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A Fourier transform infrared study of the oxidation of pyrite. The influences of experimental variables

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Abstract

The influence of variables such as moisture in the air atmosphere, heating rate and particle size on the oxidation of pyrite has been investigated. FTIR spectrometry has been used to characterize the intermediates. All three variables had an influence on the extent of oxidation and the relative abundance of the phases formed.

INTRODUCTION

In a previous paper [1], we studied the oxidation of pyrite in an air atmosphere in the temperature range 430–680°C using FTIR spectroscopy. It was found that FTIR spectroscopy is a good technique for the identification of the various phases formed. For example, it was possible to differentiate between iron(II) sulphate and iron(III) sulphate on the basis of differences in their respective spectra, and in addition it was possible to quantify the phase content by peak area integration. It was found that iron(II) sulphate was obtained as the major phase with iron(III) sulphate formed as a minor phase. The FTIR peak for the Fe–S stretching vibration in pyrite at 422 cm^{-1} was well resolved and not subject to interference from other phases, and could be used to follow the disappearance of pyrite as it was oxidized.

In this paper, the established FTIR technique for the identification of the phases formed during the oxidation of pyrite is used to study the oxidation process in more detail. The effects of various experimental

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variables, such as moisture in the atmosphere, the heating rate and the particle size, are investigated.

EXPERIMENTAL

The characteristic properties of the pyrite sample have been reported in the previous paper [1], as well as the procedures for the preparation of partially oxidized samples and the FTIR and chemical analysis. The pyrite sample, of <90 μm, was used for all experiments except the particle size studies, for which a bulk sample was sieved into four size fractions, of particle size ranges 90–75, 75–45, 45–20 and <20 μm. Oxidation experiments were carried out at heating rates in the range 2–20°C min^{-1}.

RESULTS AND DISCUSSION

Effect of moisture in the atmosphere

The source of air in our laboratory is either a compressor or a cylinder. The difference between the sources is the water vapour content, with the compressor air having a water vapour pressure that varies with the humidity. In this work programme the water content was typically between 20 and 25%. The cylinder air contains less than 0.5% of water, and was further dried by passage through a silica gel column.

The FTIR spectra of pyrite heated in dry air at 10°C min^{-1} in the range 430–650°C are given in Fig. 1. The spectra are basically similar to those of

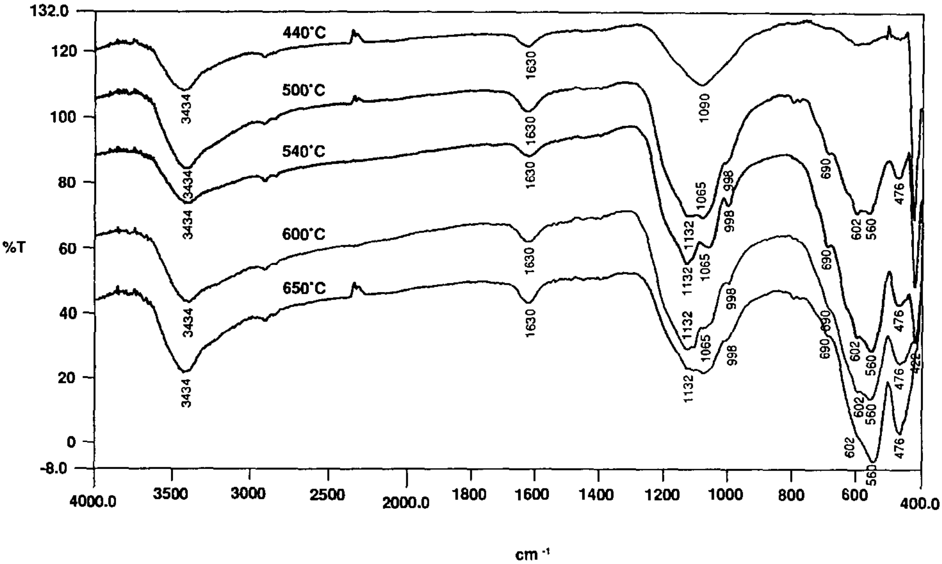

Fig. 1. FTIR spectra of pyrite heated to various temperatures in dry air.

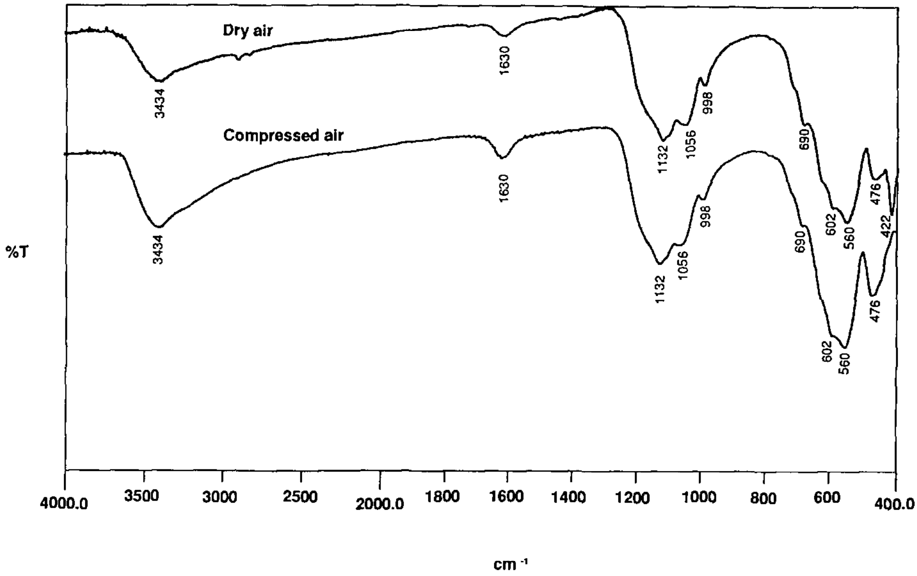

Fig. 2. A comparison of the FTIR spectra of pyrite heated to 540°C in dry and in compressed (moist) air.

pyrite heated in compressed air in the same temperature range, reported in the previous paper [1]. The phases formed during oxidation in dry air were still identified mainly as $FeSO_4$, as shown by the characteristic peaks at 1132, 1065, 998, 690 and 602 cm^{-1}. Fe_2O_3 was identified by the peaks at 560 and 476 cm^{-1}. $Fe_2(SO_4)_3$ can just be detected, and is present as a minor phase.

Figure 2 shows a comparison of the FTIR spectra of pyrite heated at 10°C min^{-1} to 540°C in compressed air and in dry air. When heated in compressed air, more pyrite was oxidized than by heating in dry air at the same temperature, as indicated by the much weaker pyrite characteristic peak at 422 cm^{-1}. More Fe_2O_3 was formed when pyrite was heated in compressed air, as shown by the increased intensity of the Fe_2O_3 peak at 476 cm^{-1}.

Chemical analysis of the partially oxidized products enabled the variation in the amount of $FeSO_4$ formed when the pyrite sample was heated in compressed air or dry air to be determined as a function of temperature. The results are presented in Fig. 3. It can be seen that, although the quantity of iron(II) sulphate remains effectively constant, the curve for the pyrite heated in compressed air was shifted to a lower temperature. The maximum formation of iron(II) sulphate occurred at $\approx$500°C for pyrite heated in compressed air and at $\approx$560°C when it was heated in dry air.

These experiments indicate that the presence of water vapour in the atmosphere enhanced the reaction rate of the oxidative process in pyrite.

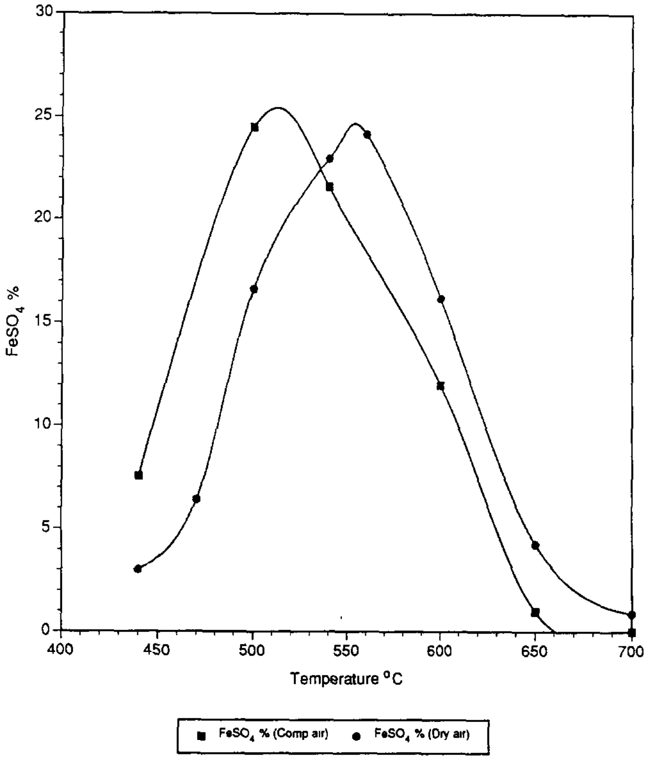

Fig. 3. Variation in the iron(II) sulphate content (determined by chemical analysis) with temperature for pyrite heated in dry and in compressed (moist) air.

Pyrite was oxidized, and sulphate formed and decomposed, at lower temperatures in the presence of moist air relative to dry air.

Effect of heating rate

Figure 4 shows the effect of changing the heating rate from 2°C min^{-1} to 20°C min^{-1} on the FTIR spectra of the pyrite sample heated to 540°C in dry air. It can be seen that more pyrite was oxidized and more Fe_2O_3 was formed at slower heating rates. This is consistent with the contracting sphere model for the oxidation of pyrite below 540°C, whereby the rate of oxidation is controlled by the diffusion of oxygen through the product layers [2]. It is interesting to note that, although the intensity of the pyrite peak at 422 cm^{-1} increased and intensity of the Fe_2O_3 peak at 560 cm^{-1} decreased with increasing heating rate, the intensity of the $FeSO_4$ peak at 998 cm^{-1} did not change significantly. Chemical analysis of the $FeSO_4$ formed at two different heating rates shows similar results (Fig. 5). Hence samples taken in the range 440–650°C and heated at rates of 5 and 10°C min^{-1} respectively had very similar $FeSO_4$ contents. However, the chemical analysis indicated that there was an increase in the quantity of

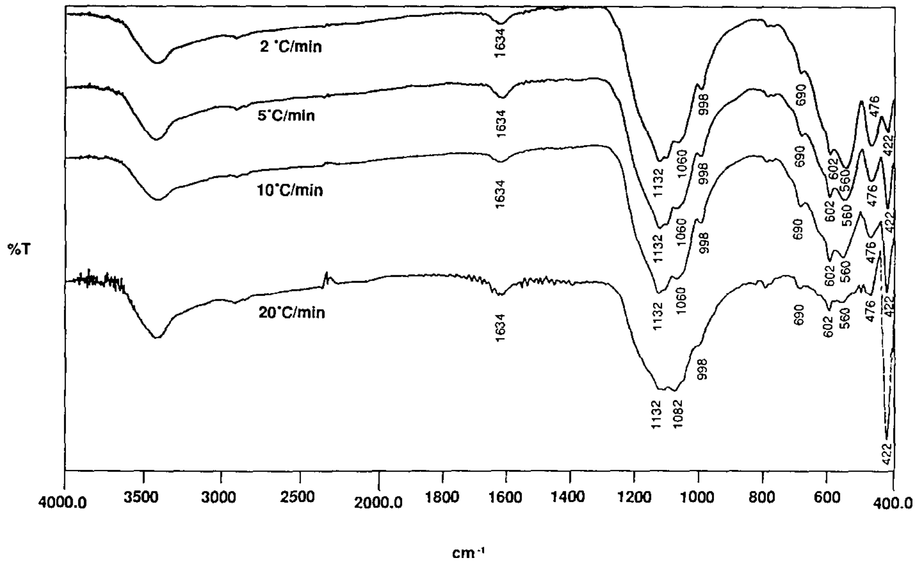

Fig. 4. FTIR spectra of pyrite heated in dry air to 540°C at different heating rates.

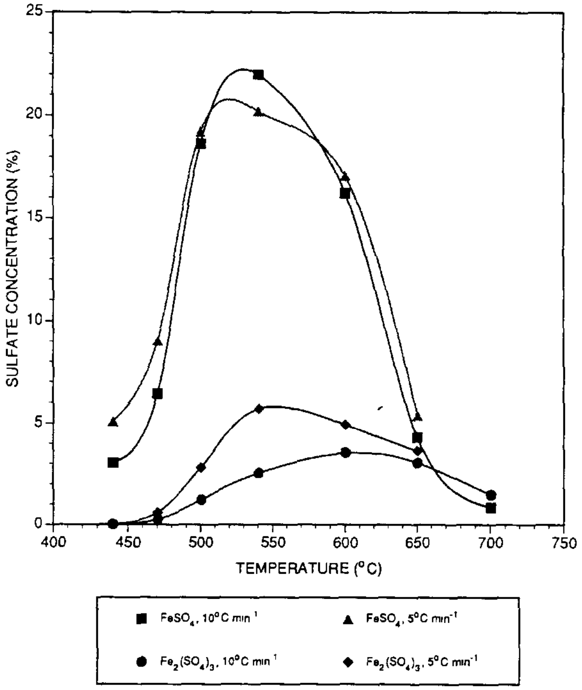

Fig. 5. Variation in iron(II) and iron(III) sulphate contents (determined by chemical analysis) with temperature in pyrite heated in dry air at two different heating rates.

TABLE 1

Effect of heating rate on the extent of reaction of pyrite heated to 540°C

Heating rate (°C min^{-1})	Unreacted pyrite (%)	Heating rate (°C min^{-1})	Unreacted pyrite (%)
2	19	10	40
5	37	20	80

$Fe_2(SO_4)_3$ formed at the slower heating rate. In a previous study [2] it was observed that an increase in heating rate decreased the formation of sulphate. This current study suggests that it is mainly a lowered formation of iron(III) sulphate that causes the decrease in sulphate formation with increase in heating rate.

Based on the area of the peak at 422 cm^{-1} for pure pyrite, the quantity of pyrite remaining unreacted at 540°C can be determined. The results are presented in Table 1. It is evident that time has a significant effect on the extent of reaction, and as the heating rate increases the amount of unreacted pyrite increases.

Effect of particle size

Figure 6 shows the FTIR spectra of the four different size fractions of pyrite heated to 540°C in a dry air atmosphere at a rate of 10°C min^{-1}. The major phases formed during the oxidation are iron(II) sulphate and

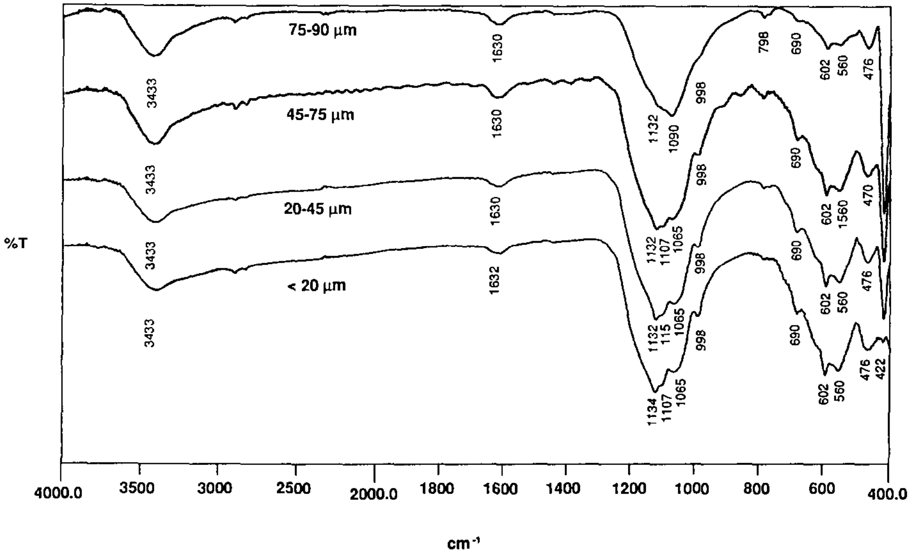

Fig. 6. FTIR spectra of pyrite of different particle sizes heated to 540°C in dry air.

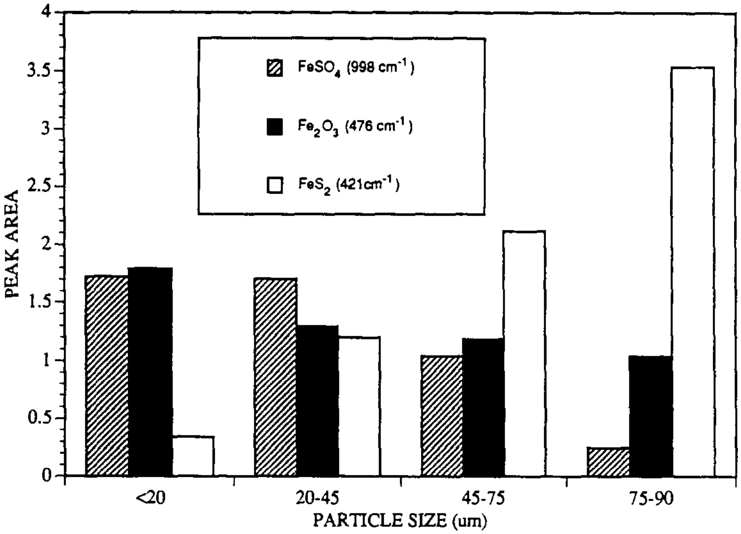

Fig. 7. Variation in iron(II) sulphate, iron(III) oxide and pyrite content for pyrite of different particle sizes heated to 540°C in dry air.

iron(III) oxide, and the presence of iron(III) sulphate was difficult to detect. There are significant changes in the area of the peaks of the phases of iron(II) sulphate, iron oxide and pyrite with change in particle size. As the particle size decreases, there is a marked increase in the rate of oxidation of pyrite, resulting in the formation of increased amounts of iron(II) sulphate and iron oxide. Figure 7 shows clearly that, as the

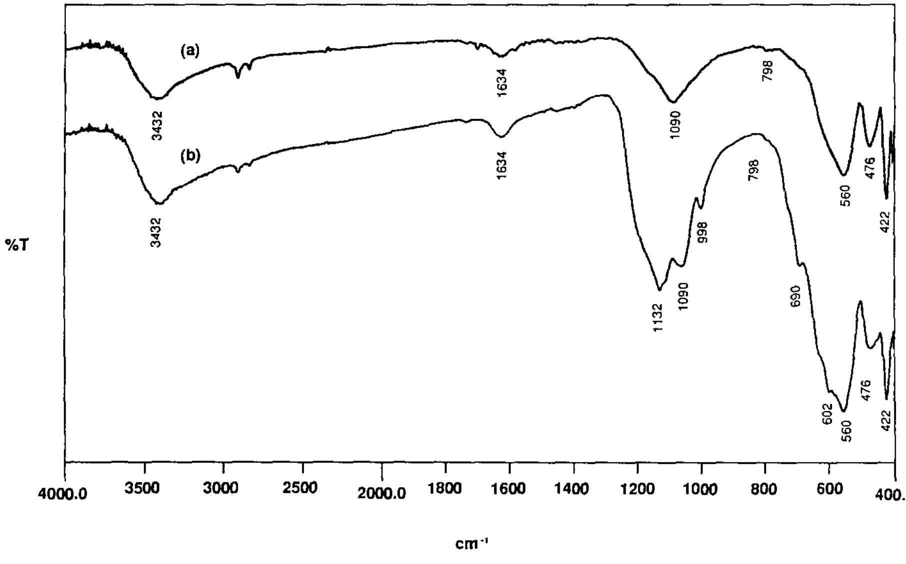

Fig. 8. FTIR spectra of pyrite heated at 10°C min^{-1} to 540°C: (curve a) after leaching with 0.1 M HCl; (curve b) unleached.

particle size increases, the rate of oxidation of pyrite decreases rapidly, and the rate of formation of iron(II) sulphate decreases rapidly as well. Although the formation of iron(III) oxide decreases, it does so at a much less rapid rate. Hence the loss of oxidation of pyrite is compensated for mainly by the lowered formation of iron(II) sulphate.

To confirm the assignment of peaks to the presence of sulphate, a sample of the 20–45 μm pyrite fraction after heating at a rate of 10°C min^{-1} to 540°C in dry air was conditioned with 0.1 M HCl solution at 70°C for 2 h. A comparison of the spectra of samples before and after the dilute acid washing (see Fig. 8) shows that, after washing, the peaks of iron(II) sulphate at 1132, 998, 690 and 603 cm^{-1} have disappeared, whereas the peaks of quartz at 1090 and 798 cm^{-1}, of iron oxide at 560 and 476 cm^{-1} and of pyrite at 422 cm^{-1} still remain.

CONCLUSIONS

The phases formed during the oxidation of pyrite were iron(II) sulphate and iron(III) oxide, with iron(III) sulphate as a minor component. The various factors examined, that is, moisture in the air, heating rate and particle size, all affect the rate of oxidation of pyrite. Moist air encourages oxidation, so that events occur at a lower temperature relative to dry air. The extent of oxidation decreased with increase in heating rate, which can be related to the time required for oxygen diffusion into the particle to take place. The extent of oxidation decreased with increase in particle size, which again can be related to the greater time required for oxygen to diffuse into large particles compared with small particles.

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