Sulphation of Chalcopyrite with Steam and Oxygen in the Presence of Some Additives

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It has been observed that the sulphides undergo weathering process to produce the metal sulphates at a very slow rate. Therefore, higher conversion to sulphates may be achieved by creating aggressive conditions at higher temperature similar to that of weathering process by using a mixture of steam and oxygen. The results obtained by this method shows a conversion of 82.32% copper sulphate from a chalcopyrite concentrate at 773 K in presence of 10% Fe₂O₃. The role of different additives like ferric oxide, ferrous sulphate and sodium sulphate on sulphation of chalcopyrite with steam and oxygen was investigated. The copper sulphate formation without any additive was found to be 71.9% whereas the values were 84.4 and 86.5% with 10% Na₂SO₄ and 20% FeSO₄ respectively at 773 K. The kinetics of the sulphation with additives has also been studied in the fixed bed in the temperature range 673–773 K in absence of external mass transfer effect due to particle size, flow rate, etc. The reaction was found to be topochemical in nature. The activation energy values using the Arrhenius equation plots were obtained as 29.2 kJ/mol with 10% Fe₂O₃, 23.57 kJ/mol with 10% Na₂SO₄ and 21.03 kJ/mol with 20% FeSO₄ in the above temperature range. The sulphated products were characterized by XRD and SEM studies.

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I. Introduction

The sulphation of chalcopyrite with oxygen is the traditional process exploited commercially to produce water soluble copper sulphate⁽¹⁾. It was shown by Neou-syngouna and Scordilis⁽²⁾ that the addition of ferric oxide during sulphation increased the SO₃ concentration thereby resulting in higher degree of sulphate formation. Das and Venkatachalam⁽³⁾ found that the powdered Fe₂O₃ eliminated tackiness and improved sulphation process kinetics. The addition of iron powder was reported⁽⁴⁾ to promote the sulphation of covellite with minimal retardation from the CuO.CuSO₄ film. The promoting effect of iron was mainly attributed to its greater affinity for oxygen and the iron surface so generated could act as a mediator between the copper sulphide lattice and molecular oxygen during sulphation. Addition of other additives like Na₂SO₄ and FeSO₄ also improved the sulphation process. Shamsuddin *et al.*⁽⁵⁾ studied the effect of Fe₂O₃ and Na₂SO₄ on sulphation roasting of an off-grade copper concentrate. The addition of sodium sulphate was found to be more effective than Fe₂O₃. Smithon and Hanway⁽⁶⁾ reported the catalytic effect of Na₂SO₄ during sulphation roasting of a complex sulphide ore as per the following cyclic reactions:

Ferric sulphate was also found to be better sulphatising agent⁽⁷⁾ and the reaction at elevated temperatures for

cupric oxide followed the Ginstling Brounshtein model. Razouk *et al.*⁽⁸⁾ observed the formation of covellite initially below 673 K which was then oxidized to oxide and sulphate. The formation of CuSO₄ was primarily due to the interaction of cupric oxide (CuO) and ferric sulphate. Investigation on the salt roasting⁽⁹⁾ of an off-grade copper concentrate employed 20 mass% NaCl to produce copper chloride. Jena *et al.*⁽¹⁰⁾ used the nucleation and growth model to explain the roasting reactions for the recovery of copper in presence of NH₄Cl. Wadsworth *et al.*⁽¹¹⁾ noticed the formation of copper sulphate with oxygen as oxidant which obeyed the parabolic rate law and calculated an activation energy of 27.21 kJ/mol. The oxidation kinetics of pelletised agglomerates studied by Agarwal and Gupta⁽¹²⁾ between 773–973 K, was explained with the help of shrinking core model, activation energy being 50 kJ/mol. Other than oxidation of chalcopyrite with oxygen in presence or absence of additive, Roberts and Williams⁽¹³⁾ studied the kinetics of roasting of chalcopyrite with steam in temperature range 673–1053 K for the formation of cupric oxide and elemental sulphur with corresponding activation energy of 42.27 kJ/mol.

It has been seen that the weathering process occurred on the surface of sulphide ore resulting in the formation of copper sulphate⁽¹⁴⁾. Therefore, the phenomenon of weathering can be created using steam and oxygen and at elevated temperature the condition can be still more aggressive for conversion. In our recent investigation⁽¹⁵⁾ on sulphation of chalcopyrite with steam and oxygen an optimum recovery of 82.32% as copper sulphate could be achieved in presence of 10% ferric oxide at 773 K. The addition of Fe₂O₃ enhanced the degree of sulphate forma-

tion. In continuation of this an attempt has been made to examine the effect of various additives viz. Fe_2O_3 , Na_2SO_4 and FeSO_4 on the sulphation of chalcopyrite, the results are described in this communication.

II. Experimental

The experimental set up used in this study was as discussed elsewhere⁽¹⁵⁾. The chalcopyrite concentrate was obtained from Indian Copper Complex, Ghatsila, Bihar. The average analysis of the sample is given in Table 1. The XRD study of concentrate showed the chalcopyrite to be the major phase along with Cu_2S and FeS_2 as the minor phases. The average particle size of the concentrate used in the study was in the range $-150+75\ \mu\text{m}$.

In a tubular furnace the experiments were carried out taking 10 g concentrate. The sample was mixed with different additives and mixed mass supported by glass wool was placed in the centre of pyrex tube reactor of 27 mm ID at about 473 K. Effective porosity in the sample was made by giving glass beads which also acted as a pre-heater. The flow of nitrogen was then commenced and temperature of furnace was raised. At a predetermined temperature the flow of nitrogen was stopped and the flow of steam-oxygen mixture was started for a specified period. It is known that the sulphation process is exothermic in nature. Therefore to offset the exothermic heat, initially furnace temperature was set at lower value and thereafter heating rate was increased to attain the desired bed temperature as discussed elsewhere⁽¹⁵⁾. In the text, the bed temperature has been reported as the temperature of reaction. After the completion of the reaction the pyrex reactor was pulled out from the furnace and cooled. The sulphated product was then leached in hot water (353 K) at pulp density of 10% for 1 h. The leach solution containing copper sulphate was analyzed iodometrically with standard sodium thiosulphate solution⁽¹⁶⁾ to know the degree of sulphation. In this studies all the chemicals used were analytical grade reagents. The off-gas obtained during the experiments was absorbed in NaOH solution containing 10% isopropyl alcohol. The absorbed gas was then analyzed by volumetric method⁽¹⁷⁾. When an alkali solution containing Na_2SO_3 and Na_2SO_4 was titrated against a dilute acid, the first end point obtained using phenolphthalein indicator, corresponds to the full neutralisation of the unreacted sodium hydroxide. The react-

ed sodium hydroxide gave the amount of absorbed SO_2 and SO_3 . Sodium sulphite in alkaline solution was analysed by oxidizing the same solution with an acidified standard I_2 solution and back titrating the residual iodine with the help of standard sodium thiosulphate.

The characterization of concentrate and sulphated product was done by SEM and XRD studies. The sample obtained was sprinkled on the graphite tape pasted on a brass stub for SEM study.

III. Results and Discussion

Having optimised the conditions for roasting of chalcopyrite in presence of ferric oxide as a catalyst⁽¹⁵⁾, it was considered essential to study the kinetics of sulphation and the influence of other additives like Na_2SO_4 and FeSO_4 on the roasting process. The effects of flow rate of gases and particle size of the concentrate/additives on roasting were discussed in earlier communication⁽¹⁸⁾. The flow of $1.6 \times 10^{-5}\ \text{m}^3/\text{s}$ for steam and oxygen each on $-150+75\ \mu\text{m}$ particle size of concentrate and additive produced a condition where external mass transfer effect was negligible. Therefore, the flow rate of oxidizing gases was maintained as mentioned above for the kinetics studies.

1. Effect of temperature on sulphation of chalcopyrite with/without additive

The effect of temperature on sulphation was studied in the range 673–773 K at the fixed flow rate ($1.6 \times 10^{-5}\ \text{m}^3/\text{s}$) of steam and oxygen each for a time period of one hour, as depicted in Fig. 1. It is apparent that fraction sulphated (α) without any addition is lower as compared to that obtained in presence of additives. The maximum sulphation was observed at 773 K with 20% FeSO_4 . At higher temperature beyond 800 K the sulphation of chalcopyrite decreased due to the decomposition of the product initially formed⁽¹⁹⁾.

Therefore it was considered worthwhile to carry out

Table 1 Chemical analysis of copper concentrate. (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

Fig. 1 Effect of temperature on sulphation of chalcopyrite with/without additive.

Fig. 2 Effect of additive on sulphation of chalcopyrite at 773 K.

experiments at around 773 K. The effect of various additives like sodium sulphate, ferric oxide and ferrous sulphate on copper sulphate formation is shown in Fig. 2. The addition of 10 (mass%) ferric oxide and sodium sulphate resulted in improvement of copper sulphate formation whereas 20% ferrous sulphate was required for optimum conversion to sulphate. The small improvement in copper sulphate formation may be accounted for their catalytic effects as discussed below. The composition of gases as shown in Table 2 indicates that without any additive the percentage conversion to SO_3 remained almost unaltered. At 773 K, the copper sulphate formation was maximum (71.9%) with the SO_2 and SO_3 levels of 3.05% and 1.23% respectively.

2. Effect of ferric oxide on sulphation of chalcopyrite

The ferric oxide has been reported to catalyze the sulphation reaction⁽⁵⁾⁽²⁰⁾. The effect of addition of 10 mass% ferric oxide of $-150+75\ \mu\text{m}$ size was studied in the temperature range 673–773 K with steam and oxygen flow rate of $1.6 \times 10^{-5}\ \text{m}^3/\text{s}$ each. Figure 3 shows the plot of fraction sulphated vs period which indicates that sulphation increased with the rising bed temperature and time of reaction. The maximum conversion to copper sulphate observed was 82.32% at 773 K in 3.6 ks. Further increase in time has not shown any major change in sulphation process.

It has been reported in our previous communication⁽¹⁵⁾ that the conversion is favoured thermodynamically at around 773 K. The sulphate formation may be assumed to take place through *in-situ* chemical reaction of gas-solid species as given below.

The product gases also react to form sulphate:

To ascertain the inference drawn on the reaction proceed-

Fig. 3 Kinetics of sulphation with the addition of ferric oxide.

Fig. 4 Variation of sulphation rate with time in presence of ferric oxide.

ing in the process, the topochemical model of kinetic expression⁽²¹⁾ may be considered as given below.

$$1 - (1 - \alpha)^{1/3} = kt \quad (6)$$

where k is the specific rate constant and t , the time of reaction. Though other models were also tried but the kinetics data was found to give the best fit following the topochemical model which is evident from Fig. 4. The straight lines obtained by plotting $1 - (1 - \alpha)^{1/3}$ vs period indicates that the sulphation occurred on the sulphate chalcopyrite interface in chemically control mode. The corresponding k values were then calculated at different temperatures with the slope of straight lines to get the Arrhenius plot. The composition of the off-gas given in Table 2 indicates that the concentration of SO_2 and SO_3 increased with increase in temperature in presence of ferric oxide. At 773 K, which is the optimum temperature for sulphate formation (82.32%), the conversion to SO_3 was found to be maximum (2.49%) with corresponding SO_2 content of 3.66% in 3.6 ks. Higher amount of SO_3 may help in generation of sulphuric acid which in turn enhanced the sulphate formation.

Table 2 Gas composition during the sulphation of chalcopyrite with steam and oxygen.

Amount of concentrate: 10 g
 Oxygen flow rate: $1.6 \times 10^{-5} \text{ m}^3/\text{s}$
 Steam flow rate: $1.6 \times 10^{-5} \text{ m}^3/\text{s}$
 Time of reaction: 3.6 ks.

Sl. No.	Condition	Amount % Off-gas and sulphate	Temperature (K)			
			693	733	773	813
1.	Without addition	SO ₂	1.98	2.35	3.05	3.52
		SO ₃	1.08	1.20	1.23	1.05
		Soluble sulphate	40.22	61.52	71.90	69.00
2.	With 10% Fe ₂ O ₃	SO ₂	2.85	3.05	3.66	3.83
		SO ₃	1.04	1.85	2.49	2.02
		Soluble sulphate	50.50	71.70	82.32	75.40
3.	With 10% Na ₂ SO ₄	SO ₂	4.96	5.15	6.21	6.32
		SO ₃	1.85	1.92	2.02	1.99
		Soluble sulphate	55.73	75.60	84.40	82.50
4.	With 20% FeSO ₄	SO ₂	4.75	5.03	5.55	5.37
		SO ₃	1.97	2.67	3.29	3.03
		Soluble sulphate	56.33	78.60	86.50	83.63

3. Effect of sodium sulphate on sulphation of chalcopyrite

Experiments were also carried out with the addition of 10 (mass%) of sodium sulphate for sulphation studies in the temperature range 673–773 K for different duration. The fraction sulphated (α) vs period plot shown in Fig. 5, indicates the increase in sulphation with the increase in temperature and time. Maximum sulphate formation was observed at 773 K in 3.6 ks of reaction and formation of sulphate remained unchanged with further increase in time. The value of fraction sulphated (α) thus obtained was found to be best fitting to eq. (6). A $1 - (1 - \alpha)^{1/3}$ vs period plot was obtained as shown in Fig. 6. With the slope of the plot different rate constant values (k) were determined. The kinetics data with respect to other models like diffusion, nucleation and growth and mixed control did not fit well and thus the reaction was ob-

Fig. 5 Kinetics of sulphation with the addition of sodium sulphate.

Fig. 6 Variation of sulphation rate with time in presence of sodium sulphate.

served to follow the topochemical model as in the case of addition of ferric oxide. The addition of sodium sulphate was found to enhance the conversion of chalcopyrite to copper sulphate due to cyclic catalytic effect⁽⁶⁾ as shown by reactions (1) and (2). The off-gas analysis given in Table 2 showed that sulphur trioxide content was 2.02% at 773 K but the copper sulphate formation was found to be 84.4%. Though sulphur trioxide level was not much different with rise in temperature, the *in-situ* cyclic reaction with Na₂SO₄ as discussed earlier and higher amount⁽²²⁾⁽²³⁾ of SO₂ were responsible for increasing sulphate formation.

4. Effect of ferrous sulphate on sulphation

The sulphates of iron are reported to enhance the sulphation rate⁽⁷⁾. It was found that ferrous sulphate (20 mass%) produced the improved sulphatising conditions at 773 K with steam and oxygen with optimum recovery of 86.5% as copper sulphate. Figure 7 shows the plot of fraction sulphated (α) with time at different temperatures. It can be seen from the figure that the trend of sulphate formation was similar to that observed with additions of sodium sulphate and ferric oxide. With increasing temperature of reaction, the decomposition of ferrous sulphate also contributed to the sulphation process. The rate of increase in sulphation may be accounted for the increase in *in-situ* SO₃ content as given in Table 2, which enhanced the sulphatising environment by producing H₂SO₄⁽¹⁵⁾ as per reactions.

With the help of values of fraction sulphated (α) the plot of $1 - (1 - \alpha)^{1/3}$ vs period was obtained (Fig. 8) for different temperatures. The best fit of kinetics data indicated that the reaction obeyed the chemically control

Fig. 7 Kinetics of sulphation with the addition of ferrous sulphate.

Fig. 8 Variation of sulphation rate with time in presence of ferrous sulphate.

mode in the temperature range studied.

The different k values obtained in the presence of three different additives were plotted against $1/T$ and shown in Fig. 9. From the slope of the straight lines the activation energy values were calculated. The activation energy was 29.2 kJ/mol when 10% ferric oxide was used, whereas the activation energy dropped to 23.57 kJ/mol in presence of 10% sodium sulphate. The addition of 20% ferrous sulphate resulted in further decrease in activation energy to 21.03 kJ/mol. Thus, the addition of different additives catalysed the sulphation process following the chemically control model with different activation energies.

The XRD phase identification of the chalcopryrite concentrate and sulphated products obtained indicate the formation of copper sulphate and ferric oxide (Table 3). In concentrate CuFeS_2 was found as the major phase along with Cu_2S , FeS_2 and SiO_2 as the minor phases. Sulpha-

Fig. 9 Arrhenius plot for sulphation of chalcopryrite in presence of additives.

Table 3 XRD identification of phases in roasted product at 773 K with steam and oxygen in 3.6 ks.

Sl. No.	Catalyst	Products major phase	Minor phase
1.	Ore	CuFeS_2	Cu_2S , FeS_2 SiO_2
2.	Fe_2O_3	CuSO_4 Fe_2O_3	$\text{Cu}_{1.96}\text{S}$ SiO_2
3.	Na_2SO_4	CuSO_4 Fe_2O_3	Na_2SO_4 $\text{Cu}_{1.96}\text{S}$ SiO_2
4.	FeSO_4	CuSO_4 Fe_2O_3	$\text{Cu}_{1.96}\text{S}$ SiO_2

tion in presence of ferric oxide, sodium sulphate and ferrous sulphate showed that CuSO_4 and Fe_2O_3 were present as major phases and chalcocite ($\text{Cu}_{1.96}\text{S}$) remained as a minor phase in the product. The presence of minor amount of sodium sulphate in the product confirmed the cyclic conversion reactions (1) and (2). Though the formation of magnetite in 3.6 ks of reaction was not observed through the XRD studies, its presence in small amount may not be ruled out in the initial phase of the roasting due to limitation of the technique⁽²⁴⁾.

The SEM micrograph of concentrate showed the sulphur rich phase in lower portion of right side in Fig. 10(a). The gangue material can be seen distributed on the surface of mineral as dark patches. The photograph of the sulphated product obtained in 3.6 ks of reaction in presence of different additives has been shown in Figs. 10(b) to (d). For the roasting in presence of Fe_2O_3 (10%) the spongy nature of sulphated product can be seen in Fig. 10(b). The iron oxide (brighter) is lying on the upper and lower left side. SEM micrograph of the product with Na_2SO_4 (10%) indicates the presence of copper rich sulphate phase as spongy clusters along with iron rich phase in the lower right side. The brighter portion at the top is

Fig. 10 SEM photograph of (a) Chalcopyrite concentrate, (b) with 10% ferric oxide (c) with 10% sodium sulphate (d) with 20% ferrous sulphate at 773 K in 3.6 ks. CH: Chalcopyrite, CS: Copper sulphate, FO: Ferric oxide, G: Gangue.

mainly due to the gangue. Figure 10(d) shows the SEM of sulphated product obtained in presence of 20 mass% FeSO_4 . The iron rich phase (bright) can be seen in the lower side and copper sulphate rich phase in the middle and upper sides as the clusters.

IV. Conclusions

The following conclusions are drawn from the results obtained in the present study.

(1) During the sulphation roasting of chalcopyrite with steam and oxygen mixture, maximum conversion of 71.9% as copper sulphate was obtained at 773 K without any additive. The kinetics of sulphation was found to be topochemical in nature in the temperature range 673–773 K under the condition of negligible external mass transfer effect.

(2) The sulphation in presence of additive also was observed to follow the topochemical model with the reaction taking place at the product and reactant phase boundary. The addition of ferric oxide enhanced the rate of sulphation by producing better *in-situ* sulphatising environment. The activation energy in this case was

29.2 kJ/mol.

(3) The sodium sulphate addition was found to catalyze the reaction by *in-situ* cyclic reaction which produced the additive. The observed activation energy value was 23.57 kJ/mol.

(4) The addition of ferrous sulphate resulted in further improvement in the rate of sulphation due to improved environment and the activation energy was found to be 21.03 kJ/mol. The concentrate and the roasted products were characterised by XRD and SEM to identify the phases which also confirmed the extent of sulphate formation.

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