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# X-Ray, DTA and TGA analysis of zinc sulfide concentrates and study of their charging for roasting in fluidized bed furnace

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Bulgaria is a major producer of zinc in Central and Eastern Europe (about 100 000 tons per year). The two zinc metallurgical plants in KCM S.A., Plovdiv and LZC S.A., Kardjali deliver the necessary raw materials from Bulgaria and abroad.

In this connection, 7 Bulgarian and imported zinc concentrates have been investigated with the use of chemical analysis, X-ray phase analysis, DTA and TGA. The following phases were established: β-ZnS; nZnS.mFeS; $CuFeS_2$; PbS; $SiO_2$ (α-quartz). The phase β-ZnS is present in all concentrates and the other established phases are represented differently in the studied concentrates.

The results obtained are interpreted from the standpoint of receipt by roasting of an appropriate zinc calcine on the basis of its chemical and phase content. For this purpose a Web-based software system, developed by mathematicians and technologists from the Paisii Hilendarski University of Plovdiv, for calculating the charges of zinc concentrates at a fixed optimizing criterion was used. This enables appropriate mixture of materials to be processed during roasting of concentrates in fluidized bed furnace. This promotes obtaining of zinc calcine with minimum insoluble zinc ferrite and content of admixtures below certain technology requests.

**Key words:** ZnS, zinc concentrates, X-ray analysis, DTA and TGA, roasting.

## INTRODUCTION

The synthesis and properties of pure ZnS [1–4] and ZnS doped with different impurities (P, Cu, Mn, Ag, Se, Te, etc.) [5–7] have been of interest for many years. This is due to the use of this sulfide in electronics, semiconductor equipment, optics, as a pigment, etc. [8–10]. Furthermore, iron ions are introduced into the crystal lattice of ZnS to obtain ZnS single-phase thin films showing ferromagnetism [11–13].

Zinc sulfide is essential zinc mineral in zinc ores [14]. Its two polymorphs are β-ZnS (Sphalerite) and α-ZnS (Wurtzite). Sphalerite is a typical hydrothermal mineral with cubic structure $F\bar{4}3m$, and tetrahedrally coordinated zinc and sulfur atoms. Wurtzite has hexagonal ($C6_3mc$) symmetry, usually stabilized by some Cd. It is a rare species.

Sphalerite is the common mineral in zinc ores. It almost always contains iron. Varieties with more than 6% Fe are named marmatite. Since marmatite has a brilliant black color like the black sphalerite, it very often goes unrecognized.

In addition to Fe, sphalerite in high-temperature deposits often contains Co, Cu, In, Sn and Se. Its impurities in low-temperature deposits are mainly Cd, Ga, Ge, Hg and Tl [14]. During the flotation of zinc ores, other mineral phases contribute Pb, $SiO_2$, $Al_2O_3$, CaO, MgO, Ni, As, Sb, Cl, F to the chemical composition of zinc concentrates.

Currently, during the incoming control of zinc concentrates in processing plants, about 20 components are analyzed to determine whether a raw material is suitable for the used technology [15].

Very often it turns out that chemical analysis alone is not sufficient to choose the most suitable conditions for the successive implementation of the process chain "roasting of zinc concentrates – calcine leaching – electrowinning of zinc". The main problem is the presence of increased contents of Fe, Pb and $SiO_2$. Iron in the zinc concentrates can be connected as $FeS_2$, $CuFeS_2$ or incorporated in the crystal lattice of ZnS [16–18]. During the oxidation of zinc concentrates in the temperature

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range 920–950 °C iron-containing sulfides oxidize and $Fe_2O_3$ is obtained. The iron (III) oxide forms ferrites with various metal oxides (mainly ZnO, obtained from the oxidation of ZnS). The formation of $ZnFe_2O_4$ [19–21] decreases the rate of leaching of zinc and necessitates further processing of the zinc-containing cake [22–24]. To reduce this unfavorable phenomenon, complete preliminary characterization of zinc concentrates is necessary.

Usually in practice various zinc raw materials are used simultaneously – often 5–6 zinc concentrates having different origins and chemical, phase and granulometric compositions. It is necessary to conduct a preliminary assessment of the possibilities for optimization of the technological process, by calculating and using appropriate charges from zinc-containing materials.

The aim of this study is to characterize most completely the Bulgarian and imported zinc sulfide concentrates by chemical, X-ray, differential thermal and thermogravimetric analysis and to use the obtained results for their optimal processing. This can be done using the Web-based expert system for calculating zinc concentrate charges [15, 25].

## EXPERIMENTAL

Seven zinc sulfide concentrates from Bulgaria, Turkey, Greece, Morocco and Peru are studied.

The X-ray phase analysis of the concentrates was carried out with an apparatus "TUR-M62" (Dresden, Germany) equipped with a computer-controlled HZG-4 goniometer with Co-$K_\alpha$ radiation and Bragg-Brentano geometry. Data base (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for the phase identification.

DTA and TGA (Q Derivatograph, Hungary) were carried out under the following conditions: sensitivity of DTA, 0.5 mV; DTG, 1 mV; TG, 100 mg; heating rate, 10° $min^{-1}$; sample mass 100 mg. A ceramic crucible was used. All the studies were performed in air medium.

A Web-based information system for calculation and prognosis of the chemical and phase composition of the mix proportions of concentrates is used [15, 25]. It is built on a modular principle using server programming language PHP. Its main modules provide opportunities for construction, management and use of Web-based database of zinc concentrates [15, 25] in the management control system relational database MySQL.

The used Web-based information system gives the following opportunities:

1. Input of the chemical composition of the used (available or in the process of being contracted to be purchased) zinc concentrates, each of which is allotted a name and a number. Thus the *main database* of the system is created. At present there are data entered for 67 concentrates with different origin (Bulgarian, Turkish, etc.).

2. From the data in the main database up to 15 concentrates can be used, with which a *working database* is created that serves for calculations.

3. With concentrates from the working database the following calculations can be made:

A) In *user mode* calculations are made at user-selected ratio of the concentrates in the working database. For that purpose the percentage share of each separate concentrate is specified, and the system calculates the composition of the charge from zinc concentrates of 18 components.

B) In *automatic mode* the system calculates charges that meet restrictive conditions with regard to 11 components that are selected together with experts in the field of zinc hydrometallurgy.

- In this specific case work was performed satisfying the following input restrictions (in mass %): Zn > 50; S – 31 ± 1%; Pb < 2.5; Fe < 9.0; $SiO_2$ < 2.5; Sb < 0.008; As < 0.12; MgO < 0.3; CaO < 0.5; F < 0.02; Ge < 30 g/t.
- Various step changes in iterations of the concentrates can be selected – from 1 to 15%.
- The content is calculated of each charge that meets the restrictive conditions and is presented under an appointed number.
- During oxidized roasting in a fluidized bed of the charge made out of zinc concentrates a zinc calcine is obtained that is extracted using solutions of sulfuric acid.
- On the basis of data from literature, own studies and experience from practice coefficients are offered with which, based on the chemical composition of the charge, calculations are made for the prognostic chemical and phase composition of the calcine.
- When more than one charge is obtained an optimization criterion is used according to which the charges are ranked in descending or ascending order.
- For the optimization criterion in this study "Zinc soluble in 7% solution of sulfuric acid" is used.
- The aim is to select a charge with maximum soluble zinc in a 7% solution of sulfuric acid so that the extraction of the calcine can be carried out at the best technical and economical indices. All calculated charges are arranged in descending order according to this technical index.
- The system also allows the use of other optimization criteria – minimal quantity of obtained zinc ferrite, maximum percentage of zinc in the charge, minimal prime cost of the charge, etc.

## RESULTS AND DISCUSSION

### *Chemical composition*

The chemical composition of the studied zinc concentrates is presented in Table 1.

Most concentrates show high content of Pb and $SiO_2$. Improper mixing of such concentrates can lead to partial aggregation of calcine and increase of the sulfide sulfur in it. Iron is particularly undesirable in terms of ferrite formation. Its harmful effects may be limited by appropriate selection of a charge, well balanced in its chemical composition. Especially unfavorable in terms of As and Sb are the concentrates with numbers 5 and 6. The strong harmful influence of these components in zinc electrowinning from zinc sulfate solutions is well known, as well as all the negative consequences [26].

### *X-ray phase analisis*

Sphalerite (β-ZnS) is the main phase in sulfide zinc concentrates. This shows that in terms of the process of oxidative roasting the majority of zinc will form oxide, which is favorable for the calcine leaching.

At the same time it can be argued with some probability that in all concentrates the phase marmatite (nZnS.mFeS) is observed. The crystal lattice of ZnS can include different amounts of iron [27–29]. Co-oxidation of zinc and iron sulfide at 920–950 °C leads to the formation of zinc ferrite that goes directly into the cake after zinc leaching. The Zn content in the cake is in the range of 15–17% the major part of which is due to the ferrite.

The studied zinc concentrates were subjected to X-ray analysis to determine their phase composition. The resulting X-ray diffraction patterns are presented in Figure 1 and summarized in Table 2.

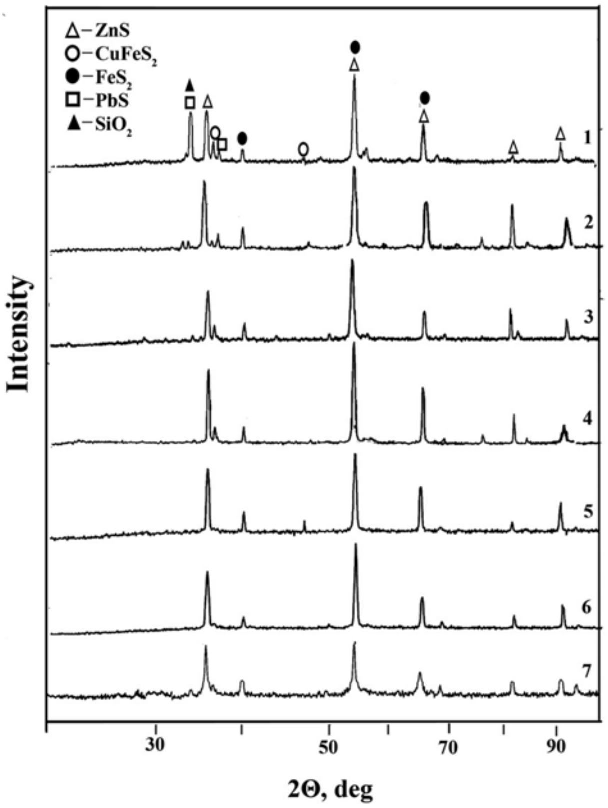

**Fig. 1.** X-ray diffraction patterns of studied zinc sulfide concentrates: Bulgaria (1, 2), Turkey (3, 4), Greece (5), Morocco (6), Peru (7)

**Table 1.** Chemical composition of sulfide zinc concentrates from Bulgaria (1, 2), Turkey (3, 4), Greece (5), Morocco (6), Peru (7)

| Component | Content (mass %) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Zn | 51.10 | 54.60 | 47.45 | 53.65 | 53.57 | 51.19 | 54.60 |
| S | 31.60 | 30.30 | 34.50 | 31.50 | 32.50 | 33.20 | 32.40 |
| Fe | 8.20 | 6.45 | 9.75 | 3.58 | 8.85 | 11.90 | 8.95 |
| Pb | 2.85 | 1.60 | 0.65 | 4.28 | 1.06 | 0.67 | 0.61 |
| $SiO_2$ | 2.25 | 4.30 | 3.30 | 3.58 | 0.95 | 0.66 | 1.75 |
| Cu | 1.96 | 1.02 | 2.06 | 0.63 | 0.27 | 0.68 | 0.38 |
| Cd | 0.29 | 0.28 | 0.23 | 0.25 | 0.30 | 0.10 | 0.09 |
| As | 0.002 | 0.005 | 0.05 | 0.029 | 1.02 | 0.099 | 0.028 |
| Sb | 0.001 | 0.001 | 0.002 | 0.003 | 0.02 | 0.002 | 0.001 |
| Co | 0.006 | 0.027 | 0.006 | 0.012 | 0.001 | 0.006 | 0.006 |
| Ni | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | 0.001 | 0.002 |
| CaO | 0.38 | 0.54 | 0.43 | 0.19 | 0.30 | 0.42 | 0.41 |

### *DTA and TGA study*

The obtained DTA and TGA curves are combined into general graphs (Figs. 2 and 3). The observed exothermic effects in the temperature range of 450–500 °C are due to oxidation of iron and copper sulfides ($CuFeS_2$, $FeS_2$). These effects are best

**Table 2.** Results from X-ray phase analysis of zinc concentrates

| № | Phases | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1. | β – ZnS | β – ZnS | β – ZnS | β – ZnS | β – ZnS | β – ZnS | β – ZnS |
| 2. | (nZnS.mFeS) | (nZnS.mFeS) | (nZnS.mFeS) | (nZnS.mFeS) | (nZnS.mFeS) | (nZnS.mFeS) | (nZnS.mFeS) |
| 3. | $FeS_2$ | | $FeS_2$ | | $FeS_2$ | | |
| 4. | $CuFeS_2$ | $CuFeS_2$ | $CuFeS_2$ | $CuFeS_2$ | | $CuFeS_2$ | |
| 5. | $SiO_2$ (α-кварц | $SiO_2$ (α-кварц) | | $SiO_2$ (α-кварц) | | | $SiO_2$ (α-кварц) |
| 6. | PbS | PbS | PbS | PbS | | PbS | |

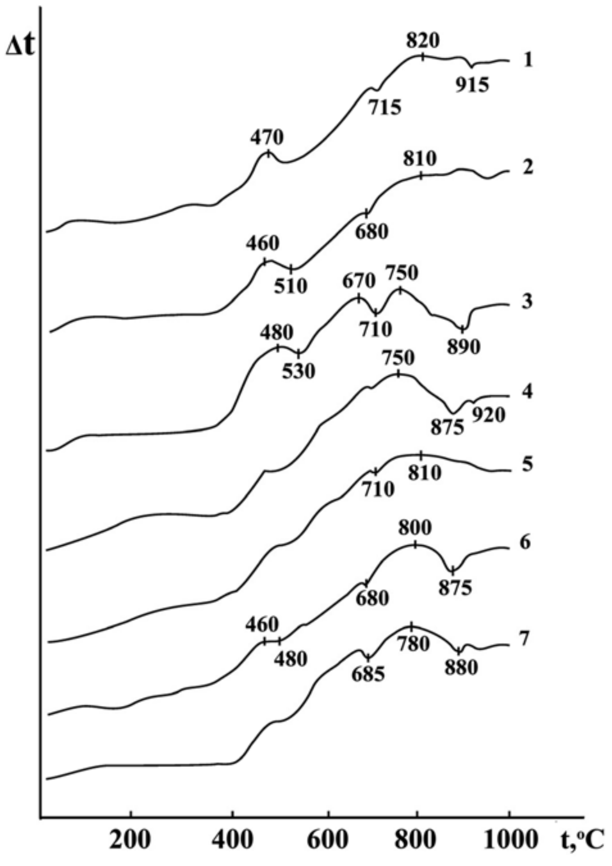

**Fig. 2.** DTA curves of the studied zinc concentrates

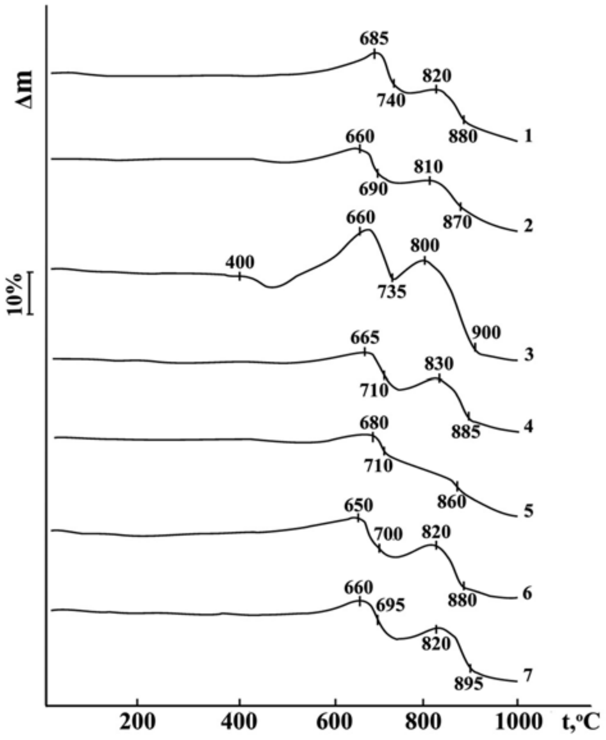

**Fig. 3.** TGA curves of the studied zinc concentrates

observed and are relatively intense in concentrates 1, 2 and 3, which is an indirect confirmation that they have separate phases of iron and copper. The X-ray study of concentrate 5 shows the presence of a $FeS_2$ line, but in the DTA curve 5 has no clear exothermic effect, which indicates that the content of pyrite in the concentrate is low.

In the other concentrates, well-expressed exothermic effects, corresponding to the oxidation of the shown copper and iron sulfides were not observed. The shown weak endothermic effects at 670–700 °C are due to dissociation of the obtained in small quantities $FeSO_4$ and $CuSO_4$. The most intensive exothermic effect is the one caused by the intensive oxidation of ZnS at 750–820 °C.

The differences observed in the zinc solubility from calcines, obtained under different conditions of roasting can be explained using the terminology introduced by us: “primary” $ZnFe_2O_4$, obtained by oxidation of marmatite and “secondary” $ZnFe_2O_4$, formed as a result of solid state interaction of ZnO (from oxidation of β-ZnS) and $Fe_2O_3$ (by oxidation of $FeS_2$). Roasting conditions influence

**Table 3.** Results from the calculation of zinc concentrate charges and chemical and phase composition of the best charge and prognostic calcine

| Charge composition from concentrate N and % of it | | | | | | |
|---|---|---|---|---|---|---|
| Conc.1 | Conc.2 | Conc.3 | Conc.4 | Conc.5 | Conc.6 | Conc.7 |
| 20 | 10 | 5 | 20 | 5 | 20 | 20 |

| Calculated chemical composition of charge, mass % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Zn | S | Fe | $SiO_2$ | Pb | Cu | Cd | As | Sb |
| 52.61 | 32.12 | 8.36 | 2.29 | 1.93 | 0.95 | 0.20 | 0.086 | 0.003 |
| Co | Ni | CaO | MgO | $Al_2O_3$ | Cl | F | Ge | Tl |
| 0.011 | 0.002 | 0.37 | 0.20 | 0.34 | 0.008 | 0.009 | 8 g/t | 7 g/t |

| Prognostic chemical composition of zinc calcine, mass % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Zn | S | Fe | SiO2 | Pb | Cu | Cd | As | Sb |
| 60.47 | 2.95 | 9.61 | 2.63 | 2.22 | 1.09 | 0.23 | 0.098 | 0.003 |
| Co | Ni | CaO | MgO | Al2O3 | Cl | F | Ge | Tl |
| 0.012 | 0.002 | 0.43 | 0.23 | 0.39 | 0.009 | 0.011 | 9 g/t | 8 g/t |

| Prognostic phase composition of zinc calcine, mass % | | | |
|---|---|---|---|
| Zn (oxide + silicate) | 52.34 | $Zn_{H2O}$ | 2.72 |
| Zn (ferrite) | 4.80 | Fe (ferrite) | 9.41 |
| Zn (sulphate) | 2.72 | Fe (oxide + silicate) | 0.19 |
| Zn (sulphide) | 0.60 | Pb (sulphate) | 1.77 |
| $Zn_{H_2SO_4}$ | 55.06 | Pb (sulphide) | 0.44 |

mainly the formation of “secondary” $ZnFe_2O_4$, while being a negligible factor in the formation of “primary” $ZnFe_2O_4$.

### *Calculation of charges*

The abovementioned Web-based expert system [15, 25] was used for calculating the optimal charges of the studied zinc concentrates. The Bulgarian 2 and Peruvian 7 concentrates were considered to be the principal ones in the charge calculation, based on available and contractual quantities of zinc concentrates for a long time period.

Best charge was obtained at the ratio of concentrates given in Table 3. Zinc, dissolved in 7% $H_2SO_4$ solution (Zn as oxide, sulphate and silicate) makes up 91.06% of the total zinc in it. This is a very high percentage and the indexes of neutral and acid leaching will be very high if the technological parameters are obeyed.

The calculated charges of zinc concentrates that meet the specified requirements are 36. They have zinc, soluble in 7% solution of sulfuric acid, in the range 90.40–91.06%. This allows to vary the choice of charge depending on the quantities of concentrates.

The results show that the use of the Web-based expert system gives very good results concerning composition of the charge and quality of the obtained calcine. The system also allows optimization on economic criteria, when the concentrate prices are known.

## CONCLUSIONS

1. X-ray, differential thermal and thermogravimetric analysis of 7 Bulgarian and imported zinc sulphide concentrate are made.
2. The relationship between the phase composition and type of the obtained DTA and TG curves is shown, highlighting the influence of $FeS_2$ and $CuFeS_2$ phases on the mass change of samples and allowing the opportunity to establish the presence of these phases in concentrates on the basis of the TG curves obtained.
3. Calculations based on the Web-based information system allow optimization of the composition of zinc concentrate charges. From all studied concentrates a charge is recommended in which zinc, soluble in 7% $H_2SO_4$ solution constitutes 91.06% of the total zinc in accordance with 11 restrictive conditions for obtaining high quality calcine in terms of its hydrometallurgical processing.

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# РЕНТГЕНОФАЗОВ, DTA И TG АНАЛИЗ НА СУЛФИДНИ ЦИНКОВИ КОНЦЕНТРАТИ И ИЗСЛЕДВАНЕ ТЯХНОТО ПЪРЖЕНЕ В ПЕЩ С КИПЯЩ СЛОЙ

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(Резюме)

България е основен производител на цинк в Централна и Източна Европа (около 100 000 тона годишно). Двата цинкови завода в КЦМ АД, Пловдив и ОЦК ЕООД, Кърджали доставят необходимите суровини от България и чужбина.

В тази връзка, 7 български и вносни цинкови концентрати бяха изследвани с използване на химичен, рентгенофазов анализ, ДТА и ТГА. В тях са установени следните фази: β-ZnS; nZnS.mFeS; $CuFeS_2$; PbS; $SiO_2$ (α-кварц). Фазата β-ZnS присъства във всички концентрати, а другите фази са представени в различна степен в изследваните концентрати.

Получените резултати са интерпретирани от гледна точка на получаване на подходяща цинкова угарка при пърженето съгласно нейния химичен и фазов състав. За тази цел е използвана Web-базирана програмна система, разработена от математици и технолози от Пловдивския университет „Паисий Хилендарски“ за изчисляване на шихти от цинкови концентрати при използване на определен оптимизиращ критерий. Това позволява по време на пърженето на концентратите в пещ с кипящ слой да се преработват подходящи по състав шихти. Това допринася за получаване на цинкова угарка с минимално количество неразтворим цинков ферит и съдържание на примесни компоненти съгласно определени технологични изисквания.