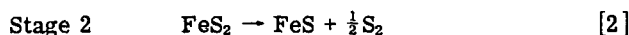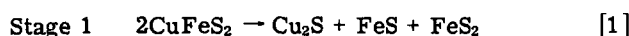# Communications

The Overall Kinetics of Roasting of Chalcopyrite

L. S. LEUNG

An intermediate step in the recovery of copper from chalcopyrite is the roasting operation in which partial removal of sulfur takes place. This operation is generally carried out in a multihearth roaster or a fluid bed roaster. The kinetics of roasting of chalcopyrite are well known.[1-4] For roasting at the operating temperature of about 650°C, the following three stages are believed to take place[2]

Stage 1 $2CuFeS_2 \rightarrow Cu_2S + FeS + FeS_2$ [1]

Stage 2 $FeS_2 \rightarrow FeS + \frac{1}{2}S_2$ [2]

     $\frac{1}{2}S_2 + O_2 \rightarrow SO_2$ [3]

Stage 3 $3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$ [4]

Taking magnetite (Fe_3O_4) as the stable iron oxide at roasting temperature the overall reaction may be written as

$$2CuFeS_2 + 4\tfrac{1}{3}O_2 \rightarrow Cu_2S + \tfrac{2}{3}Fe_3O_4 + 3SO_2 \qquad [5]$$
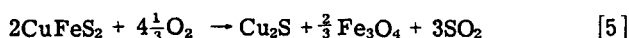
For a *given level of sulfur removal* from chalcopyrite two extreme paths may be envisaged:

1) initially all "free" sulfur in chalcopyrite is removed, *i.e.* 25 pct of sulfur in chalcopyrite is initially removed according to Eqs. [1] to [3]. Further reduction in sulfur takes place according to Eq. [4].

2) some chalcopyrite remains completely unreacted while the rest reacts to completion forming magnetite, chalcocite and sulfur dioxide according to Eq. [5].

For a given level of sulfur removal up to 75 pct of sulfur in chalcopyrite, the composition of calcine, minimum air requirement and heat of reaction are quite different for the two paths. These are compared in Table I and Figs. 1 and 2. Reaction Path 1 is referred to here as *textbook mechanism* while Path 2 is referred to as *proposed mechanism*. Table I shows that the magnetite content in calcine is considerably higher for the proposed mechanism than for the textbook mechanism over the practical range of sulfur removal in a roaster. Similarly the heat of reaction (Fig. 1) and minimum air requirement (Fig. 2) are also higher for the proposed mechanism.

In view of these differences a knowledge of what reaction path is followed in practice will be of some importance in the design and operation of roasters, particularly for the design of fluid bed roasters. Generally the textbook mechanism is accepted. Table I suggests that analysis of the calcine product from a roaster can give useful information on what reaction path is followed in practice.

Experimental As part of a comprehensive study of a 6.85 m diam, eight decks multihearth roaster, samples of calcine from various decks were collected and ana-

lyzed chemically and by X-ray diffraction. In sampling, the hot calcine was transferred quickly to sealed cans under an atmosphere of nitrogen to prevent further oxidation during cooling. Experiments were also carried out in a 102 mm diam fluid bed roaster operating within
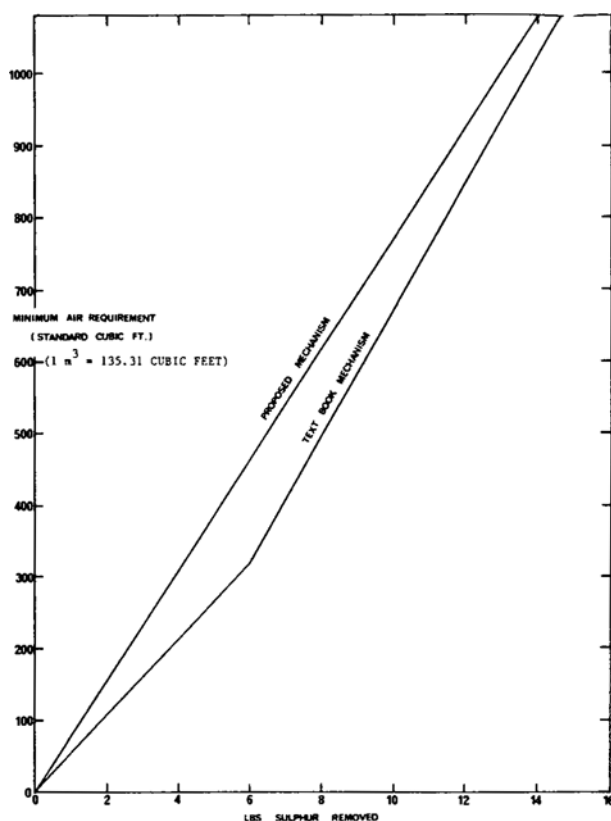

Fig. 1—Minimum air requirements for roasting of chalcopyrite (basis: 100 lb dry feed containing 24.44 lb sulfur). (1 kg = 2.205 lb).
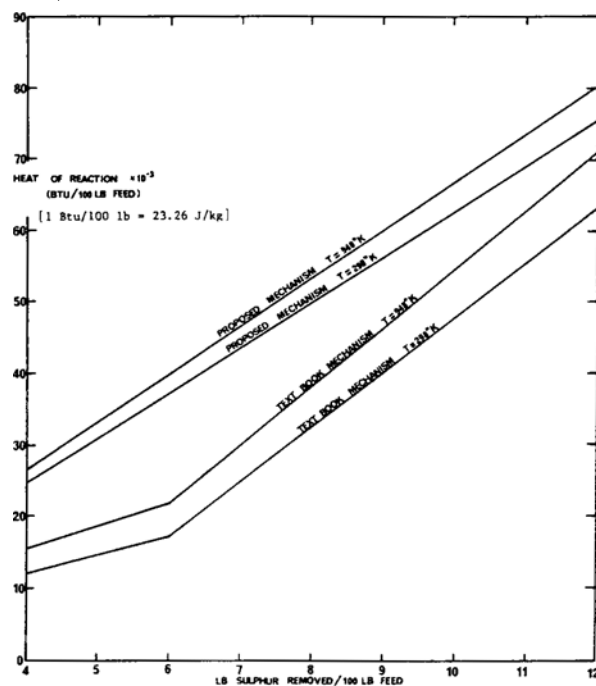

Fig. 2—Heat of reaction for roasting of chalcopyrite (basis: 100 lb dry feed containing 24.4 lb sulfur).

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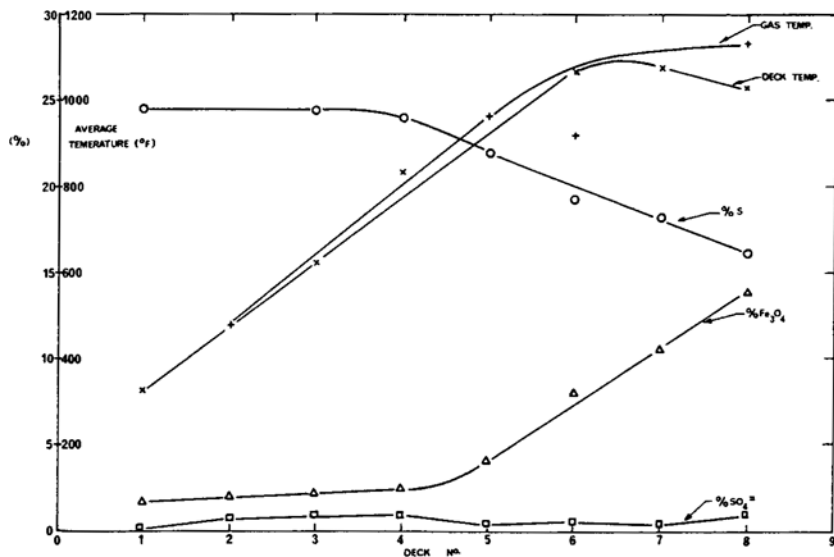
Fig. 3—Average deck and gas temperature. pct sulfur and pct magnetite variation with deck no. (test run No. 1).
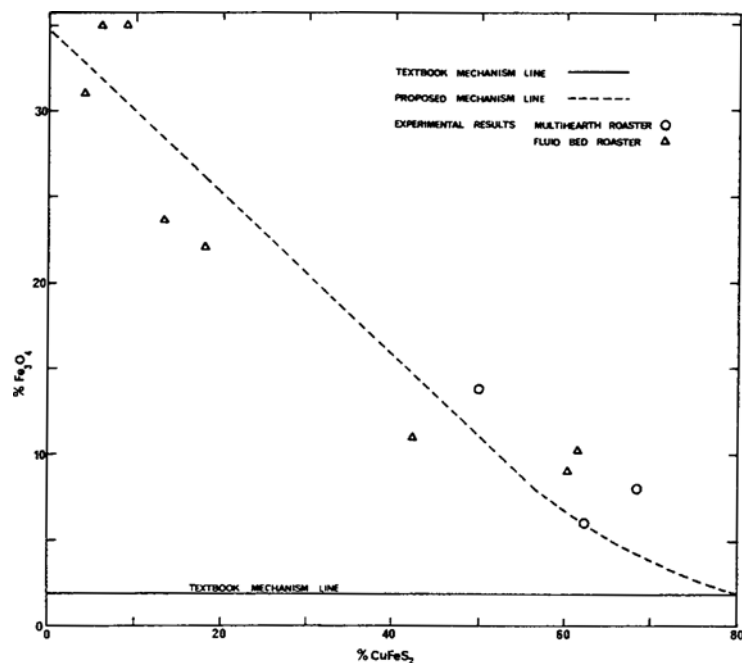

Fig. 4—Fe_3O_4 in calcine vs $CuFeS_2$ in calcine.

the temperature range of 590°C to 650°C at space veloc-ities from 0.3 m/s to 1.2 m/s. Samples of calcines from the fluid bed roaster were also collected and tested. The feed to the roaster contains an average 30.1 pct fluxes on a dry basis, the rest being mainly chalco-pyrite. The average dry feed sulfur content is 24.4 pct.

Details of the comprehensive study are given else-where.[5] Typical results from the multihearth roaster is presented in Fig. 3 showing typical deck tempera-ture, gas temperature, and analyses of calcine in var-ious decks. The results show that decrease in sulfur content in calcine is matched by a corresponding in-crease in Fe_3O_4 content, suggesting that the textbook mechanism may not be consistent with the results. Fig. 4 plots Fe_3O_4 content in calcine vs $CuFeS_2$ content in calcine both obtained by X-ray diffraction for cal-cines from the multi-hearth roaster and fluid bed roaster. Calculated lines based on the textbook mechan-ism and the proposed mechanism are also plotted for comparison. The calculated lines are based on a dry roaster feed containing an average of 1.7 pct Fe_3O_4 and 24.4 pct sulfur. Fig. 4 shows the results from the multi-hearth roaster and the fluid bed roaster are reasonably well correlated by the proposed mechanism line.

A less sensitive method of establishing the compara-tive validity of the two mechanisms is given in Fig. 5 as a plot of x (defined as pct sulfur in dry feed less pct sulfur in calcine) vs y (defined as pct Fe_3O_4 in calcine less pct Fe_3O_4 in dry feed). The figure shows that most of the experimental points lie between predictions by the two models and the proposed mechanism gives a better description of the results than the textbook mechanism. The regression line for 581 points is repre-sented by

$$y = 1.3306x + 0.1950 \qquad [6]$$

with a correlation coefficient of 0.90. Eq. [6] may be of some use for predicting magnetite content in calcine
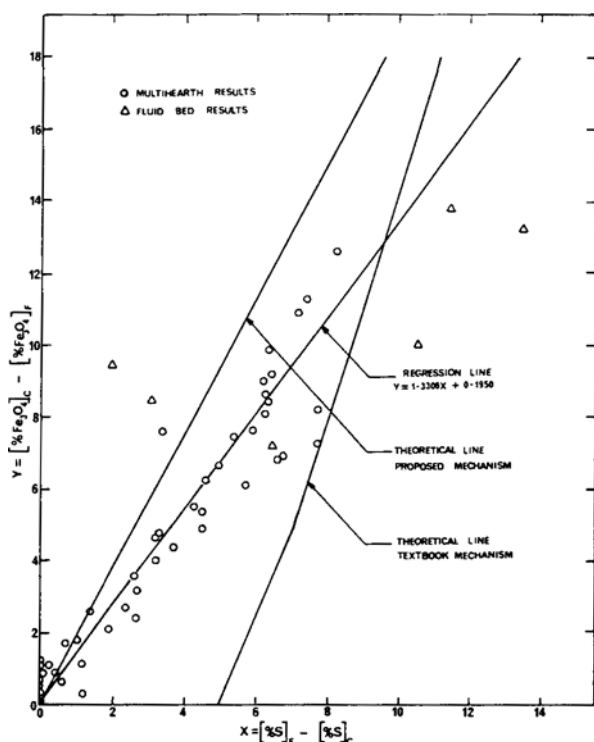
Fig. 5—$\{[\text{pct } Fe_3O_4]_{calcine}-[\text{pct } Fe_3O_4]_{feed}\}$ vs $\{[\text{pct } S]_{feed}-[\text{pct } S]_{calcine}\}$.

Table I. Comparison of Product Calcine Composition for the Two Reaction Paths, Basis 100 kg of Dry Roaster Feed Consisting of 69.9 kg Chalcopyrite and 30.1 kg of Fluxes Free of Fe₃O₄

kg of S Removed per 100 kg of Feed	Calcine Compositions							
	Textbook Mechanism				Proposed Mechanism			
	CuFeS₂	Cu₂S	FeS	Fe₃O₄	CuFeS₂	Cu₂S	FeS	Fe₃O₄
5	13.2	26.2	28.9	0	52.2	8.5	0	8.3
10	0	32.1	26.0	10	33.6	17.5	0	17.0
15	0	33.3	10.0	23.6	13.7	27.1	0	26.3
18.3	0	33.7	0	32.7	0	33.7	0	32.7

for different levels of sulfur removal for concentrate feed similar to that studied here.

Discussion It should be stressed that the present study is concerned with the overall kinetics of the roasting operation. The detailed step by step kinetics are much more complex[3,4] and have not been considered here. The present observations that in roasting, part of the chalcopyrite remains unreacted while the remainder reacts to completion to form magnetite, may be due to the fact that not all chalcopyrite is exposed to oxygen during reaction. Unexposed chalcopyrite remains unreacted while exposed chalcopyrite reacts to completion. Williams,[6] however, suggested that the observed overall kinetics can be explained in terms of the nonuniformity of activity of chalcopyrite. Thus the more active chalcopyrite with lower activation energy reacts to completion while the less active chalcopyrite remains unreacted at roasting temperature.

Conclusion Examination of calcine from a multihearth roaster and a 4 in. diam fluid bed roaster suggest that part of the concentrate feed remains unreacted while the remainder reacts to completion forming magnetite.

No systematic difference is observed between samples from the fluid bed roaster and the multihearth roaster. An empirical equation is proposed (Eq. [6]) for estimating magnetite content for different level of sulfur removal.

The work described here was carried out during a vacation school at Mount Isa Mines, Limited, Mount Isa. The author wishes to thank the management of the company for providing facilities for this work and for permission to publish this paper; the students Messrs. Bruce, Fisher, Hanrahan, Ho, Hoa, Hutton, Koh, McPherson, Moretto and Schache who carried out the experiments; and to the laboratory staff at Mount Isa Mines for carrying out the numerous analyses.

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Discussion of "Sulfide and Sulfate Solid Solubility in Lime, Magnesia, and Calcined Dolomite: Part 1. CaS and CaSO₄ Solubility in CaO"*

JAMES A. CLUM

The work by Turkdogan, et al.,[1] sets forth important thermodynamic guidelines for production of low sulfur lime products. In practice, there are a number of other factors, in addition to oxygen and sulfur potentials, which strongly affect sulfur levels of calcines. Those factors relate to the principal physical characteristics of the raw carbonate which in turn lead to the crystallite size distribution and pore distribution in the calcine.[2-6] Such characteristics include carbonate grain size and grain arrangement as well as impurity level. These features vary greatly with the origin of the carbonate as noted very briefly by Turkdogan, et al.[7] in a previous paper.

The particular carbonate specimens used[1] were carefully characterized. Unfortunately, the carbonate starting material was from a single source and thus the extreme importance of carbonate origin in application of the guidelines was not emphasized.

This note intends to point out that physical characteristics are significant parameters in calcine utilization