COPPER SLAG OXIDATION UNDER ISOTHERMAL AND NON-ISOTHERMAL CONDITIONS

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Abstract

Oxidation of copper slag in air under isothermal (at 700, 760, 800, 860 and 900^oC) and non-isothermal (25 – 1000^oC) conditions is studied using simultaneous DSC-TG and DTA-TG analysis with a flow rate of the oxidizing gas of 20 ml/min. Mechanism of the oxidizing process is proposed on the basis of the thermal curves and XRD studies. The values of the activation energy are calculated from the measured data (temperature, heating rate and weight change) using isoconversional methods. The differences in the obtained kinetic parameters are explained with the complexity and different mechanisms of the ongoing processes.

Key words: *copper slag oxidation, thermal analysis, DTA-TG, DSC-TG, kinetic data*

1. INTRODUCTION

Pyrometallurgical copper production generates large amounts of wastes like the slag that is usually discarded in landfills after processing and causes severe environmental problems (Parsons et al. 2001). On the other hand, the slag contains valuable components, which can be profitable to recover and thus contribute to the sustainable management of copper production (Gorai et al. 2003, Sanchez et al. 2004, Shen & Forssberg 2003, González et al. 2005). Various methods have been proposed for extracting residual copper and other precious metals by treating the slag with different solutions under atmospheric or high pressure (Banza et al. 2002, Berrin 2000, Altundogan et al. 2004, Yang et al. 2010, Chen et al. 2012). These methods do not lead, however, to reduction of the amount of disposed slag because the quantity of the extracted metals is negligible in comparison to the amount of slag. It is known that the basic crystal phases in the copper slag are fayalite ($2FeO.SiO_2$) and magnetite (Fe_3O_4) but fayalite prevails (Alexandrova et al. 2009), so finding a possibility of their utilization would lead to a decrease in the waste product with both ecological and economic effects. A new approach has been proposed in the EU patent No. 2 331 717 B1, which is based on the decomposition of fayalite into iron oxide and silicate phases by oxidation and subsequent hydrometallurgical treatment. As a result amorphous silicon dioxide and iron oxide have been produced and the slag has been completely utilized. The first process in this method is slag oxidation. In this regard, it is important to experimentally study the process of oxidation at the temperatures of fayalite decomposition and to obtain kinetic data characterizing the ongoing processes. These data could be used in process optimization and estimation of real-time material performance (Burnham 2006).

Mathematical methods for calculating the kinetic parameters of solid-state reactions can be divided into two groups: model-fitting or model-free (isoconversional) (Brown et al. 1980). Model-fitting methods simultaneously determine model, frequency factor and activation energy whereas isoconversional (model-free) methods generate the activation energy as a function of reaction progress without modelistic assumptions. The model-fitting method is usually applied to isothermal investigations. It requires knowledge of the equations characterizing the different stages through

which the solid-state reactions pass - nucleation, geometrical contraction, diffusion, chemical reaction, etc. (Galwey & Brown 1999). Galwey and Brown (1999) have summarized the most frequently used equations based on different assumptions and approximations. This determines the major disadvantage of the model-fitting method – its inability to uniquely determine the reaction model. Isoconversional methods evaluate the activation energy at progressive conversion values (α) (Simon 2004). This method requires several kinetic curves to perform the analysis and has therefore been called a "multi-curve" method (Zsako 1973, Zsako 1996). It gives a more real picture in the case of complicated processes with simultaneously occurring reactions.

The aims of this study are: (i) to investigate the oxidation of copper slag in air under isothermal (at 700, 760, 800, 860 and 900^{o}C) and non-isothermal (25 – 1000^{o}C) conditions using simultaneous DSC-TG and DTA-TG analysis at a constant flow rate of the oxidizing gas of 20 ml/min; (ii) to apply the isoconversional method for kinetic modeling and evaluation of experimental data. The differences in the obtained kinetic parameters are explained with the complexity and the different mechanisms of ongoing processes.

2. EXPERIMENTS AND METHODS

2.1. Materials

The copper slag used in the experiments is a waste product from the pyrometallurgical production of copper in Aurubis Bulgaria AD. The slag was sifted through a 100-mesh sieve and the fraction with particle size below 100-mesh was used in the experiment.

2.2. Non-isothermal oxidation

The non-isothermal oxidation of copper slag was carried out using the computerized combined apparatus for differential thermal and thermogravimetric analyses (DTA-TG) LABSYSEvo, SETARAM company, France, at atmospheric pressure in a flow of synthetic air (MESSER CHIMCO GAS - OOH 1056, ADR 2, 1A) in the temperature range 25 – 1000^{o}C. Corundum crucibles with a volume of 100 μl were used. The sample weight in all tests was 80±1 mg. The experiments were carried out in dynamic mode, with heating rates of 4, 8, 12, 16 and 20 ^{o}C min^{-1} and oxidizing gas flow rate of 20 ml min^{-1}. Additional experiments for identifying the intermediate solid phases were carried out under the following conditions: heating up to 300, 400, 500, 700 and 1000 ^{o}C with a heating rate of 12 ^{o}C min^{-1} and keeping at the desired temperature for two h. The oxidized samples were used in XRD analysis.

2.3. Isothermal oxidation

The isothermal oxidation of slag samples was carried out in a simultaneous thermal analyzer SETSYS 2400, SETARAM company, France at the following regimes:

- Dynamic mode: heating at 20 ºC/min from 20 to temperature on hold 700; 750; 800; 860, 900; 960 ºC; purge gas 100% Ar with 30 ml min^{-1} gas flow rate, atmospheric pressure.
- Isothermal mode: time 100 min; oxidizing gas – 100% synthetic air (MESSER CHIMCO GAS-OOH 1056, ADR 2, 1A) with 20 ml min^{-1} air flow rate;

The sample weight in all tests was 12±1 mg. The results obtained were processed with a specialized software (Calisto, v. 1.062) SETARAM, France.

2.4. XRD analyses

The XRD analyses were performed using an automatic Bruker D8 Advance powder X-ray diffractometer with Ni filtered CuKα radiation and registration by LynxEye solid-state position-sensitive detector. The X-ray spectra were recorded in the range from 5.3 to 80° 2θ with a step of 0.02° 2θ. The qualitative phase analysis was made using the PDF-2(2009) database of the International Center for Diffraction Data (ICDD) by means of the DiffracPlusEVA software package. Refinement of the unit cell parameters was made with Topas 4.2.

2.5. Kinetic analysis

The data from the TG-DTA and TG-DSC analyses were used to calculate the activation energy of the oxidation processes using the general kinetic equation:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) = A\exp(\frac{-E_\alpha}{RT}).f(\alpha) \qquad (1)$$

where: $\alpha = \frac{G_{in} - G_T}{G_{in} - G_f}$ is the degree of conversion (G_{in} is the initial weight, G_T is the (current) weight for a given temperature (or time) and G_f is the final sample weight); t – time, *k(T)* - rate constant; *f(α)* - the reaction model; *A* - the pre-exponential factor; E_a – activation energy; R – universal gas constant and T – absolute temperature.

2.5.1. Isoconversional methods for non-isothermal studies

Under non-isothermal conditions, the general kinetic equation is transformed in:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(\frac{-E_\alpha}{RT}).f(\alpha) \qquad (2)$$

where: $\beta = dT/dt$ is the heating rate.

We use two computation procedures - of Ozawa-Flinn-Wall (OFW) (Ozawa 1965, Flynn & Wall 1966) (eq.3.) and Kissinger-Akahira-Sunose (KAS) (Ozawa 1965, Flynn & Wall 1966, Akahira & Sunose 1971) (eq.4)

$$\ln\beta = \ln\frac{0.0048AE_\alpha}{g(a)R} - 1.0516\frac{E_\alpha}{RT} \qquad (3)$$

$$\ln\frac{\beta}{T^2} = \ln\frac{AE_\alpha}{g(a)R} - \frac{E_\alpha}{RT}. \qquad (4)$$

E_α is evaluated from the slope of the plot $ln\beta$ - $1/T$ or $ln(\beta/T^2)$ - $1/T$ for (α) = const.

2.5.2. Isoconversional method for isothermal studies

Under isothermal conditions the general equation can be written (Vyazovkin & Wight 1999) as follows:

$$-\ln(t_\alpha) = \ln\left(\frac{A}{g(a)}\right) - \frac{E_a}{RT} \qquad (5)$$

E_α is evaluated from the slope of the plot $\ln t_\alpha$ against 1/T.

3. RESULTS AND DISCUSSION

The copper slag used in the experiments is a waste product from the pyrometallurgical production of copper in Aurubis Bulgaria AD. The chemical composition of the slag is given in Table 1 and the phase composition is shown on Fig. 1.

Table 1 Chemical composition of the initial slag

Oxides	**mass %**	**Oxides**	**mass %**
FeO	50.93	MgO	1.43
SiO_2	31.26	CaO	1.39
Al_2O_3	6.93	CuO	0.6
Na_2O	3.02	TiO_2	0.22
K_2O	1.74	MnO	<0.01

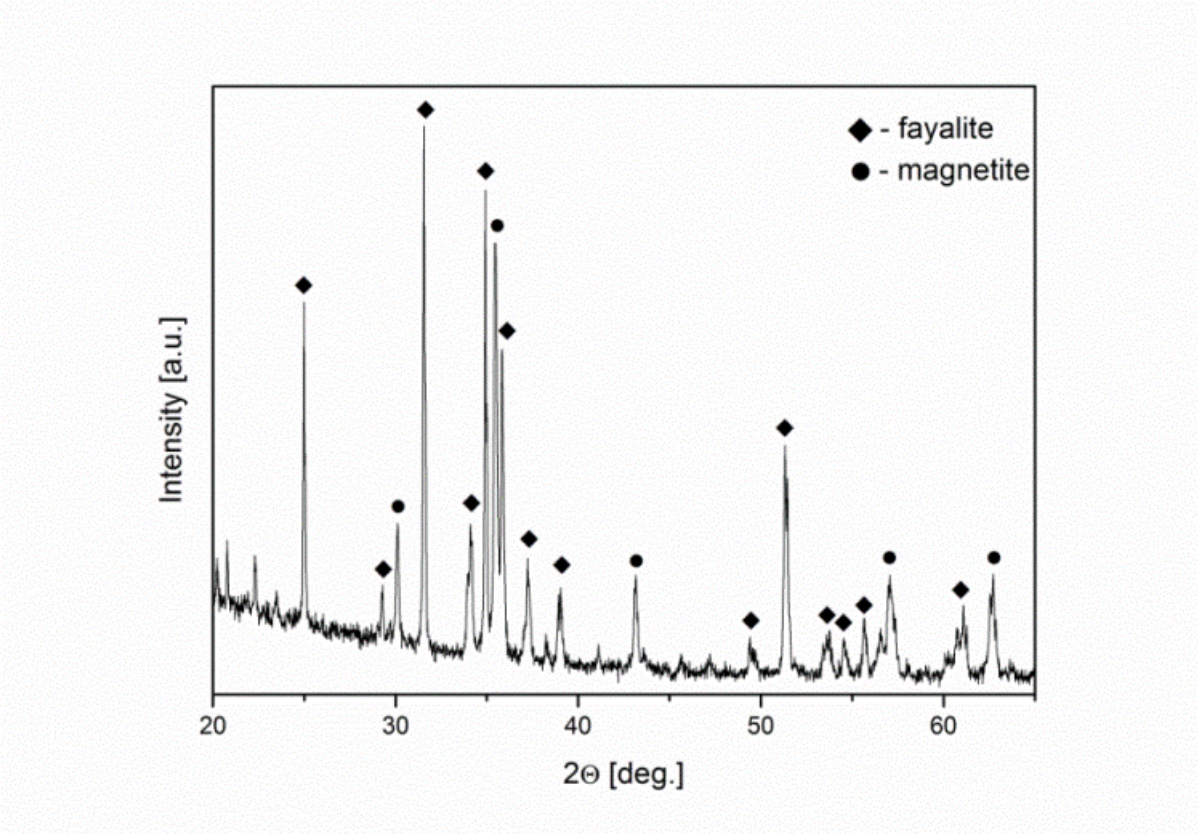


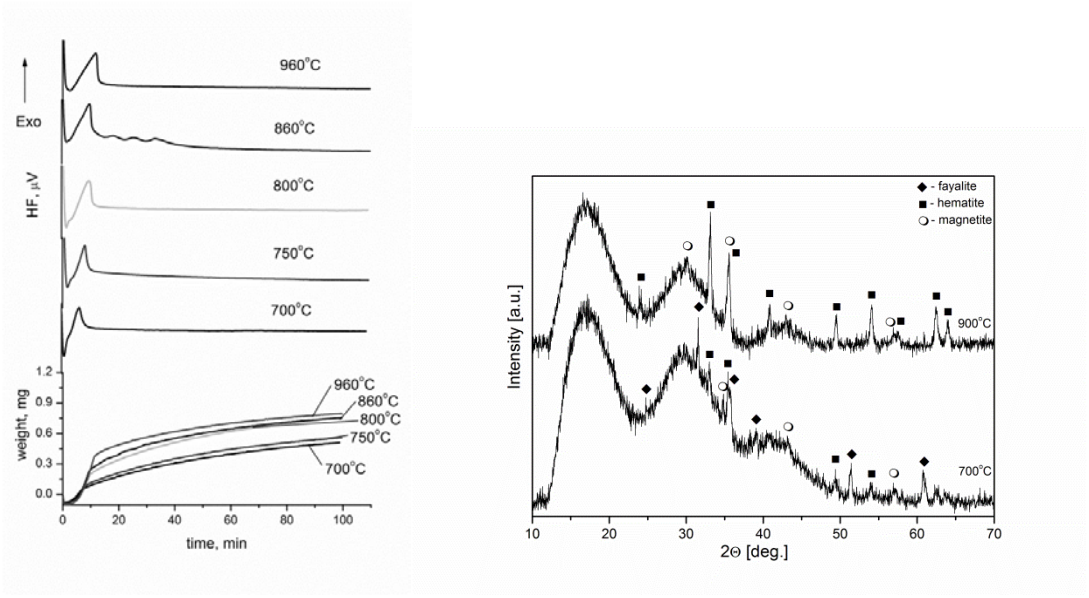
Fig. 1 XRD study of the initial slag

As we expected, the initial slag is composed of fayalite Fe_2SiO_4; a spinel type iron oxide with unit cell parameter of 8.37 Å; quartz - SiO_2; calcite - (Ca, Mg) CO_3; and calcium monocarboaluminate $Ca_4Al_2O_6CO_3.11H_2O$. The phases presented are typical for copper slag but the amount of different components may vary depending on the manufacturers. In any case, fayalite is the dominant phase in this type of slags (Gyurov 2011). The value of the unit cell parameter at room temperature of the spinel iron oxide (8.37Å) is lower than the reported values for pure magnetite: 8.3958Å (Mihailova & Mehandjiev 2010); 8.3965 Å (Wechsler et al. 1984); 8.3970Å (Haavik et al. 2000), showing that the magnetite phase is slightly oxidized.

3.1. Isothermal studies

In our previous work (Gyurov et al. 2014) we have studied the processes of non-isothermal oxidation of copper slag at different flow rates of the oxidizing gas flux and we have found no relationship between the calculated kinetic parameters and the oxidation gas flow rate, so in this study we used an oxidizing gas flow rate of only 20 ml/min. Synthetic air was used as an oxidant in order to maintain a constant oxygen partial pressure in all experiments.

The DSC-TG curves for isothermal mode at 700; 750; 800; 860, 900; 960 ºC are presented on Fig. 2a.

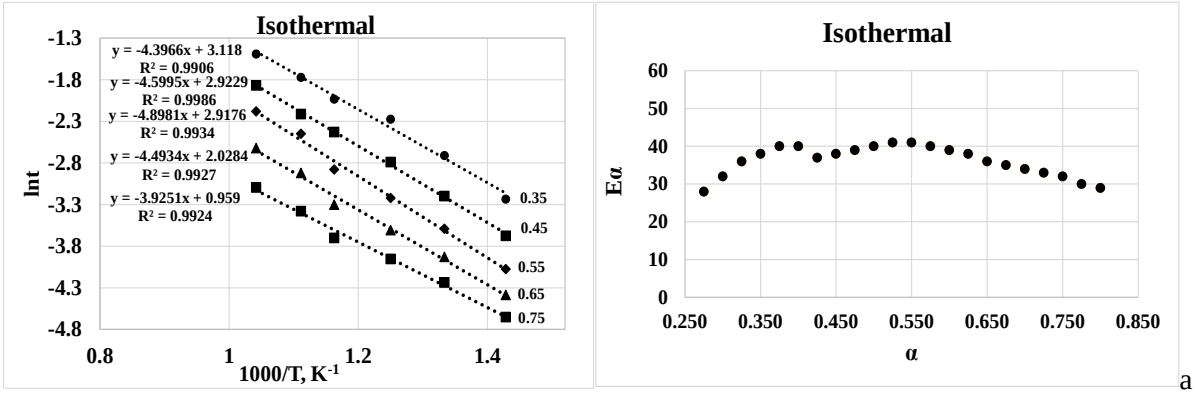


a b

Fig. 2. DSC-TG curves (a) of the oxidizing process and XRD powder patterns (b) of sample oxidized at 700 and 900°C.

An exothermic peak is clearly observed in the first 10 min of the oxidizing process, which is connected with a jump in weight change. It can be assumed that these changes are due to a chemical reaction taking place. After that a decrease in the intensity of the process is observed by the gradual increase of the weight without changing the reaction heat. Diffusion processes probably occur at this step of the oxidizing process. The shape of the TG curves shows and XRD studies (Fig. 2b) prove that at 700°C complete conversion of the slag is not reached for the time of this experiment. Peaks of residual fayalite appear together with peaks of magnetite and hematite. The conversion increases with the reaction temperature and at 900°C XRD analysis indicates the presence mainly of hematite, amorphous silicate phase and residual magnetite.

The results of the isoconversional kinetic analysis are presented on Fig. 3.



a

b

Fig. 3 Relationship between $\ln(t_\alpha)$ and $10^3/T_\alpha$ plot calculated from TG data at conversion degrees of 0.35, 0.45, 0.55, 0.65 and 0.75 (a) and (b) dependence of activation energy (E_α) on the degree of conversion (α) (E_α–α curve) for isothermal oxidation of copper slag, calculated from TG data.

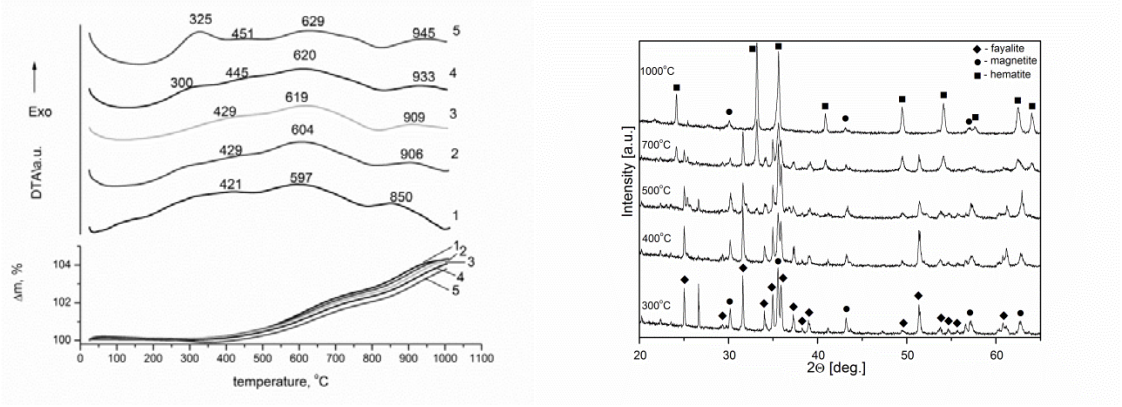
The values of the activation energy vary between 28 and 42 kJ.mol^{-1}, passing through two maxima at conversion degrees about 0.4 and 0.55.

It has been generally assumed that activation energy (E) and frequency factor (A) remain constant; it has been shown, however, that in solid-state reactions these kinetic parameters may vary with the reaction progress (α) (Vyazovkin & Wight 1999, Vyazovkin 2000, Khawam & Flanagan 2005, Galwey 2003, Vyazovkin 2003). If two or more elementary processes (each of them with its own unique activation energy) control the rate of product formation, a change in the activation energy with the reaction progress would be observed. This change will depend on the contribution of each elementary process, which gives an "effective" activation energy that varies with reaction progress. Kinetic complexities are not limited to multiple chemical processes. They may also include physical processes (e.g. sublimation, localized melting, adsorption-desorption, diffusion of a gaseous product, particle size and morphology effects, etc.) that have different activation energies.

During isothermal oxidation of copper slag, the oxidation of magnetite to hematite and the decomposition of fayalite simultaneously to silica and hematite, proceed on the surface of the slag grains. The process becomes dependent on the diffusion of oxygen through the layer of products and the geometric characteristics of this layer (morphology of the surface, amount of each phase (fayalite, magnetite), etc.) have predominant importance for the rate of the process.

3.2. Non-isothermal studies

The obtained DTA-TG curves are presented on Fig.4a. They are similar in shape for all used heating rates. Each DTA curve consists of an endothermic effect within the temperature range from 25 to about 120^{o}C and a broad exothermal effect in the temperature range from 120 to 1000 ^{o}C, where four peaks can be distinguished. The general view of the exothermic effect revealed the simultaneous run of several processes (oxidation and phase transition). The peak temperatures follow the general trend of shifting towards higher temperature values with the increase in the heating rates. The endo-effect is characterized by a minimum decrease of weight and is due to the release of residual moisture from the slag. The exo-effect is characterized by a gradual increase of weight and is due to the oxidation processes in the slag. The oxidation process is completed only at heating rates of 4 and 8 ^{o}C/min, where the TG curve reaches its plateau.

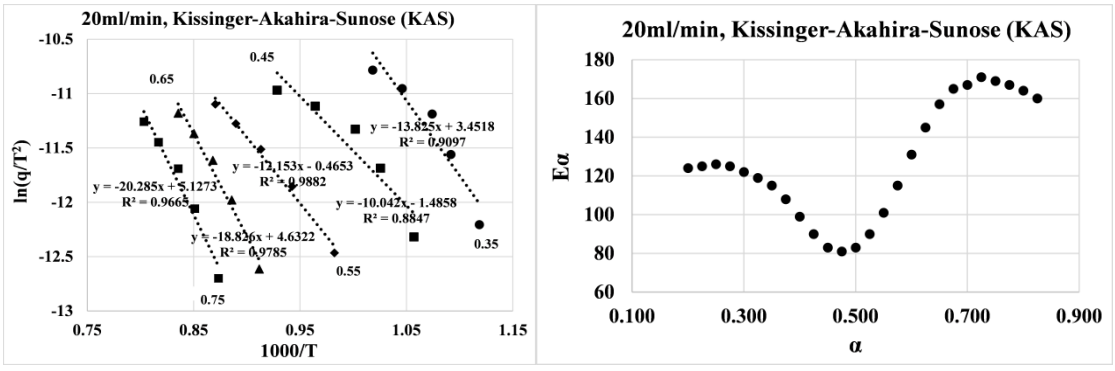


a b

Fig. 4 DTA-TG curves (a) at different heating rates (1-4°C/min; 2-8°C/min; 3-12°C/min;4-16°C/min and 5-20°C/min) and XRD powder patterns (b) of sample oxidized at 300, 400, 500 and and 900°C.

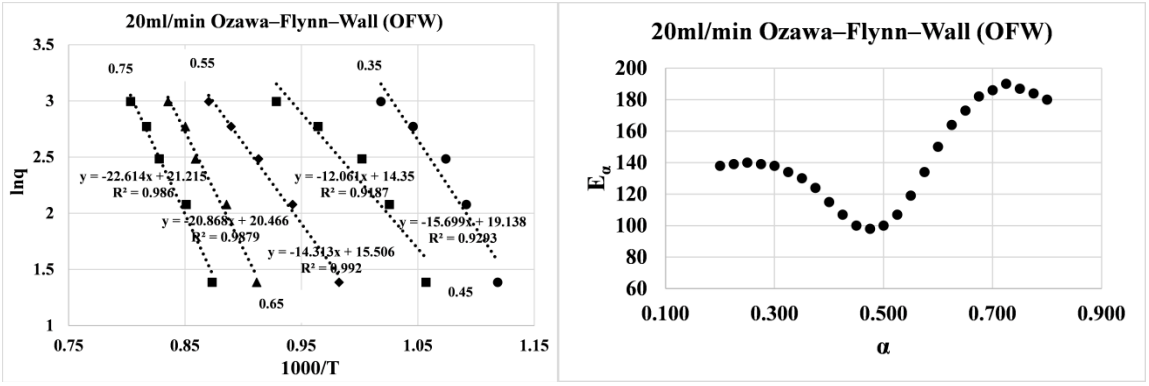
The XRD data of samples heated at different temperatures show that in the temperature range 25-400°C no changes of the slag's phase composition are observed (Fig. 4b). From 400 °C up, changes of the unit cell parameter of magnetite started due to its oxidation to maghemite. Obviously, the oxidation and transformation of the slag magnetite into hematite takes place simultaneously with the oxidation and decomposition of the slag fayalite into magnetite, hematite and amorphous silicate phase. Justification for this is the size of the magnetite crystallites. The size of the magnetite crystallites in the slag oxidized at temperatures below 600°C is greater than that of the samples oxidized at temperatures in the interval 700-1000°C. The smaller grains (the broader peaks) of the magnetite phase observed at higher temperatures indicate that the magnetite phase here is an intermediate product of the decomposition of fayalite. Slag oxidized at a temperature of 1000°C contains hematite, amorphous silicate phase and residual magnetite.

The results of the isoconversial kinetic analyses are presented on Figs. 5 and 6.



a b

Fig. 5 Relationship between $\ln(q/T_\alpha^{\ 2})$ and $10^3/T_\alpha$ — KAS plot calculated from TG data at conversion degrees of 0.35, 0.45, 0.55, 0.65 and 0.75 (a) and (b) Dependence of activation energy (E_α) on the degree of conversion (α) (E_α–α curve) for non-isothermal oxidation of copper slag, calculated from TG data by the KAS method



a b

Fig. 6 Relationship between ln(q) and $10^3/T_\alpha$ — OFW plot calculated from TG data at conversion degrees of 0.35, 0.45, 0.55, 0.65 and 0.75 (a) and (b) Dependence of activation energy (E_α) on the degree of conversion (α) (E_α–α curve) copper slag E_α depending on the degree of conversion, calculated from TG data by the OFW method

Both methods for isoconversional kinetic analyses give analogous results. The values of the activation energy vary from 80 to 170 kJ mol^{-1} (KAS) and from 100 to 180 kJ mol^{-1} (OFW), passing through two maxima at conversion degrees of about 0.25 and 0.72.

There is a disagreement between the values of the activation energy in isothermal and non-isothermal experiments. This disagreement arises from the fact that isothermal and non-isothermal experiments are necessarily conducted in different temperature regions. If decomposition involves several steps with different activation energies, the contributions of these steps to the overall decomposition rate measured in a thermal analysis experiment will vary with both temperature and extent of conversion. This means that the effective activation energy determined from thermal analysis experiments will also be a function of these two variables. For example, temperature changes could affect the kinetics not only through the rate constant but also by mechanistic changes. Elementary reaction kinetics at one temperature could differ from that at another; or complex reactions kinetics could vary with temperature due to changes in the contribution of each elementary step or change in the rate-determining step.

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REFERENCES

Akahira, T & Sunose, T. 1971, 'Joint convention of four electrical institutes. Research report (Chiba Institute of Technology)', *Sci Technol.*, vol.16, pp. 22–31.

Alexandrova, R, Paunova, R, Marinov, M & Petrov P 2014, 'Study on the behavior of flotation fayalite waste from copper production at nonisothermal heating', *Journal of Chemical Technology and Metallurgy*, vol. 49, no 1, pp. 90-93.

Altundogan, HS, Boyrazli, M & Tumen, F 2004, 'A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate', *Minerals Engineering*, vol. 17, pp. 465–467.

Banza, AN, Gock, E & Kongolo, K 2002, 'Base metals recovery from copper smelter slag by oxidising leaching and solvent extraction', *Hydrometallurgy*, vol. 67, no 1–3, pp. 63–69.

Berrin, Z 2000, 'Recovery of copper and cobalt from concentrate and converter slag' *Separation Science and Technology*, vol. 35, no. 12, pp. 1963–1971.

Brown, ME, Dollimore, D & Galwey, AK 1980, 'Reactions in the solid state', In C. H. Bamfordand C. F. H. Tipper (eds), *Comprehensive chemical kinetics*, Elsevier, Amsterdam, Chapter 3

Burnham K 2006 'A Comparison of isoconversional and model-fitting approaches to kinetic parameter estimation and application predictions', *Proceeding of NATAS 34th Annual conference Bowling Green*, KY, United States.

Chen, M, Han, Z & Wang, L 2012, 'Recovery of valuable metals from copper slag by hydrometallurgy', *Advanced Materials Research*, vol. 402, pp. 35-40.

European Patent No. 2 331 717 B1, 'Method for recycling of slag from copper production'

Flynn, JH & Wall, LA 1966, 'A Quick, direct method for the determination of activation energy from thermogravimetric data', *Polymer Letters*., vol. 4, pp. 323-328.

Galwey, AK & Brown, ME 1999, *Thermal decomposition of ionic solids: Chemical properties and reactivities of ionic crystalline phases*, Elsevier, Amsterdam, , pp. 75-115

Galwey, AK 2003, 'What is meant by the term "variable activation energy" when applied in the kinetic analyses of solid state decompositions (crystolysis reactions)?', *Thermochimica Acta*, vol. 397, no 1, pp. 249-268(20).

González, C, Parra, R, Klenovcanova, A, Imris, I & Sánchez M 2005, 'Reduction of Chilean copper slags: a case of waste management project', *Scandinavian Journal of Metallurgy*, vol. 34, no 2, pp. 143-149

Gorai, B, Jana, RK & Premchand M 2003, 'Characteristics and utilization of copper slag- a review', *Resources, Conservation and Recycling*, vol. 39, pp. 299-313.

Gyurov, S, Rabadjieva, D, Kovatcheva, D & Kostova Y 2014, 'Kinetics of copper slag oxidation under non isothermal conditions', *Journal of Thermal Analysis and Calorimetry*, vol. 116, no 2, pp. 945–53.

Gyurov, S, Kostova, Y, Klitcheva, G & Ilinkina A 2011, 'Thermal decomposition of pyrometallurgical copper slag by oxidation in synthetic air', *Waste Management & Research*, vol. 29, no 2, pp. 157–164.

Haavik, C, Stolen, S, Fjellvag, H, Hanfland, M & Hausermann D 2000, 'Equation of state of magnetite and its high-pressure modification: Thermodynamics of the Fe-O system at high pressure, Sample at P = 0 GPa', *American Mineralogist*, vol. 85, pp. 514-523.

Khawam, A & Flanagan, DR 2005, 'Role of isoconversional methods in varying activation energies of solid-state kinetics', *Thermochimica Acta*, vol. 436, no 1-2, pp. 101-112;

Mihailova I & Mehandjiev D 2010, 'Characterization of fayalite from copper slags', *Journal of the University of Chemical Technology and Metallurgy*, vol. 45, no 3, pp. 317-326.

Ozawa, TA 1965, 'New Method of Analyzing Thermogravimetric Data', *Bulletin of the Chemical Society of Japan*, vol. 38, pp. 1881-1886.

Parsons MB, Bird, DK, Einaudi, MT & Alpers CN 2001, 'Geochemical and mineralogical controls of trace element release from the Penn Mine base-metal slag dump' *California. Applied Geochemistry*, vol. 16, pp. 1567–1593.

Sanchez, M, Parada, F, Parra, R, Marquez, F, Jara, R, Carasco, JC & Palacios J 2004, 'Management of copper pyrometallurgical slags: giving additional value to copper mining industry' *Proceedings of VII Int. Conference on Molten Slags. Fluxes & Salts*, Cape Town. South Africa, vol. 25-28, pp. 543-550.

Shen, H & Forssberg E 2003, 'An overview of recovery of metals from slags', *Waste Management*, vol. 23, pp. 933–949.

Simon, P 2004, 'Isoconversional methods Fundamentals, meaning and application', *J. Therm. Anal. Cal.*, vol. 76, pp. 123-132.

Vyazovkin, S & Wight, CA 1999, 'Model-free and model-ftting approaches to kinetic analysis of isothermal and nonisothermal data', *Thermochimica Acta*, vol. 340-341, pp. 53-68.

Vyazovkin, S 2000, 'Kinetic concepts of thermally stimulated reactions in solids: A view from a historical perspective', *International Reviews in Physical Chemistry*, vol. 19, no 1, pp. 45-60.

Vyazovkin, S 2003, 'Reply to "What is meant by the term 'variable activation energy when applied in the kinetics analyses of solid state decompositions (crystolysis reactions)?"', *Themochimica Acta*, vol. 397, pp. 269-271;.

Wechsler, BA, Lindsey, DH & Prewitte, CT 1984, 'Crystal structure and cation distribution in titanomagnetites (Fe3-xTixO4) MT 100-1350', *American Mineralogist*, vol. 69, pp. 754-770.

Yang, Z, Rui-Lin, M, Wang-Dong, N & Hui W 2010, 'Selective leaching of base metals from copper smelter slag', *Hydrometallurgy*, vol. 103, no 1-4, pp. 25-29.

Zsako, J 1996, 'Kinetic analysis of thermogravimetric data. XXIX. Remarks on the "many curves" methods', *J. Therm. Anal.*, vol. 46, pp. 1845-1864.

Zsako, J 1973, 'Kinetic analysis of thermogravimetric data: VI. Some problems of deriving kinetic parameters from TG curves', *J. Therm. Anal.*, vol.5, pp. 239-251.