

S. MAŁECKI*, P. JAROSZ*

THERMOGRAVIMETRIC ANALYSIS OF THE ZINC CONCENTRATES OXIDATION CONTAINING VARIOUS IRON COMPOUNDS

TERMOGRAWIMETRYCZNA ANALIZA UTLENIANIA KONCENTRATÓW CYNKOWYCH ZAWIERAJĄCYCH RÓŻNE ZWIĄZKI ŻELAZA

This paper presents the results of oxidation of zinc concentrates containing various iron compounds. Using the thermogravimetry and thermal analysis methods it was shown that the influence of the iron form affects the thermal oxidation process. They influence the rate of, oxidation of zinc sulphide and consequently the resulting rate of oxidation of the concentrate.

Keywords: roasting, zinc concentrates, thermal analysis, iron compounds

W pracy przedstawiono wyniki badań utleniania koncentratów cynku zawierających różne związki żelaza. Wykorzystując metody termogravimetrii i analizy termicznej wykazano wpływ formy występowania żelaza na efekty cieplne utleniania. Rzutują one na szybkość utleniania siarczku cynku i związaną z tym szybkość utleniania koncentratu.

1. Introduction

In the processes of the calcination of zinc sulphide concentrates, one of the significant problems is the behaviour of various concentrate components and their impact on the oxidation of zinc sulphide, which is the dominating component of the concentrate. A particular role is attributed to the iron sulphides which, when oxidising as the first component, initiate the exothermic calcination processes and may affect the rate of the oxidation of ZnS and other components. These problems were already described in many studies, e.g. in [1-10]. The effect of pyrite on the oxidation rate ZnS [1], and the ZnS kinetics oxidation of fluidized bed [2], the possibility of zinc ferrite formation [3, 6] was investigated. In [4-6, 10] the effect of various roasting parameters (temperature, grain size, the addition of lime) on the ignition temperature and calcination products was evaluated. However, in the papers [6, 8, 9], the effects of marmatite for zinc concentrate roasting process was determined. In this study, on the basis of the thermogravimetric investigations, the analysis of the behaviour of three different zinc concentrates in calcination processes is performed.

2. Experimental

2.1. Characteristics of the investigated materials

Three various zinc concentrates, differing particularly in the form of iron occurrence, were investigated. Table 1 presents the results of the chemical analyses of the essen-

tial concentrate components and X-ray phase analysis. Fig. 1 presents an exemplary diffractogram for the "A" concentrate.

TABLE 1
Chemical analysis of the concentrates: (% wt.) and X-ray phase analysis

Component	Concentrate "A"	Concentrate "B"	Concentrate "C"
Zn	56.03	50.35	53.92
Fe	5.16	9.5	5.18
Pb	2.62	2.35	2.12
Cu	0.032	0.53	0.04
S _S	33.8	27.7	26.8
SiO ₂	0.1	4.41	5
CaO	0.4	0.2	0.17
Al ₂ O ₃	0.1	0.3	0.18
Mineralogical composition of the analysed concentrates			
ZnS	+++	+++	+++
PbS	++	++	++
FeS ₂	+++	+	-
Fe ₂ O ₃	-	+	+++
ZnSO ₄ ·3Zn(OH) ₂ ·5H ₂ O	+	++	+
Pb ₄ Al ₂ Si ₂ O ₁₁	-	++	+
CaSO ₄	++	-	-

The probability of the phase occurrence: +++ certain, ++ very likely, + unlikely, - no occurrence

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

The analysis shows that the concentrates differ in zinc content by approx. 10%. The “A” concentrate is the richest in this metal, while the “B” concentrate is the poorest in it. The iron content levels in the “A” and “C” concentrates are similar. The “B” concentrate exhibits almost twice as high content of this component. In addition, the difference in sulphide sulphur content is relevant, which may indicate the different mineralogical form of iron occurrence. As for the “B” and “C” concentrates, the SiO₂ content is also evidently higher. Other components occur in insignificant amounts.

The phase analysis shows that both the ZnS and PbS phases occur in all the concentrates. As for iron compounds, the pyrite occurrence in the “A” concentrate was found and the presence of iron (III) oxide was observed in the “C” concentrate. The “B” concentrate may contain both sulphide forms, but pyrrhotites occurrence cannot be excluded. However, their presence is difficult to prove accurately. The other compounds occur in smaller quantities, and basically their occurrence is confirmed in the “B” concentrate in case of ZnSO₄·3Zn(OH)₂·5H₂O and Pb₄Al₂Si₂O₁₁, and in the “A” concentrate for CaSO₄ (which results from the demagnetisation of the concentrate at the stage of flotation process by leaching in an H₂SO₄ solution).

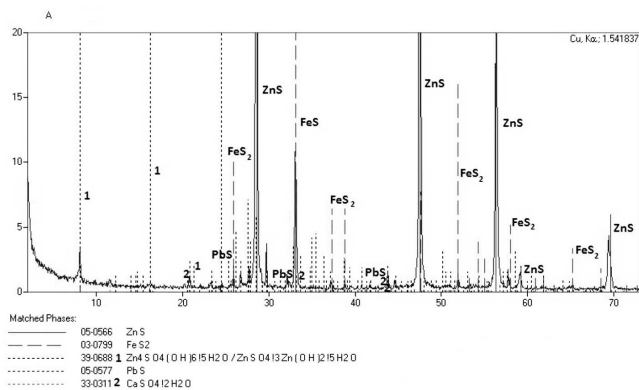


Fig. 1. “A” concentrate diffractogram

Analysis of the composition of grain size of the investigated concentrates were also carried out. The obtained results are presented in Fig. 2.

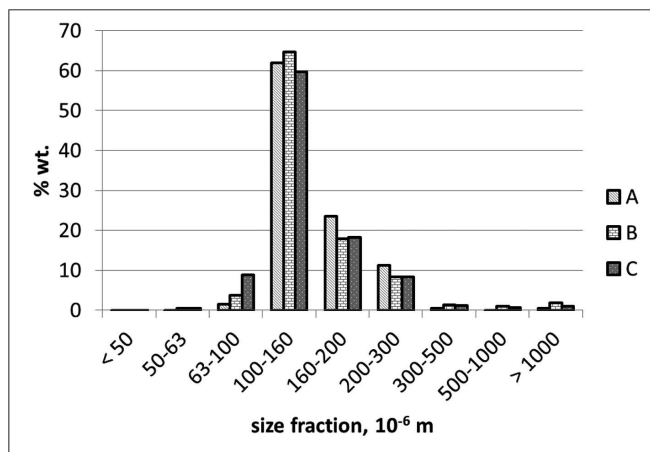


Fig. 2. Analysis of particle size distribution of the investigated concentrates

The results of particle size analysis show a very similar particle size distribution for investigated concentrates.

2.2. Thermogravimetric investigations

The materials chosen for the investigations were dried at the temperature of 100°C and then they were further investigated. No screening and/or fragmentation of the samples was carried out. The analysis of the thermographs of the investigated concentrates was conducted on the basis of the previous investigations of the oxidation of pure sulphides, the results of which are shown in Fig. 3.

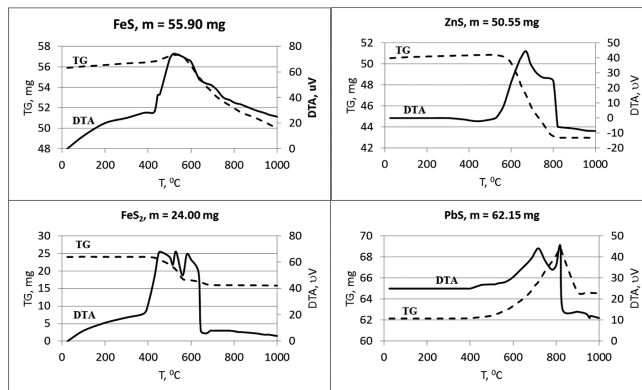


Fig. 3. Thermograms of the oxidation of pure sulphides

Next, the samples of three chosen concentrates were subjected to the thermogravimetric analysis carried out with the use of the TA Instruments SDT Q 600 thermal analyser. The first part of the investigation was conducted in the atmosphere of the air flowing with the circulation efficiency of 100 cm³/min in the temperature increasing with the rate 10 deg/min. The mass of all samples was similar and it oscillated at approx. 20 mg. The obtained results are presented in Figs. 4 to 6. On the thermograms, the mass variation curves (TG) and the heat effects (DTA) versus temperature are shown.

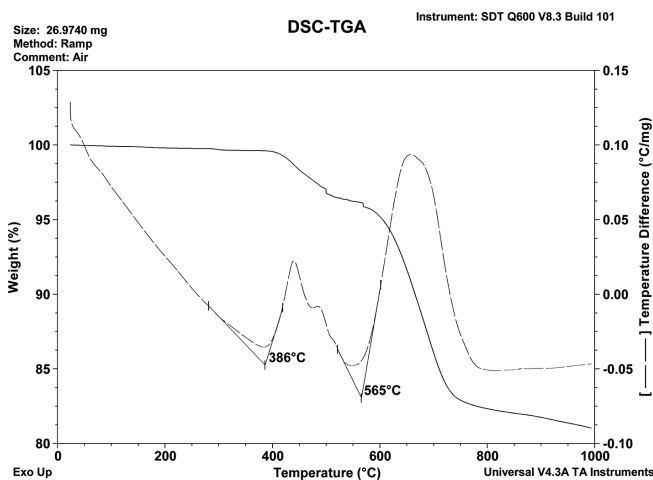
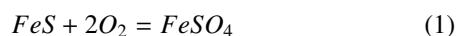


Fig. 4. “A” concentrate thermogram

The analysis of the obtained relations shows that during the oxidation process the concentrates behave in different ways. The oxidation of the “A” and “B” concentrates starts at the temperatures 384-410°C with the oxidation of iron sulphides. The temperature of the beginning of the oxidation

of iron sulphides under the experimental conditions primarily depends on grain composition and the surface development of grains, but it also may be dependent on the amount of pyrite (FeS_2) in the concentrate. Simple stoichiometric calculations allow to point out a few causes for that. In the “A” concentrate, practically all of the iron occurs in the form of pyrite, whereas in the “B” concentrate, due to the sulphide sulphur deficit, iron occurs in the form of FeS . This explains the values of the determined temperatures of the beginning of the oxidation of iron sulphides. In addition, in case of the “B” concentrate, an increase in the mass can be observed on the mass variation curve, which is characteristic for the FeS oxidation according to the reaction:



but pyrite oxidises to Fe_2O_3 , and this involves a sample mass loss. The “C” concentrate does not show any effects to the temperature up to 558°C , and this proves the absence of iron sulphides.

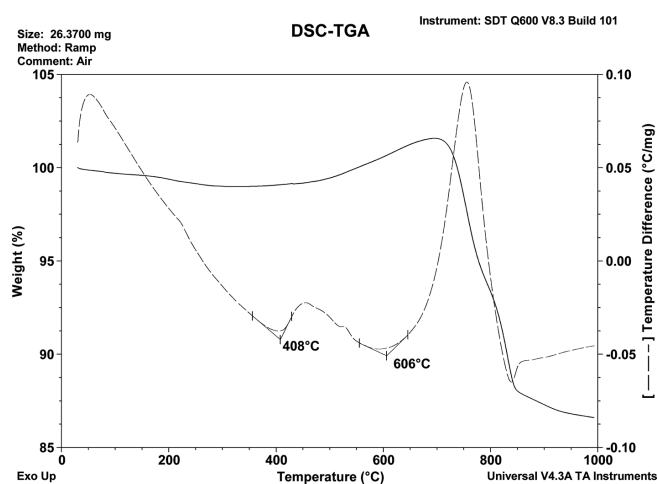


Fig. 5. “B” concentrate thermogram

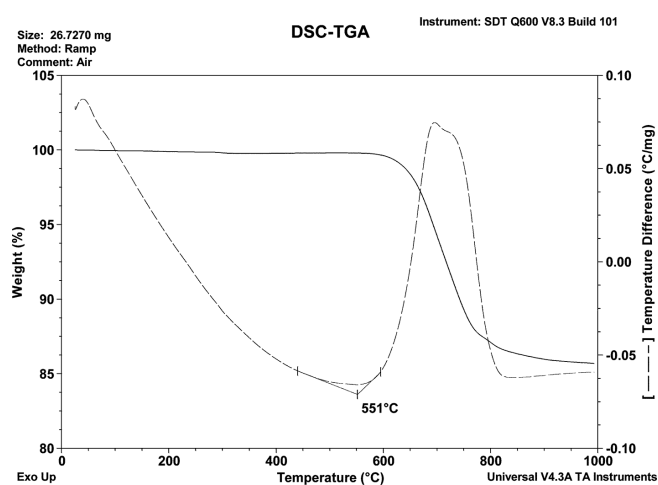


Fig. 6. “C” concentrate thermogram

Next, the effects on the thermograms are related to the mass loss and a strong exothermic effect originated by the oxidation of zinc sulphide to oxide. The beginning of this process for the concentrates “A” and “C” can be observed in the range of temperatures $500\text{--}560^\circ\text{C}$. For “B” concentrate this

temperature is 594°C . At the end of these processes, the reactions of PbS oxidation, and PbSO_4 and CaCO_3 decomposition, may occur, which are undetectable due to the superposition of individual effects.

3. Discussion

On the basis of the integration of the DTA curves, relative value of the thermal effect of the oxidation processes was determined. It is presented in Fig. 7. The thermal effect of the oxidation of the “A” concentrate was assumed as 1. The results allow for stating that the greatest thermal effect occurs for the oxidation of the “A” concentrate, and a bit smaller effect is observed for the “C” concentrate. The smallest amount of heat is generated for the oxidation of the “B” concentrate.

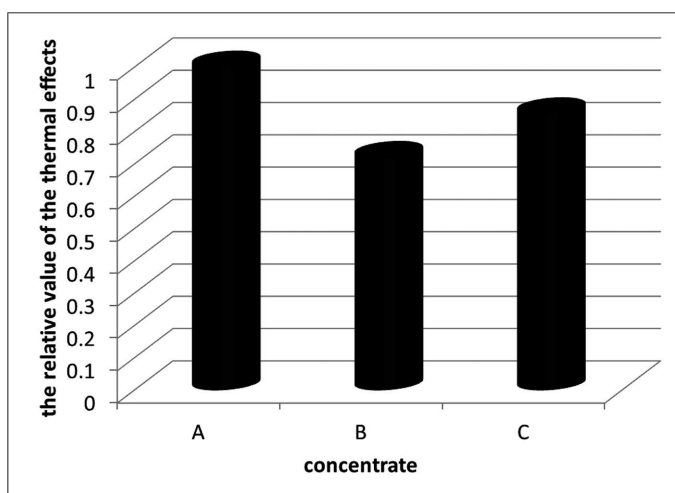


Fig. 7. The relative value of the thermal effects for the oxidation of concentrates

Another series of investigations was conducted in an argon atmosphere. The investigations were intended to determine the temperature ranges in which the mass losses connected with the thermal dissociation of the components of concentrates occur. This should allow for attributing them to relevant processes. An overall picture of the mass losses in concentrates is shown in Fig. 8.

The “A” concentrate does not undergo any changes at a temperature up to approx. 450°C , i.e. up to the temperature that is characteristic for pyrite decomposition. An approx. 4% mass loss in the temperature above 800°C is related to the decomposition of CaCO_3 , and PbSO_4 which exist in the sample in small amounts.

For the “B” concentrate, in the range of temperatures from 250 to 250°C , a small mass loss is observed, which may be related to the decomposition of alkaline zinc sulphide $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and also iron hydroxide $\text{Fe}(\text{OH})_3$. Another mass loss can be observed in the range of the temperatures from 450 to 600°C . This in turn is related to the decomposition of pyrite or pyrrhotites to FeS . An approx. 6% mass loss occurring in the temperature above 800°C is likely connected with the processes similar to those described for the “A” concentrate.

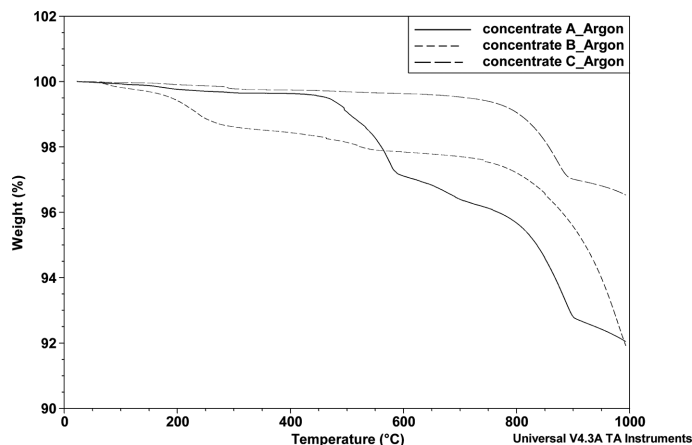


Fig. 8. The graphs of the relationship between the sample mass variation for the measurements carried out in an argon atmosphere

Finally, for the “C” concentrate, no mass loss is observed which would indicate the decomposition of iron sulphides or hydroxides. This may prove that iron occurs in the iron oxide Fe₂O₃ form only. At the temperature above 800°C, processes such as those for both “A” and “B” concentrates happen.

Further experiments were carried out in isothermal conditions. The concentrates were heated up with the maximum possible rate (100 deg/min) up to a temperature of 800°C in air atmosphere and they were maintained in these conditions until the sample reached a constant mass. An investigation of this type allowed to determine the total mass loss in this temperature and process rate, expressed as weight change over time. The results are shown in Figs. 9 and 10.

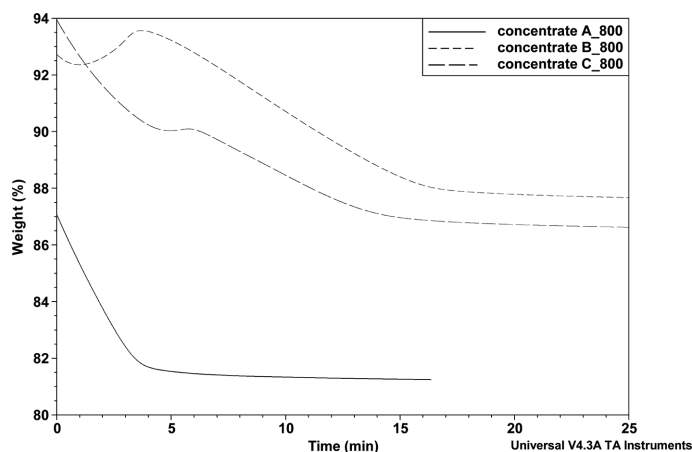


Fig. 9. The graph of the variation of the mass of the samples in the temperature 800°C

The nature of the obtained relationships is a moot problem. It is only for the “A” concentrate that a systematic mass loss is observed. In other cases, after keeping the constant temperature, small mass increases occur. They are difficult to interpret since the measurement temperature is higher than that of the dissociation of iron and zinc sulphides, whereas the formation of lead and calcium sulphides would not cause a significant mass increase. Perhaps, it is due to the fast heating up (100 deg/min.) and the processes described above would not run to the end due to the sizes of the grains in which these components occurred. The mass variation disturbances may be also caused by the formation of a small amount of a

liquid phase. It is also essential that a significant difference in the final mass loss varying by approx. from 19% for the “A” concentrate up to approx. 12.5% for the “B” one. The different change of the mass until the isothermal temperature is reached may result from the variable amount of hydroxides and iron sulphides, and their different mineralogical form.

The obtained curves (Fig. 10) allowed to compare processes rates. It should be emphasised here that the rate is referred to the “process” and not “reaction”, since the recorded mass changes also include the distribution of certain compounds occurring in the concentrates. The maximum process rate for each concentrate occurs when the isothermal temperature is reached. The presented relationships demonstrate that the highest oxidation rate is reached for the “A” concentrate. For the “B” concentrate, the observed maximum oxidation rates are almost 3 times lower. This will result in the extension of the total time of the oxidation process, despite the lower mass losses. The rate of the “C” concentrate oxidation is of an intermediate value.

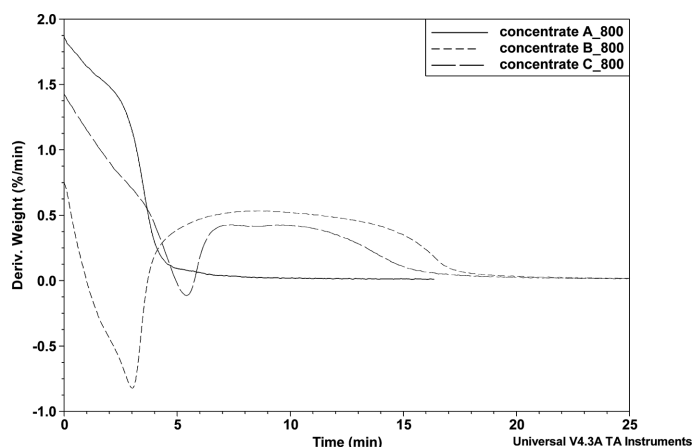


Fig. 10. Derivative of the sample weight changes over time

The rate of the oxidation processes may depend on the compounds of iron occurrence, and particularly on the pyrite amount. A strong exothermic effect of the pyrite oxidation will cause an acceleration of the zinc sulphide oxidation rate, which has been confirmed in the previous study [1].

4. Conclusions

The results and also other information gained from the present investigations allow for formulating the following conclusions:

- Significant differences occur in the chemical composition of the analysed concentrates. The differences relate to both the iron and sulphur content, and also that of silica, as well as other oxidised components (due to their small total impact on the process, it will not be further discussed).
- Essential differences in the mineralogical form of the components of the concentrates are observed. The concentrates were selected so that iron occurred in three different forms: pyrite, pyrrhotites, and iron (III) oxide. This causes various heat effects at the beginning of the concentrate oxidation process, and this is what affects the rate of the subsequent processes, hence their duration.

- In the “A” concentrate, iron occurs in the form of pyrite, which delivers a great amount of heat at the oxidation process, and consequently also accelerates zinc sulphide oxidation processes. But the “B” blend contains iron in the form of FeS, which causes its oxidation to sulphide (increase in mass) and only after that it undergoes a thermal dissociation which is an exothermic process. This in turn results in a significant lowering of the zinc sulphide oxidation rate, and consequently in an approx. triple decrease of the rate of the entire concentrate oxidation. The “C” concentrate features a high iron content, but this iron occurs in an oxidised form, which slightly affects the oxidation heat effect. Hence, the rate of the process is twice as high as that of the “B” concentrate.

REFERENCES

- [1] T. Karwan, Cz. Malinowski, S. Małeckki, *Archivum Hutnictwa* **29**, 343 (1984).
- [2] K. Natesan, W.O. Philbrook, *Metallurgical Trans.* **1**, 1353 (1970).
- [3] J.W. Graydon, D.W. Kirk, *Metallurgical Transactions B* **19B**, 141-146 February 1988.
- [4] J.E. Dutrizac, *Canadian Journal of Chemistry* **58**, 739 (1980).
- [5] J.G. Dunn, *Thermochimica Acta* **300**, 127 (1997).
- [6] B.S. Boyanov, R.I. Dimitrov, Z.D. Zivkovic, *Thermochimica Acta* **296**, 123-128 (1997).
- [7] H.Y. Sohn, D. Kim, *Metallurgical Trans.* **18B**, 727 (1987).
- [8] Z. Zivkovic, D. Zivkovic, D. Grujicic, V. Savovic, *Thermochimica Acta* **315**, 33 (1998).
- [9] R.I. Dimitrov, N. Moldovanska, I.K. Bonev, Z. Zivkovic, *Thermochimica Acta* **362**, 145-151 (2000).
- [10] J. Nyberg, *Characterization and control of the zinc roasting process*, Oulun Yliopisto, Oulu 2004.