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KINETIC STUDY AND MECHANISM OF CHALCOCITE AND COVELLITE OXIDATION PROCESS

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Results of the experimental investigation of the copper natural sulfide minerals (chalcocite and covellite) oxidation process in the air atmosphere are presented in this paper. Based on data obtained using thermal analysis methods and by construction of PSD diagrams for the Cu–S–O system at different temperatures, mechanisms of the investigated processes were determined. DTA-TG-DTG and RDA methods were used for the investigations given in this paper. Kinetic parameters as well as activation energies of investigated processes were determined using Sharp's method of reduced halftime of reaction.

Keywords: *activation energy, copper minerals, oxidation process, thermal analysis*

Introduction

Because of great practical importance in copper pyrometallurgy, oxidation processes of different copper-sulfides were subject of considerable interest [1–8].

Physicochemical characteristics of different minerals and concentrates in Cu–S system were investigated during oxidation roasting [1–3]. Also, temperatures of combustions for different sulfides were determined and presented in [4]. Special interest was exerted toward investigations of kinetics and mechanism of different pure sulfide minerals [5, 6] and concentrates oxidation processes [7, 8]. The oxidation of chalcocite processed by flash smelting methods, was investigated by Dunn *et al*. [9].

The results of kinetic study and mechanism of chalcocite and covellite oxidation process are presented in this paper. Contributing to the knowledge and understanding of copper natural sulphide minerals, complex comparative kinetic investigations were done, as well as further characterization of the oxidation products. The mechanism determined is complex, and the relationship between the kinetic conclusions and Arrhenius parameters based on TG and DTA are discussed, that is the method vide used in [10, 11].

Phase diagram for the Cu–S system [1] is presented in Fig. 1. The positions of chalcocite, Cu_2S and covellite CuS, are shown while their crystallochemical properties [1] are given in Table 1.

Experimental

For experimental investigations presented in this paper samples of natural minerals–chalcocite and covellite from Bor mine (Eastern Serbia) were used.

Experimental procedure for obtaining kinetic parameters under isothermal conditions was performed in a following manner: heating of investigated samples, during which roasting process occurred, was performed in Mars's furnace. The distinct amount of air was introduced into the reaction area, while gaseous products of reaction (SO_2 and SO_3) were generated from the tube to the absorption tanks, filled with aqueous solution of hydrogen peroxide, producing sulfuric acid. Produced sulfuric acid, in the presence

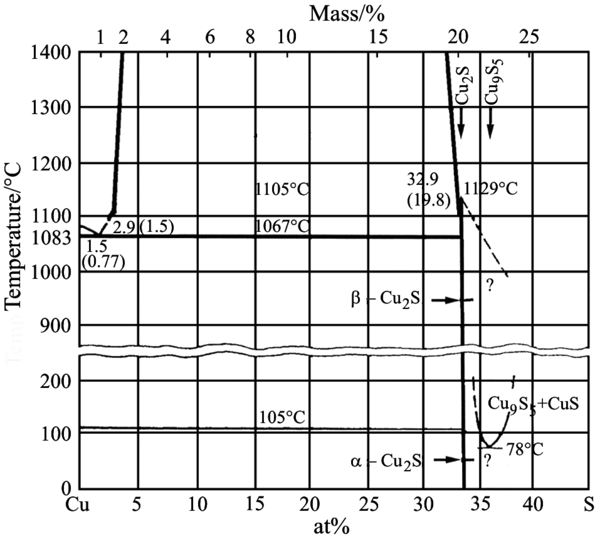

Fig. 1 Cu–S phase diagram [1]

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Table 1 Crystallochemical properties of investigated copper sulfides [1]

Sulfid	Crystal structure	Lattice spacings/m·10^{-10}			c/a	Density/g cm^{-3}
		a	b	c		
Cu_2S	rhombic	11.90	27.28	13.41	1.717	5.783 5.785
Cu_2S	hexagonal	3.89 3.95	– –	6.68 6.75	– –	– –
CuS	hexagonal	3.75	–	16.23	4.320	4.680

of indicator, reacted with measured standard solution of sodium hydroxide for the purpose of the calculation of sulfur insulated content and further degree of desulphurization during oxidation roasting.

Thermal analysis of the investigated samples was done using Derivatograph 1500 (MOM, Hungary) under following conditions: air atmosphere, heating rate of 10 K min^{-1} and T_{max}=1000°C, while alumina was used as reference material. Mineralogical characteristics of the starting sample and products of oxidation were determined by X-ray apparatus (Siemens), with Cu-anticathode and Ni-filters at 40 kV voltage and 18 mA current. Chemical analysis of the starting samples was done using a standard procedure.

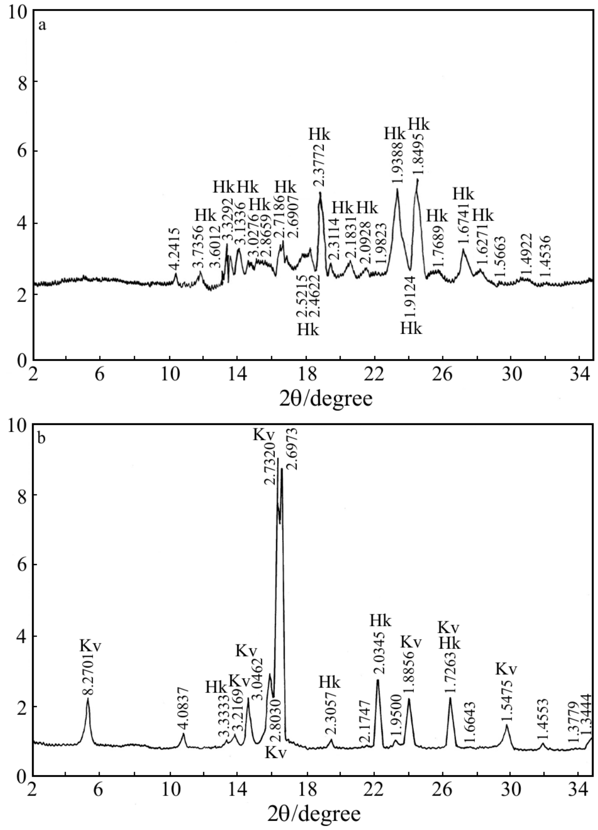

Fig. 2 X-ray results for the starting samples: a – chalcocite, b – covellite; (*Hk* – chalcocite Cu_2S; *Kv* – covellite CuS)

Results and discussion

The results of the chemical analysis for investigated copper sulfides are given in Table 2, while results of the X-ray analysis for the starting samples are shown in Fig. 2.

Obtained X-ray results confirm the presence of Cu_2S in the starting sample of chalcocite, while the presence of covellite and small quantity of chalcocite was noticed in the starting sample of covellite.

The results of thermal analysis application, which include DTA-TG-DTG recordings of investigated sulfides, are shown in Fig. 3.

Table 2 Results of the chemical analysis

Component	Chalcocite	Covellite
	content/%	
Cu	72.04	65.10
Fe	2.40	1.53
SiO_2	5.24	0.49
S	19.50	32.31
Cu-ox	0.81	1.88
Ag	0.007	0.0045
Mg	0.014	
Pb	0.0032	0.026
Sn	<0.001	0.0010
Bi	0.003	–
Ni	–	–
Ti	0.035	
Co	0.074	
V	<0.003	0.01
Ca	–	0.066
Sb	<0.01	–
Zn	<0.01	–
Mn	<0.01	0.003
As	0.1	<0.1
Ge	–	0.06
Al	–	0.008
Mo	–	<0.003
Cr	–	<0.003

In order to determine mechanisms of chalcocite, covellite and white metal oxidation processes, dependencies ΔG_T^0 *vs*. temperature for characteristic reactions were determined using [12–14] and shown in Fig. 4, while constructed 3D phase stability diagram for the system Cu–S–O, based on known thermodynamic data [8, 14, 17] for characteristic reactions occurring at the investigating temperatures is given in Fig. 5. As can be seen, sulfate formation is typical for copper sulfides oxidation at lower temperatures, while at higher temperatures oxides occurs as oxidation products.

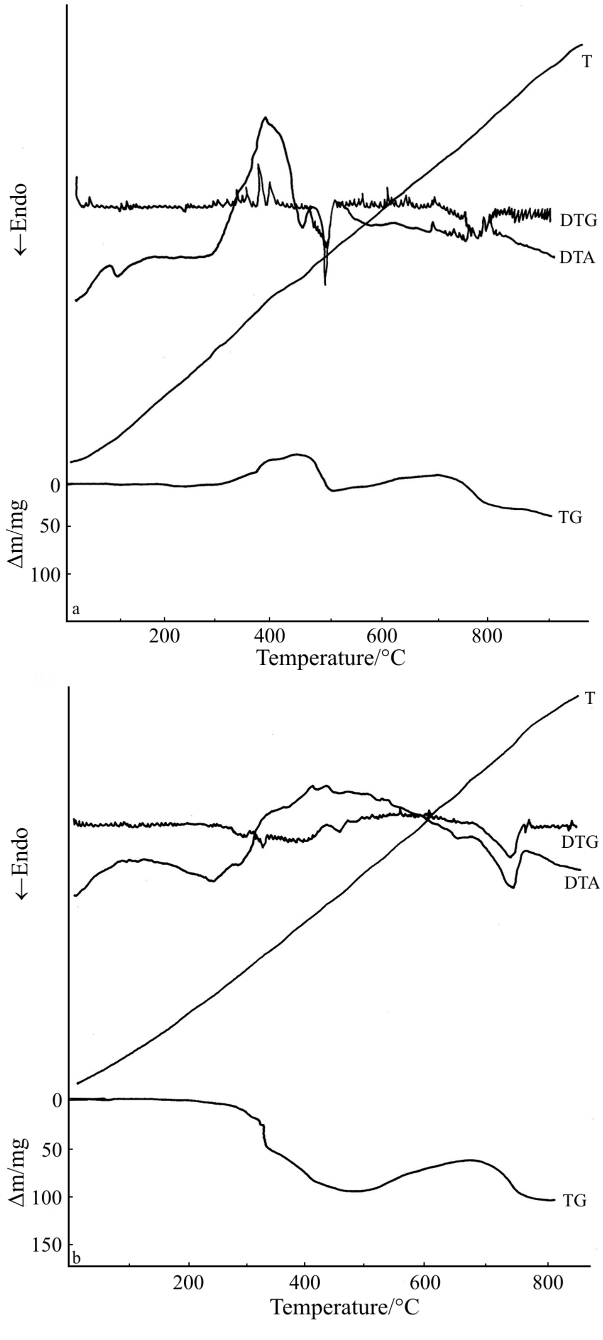

Fig. 3 DTA-TG-DTG analysis of the starting samples:
a – chalcocite, b – covellite

Based on characterization of starting sulfides, DTA-TG-DTG analysis results and phase stability investigations of Cu–S–O system, following mecha-

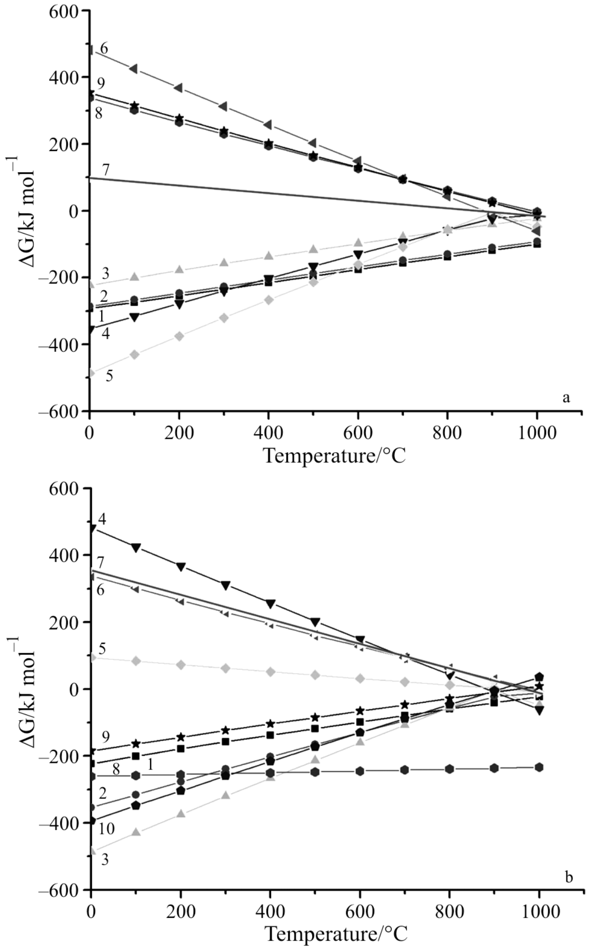

Fig. 4 ΔG_T^0 *vs*. temperature for the investigated reactions:

a – chalcocite,
1– $4/9Cu_2SO_2$=$4/9CuSO_4$+$2/9Cu_2O$,
2 – $0.4Cu_2S+O_2=0.4CuO+0.4CuSO_4$,
3 – $2Cu_2O+O_2=4CuO$,
4 – $Cu_2O+O_2+SO_2=CuO\cdot CuSO_4$,
5 – $4CuO+2SO_2+O_2=2CuO\cdot CuSO_4$,
6 – $2CuSO_4=2CuO+2SO_2+O_2$,
7 – $4/3CuSO_4=2/3Cu_2O+4/3SO_2+O_2$,
8 – $2CuO\cdot CuSO_4=4CuO+2SO_2+O_2$,
9 – $CuO\cdot CuSO_4=Cu_2O+SO_2+O_2$;
b – covellite,
1 – $2Cu_2O+O_2=4CuO$,
2 – $Cu_2O+O_2+SO_2=CuO\cdot CuSO_4$,
3 – $4CuO+2SO_2+O_2=2CuO\cdot CuSO_4$,
4 – $2CuSO_4=2CuO+2SO_2+O_2$,
5 – $4/3CuSO_4=2/3Cu_2O+4/3SO_2+O_2$,
6 – $2CuO\cdot CuSO_4=4CuO+2SO_2+O_2$,
7 – $CuO\cdot CuSO_4=Cu_2O+SO_2+O_2$,
8 – $0.8CuS+O_2=0.4Cu_2O+0.8SO_2$,
9 – $Cu_2O+SO_2+O_2=2CuO+SO_3$,
10 – $2/3Cu_2O+4/3SO_2+O_2=4/3CuSO_4$

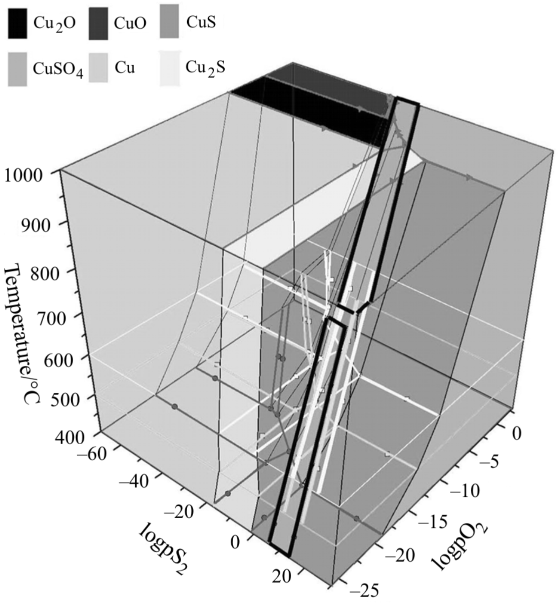

Fig. 5 3D Phase stability diagram for Cu–S–O system

nisms of chalcocite and covellite oxidation processes could be defined:

- for chalcocite:

- The exothermal peak occurring in the temperature interval 300–460°C, with the increase of mass at TG curve, responds to the oxidation of Cu_2S to $CuSO_4$ and Cu_2O [3]:

$$2Cu_2S+4.5O_2=2CuSO_4+Cu_2O \tag{1}$$

- further temperature increase (460–500°C) responds to the decrease of mass at TG curve, with exothermal peak, according to reaction of oxidation of Cu_2S to CuO and $CuSO_4$:

$$Cu_2S+2.5O_2=CuO+CuSO_4 \tag{2}$$

which is the sum of reaction (1) and reaction $Cu_2O+0.5O_2=2CuO$

- the occurrence of mass increase at TG curve at T>500°C (temperature interval 500–700°C), followed with exo-peak respond to:

$$Cu_2O+O_2+SO_2=CuO\cdot CuSO_4 \tag{3}$$

as well as:

$$2CuO+SO_2+0.5O_2=CuO\cdot CuSO_4 \tag{3a}$$

Parallel with reactions (1) and (2) until all of Cu_2S is reacted.

- the endothermal peak at temperatures over 700°C, with the mass decrease at TG curve, respond to the dissociation of sulfates and oxisulfates to Cu_2O and CuO (Eqs (4)–(7)):

$$CuSO_4=CuO+SO_2+0.5O_2 \tag{4}$$

$$2CuSO_4=Cu_2O+2SO_2+1.5O_2 \tag{5}$$

$$CuO\cdot CuSO_4=2CuO+SO_2+0.5O_2 \tag{6}$$

$$CuO\cdot CuSO_4=Cu_2O+SO_2+O_2 \tag{7}$$

- for covellite:

- the two exothermal peaks occurring in the temperature interval 280–475°C, with the decrease of mass at TG curve, respond to the oxidation of CuS to Cu_2O and CuO:

$$2CuS+2.5O_2=Cu_2O+2SO_2 \tag{8}$$

$$Cu_2O+SO_2+O_2=2CuO+SO_3 \tag{9}$$

- occurring of the exothermal peaks, with increase of mass at TG curve, in the temperature interval 475–680°C respond to reaction (3) and (3a) as well as reaction:

$$Cu_2O+2SO_2+1.5O_2=2CuSO_4 \tag{10}$$

- the endothermal peak occurring over 680°C, with decrease of mass at TG curve, respond to the dissociation of the formed sulfates, defined by Eqs (4)–(7).

In Fig. 6, results of RDA analyses of products of oxidation of chalcocite are shown. Results of X-ray analyses of products of oxidation of covellite are shown in Fig. 7.

As can be seen, from Figs 5–7 obtained results are in a good agreement with suggested mechanisms

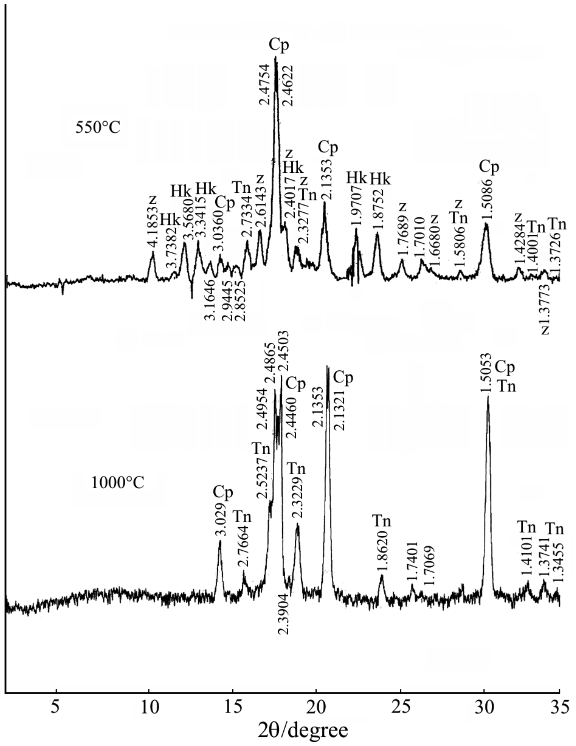

Fig. 6 X-ray analysis of products of oxidation of chalcocite at different temperatures;
(*Cp* – Cu_2O, *Hk* – Cu_2S; *z* – $CuSO_4$; *Tn* – CuO)

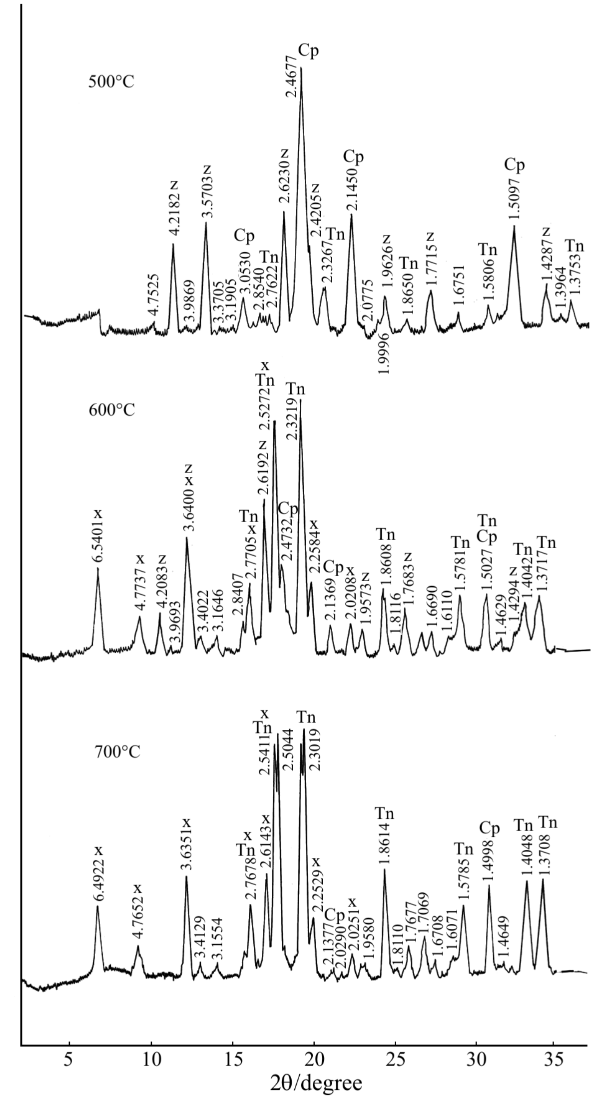

Fig. 7 X-ray analysis of products of oxidation of covellite at different temperatures;
(*Cp* – Cu_2O, *Tn* – CuO, *x* – $CuO{\cdot}CuSO_4$, *z* – $CuSO_4$)

for oxidation of all three sulfides as well as with the results presented in [9].

Experimental results for coefficient of desulphurisation (*D*) of investigated sulfides as function of time are presented at Fig. 8.

Selection of kinetic model for linearisation of experimental isotherms was done using Sharp's method of reduced halftime of reaction [15], where experimental results are presented in the form of degree of desulfurisation dependence on reduced halftime of reaction and afterwards compared with the theoretically derived curves and the usability of the selected kinetic models for description of the kinetics in such systems was estimated [16].

Values of reduced halftime of reaction for experimental data were approximate to values represent kinetic function F_1, for both investigated compounds, which means that kinetic function for linearisation of experimental results should be F_1 [$-\ln(1-\alpha)=kt$].

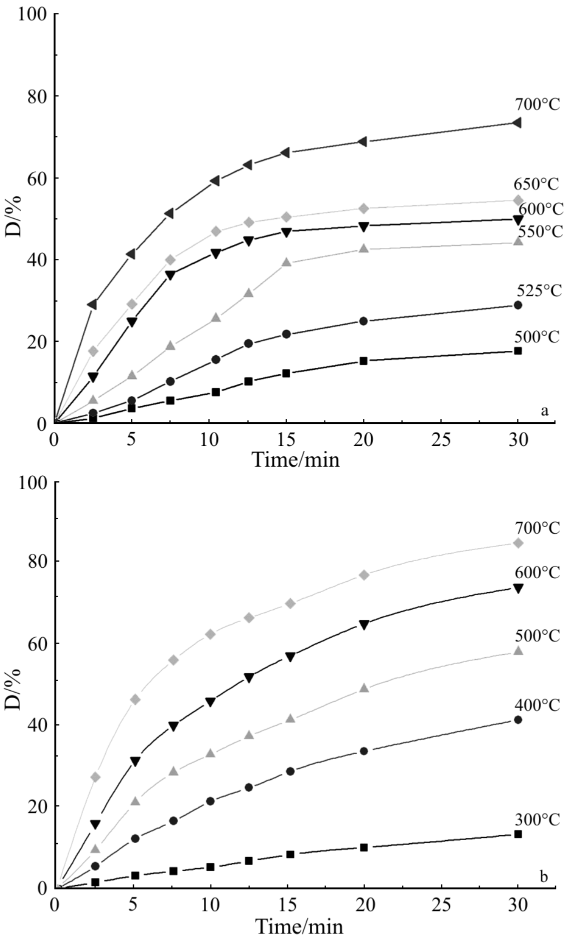

Fig. 8 Degree of desulphurisation (*D*) *vs.* time for the investigated reactions at different temperatures; a – chalcocite, b – covellite

The values for rate constant of reactions were determined using the gradient of lines representing linearised experimental data, while the values of kinetic parameters were calculated using Arrhenius equation.

Arrhenius diagrams for investigated process of oxidation of chalcocite, and covellite are presented in Fig. 9.

Results obtained by kinetic investigations of chalcocite and covellite oxidation processes are summarized in Table 3.

As can be seen from Table 3, in both cases change of a reaction mechanism occurs at following degrees of desulphurization:

- for chalcocite at α=30–40%
- for covellite at α=30–40%

In first period, up to the change of a reaction mechanism, values of activation energies decrease as follows:

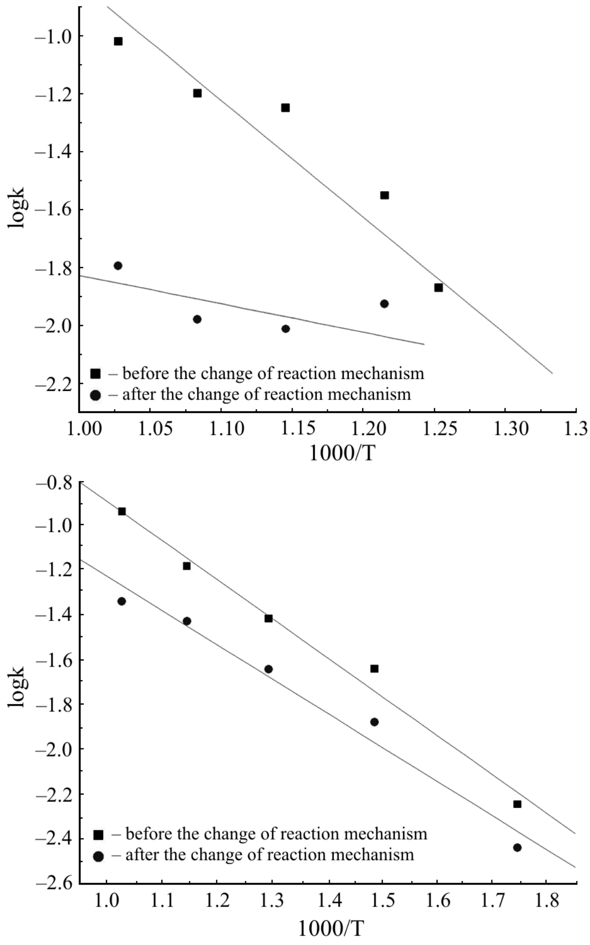

Fig. 9 Arrhenius diagrams for process of oxidation of: a – chalcocite, b – covellite

$$\xrightarrow{\text{chalcocite, 77 kJ mol}^{-1}}\xrightarrow{\text{covellite, 33 kJ mol}^{-1}}$$

while in second period, this sequence is given as:

$$\xrightarrow{\text{covellite, 29 kJ mol}^{-1}}\xrightarrow{\text{chalcocite, 19 kJ mol}^{-1}}$$

Such values obtained for activation energies point out to the fact that for both investigated samples beginning of oxidation processes are going on in a kinetic area. It should be mentioned that higher values for E_a obtained for chalcocite show dominant influence of temperature on oxidation rate, while for covellite process is near to the transition area.

After change of a reaction mechanism, at α near 40–50%, influence of diffusion is stronger, which leads to decrease of E_a values to diffusion area.

Table 3 Summarized results of kinetic investigations of Cu_2S and CuS oxidation processes

Mineral	Activation energy/kJ mol^{-1}	
	until fraction	after the fraction
chalcocite	77	19
covellite	33	29

Conclusions

Results of thermal analysis of oxidation process for natural copper sulfides chalcocite and covellite are presented in this paper. Based on the results of DTA-TG-DTG, RDA and chemical analysis, mechanisms of oxidation processes were defined and confirmed by thermodynamic analysis. Kinetic parameters and activation energies of investigated processes were determined using Sharp's method of reduced halftime of reaction.

Values of activation energies indicate that for both investigated samples oxidation process begin in kinetic, which means that temperature has overall influence on oxidation rate, and moves to diffusion area with change of a reaction mechanism.

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