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STUDIES ON THERMAL OXIDATION OF CHALCOPYRITE FROM CHITRADURGA, KARNATAKA STATE, INDIA

M. Aneesuddin, P.N. Char, M. Raza Hussain and E.R. Saxena

REGIONAL RESEARCH LABORATORY, HYDERABAD – 500 009, INDIA

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When chalcopyrite is heated in air, up to 350° there is no marked change. Between 350 and 440°, surface material is oxidised to iron sulphate, $CuSO_4$ and Fe_2O_3, while in regions not accessible to oxygen the formation of Cu_5FeS_4, FeS and S takes place. From 440 to 500° oxidation and sulphation phenomena occur. Stable compounds between 500 and 650° are iron sulphate, $CuSO_4$ and Fe_2O_3, with a minor amount of $6CuO.Cu_2O$ indicated at 650°. After the decomposition of iron sulphate, $CuSO_4$ decomposes, first to $CuO.CuSO_4$ and then to CuO. By 750° the sulphur has been totally lost from all compounds, while the oxides of copper and iron partly react to form $CuFe_2O_4$. Final products of oxidation between 800 and 850° are CuO, $CuFe_2O_4$ and Fe_3O_4.

The mechanism of thermal oxidation of chalcopyrite ($CuFeS_2$) in air has been examined in detail by many workers [1]. An attempt has been made in this paper to identify the products and to study the process of thermal oxidation of chalcopyrite in air, so as to establish a sequential relationship for the compounds formed when the mineral is progressively heated up to 850°. Techniques employed in this study are DTA, TG, X-ray diffractometry and colorimetry.

Experimental

Material

The chalcopyrite concentrates from Chitradurga, Karnataka State in South India selected for the present work contain 25% Cu, 27.90% Fe, 26.92% S, 0.75% Pb and 0.15% Zn. Non-sulphide impurities in minor amounts are CaO, MgO, Al_2O_3 and SiO_2.

Thermal analysis

DTA: Leeds and Northrup Unit provided with Pt-Pt/10% Rh thermocouples and a Robert Grim-Shaw type ceramic sample holder was used, with calcined alumina as the thermally inert reference material. The rate of heating was 2 deg per minute.

TG: The sample was heated in a platinum bucket hooked to the pan of a Mettler balance and suspended in a vertical tubular furnace of length 25 cm and diameter 2 cm. The thermocouple (Pt-Pt/13%Rh) for recording the temperature of the sample was kept very close to the bucket. The rate of heating was 2 deg per minute. Weights and temperatures of the sample were recorded simultaneously at intervals of 5 minutes.

XRD

X-ray diffractometer traces were taken on a Philips PW 1010 diffractometer with a Nonius-Guinier camera 11.46 cm in diameter, using Cu K alpha radiation.

Sample preparation for XRD studies

(a) A vertical tubular furnace 25 cm long and 5 cm in diameter, plugged at both ends with ceramic blocks, was used for roasting the samples. A 3 mm hole was provided in the plugs at both ends for inlet of the thermocouple and a natural draught of air. A 3 g sample (average particle size 44 μm), with ceramic beads distributed uniformly in the mass of the sample for easy and uniform accessiblity of air, was taken in a Gooch crucible (3.5 cm diameter and 4.5 cm height). The crucible, placed over a ceramic tripod, was kept on the ceramic plug at the bottom of the furnace. The furnace temperature was maintained at the desired value for 3 hours to ensure the formation of maximum amounts of the compounds expected at each temperature. (b) To obtain a clear XRD pattern of water-insoluble compounds formed during roasting, the masking effect of water-soluble salts was removed as follows: One g of the sample prepared as in (a) above was boiled in 20 ml distilled water for 15 minutes, after which the mixture was centrifuged and decanted. This process was repeated 5 times, after which the solids were dried, and the washings were stored for chemical analysis.

Samples thus prepared were stored in a desiccator and later subjected to X-ray analysis.

Chemical analyses

Water-soluble copper and iron in the washings obtained in (b) above were determined quantitatively by colorimetry.

Results

DTA: The DTA curve of the natural sample (Fig. 1a) shows an exothermic drift up to about 330° after which there is a series of 4 peaks on the exothermic side of the baseline till 545°. The baseline of the curve between 545 and 675° is straight, indicating this to be a region of equilibrium. Finally, in the temperature interval 675 to 780° there is a well marked double endothermic peak.

TG: The TG curve (Fig. 1b) initially shows a gradual loss in weight, this reaching a maximum of about 7% at 350°.This is followed by a continuous gain in weight with a maximum of about 20% at 540°. Between 540 and 620° there is a slight fluctuation in weight, after which there is a rapid loss in weight, which reaches a maximum of about 25% at 800°. Between 800 and 900° the changes in weight are not appreciable.

The temperature regions showing gains and losses in weight in the TG curve appear to correspond quite closely to the temperature regions showing exothermic and endothermic peaks in the DTA curve.

XRD: The DTA and TG curves show that the maximum changes take place in the temperature interval 350–800°. Chalcopyrite samples were therefore roasted at temperatures ranging from 350 to 850°, at intervals of 50°, and subjected to XRD analysis.

The X-ray diffractograms (diffraction data given in Table 1) in general exhibit weak patterns, which may be due to the lower amounts of compounds formed or a poor degree of crystallinity. The number of compounds normally being three or more, there is an obvious overlapping of lines. These factors make interpretation difficult. In cases where there is no overlapping, identification of compounds was based on the presence of the most intense reflections, whereas in cases where there was overlapping weaker reflections were taken into account to identify the specific compound (Table 2). All identifications were based on ASTM X-ray powder data.

Chemical analyses: The amounts of water-soluble Cu, determined as $CuSO_4$, and of Fe, determined as $FeSO_4$, are reported against temperature in Table 3.

The presence of $CuSO_4$ in appreciable amount is indicated in samples roasted at temperatures ranging from 400 to 700°. Iron sulphate ($FeSO_4$ and/or $Fe_2/SO_4/_3$), in traces or minor amounts, is present in samples roasted at temperatures ranging from 350 to 650°.

Discussion

When chalcopyrite is heated in air, oxygen is freely available at the surface, but could be deficient in the internal layers and at the core of each particle. This uneven distribution of oxygen accounts for the simultaneous formation of products of oxidation such as sulphates and oxides of copper and iron, and an inert atmosphere product, bornite (Cu_5FeS_4); these have not only been detected by us in XRD analysis but also reported by earlier workers [2--4].

There is no appreciable change in mineral composition up to 350° (Table 2). The exothermic drift in the DTA curve up to 360° could therefore be interpreted as being due to the oxidation of sulphur at the particle edges and to the formation of iron sulphate (Table 3). The loss in weight indicated in the TG curve up to 350° confirms the loss of sulphur, and a slight rise in weight between 300 and 350° may be due to the formation of iron sulphate.

The XRD pattern of the sample roasted at 400° is extremely weak, and nearly that for an amorphous material. Nevertheless, in addition to $CuFeS_2$ and FeS_2, the presence of Cu_5FeS_4 ($d = 1.95$ Å) and Fe_2O_3 ($d = 2.69$ Å) is indicated. Chemical analysis reveals the presence of $CuSO_4$ and iron sulphate (Table 3). The exothermic effect between 360 and 375° in the DTA curve is due to oxidation of $CuFeS_2$ at the surface, which is

Table 1 X-ray diffraction data

Temperature of roasting, °C	Natural ore		350				400			
			a		b		a		b	
	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0
	3.08	10	3.08	10	3.65	3	3.33	5	3.33	10
	3.03	100	3.03	100	3.08	9	3.16	4	3.16	15
	2.71	3	2.71	3	3.03	100	3.03	7	3.09	15
	2.40	21	1.86	20	2.63	15	2.69	3	3.07	15
	1.86	20	1.84	40	1.86	21	2.51	6	2.74	15
	1.84	40	1.63	5	1.84	35	1.95	9	2.69	10
	1.63	5	1.59	18	1.59	20	1.87	2	2.62	5
	1.59	18	1.57	14	1.57	12			2.50	15
	1.57	14							1.95	20
									1.87	5

Temperature of roasting, °C	450				500			
	a		b		a		b	
	dÅ	I/I_0	d,Å	I/I_0	dÅ	I/I_0	dÅ	I/I_0
	5.63	30	3.33	15	5.63	30	3.65	15
	5.40	36	3.09	15	5.40	30	3.33	15
	4.72	100	2.69	10	4.73	100	2.69	100
	4.13	50	2.51	15	4.13	50	2.51	80
	3.98	60	1.95	10	3.98	70	2.20	25
	3.67	80	1.68	10	3.67	100	1.83	15
	3.52	50	1.48	10	3.56	100	1.69	50
	2.96	30	–	–	3.33	40	1.60	20
	2.65	30	–	–	3.05	30	1.48	20
	2.69	100	–	–	2.69	100	1.45	20
	2.62	30	–	–	2.62	50	–	–

	2.51	80	–	–	2.51	100	–	–
	2.41	40	–	–	2.45	50	–	–
	2.19	20	–	–	2.19	50	–	–
	1.85	50	–	–	1.85	50	–	–
	1.69	50	–	–	1.69	70	–	–
	1.48	30	–	–	1.48	50	–	–
	1.45	20	–	–	1.44	50	–	–

Temperature of roasting, °C	550				600			
	a		b		a		b	
	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
	5.63	30	3.65	25	5.60	10	3.65	40
	5.40	50	2.69	100	5.40	30	2.69	100
	4.73	100	2.51	80	5.12	30	2.20	20
	4.13	50	2.20	15	4.72	80	1.83	40
	3.98	70	1.83	25	4.19	50	1.69	50
	3.67	100	1.69	50	3.98	60	1.48	30
	3.53	100	1.48	25	3.67	80	1.45	30
	3.33	40	1.45	25	3.53	80		
	3.03	30			3.33	30		
	2.75	7			3.30	20		
	2.69	100			2.69	100		
	2.62	50			2.62	80		
	2.51	100			2.57	90		
	2.41	50			2.41	60		
	2.19	50			2.32	20		
	1.85	70			2.19	30		
	1.69	70			1.85	50		
	1.48	50			1.77	30		
	1.45	50			1.69	50		
	1.				1.48	50		
					1.45	50		

Table 1. (cont'd)

Temperature of roasting, °C	650				700				750			
	a		b		a		b		a		b	
	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
	5.60	10	3.65	40	5.68	10	3.65	40	4.79	15
	5.43	10	2.69	100	5.43	10	2.69	100	3.66	25
	4.72	70	2.51	85	4.72	40	2.51	80	3.34	20
	4.18	80	2.19	25	4.19	80	2.19	20	3.49	25
	3.98	50	1.83	40	3.95	30	1.83	50	2.95	25
	3.67	70	1.67	50	3.68	70	1.67	50	2.69	40
	3.52	90	1.60	25	3.52	80	1.58	40	2.51	100
	3.30	30	1.48	25	2.69	100	1.48	30	2.42	15
	2.83	10	–	–	2.61	80	1.45	20	2.32	35
	2.69	100	–	–	2.51	90	–	–	2.20	10
	2.62	90	–	–	2.41	50	–	–	2.09	10
	2.51	90	–	–	2.30	20	–	–	1.86	20
	2.41	50	–	–	2.21	40	–	–	1.84	20
	2.30	20	–	–	1.85	50	–	–	1.69	20
	2.20	30	–	–	1.77	10	–	–	1.61	20
	2.01	20	–	–	1.69	50	–	–	1.48	20
	1.85	50	–	–	1.48	40	–	–	–	–
	1.77	40	–	–	1.45	40	–	–	–	–
	1.69	50	–	–	1.43	30	–	–	–	–
	1.48	50	–	–	–	–	–	–	–	–
	1.45	50	–	–	–	–	–	–	–	–
	1.43	20	–	–	–	–	–	–	–	–

Tempera ture of roasting, °C	800 a		850 a	
	d, Å.	I/I_o	d, Å.	I/I_o
	4.79	15	4.80	15
	3.99	55	3.49	15
	3.30	10	3.30	10
	2.95	30	2.95	40
	2.89	10	2.52	100
	2.51	100	2.48	15
	2.41	15	2.32	30
	2.32	30	2.20	5
	2.20	15	2.09	25
	2.09	20	1.71	10
	1.69	20	1.61	25
	1.61	20	1.48	20
	1.48	20		

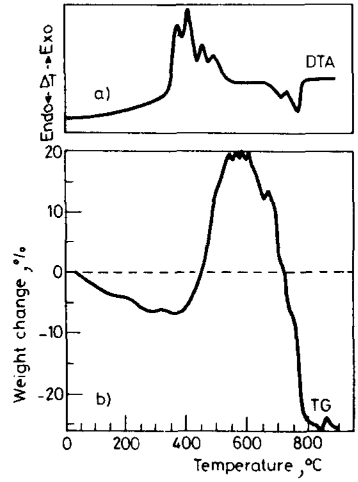

Figure 1 DTA (a) and TG (b) curves of natural chalcopyrite sample

Table 2 Results of X-ray analysis

Temperature of roasting, °C	Compounds identified in roasted products (a)	Compounds identified in roasted products after leaching in water (b)
Natural	$CuFeS_2$ (major), FeS_2 (minor) gamma-$CuFeS_2$ (traces)	––
350	$CuFeS_2$, FeS_2, gamma-$CuFeS_2$	$CuFeS_2$, FeS_2, gamma-$CuFeS_2$
400	$CuFeS_2$, FeS_2, Cu_5FeS_4	$CuFeS_2$, FeS_2, Cu_5FeS_4, Fe_2O_3
450	$CuSO_4$, $CuSO_4.5H_2O$*, $FeSO_4$, Fe_2O_3	Cu_5FeS_4, Fe_2O_3
500 to 600	$CuSO_4$, $CuSO_4.5H_2O$, $FeSO_4$, Fe_2O_3	Fe_2O_3
650	$CuSO_4$, $CuSO_4.5H_2O$, $FeSO_4$, Fe_2O_3	Fe_2O_3, $6CuO.Cu_2O$
700	$CuSO_4$, $CuSO_4.5H_2O$, $CuO.CuSO_4$, Fe_2O_3	Fe_2O_3, $6CuO.Cu_2O$
750	CuO, $CuFe_2O_4$, Fe_2O_3, Fe_3O_4	X-ray analysis not performed as all compounds are insoluble in water
800 to 850	CuO, $CuFe_2O_4$, Fe_3O_4	–do–

*Formation of $CuSO_4.5H_2O$ is due to the absorption of moisture during storage and handling.

confirmed by the gain in weight in the TG curve. The endothermic drift between 375 and 390° appears to reflect the initiation of conversion of $CuFeS_2$ to Cu_5FeS_4 in regions deficient in oxygen.

By 450° $CuFeS_2$ and FeS_2 have disappeared. Fe_2O_3 is present, with $FeSO_4$ and $CuSO_4$ (Table 2). The amount of $CuSO_4$ shows an increase (Table 3). Cu_5FeS_4 is present only in the leached sample, indicating that it is formed at the core of the particles and can be detected only after the masking effect of water-soluble substances is removed. The second exothermic peak in the DTA curve, between 390 and 440°, the continuation in weight gain in the TG curve and the increase in the amount of $CuSO_4$ represent the completion of oxidation of surface material.

The internal layers of the sample and the core of the particles are now exposed to oxygen, due to which FeS_2, FeS and S formed from bornite [5–7] undergo oxidation. This is confirmed by the fact that the characterisitic X-ray diffraction line for Fe_2O_3 (d = 2.69 Å) shows a sudden rise in intensity from 10 at 400° to 100 at 450°. The amount of $FeSO_4$ also shows an increase (Table 3). In view of this, the third exothermic peak in the DTA curve, between 440 and 480°, appears to be due to the oxidation of FeS_2, FeS and S locked up in the internal layers and the core of the particles.

Cu_5FeS_4 is absent from a sample roasted at 500°. Iron sulphate is present, and the diffraction lines of $CuSO_4$ and Fe_2O_3 are increased in intensity. In the leached sample only Fe_2O_3 is indicated (Table 2). The amount of $CuSO_4$ shows a further increase (Table 3). The fourth exothermic peak in the DTA curve therefore appears to be due to the oxidation of Cu_5FeS_4. The steep rise in weight shown in the TG curve between 425 and 500° indicates a gain in oxygen and thus supports this interpretation.

It is possible that SO_2 released during the oxidation of $CuFeS_2$, Cu_5FeS_4, FeS_2 and FeS is converted to SO_3 in the presence of Fe_2O_3; the SO_3 then attacks oxides of iron and copper to form additional amounts of the respective sulphates, due to which there is a slight increase in the amount of $CuSO_4$ formed at 550° (Table 3), which is also the maximum.

X-ray and chemical analysis indicate that $CuSO_4$, $FeSO_4$ and Fe_2O_3 are the stable compounds in the range 500–600° (Tables 2 and 3). The fourth exothermic peak in the DTA curve ends at 545° and equilibrium conditions are exhibited up to 675°. The gain in weight in the TG curve also ends at about 545°, and up to about 600° there are only slight fluctuations in weight, immediately after which the curve shows an abrupt loss in weight due to the decomposition of sulphates.

At 650°, in addition to $CuSO_4$, iron sulphate and Fe_2O_3, the presence of $6CuO.Cu_2O$ is indicated in the leached sample (Table 2).

Iron sulphate is absent from the sample roasted at 700° (Table 3). $CuSO_4$ and Fe_2O_3 are present with $CuO.CuSO_4$. In the leached sample Fe_2O_3 is present with $6CuO.Cu_2O$, which shows an increase in intensity. The amount of $CuSO_4$ is appreciably reduced (Table 3). Decomposition of $CuSO_4$ to $CuO.CuSO_4$ is represented in the DTA curve by the endothermic peak between 675 and 740° [8] and by a loss in weight in the TG curve.

Table 3 Percentage water-soluble Cu and Fe based on Cu and Fe in original ore, determined colorimetrically

Temperature of roasting, °C	Cu percentage	Fe percentage	Percentage of $FeSO_4$ as impurity in $CuSO_4$
350	nil	0.19	nil
400	22.2	0.20	1.15
450	47.28	1.77	4.46
500	81.83	0.16	0.24
550	90.68	0.22	0.32
600	84.98	0.19	0.29
650	81.78	0.18	0.29
700	67.57	–	–

In the sample roasted at 750°, Fe_2O_3 is still present, but with less intense diffraction lines, and the formation of CuO, $CuFe_2O_4$ and Fe_3O_4 is indicated (Table 2). CuO is formed from the decomposition of $CuO.CuSO_4$ which is represented by the second endothermic peak, between 740 and 780° in the DTA curve, and the continued loss in weight shown in the TG curve. $CuFe_2O_4$ is formed by the reaction between CuO and Fe_2O_3. Formation of Fe_3O_4 could have taken place in a region deficient in oxygen.

In the samples roasted at 800 and 850°, Fe_2O_3 is absent. The final products of oxidation of $CuFeS_2$ in air are CuO, $CuFe_2O_4$ and Fe_3O_4.

Sulphatation of chalcopyrite to $CuSO_4$ in air appears to take place in the following three stages: (1) Direct oxidation of $CuFeS_2$. (2) Oxidation of Cu_5FeS_4. (3) Reaction between SO_2, Fe_2O_3, SO_3 and CuO.

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Zusammenfassung — Beim Erhitzen von Chalkopyrit in Luft tritt bis 350° keine merkbare Veränderung ein. Zwischen 350 und 440° wird die Substanz an der Oberfläche zu Eisensulfat, $CuSO_4$ und Fe_2O_3 oxydiert, während in den nicht für Sauerstoff zugänglichen Teilen die Bildung von Cu_5FeS_4, FeS und S erfolgt. Im Bereich von 440–500° treten Oxydations- und Sulfatierungsphänomene auf. Zwischen 500 und 650° sind Eisensulfat, $CuSO_4$ und Fe_2O_3 stabile Verbindungen, zusammen mit dem bei 650° auftretenden $6.CuO.Cu_2O$. Nach der Zersetzung von Eisensulfat zersetzt sich $CuSO_4$ zunächst zu $CuO.CuSO_4$ und schliesslich zu CuO. Bei 750° sind alle Verbindungen vollkommen schwefelfrei und die Oxide von Kupfer und Eisen reagieren unvollständig zu $CuFe_2O_4$. Endprodukte der Oxydation sind bei 800–850° CuO, $CuFe_2O_4$ und Fe_2O_3.

Резюме — Видимых изменений не происходит с халькопиритом при нагревании его на воздухе до 350 °. Между 350 ° и 440 ° поверхность доставленных материалов окисляется до сульфата железа, сульфата меди и окиси трехвалентного железа. В местах недоступных для кислорода, образуются Cu_5FeS_4, сульфид железа и сера. Между 440 ° и 500 ° происходит реакция окисления и образоние сульфата. В области температур 500–600 ° стабильными соединениями являются сульфат железа, сульфат меди и окись трехвалентного железа, содержащая при 650 ° главную примесь $6CuO \cdot Cu_2O$. После разложения сульфата железа, сульфат меди сначала разлагается до $CuO \cdot CuSO_4$, а затем до CuO. Сера полностью удаляется из всех соединений при достижении температуры 750 °, когда окиси железа и меди частично реагируют до $CuFe_2O_4$. Конечными продуктами окисления между 800 и 850 ° являются CuO, $CuFe_2O_4$ и Fe_3O_4.