

P. JAROSZ*, S. MAŁECKI*

KINETICS OF THE FLUIDISED OXIDATION OF ZINC SULPHIDE CONCENTRATES WITH AN ADDITION OF INERT MATERIALS

KINETYKA FLUIDALNEGO UTLENIANIA SIARCZKOWYCH KONCENTRATÓW CYNKU Z DODATKIEM MATERIAŁÓW OBOJĘTNYCH

This paper presents the results of the kinetic studies of the zinc sulfide concentrate oxidation with the addition of inert, ZnO-containing materials. It was observed that about 15% of zinc oxide addition, obtained from steelmaking dust, improves the rate and maximum degree of oxidation of the concentrate. Kinetic equations of the process were determined, and the activation energy for various additions of inert material was calculated.

Keywords: roasting, zinc concentrates, inert materials, oxidation kinetics

W artykule przedstawiono wyniki badań kinetycznych utleniania koncentratów siarczkowych cynku z dodatkiem materiałów obojętnych, zawierających ZnO. Stwierdzono, że dodatek około 15% tlenku cynku, otrzymanego z recyklingu pyłów stalowniczych, zwiększa szybkość i maksymalny stopień utlenienia koncentratu. Określono równania kinetyczne procesu i energię aktywacji dla różnych dodatków materiału obojętnego.

1. Introduction

The production of zinc by the hydro-electrometallurgical process always starts with the stage of the oxidising calcination of sulphide concentrates. One type of equipment that is commonly used for this purpose is a fluidised-bed furnace. The process of calcination in the fluidisation state running in this furnace ensures the high rate of this process, energy auto-geneity, and provides a fine grain product which is beneficial for the subsequent stages of hydro-metallurgical process.

One of many problems frequently encountered in the fluidised calcination process is a high concentration of the sulphide sulphur in condensed products i.e. in the mixture from the furnace threshold and in the dust. Sulfide sulfur is present mainly in the form of ZnS, FeS, FeS₂ and PbS. According to the literature and many industrial data, the maximum content of sulphide sulphur in the materials directed to the leaching process should not exceed 0.5 wt. %. However, in some industrial plants this parameter momentarily can reach values as high as twofold higher, which significantly decreases the leaching ability, and consequently the zinc output in the entire process.

The analysis of the occurring phenomena shows that one of the reasons for the high content of the sulphide sulphur in condensed roasted products may be excessively high tem-

perature in the fluidisation bed. Under these circumstances, two roasting process products, namely ZnSO₄ (melting point T=1015 K) and PbO (melting point T=1160 K) may be subjected to partial melting. The formation of the liquid phase will result in the stoppage (or significant limitation) of the processes of the diffusion of oxygen to the reaction surface and transfer of sulphur dioxide from this surface. The grain core will, therefore, remain non-oxidised and thus the sulphide sulphur content in the calcinated ore will increase.

One of the methods to limit this adverse phenomenon is lowering the temperature in the furnace by adding to the charge energetically-inert materials of high zinc content. Such an additive is, for example, the oxide material obtained from the recycling of steel dust.

2. Experimental

Mixtures of zinc concentrates with oxide (mainly ZnO) additions were used in the investigations. The chemical and mineralogical compositions of these materials are presented in Table 1.

A photomicrograph of the concentrate sample and the size grain distribution is shown in Fig. 1.

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS METALS, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

The chemical and mineralogical composition of the materials (wt. %) used in the investigations

Element/ Formula	Zinc concentrate		Element/ Formula	Zinc oxide	
	Chemical	Mineralogical		Chemical	Mineralogical
Zn/ZnS	54.894	81.810	Zn/ZnO	68.171	84.27
Pb/PbS	2.566	2.963	Pb/PbO	5.390	5.81
Fe/FeS₂	6.028	7.050	Fe/FeO	3.519	4.03
S_s	32.580		S_s/ZnS	0.230	0.70
Others:			Others:		
FeS		4.30	Fe ₂ O ₃		0.55
CaO		0.43	CaO		0.73
MgO		0.18	SiO ₂		1.12
SiO ₂		0.10			
Al ₂ O ₃		0.10			
CO ₂		0.54			
Total	96.068	97.473	Total	77.31	97.21

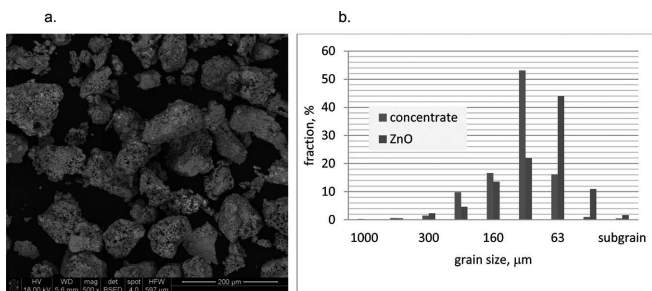


Fig. 1. SEM microphotography a) and grain size materials characteristics b)

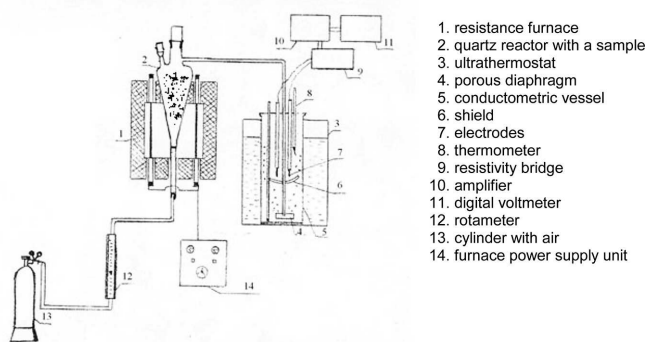


Fig. 2. Measuring apparatus diagram

These materials were used to prepare the mixtures containing an addition of oxide material within the quantitative range of 0-30% wt. For all the mixtures, the roasting process was carried out in an experimental unit in a few constant temperatures from the range of 873-1073 K. Measurements at higher temperatures were impossible due to the excessively short duration of the process, which hindered the interpretation of the obtained results. The air circulation was constant

and amounted to 10 dm³/h, which constituted a sufficient excess of gas for the full oxidation of the samples. During the measurement amount of oxidised sulphur was measured. The measurements under all conditions were repeated three times, and the final results are the average of these measurements. The scheme of the apparatus is shown in Fig. 2.

3. Results

Examples of the results of the measurements are shown in Figs. 3, 4 and 5 presenting the change in the oxidation degree versus the time for a specific additive of zinc oxide, and for all the measurements' temperatures. The degree of conversion was determined on the basis of the relationship:

$$\eta = \frac{\text{mass of the sulphur released}}{\text{mass of the sulphur in the sample}} \quad (1)$$

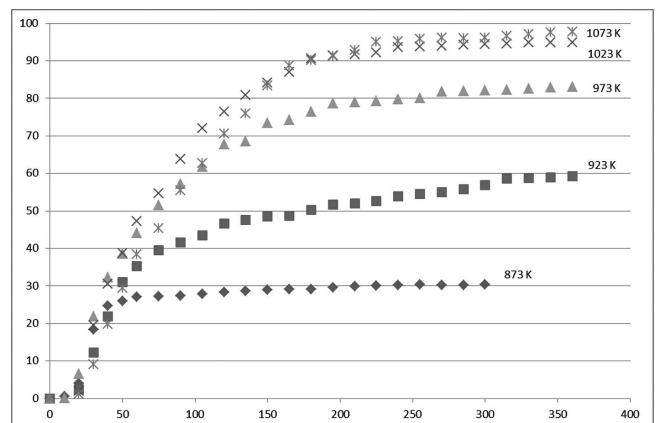


Fig. 3. The relationship between the oxidation degree, time and temperature for the mixture without zinc oxide

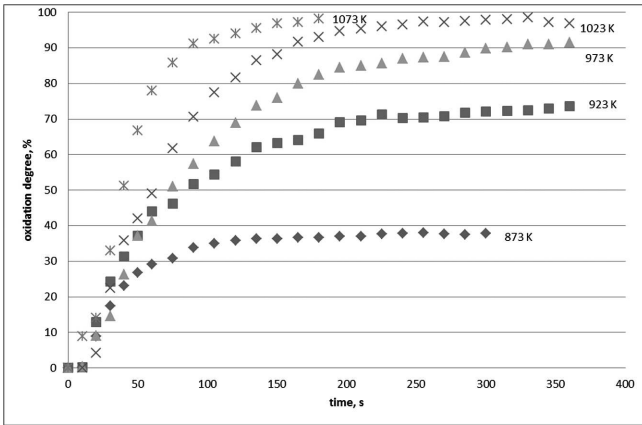


Fig. 4. The relationship between the oxidation degree, time and temperature for the mixture containing 10% per cent of the zinc oxide additive

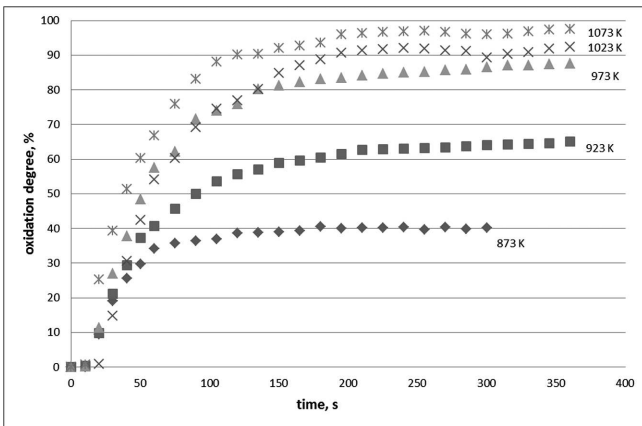


Fig. 5. The relationship between the oxidation degree, time and temperature for the mixture containing 20% of the zinc oxide additive

On the basis of the presented results, the maximum oxidation degree can be determined (as the average from the last 10 measurement points taken for a long time). These values for all the measurements' temperatures and with zinc oxide added to the charge are shown in Fig. 6.

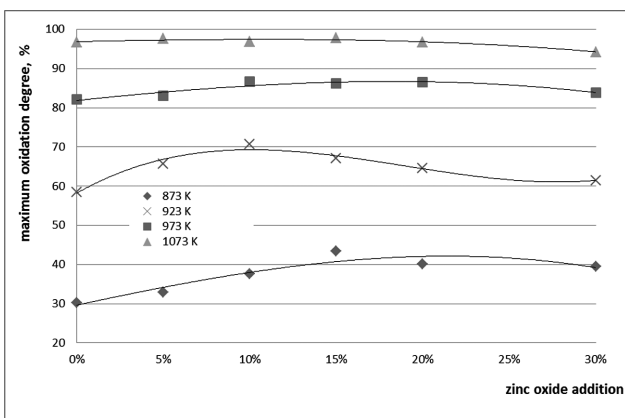


Fig. 6. Maximum degree of the final calcination of the investigated charge mixtures versus the zinc oxide addition for various temperatures

The recorded kinetic curves presented in Figs. 3-5 allow to describe the kinetics of the process. In the literature, a

number of various kinetic equations derived for reaction in heterogeneous systems can be found [1-7]. For the needs of the present analysis, the calculations for 15 different models were initially carried out, which determined the reaction kinetics in a heterogeneous system: solid phase - gaseous phase. The first step in this analysis was the transformation of all model equations to the linearized form. Next, the selection of a model according to two criteria was conducted:

1. Correlation coefficient "r" values for the individual descriptions.
2. Initial ordinate "y*₀" value for the assumed relevance level.

The calculations showed that the process can be described precisely with three models, defined in the literature as the description of the kinetic process according to the Ginstling-Brounstein (G-B) model or the "unreacted core" model, the decreasing volume (ΔV) model, and the so-called three dimensional diffusion (3-D) model [2, 3]. The main assumptions for all three models are that the process rate is limited by the diffusion of the reaction product from the surface; the reaction surface decreases during the process and it can be assumed that the solid phase has the form of ball-shaped grains. The equations describing the process rate for each model are of the form:

$$kt = \left[\left(1 - \frac{2}{3}\eta \right) - (1 - \eta)^{\frac{2}{3}} \right] \text{ for the G - B model} \quad (2)$$

$$kt = \left[1 - (1 - \eta)^{\frac{1}{3}} \right] \text{ for the } \Delta V \text{ model} \quad (3)$$

$$kt = \left[1 - (1 - \eta)^{\frac{1}{3}} \right]^2 \text{ for the 3 - D model} \quad (4)$$

where:

k – the constant proportional to the process rate, t – time [s], η – degree of conversion.

For these equations, by the least square method, the following values of the parameters were obtained for the above-referred criteria:

- ▶ G-B model: the correlation coefficient value $r = 0.9940 \pm 0.009$ with the initial ordinate $y_0 = 2 \cdot 10^{-5}$, which (with the assumed relevance level = 99%) corresponds to the assumed value $y_0^* = 0$.
- ▶ 3-D model: the correlation coefficient value $r = 0.9866 \pm 0.001$ with the initial ordinate $y_0 = 4 \cdot 10^{-5}$, which (with the assumed relevance level = 99%) corresponds to the assumed value $y_0^* = 0$.
- ▶ ΔV model: the correlation coefficient value $r = 0.9812 \pm 0.007$ with the initial ordinate $y_0 = 9 \cdot 10^{-5}$, which (with the assumed relevance level = 99%) corresponds to the assumed value $y_0^* = 0$.

The values of the slope "k" obtained for linearized dependence, being the measure of the reaction rate constants, differed insignificantly for the individual models. For further calculations the tree-dimensional diffusion model was assumed. This solution is suggested by the authors of the study [6] for the analysis of the sulphide oxidation processes. In addition, it was also used in the studies of Fukunaka, Natesan and Dimitrov [5, 9, 10]. The values of k -constants (eq. 4) for all the tested materials and all measurements temperatures are presented in Table 2.

TABLE 2

The values of constants $k \cdot 10^3$ (eq. 4) for all tested materials and temperatures

T, [K]	oxide materials addition					
	0%	5%	10%	15%	20%	30%
873	0.6	0.6145	0.768	0.79	0.8615	0.5779
923	0.9747	1.0288	1.1474	0.9733	0.9865	0.9732
973	1.1165	1.1691	1.17	1.2321	1.2844	1.19
1023	1.4243	1.5583	1.2717	1.6196	1.4882	1.3194
1073	1.45	1.6	1.7	1.68	1.6	1.555

As an example, Fig. 7 shows the accuracy of the description of experimental points obtained from the model.

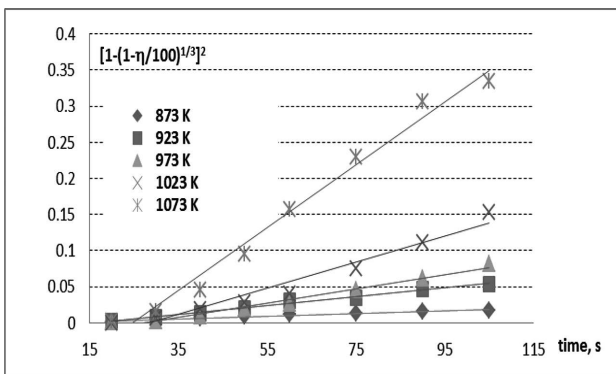


Fig. 7. The kinetics of oxidation of zinc concentrate with 10% of the oxide. Experimental points and curve model after linearization (an example)

Next, for the selected model, the initial process rates were calculated (Fig. 8).

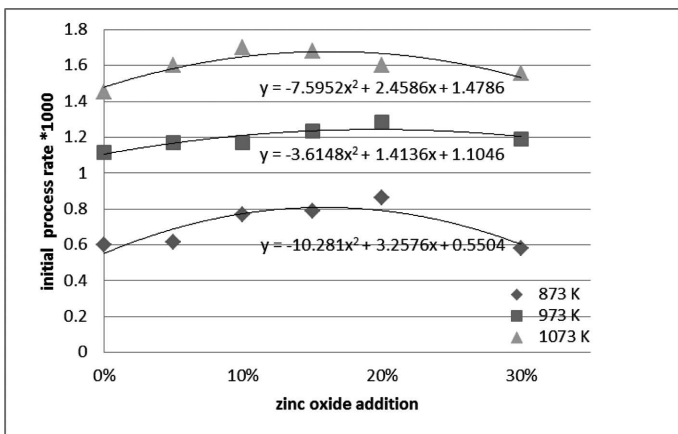


Fig. 8. The effect of addition of zinc oxide on the initial rate of the process for different temperatures

The presented results show a positive impact of the oxide additives in the mixture on the kinetics of the process and its capacity. The increase in the degree of oxidation by 10% provides a corresponding reduction of the zinc loss in the leaching step. The maximum final calcination degree in the entire temperature range has its maximum at 12-15% of oxide additives to the charge. Such an addition of energetically-inert materials makes it also possible to obtain the initial rate of

the final calcination of charge mixtures. Under industrial conditions, this corresponds to the minimisation of the sulphide sulphur content in the roasted products, and the significant process rate assumes a sufficient time for the reaction of the continuously fed charge to be completed.

With the use of the presented data the process activation energy within the analysed temperature range and the relationship between this energy and the oxide additives to the charge mixture was determined on the basis of the Arrhenius equation. The activation energy reaches its minimum for the oxide addition amounting to approx. 17.7%. The results are presented in Fig. 9 and 10.

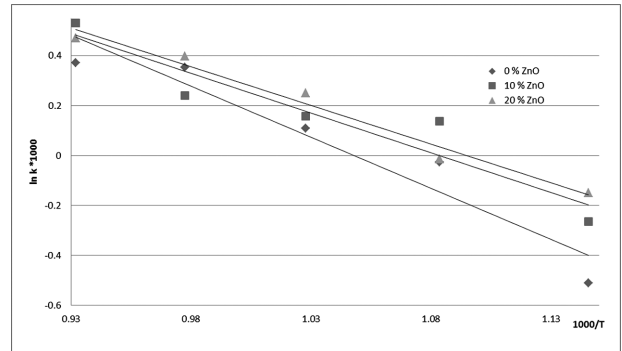


Fig. 9. Temperature dependence of the initial reaction rate constant ($\ln k = f(1000/T)$)

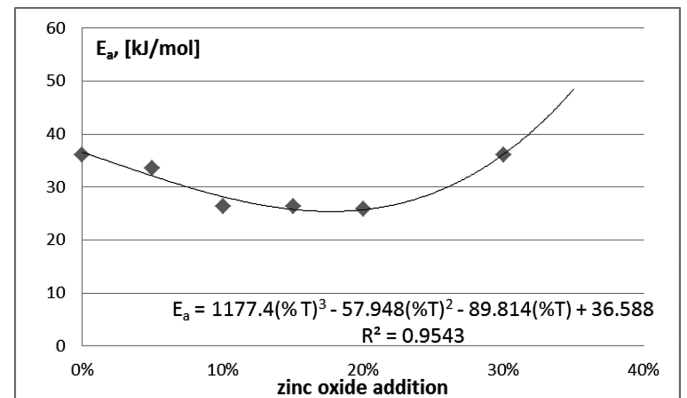


Fig. 10. The relationship between the process activation energy and the zinc oxide addition

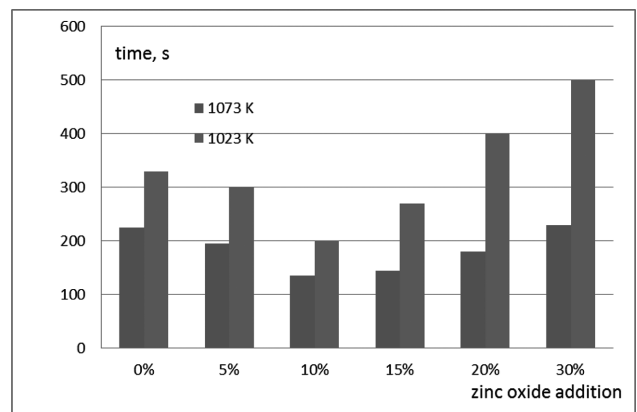


Fig. 11. The time needed for obtaining a 95% degree of final calcination for various charge mixtures at the temperatures of 1023 and 1073 K

TABLE 3

Composition of the zinc concentrate [wt. %] analysed in various studies, the process kinetic model used, and the activation energy [kJ/mole]

Work	Zn	Fe	Pb	S	Kinetics model	Activation energy
This work	54.90	6.03	2.57	32.58	$kt = \left[1 - (1 - \eta)^{\frac{1}{3}}\right]^2$	25 - 38
[3]	67.15	0.00	0.00	32.85	$kt = \left[1 - (1 - \eta)^{\frac{1}{3}}\right]$	– Isothermal investigations, T=1123 K
[4]	48.30	19.25	No data	31.80	$kt = \left[1 - (1 - \eta)^{\frac{1}{3}}\right]$ and $kt = -\ln(1 - \eta)^{\frac{1}{2}}$	31 - 96
[5]	55.70	5.50	No data	30.70	$kt = \left[1 - (1 - \eta)^{\frac{1}{3}}\right]^2$	53 - 72
[8]	56.18	5.02	0.81	33.20	$kt = \left[1 - (1 - \eta)^{\frac{1}{3}}\right]$	87
[9]	46.40	11.90	0.71	30.90	$kt = \left[1 - (1 - \eta)^{\frac{1}{3}}\right]^2$	169

The confirmation of the significant impact of the addition of inert materials on the rate of the oxidation process and its technological effectiveness is the compilation shown in Fig. 11. It presents the relationship between the time needed for obtaining a 95% degree of mixture oxidation and the oxide additive in the charge. The relationship is demonstrated for two selected temperatures. The presented values reach their minimum at the temperatures of 1023 and 1073 K for the 9.50 and 14.52% of the zinc oxide addition, respectively.

4. Discussion

The investigations carried out in this study allow for formulation of a few conclusions essential for the technology of the calcination of zinc sulphide concentrates in the fluidised state. A series of tests carried out in an experimental reactor simulating the process in the fluidised-bed furnace allowed to suggest that the degree of the charge mixture final calcination depends on its composition and temperature. The temperature increase in the range from 873 to 1073 K results in the increase of the maximum final calcination degree from the range {30; 45}% in the temperature of 873 K to the values from the range {80; 98}% at the temperature of 1073 K, and it depends on the charge mixture composition. The addition of the oxide material up to 15% makes the calcination degree higher, and the further increase of its concentration in the charge mixture makes this degree lower. The maximum calcination degree at temperatures up to 973 K is observed for the zinc oxide addition in the range from 10 up to 15%, whereas at higher temperatures this relationship is weaker and ambiguous. However, also at the temperature of 1073 K, the maximum is observed for the oxide addition at the amount of approx. 10 %. Zinc oxide addition in the amount similar to that mentioned above significantly increases the initial process rate. The results of the measurements and appropriate calculations also show that in the $\ln(k)=f(T^{-1})$ coordinate system, i.e. in the Arrhenius coordinate system, the relationship between the initial process rate constant and the inverse temperature is linear. This may prove that the process mechanism is the same within the analysed temperature range. The process activation energy

determined from the Arrhenius equation depends strongly on the amount of zinc oxide addition to the charge, and it shows its minimum for approx. 15% of ZnO in the charge mixture.

It is very difficult to compare the results obtained in this study with the data reported by other authors. The basic reason for that is the problem of the both chemical and mineralogical composition of samples, as well as the physical form (grain size, moisture content, etc.) of the concentrates. The concentrate we analysed was taken from a zinc mill, and it was subjected to a drying process in the temperature of 378 K. Its grain composition was heterogeneous (Fig. 1). The differences in the concentration of the basic components of the concentrate analysed in other studies are presented in Table 2. The authors of these studies do not give the mineralogical composition of those concentrates. In Table 3, the kinetic equations are also presented, which were used in the quoted publications, as well as the obtained values of the activation energy (or their ranges).

When analysing the reasons for the relationships observed in the investigations, a few hypotheses can be formulated. These hypotheses are connected with the chemical compositions of the charge mixture, its grain size, and both the energetics and the chemistry of the oxidation process. The charge mixture components differ significantly in their chemical composition. The oxide material used in the investigations exhibits high zinc concentration, more than a twofold higher content of lead in comparison with the concentrate, and almost complete lack of sulphide sulphur. The oxide, due to the specificity of the process in which it is formed (zinc condensation from the gaseous phase along with reoxidation), is a material of substantially lower graining than both of the concentrates used in the investigations. It also shows a lower diversity in graining. These factors directly affect the behaviour of individual charge mixture components within the process, and also indirectly its energetics.

The oxide material can be considered a charge mixture component inert from the energetic point of view. This may explain lowering of the oxidation rate, particularly for ZnS. Because the concentration of iron sulphides in the charge decreases, the reaction of the ZnS oxidation is initiated at

slightly higher temperatures, and therefore, the overall process rates relatively decrease. This decrease of the process rate is partially eliminated by a local increase of the oxygen concentration in relation with the sulphide sulphur flux. At the same time, for the oxide addition in the amount up to 15%, the maximum final calcination degree increases. This results in a lower sulphide sulphur content in the condensed products. This effect can also be interpreted with the lowering of the overall level of the energy generated during the process. In such a case, a locally lower temperature of the charge mixture grains should occur, which prevents from the partial surface melting of grains, particularly those with the increased content of lead compounds. The lack of the liquid phase on the grain surface facilitates a free access of oxygen to the reaction surface, and thus the oxidation of the entire sulphide sulphur contained in the grain. However, the formation of the liquid phase efficiently obstructs the access of oxygen, and the grain core remains non-oxidised. It can be supposed that the oxide additive in an amount of over 15% will adversely affect the process, mainly because of an excessive increase of the concentration of the lead compounds in the charge, the higher possibility of the appearance of the liquid phase, and the consumption of significant amount of heat used for heating up this material.

Summarizing, the addition of inert oxide materials, reach in zinc, within the range of 15% in the charge mixture, has a positive impact on the process of the calcination of zinc sulphide concentrates in the fluidised-bed furnace.

5. Conclusions

1. The results of our measurements show a strong relationship between the conversion degree of the charge mixture composed of sulphide zinc concentrate and oxide zinc-containing material, its composition and temperature.

2. The maximum degree of the final calcination increases with the increase of temperature, and slightly with the oxide material addition up to 15%. A further increase of the oxide material share in the charge will decrease this process index.

3. A similar effect on the initial process rate has a zinc oxide addition.

4. The process rate can be described with a very good accuracy with the formula:

$$kt = \left[1 - (1 - \eta)^{\frac{1}{3}} \right]^2$$

resulting from the three-dimensional diffusion model used for the determination of the rate of heterogeneous processes.

5. The process activation energy varies from 25 to 37 kJ/mol, and it shows its minimum for approx. 15% of the inert material addition.

6. The factor which lowers the process effectiveness is an excessive, local temperature increase occurring particularly in case of the high pyrite and pyrrhotite contents in the zinc concentrate. The possibility to limit this adverse phenomenon by adding oxidised zinc-bearing materials allows for lowering the sulphide sulphur concentration in the condensed process products.

7. In case of an increased lead content, the addition of inert zinc-bearing materials should be limited.

REFERENCES

- [1] T. H a v l i k, at al., Studium termickeho rozkladu vapenca, Hutnicke listy **4**, 277 (1989).
- [2] J. D e r e Ń, J. H a b e r, R. P a m p u c h, Chemia ciała stałego, PWN Warszawa 1977, pp. 610-638.
- [3] Cz. M a l i n o w s k i, Analysis of the effects of time factors of the oxidation rate of zinc sulphide, Arch. Met. **28**, 193 (1983).
- [4] Ž.D. Ž i v k o w i c, at al., Kinetics and mechanism of the natural mineral marmatite oxidation process, J. Therm. Anal. **54**, 35 (1998).
- [5] Y. F u k u n a k a, at al., Oxidation of zinc sulfide in a fluidized bed, Met. Trans. B **78**, 307 (1976).
- [6] V.N. Waddar, J.K. Behera, Study of kinetics involved in oxidation of nonferrous metal sulphides, thesis, National Institute of Technology, Rourkela 2010, India.
- [7] T. Karwan, Cz. Malinowski, S. Małęcki, Archiwum Hutnictwa **29**(3), 343-352 (1984).
- [8] C.A.R. Queiroz, at al., Oxidation of zinc sulphide concentrate in a fluidized bed reactor, part I & II, Braz. J. Chem. Eng. **22**, 117-124 and 127-133 (2005).
- [9] K. Natesan, W.O. Philbrook, Oxidation kinetic studies of zinc sulphide in a fluidized bed reactor, Met. Trans. **1**, 1353 (1970).
- [10] R. Dimitrov, I. Bonev, Mechanism of zinc sulphide oxidation, Thermochimica Acta **106**, 9 (1986).