SPECTROMETRIC TECHNIQUES (SEM, HR AES, XPS) APPLIED IN THE METALLURGICAL WASTE CHARACTERIZATION

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ABSTRACT

Metallurgical waste management, including the choice of its final disposal, has to be preceded by its characterization. During this process, a series of tests of physical and chemical properties of the waste and of its potential interaction with the environment is conducted. The waste material analysis applies the standard methods and techniques to determine the drying loss, specific area, sample density, water solubility, granular-metric and chemical composition. It also applies various spectrometric techniques to examine the physical and chemical characteristics.

Scanning Electron Microscopy (SEM) is often applied to test morphological and qualitative chemical composition of waste, whereas high-resolution Auger Electron Spectroscopy (HR AES) and X-ray Photoelectron Spectroscopy (XPS) are applied to determine the possible structure forms of the compounds in the sample base. The paper displays the application of these spectrometric techniques in the case the characterization of electric arc furnace (EAF) dust, which is the major representative of the hazardous metallurgical waste group.

The obtained results of the grain size test imply that the diameters of particles and their clusters range from ~ 1 μm to ~ 200 μm. The shape of EAF dust particles is mostly spherical, and very few are angular. The recorded agglomerates are mostly cluster-shaped, whereas some have wrinkled spherical surface. The results of the qualitative scanning electron microscopy of EAF dust particles imply the presence of Fe, Zn, Pb, Mn, Cu, Al, Ca, Mg, K, S, P, C, O, and Cl. Furthermore, the analysis of microscopic images and the examination of the distribution of these elements across the image surface has shown that the dust samples basically contain the compounds of the Fe-O, Zn-O, Pb-O, Ca-O, Si-O, Mg-O, and Pb-S-O type. The recorded HR AES spectra have also displayed the presence of Fe, Zn, Pb, Mo, Al, Ca, Mg, Si, S and O as well as their different quantitative distribution in the analyzed particles. The analysis of XPS spectra has confirmed the results of qualitative HR AES chemical analysis. By means of the measured bonding energy of Zn, Pb, and Ca the structural shapes of these elements were determined i.e. it was proven that zinc was tied up as ZnO, lead as PbO, PbSO₃ and/or PbSO₄, and calcium as CaO and CaCO₃.

The obtained results can provide a basis for the interpretation of potential reaction between this type of metallurgical waste and the environment and hence for the choice of the optimal management solution through the application in the plant’s own technological process (where this waste is actually generated), usage in other industrial branches, or final disposal of properly pre-treated waste at registered land fills.
Keywords: metallurgical waste; spectrometric techniques; EAFdust; characterization;

A very important waste occurring in the production of steel is the electric arc furnace (EAF) dust, which is emitted from the electric arc furnace with the fume gases. Due to its physical and chemical properties it is categorized as hazardous industrial waste. In order to assess the suitability and recycling potential of metallurgical waste, or to select the proper form of its final disposal, it is necessary to know its chemical, radiochemical, physical, morphological, mineralogical, and structural characteristics, as well as how it interacts with individual segments of environment system.

The waste material analysis applies the standard methods and techniques to determine the drying loss, specific area, sample density, water solubility, granular-metric and chemical composition. It also applies various spectrometric techniques to examine the physical and chemical characteristics. The paper displays the application of these spectrometric techniques in the case the characterisation of electric arc furnace (EAF) dust, which is the major representative of the hazardous metallurgical waste group.

In order to investigate the chemical and phase composition of EAF dust, the average monthly samples taken at the outlet of the dust suppression system were analyzed. The samples were homogenized and successive quartering provided 1000 g of each sample (average samples). All samples were dried for 2 hours at 105 °C and stored above silica gel in a desiccator.

For Scanning Electron Microscopy, the samples were prepared on a graphite support. Electron micrographs were taken on the Philips XL 30 scanning electron microscope with BSE detector and EDS analyzer. The grain morphology and mineralogical composition of EAF dust were investigated by a combination of high resolution Auger Electron Spectroscopy (HR AES) and X-ray Photoelectron Spectroscopy (XPS). Vacuum Generators Microlab 310-F system with Mg Kα X-ray source (1253.6 eV; pass energy 25 eV CAE mod; anode voltage 14.5mA × 14 kV 200 W) was used in these investigations.

Scanning electron micro-structural examination of EAF dust microstructure was performed and the results are shown in Fig. 1. Based on this microphotographs and the results of X-ray energy dispersive spectrometry (EDS), it can be seen that the samples were not completely homogeneous. The grain size of the EAF dust samples was 1– 200 μm.

Fig. 1. Scanning electron micrograph of EAF dust
The individual particles were generally spherical and very often in aggregate forms. The same samples were also subjected to the element distribution analysis (O, Zn, Mg, Al, Si, S, Pb, Ca, Mn, Fe and Cu), and the results are shown as elemental distribution images in Fig. 2. Fig. 2 shows the match of metal and oxygen distribution in accumulations, implying the possible presence of metal–oxygen structural forms, which corresponds to the XRD analysis results.

![Fig. 2. Scanning electron micrograph (SEM) and elemental distribution (BSE) image of EAF dust](image)

The references most often present the results of this type of research implying the dominancy of spherical particle, i.e. agglomerate form of comparably the same size, and the agglomerate diameter varies from 1 to around 30 μm. Spherical particles with wrinkled surface and elongated non-defined forms were also observed. Škvara et al. [1] have recorded the predominant presence of spherical particles, just like Li and Tsai [2], whereas Rocabois et al. [3] have pointed out to spherical forms of the spinel-type metal oxides (Fe, Zn, Mn)\(\text{OFe}_2\text{O}_3\), and they have proven the presence of angular shaped particles which he considers to be zinkite, ZnO.

In some of the EAF dust samples examined by means of high resolution Auger Electron Spectrometry, AES-spectra were detected at several points and they were subjected to quantitative chemical analysis. Fig. 3 shows the microphotograph of EAF dusts ample and the AES-spectrum at points P1–P5. Qualitative compositions of individual analyzed points are almost identical, and the absence of certain elements at particular points is the result of their concentration, which lies below the limit of detection.

The analysis of XPS-spectra, Fig. 4, determined the presence of zinc in the form of ZnO phase and the presence of lead in the form of PbO phase, i.e. PbSO\(_3\) and/or PbSO\(_4\) forms. Characterization of EAF dust, being one of the most significant types of hazardous metallurgical waste, was carried out through examination of its physical and chemical properties with special emphasis on chemical and structural characteristics and potential influence of this type of waste to the environment water system. For this purpose, several different spectrometric techniques were applied.
The investigation of grain morphology, chemical and the mineralogical composition of EAF dust were taken by combination of high resolution Auger Electron Spectroscopy (HR AES), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscope with BSE detector and EDS analyzer.

The examinations were performed in order to provide a more comprehensive view of the possibility to stabilize heavy metals for the purpose of their permanent disposal. At the same time, these results provide a better analysis of the possibility to use EAF dust in other industrial branches or to recover and reuse EAF dust. Only the right choice of analytical methods makes it possible to determine the physical and chemical characteristics of EAF dust as well as any other waste material and then, by knowing all of their properties, to choose form of their disposal.

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Fig. 3: Scanning electron micrograph of EAF dust (A) and HR AES spectra measured at marked points (B)

Fig. 4: XPS spectre of EAF dust, Pb 4F5/2, Pb 4F7/2 and Zn 2P3/2