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DEFINITION OF APPARENT ACTIVATION ENERGY ON DTG CURVES

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Preliminary Note – Prethodno priopćenje

The article gives the results of sulphidation oxidized copper ores and tailings with sulfur. Defined by the apparent activation energy in the conditions of heating the mixture of substances interacting with a constant speed by differential thermogravimetry (DTG).

It was established that the sulfiding may occur in a kinetic mode , since the interaction is charged, in the presence of liquid and gaseous sulfur , i.e. transport of sulfur to the surface of the mineral is not a limiting process.

Key words: copper ores, industrial waste, oxidation, sulfur, activaition energy

INTRODUCTION

Methods of thermal and thermogravimetric analysis are widely used during study of phase transformation, reaction of sulfurizing, restoration, oxidizing, dehydrating and other, in other words, processes related to change of substance enthalpy and mass [1].

The advantage of the methods of non-isothermal kinetics is that all kinetic constants energy activation (E_{act}), preexponential factor (A) and reaction order (n) [2] can be defined by one experiment.

This can be calculated by Arrhenius equation:

$$K=A\cdot \exp(-E_{act} / RT) \quad (1)$$

Where: K – kinetic constant;

A – preexponential factor, temperature-in dependent in short temperature interval;

E_{act} – energy activation;

R – gas constant;

T – absolute temperature.

In order to study and optimize temperature and time mode of sulfurizing of oxide copper ore, it is necessary to know kinetic process parameters, particularly, the apparent activation energy of sulfur interaction with oxide minerals.

In order to define kinetic constant (k) at isothermal thermogravimetry with continuous registration of loss in weight, it is necessary to perform the number of experiments at different temperatures.

At present new methods to study solid-state reaction have been developed, including definition of apparent activation energy in the terms of heating the mixture of interacting substances with constant speed with the help of differential thermogravimetry (DTG).

Definition of apparent activation energy value is significantly simplified if the dependence graphs are developed instead of dependence lg K – $f(1/T)$ for deviation from base lines of DTG curves in lg Δt – $f(1/T)$ coordinates. Value Δt is measured directly by DTG curves in the unit of length.

Some authors [3, 4] in their papers defined the value of activation energy of endothermic processes by non-isothermal kinetics methods. The authors [5] proposed the method to define kinetic parameters, where for endothermic processes had the biggest deviation of DTG line complied with maximum process speed, while for exothermic effect the peak point of DTG curve coincides with transformation completion moment.

EXPERIMENTAL AND DISCUSSION

This is to be considered during defining the apparent activation energy on DTG curves.

In the present work this method was used for calculation of kinetic parameters of endothermic and exothermic processes, where activation energy is calculated by DTG curve. Also, it is proposed to use this method for calculation of E_{act} processes of sulfurizing oxide copper ore by elemental sulfur. Thermal analysis has been performed on derivatograph Q-1000/D of F. Paulik, J. Paulikand L. Erdeysystem of "MOM" firm, (Budapest).

The method is based on registration of thermochemical and physical changes of substance parameters by the tool, accompanied by heat emission or the absorption at its heating. Thermochemical state of the sample is described by the curves: T (temperature), DTA (differentiated thermo-analytical), TG (thermogravimetric) and DTG (differential thermogravimetric), which is derivative of TG–function.

A survey was performed in the aerial environment in the range of temperature 20 - 1 000 °C.

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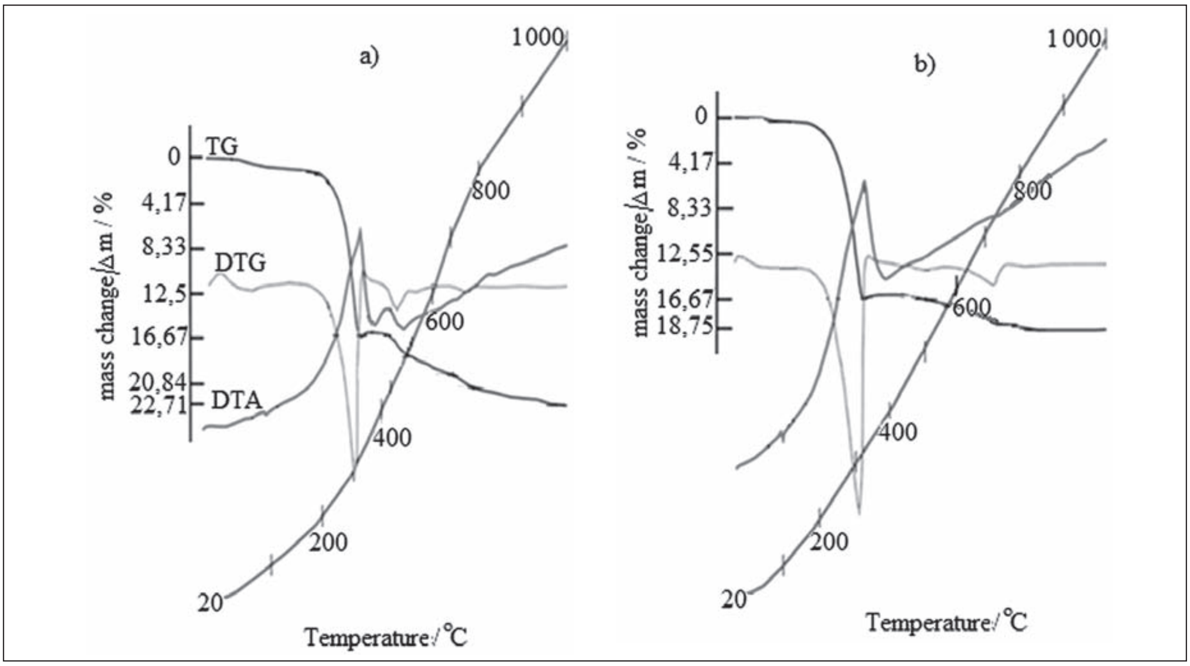

Figure 1 Thermogram of the samples:(a)oxide copper ore + sulfur, (b) mill tailing + sulfur surveyed at the range of temperature from 25 °C to 1 000 °C

Due to the peculiarity of the thermal behavior of the oxidizing substances, included in the rocks (low oxidizing temperature), the heating of some samples was limited to the range of 20 ~ 650 ^{o}C. The heating mode is dynamic (dT/dt = 10 $\frac{grad}{\min}$), comparison substance – heat-treated Al_2O_3, sample – 100 mg.

Sensitivity of the measurement systems of the tool was set at the same for all samples: DTA = 250 μV, DTG = 500 μV, T = 500 μV, TG – 100 at line sensitivity - 500 μV, sample -500 mg. The results of thermal analysis are presented on the Figure 1 a) and b).

Starting from a temperature of 200 °C the results should be related to the reaction of sulfurizing. As the temperature rises, the other processes are imposed such as sulfur evaporation and its' oxidizing, oxidizing of copper sulfide, that is why the effects and therefore the effects of weight loss include the overall process.

Exo-effects on DTG curve and relevant loss of weight, in my opinion, relate to the main reactions proceeding in parallel:

$2\,CuCO_3 + 4\,S = 2\,CuS + SO_2 + 2\,CO_2$ (200 – 435 °C).

$S + O_2 = SO_2$ before 435 °C (sulfur boiling point 444 °C), then as the temperature rises, it is accompanied by sulfide oxidizing to sulfate, since DTG was performed in aerial environment $CuS + 2\,O_2 = CuSO_4$ (435 – 660 °C). Thermal effects are shown in the Table 1.

The same changes in thermograms can be seen with mill tailings during the interactions with sulfur, due to the same processes, and the only difference is that components content is low.

The interpretation of thermal behavior of powdered sample was done by morphology of thermal curves and numerical value of intensity of endo- and exothermic effects, using conjugated thermogravimetric indices of TG-lines.

Table 1 **Thermal effects / °C**

№ peak	Materials		Notes
	a)	b)	
1	200	240	$S_{solid} \rightarrow S_{gaz}$
2	240	380	$2\,CuCO_3 + 4\,S = 2\,CuS + + SO_2 + 2\,CO_2$
3	435	660	$S + O_2 = SO_2$ and $CuS + 2\,O_2 = CuSO_4$

Two burden mixtures, containing oxide copper ore with sulfur and mill tailing with sulfur were under thermographic analysis in the terms of air access limits.

Figure 2 shows the results of linearization of the ascending branch of DTG peak in the lgΔt – 1/T coordinates.

Activation energy E_{act} is defined by a slope ratio lgΔt = f (1/T), obtained by logarithmation of Arrhenius equation (1), and Δt by the following equation:

$$\Delta t = \frac{P_к - P_i}{P_н - P_к} \tag{2}$$

Where: P_k – final weight;
P_i – total weight;
P_n – initial weight.

Dependence is developed in the lg Δt – 1/T coordinates for each thermal effect based on the definition of the temperature value and DTG curve deviation from the specified direction; and $E_{act.}$ process values were calculated by lg Δt – 1/T slope ratio of dependence line with respect to the peaks on thermograms.

The value of activation energy E_{act} and logarithm of pre-exponential factor A can be defined in the graphic form.

$$tg\alpha = \frac{E_{act}}{R} \tag{3}$$

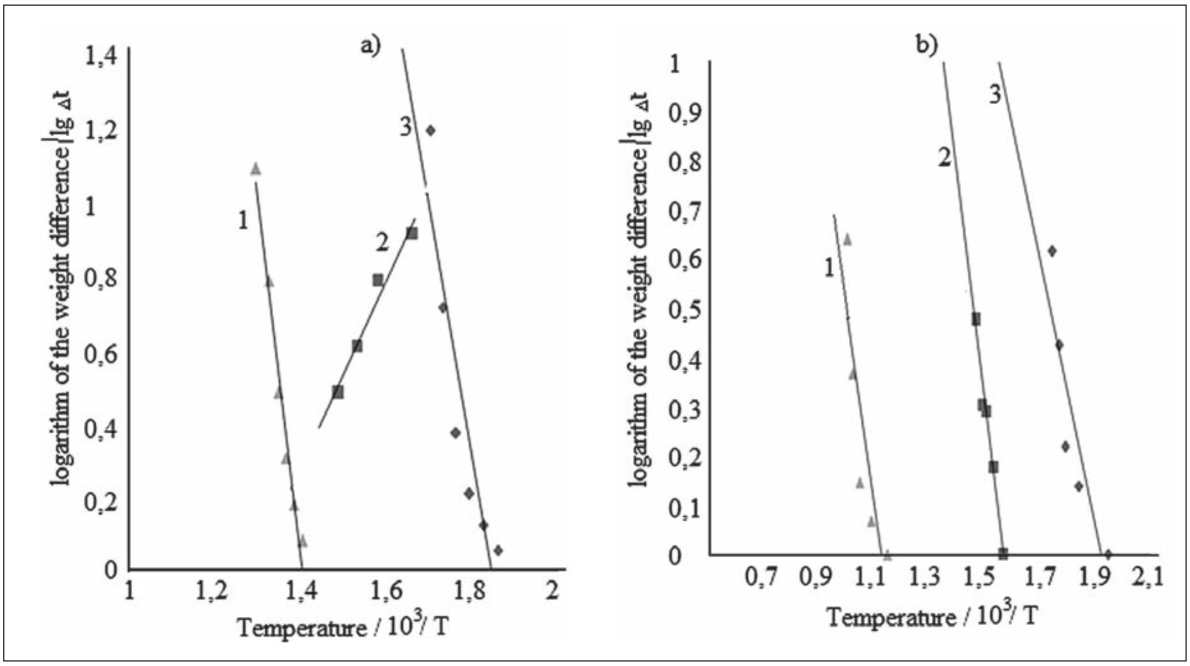

Figure 2 Dependence of as cend height of DTG curve peak for relevant temperature in semilogcoordinates from the reciprocal temperature loss in weight relate to the overall processes.

Table 2 **Value of apparent activation energy defined by dependence slope lgΔt – 1/T**

№	Material	Equation	Correlation Coeff. R	E_{act} / kJ/mol·K	Temperature range /°C
1	Copper ore+sulfur	lg Δt = - 6,751/T + 12,44	0,855	62,15	200-240
		lg Δt = 2,517/T - 3,245	0,968	20,77	240-435
		lg Δt = - 9,620/T + 13,49	0,976	82,9	435-515
2	Mill tailings+sulfur	lg Δt = - 2,682/T + 5,160	0,795	31,2	240-320
		lg Δt = - 4,558/T + 7,142	0,976	41,55	365-435
		lg Δt = - 3,878/T + 4,346	0,767	27,7	600-765

The results of the calculation are indicated in the Table 2.

Temperature range 200 – 435 °C can be related to the reaction of sulfurizing, and above 435 °C – to overall oxidizing reactions (Table 2).

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CONCLUSIONS

Thus, the proposed method for defining the apparent activation energy(oxide copper ore + sulfur and mill tailings + sulfur) on DTG curves was used for detection of exothermic and endothermic effects.

More likely, sulfurizing can proceed in kinetic mode, since the interaction is in the burden, and the presence of liquid and gaseous sulfur, in other words, sulfur transportation to the mineral surface, is not the process for limitation. Oxidizing of the sulfur and copper sulfide (overall process) is in the kinetic mode, since the air comes from the outside, and oxygen contacts with the sulfur and copper sulfide at the mixture surface only.

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Note: The responsible for English language is Serikbayeva A.K. the associate professor from the University named after Sh. Esenov.