Mechanism of Sulfate Formation During the Roasting Of Cuprous Sulfide

by C. L. McCabe and J. A. Morgan

IN the art of roasting sulfides it is well known that the lower the temperature and the higher the pressure of SO_3 , the larger will be the amount of sulfate present in the product. However, the mechanism of sulfate formation is not generally understood. The following experiment* demonstrates in a direct way

*Peretti¹ has reported observations similar to those in this note.

that, in the roasting of Cu_2S , the sulfate forms from the reaction of Cu_2O , formed by the oxidation of Cu_2S , with gaseous SO_2 (or SO_3) and O_2 . Thus, the sulfate does not form at the sulfide surface. The reaction at the sulfide surface is the same whether or not sulfate is formed. Using an indirect method, Ong, Fassell, and Wadsworth² infer that sulfate forms after oxidation, during the roasting of sphalerite, agreeing with the observations of this paper. The method presented here of demonstrating that sulfate forms after formation of Cu_2O is to roast a sample of Cu_2S and then to locate and identify the phases formed.¹

A solid cube of cuprous sulfide, made by melting Fisher reagent grade Cu_2S powder and measuring about 1.5 cm on edge, was placed on a Nichrome wire grid suspended over the top of an Alundum combustion boat. The assembly was placed in a tube furnace at 600°C and oxygen gas, flowing at 0.60 liters per min, was passed around the specimen for 24 hr. The furnace tube diameter was 1.5 in. The partially roasted sample was removed from the furnace and impregnated with resin No. BR 0014, obtained from the Palmer Products Co., and the impregnated sample was then mounted in Lucite. A cross section was obtained by grinding and the surface was prepared by the following steps: 1) grinding—60 grit, 3M disk, dry; 2) preliminary polishing—60 through 600 grit, 3M disk, dry; 3) polishing—8 μ diamond putty, silk cloth; and 4) final polishing—levigated magnesia in isopropyl alcohol, Selvyt cloth.

The color micrograph of the polished surface is shown in Fig. 1. The layers present in the micrograph are given along the side.

The compositions of the various layers were established by Debye-Scherrer patterns. From this evidence the following sequence of reactions which occur in the roasting of Cu_2S is inferred:

1) The oxidation of Cu_2S occurs with oxygen which has been transported through the oxide-sulfate layer by either gaseous or solid state diffu-

Fig. 1—Color micrograph shows outer oxide and sulfate layers formed during the roasting of Cu_2S . Unetched specimen was photographed under polarized light. X100. Area reduced approximately 10 pct for reproduction.

sion. The products of this reaction at the Cu_2S surface are Cu_2O and SO_2 .

2) The SO_2 diffuses out through the pores in the Cu_2O and finally reaches a position in the Cu_2O where the oxygen pressure and the SO_2 pressure have values such that the thermodynamic conditions for the formation of CuSO_4 are fulfilled. Then, the mixture of SO_2 , SO_3 , and oxygen reacts with the Cu_2O to form CuSO_4 .

3) The CuSO_4 decomposes by the evolution of SO_3 , or SO_2 and O_2 , to form the basic sulfate. This is reasonable, since the SO_3 gradient will decrease toward the oxygen gas phase from the CuSO_4 layer.

4) For this same reason the basic sulfate will decompose to form CuO .

The above sequence of events is based on the assumption that diffusion through the oxide and sulfate layers, rather than the reaction at the sulfide-oxide interface, is rate-determining. This assumption is supported by the observation that these oxide and sulfate layers combined are almost nonpermeable to the flow of gases through them.

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