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Thermal behavior of zinc sulfide concentrates with different iron content at oxidative roasting

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ABSTRACT

Processing of sulfide concentrates with high iron content in the hydrometallurgy of zinc increases the amount of obtained cakes containing 15–20% Zn and 25–30% Fe. The main reason for this undesirable process is the presence of a part of the zinc as insoluble ZnF_2O_4.

In this regard, 6 zinc concentrates of different origins were investigated using Mössbauer spectroscopy as well as chemical, XRD, DTA and TGA analyses. The relation between the phase content and the received TG and DTA curves, as well as the behavior of the main phases in the concentrates during their oxidation was established. On the basis of the Mössbauer spectra, the iron containing phases and their influence on the oxidation process were determined.

The results are used to choose the charge of concentrates for optimal oxidative roasting in fluidized bed furnace and for minimizing ferrite formation.

1. Introduction

Zinc is produced from zinc sulfide concentrates and by-products (slag, zinc dross and cakes, etc.) using pyro- or hydrometallurgical methods. Currently, more than 80% of the world production of zinc is carried out by the hydrometallurgical method, the first stage of which is oxidizing roasting of zinc sulfide concentrates in a fluidized bed furnace (FBF) [1].

Roasting of zinc sulfide concentrates is one of the most important processes in zinc hydrometallurgy. During the roasting process the sulfur in the concentrate is removed at a temperature of about 930–980 °C, wherein zinc sulfide is oxidized mainly to zinc oxide. The following zinc containing phases: $ZnSO_4$, $ZnFe_2O_4$, Zn_2SiO_4, are also obtained with a small quantity of unreacted ZnS. Despite many studies related to oxidative roasting of zinc concentrates, the roasting of low-grade zinc concentrates continues to be of interest due to the variation in chemical and mineral compositions and particle size distributions [2–6].

This is important especially today because zinc concentrates of different origins are processed and most of zinc producing plants import concentrates from various countries around the world. KCM S.A., Plovdiv, Bulgaria, for example, has imported and processed concentrates from Canada, USA, Peru, Australia, Morocco, Iran, almost all Balkan countries and others.

Sphalerite is the most common sulfide zinc mineral in nature. It almost always contains iron. Iron in the zinc concentrate can be in the form of FeS_2, $CuFeS_2$, or incorporated in the crystal lattice of ZnS [4,7–9]. Sphalerite containing more than 6% Fe in its crystal lattice is called marmatite.

The increased iron content in the processed zinc concentrates is a significant technological problem for zinc plants [10,11]. Upon oxidizing roasting in FBF, solid phase interactions between oxides of zinc and other non-ferrous metals (Cu, Cd and Pb, etc.) and Fe_2O_3 (formed by oxidation of FeS_2, (Zn,Fe)S, and $CuFeS_2$) take place, and ferrites are obtained as a result [1,12,13]. They are very stable [14] and poorly soluble compounds. Obtaining mainly $ZnFe_2O_4$ reduces the rate of zinc leaching and the zinc-containing cake needs further processing. The ferrite, which contains about 15% of the total zinc, remains insoluble in low-acid conditions [1,15–17].

In order to reduce this adverse ferrite formation, a complete preliminary characterization of the zinc concentrates is required. Different number of zinc concentrates (often 10–12) of different origins, chemical compositions and grain sizes are usually used simultaneously in the practice of oxidative roasting. Various zinc-containing raw materials can be successfully processed using suitable charging, thus optimizing the technological process of roasting in fluidized bed furnace. The processing of low-grade zinc concentrates containing more than 8% iron causes difficulties in the leaching of zinc from the calcine obtained at roasting [18–20].

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Table 1
Chemical composition of zinc sulfide concentrates from Macedonia (C1, C4), Bulgaria (C2), Peru (C3), Bosnia and Herzegovina (C5, C6).

Components	Content (wt%)					
	C1	C2	C3	C4	C5	C6
Zn	55.25	**49.30**	53.75	**47.60**	**49.80**	**48.72**
S	31.35	30.00	32.20	31.35	31.75	**33.15**
Fe	4.69	6.90	**9.05**	**10.55**	**11.46**	**13.22**
Cu	0.98	**1.96**	0.55	**1.04**	0.22	0.30
Cd	**0.42**	0.29	0.09	**0.42**	0.28	**0.49**
Co	**0.01**	0.006	0.002	**0.011**	0.001	0.001
Ni	0.001	**0.002**	0.001	0.001	0.001	0.001
Al_2O_3	0.28	0.17	0.14	0.22	0.17	0.08
Tl(g/t)	9	0	5	9	7	10
Pb	**3.31**	**2.85**	0.56	1.50	1.75	1.89
SiO_2	1.90	**2.25**	1.70	**2.60**	1.85	0.62
Ge(g/t)	<5	<5	<5	<5	<5	<5
Sb	0.001	0.001	0.001	0.001	**0.064**	**0.012**
As	0.002	0.002	0.02	0.01	0.04	**0.18**
MgO	0.13	0.08	0.13	0.16	0.08	0.10
CaO	0.38	0.38	0.14	**1.57**	0.09	0.40
Cl	0.01	0	0.01	0.01	0.01	0.01
F	0.01	0	0.013	0.01	0.01	0.008

Note: Underlined and bold values do not meet compositional requirements.

Currently, there is strict input control of zinc concentrates in zinc hydrometallurgical plants. Over 20 components are analyzed in order to determine whether the material is suitable for use in processes of concentrates roasting and calcine leaching [21].

For a profitable zinc production, the use of high quality concentrates containing more than 50% zinc, and up to 8% iron is required [22]. As a result of the depletion of the zinc-rich raw materials with a low iron content, currently zinc concentrates having sometimes an iron content of up to 12–14% are processed [23,24]. The amount of the obtained cakes rapidly grows and they contain up to 15–20% Zn and 25–30% Fe. This requires further processing of these by-products, both for economic reasons and because of environmental constraints [25].

In this connection, the purpose of this study is to characterize 6 zinc sulfide concentrates of various origins using chemical, XRD analysis, DTA, TGA and Mössbauer spectroscopy. The results can be used for selecting a charge of the concentrates in order to obtain zinc calcine with the most appropriate chemical and phase composition. To accomplish this, a WEB-based programming system [23,26] for calculating the charge on the basis of technological and economic optimization criteria was used.

2. Experimental

In this study six sulfide zinc concentrate originating from Bulgaria, Macedonia, Peru, Bosnia and Herzegovina were analyzed by different methods.

The XRD 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. Database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia, PA, USA, 1997) was used for the phase identification.

Mössbauer spectra (MS) were obtained at room temperature with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) at a constant acceleration mode. A ^{57}Co/Cr (activity ≅ 45 mCi) source and an α-Fe foil standard were used. The obtained spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (H_{eff}) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectra were determined.

Thermogravimetric and differential thermal analyses (TG–DTG–DTA) were performed on a Stanton Redcroft thermal analyzer STA 780 (England) in the temperature range 20–1100 °C, with a heating rate of 10 °C min^{-1}, sample mass of 10.0 ± 0.3 mg. Zirconium melting pots of $d = 4.5$ mm were used and the purging gas was 100% air with a flow of 50 mL min^{-1}.

The oxidation of sulfide concentrates was performed in a fix bed in tube furnace. The air flow was 0.8 L min^{-1} and the temperature range of study – 700–900 °C. Ceramic crucibles were used and the sample mass was 0.5 g.

The degree of desulfurization of the concentrates is calculated on the basis of sulfur content obtained by using the apparatus SC632 Carbon/Sulfur Determinator by LECO Corporation, USA. The analysis of sulfur is carried out in the range 0.001%–20% at 1% RSD. The sample mass is 0.1 g, and the sample is roasted in an infrared absorption furnace in an oxidized medium (99.5% oxygen).

To obtain the content of zinc soluble in sulfuric acid, 1 g of the sample was dissolved for 1 h in a 7% sulfuric acid solution. After filtering, the zinc content in the solution was determined, and the respective calculations were made.

A Web-based information system for the calculation of the chemical compositions of the charges of concentrates is used. It is built on a modular principle using server programming language PHP. Its main modules allow the construction, management and use of Web-based database of zinc concentrates [23,26]. 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 (wt%): Zn > 50; S – 31 ± 1%; Pb < 2.5; Fe < 8.0; $SiO_2 < 2.5$; Sb < 0.008; As < 0.08; MgO < 0.3; CaO < 0.5; F < 0.02; Ge < 30 g/t.

3. Results and discussion

3.1. Chemical composition

The chemical compositions of the zinc concentrates used in this study are presented in Table 1 where higher numbers correspond to higher iron content. It is clearly evident that all zinc concentrates do not fully meet compositional requirements mentioned above. Therefore in practice, these concentrates are not suitable for individual processing. Part of the undesired impurities will remain in the calcine, and then in the solution after leaching.