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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

QUANTITATIVE DETERMINATION OF PHASES PRESENT IN OXIDISED CHALCOCITE

J. G. Dunn[1], *A. Ginting*[1] *and B. H. O'Connor*[2]

[1]School of Applied Chemistry, Curtin University, Perth,
[2]Department of Applied Physics, Curtin University, Perth, Western Australia

Abstract

A sample of chalcocite (Cu_2S) of particle size 45–75 μm was heated in air at 10°C min^{-1} in a simultaneous TG-DTA apparatus. The phase compositions of the products at various temperatures were quantitatively determined by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and wet chemical analyses. Copper(II) sulfate, of amount 1.7% by mass, was observed at 435°C and increased rapidly in concentration to 56% at 570°C. From 570–670°C, there was a rapid decrease in $CuSO_4$ content to 9.8% as the phase converted to $CuSO_4{\cdot}CuO$, with the $CuSO_4$ not being detected at 775°C. From 435–570°C, Cu_2O formed, but at a rather slower rate, reaching 47% at 570°C. The Cu_2O level then decreased to 38% over the range 570–670°C. $CuSO_4{\cdot}CuO$ was first detected at 570°C by FTIR, although it was not detected by XRD at this temperature. The content of this species reached 41% at 670°C, decreased to 24% at 775°C, and was not detected at 840°C. CuO first appeared at 670°C and rose steadily in concentration until at 840°C it was the only compound present.

Keywords: chalcocite, TG-DTA

Introduction

In a previous publication [1], we have described a thermal analysis study of the oxidation of chalcocite, Cu_2S. Part of the research strategy involved the isolation of partially-oxidised material taken at various temperatures, followed by phase determination using primarily XRD and FTIR spectroscopy. From these data it was possible to assign reactions to each of the thermal events.

This paper describes the quantitative determination of phases present in these samples. Copper(I) and copper(II) oxides were determined by XRD, using the reference intensity ratio (RIR) method which obviates the need to use suites of calibration standards. RIR factors (designated here as *R*) may be determined from the most intense lines of the phase being measured and an internal standard [2]. The intensity (*I*) for line *i* of phase *j* is given by Eq. (1),

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$$I_{ij} = k_{ij} \times X_{ij} / \mu \tag{1}$$

and that for a selected diffraction line for the internal standard, I_q, by Eq. (2),

$$I_q = k_q \times X_q / \mu \tag{2}$$

where k=constant, X=mass fraction, μ=mass absorption coefficient of the specimen. Symbol q signifies the phase α-quartz which was employed as the internal standard.

Combination of (1) and (2) gives:

$$I_{ij}/I_q = (k_{ij}/k_q) \times X_{ij}/X_q \tag{3}$$

where k_{ij}/k_q, is the reference intensity ratio R for the selected lines.

The mole fraction of each phase being analysed can be calculated from Eq. (4):

$$X_{ij} = I_{ij}/I_q \times (X_q/R) \tag{4}$$

When the strongest line intensity, intensity I^{100}, suffers from overlap, a secondary line of intensity I^{y} can be chosen for the analysis. The intensity of the secondary line I^{y} must then be scaled by the factor $100\,y^{-1}$. In planning analytical strategy, it is useful to determine the mean phase composition levels using independent pairs of lines for the unknown phase and internal standard, as performed in this study.

The reliability of quantitative XRD analysis is limited by bias associated with microabsorption, preferred orientation, primary extinction and line overlap. In addition to minimising the influence of these factors, the specimen must have sufficient thickness to satisfy the 'infinite-thickness' criterion [3].

Copper(II) sulfate and copper(II) oxysulfate were quantified using FTIR, as these phases are difficult to detect by XRD at levels lower than 5%. In the mid IR region the sulfates have unique absorption bands that are free from interference by other species in the oxidised chalcocite.

Experimental

The chalcocite sample selected for the study has been described in a previous publication [1]. The particle size range was 45–75 μm.

Simultaneous TG-DTA measurements were performed by heating approximately 5 mg of sample at 10°C min^{-1} from ambient temperature to a maximum temperature of 1000°C. An air flow of 35 mL min^{-1} was passed through a silica gel scrubber to remove water. The heating was stopped at the beginning and at the end of exothermic or endothermic events. The oxidation atmosphere was switched to nitrogen to avoid further oxidation and the sample allowed to cool to room temperature. To provide sufficient partially-oxidised chalcocite samples for further analysis, the oxidation was performed several times under the same experimental conditions, and the samples combined.

XRD measurements were performed using a Siemens D500 Bragg-Brentano diffractometer consisting of a rotating specimen stage, a copper X-ray tube (operating at 40 kV, 30 mA) and a sodium iodide detector. CuK_α radiation was employed with a graphite diffracted-beam monochromator being used to eliminate the CuK_β component. Data were collected for the 2Θ range 10–100° with a goniometer step at 0.04° 2Θ and counting time of 1 s/step. The CuK_{α_2} component radiation was eliminated mathematically during the data reduction process. Accordingly, the final data set was assembled for CuK_{α_1} (λ=1.540598 Å). The 2Θ and *I* values were obtained using the EVA software package supplied by Socabim-Sarl a bis, villa du Bel-Air, Paris. The resulting data were assessed with the Powder Diffraction File (PDF). The pairs of 2Θ and *I* values in the observed and PDF data sets were then used to assess the reliability of the presence of a phase. Lines not suffering from overlap and with reasonable counting statistics were selected for quantitative analysis.

R values were measured with pure copper(I) oxide and copper(II) oxide, Cu_2O and CuO, samples which were synthesised for this purpose. Copper(I) oxide was synthesised by reduction of cupric acetate, $Cu(CH_3COO)_2$, with glucose, $C_6H_{12}O_6$ [4] while copper(II) oxide was the end oxidised product of chalcocite at 1000°C. Each of these oxides was mixed with α-quartz in the ratio 85:15% by mass respectively. Approximately 20 mg of the mixture was mounted on the sample holder for XRD analysis, and the best five lines in the 2Θ range 10–100° were chosen for quantitative determination.

FTIR spectra were recorded with a Perkin Elmer 1720 Infrared Fourier Transform Spectrometer with a TGS detector. The sample was lightly ground to less than 10 μm, and about 1 mg was accurately weighed and gently mixed with approximately 199 mg of KBr powder (spectrometry grade) in an agate mortar. The mixture was transferred into a cylindrical stainless steel die and pressed at a pressure of 7 tonne total load. Data collection for each sample involved 10 scans at a mirror velocity of 0.2 cm^{-1} s^{-1} and a resolution of 4 cm^{-1}. The spectra were analysed using IRDM software supplied by Perkin Elmer.

Results and discussion

Thermal analysis

The TG-DTA traces for the oxidation of chalcocite under the conditions specified are shown in Fig. 1, together with the temperatures at which samples were collected for quantitative analysis. Mass gains were evident in the TG trace in the temperature ranges 425–510 and 510–560°C. The first mass gain was approximately 13% while the second was 11%. From 560–725°C there was a slower increase in mass of about 5%, followed by a mass loss of 30% from 725–810°C, and then a further 2% mass loss up to 1000°C.

In the DTA trace, two endothermic peaks were present in the temperature ranges 107–117 and 720–810°C. The first endotherm had no associated mass

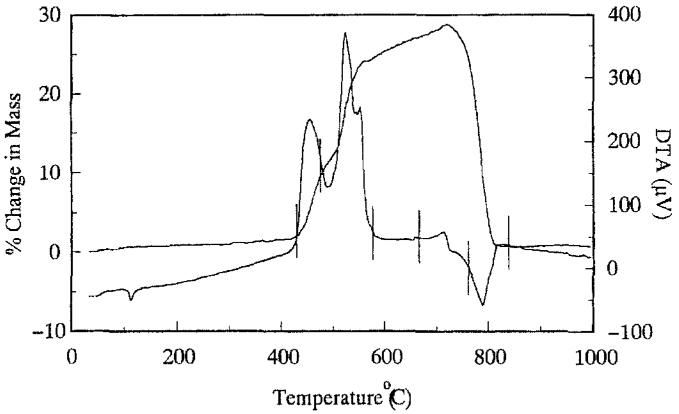

Fig. 1 TG-DTA trace for the oxidation of chalcocite. The vertical lines indicate the temperatures at which partially oxidised samples were taken for analysis

loss, and as before can be assigned to the transformation of orthorhombic to hexagonal chalcocite. The two exothermic peaks, which occurred in the temperature ranges 425–490 and 490–585°C, were associated with the first two mass gains.

Quantitative analysis for oxides by XRD

Standard samples for R determinations were made up from mixtures of pure Cu_2O and α-SiO_2, in the copper oxide:standard ratio 85:15 by mass. Approximately 30 mg of the mixture was mounted over a square area (~1 cm^2) on a low background quartz crystal sample holder. The thickness of the mixture exceeded the limit of the thickness for the experimental conditions employed. The intensities of five strong lines, for both the copper oxide and α-SiO_2 phases, were measured for each mixture. Equation 3 was used to calculate the RIR values for each of the selected line pairs. The R values are given in Table 1.

A similar procedure was adopted for the determination of R values for CuO. The R values are given in Table 2.

The XRD patterns for the partially oxidised chalcocite samples were measured using α-SiO_2 as an internal standard method, again in the mass ratio 85:15. Approximately 25 mg of the mixture was mounted on the sample holder over a square area (~1 cm^2). The amount of the mixture analysed was maintained constant for all the experiments. The 2Θ and I values for the Cu_2O, CuO and α-SiO_2 phases are given in Tables 3 and 4, respectively. Phase composition values for Cu_2O and CuO were calculated for each of the selected line pairs as summarised in Tables 5 and 6, respectively. Standard error values were calculated from the individual line pair results using

$$\sqrt{\sum(\bar{x}-x)^2/n(n-1)}\,.$$

Table 1 Reference intensity ratio (R) data for XRD analysis of Cu_2O

Cu_2O		2Θ(°)	I	2Θ(°)	I	2Θ(°)	I	2Θ(°)	I	2Θ(°)	I
		29.60	49	36.46	1000	42.35	268	61.43	225	73.61	163
α-SiO_2		R		R		R		R		R	
2Θ(°)	I										
20.87	23	0.38		7.67		2.06		1.73		1.25	
26.65	143	0.06		1.23		0.33		0.28		0.20	
39.48	10	0.86		17.65		4.73		3.97		2.88	
50.21	23	0.38		7.67		2.06		1.73		1.25	
60.01	15	0.58		11.76		3.15		2.65		1.92	

XRD line intensities (I) and angle values (2Θ) for Cu_2O:α-SiO_2 mixture, 85:15% by mass

Table 2 Reference intensity ratio (R) data for XRD analysis of CuO

Cu_2O		2Θ(°)	I	2Θ(°)	I	2Θ(°)	I	2Θ(°)	I	2Θ(°)	I
		33.56	913	38.76	1000	48.79	327	61.602	255	66.299	209
α-SiO_2		R		R		R		R		R	
2Θ(°)	I										
20.89	58	2.78		3.04		0.99		0.78		0.64	
26.65	262	0.62		0.67		0.22		0.17		0.14	
39.50	45	3.58		3.92		1.28		1.00		0.82	
50.18	67	2.40		2.63		0.86		0.67		0.55	
55.99	55	2.93		3.21		1.05		0.82		0.67	

XRD line intensities (I) and angle values (2Θ) for CuO:α-SiO_2 mixture, 85:15% by mass

Quantitative analysis for sulfates by FTIR

Copper(II) sulfate and copper(II) oxysulfate were quantified using FTIR spectrometry. Standard calibration curves were constructed using the two pure sulfates in suitable matrices. The height of the characteristic peaks of copper(II) sulfate and copper(II) oxysulfate at 704 and 439 cm^{-1} respectively, which were unaffected by band overlap, were used to construct calibration curves and to determine the concentrations in the partially oxidised samples.

Table 3 XRD 2Θ and *I* values for selected lines of Cu_2O (analyte phase) and α-SiO_2 (internal standard) following the heating of chalcocite to specified temperatures

T/°C	Observed data for Cu_2O		Observed data for α-SiO_2	
	2Θ (°)	*I*	2Θ (°)	*I*
435	36.42	77	20.87	223
	61.55	38	26.65	1000
			50.19	225
			60.00	129
470	36.58	205	20.87	204
	73.82	59	26.65	1000
			50.18	214
570	36.42	1000	26.65	287
	61.38	282	39.50	21
	73.53	185		
670	29.55	55	20.87	57
	36.42	1000	26.65	366
	73.56	193	60.00	35

Table 4 XRD 2Θ and *I* values for selected lines of CuO (analyte phase) and α-SiO_2 (internal standard) following the heating of chalcocite to specified temperatures

T/°C	Observed data for CuO		Observed data for α-SiO_2	
	2Θ (°)	*I*	2Θ (°)	*I*
670	35.589	107	20.869	57
	48.837	32	60.001	35
775	35.555	849	20.841	55
	38.769	1000	26.652	303
	48.785	299	59.949	64
	61.607	207		

Table 5 Estimated amounts of Cu_2O present in the partially oxidised chalcocite determined by XRD

T/°C	Cu_2O content (% by mass)		
	value	mean	std. error
435	0.7, 0.9, 0.7, 0.8, 1.5, 2.0, 1.5, 1.7	1.2	0.2
470	2.0, 2.5, 1.9, 3.5, 4.4, 3.3	2.9	0.4
570	42.5, 40.5, 52.6, 50.7, 48.3, 45.9	46.8	1.7
670	38.1, 37.6, 40.6, 34.3, 33.3, 36.4, 40.6, 39.5, 43.1	38.2	1.0

Table 6 Estimated amounts of CuO present in the partially oxidised chalcocite determined by XRD

T/°C	CuO content (% by mass)		
	value	mean	std. error
670	10.1, 15.7, 8.5, 13.1	11.8	1.6
775	83.3, 67.8, 67.9, 89.7, 73.9, 73.0, 82.4, 67.3, 66.7, 72.4, 60.3, 59.2	72.0	2.7

Copper(II) sulfate analysis

Initial attempts to construct calibration curves for $CuSO_4$, which had been heated to various temperatures and dispersed in a pressed KBr disc, produced non-linear relationships with concentration. On monitoring the peak at 704 cm^{-1}, it was found that the peak height varied with temperature. This effect occurred for all

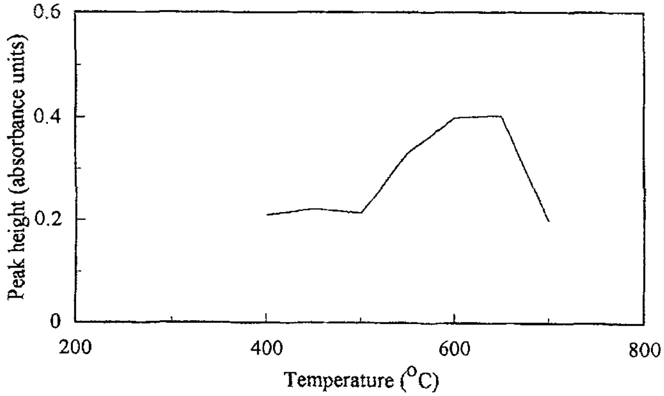

Fig. 2 FTIR peak height at 704 cm^{-1} as a function of temperature for $CuSO_4$

characteristic peaks that were not interfered with by the characteristic peaks from other species. The intensity of the peak at 704 cm^{-1} is plotted in Fig. 2 as a function of temperature. It is seen that the peak height of copper(II) sulfate at 704 cm^{-1} is approximately constant in the temperature range 400–500°C. The peak height then dramatically increases up to 650°C. At 700°C the peak height decreases, as a result of the decomposition of copper(II) sulfate to copper(II) oxysulfate. A similar profile was obtained for the characteristic peaks at 962 and 589 cm^{-1}.

The temperature dependence of absorbance of $CuSO_4$ was investigated by making two KBr discs which contained samples of copper(II) sulfate which had been heated to 400 and 600°C, respectively. The initial spectra of the sample discs were obtained at zero time. The discs were then left in an open atmosphere for 30, 60, and 120 min before the spectra were taken from the same disks. The plot of peak heights at 704 cm^{-1} against time of data collection is given in Fig. 3. It can be seen that the absorbance of the 704 cm^{-1} peak of copper(II) sulfate in a KBr disc changes significantly during the first 30 min of exposure. The copper(II) sulfate sample heated to 400°C changed more than the sample heated to 600°C. The peak height had diminished to 17% of the original value at 400°C, but only to 68% for the sample heated to 600°C. Beyond this time the rate of change of absorbance diminished.

These effects can be related to the tendency of anhydrous $CuSO_4$ to adsorb water. It is difficult to obtain a spectrum of pure anhydrous $CuSO_4$, as adsorption of water produces the monohydrate which has a different symmetry and hence a different spectrum. This diminishes the intensity of the anhydrous form as the concentration of the monohydrate increases with time. After 30 min the rate of water adsorption slows, and so the peak intensities stabilise to some extent. The sample heated to the higher temperature has less tendency to adsorb water, prob-

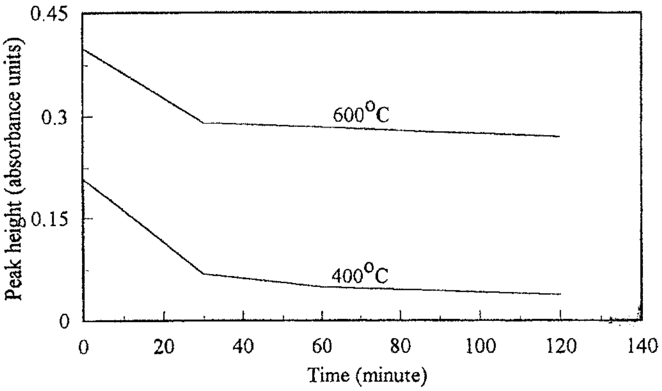

Fig. 3 FTIR peak height at 704 cm^{-1} as a function of time of $CuSO_4$ heated to 400 and 600°C

ably because of changes in crystallinity, and so the loss of peak intensity for that sample was less than for the sample heated to 400°C.

In view of the different responses that $CuSO_4$ showed with temperature, it was obviously not possible to construct a calibration curve which could be used to determine the $CuSO_4$ content in oxidised chalcocite samples heated to different temperatures. Instead, the $CuSO_4$ content was determined by heating samples to temperatures on either side of the temperature at which the chalcocite was taken, and a simple ratio technique used. The copper(II) sulfate levels were estimated by direct comparison of the peak height at 704 cm^{-1} of pure copper(II) sulfate in a KBr disc to the peak height of unknown at the same wave number. The spectra of the standards and samples were obtained after 30 min exposure to the atmosphere in order to eliminate differences due to water absorption of the disc.

The matrix of the standards was chosen to simulate the composition of the partially oxidised sample. For example, the matrix of the standard at 435°C was a mixture of Cu_2S, Cu_2O, and $CuSO_4$; whereas the matrix of the standard at 670°C was a mixture of Cu_2O, $CuSO_4$, $CuSO_4 \cdot CuO$, and CuO. Peak heights at 704 cm^{-1} for $CuSO_4$ standard at various concentrations and various temperatures are given in Table 7 and Fig. 4.

Table 7 Estimated amounts of $CuSO_4$ present in the partially oxidised chalcocite determined by FTIR

T/°C	Average peak height	[$CuSO_4$] (%)
435	0.0012	1.7
470	0.0187	12.8
570	0.1228	55.6
670	0.0293	9.8

The same method applied to the standard was applied to determine the spectra of the partially oxidised chalcocite. The peak height of the sample at 704 cm^{-1} was used to calculate the concentration of $CuSO_4$ present in the partially oxidised chalcocite, which is given in Table 7. The values presented in the Table 7 were calculated from the mean values both of standard and the sample.

The values of $CuSO_4$ in the chalcocite samples, as determined by FTIR, were checked by wet chemical analysis. Samples of partially oxidised chalcocite at temperatures of 435, 470, and 570°C were obtained from multiple experiments on the TG-DTA apparatus and leached with water. The soluble sulfate was precipitated as $BaSO_4$ and determined gravimetrically. The sample oxidised at 670°C could not be analysed for $CuSO_4$ because the $CuSO_4 \cdot CuO$ was also present in the product. This species was found to be slightly soluble in water and would increase the concentration of $CuSO_4$ in the solution. The values of $CuSO_4$

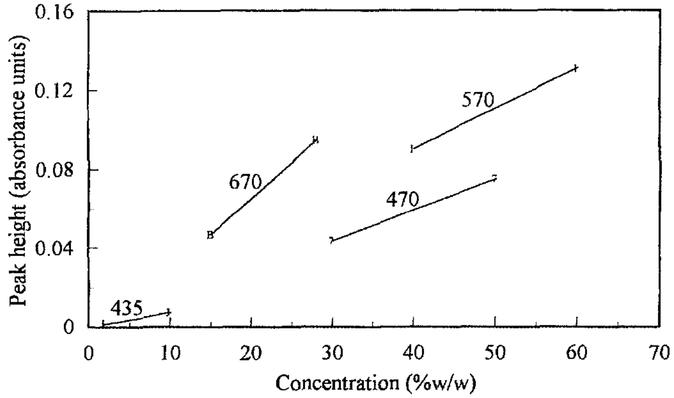

Fig. 4 FTIR absorbance values for standard samples of $CuSO_4$ at various temperatures

in the partially oxidised chalcocite at 435, 470, and 570°C were 1.02, 10.66, and 50.76%, respectively. The wet chemical analysis data for $CuSO_4$ showed a similar trend to, but with values slightly lower than, the data obtained with the FTIR method.

Copper(II) oxysulfate analysis

A calibration curve for $CuO{\cdot}CuSO_4$ was constructed by measuring the peak height of one of its characteristic peaks at 439 cm^{-1} and plotting this against concentration. The spectra of the standards was obtained from a mixture of a certain amount of $CuSO_4{\cdot}CuO$ in a matrix of Cu_2O, CuO, and $CuSO_4$. The ratio among them was adjusted to a similar composition of the species present in the partially oxidised chalcocite. The peak height data at 439 cm^{-1} for standard $CuO{\cdot}CuSO_4$ were determined and the mean values of the peak height against concentration plotted to construct a calibration curve (Fig. 5). The mean values of the characteristic peak for $CuSO_4{\cdot}CuO$ obtained from the partially oxidised chalcocite were measured. These values were then related to the calibration curve in the usual way to obtain the amount of $CuO{\cdot}CuSO_4$ present in the sample. The results are given in Table 8.

Phase composition results

The quantitative analysis results for the phases present in the partially oxidised chalcocite are given in Table 9. During the oxidation of chalcocite, the rate of the formation of $CuSO_4$ is faster than that for Cu_2O. The two species increased in concentration dramatically from 2 and 1% for $CuSO_4$ and Cu_2O, respectively, at 435°C to amounts of 56 and 47% at 570°C. At this temperature, 2% of

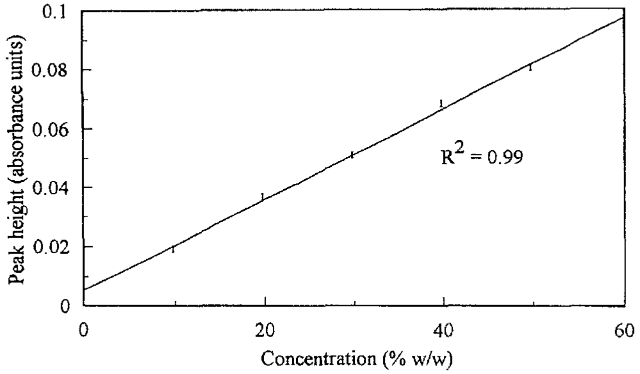

Fig. 5 FTIR calibration curve for $CuSO_4 \cdot CuO$

Table 8 Estimated amounts of $CuSO_4 \cdot CuO$ present in the partially oxidised chalcocite, determined by FTIR

T/°C	No. experiment	Peak height	Average	[$CuO \cdot CuSO_4$]
570	1	0.0047		
	2	0.0038	0.0043	1.9
670	1	0.0669		
	2	0.0743	0.0706	41.2
775	1	0.0458		
	2	0.0397	0.0427	23.8

$CuO \cdot CuSO_4$ has been formed. The sample taken at 670°C showed that both $CuSO_4$ and Cu_2O have decreased in level.

The rate of disappearance of $CuSO_4$ was faster than Cu_2O. One possible reason for this is that the former can be involved in the formation of $CuO \cdot CuSO_4$ via two routes of reaction, only one of which involves Cu_2O. The content of $CuO \cdot CuSO_4$ increased to 41%. As well, Cu_2O was oxidised in this temperature range to form 9% CuO. Samples taken at 775°C showed no indication of the presence of $CuSO_4$ and Cu_2O. Two phases identified as being present were 24 and 72% of $CuO \cdot CuSO_4$ and CuO, respectively. The copper(II) oxysulfate was stable up to 775°C. The end product of the oxidation of chalcocite at 840°C was CuO. There was no indication of the presence of Cu metal at any stage of the reaction sequence.

The total mass percent of the species present in the partially oxidised chalcocite was reasonably close to 100%. The error in the first two sets of data could not be estimated as the content of Cu_2S was calculated by difference. The last

Table 9 Quantitative data for phase analysis of partially oxidised chalcocite

T/°C	Mass percent of the species in the products					Total
	Cu_2S	Cu_2O**	$CuSO_4$	$CuO\cdot CuSO_4$	CuO**	
435	97.1*	1.2±0.4	1.7±0.4			100
470	83.5*	3.7±0.8	12.8±0.9			100
570		46.8±3.4	55.6±2.8	1.9±0.1		104.3±6.3
670		38.2±2.0	9.8±1.0	41.2±1.4	11.8±3.2	101.0±9.0
775				23.8±0.8	72.0±5.4	95.8±6.2
840					100	100

*calculated by difference

**uncertainties for Cu_2O and CuO levels set at 2 × standard errors

data set was assumed to comprise 100% CuO as no other product was detected by any of the characterisation methods.

Conclusions

Quantitative XRD and FTIR techniques were used to determine the oxide and sulfate phase compositions, respectively, of chalcocite at various stages of oxidation. The XRD technique was quite straight forward, but the FTIR technique was not all that suitable for the determination of the $CuSO_4$ content. This was primarily to do with the ability of anhydrous $CuSO_4$ to rehydrate at different rates dependent on the temperature to which the sample was heated prior to analysis. Thus a linear calibration curve could not be obtained, and standard samples needed to be prepared at temperatures corresponding to the oxidation temperature of the chalcocite. On the other hand, the FTIR technique provided a simple and sensitive method for the quantitative determination of $CuSO_4\cdot CuO$ in partially oxidised chalcocite samples.

Using these techniques, it was possible to follow quantitatively the appearance and disappearance of various phases during the oxidation of chalcocite.

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