heptahydrate and iron(III) sulfate decahydrate used were both analytical reagent grade. The anhydrous iron(II) sulfate was prepared in this laboratory by heating iron(II) sulfate heptahydrate to 500°C in a nitrogen atmosphere. The anhydrous iron(III) sulfate was prepared in this laboratory by heating the iron(III) sulfate decahydrate to 400°C.

Techniques

Preparation of partially oxidized pyrite samples

Approximately 5 mg of the pyrite sample was heated in a Linkam hot stage driven by a TMS 90 temperature controller at a rate of 10°C min^{-1} in an air atmosphere. The heating process was stopped at certain selected temperatures between 400 and 700°C. The atmosphere was replaced with nitrogen, and the sample was cooled to room temperature and analyzed by FTIR spectroscopy. Several identical experiments were carried out to provide a sufficient sample size for chemical analysis.

FTIR analysis

FTIR spectra were recorded with a Perkin-Elmer 1720 FT-IR spectrometer with a TGS detector. Ten scans were taken on each sample at a mirror velocity of 0.2 cm s^{-1} and a resolution of 4 cm^{-1} throughout the range 4000–400 cm^{-1}. A sample shuttle was used to take the interferograms of the background and the sample alternately in order to minimize the influence of CO_2 and moisture in the atmosphere on the spectra.

Samples were prepared by mixing approximately 1 mg (accurately weighed) of the ground sample with 100 mg of potassium bromide powder. The mixture was transferred into a cylindrical stainless steel die and pressed at a pressure of 9 tonne total load. The die was evacuated for one minute before being pressed and evacuation was continued throughout the pressing time of 3 min. The resulting pellet was 13 mm in diameter and about 0.2 mm thick.

Chemical analysis

Chemical analysis of the soluble divalent and trivalent iron in the heated pyrite samples was performed using a standard procedure [8]. Anhydrous iron(II) sulfate in the samples was calculated from the soluble divalent iron, and anhydrous iron(III) sulfate from the soluble trivalent iron.

RESULTS AND DISCUSSION

The FTIR spectrum of the pyrite sample before heating is given in Fig. 1, together with the spectrum of the commercial quartz. The spectrum of the pyrite sample indicates the presence of quartz as a minor impurity, as shown by the three characteristic peaks at 1090, 798 and 470 cm^{-1} and the two strong shoulders at 1170 and 516 cm^{-1}. The strongest peak at 422 cm^{-1} matches the peak of pyrite [9].

The FTIR spectra of pyrite samples heated to 430, 445, 470 and 540°C respectively are given in Fig. 2. The spectra of the iron(II) and iron(III)

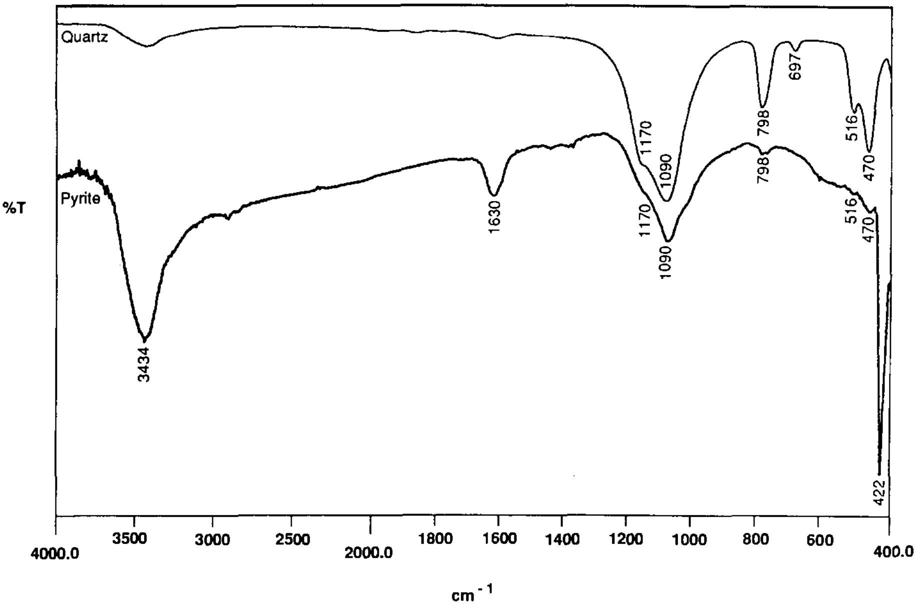

Fig. 1. FTIR spectra of pyrite and quartz.

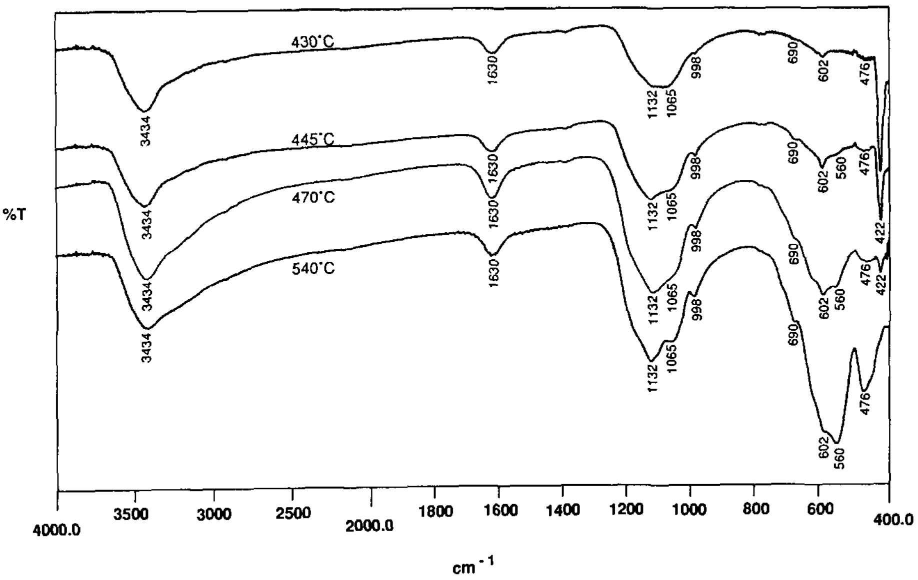

Fig. 2. FTIR spectra of pyrite samples heated to different temperatures in air. Heating rate 10°C min^{-1}.

anhydrous and hydrated sulfates are given in Fig. 3, together with the spectrum of the pyrite sample heated to 445°C. The spectrum of the pyrite

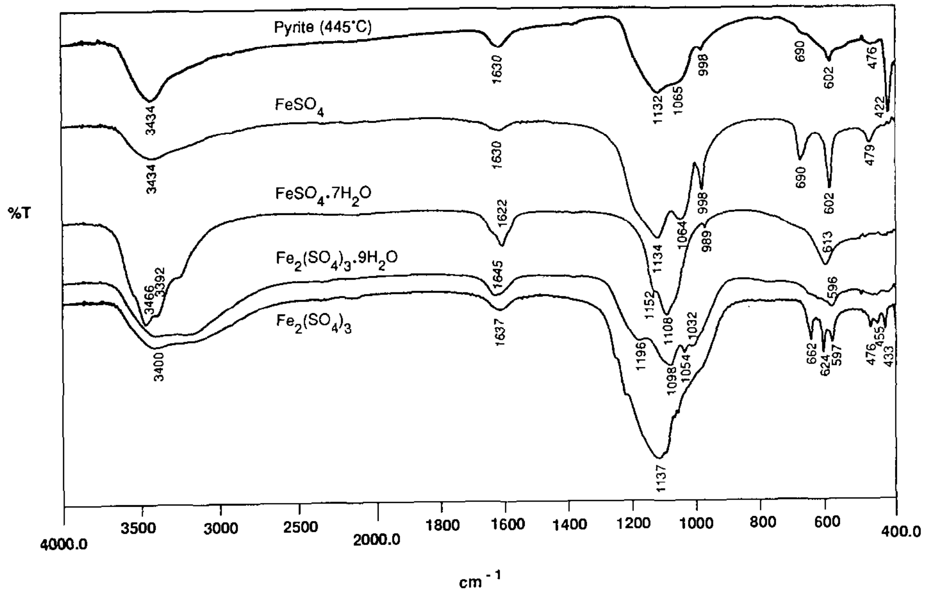

Fig. 3. FTIR spectra of iron(II) and iron(III) anhydrous and hydrated sulfates and pyrite heated to 445°C in an air atmosphere at a heating rate of 10°C min^{-1}.

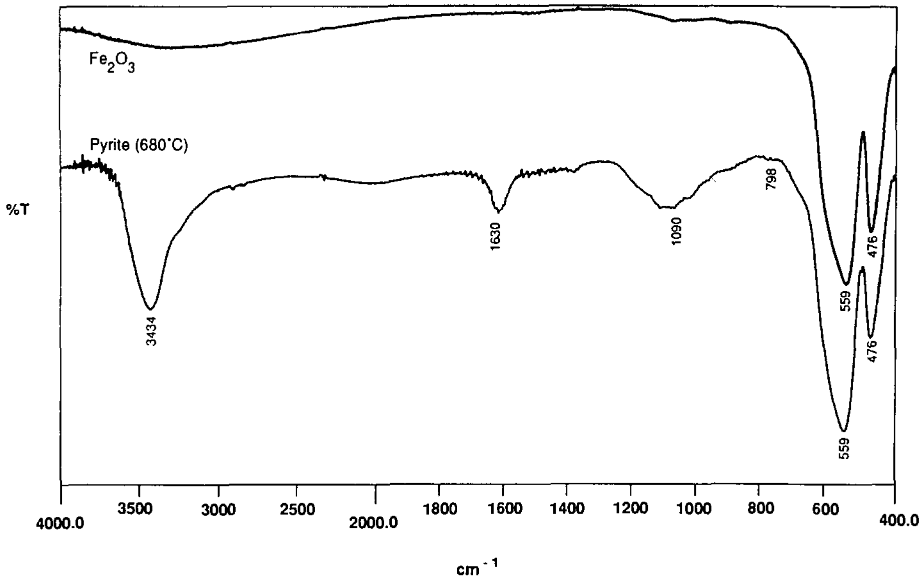

Fig. 4. FTIR spectra of iron(III) oxide and pyrite heated to 680°C in an air atmosphere at a heating rate of 10°C min^{-1}.

sample heated to 680°C is shown in Fig. 4, as well as that of iron(III) oxide.

The weight percentages of $FeSO_4$ and $Fe_2(SO_4)_3$ in the heated pyrite samples as determined by chemical analysis are shown in Table 1 and Fig. 5, as well as the percentage of $Fe_2(SO_4)_3$ in the total iron sulfates.

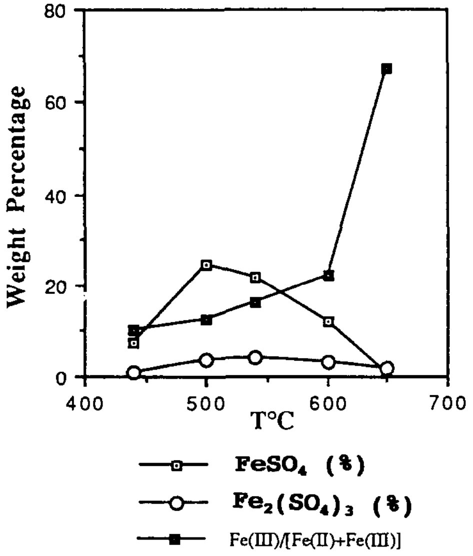

Fig. 5. Determination of soluble iron sulfates in partially oxidized pyrite samples by chemical analysis.

TABLE 1

Chemical analysis of iron sulphates in heated pyrite

	T (°C)				
	440	500	540	600	650
$FeSO_4$ (%)	7.56	24.47	21.60	12.02	0.98
$Fe_2(SO_4)_3$ (%)	0.86	3.51	4.24	3.40	2.00
$\frac{Fe_2(SO_4)_3}{FeSO_4 + Fe_2(SO_4)_3}$ (%)	10.21	12.54	16.41	22.05	67.11

Sulfate determination

The spectra of the pyrite sample heated to 430, 445, 470 and 540°C (Fig. 2) show absorption peaks in the two regions 900–1200 cm^{-1} and 500–700 cm^{-1}. These regions correspond to the characteristic absorption peaks of iron sulfates. The fundamental frequencies of the tetrahedral sulfate ion when retaining its full T_d symmetry are given by Ross [10] as 1105 cm^{-1} (ν_3), 983 cm^{-1} (ν_1), 611 cm^{-1} (ν_4) and 450 cm^{-1} (ν_2). The ν_1 (symmetric stretching) and ν_2 (symmetric bending) modes are Raman active only, whereas the ν_3 (asymmetric stretching) and ν_4 (asymmetric bending) modes are both infrared and Raman active. In sulfate compounds and minerals, the distortion of the tetrahedron will lower the symmetry, causing the non-active vibrations ν_1 and ν_2 to absorb in the infrared and removing the degeneracy of the infrared active ν_3 and ν_4 vibrations. The strongest peaks of sulfates are usually found in the region between 1210 and 1040 cm^{-1}, which correspond to the ν_3 vibration. The second strongest peaks of sulfates are frequently found in the range between 680 and 570 cm^{-1}, corresponding to the ν_4 vibration.

A single sharp peak in the region 1030–960 cm^{-1} corresponds to the ν_1 vibration, while a weak peak in the region between 430 and 500 cm^{-1} corresponds to the ν_2 vibration. A number of factors, such as site symmetry, the perturbation by water molecules and the possibility of co-ordination between metal and the anion, may affect the spectra [11]. The ν_3 vibration may be split to give rise to two or three absorption peaks, whereas the ν_4 vibration may be split into three absorption peaks. Thus the spectra vary considerably in the number, position and intensity of the absorption peaks between the iron(II) and iron(III) anhydrous and hydrated sulfates, as shown in Fig. 3.

The spectrum of the pyrite sample heated to 445°C (Fig. 3) shows strong peaks in the two characteristic regions of sulfates, indicating the formation of sulfate during the oxidation of pyrite. Further analysis by comparing the spectrum with those of the various types of iron sulfates indicates that the compound formed is an anhydrous iron(II) sulfate. The frequencies of the peaks of the heated pyrite sample at 1132, 1065, 998, 690, 602 and 476 cm^{-1} match those in the spectrum of anhydrous iron(II) sulfate within the resolution of the instrument (4 cm^{-1}). The relative intensities of the peaks are also compatible with each other. The characteristic peaks of anhydrous iron(III) sulfate at 1137, 662 and 624 cm^{-1} (Fig. 3) are almost undetectable in the spectrum. The chemical analysis of the pyrite sample heated to 440°C (Table 1) indicates the sulfate formed as being mainly iron(II) sulfate with only a small amount of iron(III) sulfate present.

According to the infrared data and assignment by Pannetier and Bregeault [12] (Table 2), the compound formed when the pyrite sample was heated to 445°C can be identified mainly as $FeSO_4$ with a C_{2v} site symmetry. The peaks at 1132 and 1065 cm^{-1} can be assigned to the asymmetric stretching vibration (ν_3), the peak at 998 cm^{-1} to the symmetric stretching vibration (ν_1), the peaks at 690 and 602 cm^{-1} to the asymmetric bending vibration (ν_4), and the peak at 476 cm^{-1} to the symmetric bending vibration (ν_2).

From the spectra of the pyrite sample heated to the various temperatures from 430 to 450°C (Fig. 2), it can be seen that no change in the frequencies of the characteristic peaks of the anhydrous iron(II) sulfate at 1132, 1065, 998, 690 and 602 cm^{-1} is observable. This suggests that, during the heating process of the pyrite sample between 430 and 540°C, iron(II) sulfate was the dominant sulfate present. This is consistent with the chemical analysis shown in Table 1 and in Fig. 5, although up to 4.24% of iron(III) sulfate was also determined in the sample. However, because the proportion of iron(III) sulfate in the sample was low, the characteristic peaks at 1137 and 624 cm^{-1} were masked by the strong peaks of the iron(II) sulfate at 1132 and 602 cm^{-1}, respectively. The iron(II) sulfate began to decompose above 500°C, and hence its content decreased

TABLE 2

Band frequencies in the spectra of ferrous sulfates and heated pyrite (445°C)

Compound	ν_1	ν_2	ν_3	ν_4	Site symmetry
β-$FeSO_4$ [a]	996	479	1195, 1131, 1060	678, 599	C_{2v}
$FeSO_4$ [b]	998	479	1134, 1064	690, 602	C_{2v}
Pyrite (445°C)	998	476	1132, 1065	690, 602	C_{2v}

[a] Data from Pannetier and Bregeault [12].
[b] $FeSO_4 \cdot 7H_2O$ heated to 500°C in N_2.

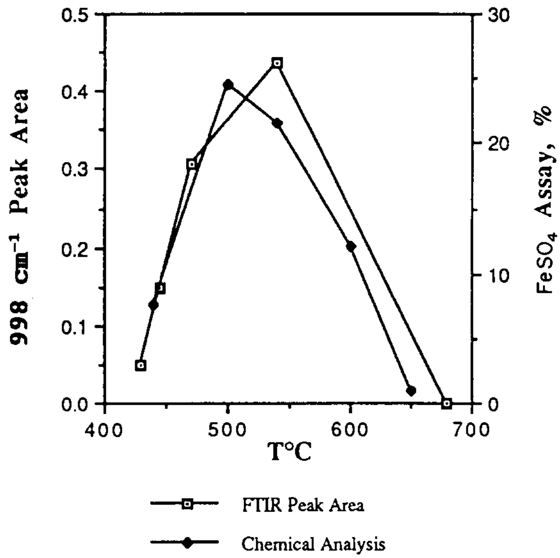

Fig. 6. Comparison of the $FeSO_4$ content of oxidized pyrite samples determined by chemical analysis and area integration of the peak at 998 cm^{-1} in the FTIR spectrum.

steadily up to 650°C. Iron(III) sulfate was relatively constant in the same temperature range, although it too had begun to decompose slowly above 550°C, so that the iron(III)/iron(II) ratio increased from 500–650°C (see Fig. 5).

The $FeSO_4$ peak at 998 cm^{-1}, which showed no interference from other phases, was integrated and plotted as a function of temperature (see Fig. 6), together with the values obtained from chemical analysis. Good agreement was found between the two sets of results, which indicated a maximum content of $FeSO_4$ occurring between 500 and 550°C.

Sulfide and oxide determination

The iron(III) oxide sample (Fig. 4) shows two major peaks in the FTIR spectrum at 559 and 476 cm^{-1}, and these peaks were used to identify the oxide in the oxidized pyrite samples.

The two peaks at 559 and 476 cm^{-1} are hardly visible in the pyrite sample heated to 430°C, but started to appear in the sample heated to 470 and 540°C (Fig. 2). This means that iron(III) oxide has formed between 430 and 445°C. Although the peak of iron(III) oxide at 559 cm^{-1} can hardly be seen at 430°C, the peaks of anhydrous iron(II) sulfate at 1132, 998 and 602 cm^{-1} are clearly shown. This suggests that anhydrous iron(II) sulfate formed at or below 430°C, whereas iron(III) oxide formed above 430°C and might be a product of the oxidation of iron(II) sulfate.

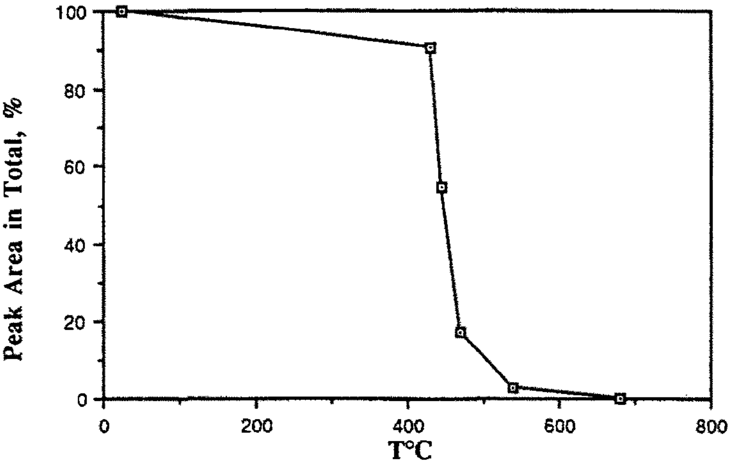

Fig. 7. Pyrite content as a function of temperature determined by quantitative FTIR spectrometry.

An attempt was made to quantify the change in composition of the oxide and sulfide components of the oxidized samples by integration of the appropriate peak areas in the FTIR spectra. However, this could not be realized for Fe_2O_3 because there was no peak available that did not have some interference from other phases. On the other hand, the peak at 422 cm^{-1} belongs exclusively to pyrite and is well resolved. The integrated peak areas as a function of temperature are given in Fig. 7.

The pyrite content decreases rapidly beyond 430°C. If the content at room temperature is taken to be 100% pyrite, then by 430°C this has fallen to 91%, by 445°C to 54%, to 17% by 470°C and 2.5% by 540°C. These values follow a similar trend to that reported by Dunn et al. [7], who used quantitative X-ray diffraction to obtain values of 90% of pyrite at 430°C, 36% at 470°C, and 10% at 505°C. Direct comparison is difficult as different apparatus was used to prepare the partially oxidized samples.

Reaction schemes

From the four components identified in the oxidized samples (FeS_2, $FeSO_4$, $Fe_2(SO_4)_3$ and Fe_2O_3) by FTIR and chemical analysis, the following reactions may be assumed

$$2FeS_2 + 5.5O_2 \rightarrow Fe_2O_3 + 4SO_2 \quad (1)$$

$$FeS_2 + 2O_2 \rightarrow FeSO_4 \quad (2)$$

$$2FeS_2 + 7O_2 \rightarrow Fe_2(SO_4)_3 + SO_2 \quad (3)$$

$$2FeSO_4 \rightarrow Fe_2O_3 + 2SO_2 \quad (4)$$

$$4FeSO_4 + 6O_2 \rightarrow 2Fe_2(SO_4)_3 + 2SO_2 \quad (5)$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_2 + 1.5O_2 \quad (6)$$

Other reactions are possible, but were not established in this study.

An examination of the changes in phase composition as presented in Figs. 2, 5 and 6 enables the temperature ranges in which the reactions occur to be defined. Between ambient temperature and 450°C, iron(II) sulfate, a small amount of iron(III) sulfate and Fe_2O_3 were formed. The last was quite difficult to detect by FTIR, although significant amounts must be present as the summed amount of pyrite and sulfate only accounted for about 65% of the total. The formation of $FeSO_4$ increased considerably with temperature up to 500–540°C, as indicated by both the chemical analysis and FTIR results. Between 450 and 550°C, all six reactions could take place, because all the four components were present in significant amount. However, as the proportion of $FeSO_4$ was much higher than that of $Fe_2(SO_4)_3$, reaction (2) was more likely to have occurred than reaction (3). Because $FeSO_4$ increased continuously in this temperature region, the oxidation of pyrite to $FeSO_4$ would certainly have taken place. The oxidation of pyrite into $Fe_2(SO_4)_3$ and Fe_2O_3 was less likely to occur because less than half of the original pyrite was left in this region. Hence increases in the Fe_2O_3 content were most likely attributable to the oxidation of $FeSO_4$ in reaction (4).

Between 550 and 580°C, because almost all the pyrite had been oxidized, the reactions (1)–(3) were unlikely to occur. Thus, no more $FeSO_4$ would form, which is supported by its continuous decrease (Fig. 6) and the considerable increase in the proportion of iron(III) sulfate in the total iron sulfates (Fig. 5). The oxidation of $FeSO_4$ might result in the formation of both iron(III) oxide and iron(III) sulfate (reactions (4) and (5)). The continuous decrease in iron(III) sulfate above 550°C indicates clearly the existence of reaction (6).

CONCLUSIONS

FTIR spectroscopy can be used to identify and monitor the change of various phases in pyrite during the process of oxidation. This technique is particularly useful because it directly measures the presence of sulfate phases, which is not possible by X-ray diffraction. The dominant sulfate phase present was iron(II) sulfate, with a C_{2v} site symmetry. Iron(III) sulfate also occurred, but only as a minor component. Pyrite oxidized rapidly between 430–470°C, with only 17% of pyrite remaining at the higher temperature. The first oxidized phase detected was anhydrous iron(II) sulfate at about 430°C, whereas iron(III) oxide was not detected until 430–450°C.

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