INVESTIGATION OF MECHANISM AND KINETICS OF CHALCOPYRITE CONCENTRATE OXIDATION PROCESS

The oxidation process of chalcopyrite concentrate ″Rudnik″ (Serbia) was investigated by DTA-TG measurements under air conditions in the temperature range of 298 – 1173 K, as well as by XRD analysis of the oxidation products at 723, 873 and 1173 K. Based on the results obtained, the mechanism of chalcopyrite concentrate oxidation process was given, contributing to the understanding of the successive chemical reactions accompanying the formation of intermediate products. The kinetic study of the investigated process was done according to the methods of Kissinger and Ozawa, which enabled determination of the activation energy values of the chemical reactions proceeding during the chacopyrite concentrate oxidation.

Key words: chalcopyrite, oxidation, DTA-TG, XRD, kinetics

Istraživanje mehanizma i kinetika procesa oksidacije halkopiritnog koncentrata. Proces oksidacije halkopiritnog koncentrata ″Rudnik″ (Srbija) ispitivan je DTA-TG mjerenjima u atmosferi zraka i temperaturnom intervalu 298–1173 K, kao i XRD analizama produkata oksidacije na 723, 873 i 1173 K. Na temelju dobijenih rezultata predložen je mehanizam oksidacije halkopiritnog koncentrata uključujući i kemijske reakcije koje prate stvaranje odgovarajućih međuproizvoda. Za ispitivanje kinetike procesa rabljene su metode Kissinger i Ozawa, kojima su određene vrijednosti energija aktivacije kemijskih reakcija tokom oksidacije halkopiritnog koncentrata.

Ključne riječi: halkopirit, oksidacija, DTA-TG, XRD, kinetika

INTRODUCTION

The roasting of chalcopyrite, the most exploited copper mineral, presents a very important step in the copper extraction during the traditional smelting-refining process, as well as in advanced processes in copper metalurgy [1-2].

Consequently, numerous researches have been investigated, in order to study the chalcopyrite oxidative roasting parameters, its mechanism and reactions involved [1-16]. These references deal with pure chalcopyrite mineral oxidation and with the oxidation process of chalcopyrite concentrates, also. Although there are slight differences in the sequence of phase changes occurring in Cu-Fe-S-O system [1, 5, 6, 10], following main reactions proceed during the roasting of chalcopyrite as suggested in [1]:

$$2CuFeS_2 + 7.5O_2 \rightarrow 2CuSO_4 + Fe_2O_3 + 2SO_2 \qquad (1)$$

$$2CuFeS_2 \rightarrow Cu_2S + 2FeS + S \qquad (2)$$
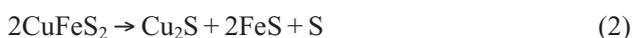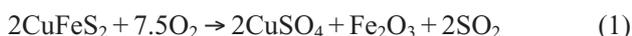
Meunier at al. [3] studied the behaviour of pieces of chalcopyrite in a stream of air at 573-1173 K. At the temperature of 773 K a layer of bornite surrounded by Fe_2O_3 and $CuSO_4$ was found. At 1073 K, CuO and

Fe_2O_3 with $CuFe_2O_4$ were formed. From sulphide ores, the formation of copper sulphate was also reported [4]. Heating in presence of air at 773-823 K transforms the sulphides to sulphates and oxides at higher temperature, which was confirmed by microscopic studies.

The complexity of the chalcopyrite oxidation process makes this topic still an interesting one, due to the number of reactions being occured simultaneously and frequently influencing one another. As a contribution to the better knowledge of this process, the mechanism and kinetics of the oxidation process of chalcopyrite concentrate from "Rudnik" mine (Serbia), using comparative analysis of data obtained by DTA-TG measurements and XRD of oxidation products at selected temperatures, are presented in this paper.

EXPERIMENTAL

The chalcopyrite concentrate from "Rudnik" mine (Serbia), having chemical composition presented in Table 1, was used for experimental investigation.

Participation of the main minerals in the concentrate is shown in Table 2.

DTA and TG measurements were carried out using a thermal analyser NETZSCH STA 409 EP. Chalcopyrite samples of 100 mg were used and recordings were car-

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Table 1. **Chemical analysis of the chalcopyrite concentrate**

Element	Cu	Zn	Pb	Fe
wt / %	27,97	3,93	2,67	27,47

Table 2. **Mineralogical composition of the chalcopyrite concentarate**

Mineral	$CuFeS_2$	ZnS	PbS	FeS_2	other
wt / %	80,76	5,85	3,08	7,86	2,45

ried out in air atmosphere, at heating rates 2, 5, 10, 15 and 20 °/min, over the temperature range 298 – 1173 K. Alumina was used as a reference material.

X-ray analysis was performed to determine the phase composition of the intermediate products formed during the chalcopyrite oxidation. The PHILIPS X-ray diffractometer, model PW-1710, with graphite-monochromatized CuK_α radiation (λ=1.54178 Å) was used. Diffraction patterns were recorded in $0,02\theta$ 2è intervals, 0,25 s sampling time and over a range 4° - 70° 2θ.

RESULTS AND DISCUSSION

The results of DTA-TG measurements for the oxidation process of investigated chalcopyrite concentrate from „Rudnik" mine, obtained at diferent heating rates, are presented in Figures 1 and 2.

The DTA curves, recorded at different heating rates, have similar shape, as their peaks are gradually shifted to the higher temperatures with increasing the heating rate from 2 to 20 °/min. Also, each DTA curve consists of two parts - the first, at lower temperatures, corresponds to the sulphides oxidation process and includes three exothermic peaks, while the second involving endothermic peaks, corresponds to the dissociation of the previously formed sulphates and copper oxy-sulphate.

The DTA curves, given in Figure 1, show that oxidation of the chalcopyrite surface layers, depending on the
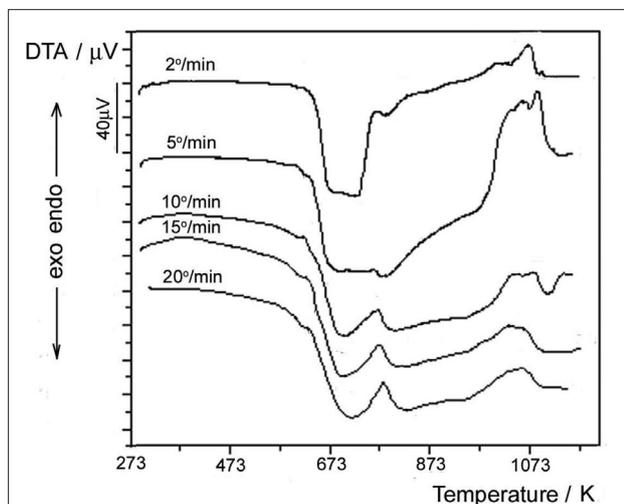
Figure 1. DTA curves of chalcopyrite concentrate oxidation at different heating rates
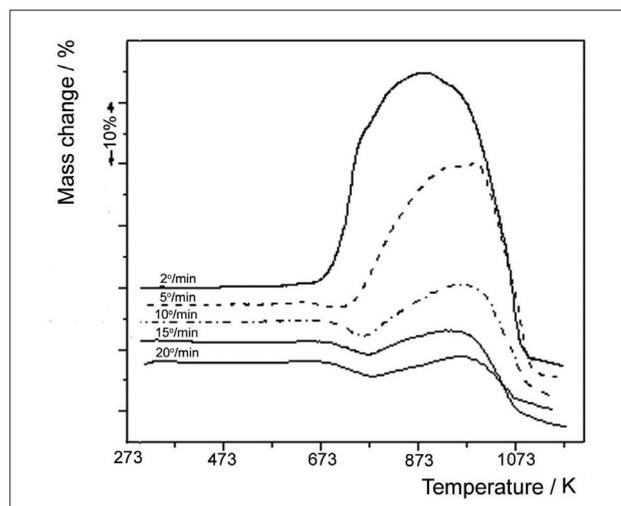
Figure 2. TG curves of chalcopyrite concentrate oxidation at different heating rates

heating rate, begins at 603-630 K, as indicated by the small exothermic peak at such temperatures, without a noticable mass change on the TG curves:

$$2CuFeS_2 + O_2(g) \rightarrow Cu_2S + 2FeS + SO_2(g) \qquad (3)$$
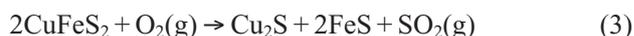
This is followed immediately by a distinct exothermic peak with a maximum on the DTA curves in the temparature interval 677-713 K, accompanied by a decrease in the sample mass, which reflects intensive oxidation of the inner layers of the chalcopyrite sample and the simultaneous dissociation of the pyrite present in the sample:

$$2CuFeS_2 + O_2(g) \rightarrow Cu_2S + 2FeS + SO_2(g)$$

$$2FeS_2 + 2O_2(g) \rightarrow 2FeS + 2SO_2(g) \qquad (4)$$

This stage of the process is manifested by a decrease in the sample mass of about 3 % due to the released elemental sulphur.

On further heating, the sample mass starts increasing and the medium exothermic peaks with maximum for different heating rates in the temperature range 775-828 K are observed in the DTA curves. In this stage of the roasting process, iron sulphate, copper sulphate and copper oxy-sulphate are formed, which can be sumarised as:

$$FeS + 2O_2(g) \rightarrow FeSO_4$$

$$Cu_2S + SO_2(g) + 3O_2(g) \rightarrow 2CuSO_4 \qquad (5)$$

$$2Cu_2S + 5O_2(g) \rightarrow 2CuO \cdot CuSO_4$$
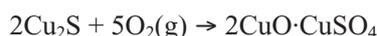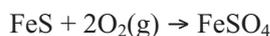
With further rise of temperature, the dissociation of iron sulphate begins which reflects thrugh the slower mass growth on the TG curve and the weak endothermic peak with maximum in the temperature range 827-886 K, depending on the heating rate:

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2(g) + SO_3(g) \qquad (6)$$
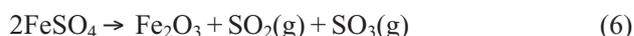
At the temperatures above 1023 K, the dissociation processes of the previously formed sulphates start:

$$CuSO_4 \rightarrow CuO + SO_3(g) \qquad (7)$$

$$CuO \cdot CuSO_4 \rightarrow 2CuO + SO_3(g) \qquad (8)$$
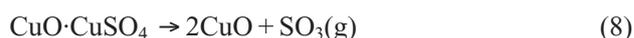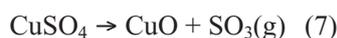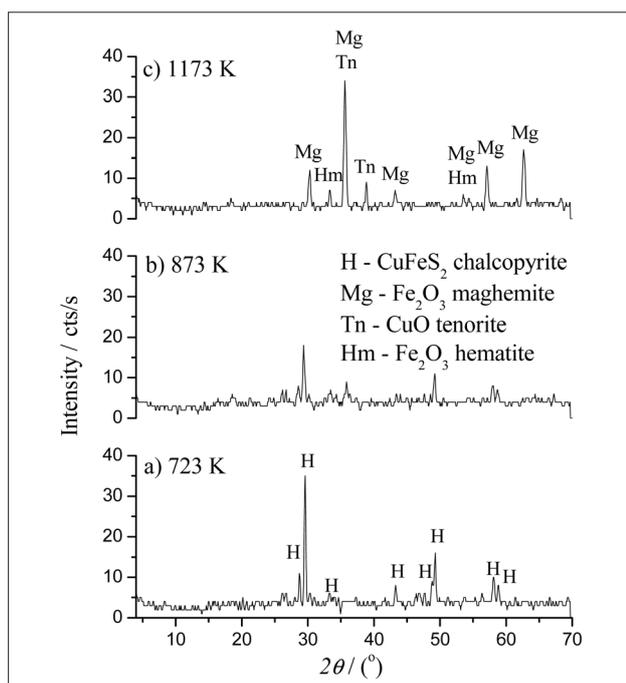
Figure 3. X-ray recordings of the chalcopyrite concentrate oxidation products at 723 K (a), 873 K (b) and 1173 K (c)

Figure 4. The Kellogg diagrams for Cu-S-O (a) and Fe-S-O (b) systems at the temperatures typical for oxidation roasting process - 723, 873 and 1273 K [15]

which is manifested by the two endothermic peaks on the DTA curves and a mass loss on the TG curves at such temperatures. At the lowest heating rate of 2 °/min, the peaks corresponding to the copper sulphate and the copper oxy-sulphate dissociation are clearly separate with the maximums at 1026 and 1073 K, respectively. With increasing the heating rate, the dissociations of copper sulphate and copper oxy-sulphate start to proceed simultaneously in some degree and consequently their peaks begin to overlap.

XRD recordings of the oxidation products at 723, 873 and 1173 K are presented in Figure 3. It should be stated that the sulfates and sulfides formed during the oxidation are not registered on the X-ray recordings, probably due to the insufficient time for their crystallization.

The results shown in Figure 3 confirm the above proposed mechanism of the oxidation process and the obtaining of Fe_2O_3 and CuO as the final products of investigated chalcopyrite concentrate oxidation, which is also in accordance with theoretical, thermodynamic considerations - Kellog diagrams (Figure4) constructed for the systems Cu-S-O and Fe-S-O at investigated temperatures.

The complex mechanism of the oxidation process of chalcopyrite concentrate from „Rudnik" mine (Serbia), involving numerous reactions and some of them proceed simultaneously, shows certain similarity with literature data [2, 8, 10, 19]. But, nature and origin of the starting and its associated impurity constituents have significant influence on the phase transformation in thermal treatment of sulphides.

Apart from the sequence of reactions during the roasting, it is important to know which reaction controls the rate of conversion, and thus a kinetic study is critical for the process. Therefore, the kinetic analysis of DTA data, obtained in this work for different heating rates in the range from 2 to 20 ^{o}min^{-1}, was performed using Kissinger [17] and Ozawa [18] methods, which can be represented by following expressions:

– Kissinger method [18]:

$$ln\,(\o\,/Tm^2) = C_1 - Ea/RTm \qquad (9)$$

– Ozawa method [19]:

$$ln\,\o = C_2 - Ea/RTm \qquad (10)$$

where ø is heating rate (in ° min^{-1}); Tm is absolute maximum temperature on DTA curve (K); Ea is activation energy of the process (kJ mol^{-1}); C_1, C_2 are integration constants and R is universal gas constant, 8.314 J K^{-1} mol^{-1}.

The peaks of maximum temperature (Tm) as a function of heating rate for the processes (5)-(8), given in Figure 5, show that the increase in heating rate shifts the maximum temperature Tm to a higher value. Due to the overlaping, it is not possible to determine the maximum temperature (Tm) of the copper sulphate and the copper oxy-sulphate dissociation peaks, so the processes (9) and (10) were eliminated from the kinetic consideration.

From the slopes of both, the plot of $ln\,(\o/Tm^2)$ versus $1/Tm$ for Kissinger method (Figure 6) and the plot of $ln\o$ versus $1/Tm$ for Ozawa method (Figure 7), the activa-
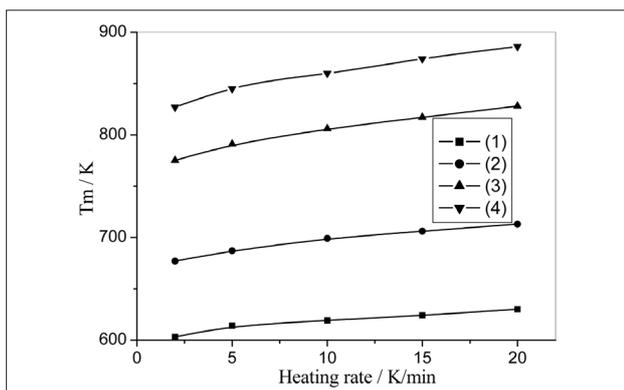
Figure 5. Dependence of *Tm* on heating rate for the processes (5) – (8) occuring during the chalcopyrite concentrate oxidation

tion energy values for the processes (5) – (8) were calculated and presented in Table 3.

Relatively high values of activation energy, calculated from DTA experiments using Kissinger and Ozawa methods, indicate that the processes (5) – (8) during the chalcopyrite concentrate oxidation proceed in the kinetic area.
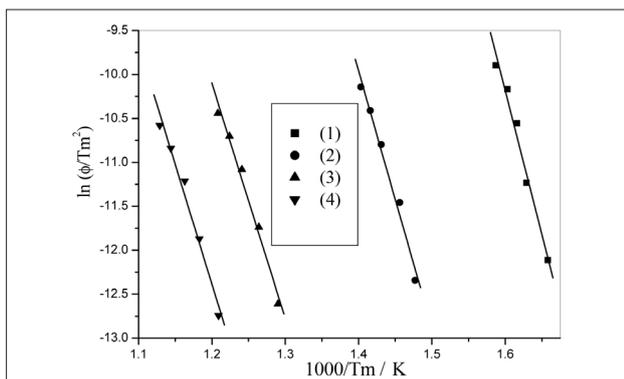
Figure 6. Linear correlation between *ln (ø/Tm²)* and *1/Tm* for the processes (5) – (8) occuring during the chalcopyrite concentrate oxidation
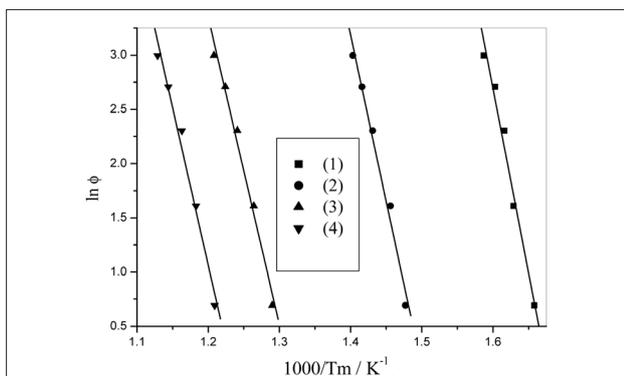
Figure 7. Linear correlation between *ln ø* and *1/Tm* for the processes (5) – (8) occuring during the chalcopyrite concentrate oxidation

The comparison between the kinetic parameters obtained in this work and literature [1, 2, 10] indicate to weaker agreement for some reactions, which may be expected considering that roasting kinetics follow differ-

Table 3. Ea values determined by Kissinger and Ozawa methods for the processes (1)–(4)

Process	Ea / kJ mol⁻¹	
	Kissinger method	Ozawa method
1	272	282
2	243	254
3	222	235
4	227	241

ent models - depending on the conditions, particle size, atmosphere, reacting gases, temperature, type of bed used, complexity of the starting sulfide concentrate, presence of other sulfides, etc.

Oxidation roasting is an important technique in order to recover copper from chalcopyrite. Products, such as copper oxide or sulphate, can be preferentially obtained by applying knowledge of the thermodynamics of the M-S-O system and choosing appropriate roasting conditions - temperature, oxidising gases, additives etc. [1] Further efforts may be directed towards the use of catalytic promoters and gaseous mixtures which can control the kinetics and permit the reactions to proceed at lower temperatures with high yield, but most of all having in mind environmentally competitivness of the roasting processes .

CONCLUSION

The comparative DTA and TG analyses of the chalcopyrite concentrate oxidation in air indicate complexity of the process, i.e., the process occurs through a number of reactions accompanied by the formation of the intermediate products. XRD of the oxidation products shows that the chalcopyrite concentrate oxidation leads to the obtaining of Fe_2O_3 and CuO as the final products at 1173 K.

DTA curves recorded at different heating rates display the exothermic peaks at lower temperatures, corresponding to the sulphides oxidation to sulphates and the endothermic peaks at temperatures above 823 K, representing the dissociation of the previously formed sulphates.

The maximum temperatures of the peaks were taken for the kinetic calculation which was performed using Kissinger and Ozawa methods. The values of activation energy for the processes occuring during the chalcopyrite concentrate oxidation range from 222 to 272 kJ mol⁻¹ (Kissinger method) and from 235 to 282 kJ mol⁻¹ (Ozawa method). The ralatively high values of activation energy indicate that the chalcopyrite concentrate oxidation process occurs in the kinetic area.

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Note: The Author M. Sokic is responsible for English language in the Article.