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Non-isothermal thermoanalytical studies on the salt roasting of chalcopyrite using KCl

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Abstract

In an earlier study [1], the isothermal kinetics of salt roasting of chalcopyrite under an oxidizing atmosphere using KCl was studied in the temperature range 523–773 K. The salt roasting reaction was found to be chemically controlled at temperatures below 600 K both under static air and oxygen atmosphere. At higher temperatures, the process was not thermally activated because of a change in the chemistry of the process. In the present study, the salt roasting of chalcopyrite using KCl under oxygen and static air atmosphere was studied by non-isothermal thermoanalytical studies up to 723 K. The effect of salt content, heating rate and particle size on the salt roasting behavior was studied using TG/DTA techniques at a programmed linear heating rate. The TG and DTA studies reveal two distinct chemical processes, one operative up to 620 K and the other from 620 to 723 K. The integral method of Coats and Redfern was used for the treatment of non-isothermal kinetic data. The non-isothermal analysis confirmed the chemical control mechanism at temperatures below 620 K. However, the activation energy for the process derived from non-isothermal thermogravimetric analysis is almost twice as that deduced from isothermal measurements. In the temperature range 620–723 K, the kinetic data still obeys the interfacial reaction control model although the activation energy in this temperature range is very low.

Keywords: Non-isothermal analysis; Salt roasting; Chalcopyrite

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1. Introduction

The traditional method of copper production from chalcopyrite is based on the pyrometallurgical route of flash smelting, converting and fire refining. Modern practice such as the Noranda process utilize a single reactor to carry out smelting and converting and the furnace off gases are sufficiently rich in SO_2 for the production of sulfuric acid. Despite the several developments made in reducing the energy consumption and pollution levels in the pyrometallurgical processing of copper during the past few decades, several alternative routes have been explored for the extraction of copper from sulfide ores. These are summarized in the recent handbook on extractive metallurgy by Habashi [2]. Salt roasting of sulfide ores using alkali chlorides appears promising because of the low temperatures of formation of water soluble chloride and sulfate salts and the prospect of recovering sulfur in the non-polluting elemental form. Another advantage in the salt roasting of sulfide ores containing pyrites is the formation of intermediate ferric chloride and sulfur chloride gases which are excellent chloridizing agents.

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In an earlier study [1], the kinetics of salt roasting of chalcopyrite was investigated in the temperature range 523–773 K under argon, static air and oxygen atmospheres by isothermal thermogravimetry. Both, the rate of weight gain as well as the net weight gain was found to be higher under a flowing oxygen atmosphere than in a static air atmosphere. A small weight loss was observed when salt roasting is carried out under an inert atmosphere. The chemistry of the salt roasting process was found to be very complex because several processes such as oxidation, sulfation, in situ chlorination and evaporation of volatile species occur simultaneously or sequentially. The salt roasting reaction was found to conform to a chemical control mechanism up to 600 K both under static air and pure oxygen atmospheres. At higher temperatures, the process was found not to be thermally activated because of a change in the chemistry of the process. The activation energy for the salt roasting reaction deduced from isothermal thermogravimetric studies was found to be 102 kJ/mol under a static air atmosphere and 77 kJ/mol under a flowing oxygen atmosphere.

Isothermal studies for the analysis of the kinetics of reactions has certain limitations [3]: (a) reactions associated with enthalpy changes disturb the isothermal conditions leading to deviation of the temperature of the sample from the set value, (b) it is not realistically possible to attain thermal equilibrium with the environment without significant pre-reaction. This is especially valid for processes such as salt roasting associated with low activation energies, (c) the physical characteristics of the sample may change in different runs, (d) the actual process of salt roasting is carried out under conditions of gradual heating to the required temperature and therefore, isothermal conditions do not represent a realistic situation and (e) the kinetic parameters of the Arrhenius type expression may not have identical values under isothermal and non-isothermal conditions. Therefore, reaction rates determined under isothermal conditions may not be applicable for actual processes taking place non-isothermally.

In the present study therefore, the salt roasting of chalcopyrite using KCl under oxygen and static air atmosphere was studied by non-isothermal thermoanalytical studies and the results compared with those obtained from isothermal studies. In general, the overall stoichiometry of the salt roasting reaction can be expressed either as [5]:

$$\mathrm{CuFeS_2} + 2\mathrm{KCl} + \tfrac{15}{4}\mathrm{O_2} = \mathrm{CuCl_2} + \tfrac{1}{2}\mathrm{Fe_2O_3} + \mathrm{K_2SO_4} + \mathrm{SO_2} \qquad (1)$$

$$\Delta G^0 = -1290818 + 25.2T\ln T + 306T \quad (\mathrm{J/mol})$$

or as:

$$\mathrm{CuFeS_2} + 4\mathrm{KCl} + \tfrac{17}{4}\mathrm{O_2} = \mathrm{CuCl_2} + \tfrac{1}{2}\mathrm{Fe_2O_3} + 2\mathrm{K_2SO_4} + \mathrm{Cl_2} \qquad (2)$$

$$\Delta G^0 = -1577487 - 22.5T\ln T + 863T \quad (\mathrm{J/mol})$$

It is seen that reaction (2) is favored at low temperatures and reaction (1) at higher temperatures. The stoichiometric mass gain for reaction (1) is 16.8% and for reaction (2) is 13.7%. The formation of other species such as $\mathrm{KFe(SO_4)_2}$, $\mathrm{K_2CuSO_4Cl_2}$, $\mathrm{K_2CuCl_4}$, $\mathrm{CuSO_4}$, $\mathrm{FeCl_3}$, CuCl and $\mathrm{(CuO)CuSO_4}$ during the salt roasting of chalcopyrite has also been reported [1,4]. Determination of the equilibrium phases by free energy minimization calculations also provide incomplete information because of the lack of thermodynamic data of several of these complex phases [1].

2. Experimental

Chalcopyrite samples received from Hindustan Copper, Ghatsila, Bihar, India was refloated to further remove the impurities. The X-ray diffraction pattern of the refloated concentrate indicated predominantly the presence of chalcopyrite and small amounts of pyrite. The chemical analysis of the concentrate used for the salt roasting experiments is given in Table 1. Pure analar grade anhydrous KCl was used for the salt roasting experiments.

Table 1
Analysis of chalcopyrite concentrate used for salt roasting experiments

Constituents	Chemical analysis (wt.%)
Cu	31.5
Fe	31.09
S	35.65
$\mathrm{SiO_2}$	1.61
MgO	0.18
$\mathrm{Al_2O_3}$	0.052

Table 2
Experimental conditions of thermoanalytical measurements

Amount of sample material	~50 mg of $CuFeS_2$ + KCl
Reference material	Annealed α-Al_2O_3
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_2 at a flow rate of 150 ml/min and static air
Sample holder	Pt crucible, Φ, 5 mm
Thermocouples	Pt–Pt/Rh, 13%
Heating rate and temperature	3 and 5 K/min Ambient to 723 K
Packing density	Loose packed, no pressing

Thermoanalytical experiments were carried out in a simultaneous TG/DT (SEIKO, model no. 320) analyzer. The conditions adopted for the thermoanalytical measurements are given in Table 2. About 50 mg of chalcopyrite and KCl of required stoichiometry were mixed thoroughly and ground in an agate mortar prior to the experiment. For most of the experiments, the sample size was in the range of 75–105 μm and was heated at a linear heating rate of 3 K/min. Experiments were carried out in static air and a flowing oxygen atmosphere at a flow rate of 150 ml/min. The effect of salt content, heating rate and particle size on the salt roasting behavior was studied. The stoichiometric requirement of KCl for reaction (2) is twice that of reaction (1). The stoichiometric amount of KCl mentioned throughout this paper is with reference to reaction (1).

3. Results and discussion

3.1. Effect of heating rate

The TG and DTA plots obtained with heating rates of 3 and 5 K/min for salt roasting using 3.33 times stoichiometric KCl under a flowing oxygen atmosphere are shown in Figs. 1 and 2, respectively. The DTG plot corresponding to Fig. 1 is also shown in Fig. 3. At lower heating rates (3 K/min), both, the extent and rate of mass gain is higher and the various exothermic peaks observed around 578, 603, 624 and 666 K are clearly resolved. At temperatures above 700 K, the mass decreases with temperature because of the onset of vaporization. The peak positions compare well with those obtained in the earlier study

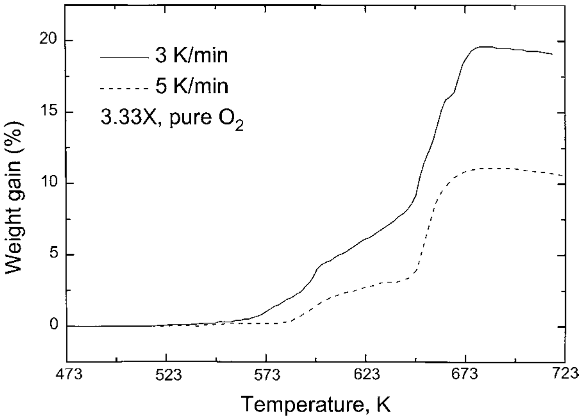

Fig. 1. Thermogravimetry plot to demonstrate the effect of heating rate on the salt roasting process under a flowing oxygen atmosphere.

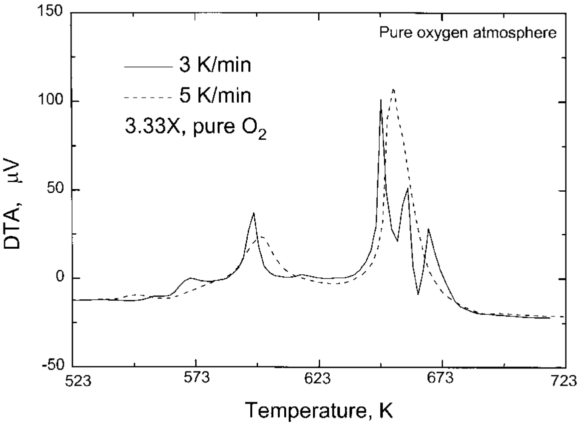

Fig. 2. Effect of heating rate on the salt roasting behavior from DTA.

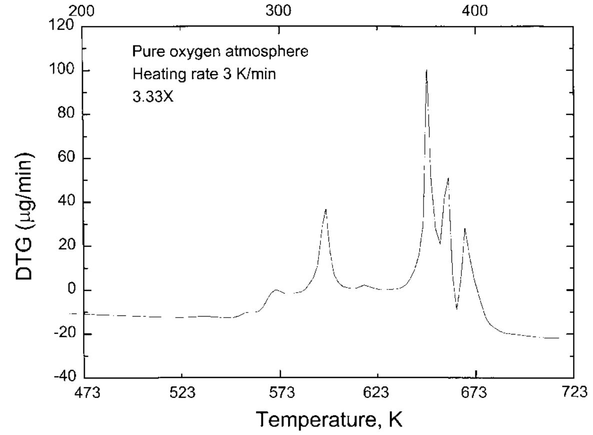

Fig. 3. DTG plot for 3.33X KCl at a heating rate of 3 K/min.

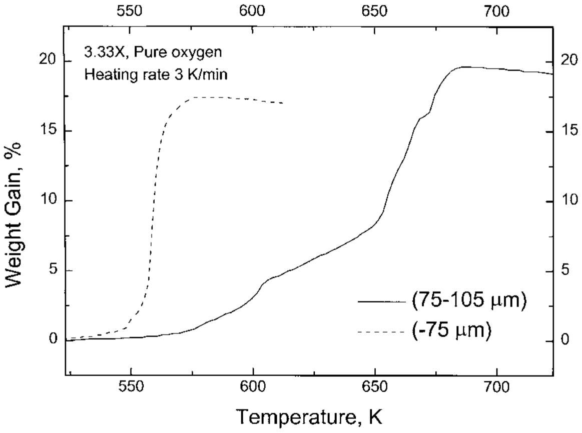

Fig. 4. The effect of particle size on the salt roasting behavior of chalcopyrite under a flowing oxygen atmosphere.

[1]. These exothermic peaks were earlier correlated to the oxidation, chlorination and sulfation processes. Both, the DTG and DTA results indicate two general exothermic processes, one from 523–620 K and the other from 620–723 K. The first region probably corresponds to the chlorination reaction and the second region to the sulfation and other complex processes. At a heating rate of 5 K/min, the peak positions shift to higher temperatures and further the high temperature exothermic processes are not clearly resolved. All subsequent experiments were carried out at a linear heating rate of 3 K/min.

3.2. *Effect of particle size*

The effect of the variation of particle size on the TG and DTA characteristics during the salt roasting of chalcopyrite under a flowing oxygen atmosphere is delineated in Figs. 4 and 5, respectively. It is seen (Fig. 4) that the salt roasting reaction initiates and completes at much lower temperatures (540–570 K) when the charge was of −200 mesh (−75 μm) than with particles in the size range of 75–105 μm. The DTA plot (Fig. 5) also indicates a single large exothermic peak at around 560 K for the −75 μm particles.

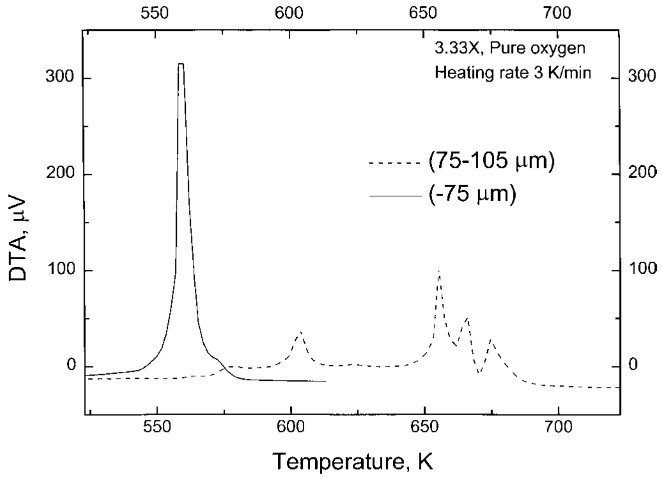

Fig. 5. DTA curves showing the effect of particle size on the salt roasting process.

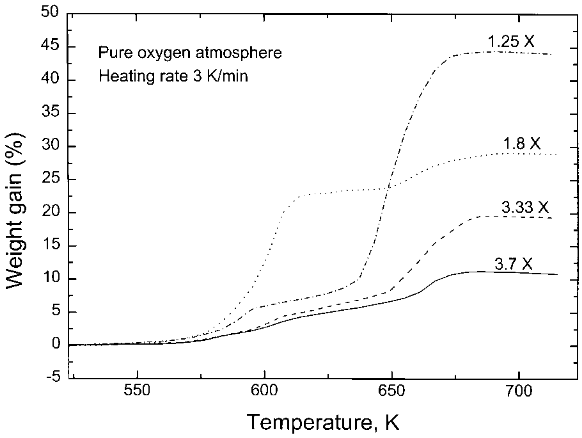

Fig. 6. Variation in the thermogravimetric behavior with salt content during the salt roasting of chalcopyrite under an oxygen atmosphere.

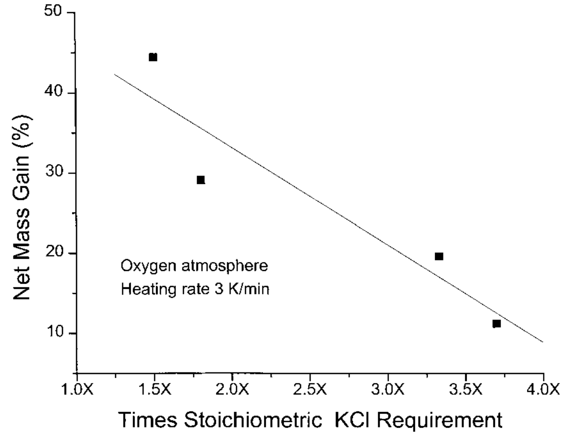

Fig. 8. Variation of maximum weight gain with salt content.

The merger of the peaks indicate that all the exothermic processes occur simultaneously for lower particle size than sequentially for larger particle size charge. In all the subsequent experiments, the charge with particle size in the range of 75–105 μm was adopted.

3.3. *Effect of salt concentration*

The end products of the salt roasting reaction can be a combination of chlorides, sulfates, oxides or complex chloride sulfates. The exact phases that form and their amounts depend on the process conditions. Salt roasting studies were therefore carried out by varying the salt concentration from 1.25 times stoichiometry to 3.7 times stoichiometry (based on reaction (1)). The TG and DTA results obtained for salt roasting in a flowing oxygen atmosphere are depicted in Figs. 6 and 7, respectively. The variation of the net weight gain with salt concentration is also shown in Fig. 8. It is observed that the net weight gain or extent of reaction increases linearly with increase in salt concentration indicating that the same chemistry operates immaterial of the salt concentration in the range investigated. The net maximum weight gain increases from 11.2%

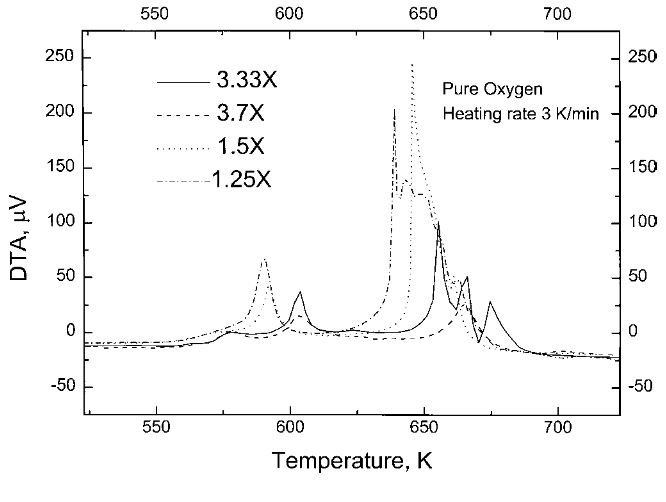

Fig. 7. DTA plots showing the effect of salt concentration on the salt roasting process under oxygen atmosphere.

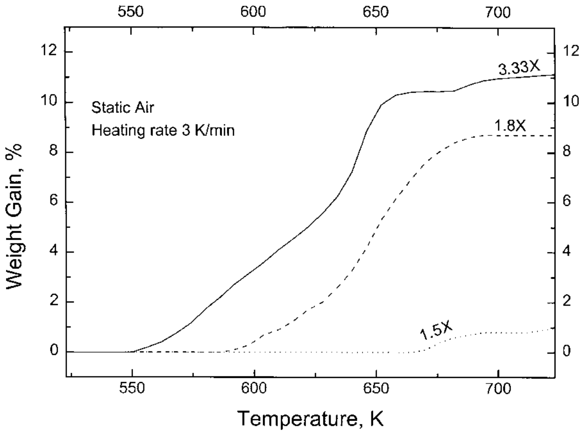

Fig. 9. Variation in the thermogravimetric behavior with salt content during the salt roasting of chalcopyrite under a static air atmosphere.

in the case of 3.7 times stoichiometric KCl to 44.4% in the case of 1.25 times stoichiometric KCl. In all cases, mass loss is observed at temperatures higher than 700 K. The fact that the chemistry of the process is independent of salt concentration is confirmed by the DTA results although the exothermic peaks shift marginally towards higher temperature as the salt content is increased.

The results of the salt roasting experiments with varying salt concentration carried out under a static air atmosphere are delineated in Figs. 9 and 10, respectively. In contrast to the salt roasting experiments under a flowing oxygen atmosphere, the weight gain as well as the reaction rate increases with increase in salt concentration. The extent of reaction is insignificant below 1.8 times the stoichiometric amount of KCl. A maximum of 10 wt.% gain is observed with 3.33 times the stoichiometric KCl. The presence of an oxidizing atmosphere is therefore essential for the salt roasting of chalcopyrite.

3.4. Non-isothermal kinetic analysis

The fundamental method for the treatment of kinetic data derived from non-isothermal experiments have been given by MacCullum and coworkers [6] and described in detail by Ray [3]. The differential form of the kinetic law can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)\Phi(\alpha, T) \tag{3}$$

where α is the fraction reacted, t the time, T the temperature, $k(T)$ the rate constant which is a function of temperature, $f(\alpha)$ is a function of the fraction reacted and $\Phi(\alpha, T)$ is a function of α and temperature. Generally $\Phi(\alpha, T)$ is assumed to be unity [3]. If we assume that the kinetic rate constant $k(T)$ follows an Arrhenius type of expression, i.e.

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{4}$$

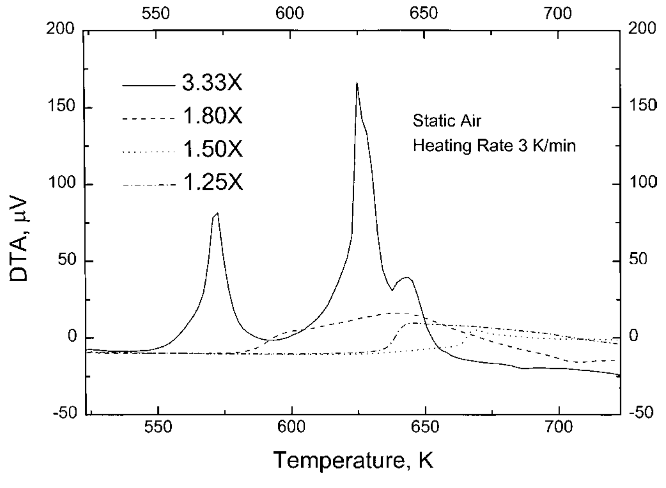

Fig. 10. DTA plots showing the effect of salt concentration on the salt roasting process under a static air atmosphere.

where A is the pre-exponential factor, E the activation energy and R the gas constant, then Eq. (3) assumes the form:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

If the heating rate is linear with respect to time, then Eq. (5) reduces to:

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{B}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{6}$$

Integrating Eq. (6), one obtains

$$\int\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{B}\int\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{7}$$

It may be mentioned that it is necessary to know the functional form of $f(\alpha)$ to integrate the LHS of Eq. (7) and further the RHS of Eq. (7) cannot be integrated in a finite form. One of the popular method of analysis of Eq. (7) was provided by Coats and Redfern [7]. With some approximations, Eq. (7) reduces to [7]:

$$\int\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{ART^2}{BE}\exp\left(-\frac{E}{RT}\right)\left[1-\frac{2RT}{E}\right] \tag{8}$$

In an earlier study employing the isothermal approach [1], it was deduced that the salt roasting of chalcopyrite using KCl follows the interfacial reaction control model for spherical particles at temperatures up to 600 K. For a interfacial reaction model, $f(\alpha)$ takes the form $(1-\alpha)^n$, where the value of n is 2/3 for spherical particles. Incorporating the functional form of $f(\alpha)$ in Eq. (8) and integrating:

$$\frac{[1-(1-\alpha)^{1-n}]}{(1-n)T^2} = \frac{AR}{BE}\left[1-\frac{2RT}{E}\right]\exp\left(-\frac{E}{RT}\right) \tag{9}$$

It has been suggested that the pre-exponential term in Eq. (9) is a constant and, therefore, a plot of ln(LHS)

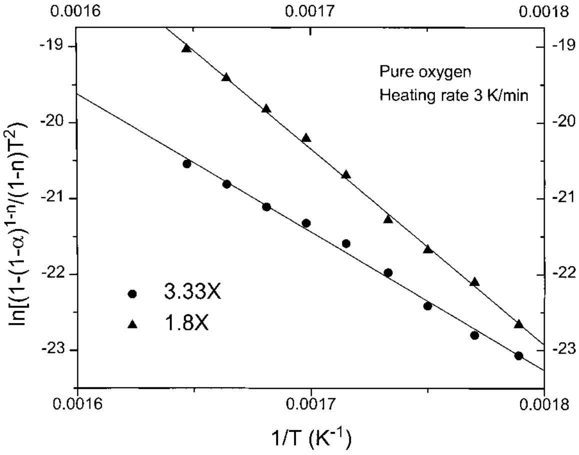

Fig. 11. Coats–Redfern plot for non-isothermal analysis of kinetic data of the salt roasting process under an oxygen amosphere in the temperature range 523–620 K.

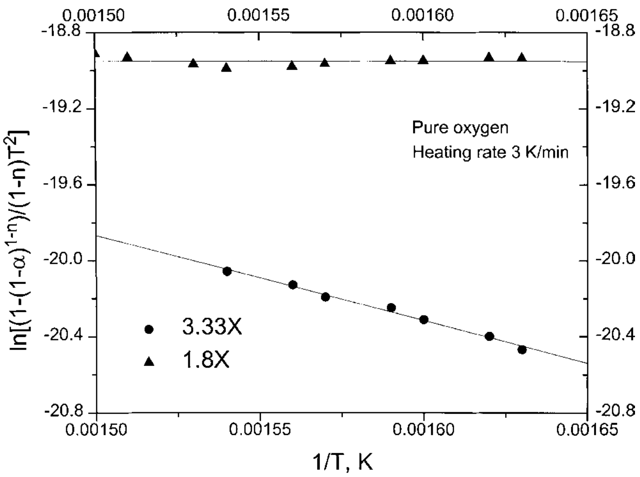

Fig. 12. Coats–Redfern plot for non-isothermal analysis of kinetic data of the salt roasting process under an oxygen amosphere in the temperature range 620–723 K.

versus $1/T$ should yield a straight line with a slope of $(-E/R)$ [3].

An analysis of the behavior of the function $\ln[1-(1-\alpha)^{1-n}]/(1-n)T^2$ with the reciprocal of temperature for salt roasting under an oxygen atmosphere showed two distinct linear regions of varying slope, one in the temperature range 523–620 K and the other in the range 620–723 K. The plots for both these temperature ranges are depicted in Figs. 11 and 12, respectively. It was observed that this function showed a small variation with the salt concentration. In the temperature range 523–620 K, the activation energy derived from the slope of the plot was found to be 151.8 kJ/mol for 3.33 times stoichiometric KCl and 175 kJ/mol for 1.8 times stoichiometric KCl. An activation energy of 77 kJ/mol was earlier derived from isothermal experiments for the salt roasting of chalcopyrite with 1.8 times stoichiometric KCl under a flowing oxygen atmosphere [1]. For the temperature range 620–723 K, although the Coats–Redfern plot conformed to interfacial reaction control model, the activation energy derived from the plot was very low. With 1.8 times stoichiometric KCl, the activation energy was found to be less than 0.5 kJ/mol and with 3.33 times stoichiometric KCl, the activation energy was derived to be 37 kJ/mol.

4. Conclusions

The salt roasting of chalcopyrite using KCl under oxygen and static air atmosphere was studied by non-isothermal thermoanalytical studies. Both, smaller mean particle size as well as higher heating rates accelerated the salt roasting reaction. Under pure oxygen atmosphere, the amount of salt does not alter the chemistry of the process, although the peak positions shift to higher temperature with increase in salt content. Under a static air atmosphere, the reaction rates were not appreciable at lower salt concentrations. The integral method of Coats and Redfern was used for the treatment of non-isothermal kinetic data. The non-isothermal analysis confirmed the chemical control mechanism at temperatures below 620 K. The activation energy for the process derived from non-isothermal thermogravimetric analysis is almost twice (175 kJ/mol) as that deduced from isothermal measurements (77 kJ/mol) in the temperature range 523–620 K. In the temperature range 620–723 K, although the reaction mechanism conformed to the interfacial reaction control model, the activation energy of the process was very low. These conclusions are qualitatively consistent with those deduced from the isothermal kinetic studies reported earlier.

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