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Thermal behaviour of low-quality zinc sulphide concentrate

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Abstract

DTA, TGA and *X*-ray diffraction analysis of a low-quality zinc concentrate from Maidanpek deposit in Yugoslavia have been made. High content of marmatite has been found in it, which results in the formation of $ZnFe_2O_4$ when roasted. Behaviour of Yugoslavian concentrate during oxidation is compared to those of Bulgarian, Polish and Canadian concentrates. The results obtained from the thermal treatment of the concentrates and the calculations made, make possible to recommend optimal composition of mixtures for roasting in fluid bed. They are made up of Bulgarian, Polish and Canadian concentrate and Yugoslavian concentrate in them should be up to 8%. © 1997 Elsevier Science B.V.

Keywords: Thermal behaviour; Zinc; Sulphide; DTA; TGA

1. Introduction

While processing zinc concentrates, using classical hydrometallurgical technologies, there is a number of requirements concerning their chemical, granulometric and phase composition. Our observations and research of over 100 concentrates from more than 20 countries, show that zinc concentrates meet most of the requirements [1,2]. A suitable mixing can reduce or totally eliminate the harmful effects of some of their components.

The case is more complicated when, due to various reasons (technological or economic), low-quality out-of-standard zinc concentrates are obtained after flotation. They are often of complex nature and composition and contain more Fe, Cu, Pb, SiO_2, etc. in comparison with the requirements. The form of zinc and iron sulfides in concentrates is of considerable importance. Presence of marmatite results in a considerable increase in the formation of zinc ferrite [3,4] which is insoluble in diluted solutions of sulphuric acid.

Processing of zinc concentrates with higher Cu content causes serious difficulties. These concentrates can be considered as copper–zinc ones. Sometimes they contain 10–25% Zn and 8–15% Cu [5]. While choosing a technology for processing such raw materials, it is necessary to have in mind their quantity, chemical and phase composition [6–10]. One of the initial steps in their study is to test their behaviour when thermally treated [9] and to check up the possibilities to mix them with the produced and processed at this stage zinc concentrates.

The purpose of this study is to investigate the low-quality zinc concentrate by using DTA and TGA which contains marmatite, to compare the results with

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those obtained from other zinc concentrates and judge the possibility for its mixing and processing with them. The zinc concentrate was obtained from Maidanpek deposit in Yugoslavia. For this purpose software [11] which we have worked out and upgraded is used.

2. Experimental

DTA and TGA were made using a Derivatograph Q manufactured by the Hungarian firm MOM. The analysis was made in static air atmosphere at a heating rate of 10 K min^{-1}. The following sensitivities were used: DTA – 0.5 mV; DTG – 1 mV; TG – 50 mg. The mass of all samples was 100 mg and a platinum crucible was used during the investigation.

X-ray diffraction analysis was made by a diffractometer TUR -M61 (Germany) with a copper or cobalt lamp and an iron filter.

A study was made of the characteristics of a large number of Bulgarian and imported zinc concentrates. This paper presents the results of the study of concentrates from Poland, Bulgaria, Canada and Yugoslavia, which are quite different in chemical, mineralogical and phase composition.

3. Results and discussion

Results from the chemical analysis (Table 1) show that the tested concentrates considerably differ in the content of some main components. These differences in the chemical composition make necessary a preliminary testing of their behaviour during oxidation.

The essential conclusion which can be made on the basis of the chemical composition is that processing of each concentrate alone would lead to certain difficulties. This is due to exceeding the allowable content of the components which is required for normal functioning according to classical hydrometallurgical technology for processing zinc concentrates.

Results from the X-ray diffraction analysis show that prevailing phase in all concentrates is β-ZnS.

The form in which iron exists in the concentrates is quite important. It is a fact that when it is in the form of marmatite (nZnS.mFeS) formation of ferrite increases and this results in decrease of zinc extraction [4]. Presence of pyrite (FeS_2) lowers the initial temperature of concentrate oxidation [12,13].

X-ray diffraction analyses show that FeS_2 is present in all concentrates. The Polish concentrate has the least amount of FeS_2 while the Yugoslavian one has the maximum. Marmatite phase was observed in the Yugoslavian, Bulgarian and Canadian concentrates. PbS phase is observed in the Bulgarian and Polish concentrates. The main copper containing phase in the Yugoslavian and Bulgarian concentrates is $CuFeS_2$. In the Bulgarian concentrate the lines of α-SiO_2 are observed, while they are not clearly expressed on the X-ray patterns of the other concentrates.

Table 1
Chemical composition of the investigated zinc concentrates

Component	Composition, mass.%			
	Polish	Bulgarian	Canadian	Yugoslavian[a]
Zn	54.7	49.6	53.7	32.0
Fe	1.8	7.7	8.9	18.0
Pb	2.7	2.3	0.05	1.18
SiO_2	0.57	2.9	1.08	1.30
Cu	0.09	1.00	0.80	3.86
S	30.3	30.0	33.0	32.0
Cd	0.28	0.24	0.28	0.11
Ge(g/t)	10	3	1	7
Sb	0.002	0.001	0.001	0.009
As	0.26	0.02	0.012	0.074
MgO	1.91	0.29	0.1	0.05
CaO	4.32	0.5	0.1	0.83
F	0.02	0.03	0.34	0.02

[a] indicates zinc concentrate from Maidanpek deposit in Yugoslavia.

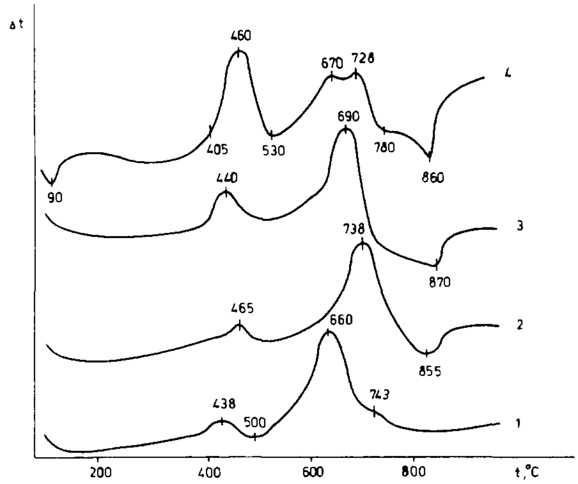

Fig. 1. DTA curves of zinc concentrates: 1 – Polish; 2 – Bulgarian; 3 – Canadian; 4 – Yugoslavian.

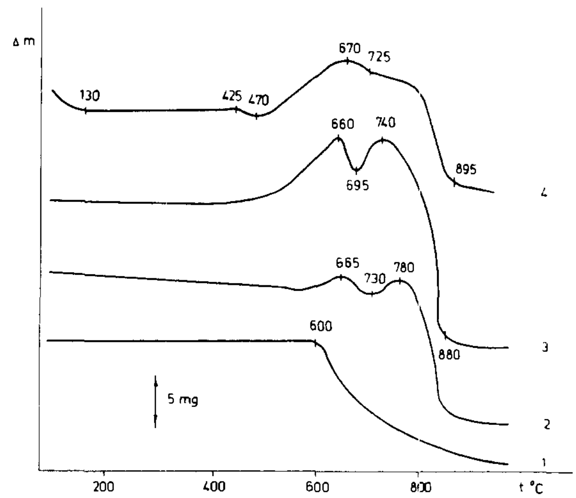

Fig. 2. TG curves of zinc concentrates: 1 – Polish; 2 – Bulgarian; 3 – Canadian; 4 – Yugoslavian.

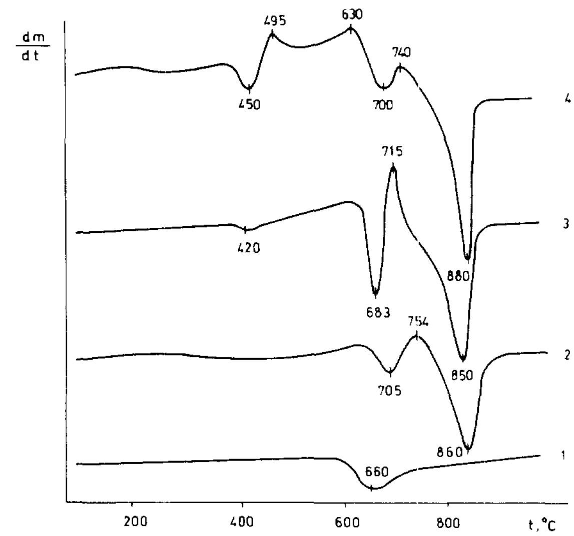

Fig. 3. DTG curves of zinc concentrates: 1 – Polish; 2 – Bulgarian; 3 – Canadian; 4 – Yugoslavian.

The DTA we made shows considerable differences in the behaviour of the different concentrates when thermally treated. Depending on phase composition, in the temperature range 400–550°C exoeffects are observed due to oxidation of FeS_2 and $CuFeS_2$ (Fig. 1). The most noticeable peak in this interval is observed with the Yugoslavian concentrate.

The intensive exoeffects in the temperature range 600–800°C are a result of β-ZnS oxidation. Differences are observed in the temperatures of the maximums and in the intensity and type of peaks. The process which follows is a dissociation of the obtained $ZnSO_4$, which is manifested on the DTA curves by an endoeffect at temperature about 860 °C.

The TG curves vary a lot. (Fig. 2). At temperature 600°C a reduction in the mass of the Polish concentrate sample is observed, which implies that ZnO was obtained directly. An increase in the mass of samples of the other concentrates is noticed at first, followed by a two-stage decrease. The initial increase in the mass of the samples is due to the obtaining of $FeSO_4$; then its dissociation follows (the mass decreases) and $ZnSO_4$ is obtained. After that it dissociates at temperatures over 725°C and the main product of oxidation - ZnO is obtained. These processes are proved by the obtained DTG curves (Fig. 3).

On the basis of data from DTA è TG curves the process of oxidizing metal sulfides and sulfide zinc concentrates [9,14,15] can be characterized by the temperatures given in [12]. For the tested zinc concentrates the temperatures are shown in Table 2. The following symbols are used:

- T_1–temperature at the beginning of the oxidation process;
- T_2'–temperature of the beginning of intensive oxidation of the easiest-to-oxidize sulfide;

Table 2
Characteristic temperatures (°C) of the investigated zinc concentrates

No	Concentrate	T_1°C	T_2'°C	T_2''°C	T_3°C	T_4°C
1	Polish	380	400	505	660	890
2	Bulgarian	430	450	650	730	900
3	Canadian	390	405	640	690	880
4	Yugoslavian	375	405	530	728	900

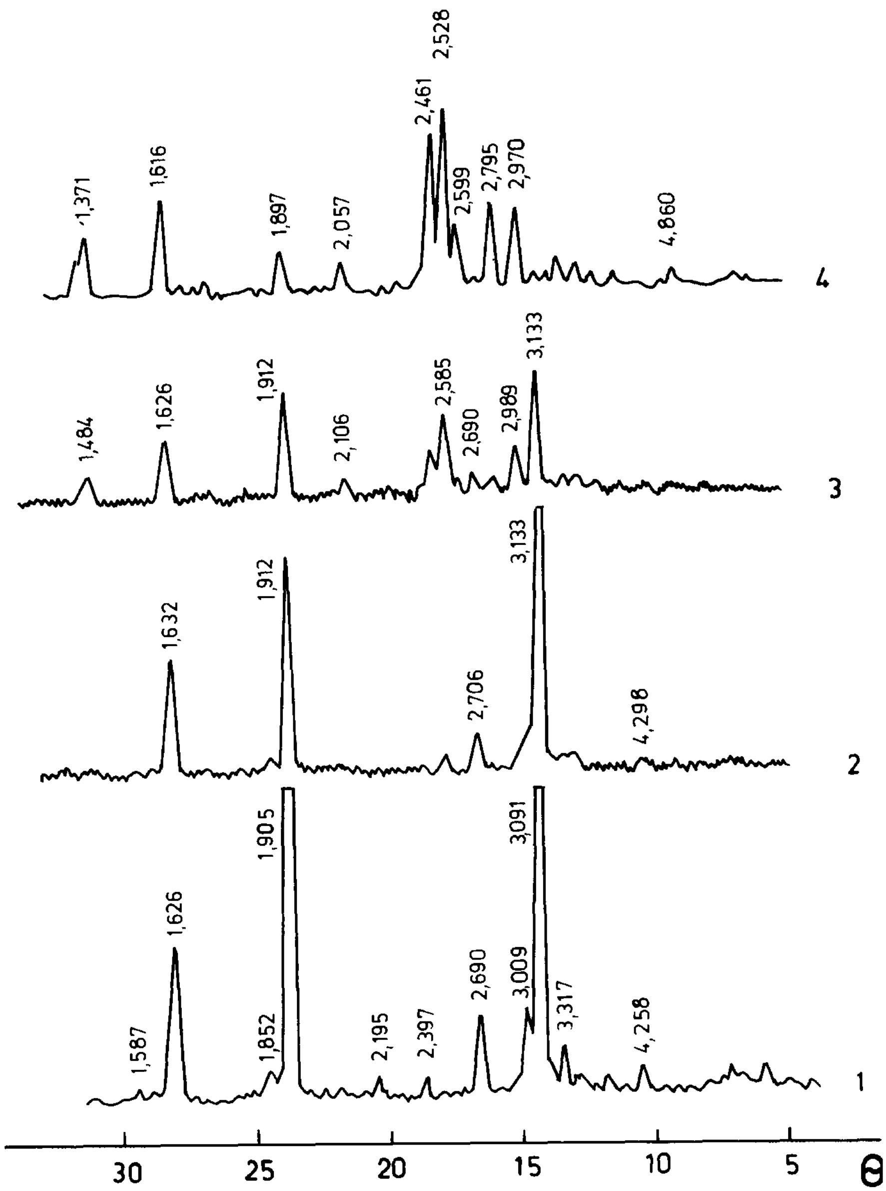

Fig. 4. X-ray patterns of Yugoslavian concentrate (1) and products of its oxidation at 450°C (2); at 700°C (3) and at 1000°C (4).

- T_2''–temperature of the beginning of oxidation of the main sulfide;
- T_3–temperature at which intensive oxidation takes place;
- T_4–minimal temperature over which processes take place at a high speed up to the stage of desulphurisation required.

Greatest differences are observed in the values of the temperatures T_2'' and T_3. Intensive oxidation of zinc minerals takes place in a wide temperature range: 630–800°C. This is probably due to the different content of iron in β–ZnS and to the different granulometric composition of concentrates.

The thermal treatment of the Yugoslavian concentrate at different temperatures shows the sequence of formation of the main phases (Fig. 4). At 450°C some diffraction maximums are not observed due to presence of FeS_2 and $CuFeS_2$ in the concentrate. A decrease in the intensity of the lines of the main phase - nZnS.mFeS is also observed. At 700°C the lines of the phases ZnO and Fe_2O_3 appear. They are products of oxidation. At 1000°C $ZnFe_2O_4$ and ZnO are the prevailing phases.

The predictions made by the software system [11] about the composition of the calcine obtained from roasting Yugoslavian zinc concentrate alone, show that it contains 10.34% ferrite zinc, and only 26.07% zinc soluble in 7% H_2SO_4 solution.

The study of the behaviour of low-quality Yugoslavian concentrate under thermal treatment shows that processing it alone is not effective. Therefore it is possible to look for ways for its mixing together with other zinc concentrates. The Bulgarian, Polish and Canadian concentrates, presented above, are not of the best possible quality but the software for mixing zinc concentrates, which we have developed, makes possible the determination of optimal ratio between them and the Yugoslavian one, so that good technical and economic results can be achieved by processing them together.

Table 3 presents the influence of the Yugoslavian concentrate on the content of the main components in the mixture of concentrates: Polish – 10%, Canadian – 5%, and the Bulgarian and Yugoslavian make up to 100%. This ratio has been chosen on the basis of composition recommended by the software system, and namely: Bulgarian concentrate – 80%, Polish – 10%, Canadian – 5% and Yugoslavian – 5%.

Table 3
Chemical composition of the recommended mixtures and expected chemical composition of the calcine

	Component	Content of Yugoslavian concentrate (mass.%)						
		0	2	4	5	6	8	10
M	Zn	50.32	49.97	49.61	49.44	49.26	48.91	48.56
I	Fe	7.17	7.38	7.58	7.69	7.79	8.00	8.20
X	Pb	2.23	2.20	2.18	2.17	2.16	2.14	2.11
T	SiO_2	2.58	2.54	2.51	2.49	2.48	2.45	2.42
U	Sb	0.001	0.001	0.001	0.002	0.002	0.002	0.002
R	As	0.044	0.045	0.046	0.046	0.047	0.048	0.049
E	CaO	0.86	0.87	0.87	0.88	0.88	0.89	0.90
S	Cl	0.051	0.054	0.057	0.059	0.061	0.064	0.067
	F	0.029	0.029	0.029	0.029	0.029	0.28	0.028
	Ge(g/t)	3.6	3.7	3.8	3.8	3.8	3.9	4.0
C	Zn	57.84	57.43	57.03	56.82	56.62	56.22	55.81
A L	Zn soluble in H_2SO_4	53.14	52.62	52.10	51.84	51.58	51.06	50.54
C I	Zn (ferrite)	4.12	4.24	4.36	4.42	4.48	4.60	4.71
N E	Zn (sulfate)	2.60	2.58	2.57	2.57	2.55	2.53	2.51
S	Zn (sulfide)	0.58	0.57	0.57	0.57	0.57	0.56	0.56

The influence of Yugoslavian concentrate on the composition of the mixture and calcine is not entirely positive or negative. It can be defined as follows:

1. *Negative influence*: reducing the total Zn content in the mixture and the content of Zn soluble in 7% H_2SO_4 solution; increase of the Fe content in the mixture and calcine and also the content of ferrite zinc.
2. *Positive influence*: reducing the content of Pb and SiO_2 in the mixture.
3. Minor influence on the content of Sb, As, Ge, Cl, Fè, CaO in the mixture.

The data from the table shows that up to 8% Yugoslavian concentrate can be processed with the so formed mixture. Critical limit is the value of Fe content – 8%. This index has been accepted on the basis of the work of a zinc plant following classical hydrometallurgical technology over a long period of time. When Fe in the mixture exceeds 8%, the content of $ZnFe_2O_4$ becomes high enough and the indexes of the processing of calcine worsen considerably. Under the above mentioned conditions the quantities of the rest of the components meet the preset requirements. In case of other suitable concentrates of higher quality the part of Yugoslavian concentrate in the processed mixtures could increase.

4. Conclusions

1. The DTA, TGA and X-ray diffraction analysis carried out show that while oxidizing Yugoslavian concentrate from Maidanpek deposit, a considerable amount of $ZnFe_2O_4$ is obtained, due to high content of Fe and presence of marmatite in the concentrate.
2. The behaviour of the Yugoslavian zinc concentrate during oxidizing is compared to the one of Bulgarian, Polish and Canadian concentrate. Common features and differences are pointed out.
3. Predicting the composition of the mixture and calcine, using our software for mixing of zinc concentrates, shows that Yugoslavian zinc concentrate from Maidanpek deposit is impossible to be processed alone because of the high degree of ferrite formation and unfavourable chemical composition..
4. The behaviour of Yugoslavian zinc concentrate under thermal treatment and the calculations made, make possible to recommend mixtures comprised of Bulgarian, Polish and Canadian concentrates, where Yugoslavian concentrate can be up to 8%.

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