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THERMAL ANALYSIS AND KINETICS OF THE CHALCOPYRITE-PYRITE CONCENTRATE OXIDATION PROCESS

The paper presents the results of experimental investigation of the chalcopyrite-pyrite concentrate oxidation in the air. Characterisation of the initial sample and oxidation products was done by ICP-AES, XRD, EDXRF methods. Phase stability diagrams were constructed for Cu-Fe-S-O system at 25, 450, 650 and 900 °C. Equilibrium composition of the charge for the optimal oxidation process was calculated. DTA-TG analysis was used for monitoring the oxidation process. Kinetic parameters in non-isothermal conditions were determined, based on Kissinger and Ozawa methods. Values of activation energies showed that all stages of the oxidation process occur in the kinetic field.

Key words: thermal analysis, copper concentrate, oxidation

INTRODUCTION

Although many investigations were done in the field of Cu-Fe-S-O system [1-5], and chalcopyrite, as the most used sulphide copper mineral in pyrometallurgical copper production, has been theoretically and experimentally studied by various authors [6-14], there is still lack of knowledge about thermal characteristics and kinetic behaviour of low grade polymetallic copper concentrates.

For the purpose of better understanding of the thermodynamic characteristics, kinetic parameters and reaction mechanisms during oxidation, polymetallic chalcopyrite-pyrite concentrate and its oxidation products were subjected to comparative analysis based on data obtained from chemical analysis, PSD, XRD, EDXRF, and DTA/TG measurments at certain temperatures. The equilibrium composition diagram of the investigated concentrate was calculated depending on the gas temperature at gas vs. charge molar ratio of 20:1.

Kinetic parameters and activation energies for characteristic stages of the oxidation process in non-isothermal conditions were determined, based on Kissinger and Ozawa methods.

EXPERIMENTAL

Chalcopyrite-pyrite concentrate from Bor mine (Serbia), with chemical composition given in Table 1, was used for the investigation. Chemical analysis was done by ICP-AES, AAS and electrogravimetry. XRD was done on X-ray diffractometer "Phillips" PW 1710,

with a curved graphite monochromator and a scintilarion counter on polycrystalline powder samples. X-rays intensity CuKα (λ = 1,54178 Å) was measured at room temperature at 0,02 ° 2θ intervals and time 0,5 second, in the range 4 – 65 ° 2θ. X-ray tube was loaded with 40 kV voltage and 30 mA current. XRD analysis was done for the initial sample, and for samples roasted one hour at 450, 650 and 900 °C. EDXRF spectroscopy of the initial sample of 0,50 g was done on spectrometer „Canberra", with radioisotopes Cd-109 (22,1 keV) and 33 seconds measurement duration.

DTA/TG analysis was done on thermal analyzer "Netzsch" STA 409 EP on a sample of 100 mg, under heating range 25 – 1 000 °C in the air atmosphere, at heating rates 5, 10, 15 and 20 °C min^{-1}.

Table 1 **Chemical composition of initial concentrate sample / wt %**

Chemical composition / wt %				
Cu	Fe	S	Zn	Pb
15,84	33,19	35,80	0,88	0,062
Cd	Sb	Ni	As	Hg
0,0011	0,016	0,032	0,0084	0,00005

RESULTS AND DISCUSSION

EDXRF spectrum of the initial chalcopyrite-pyrite concentrate sample is given in Figure 1. Intensive reflections for Cu and Fe and detection of S, Zn and Pb are in consistency with chemical analysis results.

Phases in Cu-Fe-S-O system at 25, 450, 650 and 900 °C, according to PSD diagrams, are given in Figure 2. Results of X-ray phase analysis of the initial sample and oxidation products at 450, 650 and 900 °C is given in Figure 3.

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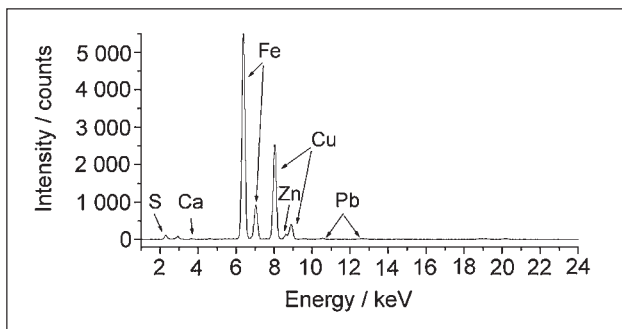
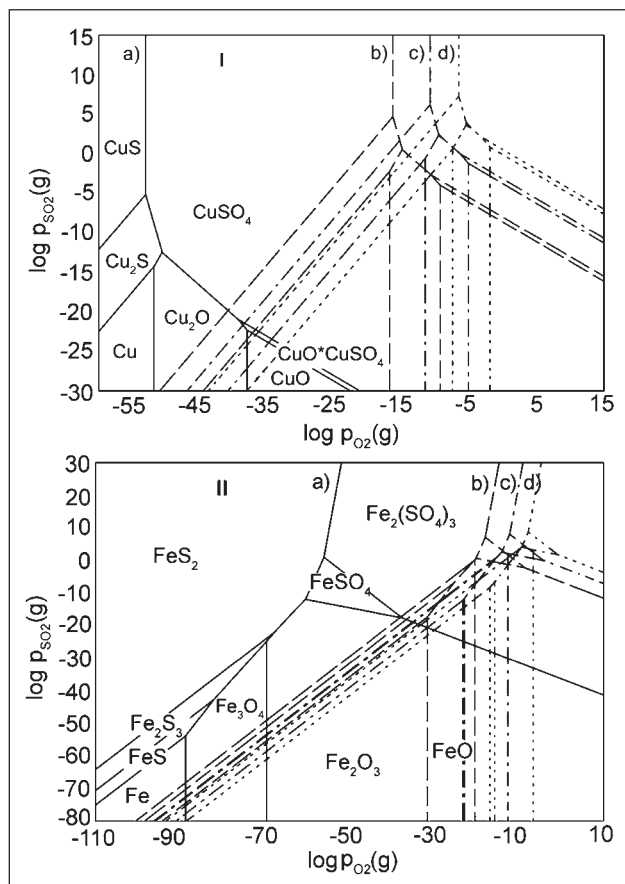**Figure 1** EDXRF elemental analysis of the initial concentrate sample

Figure 2 Phase stability diagrams for the Cu-S-O system (I) and Fe-S-O system (II) at 25 °C (a), 450 °C (b), 650 °C (c) and 900 °C (d)

Figures 2 and 3 indicate that in the given temperature range, during heating in the air atmosphere, at lower temperatures, in the Cu-Fe-S-O system (i.e. investigated copper concentrate) present sulphides (chalcopyrite, pyrite and bornite) oxidize into sulphates and oxysulphates (chalcocyanite and dolerophanite), while at higher temperatures those phases decompose into oxides (tenorite, hematite and magnetite). In the formed calcine at 900 °C, copper ferrite ($CuFe_2O_4$) is found, as a result of native solid phase diffusion of chalcopyrite into spinel form ferrite. This phase occurs inside of grains, through the intermediate phases $CuSO_4$, Fe_3O_4, CuO and Fe_2O_3 [14-16].

Comparative DTA and TG results at different heating rates are given in Figures 4 and 5. The DTA curves
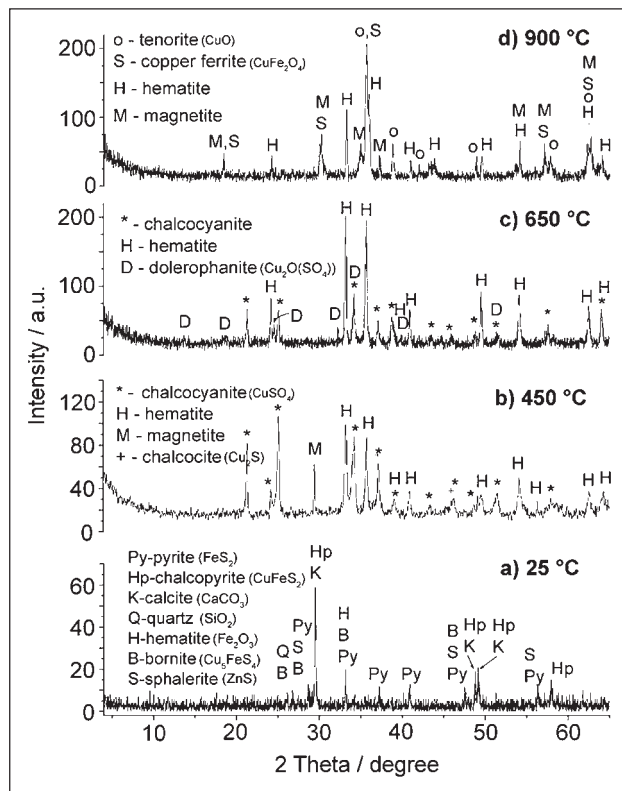

Figure 3 Diffractograms of the initial sample (a) and the oxidation products at 450 °C (b), 650 °C (c) and 900 °C (d)

are similar in shape, while the peaks shift to higher temperatures with the heating rate increase.

Heating from 40 °C to 138 °C corresponds to moisture loss (mass decrease in TG curve and an endothermic peak in the DTA at 107 °C). In the interval 173 - 261 °C, pyrite starts oxidizing (mass loss on TG curve and the DTA exothermic peak at 248 °C) according to following reactions:

$$FeS_2 + O_2(g) \rightarrow FeS + SO_2(g) \qquad (1)$$

$$S_2 + 2O_2(g) \rightarrow 2SO_2(g) \qquad (2)$$

In the interval 275 - 596 °C, FeS further oxidizes forming $FeSO_4$, Fe_3O_4 and Fe_2O_3, which is followed by
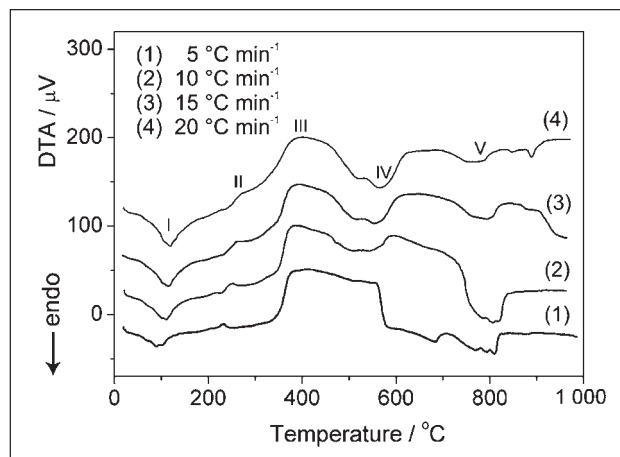

Figure 4 DTA curves for the oxidation process of the chalcopyrite-pyrite concentrate at different heating rates
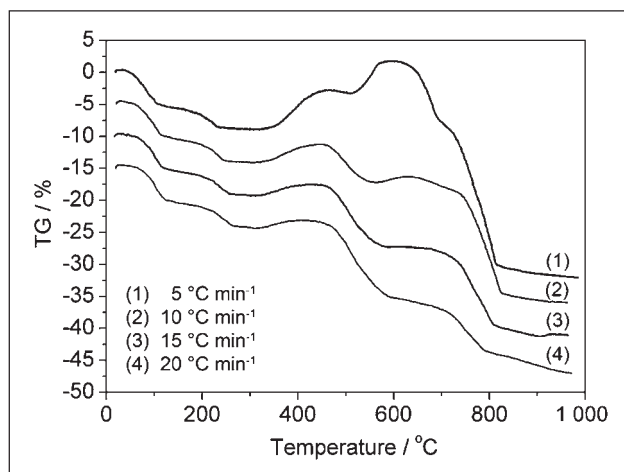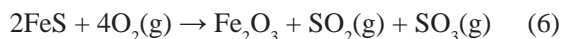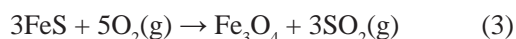
Figure 5 TG curves for the oxidation process of the chalco-pyrite-pyrite concentrate at different heating rates

mass increase on TG curve in the range 275 - 393 °C. At the same time, chalcopyrite and bornite decompose into Cu_2S, $FeSO_4$, Fe_3O_4 and Fe_2O_3, which is accompanied by a mass decrease on TG curve in the range 423 - 564 °C. These processes can be described by reactions (3-8):

$$3FeS + 5O_2(g) \rightarrow Fe_3O_4 + 3SO_2(g) \qquad (3)$$

$$FeS + 2O_2(g) \rightarrow FeSO_4 \qquad (4)$$

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2(g) + SO_3(g) \qquad (5)$$

$$2FeS + 4O_2(g) \rightarrow Fe_2O_3 + SO_2(g) + SO_3(g) \qquad (6)$$

$$2CuFeS_2 + O_2(g) \rightarrow Cu_2S + FeS + SO_2(g) \qquad (7)$$

$$2Cu_5FeS_4 + O_2(g) = 5Cu_2S + 2FeS + SO_2(g) \qquad (8)$$

After chalcopyrite dissociation, formed FeS is oxidized according to the above reactions, then Cu_2S oxidizes into sulphates and oxysulphates, described by Eqs. (9-10). The reactions end at 620 °C, accompanied by the mass increase on TG curve and exothermic peak at 596 °C.

$$Cu_2S + SO_2(g) + 3O_2(g) \rightarrow 2CuSO_4 \qquad (9)$$

$$Cu_2S + 2,5O_2(g) \rightarrow 2CuO \cdot CuSO_4 \qquad (10)$$
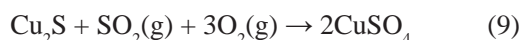
At 474 °C formed magnetite starts oxidizing into hematite by reaction:

$$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3 \qquad (11)$$
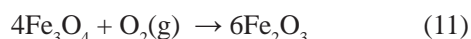
Above 700 °C magnetite is stable, so the part of hematite transforms into magnetite, according to Eq. 12:

$$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2(g) \qquad (12)$$
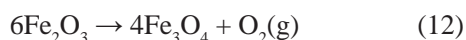
In the temperature range 714 - 847 °C, $CuO \cdot CuSO_4$ and $CuSO_4$ start decomposing into CuO, which is followed by mass loss on TG curve, with the maximum dissociation rate at 800 °C and endothermic peak at 806 °C on the DTA curve (Eqs. 13-14):

$$CuO \cdot CuSO_4 \rightarrow 2CuO + SO_3(g) \qquad (13)$$

$$CuSO_4 \rightarrow CuO + SO_3(g) \qquad (14)$$

Copper ferrite was identified on the diffractogram at 900 °C (Figure 3d), which is formed according to Eq. 15:

$$CuO + Fe_2O_3 \rightarrow CuFe_2O_4 \qquad (15)$$

For the equilibrium composition calculation, the initial conditions and condensed phases were defined according to chemical and XRD analysis results (Table 2). Gas pressure of 1 bar was taken for the calculation.

If the molar ratio of the gas and charge is 20 : 1, there is enough oxygen in the system for the oxidation of all present sulphides. Formed copper and iron sulphates are stable up to 600 °C, where their amount rashly decreases, on the account of Fe_2O_3 formation. Above 700 °C in the reaction products Fe_3O_4 is found. Copper sulphide is completely oxidized, and above 600 °C in the reaction products CuO is found, according to Figure 6.

Kinetic analysis was done using Kissinger [17] and Ozawa [18] methods, according to DTA results at heating rates 5, 10, 15 and 20 min. According to Figure 4, five peaks which describe certain process were taken into account for the activation energies calculation. Summary of results for the calculated activation energies are presented in Table 3.
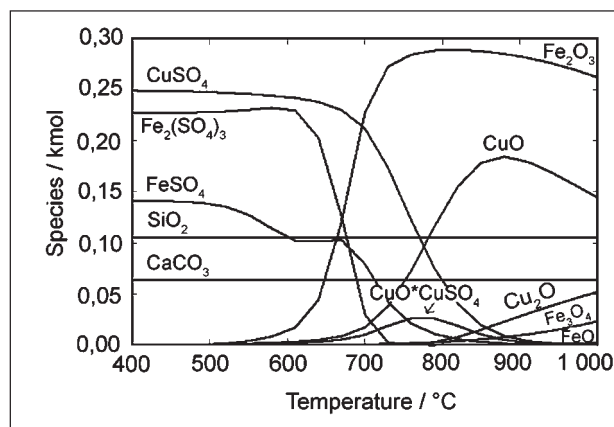

Figure 6 Calculated equilibrium composition diagram of the system in $CuFeS_2 + FeS_2 + CaCO_3 + SiO_2 +$ gas (71 % N_2, 19 % O_2, 10 % CO_2), depending on the gas temperature at molar ratio of 20 : 1 (gas : charge)

Table 2 **Initial conditions for equlibrium composition calculation**

Gas amount / kmole			Charge amount / kg	Gas vs. charge molar ratio
N_2 (g)	O_2(g)	SO_2(g)	41,56kg FeS_2; 45,78kg $CuFeS_2$; 6,33kg $CaCO_3$; 6,33 kg SiO_2	20 : 1
5,432 (71%)	1,453 (19%)	0,765 (10%)		
C o n d e n s e d p h a s e s				
Metals			Cu, Fe	
Sulphides			$CuFeS_2$, Cu_5FeS_4, CuS, Cu_2S, FeS, FeS_2	
Oxides, sulphates, oxysulphates, ferrites, carbonates			CuO, Cu_2O, $CuO \cdot CuSO_4$, $CuSO_4$, Cu_2SO_4, FeO, Fe_2O_3, Fe_3O_4, $FeSO_4$, $Fe_2(SO_4)_3$, SiO_2, $CaCO_3$	

Table 3 **Activation energy values for the chalcopyrite-pyrite oxidation process**

Peak	E_a / kJ mole^{-1}	
	Kissinger	Ozawa
I	63	70
II	70	78
III	253	264
IV	188	203
V	106	120

Calculated values of the activation energy for the chalcopyrite-pirite oxidation indicate that all stages of the process occur in the kinetic field.

CONCLUSIONS

The chalcopyrite-pyrite concentrate from the Bor mine (Serbia) was used for the thermal and kinetic investigation during oxidation in the air atmosphere.

Thermoanalytical study of the initial sample, intermediates (at 450 °C and 650 °C) and final oxidation products (at 900 °C) provided valuable informations about the reactions occuring in this process.

Initial sample consisted of following copper and iron minerals: chalcopyrite, pyrite, bornite, and hematite. It was found that exothermic oxidation reactions predominate in the lower temperatures area, with intermediate products: chalcocyanite, chalcocite, dolerophanite, hematite and magnetite (below 650 °C). At higher temperatures, these sulphates and oxysulphates decompose by endothermic reactions, forming final products: tenorite, hematite, magnetite and copper-ferrite at 900 °C. According to these results, reaction mechanism was proposed.

Calculated equilibrium composition showed that the optimal roasting conditions were achieved under gas-charge molar ratio of 20:1. Under these conditions, copper sulphides are completely oxidized. Above 600 °C tenorite (CuO) is found in the reaction products, which is in accordance with the presented experimental results.

Kinetic analysis in non-isothermal conditions, under heating rates of 5, 10, 15 and 20 °C min^{-1} was done and activation energy values were calculated. Five peak temperatures were taken for the activation energy calculation. The obtained results of 63 - 106 kJ mole^{-1} by Kissinger method and 70 - 120 kJ mole^{-1} by Ozawa method, showed that all stages of the oxidation process occurred in the kinetic field.

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