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THERMOANALYTICAL STUDIES ON COPPER–IRON SULPHIDES

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Abstract

The direct production of copper sulphate from copper ore is an important route to recover copper. The condition, however, is dependant on temperature and sulphatising environment. The oxidation of chalcopyrite in static air bed condition has been studied byTG/DTA and DSC techniques. The addition of catalysts, improved the sulphation by in-situ producing better condítions. The mutual effects of sulphides were further confirmed by studying the oxidation reaction on pure copper-iron sulphides and results so obtained were corroborated with X-ray diffractrograms. With only chalcopyrite a mass gain of 8% (TG) corresponding to copper sulphate formation was observed, in the temperature range 628–738 K. The TG plots showed respective mass gain of 14, 17 and 12% in presence of Fe_2O_3, Na_2SO_4 and $FeSO_4$ with chalcopyrite in the wider temperature range 628–923 K. As such the cupric sulphide had a negligible tendency of sulphation, which increased with the addition of ferrous sulphide mixture under the temperature range studied. At higher temperature copper ferrite formation was found.

Keywords: catalysis, copper sulphate, reaction sequence, sulphation

lntroduction

The oxidation of sulphide is complex in nature and it is very difficult to predict the actual course of reaction. This is mainly due to several other reaction taking place with one or other intermediate products. The associated solid state transformations depend upon various other factors like characteristics of mineral, the gaseous environment, temperature, associated impurities, catalyst and rate of heating. The thermal analysis (TA) technique is most useful tool for understanding the selectivity, phase changes and to predict a particular temperature range for a desired product. With the help of TA and XRD the approach for sequence of reaction may also be made.

Aneesuddin *et al.* [1] and Kurian *et al.* [2] have initiated the studies on Indian chalcopyrite mineral with the help of TG/DTA under different gaseous conditions. But, there are discrepancies presumably due to different oxidising conditions [3] and presence of impurities. In order to know the actual transformations during the roasting of chalcopyrite the present investigation has been undertaken. A mixture of bi-

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nary sulphides of copper and iron was also subjected to thermal treatment to predict the actual mode of conversion.

Materials and methods

The chalcopyrite concentrate obtained from Indian Copper Complex, Ghatsíla, Bíhar, was used in the present studies. The chemical composition of the concentrate is given in Table 1. The other additives and chemicals used were AnalaR grade reagents. The particle size of the materials used in the study was in the range of 106 to 75 μm. The thermal experiments were carried out in static air with the help of simultaneous TG/DTA Sieko-320 derivatograph. About 30–50 mg of sample was packed in a platinum crucible. The heating rate of 10°C per minute was employed. The curves for TG, DTG and DTA with temperature were simultaneously recorded. The X-ray diffractrograms of specific powder sample were taken with Siemens D-500 X-ray difiractometer in a 2θ range of 15–90° at a scanning speed of 2^o min^{-1} with CoK_α target. Identifications of phases were based on ASTM X-ray powder data file.

Table 1 Chemical analysis of copper concentrate

Constituent	Mass/ %
Cu	25.2
Fe	28.28
S	31.6
Ni	0.425
Co	0.168
Mo	0.09
Al_2O_3	4.84
SiO_2	6.14
MgO	0.5
Moisture	2.71

Results and discussion

In order to know the oxidation characteristics with temperature of the various sulphide samples, the curves of thermal analyses, for TG, DTG and DTA with temperature were simultaneously recorded. In some cases DSC technique was also employed.

These studies were carried out in the following manner:

(i) Oxidation reaction of chalcopyrite mineral without/with additives.
(ii) Comparison of results with the synthetic copper and iron sulphides.

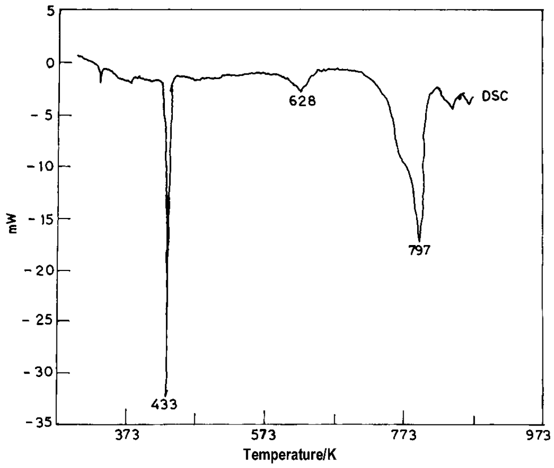

Fig. 1 DSC curve for the decomposition of chalcopyrite in inert atmosphere

Initially, the effect of temperature on chalcopyrite was studied with DSC in an inert atmosphere (Fig. l). The DSC curve obtained depicts the conspicuous absence of any of reactions that have occurred in air, except the first sharp endothermic peak at 433 K, which may be due to the initial phase transformation of chalcopyrite to bornite as discussed by Vaughan and Craig [4]. The small peak at 628 K represents the removal of sulphur from pyrite to produce iron sulphide (FeS). A well defined endothermic transition at 797 K has been observed and this is due to the following reaction [5].

$$2CuFeS_2=Cu_2S+2FeS+S^0 \quad (1)$$

The simultaneous loss in mass was also reported by Bayer *et al.* [6] for the thermal analysis of chalcopyrite in inert atmosphere. This was mainly due to the removal

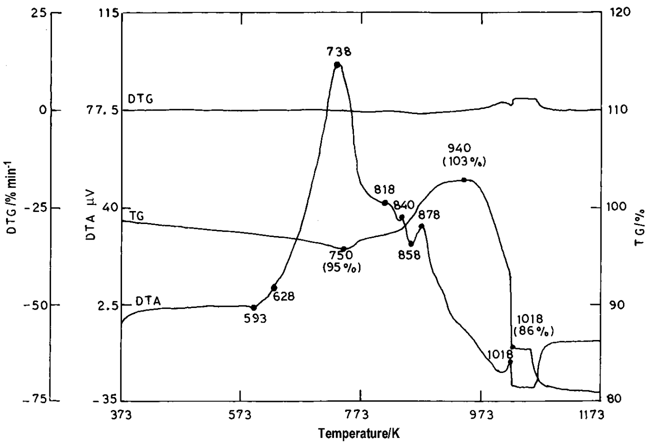

Fig. 2 TA curves for oxidation of chalcopyrite

Table 2 Phase identification by XRD analysis in roasting of cupric sulphide in presence of 10 wt% ferric oxide

Sample	Temp./ K	Time/ min	Gas	Roasted products	
				major phase	minor phase
1	573	60	oxygen	$CuSO_4$	CuO Cu_2O, CuS
2	773	60	oxygen	CuO	$CuSO_4$ Cu_2O
3	573	60	steam	Cu_2O $Cu_{1.96}S$	CuO CuS
4	773	60	steam	Cu_2O	$Cu_{1.96}S$ CuO CuS
5	773	15	oxygen+ steam	$CuSO_4$ Cu_2S CuS	Cu_2O CuO Fe_2O_3
6	773	30	oxygen+ steam	$CuSO_4$ CuS	Cu_2S Cu_2O $Cu_{1.96}S$ CuO Fe_2O_3
7	773	45	oxygen+ steam	Cu_2O CuO	$CuSO_4$ $Cu_{1.96}S$ Fe_2O_3
8	773	60	oxygen+ steam	CuO	$Cu_{1.96}S$ Fe_2O_3

Flow rate of inidividual gases: 0.016 L s^{-1}

of sulphur from the decomposition of chalcopyrite. In TA study with static air, oxygen is freely available at the surface as compared to the internal layers and at the core of each particle. Due to presence of areal oxygen the oxidation of copper and iron sulphide is possible.

A typical TA (DTA, TG, DTG) curve for chalcopyrite oxidation is shown in Fig. 2.

When chalcopyrite was heated in static air, there was no marked change upto 593 K. The exothermic peak started at 628 K (as the onset of ignition) and continued till 738 K (peak maxima in DTA). This was also marked by mass gain (8%) in the temperature range 750–940 K. These changes are mainly attributed to either direct formation of copper sulphate and iron sulphate/oxide or via oxidation of Cu_2S/CuS and FeS, obtained after decomposition of chalcopyrite. Both routes have the thermodynamic feasibility at 773 K.

$$2CuFeS_2+7.5O_2=2CuSO_4+Fe_2O_3+2SO_2 \qquad (2)$$

$$\Delta G_{773} = -1815 \text{ kJ mol}^{-1}$$

$$2CuFeS_2+O_2=Cu_2S+2FeS+SO_2 \tag{3}$$

$$\Delta G_{773}= -235.2\ \mathrm{kJ\ mol^{-1}}$$

$$CuS+2O_2=CuSO_4 \tag{4}$$

$$\Delta G_{773}= -433.6\ \mathrm{kJ\ mol^{-1}}$$

$$FeS+2O_2=FeSO_4 \tag{5}$$

$$\Delta G_{773}= -555.8\ \mathrm{kJ\ mol^{-1}}$$

The stable copper sulphate phase identified by XRD (Table 2) in the roasting of chalcopyrite with oxygen at 773 K further substantiates such a transformation. Also, iron sulphate initially formed decomposes to ferric oxide as inferred from the XRD phase identification. At above 940 K, a drastic loss in mass may be attributed to the decomposition of copper sulphate until 1018 K, where it forms copper ferrite ($CuO\cdot Fe_2O_3$) due to solid state reaction.

The oxidation/sulphation of chalcopyrite with the formation of $CuSO_4$ and Fe_2O_3 at 773 K was also thermodynamically studied by Ingraham [7]. However, in a further study [8, 9] researchers concluded from investigation of the copper sulphide oxidation that primary product is the copper oxide and not the sulphate. The formation of copper sulphate as the reaction product is mainly due to in-situ reactions of CuO with SO_2–O_2 and SO_3, as shown in reactions 4 and 5. Thus, the formation of copper sulphate from copper sulphide (Cu_2S/CuS) generated from chalcopyrite is the route of transformation rather than direct conversion of chalcopyrite to copper sulphate [10]. Therefore, an oxidising catalyst viz Fe_2O_3 was added to investigate the roasting reactions by TA.

It is quite likely that SO_2 released during the oxidation of $CuFeS_2$, Cu_2S, CuS and FeS is converted to SO_3 in the presence of Fe_2O_3 [11]. The SO_3 then interacts with

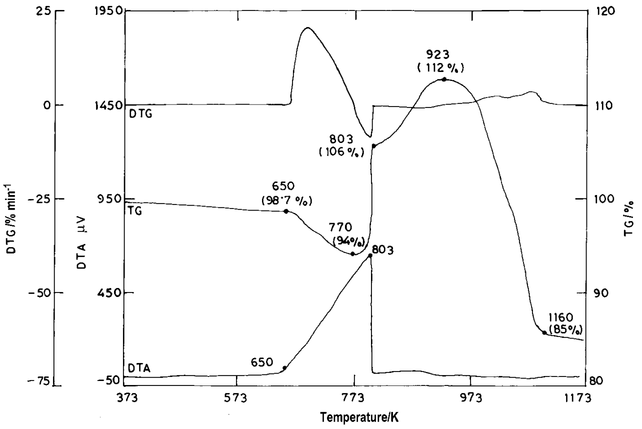

Fig. 3 TA curves for oxidation of chalcopyrite+ferric oxide

the oxides of copper to form additional amount of sulphate. This catalytic activity can clearly be seen from Fig. 3 for TA curves of chalcopyrite in presence of Fe_2O_3 (10%). The enhanced level of sulphation, resulting in higher mass gain (14%) in the temperature range 769–923 K was observed in the TG curve. The onset of ignition in this case (DTA) was 650 K compared to 628 K found for chalcopyrite. The peak intensity (enthalpy change) was found very high with exothermic maxima (DTA) at 803 K. This is due to initial burning of sulphur to SO_2 which immediately oxidises to SO_3 in the presence of ferric oxide and reacts with intermediate product, CuO to form higher amount of copper sulphate.

The XRD analysis of calcine, produced in roasting of chalcopyrite in presence of 10% Fe_2O_3 with oxygen also shows the $CuSO_4$ as a major phase at 773 K (Table 3). Formation of CuO in the initial period was observed in the XRD pattern. The oxy–sulphate ($CuO{\cdot}CuSO_4$), which was present as the major phase during oxidation of chalcopyrite, subsequently appeared in the minor amount when roasted in presence of ferric oxide. Therefore, the following sequenee can be assumed to take place in the sulphation roasting of chalcopyrite with ferric oxide.

$$CuFeS_2 \rightarrow Cu_2S \rightarrow Cu_2O \rightarrow CuO \rightarrow CuO{\cdot}CuSO_4 \rightarrow CuSO_4 \tag{6}$$

The similar sequence of reaction was proposed by Wadsworth *et al.* [9] and Hocking *et al.* [12]. Addition of ferric oxide during the sulphation roasting of chal-

Table 3 Phase identification by XRD analysis in roasting of ferrous sulphide

Sample	Temp./ K	Time/ min	Gas	Roasted products	
				major phase	minor phase
1	573	60	oxygen	Fe_2O_3	Fe_3O_4 FeS, $Fe_{(1-x)}S$
2	773	60	oxygen	Fe_2O_3	Fe_3O_4 $Fe_{(1-x)}S$
3	573	60	steam	Fe_3O_4 $Fe_{(1-x)}S$	FeS
4	773	60	steam	Fe_3O_4 $Fe_{(1-x)}S$	–
5	773	15	oxygen+ steam	Fe_2O_3 Fe_3O_4	FeS $Fe_{(1-x)}S$
6	773	30	oxygen+ steam	Fe_2O_3 Fe_3O_4 $Fe_{(1-x)}S$	FeS
7	773	45	oxygen+ steam	Fe_2O_3	Fe_3O_4 $Fe_{(1-x)}S$
8	773	60	oxygen+ steam	Fe_2O_3	Fe_3O_4 $Fe_{(1-x)}S$

Flow rate of individual gases: 0.016 L s^{-1}

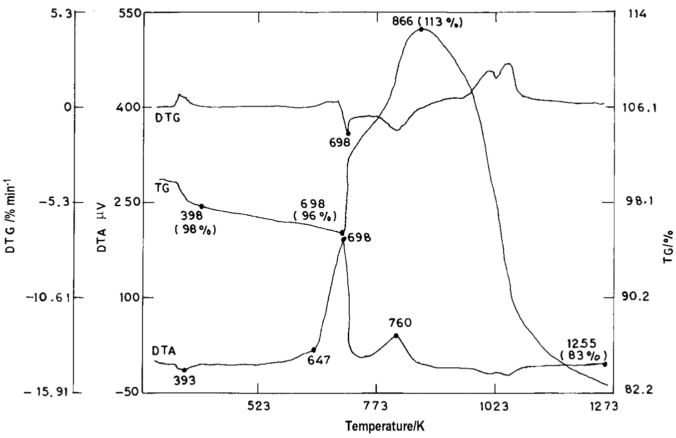

Fig. 4 TA curves for the oxidation of chalcopyrite+sodium sulphate

copyrite, thus, not only catalyses the reaction in the initial period but also stabilises the copper sulphate formed. Beyond 923 K, decomposition of copper sulphate was observed as shown in TG.

Addition of sodium sulphate as promoter causes an efficient conversion of the sulphides to soluble sulphates [13]. Hence, in the thermal study, sodium sulphate (10%) was added [14, 15] with chalcopyrite and subjected to heating with stagnant air. Figure 4 infers the initial removal of moisture at around 393 K in DTA curve as an endothermic peak. With onset of ignition at 647 K, the vigorous oxidation takes place at about 698 K resulting in a major exothermic peak. This was accompanied by a corresponding increase of mass in TG. The flash due to vigorous oxidation is evident from DTG minima at 698 K. This is mainly due to the formation of copper sulphate by oxidation of copper sulphide. The TG plot shows further gain in mass (17%) indicating the completion of sulphate formation. This additional increase in mass representing copper sulphate formation in presence of sodium sulphate compared to that observed for chalcopyrite (8%) without any Addition, is mainly due to promoting effect of sodium sulphate as per reaction.

$$\mathrm{CuS+Na_2SO_4=CuSO_4+Na_2S} \tag{7}$$

An additional exothermic peak (DTA) was found in plot 4 at 760 K. This peak may be attributed to the oxidation of Na_2S, which regenerates sodium sulphate in situ and confirms the occurrence of cyclic reaction [14].

$$\mathrm{Na_2S+2O_2= Na_2SO_4} \tag{8}$$

The presence of higher amount of copper sulphate and sodium sulphate was confirmed by XRD analysis of roasted product obtained from chalcopyrite with oxygen flow at 773 K. With the increase in temperature, the decomposition of copper sulphate was observed in this case also.

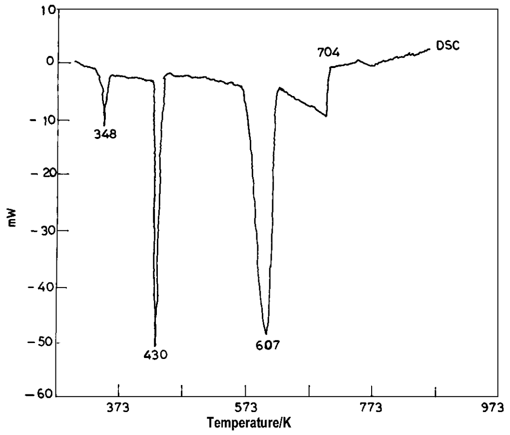

Fig. 5 DSC curve for decomposition of ferrous sulphate in the inert atmosphere

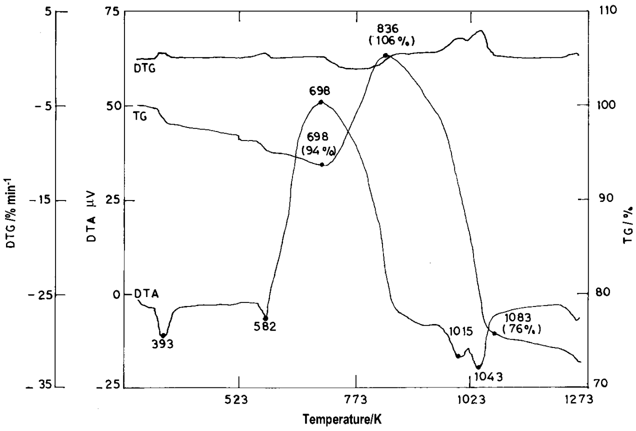

Fig. 6 TA curve for oxidation of chalcopyrite+ferrous sulphate

The sulphatising roasting of metal sulphide and oxide in the presence of iron sulphate is well known in the extraction of metals [15], under carefully controlled conditions. Figure 5 shows the DSC curve for the decomposition of $FeSO_4$ in an inert atmosphere. The decomposition of $FeSO_4$ starts at 430 K and found maximum at 607 K as shown in the DSC curve with endothermic peak. Therefore, the actual role of ferrous sulphate for sulphation of chalcopyrite is possible only after 610 K by its decomposition, thereby producing certain amount of SO_2 and SO_3, which enhances the rate and extent of sulphation process.

To ascertain the role of ferrous sulphate, its mixture (20%) with chalcopyrite was subjected to TG/DTA studies. Apart from removal of moisture at 393 K, another endothermic drift (Fig. 6) was observed at around 582 K, which signifies the decomposition of ferrous sulphate. After this, an exothermic peak in DTA followed the sul-

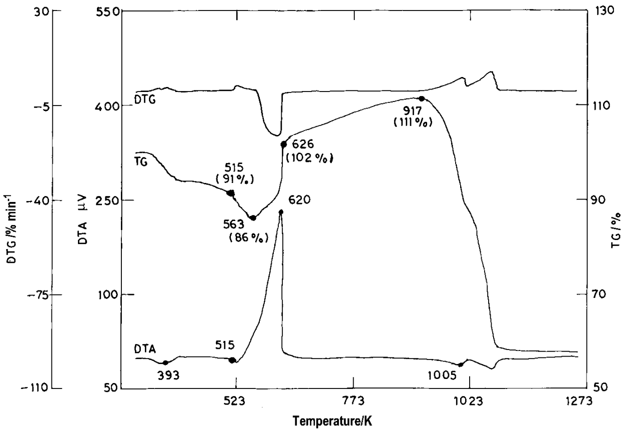

Fig. 7 TA curve for oxidation of cupric sulphide

phation reaction with maxima at 698 K. The simultaneous increase in mass at this temperature also started which confirms the formation of copper sulphate as seen in TG plot. The increase in mass (12%) continues up to the temperature 836 K. Improved sulphation in presence of $FeSO_4$ is apparently related to increased level of in situ SO_2 and SO_3 concentration as reported earlier [16] as per reaction.

$$SO_2+1/2O_2=SO_3 \tag{9}$$

Above 840 K, a drastic mass loss is observed, which is apparently due to the decomposition of copper sulphate. The decomposition of $CuSO_4$ to $CuO{\cdot}CuSO_4$ and then CuO may be represented by the drift at 1015 and 1043 K respectively as reported earlier by Opera [17], which is accompanied by mass loss as well during the oxidation of pure cupric sulphide.

$$2CuSO_4=CuO{\cdot}CuSO_4+SO_2+0.5O_2 \tag{10}$$

$$CuO{\cdot}CuSO_4=2CuO+SO_2+0.5O_2 \tag{11}$$

In order to know the actual path of roasting reactions of chalcopyrite, it was considered worthwhile to study the roasting of individual copper and iron sulphides and their mixture. Therefore, a pure synthetic cupric sulphide (CuS) was subjected to thermal studies and the TA curve is shown in Fig. 7. The first endothermic peak at around 393 K is due to loss of moisture. At 515 K, an exothermic peak started (as onset of ignition), which continued up to 620 K (peak maxima in DTA). A DTG peak at this temperature may be assigned to part removal of sulphur that was followed by TG also. The reaction up to 563 K may be represented as,

$$2CuS+O_2=Cu_2S+SO_2 \tag{12}$$

The major mass gain observed in TG up to 626 K which continued till 917 K, is mainly due to the formation of $CuSO_4$ via the following reactions which may occur simultaneously.

$$Cu_2S+1.5O_2=Cu_2O+SO_2 \tag{13}$$

$$Cu_2O+0.5O_2=2CuO \tag{14}$$

$$CuO+SO_2+0.5O_2=CuSO_4 \tag{15}$$

$$CuS+2O_2=CuSO_4 \tag{16}$$

This type of mass gain was also observed by Razouk *et al.* [18] and Khalafalla *et al.* [19]. At higher temperature, the loss in mass represented decomposition of copper sulphate as reported by several workers including Kellogg [20]. The DTA plot, shows an endothermic peak at 1005 K corresponding to the formation of CuO from copper sulphate.

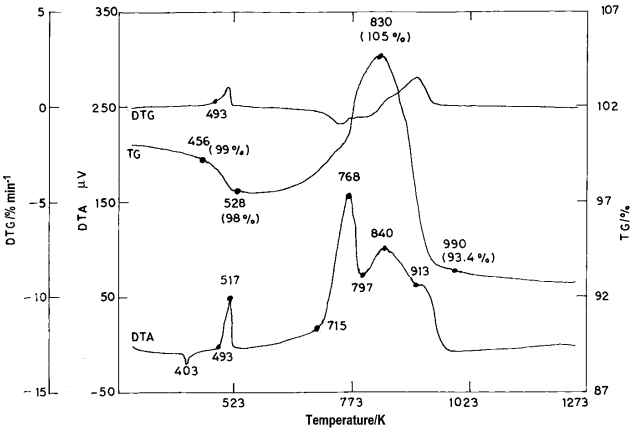

Fig. 8 TA curve for oxidation of ferrous sulphide

Thermal analysis of another component ferrous sulphide (FeS) was also carried out under static air. The curves are shown in Fig. 8. In the initial period up to 528 K the mass loss shown in TG and DTG is due to surface reaction wíth loss of sulphur followed by oxidation of iron sulphide. The first exothermicity started at 493 K, which is an onset of oxidation of FeS, with the change in mass (DTG) and continued up to 517 K. This was followed by a vigorous increase in exothermic heat with a peak at 768 K. The rate of mass gain (TG) observed was mainly due to ignition and formation of pyrrhotite and magnetite/hematite as well as ferrous sulphate.

$$FeS+2/3xO_2=Fe_{(1-x)}S+x/3Fe_3O_4 \tag{17}$$

$$FeS+2O_2=FeSO_4 \tag{18}$$

The presence of pyrrhotite and magnetite was confirmed by XRD analysis of calcine obtained in the roasting of FeS with oxygen at 573 K (Table 4). At above 830 K a sharp decrease in mass was observed in the TG. This may be due the decomposi-

Table 4 Phase identification by XRD analysis during roasting of CuS–FeS mixture in presence of 10 wt% ferric oxide

Sample	Time/ min	Roasted products	
		major phase	minor phase
1	15	Fe_2O_3 $CuSO_4$	Cu_2S Cu_2O Fe_3O_4 $Fe_{(1-x)}S$
2	30	Fe_2O_3 $CuSO_4$	CuO $Cu_{1.96}S$ Fe_3O_4
3	45	$CuSO_4$ Fe_2O_3	CuO $Cu_{1.96}S$
4	60	$CuSO_4$ Fe_2O_3	CuO

Temperature: 773 K, Flow rate of oxygen and steam: 0.016 L s^{-1} each

tion of ferrous sulphate. The Fe_3O_4 initially formed, oxidised to Fe_2O_3, which is apparent with the endothermic peak at 797 and 913 K, as reported by Coombs *et al.* [21].

A synthetic mixture of CuS and FeS in I:1 ratio was also made and subjected to thermal studies under the similar conditions. The results of thermal treatment are shown in Fig. 9. The exothermic peak (DTA) of the mixture corresponding to the formation of sulphate starts at 555 K as onset of ignition, compared to 628 K in case of chalcopyrite concentrate.

The change in enthalpy with the pure system is also more than the concentrate. The lower temperature of sulphation and high enthalpy change of synthetic system is mainly due to the fact that the individual sulphides (CuS–FeS) are freely available

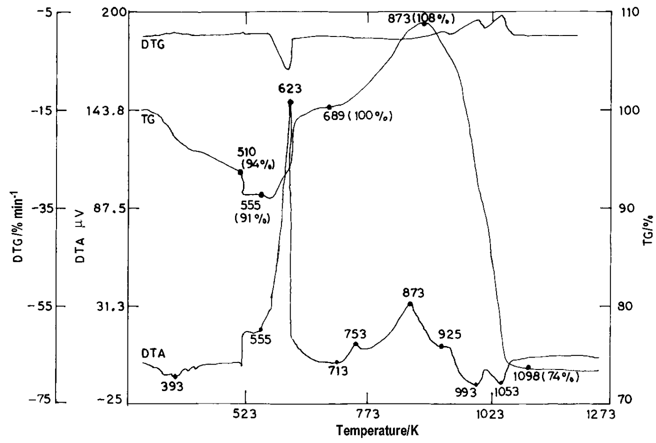

Fig. 9 TA curve for oxidation of cupric sulphide+ferrous sulphide

and easily oxidised than that of chalcopyrite ($CuFeS_2$), which has these sulphides in combined form [22]. In the plot it can be observed that the peak maxima of DTA is at 623 K, with a drip in DTG at this temperature. At around 555 K the mass loss may be assigned to part removal of sulphur that was followed by major mass gain (18%) observed in TG up to 873 K. The mass gain is mainly due to the formation of copper sulphate via the reactions (13–16) mentioned earlier.

The other two exothermic peaks in DTA curve at 753 and 873 K may be due to in situ oxidation reaction of internal core particles, which causes the additional formation of copper sulphate, in presence of FeS by producing high concentration profile of SO_2 and SO_3. The presence of $CuSO_4$ and Fe_2O_3 as major phases was confirmed by XRD analysis (Table 4) when mixture was roasted with oxygen. At higher temperature, the TG plot shows the loss in mass, which must be due to the decomposition of $CuSO_4$ to CuO as observed in the case of chalcopyrite oxidation. The endotherm at 993 and 1053 K further confirms the possibility of ferrite formation.

Conclusions

Following conclusions are drawn from the thermal studies.

(i) To understand the conversion of chalcopyrite to copper sulphate, the thermal studies have been found to be a useful tool. The TA pattern shows the mass gain corresponding to copper sulphate formation from the chalcopyrite concentrate in the temperature range 628–738 K.

(ii) The synthetic mixture (l:l) of CuS–FeS shows the transformation for copper sulphate in the temperature range 555–873 K. The temperature range of 698–923 K was suitable for copper sulphate formation from chalcopyrite in presence of additives like Fe_2O_3, Na_2SO_4 and $FeSO_4$.

(iii) In the oxidation/sulphation process of chalcopyrite with oxygen, the formation of Fe_2O_3 through the intermediate Fe_3O_4 phase was not detected, unlike the presence of Fe_3O_4 clearly observed in TA of FeS.

(iv) It is thus quite likely that chalcopyrite first converts to Cu_2S and FeS. Transformation of Cu_2S to Cu_2O is followed by formation of CuO. Copper sulphate is finally converted from oxy–sulphate ($CuO \cdot CuSO_4$). The oxidation of FeS to Fe_2O_3 with intermediate phase (Fe_3O_4) leads to solid state reaction forming copper ferrite ($CuO \cdot Fe_2O_3$) at higher temperature (1000 K).

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