The Action of Sulfur Trioxide on Chalcopyrite

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Chalcopyrite reacts readily with SO_3 at about 100°C to form water-soluble sulfates; the reaction is approximately:

$$3CuFeS_2 + 26SO_3 \rightarrow 3CuSO_4 + FeSO_4 + Fe_2(SO_4)_3 + 25SO_2$$

The presence of about 4 pct O_2 in the gas phase greatly accelerates the reaction presumably due to the complete transformation of ferrous into ferric sulfate in an extremely porous form:

$$2\mathrm{Cu}\,\mathrm{FeS}_2 + 17\mathrm{SO}_3 + \frac{1}{2}\mathrm{O}_2 \rightarrow 2\mathrm{Cu}\,\mathrm{SO}_4 + \mathrm{Fe}_2(\mathrm{SO}_4)_3 + 16\mathrm{SO}_2$$

A stoichiometric mixture of $SO_2 + \frac{1}{2}O_2$ behaves towards chalcopyrite in nearly the same way as SO_3 although only in the temperature range 350° to 700°C.

VERY little is known about the reaction of sulfides with SO_3 . Sommer and Kellogg¹ showed in brief tests that sphalerite was converted to zinc sulfate at 360° to 527°C according to the equation:

$$ZnS + 4SO_3 \rightarrow ZnSO_4 + 4SO_2$$
 [1]

At that temperature neither oxygen nor SO_2 had any significant action on sphalerite. Jonas and $Guth^2$ reacted pyrite with pure SO_3 to get pure SO_2 suitable for liquefaction. The present study is concerned with the reaction between chalcopyrite and SO_3 .

EXPERIMENTAL

Tests were conducted on a -400 mesh chalcopyrite flotation concentrate from Twin Buttes, Arizona analyzing 29.6 pct Cu, 23.6 pct Fe, and 29.6 pct S. Sulfur trioxide used was pure, colorless liquid SO₃ marketed under the trade name Sulfan by Baker and Adamson. The supplier guarantees a minimum of 99.4 pct SO₃, a maximum of 0.3 pct H₂SO₄, and 0.25 pct stabilizer (e.g., SbCl₅, SbF₅, or boron compounds), and a boiling point of 44.8°C.

The action of liquid as well as gaseous SO₃ was investigated. In the first case, a flask containing 5.7 g chalcopyrite and 10 ml liquid SO₃ were contacted at room temperature with occasional shaking. The purpose of these tests was to use as low a temperature as possible in an attempt to eliminate the interaction of SO₃ with any elemental sulfur that might be liberated.³ Nitrogen was used to flush the flask at the end of the test to vaporize away any unreacted SQ₃. In the second case, gaseous SO₃ was generated by boiling Sulfan at 50°C. The amount of liquid SO₃ vaporized was 25 ml/h which equaled to 13,400 ml of gaseous SO_3/h . Chalcopyrite as 1 g samples were charged in a porcelain boat in a transparent Vycor tube and heated in a hinged type tube furnace (Lindberg) with a temperature control ± 0.5 °C for 1 or 2 h. The upper half of the furnace could be opened for inspecting the sample in the boat without interrupting the reaction.

At the end of each test, the flow of SO_3 and the heating were stopped and the reaction tube purged with nitrogen for a sufficient time to assure the absence of adsorbed SO_3 or SO_2 in the samples. It was also possible to remove the reaction tube out of the furnace to accelerate the cooling. The solid samples were then leached with water to determine the water-soluble copper and iron, while the total copper and iron were determined in the residue. Solubility in 5 pct H_2SO_4 was also determined but these were not included on the diagrams for the sake of clarity. All determinations were made by atomic absorption. Although great care has been taken in minimizing contact with air, e.g., use of dessicator and dry box, yet because of the extremely hygroscopic nature of the samples high precision cannot be claimed.

RESULTS AND DISCUSSION

Tests using liquid SO₃ showed that the reaction is slow; contacting chalcopyrite with liquid SO₃ at 30°C for 16 h converted about 30 pct of the copper into a water-soluble form and 8.8 pct of the sulfur into the elemental form. Heating at the boiling point for 8 h under a reflux condenser converted about 20 pct of the copper into a soluble form and 7.3 pct of the sulfur into the elemental form. The reaction

$$S + 2SO_3 \rightarrow 3SO_2$$
 [2]

is greatly accelerated by temperature rise such that above the boiling point of SO_3 no elemental sulfur can be found in the reaction product.³

Table I. Ferrous and Ferric Ion Contents in Solutions Obtained by Leaching the Reaction Products With Water, 1 g Samples, 2 h

Reactant		Water Soluble Iron		
	Temp., °C	Fe ²⁺ , g/l	Fe ³⁺ , g/l	Fe ³⁺ /Fe ²⁺
SO ₃	65	1.9	4.3	2.3
	95	2.2	4.4	2.0
	120	2.4	4.8	2.0
$SO_3 + O_2$	125	0.8	8.9	11.1

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Fig. 1-Water solubility of copper and iron on reacting chalcopyrite with SO₃ \bigcirc 1 h \triangle 2 h.

The rate of reaction of chalcopyrite with gaseous SO_3 is increased with temperature as shown in Fig. 1 up to a maximum at 100°C beyond which the rate decreases. Solutions obtained by leaching samples reacted at 65° to 120°C, Table I, showed that the Fe³⁺/ Fe²⁺ ratio is nearly 2. Therefore, the equation representing the reaction may be formulated as follows:

$$3CuFeS_2 + 26SO_3 \rightarrow 3CuSO_4 + FeSO_4 + Fe_2(SO_4)_3 + 25SO_2 \qquad [3]$$

The unexpected decrease in the rate in the temperature range 150° to 250°C is most probably due to the partial decomposition of SO₃ catalytically³ according to the Eq. [4]:

$$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$$
 [4]

This assumption is supported by the fact that the reacted samples after leaching with water were unreacted chalcopyrite as identified visually, by X-rays, and by chemical analysis. There is no reason to assume that only in this temperature range the sulfates produced form a protective layer on chalcopyrite which prevent further reaction with SO₃. Above 300°C, the residual SO₃ together with O₂ formed by the above reaction act rapidly on chalcopyrite resulting in a high reaction rate as observed experimentally in the increasing solubility of copper and iron.

At 500°C, the solubility of iron reaches a maximum since beyond this temperature ferrous sulfate is known to decompose to Fe_2O_3 . This can readily be judged by the red color of the reacted sample, and was confirmed by X-ray analysis.

The water solubility of copper reaches a maximum



Fig. 2—X-ray diffraction pattern (middle) of residue obtained by heating chalcopyrite in SO₃ atmosphere at 540°C then leaching with 5 pct H_2SO_4 to remove soluble reaction products. The patterns of chalcopyrite (top) and bornite (bottom) are included for comparison.

for a roasting temperature of 650°C since above this temperature decomposition to oxysulfate, $CuO \cdot CuSO_4$, takes place as can be judged by the insolubility in water but solubility in 5 pct H₂SO₄. At higher temperatures the formation of ferrite was confirmed by X-rays as well as by the fact the product was insoluble in 5 pct H₂SO₄.

There is evidence by X-ray diffraction and chemical analysis that bornite is formed as an intermediate in the temperature range 300° to 600°C. Fig. 2 shows the X-ray pattern of a residue obtained by heating chalcopyrite in SO₃ atmosphere at 540°C then leaching with 5 pct H_2SO_4 to remove soluble reaction products. The pattern shows the lines of bornite.

Effect of Oxygen

During the course of studies, it was observed that the presence of small amounts of air in the reaction tube greatly accelerated the rate of reaction. Therefore, a series of tests were planned to clarify this process. This was studied by allowing some of the oxygen to bubble through liquid SO_3 at a certain predetermined rate to obtain the required composition of the gas mixture. The oxygen lines contained calibrated flowmeters. The amount of liquid SO_3 evaporated per hour was noted by the difference in level in the graduated flask holding the SO_3 during each test.

The amount of liquid SO_3 vaporized was the same as in the previous tests. Oxygen concentration in the gas phase was maintained at 60 pct by volume. Fig. 3 gives the results of these tests which show the increase in water-soluble copper and iron in the low temperature range. Solutions obtained by leaching the reaction product were analyzed for ferrous and ferric contents, and compared with samples of chalcopyrite subjected to the action of SO_3 alone. A temperature range was so selected where no side reactions, *i.e.*, decomposition of sulfates, take place. It can be seen from Table I that when oxygen was added to SO_3 , the iron in the reaction product was mainly in the ferric state. In this case, therefore, the overall reaction would be:

$$2Cu FeS_2 + 17SO_3 + \frac{1}{2}O_2 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + 16SO_2$$
[5]

The effect of O_2 concentration in the gas mixture was consequently studied at a constant total gas flow. Fig. 4 gives the results of these tests. It can be seen that the maximum rate of reaction of chalcopyrite takes place when the concentration of oxygen in the gas mixture is about 4 pct which is near to the stoichiometric concentration of 2.9 pct according to the suggested equation. It should be also noted that pure oxygen has practically no effect on the rate of reaction of chalcopyrite at that temperature. Although the role of oxygen is believed to be secondary, yet it has a great effect on the





400

500

Temperature , ° C

600

700

800

200

300

100



Fig. 4—Effect of O_2 concentration in the gas mixture at 125°C for 2 h.



Fig. 5-Water solubility of copper and iron on reacting chalcopyrite with SO_2-O_2 mixture at different temperatures for 2 h.



Fig. 6—Water solubility of copper and iron on reacting chalcopyrite with O_2 at different temperatures for 2 h.

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rate of the reaction due to influencing the physical character of the product. The material becomes more porous and therefore more reactive than when SO_3 is used alone.

The reaction of chalcopyrite with SO_3-O_2 mixture was rapid at 125°C. In 15 min 71.2 pct of the copper was already converted into a water-soluble form.

Application to Other Minerals

A mixed copper ore containing chalcocite, covellite, chalcopyrite, chrysocolla, malachite, and azurite was treated by SO₃. It was found that 91.5 pct of the copper was converted into a water-soluble form after 15 min reaction with SO₃ at 150°C, and 99.1 pct when SO₃-O₂ mixture was used at 200°C.

The Action of SO₂-O₂ Mixture

Tests were conducted using a stoichiometric mixture of $SO_2 + \frac{1}{2}O_2$ to compare it with SO_3 . Results are shown in Fig. 5 from which it can be seen that the stoichiometric mixture is as effective as SO_3 in the temperature range 350° to 700°C, only. The low temperature reaction at 100°C is characteristic of SO_3 . The behavior of the stoichiometric mixture is also different from pure O_2 , Fig. 6. In case of O_2 , the sulfide ignites and the temperatures indicated are not certain.

CONCLUSION

1) SO₃ reacts with chalcopyrite at about 100°C to form water-soluble sulfates and SO₂.

2) SO_3 containing about 4 pct O_2 reacts more rapidly than SO_3 alone at that temperature apparently due to the complete transformation of $FeSO_4$ into ferric sulfate in an extremely porous form.

3) At that temperature a stoichiometric mixture of $SO_2 + \frac{1}{2}O_2$ has no effect on chalcopyrite but becomes similar only in the temperature range 350° to 700°C.

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