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# Thermal oxidation of covellite (CuS)

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## Abstract

The thermal oxidation of covellite of particle size 45–90 μm was studied by heating 5–6 mg samples at 20°C min$^{-1}$ in dry air in a simultaneous thermogravimetry–differential thermal analysis (TG–DTA) apparatus. Evolved gases were analysed by coupled FTIR equipment. The unreacted and the partially oxidised covellite samples were characterised for phase composition by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and optical microscopy (OM).

By 330°C, a small amount of decomposition of covellite had occurred with the formation of cubic digenite ($Cu_{1.8}S$). A mass loss was evident between 330 and 422°C associated with an exothermic peak. This event was assigned to the decomposition of CuS to $Cu_2S$ followed by oxidation of the evolved sulfur. Between 422 and 474°C, an exothermic peak accompanied by a mass gain was observed. The exothermic peak was attributed to the oxidation of $Cu_2S$, and the mass gain to the formation of $CuSO_4$. This was followed by a further exothermic peak and mass gain in the temperature range 474–585°C. This event was attributed to a solid–solid reaction between $Cu_2S$ and $CuSO_4$ which caused a melt to form. Until this stage, the reaction had proceeded by a shrinking core mechanism inhibited by oxide and sulfate coatings. However, the formation of a melt effectively destroyed this inhibition and permitted further oxidation of the sulfide and formation of sulfate. At 583°C $CuO{\cdot}CuSO_4$ was detected, and continued to form up to 653°C. Finally an endothermic event and mass loss observed in the temperature range 653–820°C were due to the decomposition of $CuO{\cdot}CuSO_4$ into CuO. Various other reactions were identified which did not produce significant events on the TG–DTA record. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Covellite; Oxidation; TG–DTA–FTIR

## 1. Introduction

Covellite usually exists in small quantities associated with other copper sulfides such as chalcocite ($Cu_2S$), chalcopyrite ($CuFeS_2$) and bornite ($Cu_5FeS_4$). It is found in the zone of secondary enrichment formed as a result of the alteration of primary sulfides [1]. It can occur as thin crusts or as deep blue-black powdery or sooty masses [2], as well as grains in geothite, malachite and areas of gangue [3].

Heating covellite in an inert atmosphere causes decomposition with the formation of copper deficient compounds. Anilite ($Cu_7S_4$) is reported to form from covellite in the temperature range 278–354°C, followed by decomposition to $Cu_2S$ between 500 and 615°C [4]. In another study, four endothermic peaks were observed commencing at 280, 450, 550, and 830°C, respectively. These were assigned to the

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transformation of CuS into cubic digenite ($Cu_{1.8}S$), then cubic djurleite ($Cu_{1.94}S$), then $Cu_2S$ and finally to copper [5].

There are several reports on the thermal oxidation of natural and precipitated covellite [6–12]. The initial mass loss in the TG curve is usually ascribed to the formation of either $Cu_2S$ or digenite, with oxidation of the evolved sulfur giving rise to an exotherm in the DTA curve, according to the equations

$$1.8CuS + 0.8O_2 \rightarrow Cu_{1.8}S + 0.8SO_2$$

$$2CuS + O_2 \rightarrow Cu_2S + SO_2$$

The first reaction was reported to occur in the temperature range 220–260°C [6], and 345–400°C [7], and the second reaction between 300 and 370°C [8,9]. Following this, oxidation of the sulfide takes place with the formation of copper(I) oxide, and copper(II) sulfate, commencing around 360°C [8]. It has been proposed that copper(II) sulfate is formed either by direct oxidation of the sulfide, or reaction between liberated $SO_2$, air and the newly formed copper(I) oxide. Certainly all of the reactants are found in the same temperature range, so both routes are possible. Various reactions have been proposed, although often without confirmatory evidence.

$$Cu_2S + 4O_2 \rightarrow 2CuSO_4 \qquad [10]$$

$$2Cu_2S + 4.5O_2 \rightarrow 2CuSO_4 + Cu_2O \qquad [11]$$

$$Cu_2O + 2SO_2 + 0.5O_2 \rightarrow 2CuSO_4 \qquad [11]$$

Oxidation of the copper(I) oxide to copper(II) oxide occurs at some stage, although there has been a large range of temperatures reported for this reaction. For example, CuO has been reported in the range 360–690°C [11], after a large exotherm that was complete at 520°C [8], and between 650 and 800°C [6]. It has also been suggested that this reaction takes place by the direct oxidation of $Cu_2S$ in the temperature range 350–400°C [12].

$$Cu_2S + 2.5O_2 \rightarrow CuO + CuSO_4$$

The presence of copper oxysulfate has been detected [6,10]. Based on XRD data, it was suggested that $CuO{\cdot}CuSO_4$ formed prior to $CuSO_4$, in the temperature range 360–470°C, by reaction between copper(II) oxide and liberated $SO_2$ [12].

$$2CuO + SO_2 + 0.5O_2 \rightarrow CuO \cdot CuSO_4$$

Beyond 850°C this compound decomposed to CuO [6], which decomposes above 1000°C to form $Cu_2O$.

$$CuO \cdot CuSO_4 \rightarrow 2CuO + SO_3$$

The objective of this paper is to identify the phases formed at each stage of the oxidation of covellite, using a well-characterised starting material.

## 2. Experimental

XRD curves were obtained with a Philips automatic powder diffractometer using a cobalt source. A Perkin-Elmer 1720 FTIR spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector was used for recording FTIR spectra, using the KBr disc method. A Jeol JSM-5800LV scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyser (EDAX) detector was used to obtain micrographs of the mounted carbon coated samples, and for the analysis of selected regions of individual particles. Optical microscopy (OM) of the uncoated polished samples was carried out with a Nikon microscope used in conjunction with an Olympus OMB-2 photographic camera.

The covellite sample was supplied by Ward's Natural Science Establishment, Inc., New York. A subsample was ground to give a particle size of 45–90 μm, and stored in a desiccator under nitrogen. Wet chemical analysis of the sample gave 66.9 wt.% Cu and 32.6 wt.% S (theoretical values for covellite 66.5 wt.% Cu and 33.5 wt.% S). XRD analysis indicated covellite as the only detectable phase. No infrared activity was noted in its FTIR spectrum. Analysis of 50 particles by EDAX showed no significant variation in particle-to-particle composition. The atomic ratio was confirmed as 1:1. The results of the EDAX analysis averaged over the 50 particles are presented in Table 1.

Optical micrographs taken of the unreacted CuS sample showed various textures of blue ranging from dark blue to bluish-white, in agreement with the work

Table 1
Average of results obtained from EDAX analysis of 50 particles of covellite

| Mass ratio | | Atomic weight percent | | Empirical formula | |
|---|---|---|---|---|---|
| Cu | S | Cu | S | Cu | S |
| 65.82 | 34.18 | 1.035 | 1.068 | 1 | 1.030 |

published by others [1,2,13]. The orange/red colour which results from the anisotropic properties of CuS was evident [14]. A very few minute grains, predominantly yellow, were evident, and suggested the presence of chalcopyrite which is commonly associated with covellite [1,2].

Thermal analysis experiments were performed with a Netzsch STA 409C simultaneous TG–DTA apparatus coupled to an FTIR apparatus for evolved gas analysis. Cylindrical alumina crucibles of diameter 4 mm and depth 2 mm were used. Approximately 5–6 mg of sample was heated in dried air at a flow rate of 40 ml $\mathrm{min}^{-1}$ and a heating rate of 20°C $\mathrm{min}^{-1}$ from ambient temperature to a maximum of 820°C. Samples were isolated after arresting the heating process and immediately replacing the oxidising atmosphere with nitrogen. The partially oxidised product was allowed to cool to room temperature before being collected into a capped bottle for storage in a desiccator under nitrogen.

## 3. Results and discussion

Covellite samples were thermally oxidised in dry air using a simultaneous TG–DTA–FTIR apparatus. Partially oxidised products were analysed at various temperatures by techniques such as XRD, SEM, OM and FTIR spectroscopy. A typical TG–DTA–FTIR trace is shown in Fig. 1. The Gramm Schmidt plot is the integrated gas evolution profile. The phases detected by the techniques used at various temperatures are shown in Table 2.

A small gradual mass loss took place from 130 to 330°C and was accompanied by a broad exothermic drift. A sample taken at 330°C and analysed by XRD showed two phases, the major one being unreacted covellite and the other cubic digenite ($Cu_{1.8}S$). Like the unreacted covellite, no infrared active phases were detected in the FTIR spectrum (Fig. 2a). Hence in this temperature range a slow decomposition of some of the covellite to digenite occurred, with subsequent oxidation of the liberated sulfur. No oxides or sulfates were detected by any of the techniques up to 330°C.

$$1.8CuS = Cu_{1.8}S + 0.8S \quad (1)$$

$$0.8S + 0.8O_2 = 0.8SO_2 \quad (2)$$

Reaction (1) is responsible for the mass loss, and reaction (2) for the exothermic peak. These reactions agree with previous reports [8–10]. The lack of detection of $SO_2$ may be due to the relatively minor and kinetically slow reaction producing low concentrations of the gas which were below the detection limits of the equipment.

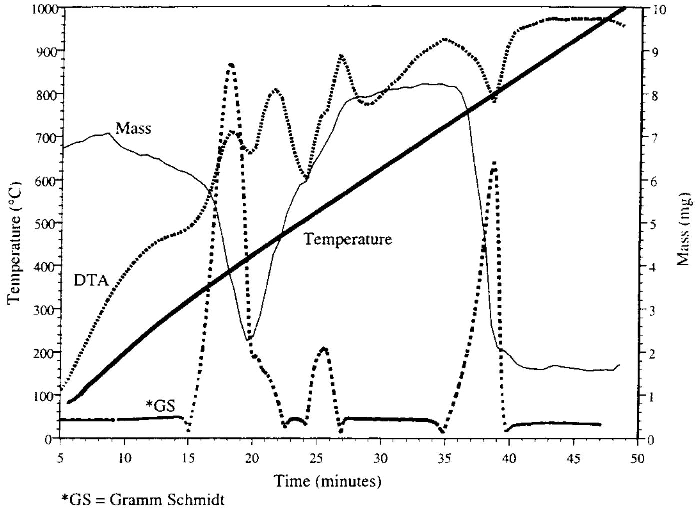

Fig. 1. TG–DTA–FTIR records for the oxidation of covellite, particle size 45–90 μm, from ambient to 820°C in dry air at a heating rate of 20°C $\mathrm{min}^{-1}$.

Table 2
Summary of phases identified at various temperatures during the oxidation of covellite

| Temperature (°C) | Major phase | Identifying technique | Minor phase | Identifying technique |
|---|---|---|---|---|
| 330 | CuS | XRD, OM | $Cu_{1.8}S$ | XRD |
| 422 | $Cu_2S$ | XRD, OM, SEM | $Cu_{1.96}S$<br>$Cu_{1.8}S$<br>$Cu_2O$<br>$Cu_2SO_4$<br>$CuSO_4$ | XRD, SEM<br>XRD<br>XRD, FTIR, OM<br>XRD, SEM<br>XRD |
| 474 | $Cu_2O$<br>$CuSO_4$ | XRD, OM, FTIR, SEM<br>XRD, FTIR | $Cu_2S$<br>$Cu_{1.96}S$<br>$Cu_{1.8}S$ | XRD, OM, SEM<br>XRD, SEM<br>XRD |
| 585 | $Cu_2O$<br>$CuSO_4$ | XRD, FTIR, OM, SEM<br>XRD, FTIR, SEM | $CuO \cdot CuSO_4$ | XRD, FTIR |
| 653 | $CuO \cdot CuSO_4$ | XRD, FTIR | $Cu_2O$<br>$CuSO_4$<br>CuO | XRD, OM<br>XRD, FTIR<br>XRD, FTIR |
| 820 | CuO | XRD, FTIR, SEM | | |

Between 330 and 422°C, there was a major mass loss accompanied by an exothermic peak and the evolution of $SO_2$ gas. XRD analysis performed on the sample taken at 422°C indicated the presence of $Cu_{1.8}S$, $Cu_{1.96}S$, $Cu_2S$, $Cu_2O$, $CuSO_4$ and $Cu_2SO_4$ phases. FTIR analysis was also performed on the sample and a peak at 617 cm$^{-1}$ was assigned to $Cu_2O$ [15]. Although not identifiable by XRD, $CuSO_4 \cdot H_2O$ showed one peak on the FTIR spectrum at 1109 cm$^{-1}$ [16]. Its presence is due to the hydration of anhydrous copper(II) sulfate, one of the products formed at this temperature interval. This rapid reaction probably occurred during the transfer of the oxidised sample from the TG–DTA instrument into the storage container. Micrographic images taken at 422°C showed the formation of thin rims around the particles. The colour of the particles as seen through the optical microscope corresponded to that of $Cu_2S$ constituting the central core, and $Cu_2O$ making up the thin rim around the particles. EDAX work performed on the thin light grey rim gave formulas of $Cu_2SO_4$ and $Cu_3SO_5$, the latter possibly being a mixture of $Cu_2O$ and $CuSO_4$. The central core of the particles consisted of $Cu_2S$ and $Cu_{1.96}S$.

According to the phases confirmed present in the region of 330–422°C, the following reactions are proposed. The major reaction, which causes both the mass loss and the exothermic peak, is

$$2CuS + O_2 \rightarrow Cu_2S + SO_2 \quad (3)$$

The minor reaction is

$$Cu_2S + 0.01O_2 \rightarrow Cu_{1.96}S + 0.02Cu_2O \quad (4)$$

It is commonly thought that the formation of $Cu_2O$ is followed by oxidative sulfation of some of the oxide by the $SO_2$ liberated in the first reaction.

$$Cu_2O + SO_2 + 0.5O_2 \rightarrow Cu_2SO_4 \quad (5)$$

$$Cu_2O + 2SO_2 + 1.5O_2 \rightarrow 2CuSO_4 \quad (6)$$

There were seven well resolved peaks in the XRD pattern which matched the PDF file pattern for $Cu_2SO_4$ There was also supplementary support for its presence from the EDAX analysis of the rim material.

A gradual mass gain occurred in the temperature range 422–474°C associated with an exothermic peak and the evolution of $SO_2$. The phases identified by XRD for the sample taken at 474°C were $Cu_2S$, $Cu_{1.96}S$, $Cu_{1.8}S$, $Cu_2O$ and $CuSO_4$. FTIR analysis performed on the sample detected the presence of $CuSO_4$ as evidenced by a peak at 1144 cm$^{-1}$ [16]. SEM micrographs and colour OM photographs taken at 474°C both revealed the emergence of a second outer porous rim on the particles. There was an

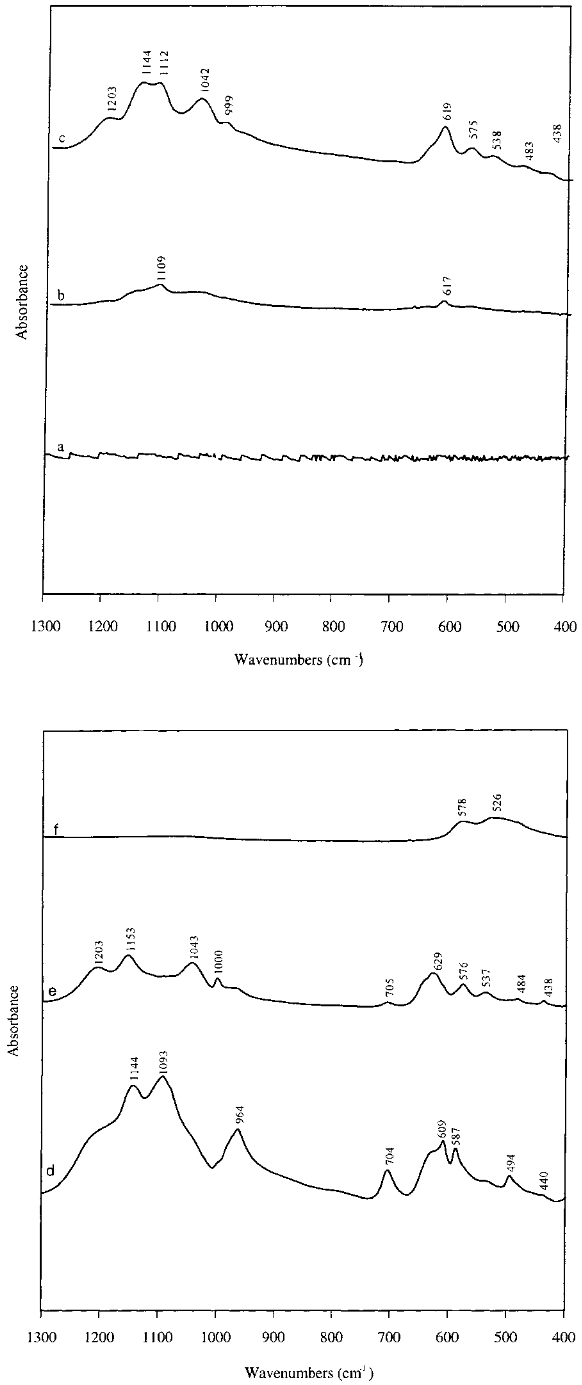

Fig. 2. FTIR spectra for partially oxidised covellite, at temperatures: (a) 330°C; (b) 422°C; (c) 474°C. (d) 585°C; (e) 653°C; (f) 820°C.

observable decrease in the sizes of the unreacted cores compared with the previous sizes, confirming that further oxidation of the core sulfides had taken place with the increase in temperature. OM colour photographs indicated the presence of $Cu_2O$ forming the inner porous rim. EDAX analysis was performed on the outer rim which consisted of a white phase mixed with a light grey phase. The white phase consisted of $Cu_2O$ and the light grey phase was composed of $Cu_3SO_5$ which is probably a mixture of $Cu_2O$ and $CuSO_4$. The other phases identified were unreacted $Cu_2S$ and $Cu_{1.96}S$ forming the inner core. This temperature interval was also marked by the disappearance of CuS and $Cu_2SO_4$ phases and the appearance of additional phases. From the results obtained using the different techniques it can be suggested that the formation of $Cu_2O$ and $CuSO_4$ continued. A previously unreported reaction involving the decomposition of $Cu_2SO_4$ is proposed in this temperature interval.

The major reactions in this temperature region were

$$Cu_2S + 1.5O_2 \rightarrow Cu_2O + SO_2 \qquad (7)$$

$$Cu_2O + 2SO_2 + 1.5O_2 \rightarrow 2CuSO_4 \qquad (8)$$

The minor reactions in this temperature region were

$$3Cu_2SO_4 \rightarrow 2Cu_2O + 2CuSO_4 + SO_2 \qquad (9)$$

$$Cu_2SO_4 + \text{oxidation} \rightarrow 2CuSO_4 \qquad (10)$$

The exothermic peak is due to reaction (7), and the mass gain to reaction (8).

The third exothermic peak was associated with a further mass gain and evolution of $SO_2$ in the temperature range 474–585°C. XRD analysis performed on the samples collected at 585°C identified the presence of $Cu_2O$, $CuSO_4$, and $CuO{\cdot}CuSO_4$. The FTIR spectrum of the sample collected at 585°C confirmed the presence of $Cu_2O$, $CuSO_4$ and $CuO{\cdot}CuSO_4$ (Fig. 2d). A peak at wavenumber 704 cm$^{-1}$ in the FTIR spectrum was characteristic of $CuSO_4$ [16], and another peak at 440 cm$^{-1}$ was used to identify $CuO{\cdot}CuSO_4$ [17]. Computer enhancement of the regions close to these weak peaks clearly showed their presence. BSE images and OM photographs taken at 585°C showed the complete disappearance of the sulfide core with particles becoming extremely porous especially on the innermost regions of the particles. It appeared that melting of the particles had occurred. The particles showed different textures ranging from white, light grey through to dark grey. Microscopic examination of the products of the reaction also showed that most of the size reduction occurred during the melting of the particles and showed that it was caused by droplets being pinched off from larger molten or semi-molten particles. EDAX work performed on the different regions of the particles at this temperature showed the presence of $CuSO_4$ in the dark grey regions of the particles and $Cu_2O$ was detected in the white region.

Previous work on the oxidation of chalcocite had suggested that the sulfate and oxide coatings formed on the surface of the particles were protective, and inhibited further reaction [17]. However, in the region of 480°C it was demonstrated that a solid state reaction occurred between $Cu_2S$ and $CuSO_4$ which produced a melt. This destroyed the protective coating and so further oxidation could take place. This explanation also applies for the events observed in the temperature range 474–585°C for this present study. Thus, the reaction slows at about 450°C and the DTA curve returns towards the baseline. At 474°C the solid state reaction occurs which causes melting and further rapid oxidation of the remaining sulfide (reaction (11)) and sulfation of the oxide formed (reaction (12)).

$$Cu_2S + 2CuSO_4 \rightarrow 2Cu_2O + 3SO_2 \quad (11)$$

$$Cu_2O + 2SO_2 + 1.5O_2 \rightarrow 2CuSO_4 \quad (12)$$

The exothermic peak is caused by reaction (11), and the sulfation process is responsible for the mass gain that is observed in this temperature region (reaction (12)). $CuO{\cdot}CuSO_4$ is the new product appearing in this interval, and may be formed from either of the following reactions [18].

$$2CuSO_4 \rightarrow CuO \cdot CuSO_4 + SO_2 + 0.5O_2 \quad (13)$$

$$Cu_2O + 4CuSO_4 \rightarrow 3CuO \cdot CuSO_4 + SO_2 \quad (14)$$

The presence of both the $CuSO_4$ and $Cu_2O$ phases at this temperature interval makes either of the two suggested routes possible.

In the fourth region, from 585 to 653°C, accompanying a small mass gain is a very weak exothermic drift. XRD at 653°C detected the presence of $Cu_2O$, $CuSO_4$, and $CuO{\cdot}CuSO_4$. FTIR analysis of the sample indicated the presence of $CuSO_4$, $CuO{\cdot}CuSO_4$, and $CuSO_4{\cdot}H_2O$ as before (Fig. 2e). SEM images showed particles that were completely porous, most of them with very large holes in the centre possibly due to melting. The OM photographs indicated a decrease in the intensity of the reddish-brown colour characteristic of $Cu_2O$, and an increase in the outer white phase. SEM confirmed the presence of CuO.

In this temperature interval, a new product, CuO, was formed by the oxidation of $Cu_2O$, and accounts for the slight increase in mass. $CuO{\cdot}CuSO_4$ increased in concentration as evidenced by the FTIR results, but the absence of any $SO_2$ in the evolved gas stream indicated that reactions (13) and (14) were not valid to describe the formation of this compound. Rather, it appears that the conversion of $Cu_2O$ to CuO is followed by reaction of the latter with $CuSO_4$ to produce the oxysulfate.

$$Cu_2O + 0.5O_2 \rightarrow 2CuO \quad (15)$$

$$CuO + CuSO_4 \rightarrow CuO \cdot CuSO_4 \quad (16)$$

The final stage of oxidation took place in the temperature range of 653–820°C. A major mass loss was accompanied by an endothermic peak. A very intense and sharp peak showing the evolution of $SO_2$ was observed in the FTIR spectrum for the evolved gas analysis. Only CuO was detected above 820°C, as indicated by XRD analysis and by the presence of only two peaks in the FTIR spectrum at 578 and 526 $cm^{-1}$ [19] (Fig. 2f). The final stage of the oxidation of CuS is therefore, the decomposition of the copper oxysulfate into CuO with the evolution of sulfur dioxide gas as proposed in the following reaction.

$$CuO \cdot CuSO_4 \rightarrow 2CuO + SO_2 + 0.5O_2 \quad (17)$$

## 4. Conclusions

Thermal oxidation of covellite has been investigated under a set of well defined and controlled experimental conditions in a simultaneous TG–DTA–FTIR apparatus. Using the various characterisation techniques, it was possible to assign the various thermal events to specific reactions in the appropriate temperature ranges. The order of the main chemical reactions taking place was established and is presented below.

| | | |
|---|---|---|
| 330–422°C | $2CuS + O_2 \rightarrow Cu_2S + SO_2$ | Major reaction |
| | $Cu_2O + SO_2 + 0.5O_2 \rightarrow Cu_2SO_4$<br>or $Cu_2S + 2O_2 \rightarrow Cu_2SO_4$ | Minor reactions |
| 330–474°C | $Cu_2S + 0.01O_2 \rightarrow Cu_{1.96}S + 0.02Cu_2O$ | Minor reaction |
| 422–585°C | $Cu_2O + 2SO_2 + 1.5O_2 \rightarrow 2CuSO_4$ | Major reaction |
| 422–474°C | $3Cu_2SO_4 \rightarrow 2Cu_2O + 2CuSO_4 + SO_2$ | Minor reaction |
| 422–585°C | $Cu_2S + 1.5O_2 \rightarrow Cu_2O + SO_2$ | Major reaction |
| 474–585°C | $Cu_2S + 2CuSO_4 \rightarrow 2Cu_2O + 3SO_2$ | Major reaction |
| 585–653°C | $Cu_2O + 0.5O_2 \rightarrow CuO$ | Major reaction |
| | $CuO + CuSO_4 \rightarrow CuO \cdot CuSO_4$ | Major reaction |
| 653–820°C | $CuO \cdot CuSO_4 \rightarrow 2CuO + SO_3$ | Major reaction |

This was the first time that $Cu_2SO_4$ had been identified during the oxidation of covellite. This was also the first time that the formation of $CuO \cdot CuSO_4$ had been proposed from the direct combination of CuO and $CuSO_4$. The absence of any evolved $SO_2$ in the temperature range 585–653°C made the previous propositions, which involved reactions which produced $SO_2$, untenable. Although the solid state reaction between $Cu_2S$ and $CuSO_4$ to produce a melt had been found in the oxidation of chalcocite [17], it had not been previously identified in the oxidation of CuS.

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