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THERMAL ANALYSIS AND KINETICS OF THE COPPER-LEAD MATTE ROASTING PROCESS

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In this paper, the results of copper-lead matte investigations are presented. Investigated copper-lead matte is intermediate product of the lead production in TREPCA-Zvečan. In the first part of the paper characterization of starting material is presented, consisting of: chemical composition analysis (XRQ), scanning electron microscopy (SEM) and diffractometry (XRD). Thermal properties of investigated matte were determined using differential thermal analysis (DTA) at characteristic temperatures. Using results of induced analysis, mechanism of matte oxidation process was determined. In the second part of the paper kinetic parameters describing oxidative roasting of copper-lead matte are presented. For activation energy calculations, non-isothermal methods defined by Kissinger and Ozawa were used [1, 2]. Kinetic equation describing oxidation process was determined using Sharps method of reduced half time of reaction [3].

Keywords: *copper-lead matte, DTA, leaching, oxidative roasting, SEM, XRD*

Introduction

Besides metallurgical slag, sulfide mattes are the other, also important waste material obtained as the result of primary and secondary material smelting. Mattes can be defined as high-tempearature solid solutions of metal sulfides that are much denser than the slag [4]. In the smelting operations mattes are used for collection of basic noble metals (smelting of Cu and Ni) or for collecting of sulfur and the impurities as sulfide phase (smelting of Pb) [4]. In lead metallurgy, only mattes rich in copper can be recycled for copper utilization in the operation of secondary materials smelting [5]. Otherwise, mattes are regarded as waste material and are discarded. From ecological aspect mattes obtained in lead smelting are defined as 'toxic waste' No.10 04 00 according to European catalog of wastes (comity decision No. 94/3EC) [6].

Knowledge of metal distribution and phase compositions of metallic phases in mattes is of special interest for determination of possibility of their further processing or safe disposal. In that sense information about mechanism and kinetics parameters describing process of mattes utilization treatments are important.

Great percent of lead and copper in, lead production intermediate copper-lead matte, leads to the fact that number of authors investigated problems concerning valorization of the valuables from that material. This is why number of procedures describing copper-lead mattes processing are present [7–14]. Copper-lead mate is mixture of sulfides [15], mostly PbS and Cu_2S. Berg [16] in his monograph did publish results of the Pb–Cu–S system investigations. Structure of lead sulfides was subject of interest for Hansen [17], while phase diagram of the system PbS–Cu_2S was presented by Čižakov [18]. Investigation, describing melting of sulfides was presented by Voghan [19].

Experimental

Characterizations of copper-lead mate were done using scaning electron microscopy (SEM) with EDEX-9100 analyses and PAX software package, with resolution of 1 nm (30 kV), excitation voltage of 0.2–30 kV, maximum magnification of 500000× and with the secondary electron detector. Mineralogical investigations were performed at the atomic powder diffractometer APD SYSTEM PW 1710 'PHILIPS', under following conditions: 2θ range (4–90°), velocity $0.05°\ s^{-1}$, Cu anti-cathode (CuK_α=1.54178 Å) with 30 mA current and voltage of 40 kV. Chemical composition of starting sample was determined using X-ray quantum-meter (ARL 86480).

DTA investigations were performed at the apparatus DTA STA 409 (Netzsch, Germany). Sample mass for DTA was 30 mg and heat rate in the range of $15–30°\ min^{-1}$.

Heating of investigated sample, under isothermal conditions, was performed in Mars's (electroresistant) furnace. The distinct amount of air was introduced in to the reaction area, while gaseous product of reaction

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Table 1 Chemical composition of the copper-lead matte

Cu/%	Pb/%	S/%	Sb/%	As/%	Zn/%	Ni/%	Fe/%	Rest
45.3	41.1	10.6	0.931	0.636	0.376	0.289	0.278	0.49

(mostly SO_2), was generated from the tube to the absorption tanks, filed with aqueous solution of hydrogen peroxide, producing sulfuric acid. Produced sulfuric acid, in the presence of indicator, was reacted with measured standard solution of sodium hydroxide for the purpose of calculation of sulfur insulated content as well as degree of desulphurization during oxidation roasting.

Results and discussion

Characterization of the starting sample

For experimental investigations presented in this paper sample of copper-lead matte was used, chemical composition of the starting sample is presented in Table 1.

With rest presenting series of elements: Si, Ca, Se, Hg, Sn, Te, Mn, Sr, Pd, Mo and Cs. If observing results presented in Table 1, it is obvious that amount of valuable elements, copper and lead in this case, is very high.

Results of X-ray analyses of starting sample are given in Fig. 1. There are three main crystal phases identified: Cu_2S (chalcocite), PbS (galena) and small amount of $CuSO_4$ (chalcocyanite).

Results of the SEM analysis of the starting sample are presented in Fig. 2. Results of semi-quantitative analyses are shown in Table 2.

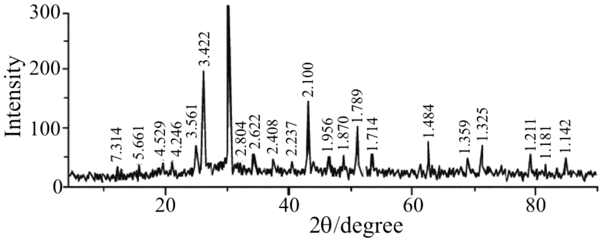

Fig. 1 X-ray results for the starting sample of copper-lead matte

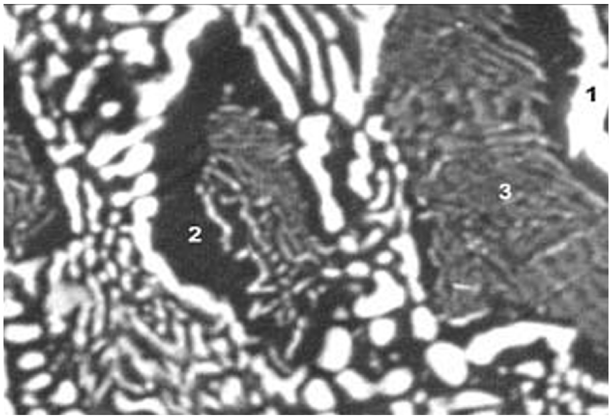

Fig. 2 Microstructure analyses of the copper-lead matte surface, magnification ×1025

Table 2 Semi-quantitative analyses of compositions presented in Fig. 2

Elements	Amount/%			
	Surface	Point 1	Point 2	Point 3
Cu	45.28	4.75	91.35	47.02
Pb	36.55	91.78	1.19	38.7
S	16.46	2.27	6.36	11.2
Sb	0.4	0.65	0.48	0.65
As	0.35	0.742	0.72	0.51
Zn	0.48	0.12	0.11	0.23
Ni	0.2	0.014	0.38	0.12
Fe	0.27	0.13	0.21	0.19

For the elements: Cu, S, Pb, Sb and Ag line analysis was performed as well. Results are presented in Fig. 3.

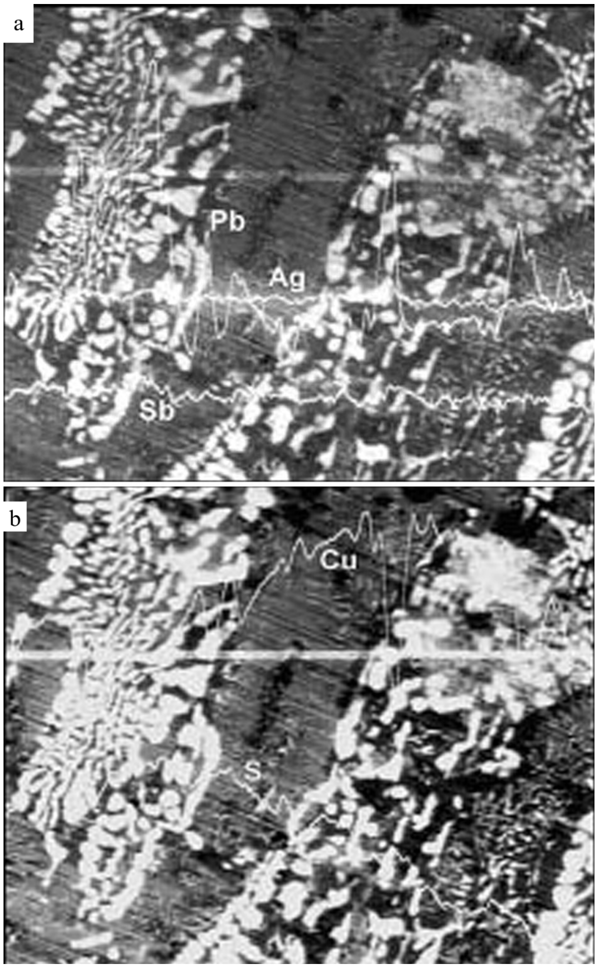

Fig. 3 Microstructure including line analysis: a – Pb, Sb and Ag; b – Cu and S

According to the results presented, it is obvious that lead and copper are segregated in separate phases. Black colored phases are enriched in copper while light ones in lead. Sulfur is present in both with the amount higher in copper enriched phase. Surface analysis presented in Table 2, shows that sulfur content in investigated sample is about 17% (mass) that is in agreement with the X-ray results. According to the point analysis sulfur content is much less than 17%. The discrepancy of point analysis is too large, especially if compared with the results of chemical analysis (Table 1). If results of the point analysis were correct, for whole volume of the sample, X-ray analysis would detect copper and lead as separate phases. Since those phases were not detected and surface analysis are closer to the chemical composition presented in Table 1, authors assume that point analysis results are not representing the real composition of the sample (being semi-quantitative in nature) and that the areas chosen for analysis were not of homogenous composition.

Thermal analysis and mechanism of copper-lead matte oxidative roasting

Results of DTA analysis of the copper-lead matte sample are presented in Fig. 4, for the heating rate of 25° min^{-1}.

At the DTA curve, Fig. 4, two exothermal peaks are present in temperature interval 450–580°C and one in 620–680°C. Further temperature rise leads to appearance of endothermal behavior in temperature interval 700–740°C, after which new exothermal peak appears in interval 800–840°C.

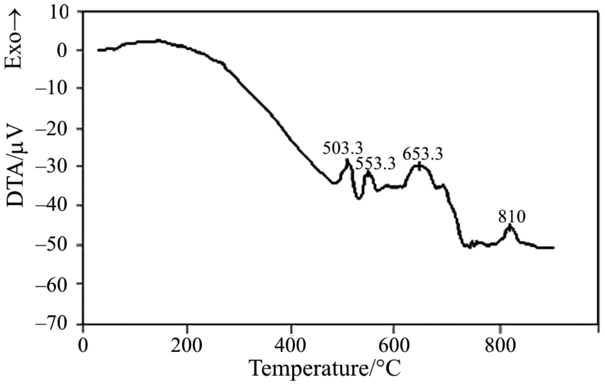

Fig. 4 DTA analysis of copper-lead matte; sample mass=30 mg, heating rate ν=25°C min^{-1})

For the products of oxidative roasting of mattes, at the temperatures 550, 650 and 900°C, X-ray analysis were done with purpose to describe thermal behavior of copper-lead matte. Phase composition of the starting sample and samples oxidative roasted at 550, 650 and 900°C, are given in Table 3.

Using the results of DTA analysis, Fig. 4, combined with results of X-ray analysis, Table 3, and thermodynamics analysis of the system Cu–Pb–S–O [19, 20], Fig. 5, it is possible to define mechanism of copper-lead mattes oxidative roasting.

Two exothermal peaks appearing in temperature interval 450–580°C are related to beginning of oxidation of the sulfides present, according to two dominant reactions:

$$3/4PbS+3/2O_2=3/4PbSO_4 \quad (1)$$

$$1/2Cu_2S+1/2SO_2+3/2O_2=CuSO_4 \quad (2)$$

and less significant reaction:

$$Cu_2S+3/2O_2=Cu_2O+SO_2 \quad (3)$$

Further temperature rise leads to new exothermal peak in temperature interval 620–680°C, which can be characterized with intensification of reactions (1)–(3) and appearance of reaction:

$$3/4Cu_2S+3/2O_2=3/2CuO+3/4SO_2 \quad (4)$$

Further temperature rise leads to appearance of the endothermal peak in temperature interval 700–740°C which can be described with reaction of dissociation of copper sulphate formed:

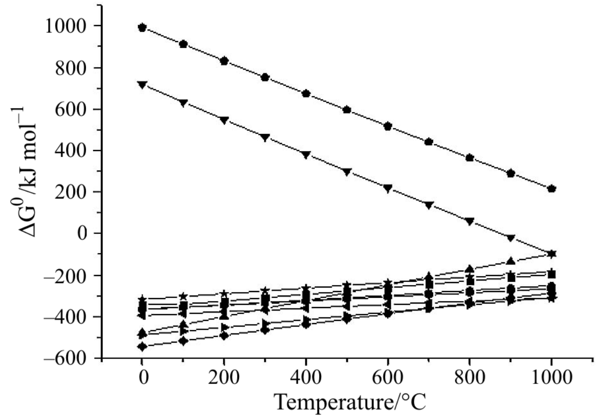

Fig. 5 Results of Gibbs free energy dependence on temperature for the characteristic reactions describing oxidation in the Pb–Cu–S system

Table 3 Phase composition of starting sample of investigated copper-lead matte and mattes roasted at different temperatures

	Starting sample	500°C	600°C	700°C	900°C
Crystal phases containing lead	PbS	PbS, $PbSO_4$	$PbSO_4$, PbS	$PbSO_4$, PbS	$PbOPbSO_4$, $Pb_3O_2(SO_4)$, $PbSO_3$, PbO_2, Pb_3O_4
Crystal phases containing copper	Cu_2S, $CuSO_4$	Cu_2S, $CuSO_4$	Cu_2S, Cu_2O, CuO, $CuSO_4$	Cu_2S, CuO	not identified

$$3CuSO_4=3CuO+3SO_2+3/2O_2 \quad (5)$$

With further temperature rise following reaction is predominant:

$$PbS+3/2O_2=PbO+SO_2 \quad (6)$$

As well as the reactions:

$$PbO+PbSO_4=PbO\cdot PbSO_4 \quad (7)$$

$$6/7PbS+3/2O_2=3/7PbO\cdot PbSO_4+3/7SO_2 \quad (8)$$

Parallel with reactions (6)–(8) in the temperature interval 800–840°C, characterized with significant exothermal peak at the DTA curve, following reactions are possible:

$$3/4PbS+3/2O_2=3/4PbO_2+3/4SO_2 \quad (9)$$

$$9/10PbS+3/2O_2=3/10Pb_3O_4+9/10SO_2 \quad (10)$$

$$PbO+SO_2=PbSO_3 \quad (11)$$

Crystal phases of copper are not identified at the diffractogram for sample roasted at 900°C. Reason for such an appearance is higher dissipation of X-rays at lead then on copper atoms. This is why Cu phases reflections are with low intensities even when their presence is not small.

Calculation of kinetic parameters for the process of oxidative roasting of copper-lead matte

Non-isothermal investigations

The initial sample examined was subjected to oxidation in air atmosphere at different heating rates from 15 to 30°C min^{-1} under the same conditions, and the results obtained for the maximum temperatures of DTA peaks dependence on the heating rate are shown in Fig. 6.

Kinetic analysis of the investigated oxidation process of copper-lead matte was performed according to methods developed by Kissinger and Ozawa. Those methods are widely used and in literature well described [21–23], because of the accuracy of the results obtained. Figure 7 shows the dependences of $\ln(\Phi/T_m^2)$ and $\ln\Phi$ as a function of $1/T_m$, where Φ is the heating rate and T_m is the temperature of the maximum of the peeks present on the DTA curve.

Based on these results, the corresponding values for activation energy E and the integration constants C and C_1 have been calculated for the process and results are presented in Table 4.

These values are consistent with oxidation of copper-lead matte taking place in kinetic region, which implies the reaction surface and temperature have the limiting influence on reaction rate.

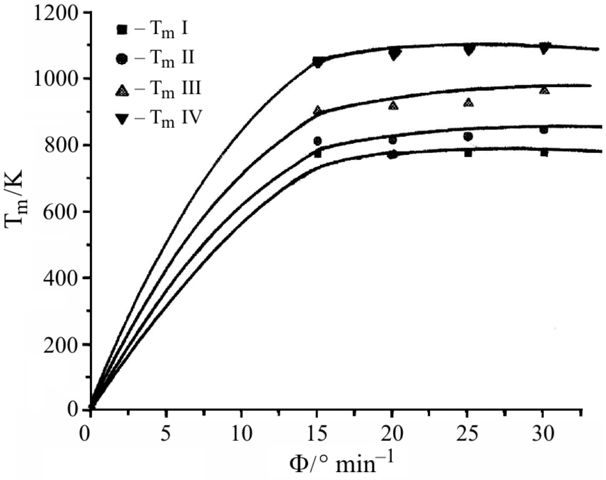

Fig. 6 Dependence of T_m on heating rate for DTA results (I – 15° min^{-1}; II – 20° min^{-1}; III – 25° min^{-1}; IV – 30° min^{-1})

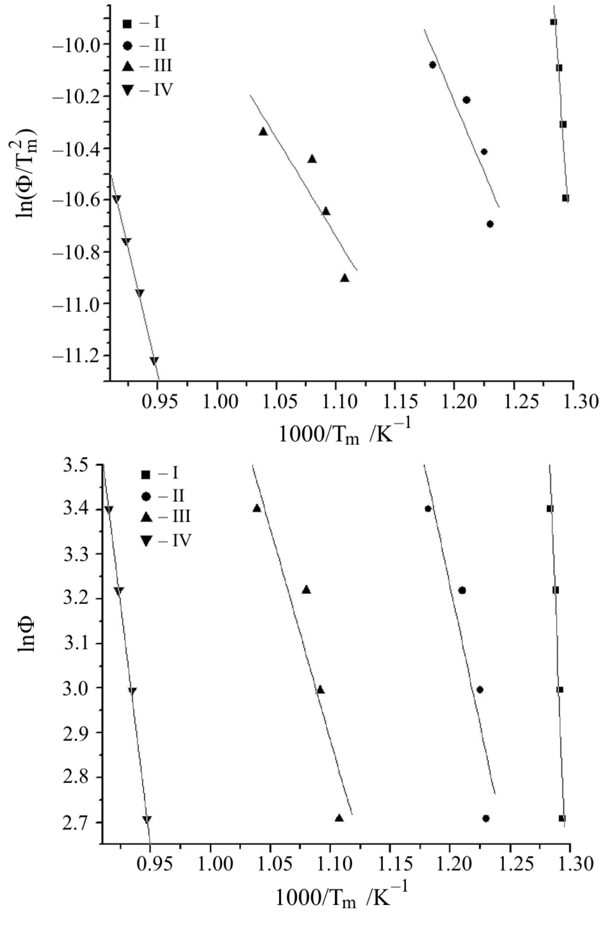

Fig. 7 a – Dependencies of $\ln(\Phi/T_m^2)$ *vs.* $1/T$ and b – $\ln\Phi$ *vs.* $1/T$ for the copper-lead matte oxidation process

Isothermal investigations

Oxidative roasting was performed by introducing distinct amount of air in the tube furnace reaction space. Roasting temperatures were in the range of 400–700°C.

Table 4 Calculated values of activation energy and integration constants for the oxidation process of copper-lead matte under non-isothermal condotions

Process	Method			
	Kissinger		Ozawa	
	E/kJ mol^{-1}	C	E/kJ mol^{-1}	C1
I	541	$9.84\cdot10^{31}$	554	$4.38\cdot10^{38}$
II	102	98.124	104	$8.54\cdot10^{7}$
III	63	0.089	78	$5.71\cdot10^{5}$
IV	162	1340.677	180	$1.14\cdot10^{10}$

Analysis of kinetic parameters for the process of oxidative roasting of copper-lead matte, under isothermal conditions, was done using method defined by Sharp. Results presenting degree of desulfurization as the function of time at different roasting temperatures are given in Fig. 8.

According to the results present in Fig. 8 it is obvious that most desulfurization is obtained at 700°C during 30 min and maximum value is 46%.

Linearization of experimental results, presented on Fig. 8, was tested using nine different kinetic equations, proposed by Sharp [3]. Criteria for accepting equation as best for linearization of experimental data was least square deviation of linearizated data in comparison with linear fitting of experimental data obtained by iteration model that MLAB software provide [24]. Square derivation was calculated for all nine equations using formula:

$$SD=\frac{1}{n}\sqrt{\sum_{i=1}^{n}(y_{M}-Y_{F})_{i}^{2}}$$

where: SD – square derivation, n – number of points regarded, Y_M – values of straight-line points obtained using MLAB software iteration model, Y_F – values for linearized experimental data obtained using nine different kinetic equations proposed by Sharp.

Using equation D4: $(1–2/3\alpha)–(1–\alpha)^{2/3}=kt$; where α – degree of reaction, t – time, k – rate constant; best linearization of experimental data was performed (i.e. minimum square deviation for all isotherms). From the inclination of linearized isotherms, rate constants were determined and Arrhenius diagram, Fig. 9, constructed.

According to the Arrhenius diagram, activation energy of the process, under isothermal conditions, was calculated and its value is 168 kJ mol^{-1}. Kinetic parameters of the process are presented in Table 5.

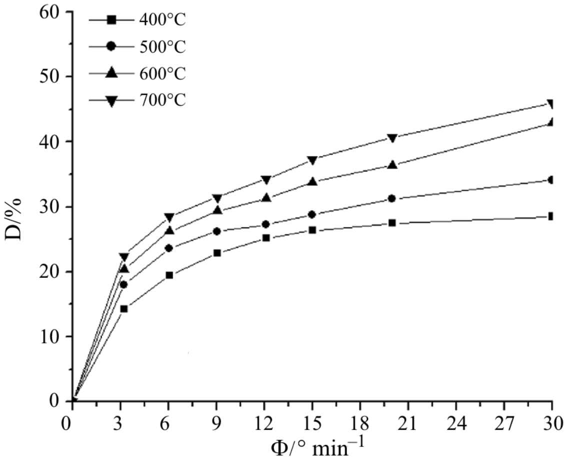

Fig. 8 Degree of desulfurization of copper-lead matte as the function of time and roasting temperatures

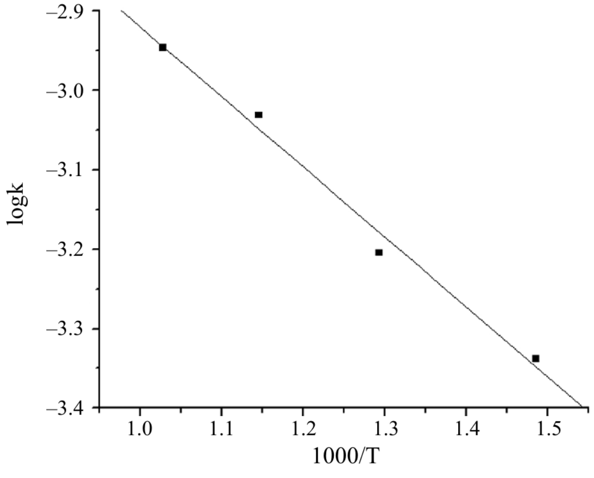

Fig. 9 Arrhenius diagram for the process of copper-lead matte oxidative roasting

Table 5 Kinetics parameters for the process of copper-lead matte oxidative roast, under isothermal condotions

Oxidative roast of the matte	Rate constant/s^{-1}	$k_1=9.1\cdot10^{-3}\exp\left(\frac{-20260}{T}\right)$
	Kinetics equation	$(1–2/3\alpha)–(1–\alpha)^{2/3}=k_1t=9.1\cdot10^{-3}\exp\left(\frac{-20260}{T}\right)t$

Conclusions

Copper-lead matte oxidation process has been experimentally investigated using DTA-TG-DTG, SEM and X-ray analysis. The results including heat effects, kinetic parameters and mechanism of the investigated process have been determined and presented in this paper.

Using results of analysis above listed, mechanism of copper-lead matte oxidation was concluded which was confirmed by calculated Gibbs energy change *vs*. temperature, and literature data [15]. Kinetic analysis, under non-isothermal conditions, carried out according to Kissinger [1] and Ozawa [2] showed that the values of activation energy are consistent with oxidation of copper-lead matte taking place in kinetic region, which implies that reaction surface and temperature have the limiting influence on the reaction rate. Using kinetic analysis, under isothermal conditions, kinetic equation was defined.

Acknowledgements

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