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Kinetics of the oxidation process in the system Zn–Fe–S–O[1]

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Abstract

The process of roasting marmatite and marmatite concentrate was investigated experimentally. Results obtained by DTA under non-isothermal conditions were used for determining kinetic parameters for the oxidation process in the system Zn–Fe–S by using Kissinger and Ozawa methods. The activation energy for the marmatite concentrate oxidation process is 187 and 194 kJ/mol, according to the Kissinger and Ozawa methods, respectively. In the case of the pure mineral marmatite, the corresponding values for activation energy are 69 and 86 kJ/mol. Mineralogical characterization was done by X-ray analysis, which enabled determination of the phases that were present during the oxidation process. © 1998 Elsevier Science B.V.

Keywords: Kinetics; DTA; Marmatite; Oxidation process; X-ray analysis

1. Introduction

In recent times, the availability of zinc concentrates with higher marmatite content has required more complete investigation of the oxidation process of marmatite. This is of both theoretical and practical interest for continued treatment in existing hydrometallurgical plants for zinc production, because the oxidative roasting of sulfide concentrates precedes the leaching process.

Available literature data about the process of oxidatively roasting zinc concentrates in the extractive metallurgy of zinc, deals with theoretical and practical aspects [1–12]. In the research works of R. Dimitrov and collaborators [1–8], kinetics and mechanism of zinc concentrates oxidative roasting are elaborated in detail. Mentioned data are mostly related to the investigation of sphalerite concentrate oxidation [9–12], except one that refers to marmatite oxidation [8].

As a contribution to the better knowledge of the oxidation of marmatite, kinetics and mechanism of the processes in the system Zn–Fe–S–O were investigated and presented in this paper. Bearing in mind that marmatite concentrates are accompanied by a higher content of chalcopyrite and pyrite, their influence on the oxidation process of such a complex system must be taken into consideration [13,14].

2. Experimental

Simultaneous DTA-TG-DTG technique was used for the experimental investigations and was performed on a derivatograph MOM, Budapest. Identification of the phases formed during the investigated process was carried out on Siemens X-ray equipment with a Cu anode and Ni filter at a voltage of 40 kV and current of 18 mA. Samples were in the powder state.

Mineral marmatite from Stari Trg (Serbia, Yugoslavia) and marmatite concentrate from the industrial production in Majdanpek Flotation (Serbia, Yugoslavia) were used for the experimental investigations.

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Table 1
Chemical composition of the marmatite concentrate

Component	Zn	Fe	S	Pb	Cu	SiO_2	Cd	Ge	Sb	As	Mg	F
Content (wt%)	32	18	32	1.2	3.8	1.3	0.11	7	0.00	0.07	0.05	0.02

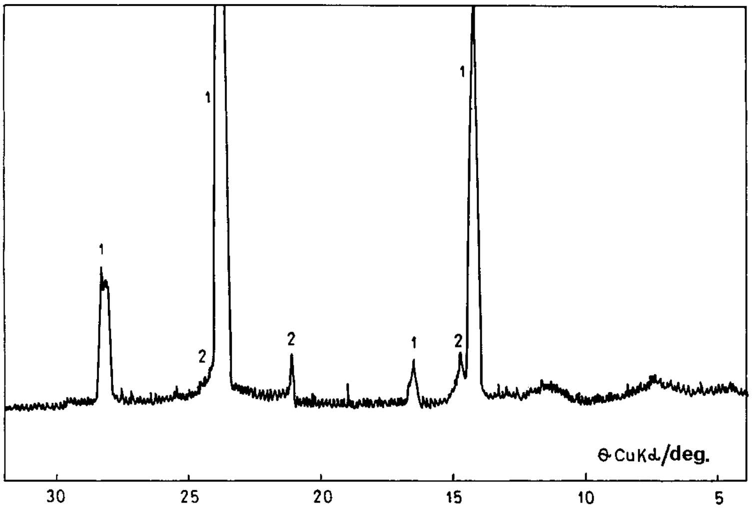

Fig. 1. X-ray diagram for the marmatite concentrate; (1) marmatite, (2) chalcopyrite.

Chemical composition of the marmatite concentrate, obtained by the standard chemical analysis methods, is given in Table 1. Particle size was the same in all cases investigated (−100+80 μm).

An X-ray diagram for the marmatite concentrate is shown in Fig. 1. It can be seen that, in the investigated concentrate, mineral marmatite has the dominant content (label 1 in Fig. 1), and that chalcopyrite – as the main copper bearer (label 2 in Fig. 1) – is also registered.

3. Results and discussion

During the oxidative roasting of such a complex system, numerous processes are occurring. A phase stability diagram for characteristic sulfides at temperature 1300 K, typical for the oxidative roasting process, was constructed on the basis of the known thermodynamic values for reactions in systems Me–S–O (Me=Zn–Fe–Cu–Pb–Ni) and shown in Fig. 2. For SO_2 partial pressure of 10^4 Pa, which is common under the industrial conditions [15], the following

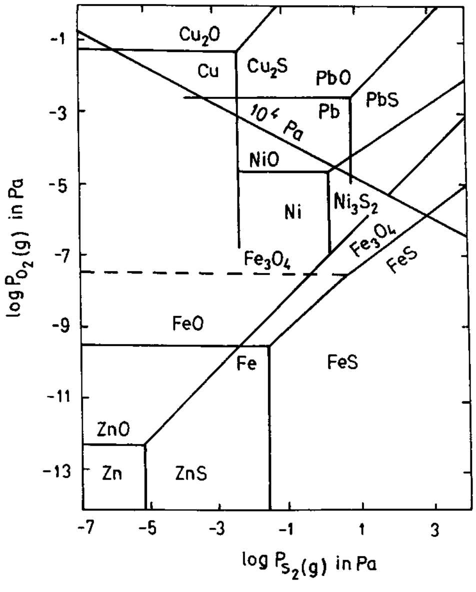

Fig. 2. $\log ps_2 = f(\log po_2)$ for different sulfides at 1300 K. Stability diagram calculated from known thermodynamic data.

order for sulfide oxidation is obtained. FeS–ZnS–PbS–Ni_3S_2–Cu_2S.

The X-ray analysis confirmed the presence of numerous phases (ZnO, $ZnFe_2O_4$, $ZnSO_4$, ZnO, $ZnSO_4$, CuO, $PbSO_4$, SiO_2, $CaSO_4$, etc.) in the samples obtained by roasting different concentrates.

During the marmatite roasting:

$$2(\mathrm{Zn,Fe})\mathrm{S} + 4.5\mathrm{O}_2 = \mathrm{ZnO} + \mathrm{ZnFe}_2\mathrm{O4} + 2\mathrm{SO}_2 \qquad (1)$$

the probability of zincferrite formation is greater Zn and Fe are already present in the same crystal lattice. Under the conditions of an oxidative roasting of marmatite concentrate, the following reaction is also possible [16]:

$$\mathrm{ZnFe}_2O_4 + \mathrm{CuO} = \mathrm{Cu}_x\mathrm{Zn}_{1-x}\mathrm{Fe}_2O_4 + x\mathrm{ZnO} + (1-x)\mathrm{CuO} \qquad (2)$$

where $0 \leq x \leq 1$. At elevated temperatures, decomposition of zincferrite with other oxides is possible by the general reaction:

$$\mathrm{ZnFe}_2\mathrm{O}_4 + \mathrm{MeO} = \mathrm{MeFe}_2\mathrm{O}_4 + \mathrm{ZnO}, \qquad (3)$$

but this reaction occurs to only a limited extent under industrial conditions, because of the roasting temperature.

Kinetics of the marmatite and marmatite concentrate oxidation were investigated by DTA. The DTA curves were obtained at different heating rates: 2.5, 5, 10 and 20°C min^{-1} and are presented in Figs. 3 and 4. All investigations were carried out in air.

In Fig. 3 and Fig. 4, which show DTA curves for marmatite and marmatite concentrate respectively, the exothermic peak at 350°C–400°C, corresponds to the pyrite oxidation process [14]. In the temperature interval 550°C–900°C, a weakly defined peak corresponding to the marmatite oxidation is noticed. This peak is obviously composed of two parts, where the first part corresponds to FeS oxidation and the other to ZnS oxidation. For confirmation of this statement, some additional investigation is needed. Mean values of the peak maxima were taken for the kinetic calculation, so results obtained must be considered as approximate. The differences in DTA curves in Fig. 3 and Fig. 4 exist because of the differences in the chemical composition of the samples investigated (pure mineral marmatite and marmatite concentrate).

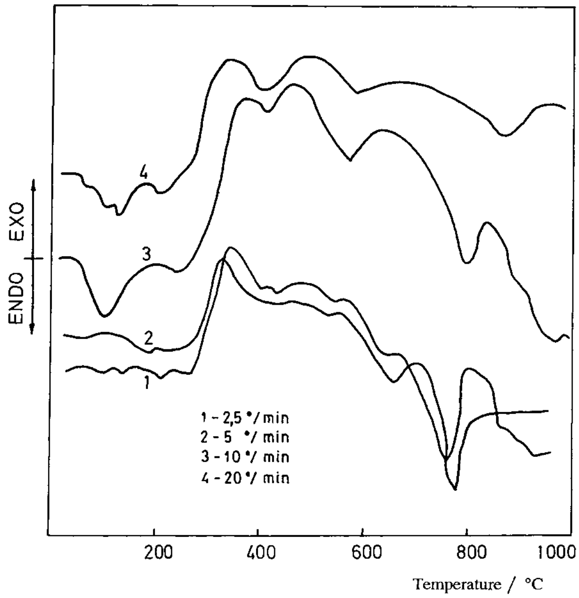

Fig. 3. DTA curves for marmatite at different heating rates

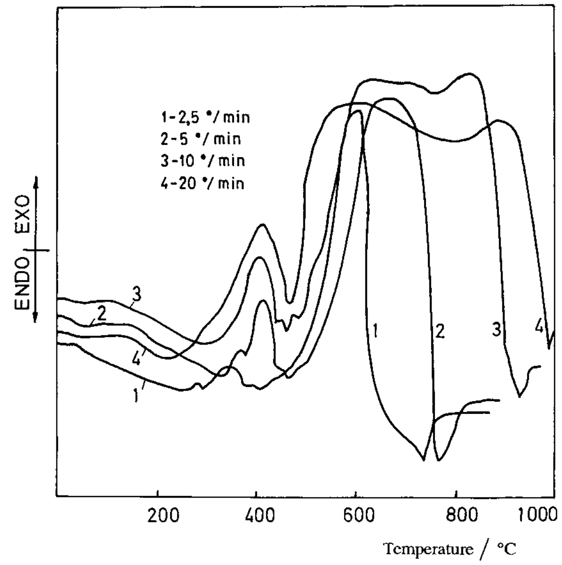

Fig. 4. DTA curves for marmatite concentrates at different heating rates

Based on results shown in Fig. 3 and Fig. 4, dependence of the maximum temperature (T_m) on a heating rates for the oxidation process is given in Fig. 5.

For the kinetic elaboration of the obtained DTA results DTA results, Kissinger and Ozawa methods

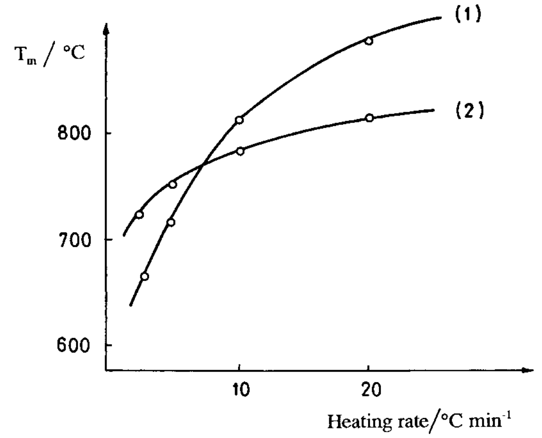

Fig. 5. Dependence of T_m on heating rate for the oxidation process of marmatite (1) and marmatite concentrate (2)

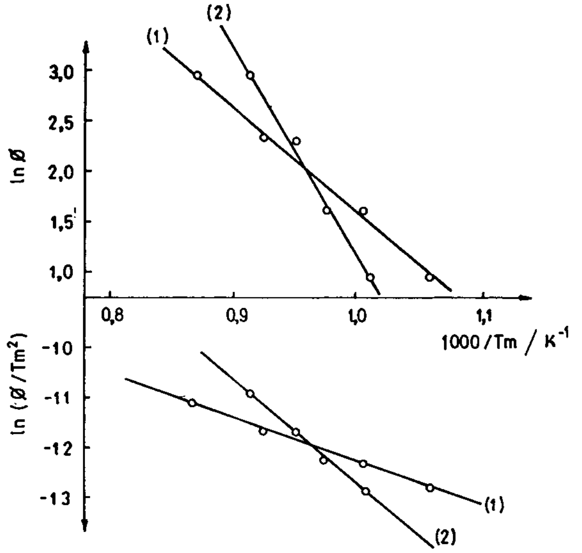

Fig. 6. Dependencies $\ln(\phi/T_m^2) = f(1/T_m)$ and $\ln\phi = f(1/T_m)$ for the oxidation process of marmatite (1) and marmatite concentrate (2)

were used, according to the following approximate relations:

(a) Kissinger method [17]:

$$\ln(\phi/T_m^2) = C - E_a/RT_m \tag{4}$$

(b) Ozawa method [18]:

$$\ln\phi = C_1 - E_a/RT_m \tag{5}$$

where: ϕ is heating rate, T_m is temperature of maximum on DTA curve, E_a is activation energy of the process, R is the universal gas constant and C, C_1 are integration constants.

Considering Eqs. (4) and (5), dependencies $\ln(\phi/T_m^2) = f(1/T_m)$ and $\ln\phi = f(1/T_m)$ are obtained for the oxidation process of marmatite and marmatite concentrates, and are shown in Fig. 6. From the slopes of the lines in Fig. 6, values for the activation energies of the investigated processes were determined, as well as the values for constants C and C_1. These results are presented in Table 2.

X-ray diagrams for the initial marmatite concentrate, as well as for the products formed during the roasting process at 298 K, 683 K, 973 K and 1273 K are presented in Fig. 7.

The results show that the oxidation process of marmatite and marmatite concentrate occurs in the kinetic field, which means that temperature has the dominant influence on the rate of the process. Higher values for the activation energy in the case of the marmatite concentrate compared to the pure marmatite are the consequence of the following two factors: (a) smaller particles of concentrate produced by the flotation concentration, and (b) the presence of chalcopyrite, which oxidises to form copper (II) oxide; this oxide destroys zinc ferrite (reaction (2)) and moves the reaction equilibrium towards marmatite oxidation. Copper ferrite which is formed according to reaction (2) is registered by chemical analysis; however it is not defected by X-ray diffraction probably due to its amorphous state (because low temperatures and short time preclude full crystallization).

Table 2
Calculated values for the activation energy and integration constants for the oxidation process of marmatite and marmatite concentrate

Process	Marmatite oxidation		Marmatite concentrate oxidation	
Kinetic parameters	E_a/kJ mol^{-1}	C	E_a/kJ mol^{-1}	C_1
Kissinger method	69	0.47×10^2	187	1.6×10^5
Ozawa method	86	1.6×10^4	194	3.9×10^4

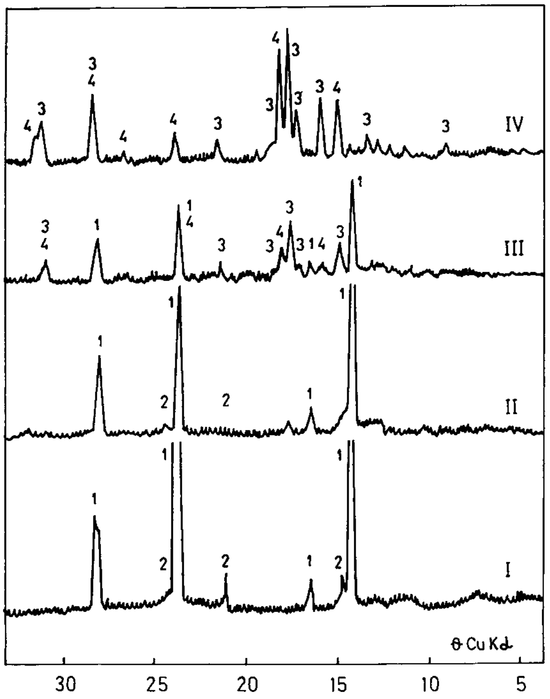

Fig. 7. X-ray diagrams for the marmatite concentrate at different temperatures: (I) 298 K; (II) 683 K; (III) 973 K; (IV) 1273 K. Phases: (1) (Zn, Fe)S; (2) $CuFeS_2$; (3) $ZnFe_2O_4$; (4) ZnO.

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