

# Kinetics of salt roasting of chalcopyrite using KCl

M. Chakravorty<sup>a</sup>, S. Srikanth<sup>b,\*</sup>

<sup>a</sup>Non-Ferrous Process Division, National Metallurgical Laboratory, Jamshedpur, 831007 Bihar, India

<sup>b</sup>NML Centre, CSIR Madras Complex, Chennai, 600113 TN, India

Received 21 October 1999; accepted 17 February 2000

## Abstract

The process of salt roasting appears to be very promising because it lowers the reaction temperature and leads to water soluble chloride salt. This paper presents the kinetics of salt roasting of chalcopyrite using KCl as the chlorinating agent. Isothermal thermogravimetric studies were carried out in the temperature range of 523–773 K under oxygen, static air and argon atmospheres. It is observed that the weight gain is more in the presence of oxygen than in static air. Weight loss is observed when salt roasting is carried out under an inert atmosphere. It is deduced that the reaction is chemically controlled at temperatures below 600 K both under static air and oxygen atmosphere. At higher temperatures, the process is not thermally activated. The weight gain decreases with increase in temperature because of a change in the chemistry of the process. The roasting experiments carried out in a horizontal electric tube furnace under an oxygen atmosphere shows that up to 96% Cu can be recovered from the chalcopyrite by salt roasting with KCl and subsequent water leaching. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Kinetics; Chalcopyrite; Chloridising roasting

## 1. Introduction

Various pyro- and hydro-metallurgical processes for the extraction of metals from sulphides have been practised for several decades. Chloridising roasting of sulphides under an oxidising atmosphere with common salts for the extraction of metals has continued to remain a subject of interest. The process is interesting, since it produces soluble chloride of metals with simultaneous rejection of iron.

Chloridising roasting of metal oxide and sulphide in the presence of common salt has been reported by a number of workers [1–7]. The processing of nickel sulphide concentrate with MgCl<sub>2</sub> was first patented in

1929 [1]. Kershner and Hoertel [2] reported that >95% of Co, Ni and Cu could be extracted from cobalt and nickel bearing complex sulphide concentrate in the presence of sodium chloride after leaching the roasted product with hydrochloric acid at unit pH. Dahlstedt et al. [3] have carried out a thermodynamic analysis of salt roasting of lean complex sulphide concentrate in the presence of NaCl and O<sub>2</sub> at 1000 K. They have suggested that the condensed chlorides of valuable metals can be separated out from the gangue materials. Rajmohan and Jacob [4] suggest that the presence of SO<sub>2</sub> is essential in the salt roasting of lean oxide ores to convert NaCl to Na<sub>2</sub>SO<sub>4</sub> which is thermodynamically more stable, whereas in case of sulphides, SO<sub>2</sub> is produced in situ by roasting. Bayer and Weidemann [7] have carried out extensive studies on salt roasting of common sulphides and chalcopyrite at low temperatures (473–513 K) by thermoanalytical technique.

\* Corresponding author. Tel.: +91-44-2350077;

fax: +91-44-2301027.

E-mail address: s\_srikanth\_99@yahoo.com (S. Srikanth).

They have observed that the mixture of KCl-CuFeS<sub>2</sub> can be heated more rapidly to the reaction temperature than other salts, such as NH<sub>4</sub>Cl, because KCl does not volatilise during heating. Bayer and Weidemann [7] have also observed that the salt-roasting reaction is spontaneous for KCl, slower for NH<sub>4</sub>Cl and of variable rate for NaCl. They have obtained a strong weight gain in the presence of O<sub>2</sub> (41%), whereas no reaction was observed in nitrogen atmosphere. They also reported that, at a higher temperature (>553 K), the Fe-sulphate and Cu-chlorides decomposed with weight loss. Ngoc et al. [6] have studied the salt roasting of Sikkim complex sulphide concentrate using NaCl at low temperatures (523 K). They have concluded that the process is suitable for the extraction of metal values from the off-grade concentrate and the chemistry of the process is very complex since a number of reactions involving oxidation, sulphation and in situ chlorination may take place simultaneously or sequentially. The principle reaction is:



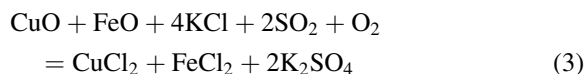
On account of the complexity of sulphide concentrate and because of the availability of oxygen during salt roasting, a number of reactions other than the principle reaction may take place sequentially or simultaneously. Dahlstedt et al. [3] have reported in their study that there are several paths through which each sulphide mineral may undergo reaction and the kinetic factors influence the roasting process. In this study, the kinetics of salt roasting of chalcopyrite from the Singhbhum district in India using KCl as the chlorinating agent were carried out by thermogravimetry as well as by analysing the leach recovery of copper obtained from salt roasting – water leaching experiments.

## 2. The chemistry of salt roasting

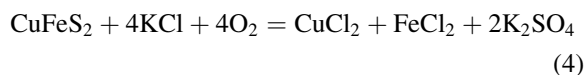
The chemistry of salt roasting is very complex because several processes such as oxidation, sulphation, in situ chlorination and evaporation of volatile species occur either simultaneously or sequentially. The various possible reactions that could occur during the salt roasting of chalcopyrite using KCl are [3,5–7]:



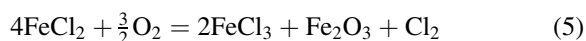
$$\Delta G^0 = -711\,064 + 149.064T$$



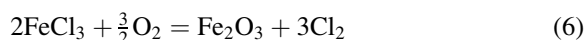
$$\Delta G^0 = -665\,055 + 538.7587T$$



$$\Delta G^0 = -1\,376\,119 + 687.822T$$



$$\Delta G^0 = -72\,865 + 49.09T$$

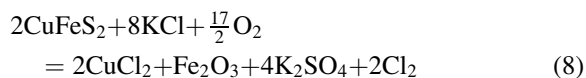


$$\Delta G^0 = -121\,736 + 19.833T$$

All these reactions are exothermic and are feasible at low temperatures. Reaction (4) is associated with a weight gain of 26.6%, whereas, reactions (5) and (6) are associated with weight loss. Bayer and Weidemann [7] also reported that various other species like KFe(SO<sub>4</sub>)<sub>2</sub>, K<sub>2</sub>CuSO<sub>4</sub>Cl<sub>2</sub> and K<sub>2</sub>CuCl<sub>4</sub> may form during the roasting of chalcopyrite with KCl in the presence of oxygen. In addition, the phases CuSO<sub>4</sub> and (CuO)CuSO<sub>4</sub> and other complex sulphate phases may also form depending on the prevailing oxygen potential. In general, the overall stoichiometry of the salt roasting reaction can be expressed as:



or



The stoichiometric mass gain in reaction (7) is 16.8%, and in reaction (8) it is 13.7%. It is difficult to describe the salt-roasting reactions by simple chemical equations, because a number of reactions take place simultaneously and/or sequentially. Therefore, the equilibrium condensed and gas phase compositions for the salt roasting of CuFeS<sub>2</sub> with KCl (1.8 times the stoichiometry as indicated by reaction 7 which corresponds to 0.9 times the stoichiometric amount as indicated by reaction (8) under an atmosphere of static air at temperatures in the range of 523–773 K were determined through free energy minimisation

calculations using the SOLGASMIX programme [8]. All the relevant condensed and gas phases whose thermodynamic data is available in the literature was included for the free energy minimisation calculations. Thermodynamic data for all the species were taken from standard compilation [9,10]. Since thermodynamic data is not available for the species  $\text{KFe}(\text{SO}_4)_2$ ,  $\text{K}_2\text{CuSO}_4\text{Cl}_2$  and  $\text{K}_2\text{CuCl}_4$ , they could not be included for the calculations. The results of the free energy minimisation calculations indicate the formation of the condensed phases  $\text{K}_2\text{SO}_4$ ,  $\text{CuCl}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CuSO}_4$  at 523 and 573 K,  $\text{K}_2\text{SO}_4$ ,  $\text{CuCl}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $(\text{CuO})\text{CuSO}_4$  at 573 K and  $\text{K}_2\text{SO}_4$ ,  $\text{CuCl}$ ,  $\text{Fe}_2\text{O}_3$  and  $(\text{CuO})\text{CuSO}_4$  up to 773 K. The species  $\text{CuCl}$  is liquid in the temperature range 696–823 K and  $\text{FeCl}_3$  exists as a liquid between 577 and 603 K and as a gas above 603 K. The gas phase comprises predominantly of  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $(\text{CuCl})_3$  and  $\text{SO}_3$  and small amounts of  $\text{KCl}$ ,  $\text{FeCl}_3$  and  $\text{SO}_2$ . The free-energy minimisation calculations predict a maximum weight gain of 17.95% up to 600 K and a decrease in weight thereafter. Non-availability of thermodynamic data for the complex species, such as  $\text{KFe}(\text{SO}_4)_2$ ,  $\text{K}_2\text{CuSO}_4\text{Cl}_2$  and  $\text{K}_2\text{CuCl}_4$ , is a serious limitation towards the analysis of the thermodynamics of the salt-roasting process using free energy minimisation calculations.

### 3. Experimental

The chalcopyrite received from Hindustan Copper, Ghatsila, Bihar, India, was used for the salt-roasting experiments. Reflotation of the concentrate was done to remove the impurities. The X-ray diffractogram of the concentrate indicated predominantly the presence of chalcopyrite and small amounts of pyrite. The chemical analysis of the chalcopyrite concentrate used is given in Table 1. The scanning electron micrograph of the concentrate is shown in Fig. 1. The elemental composition of the concentrate determined from EDAX analysis is also given in Table 1. Pure analar grade anhydrous  $\text{KCl}$  was used for the salt-roasting experiments.

#### 3.1. Thermoanalytical experiments

Thermoanalytical studies were carried out in a simultaneous TG/DTA (SEIKO, model No. 320).

Table 1

Analysis of chalcopyrite concentrate used for salt-roasting experiments

Constituents	Chemical analysis (wt.%)	EDAX analysis (wt.%)
Cu	31.5	35.33
Fe	31.09	31.43
S	35.65	33.24
$\text{SiO}_2$	1.61	
$\text{MgO}$	0.18	
$\text{Al}_2\text{O}_3$	0.052	

Kinetic studies were carried out by thermogravimetry under isothermal conditions in the temperature range 523–773 K. The conditions adopted for the thermoanalytical measurements are given in Table 2. About 50 milligrams of  $\text{KCl}$  and chalcopyrite of required stoichiometry were mixed thoroughly in an agate mortar prior to the experiment. The samples were

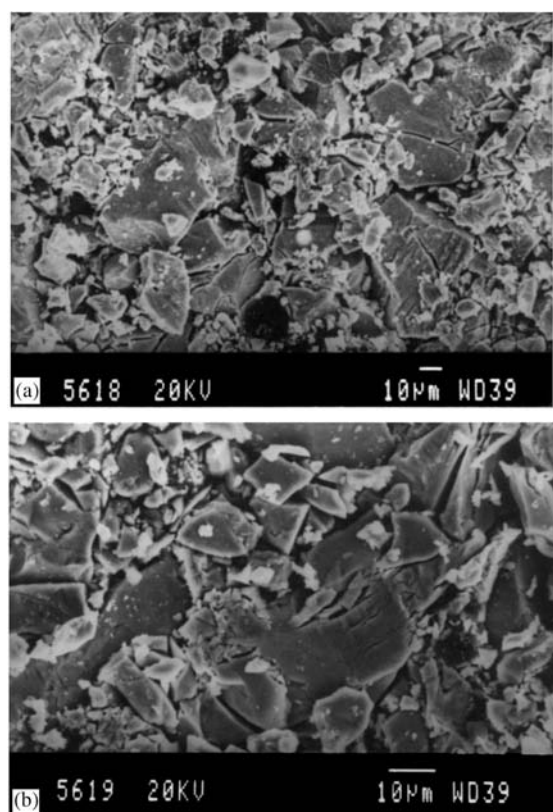


Fig. 1. SEM photograph of the chalcopyrite concentrate used for salt-roasting experiments.

Table 2  
Experimental conditions of thermoanalytical measurements

Amount of sample material: 50 mg of CuFeS <sub>2</sub> + KCl	
Reference material	Annealed $\alpha$ -Al <sub>2</sub> O <sub>3</sub>
Mean particle size of the test material:	0.104 mm
Situation of sample material	Thermocouples exactly in the centre of the sample with direct contact to the heated substance
Furnace atmosphere	O <sub>2</sub> and Ar at a flow rate of 150 ml/min
Sample holder	Pt crucible, $\Phi$ 5 mm
Thermocouples	Pt–Pt/Rh 13%
Heating rate and temperature	100°C/min, 523–723 K
Packing density	Loose packed, no pressing

heated up to the reaction temperature at a heating rate of 100°C/min for all the isothermal experiments. Experiments were carried out in static air, oxygen and argon atmosphere at a flow rate of 150 ml/min. Samples were held for 3 h at the specified temperature in each isothermal roasting experiment. To characterise the salt-roasting process, in one of the non-isothermal experiments, a heating rate of 3°C/min was adopted for better resolution and interpretation of the TG/DTA plot.

### 3.2. Tube furnace roasting experiments

Salt-roasting experiments on chalcopyrite mixed with KCl in the desired stoichiometry was also performed in a horizontal electric Inconel tube furnace. These roasting experiments were carried out in the 3–4 g scale. KCl and CuFeS<sub>2</sub> of required stoichiometry were mixed thoroughly and taken in a pre-weighed alumina boat. The weight of the alumina boat with charge was recorded and the boat was introduced inside the hot zone of the furnace after the temperature had equilibrated at the set value. The temperature of the sample was monitored using a Chromel–Alumel thermocouple placed in contact with the alumina boat. All the tube furnace roasting experiments were carried out under a flowing oxygen atmosphere at a flow rate of 200 ml/min. After each roasting experiment, the roasted mass was leached with distilled water at 70°C to bring all the copper into the solution. The leach solution was filtered and the residue was collected and kept in an oven for 4 h at 105 ± 2°C. The amounts of Cu and Fe in the leach liquor were determined by atomic absorption spectrophotometer and the amounts of K<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>-</sup> were determined by conventional analysis. X-ray diffraction analysis was carried

out on the leach residue. XRD studies could not be conducted on the roasted product because of its extreme hygroscopic nature.

## 4. Results and discussion

### 4.1. Non-isothermal TG/DTA studies

The differential thermal analysis plot of the chalcopyrite mixed with 80% excess KCl (excess of stoichiometry as indicated by reaction (7) or 0.9 times the stoichiometric amount as indicated by reaction (8)) up to 700 K under an oxygen atmosphere is shown in Fig. 2. The DTA plot indicates that the reaction initiates at around 550 K. Two major exothermic peaks are observed at 580 and 603 K, two minor peaks at 626 and 652 K and a small endothermic peak at 704 K. The two major exothermic peaks probably

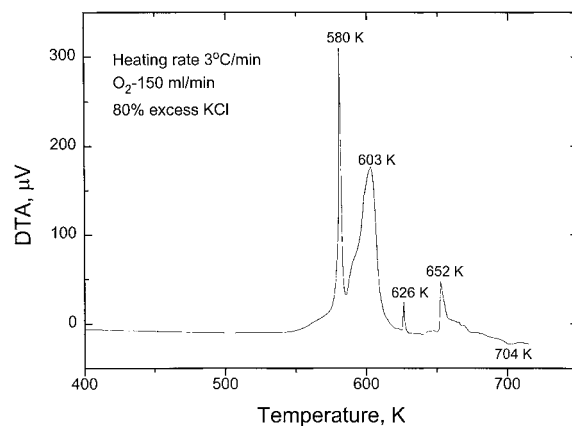


Fig. 2. The differential thermal analysis plot for the salt roasting of chalcopyrite under an oxygen atmosphere.

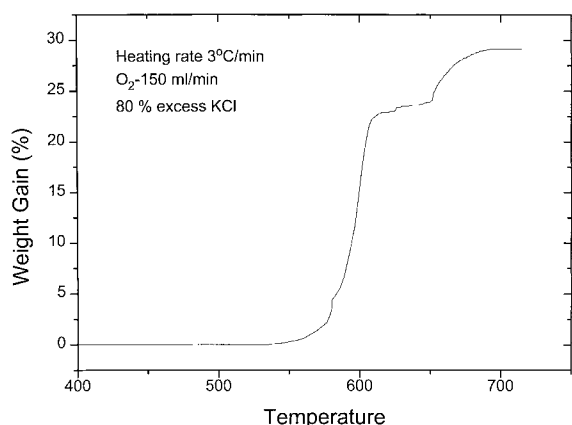


Fig. 3. Thermogravimetric plot for the salt roasting of chalcopyrite under an oxygen atmosphere.

correspond to the oxidation of chalcopyrite as represented by reaction (2) and the chlorination reaction as represented by reaction (3). The two minor peaks probably correspond to the sulphation and other complex phase formations. The small endothermic peak at 704 K corresponds to the melting of CuCl. These observations are substantiated by the TG and DTG results shown in Figs. 3 and 4, respectively. The TG results indicate two distinct regions, the oxidation and chlorination reactions (reactions (2–4)) between 550 and 620 K with a weight gain of 22.8%, and the sulphation and other complex reactions between 650 and 700 K with a weight gain of 6.3%. The weight gain of 22.8% for the first stage of the reaction agrees

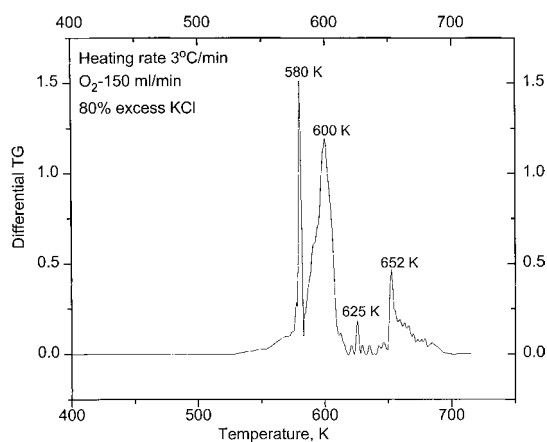
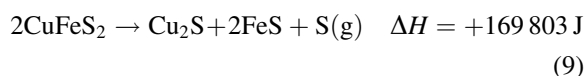


Fig. 4. Differential thermogravimetric plot for the salt roasting of chalcopyrite under an oxygen atmosphere.

well with the theoretical weight gain computed for reaction (4). However, the thermogravimetric results do not support the occurrence of either the overall reaction (7) which indicates a theoretical weight gain of only 12.4% or the overall reaction (8) which is associated with a weight gain of 18%. The differential thermogravimetric plot has the same features as the DTA plot.

The differential thermal analysis plot of the chalcopyrite mixed with 80% excess KCl under an inert atmosphere (Ar) indicates an endothermic peak probably corresponding to the dissociation of chalcopyrite according to the reaction:



#### 4.2. Isothermal thermogravimetric studies

##### 4.2.1. Effect of salt

The effect of the salt (KCl) quantity on the roasting of chalcopyrite in a static air atmosphere at 623 K is shown in Fig. 5. Under oxygen atmosphere, the weight gain approaches the maximum even at low concentrations of KCl and within a short time. In the case of static air, it is observed that, at low amounts of KCl, there is no reaction even up to 1 h of roasting. On the contrary, a minor weight loss is observed for higher periods of roasting probably due to the partial decomposition of chalcopyrite or the evaporation of KCl. The rate of weight gain increases with increase in salt

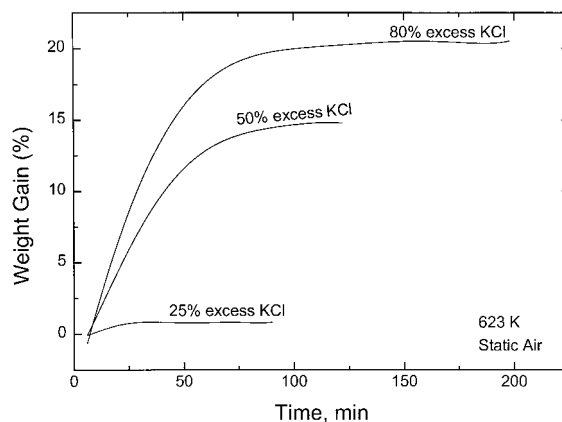


Fig. 5. Effect of salt (KCl) quantity on the roasting of chalcopyrite under an oxygen atmosphere.

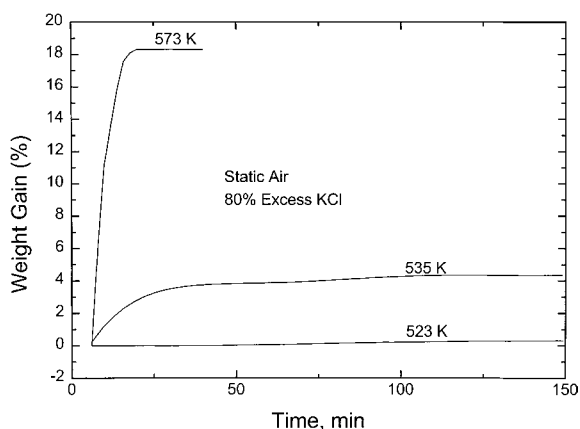


Fig. 6. Effect of temperature and time on the salt roasting of chalcopyrite under a static air atmosphere for low temperatures.

quantity and time. At higher concentrations of KCl, the roasted mass tended to become sticky and effuse out of the crucible.

#### 4.2.2. Effect of temperature

The effect of temperature and time on the salt roasting of chalcopyrite in a static air atmosphere is shown in Figs. 6 and 7. At 523 K, virtually no reaction or weight gain was observed even after two-and-a-half hours of roasting. At 535 K, a small weight gain of up to 4.5% was observed, probably corresponding to the partial oxidation of chalcopyrite. However, at 573 K, both the rate and extent of weight gain increases strongly. Up to 18.3% weight gain is observed within

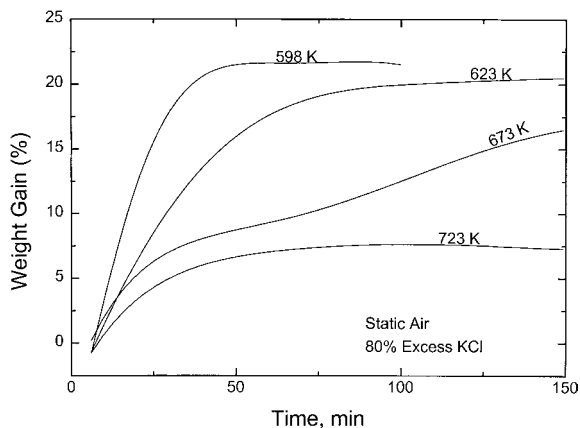


Fig. 7. Effect of temperature and time on the salt roasting of chalcopyrite under a static air atmosphere for high temperatures.

30 min. The extent of weight gain increases with temperature up to 598 K. A maximum weight gain of 21.7% is observed, which is close to the value of 18% calculated for the formation of  $K_2SO_4$ ,  $Fe_2O_3$ ,  $CuCl_2$  and some amount of  $CuSO_4$  from free energy minimisation calculations. From Fig. 7 it is seen that, as the temperature is increased further, the net weight gain decreases. At 723 K, the net weight gain is only 8%. At temperatures above 623 K, a small weight loss (up to 1.5%) is observed initially during the heating period, after which a weight gain is recorded. The initial weight loss may be attributed to the partial decomposition of  $CuFeS_2$  and some evaporation of KCl. The decrease in weight gain at temperatures  $>600$  K can be attributed to the change in the chemistry of the process as predicted by the free-energy minimisation calculations. Up to 590 K, the condensed phases predicted to form are  $K_2SO_4$ ,  $CuCl_2$ ,  $Fe_2O_3$  and  $CuSO_4$ . Above 598 K,  $(CuO)CuSO_4$  forms instead of  $CuSO_4$  and at temperatures above 623 K,  $CuCl$  forms instead of  $CuCl_2$ . It may, however, be mentioned that the formation of complex species such as  $KFe(SO_4)_2$ ,  $K_2CuSO_4Cl_2$  and  $K_2CuCl_4$ , which have been reported to form during the salt roasting of chalcopyrite with KCl [7], have not been taken into account in the free-energy minimisation calculations. At temperatures  $>700$  K, the samples were sticky and tend to flow out of the crucible because of the melting of  $CuCl$ .

The effect of temperature in the range of 513–593 K and time on the salt roasting of chalcopyrite under a flow of oxygen is shown in Fig. 8. At temperatures  $>600$  K, the sample melted and reacted with the Pt crucible and, therefore, salt-roasting experiments under a flow of  $O_2$  could not be carried out  $>600$  K. Both, the total weight gain as well as the rate of weight gain was more under a flow of oxygen than under a static air atmosphere. In this case also, there was virtually no reaction at 523 K (weight gain of 2.1%) even after two-and-a-half hours of roasting. However, the rates of reaction were very high at 563 and 593 K. The weight gain was slightly more at 563 K (22.2%) than at 593 K (20.2%), probably because of the decomposition of  $CuCl_2$  to  $CuCl$  and the oxidation of  $FeCl_2$  at higher temperatures. Under oxygen atmosphere, there was a strong weight loss during the initial period (3.9% at 563 K and 15.5% at 593 K) before weight gain was observed. Under a strong oxidising

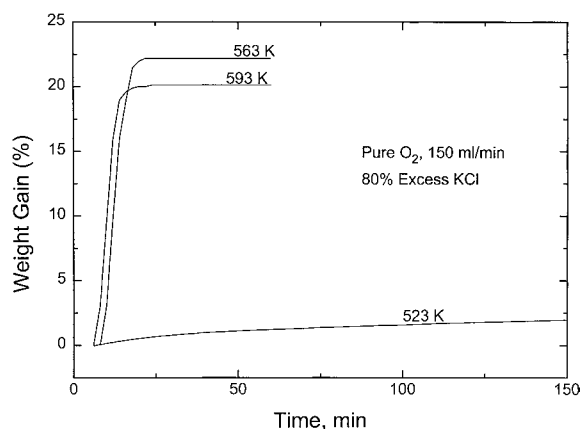


Fig. 8. Effect of temperature and time on the salt roasting of chalcopyrite under an oxygen atmosphere.

atmosphere, the formation and evaporation of ferric chloride may contribute to the weight loss in addition to the other processes mentioned previously.

#### 4.2.3. Effect of gas atmosphere

Salt-roasting experiments were carried out under argon, static air and oxygen atmospheres to determine the effect of oxygen potential on the salt-roasting process. The results of the thermogravimetry experiments under a flowing Ar atmosphere at three different temperatures are shown in Fig. 9. Under an argon atmosphere, there is virtually no reaction and there is a weight loss (up to 4%) which decreases exponentially with time. The condensed phases that were predicted

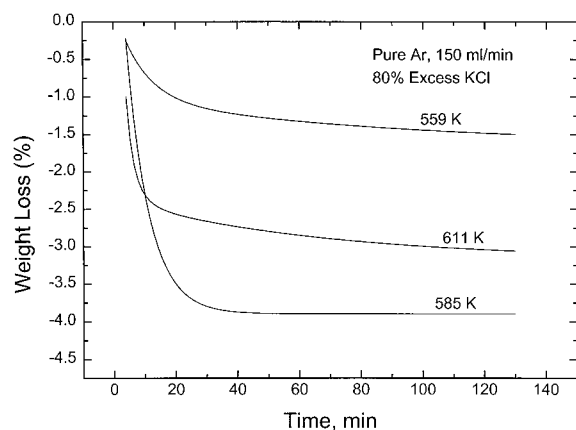


Fig. 9. Results on the salt roasting of chalcopyrite under an inert (Ar) atmosphere.

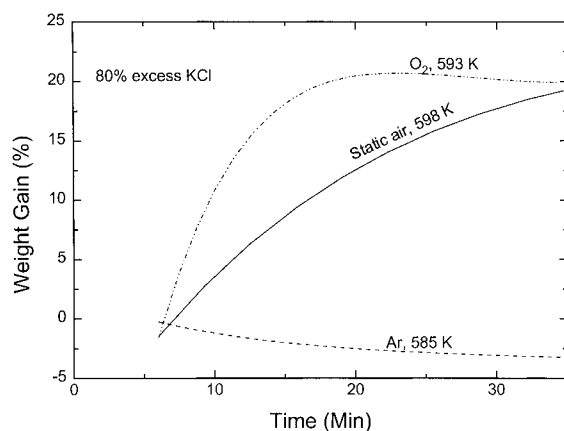


Fig. 10. Effect of gas atmosphere on the salt roasting of chalcopyrite.

to form in the temperature range 523–723 K under an inert atmosphere were  $\text{CuCl}$ ,  $\text{FeS}_2$  and  $\text{FeCl}_2$  other than the unreacted  $\text{CuFeS}_2$  and  $\text{KCl}$ . The gas phase contains small amounts of  $\text{S}_2$ ,  $\text{KCl}$ ,  $\text{FeCl}_2$  and  $\text{Cu}_3\text{Cl}_3$  in addition to Ar. The predicted mass loss is in good agreement with the observed values. The relative effect of oxygen, static air and argon on the salt-roasting process is demonstrated in Fig. 10. Both the rate of weight gain and the net weight gain is more with the use of a pure oxygen atmosphere.

#### 4.3. Tube furnace roasting

##### 4.3.1. Effect of particle size and bed depth

The effect of particle size on the recovery of copper derived from the salt-roasting process is given in Table 3. The mean particle size of chalcopyrite was varied in the range of 0.07 to 0.152 mm. It is observed that copper recovery improves with decrease in particle size. However, at particle size  $<0.1$  mm, the roasted mass was sticky and sintered to the alumina boat and, consequently, leach recovery of Cu dropped.

Table 3  
Effect of particle size on salt roasting of chalcopyrite

Mean particle size (mm)	Leach recovery of Cu (%)
0.152	21.00
0.104	57.00
0.070	44.00

Table 4  
Effect of quantity of charge on the salt-roasting process

Time (min)	3-g scale		4-g scale	
	Cu recovery (%)	Fe recovery (%)	Cu recovery (%)	Fe recovery (%)
60	50.5	36	51	37
120	71.0	27	69	30

It is seen that the Cu recovery is maximum for 0.104 mm mean particle size.

In order to investigate the effect of bed depth on the salt-roasting process, experiments were carried out using different quantities of charge from 3 to 8 g. Some of these results are presented in Table 4. It appears that bed depth does not have a significant influence on the salt-roasting process within the range studied. Therefore, all the subsequent salt-roasting experiments were carried out on the 3-g scale with a mean particle size of 0.104 mm.

#### 4.3.2. Effect of salt quantity

The amount of salt required for the good recovery of Cu is one of essential factors for the salt roasting of chalcopyrite. Accordingly, a set of experiments were carried out by varying the amount of KCl from 25 to 80% excess of stoichiometry (based on reaction (7)) at 573 K for 1 h at a flowing oxygen flow rate of 200 ml/min. The results are presented in Fig. 11. It is seen that the leach recovery of copper increases with increase in KCl content up to about 50% and thereafter remains at a steady value. For 80% excess of KCl, the Cu

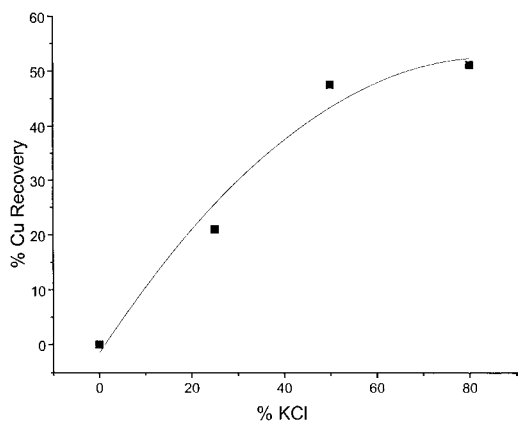


Fig. 11. Effect of salt (KCl) quantity on the leach recovery of copper.

recovery is 52% in 1 h of roasting at 573 K, whereas it is 50% with 50% excess of KCl under the same conditions of roasting.

#### 4.3.3. Effect of roasting time

The effect of time of salt roasting on the leach recovery of Cu at several temperatures is delineated in Fig. 12. It is seen that the leach recovery of copper increases with time up to 180 min after which a steady state is reached. One of the objectives of the salt-roasting process under an oxidising atmosphere is to convert all the copper to its chloride and the iron to oxide form to minimise the amount of iron in the leach liquor in the subsequent water leaching stage. The amount of Cu and Fe in the leach solution for different times of roasting is depicted in Fig. 13. It is seen that the recovery of Fe in the leach solution is <10% for roasting periods above 180 min.

#### 4.3.4. Effect of roasting temperature

The effect of roasting temperature in the range of 523 to 623 K on the leach recovery of Cu is depicted in Fig. 12. In this temperature range, the Cu recovery

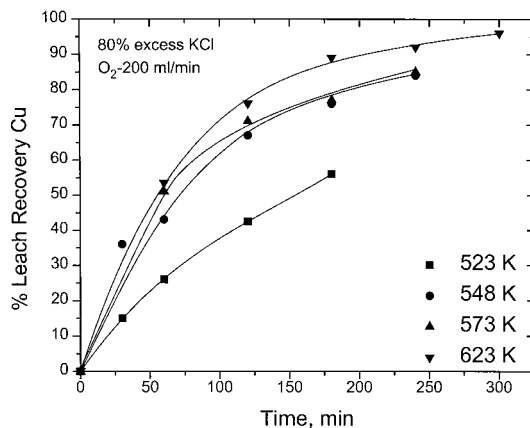


Fig. 12. Effect of temperature of salt roasting on the leach recovery of Cu.



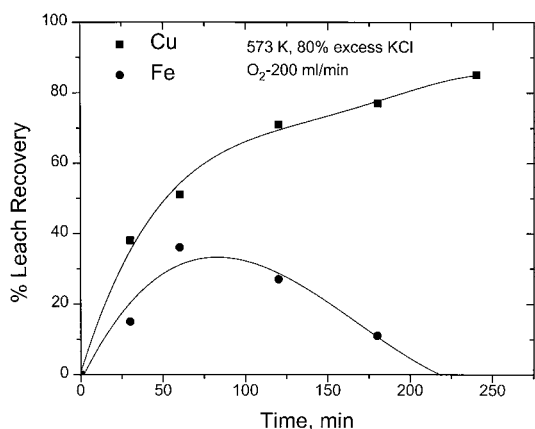


Fig. 13. Effect of time of roasting on the copper and iron concentrations in the leach liquor.

increased with increase in temperature. Here, up to 96% Cu could be recovered by salt roasting at a temperature of 623 K for 5 h. This trend is somewhat different compared to the thermogravimetric results. As mentioned earlier, in the TG experiments under a flow of pure oxygen, the weight gain decreased slightly at temperatures >575 K. For roasting temperatures >623 K, the roasted mass had fused and seeped out of the alumina boat resulting in low Cu recovery. This may be attributed to the formation of liquid CuCl and some FeCl<sub>3</sub>. For example, a roasting experiment carried out at 673 K for 2 h under a flowing O<sub>2</sub> atmosphere yielded Cu and Fe recoveries of 15 and 26%, respectively.

It is difficult to distinguish whether copper is present as chloride or sulphate in the roasted product since both these species are water soluble. Free-energy minimisation calculations indicate the formation of some copper sulphate at all temperatures. Thermo-

gravimetric results indicate the formation of complex sulphates with a strong weight gain. X-ray diffraction studies could not be carried out on the roasted product because of its extreme hygroscopic nature. The concentrations of K<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in the leach liquor for various conditions of roasting are given in Table 5. The high concentration of sulphate ion in the leach liquor also indicates some copper sulphate and other complex sulphate and chloride formation during salt roasting. The X-ray diffraction analysis of the leach residue indicates predominantly the presence of K<sub>2</sub>CuSO<sub>4</sub>Cl<sub>2</sub> and minor amounts of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O and KFe(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Table 5).

#### 4.4. Kinetic analysis of the salt-roasting process

Various kinetic models were examined to ascertain the mechanism of the salt-roasting process of chalcopyrite. Because of the decomposition of the chalcopyrite and the several gaseous species evolving during the salt-roasting process, it may be expected that the reaction product would be porous and the process may be controlled by chemical reaction at the interface. For such a process, the rate of roasting is proportional to the interfacial area:

$$-\frac{1}{\eta} \frac{dW}{dt} = -\frac{dV}{dt} \cong kA$$

where  $\eta$  is the density,  $W$  the weight of chalcopyrite,  $V$  the volume of the particle at time  $t$ ,  $A$  the interfacial area and  $k$  the rate constant. If the particles are assumed to be spherical, the above equation assumes the form:

$$[1 - (1 - \alpha)^{1/3}] = kt$$

Table 5  
Ionic concentration in the leach liquor

Temperature of roasting (K)	Time of roasting (min)	K <sup>+</sup> (g/l)	Cl <sup>-</sup> (g/l)	SO <sub>4</sub> <sup>2-</sup> (g/l)
573	60	4.99	13.84	12.50
573	120	3.42	12.07	13.16
623	60	3.61	13.13	11.84
623	120	4.48	13.13	8.96
623	240	3.42	12.7	9.05
673	30	3.20	10.65	8.63
673	60	4.68	13.49	7.89
673	120	6.31	13.49	6.9

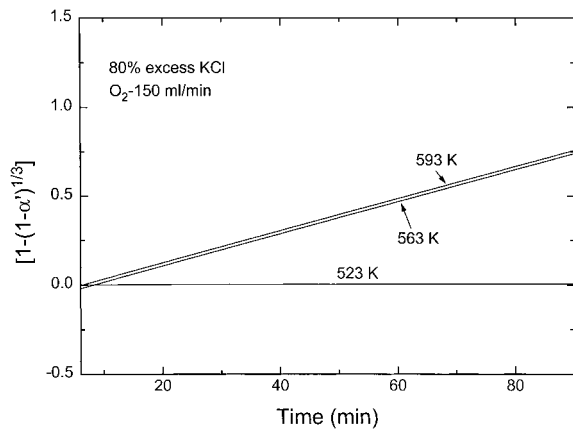


Fig. 14. Plot of  $[1-(1-\alpha')^{1/3}]$  vs. time from thermogravimetric data for the salt roasting of chalcopyrite under a flowing oxygen atmosphere.

which is the topochemical kinetic model, where  $\alpha$  is the fraction reacted,  $k$  the rate constant and  $t$  the time.

For the thermogravimetry measurements, it is difficult to deduce the fraction reacted because of the complexity of the salt-roasting process and, therefore, the fractional weight gain ( $\alpha'$ ) was used instead of the  $\alpha$  parameter to denote the fraction reacted. Fig. 14 shows a plot of  $[1-(1-\alpha')^{1/3}]$  as a function of time in the temperature range 513 to 593 K derived from the thermogravimetric data for salt roasting with 80% excess KCl in a flowing oxygen atmosphere. The plots are linear, indicating that the salt-roasting reaction follows the shrinking core model in the temperature range of 523–600 K. The rate constant,  $k$ , obtained from the slope of the lines shown in Fig. 14, was used to draw an Arrhenius plot shown in Fig. 15 from which an apparent activation energy of 77 kJ/mol was obtained for the salt-roasting process under an oxygen atmosphere.

A similar kinetic analysis was carried out on the thermogravimetric data for salt roasting with 80% excess KCl in a static air atmosphere. The activation energy for the salt-roasting process under a static atmosphere at low temperatures was deduced to be 102 kJ/mol, which is understandably more than that derived under an oxygen atmosphere. As mentioned earlier, at temperatures above 600 K in a static air atmosphere, the weight gain decreases with increase in temperature because of a change in the chemistry of the process at higher temperatures. This indicates that

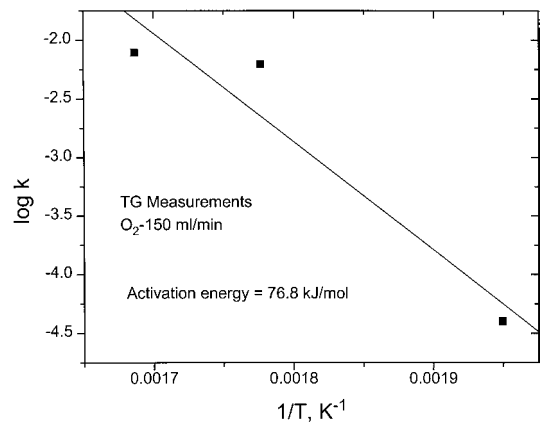


Fig. 15. The Arrhenius plot for the salt roasting of chalcopyrite under a flowing oxygen atmosphere.

the salt-roasting process is not thermally activated at temperatures >600 K.

A similar kinetic analysis can be performed using the leach recoveries of Cu derived from the salt-roasting experiments carried out in the tube furnace. Fig. 16 shows the plot of  $[1-(1-\alpha)^{1/3}]$  versus time in the temperature range based on the results obtained in the roasting experiments conducted in the tube furnace. In this case,  $\alpha$  is the fractional recovery of copper in the leach solution. The plots are linear over the entire temperature range.

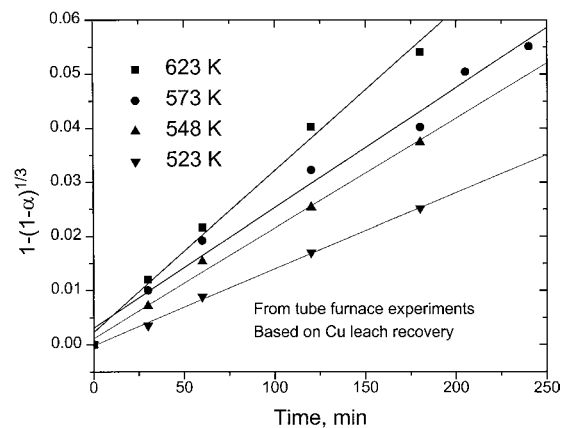


Fig. 16. Plot of  $[1-(1-\alpha)^{1/3}]$  vs. time from Cu recoveries using the salt roasting-water leaching experiments under a flowing oxygen atmosphere.

## 5. Conclusion

Based on the thermogravimetric and salt-roasting studies carried out in the present investigation, the following conclusions can be drawn:

1. The chemistry of the salt-roasting process is very complex because several processes, such as oxidation, sulphation, in situ chlorination and evaporation of volatile species, occur either simultaneously or sequentially. The free-energy minimisation calculations indicate the formation of the condensed phases  $K_2SO_4$ ,  $CuCl_2$ ,  $Fe_2O_3$  and  $CuSO_4$  at 523 and 573 K,  $K_2SO_4$ ,  $CuCl_2$ ,  $Fe_2O_3$  and  $(CuO)CuSO_4$  at 573 K and  $K_2SO_4$ ,  $CuCl$ ,  $Fe_2O_3$  and  $(CuO)CuSO_4$  up to 773 K. However, the non-inclusion of complex species, such as  $KFe(SO_4)_2$ ,  $K_2CuSO_4Cl_2$  and  $K_2CuCl_4$  which have been reported to form during the salt roasting of chalcopyrite with KCl [7], is a serious limitation in the analysis of the chemistry of the process.
2. The non-isothermal thermal analysis results distinctly indicate four exothermic processes at 580, 603, 626 and 652 K with a weight gain and a minor endothermic process at 704 K. These have been correlated to the oxidation, chlorination, sulphation and liquefaction reactions occurring in the salt-roasting process.
3. The isothermal thermogravimetric studies in a static air atmosphere indicate increase in weight gain with increase in salt quantity up to 80%, increase in temperature up to 600 K. A maximum weight gain of 21.7% is recorded at 598 K. At temperatures >600 K, the extent of weight gain decreases with increase in temperature. This is attributed to the change in the chemistry of the process. A similar trend is observed in the thermogravimetric measurements carried out under a flowing oxygen atmosphere. A maximum weight gain of up to 22.2% could be achieved under oxygen atmosphere.
4. Both, the rate of weight gain as well as the net weight gain are higher under a flowing oxygen atmosphere than in a static air atmosphere. However, there is a small weight loss (up to 4%)

when salt roasting is carried out under an inert atmosphere (Ar).

5. Salt roasting in the tube furnace followed by water leaching experiments indicates an increase in Cu recovery with temperature up to 623 K and 3 h of roasting. Up to 96% Cu could be recovered by salt roasting at a temperature of 623 K beyond 3 h. The amount of Fe in the leach solution decreases with increasing times and temperatures of roasting. The recovery of Fe in the leach solution is <10% for roasting periods above 180 min.
6. X-ray diffraction studies of the leach residue as well as ionic concentration analysis in the leach liquor indicate that copper is present predominantly as chloride, but complex sulphates and chlorides also exist.
7. The kinetics of the salt-roasting process conforms to the chemical control mechanism up to 600 K both under static air and pure oxygen atmospheres. However, the activation energy of the process is higher under a static air atmosphere (102 kJ/mol) than under a pure oxygen atmosphere (77 kJ/mol).

## References

- [1] E.L. Duffield, Nickel, iron, copper, etc. from sulphide ores, British Patent, 328, 698 (1929).
- [2] K.K. Kershner, E.W. Hoertel, Recovery of cobalt and nickel from complex sulphide ores of South Eastern Missouri, U.S. Bureau of Mines Rep. Invest. 5740, 1961, 16 pp.
- [3] A. Dahlstedt, S. Seetharaman, K.T. Jacob, *Scand. J. Metall.* 21 (1992) 242–245.
- [4] N. Rajmohan, K.T. Jacob, *Min. Eng.* 5 (2) (1992) 235–243.
- [5] T.K. Mukherjee, P.R. Menon, P.P. Shukla, C.K. Gupta, *J. Metals* (1985) 28–33.
- [6] N.V. Ngoc, M. Shamsuddin, P.M. Prasad, *Hydrometallurgy* 21 (1989) 359–372.
- [7] G. Bayer, G.H. Weidemann, *Thermochim. Acta* 198 (1992) 303–312.
- [8] H. Flynn, A.E. Morris, D. Carter, Using the UMR PC/SOLGASMIX Software Package, University of Missouri-Rolla, 1986.
- [9] I. Barin, *Thermochemical Data of Pure Substances*, third edn., VCH Publishers, Weinheim, 1995.
- [10] D.R. Stull, H. Prophet: *JANAF Thermochemical Tables*, second edn., U.S. Department of Commerce, Washington, 1975.