The use of selected structural tests in the determination of phase composition of industrial wastes based on the example of Zn-Pb slags

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Abstract. The article presents the results of phase composition analyses of Zn-Pb slags based on selected structural tests. Based on these tests it has been found that the application of several complementary research techniques may provide reliable information regarding the presence of individual phases. In view of obtaining qualitative characteristics of the components of slags, the phase identification tests by means of X-ray diffraction were found to be precise. Based on them, also the percentage of the individual crystalline phases and the percentage of the amorphous substance have been determined. Studies using electron scanning microscopy and X-ray spectral microanalysis allowed for the determination of the chemical composition of the individual components. In that case, the X-ray spectral microanalysis was found to be more precise and it allowed for the identification of substitutions of elements occurring in small amounts in the crystalline phases, i.e. the rare earth elements.

1. Introduction
Steel production is one of the branches of industry that produces significant amounts of wastes, including slags. For years the slags were deposited to dumps. Today, however, seeking the possibilities of reusing the slags i.e. in production of various aggregates that serve as an additive to cement is increasingly common [1-8].

There are also known testes to recover metals from metallurgical wastes; very interesting are researches conducted in China – process of coal-based direct reduction followed by magnetic separation was conducted to extract metallic iron and separate Pb and Zn from lead slag [9]. A study on the recovery of copper, cobalt and zinc from copper smelter and converter slags by roasting with sulfuric acid has been conducted by Turkish scientists. In their experiment they show that a total of: 88% of copper, 87% of cobalt, 93% of zinc, and 83% of iron were extracted in 2 h of roasting at 150°C and 3:1 acid/slag ratio [10].

These type works are determined by the necessity to conduct diverse research of slags, especially mineralogical and chemical analyses – as due to the phase composition, smelter slags are one of the most differentiated groups among waste materials. To exemplify this, among the slags produced in the processing of Zn-Pb ores in Bukowno, Kucha and Jędrzejczyk [11] have distinguished i.e. augite, omphacite, kirschsteinite, diallage, chromite, magnetite, wustite, periclase, Fe and Al carbides, phosphides and silicides as well as metallic phases of Fe and Pb. Among the slags from copper
production, Muszer [12,13] has distinguished metallic phases, sulphides, arsenides, antimonides and oxides rich in Ag, Pb, Cu, Ni, Co, Sb, As, Zn, Fe, Cr. The following, on the other hand, are dominant in the phase composition of steel production slags from the Gliwice-Ląbędy dump: iron oxides represented by wustite, magnetite, hematite and pericase, perovskite, melilites, dicalcium silicates and pyroxenes [14,15].

In the world, research of metallurgical slags are conducted, among others in Portugal [16], in the United States of America [17] and the Czech Republic [18], as also by the Russian scientists, who were conducted tests on the vanadium slag samples. The evolution of the compositions of spinelide, silicate, and metallic phases was investigated [19]. Babenko et al. [20] describe a phase composition of magnesia converter slag in which they distinguished larnite, brownmillerite and ferruginous periclase, with a series of solid solutions of magnesiowustite, magnesioferrite and calcium ferrites.

The diversity of the phase composition of slags results in the fact that each of them should be considered separately. Excessive generalizations are not allowable as the phase composition of slags changes depending on the steel production process, the type of the furnace charge material, the use of additives and fluxing agents.

Phases that crystallize in the conditions of a metallurgical furnace are identified as materials which are formed as a result of natural geological processes. Their chemical composition, however, is often much richer than their natural counterparts. They may also contain impurities, namely various elements which form substitutions in their internal structure.

One should also note that phase components of slags form highly diversified forms which are the result of the variable crystallization conditions. The intensity of the slag cooling process has an impact on the size and form of the crystals. In slags, well-formed crystals of mineral phases, the crystallization of which proceeded in the conditions of slow setting may be found as well as fine crystallites in glaze mass – if the crystallization process was interrupted due to sudden cooling of the slag.

This paper presents the results of the mineralogical analysis of Zn-Pb slags conducted using selected research methods. In view of the diversified and variable phase composition of slags, we have aimed at exhibiting the importance of the selection of research methods in such a study.

2. The scope and methodology of research

The range of the study incorporated highly weathered Zn-Pb smelter slags that have been deposited to the dump in Ruda Śląska-Wirek over a hundred years ago. The liquidation works conducted for a certain period and the extraction of material from the central part of the dump has made the acquisition of samples from the base of the dump possible. 10 samples of wastes, 2 kg each, have been collected. The samples were subject to microscopic observation and described. 3 of the samples were selected for further laboratory research. Before commencing laboratory analyses, the samples were dried and reduced by quartering. A part of each of the samples was ground in a bead mill, while the other part served as preparations for the microscopic study – 2–3 preparations were made from each of the samples.

Within the study, identification of phases using X-ray diffraction method was applied. Moreover, electron scanning microscopy and X-ray spectral microanalysis were used.

X-ray structural tests were conducted in the Institute of Ceramics and Building Materials, Refractory Materials Division in Gliwice, Structural, Thermal and Thermomechanical Testing Laboratory. The analysis of the phase composition using X-ray diffraction (XRD) was conducted using a PANalytical XPERT PRO MPD powder diffractometer with an X-ray lamp with a Cu anode, a graphite monochromator at the diffracted beam side, X'Celerator semiconductor strip counter and a spinner. X-ray diffractograms were made for the range of angles of 5–80° 2Θ at lamp operational parameters of 35 mA and 45 kV. To identify the phase composition, HighScore software by PANanalytical as well as the ICDD PDF-4+ (2011 issue) database were used. The quantitative analysis of the phase composition was conducted using the Rietveld Method with the SIROQUANT software. The following corrections were applied in the analyses: the effect of anomalous X-ray
scattering and the microabsorption. The elementary cell parameters were determined using the Rietveld method only for the phase components in case of which the diffraction spectrum was well-formed. The results of the determinations of the elementary cell parameters were compared with catalogue data of the ICCD PDF 4+2012 database to identify solid solutions.

The tests using electron scanning microscopy were conducted in the Institute of Ceramics and Building Materials, Refractory Materials Division in Gliwice with the use of a microscope equipped with an electron gun in the form of Schottky emitter (accelerating voltage of 200 V−30 kV) and a Wide Field Optics optical system comprised of three electron lenses. Microscopic images were obtained using detectors: backscattered electrons detector BSE (2.0 nm resolution at 30 kV), secondary electrons (SE) detector (1.2 nm) working in high-vacuum mode, LVSTD low vacuum secondary electron detector (1.5 nm) and a CL cathodoluminescence detector (radiation range of 350−650 nm).

The X-ray microspectral analysis was conducted in the Institute of Non Ferrous Metals (Department of Material Engineering and Powder Metallurgy) in Gliwice, using an X-ray JXA 8230 microanalyser manufactured by JEOL. The analyses were conducted using metallographic specimens dusted with a thin layer of carbon to transfer the electric charge. X-ray mapping of elements was conducted using Energy Dispersive Spectroscopy. Local quantitative analyses of selected grains were conducted.

3. Results

3.1. X-ray diffraction

Tests conducted using the X-ray diffraction method allowed for a precise determination of the phase composition of slags, both in terms of quality and quantity.

It has been exhibited that the amorphous substance is dominating in the composition of the analyzed Zn-Pb slags, apart from which the crystalline phases occur and are represented by: oxides (hematite, magnetite, corundum, solid solution of spinel, hercynite) and silicates (mullite, quartz, cristobalite, anorthite, melilite, sanidine, sekaniinaite) as well as phases which were subject to secondary crystallization in the dump, among which the following were distinguished: carbonates (calcite, agagonite), sulphates (gypsum, epsomite, hexahydrite) and hydroxides (ferrihydrite). The results of the analysis have been presented in table 1.

The amorphous substance constitutes the main component of slags and its content varies in the range from 45.00 to 74.60%. The formation of such significant amounts of amorphous substance is related to the rapid setting of slag during its release to the so-called slag pits. Additionally, such slag may be sprayed with water which increases the rate of the setting process. In such conditions, a material resembling glaze is formed.

Amorphous substance rarely occurs in the entire volume of the slag melt, but it usually co-exists with the crystalline phase. In such substances, domains of crystalline phase appear (known as crystallites in mineralogy), mixed with the domains of amorphous phase. By changing the conditions of liquid cooling, it is possible to change the proportions of one phase to another in a relatively wide range. In case of smelter slags, however, the crystallites constitute a small percentage among other components surrounding them. The crystallization commences in the conditions of the furnace, but the process is suddenly interrupted during the cooling of the slag melt, which results in the formation of fine crystals surrounded by amorphous substance. Their clear identification is impossible in e.g. microscopic observations in thin section, however tests using X-rays provide a reliable image of the presence of crystalline phases. In case of the tested Zn-Pb slags, among the crystalline components identified using such a method, the finding of the solid solution of spinel characterized by variable chemical composition was interesting. In sample No. 2 the spinel was found to have an iron impurity, while the spinel found in sample No. 3 contained substitutions of zinc. The X-ray diffraction method also provides good results in terms of the identification of hydroxides, the determination of which in
microscopic studies may be difficult due to the microcrystalline structure. The presence of one of the iron hydroxides – ferrihydrite – was found in the tested slags.

**Table 1.** Phase composition of slags based on X-ray diffraction.

| No. of sample | Phase composition                                                                 | Quantitative participation (%) |
|---------------|-----------------------------------------------------------------------------------|--------------------------------|
| 1             | Amorphous substance                                                              | 74.6 ± 0.5                     |
|               | CaSO$_4$·2H$_2$O – Gypsum                                                       | 1.3 ± 0.1                      |
|               | Al$_6$Si$_2$O$_{13}$ – Mullite                                                   | 15.0 ± 0.2                     |
|               | Fe$_2$O$_3$ – Hematite                                                           | 1.8 ± 0.1                      |
|               | Fe$_3$O$_4$ – Magnetite                                                          | 1.6 ± 0.1                      |
|               | Al$_2$O$_3$ – Corundum                                                           | 1.4 ± 0.1                      |
|               | SiO$_2$ – Quartz                                                                  | 1.3 ± 0.1                      |
|               | CaCO$_3$ – Calcite                                                                | 1.8 ± 0.1                      |
|               | CaCO$_3$ – Aragonite                                                              | 1.1 ± 0.1                      |
| 2             | Amorphous substance                                                              | 56.5 ± 0.5                     |
|               | Ca [Al$_2$Si$_2$O$_8$] – Anorthite                                               | 17.1 ± 0.2                     |
|               | Fe$_2$O$_3$ – Hematite                                                           | 1.6 ± 0.1                      |
|               | Fe$_3$O$_4$ – Magnetite                                                           | 5.7 ± 0.1                      |
|               | CaSO$_4$·2H$_2$O – Gypsum                                                       | 2.5 ± 0.1                      |
|               | Al$_6$Si$_2$O$_{13}$ – Mullite                                                   | 5.5 ± 0.2                      |
|               | (Fe,Mg)Al$_2$O$_4$ – Spinel solid solution                                        | 2.8 ± 0.1                      |
|               | (Ca,Na)$_2$[(Al,Mg,Fe$^{2+}$)][(Al,Si)SiO$_7$] – Melilite                      | 0.7 ± 0.1                      |
|               | FeAl$_2$O$_4$ – Hercynite                                                        | 6.9 ± 0.1                      |
|               | SiO$_2$ – Quartz                                                                  | 0.8 ± 0.1                      |
| 3             | Amorphous substance                                                              | 45.0 ± 1.0                     |
|               | SiO$_2$ – Quartz                                                                  | 10.2 ± 0.5                     |
|               | KAlSi$_3$O$_8$ – Sanidine                                                        | 3.7 ± 0.3                      |
|               | MgSO$_4$·7H$_2$O – Epsomite                                                      | 10.0 ± 1.0                     |
|               | Fe$_2$O$_3$ – Hematite                                                           | 1.2 ± 0.1                      |
|               | Fe$_3$O$_4$ – Magnetite                                                           | 1.0 ± 0.2                      |
|               | CaSO$_4$·2H$_2$O – Gypsum                                                       | 2.1 ± 0.2                      |
|               | (Fe$^{2+}$, Mg)$_2$Al$_4$Si$_5$O$_{18}$ – Sekaninaite                           | Below the limit of determination|
|               | (Mg,Zn)Al$_2$O$_4$ – Spinel solid solution                                        | 1.0 ± 0.1                      |
|               | Fe$_{1.4}$O$_{12}$ (OH)$_{3.68}$ – Ferrihydrite                                 | Below the limit of determination|
|               | SiO$_2$ – Cristobalite                                                           | 6.3 ± 0.4                      |
|               | MgSO$_4$·7H$_2$O – Hexahydrate                                                   | 19.0 ± 1.0                     |

3.2. Scanning electron microscopy
The tests using electron scanning microscopy made it possible to identify the components of the slags as well as to exhibit their chemical composition (figure 1, table 2).
Figure 1. Microphotography of Zn-Pb slag; scanning electron microscopy.

Table 2. Chemical composition of Zn-Pb slag phases; points of analyzes according to figure 1.

| Element | 1     | 2     | 3     | 4     | 5     |
|---------|-------|-------|-------|-------|-------|
| O       | 58.33 | 57.53 | 63.92 | 75.82 | 74.32 |
| Na      | -     | -     | 0.19  | -     | -     |
| Mg      | 1.56  | 1.93  | 14.93 | -     | -     |
| Al      | 14.53 | 23.29 | 0.89  | -     | -     |
| Si      | 2.15  | -     | 19.04 | -     | 0.18  |
| P       | -     | -     | -     | -     | -     |
| S       | -     | -     | -     | 12.42 | 13.16 |
| K       | -     | -     | -     | -     | -     |
| Ca      | 0.20  | -     | 0.14  | 11.53 | 11.89 |
| Ti      | 0.69  | 0.29  | 0.12  | -     | -     |
| Fe      | 22.54 | 16.96 | 0.78  | 0.23  | 0.45  |
| Total   | 100.00| 100.00| 100.00| 100.00| 100.00|

Explanations: 1−2 hercynite, 3 forsterite, 5−6 gypsum

The microphotography and the analyses presented in table 2 have been supplemented by the EDS spectra, which are the dependence of counts vs. the radiation energy. The spectra allow for the identification of elements constituting components of a given phase and – in a quite evident manner – for exhibiting the chemical composition in the analyzed micro areas (figure 2).
Based on the analysis conducted using electron scanning microscopy, the presence of most of the components identified using the X-ray diffraction was found, i.e. the hercynite (figure 1, table 2, analysis 1-2), as well as forsterite which was not identified in X-ray structural tests (figure 1, table 2, analysis 3). This may be explained by the form of the forsterite, which constitutes very fine crystallites which result in low results in the phase identification using X-ray diffraction. In such case, the reflections of the better crystallized phase components occurring in larger amounts may overlap the forsterite peaks.

Observations using electron scanning microscopy have also allowed for the assessment of the structure of the individual phases, including the morphology, dimensions and their mutual co-occurrence. Figure 1 presents numerous fine euhedral hercynite crystals accompanied by fine crystallites of fosterite and agglomerations of gypsum filling the pores formed in the slag.

Microphotographs of fractures or the surface of slag are helpful in preparing morphological descriptions of crystalline phases. Especially the structure of secondary phases filling the pores and fissures formed in the slag during the setting process were well observable. Figures 3 and 4 depict gypsum crystal tiles.

**Figure 2.** EDS spectrums; scanning electron microscopy (from the left: EDS spectrums from 1 to 5 point – points according to figure 1).
Figures 3, 4. Tabular habit of gypsum; scanning electron microscopy.

Tests conducted using the electron scanning microscopy as well as the studies conducted using X-ray spectral microanalysis, described in a subsection below, allow for the creation of element maps exhibiting the distribution of elements at the analyzed area of the sample.

Figure 5. Maps of main elements in the Zn-Pb slag amorphous substance; scanning electron microscopy.
Figure 5 presents the surface distribution of the main elements occurring in the amorphous substance separated in the tested Zn-Pb slags, where silicon, aluminum and potassium were dominant besides oxygen.

3.3. X-ray spectral microanalysis

The tests conducted using the X-ray spectral analysis have confirmed the presence of phases in the analyzed slags that have been identified using the X-ray diffraction method. Additionally, based on these tests iron sulphides have been identified, which were not found using other methods (figure 6, table 3).

![Figure 6. Microphotography of Zn-Pb slag; X-ray spectral microanalysis.](image)

Iron sulphides occur in the form of fine spherical inclusions surrounded by amorphous substance. In their chemical composition, the content of iron is from approx. 52 to over 58%, while the content of sulphur varies between 37 and 39%. Such a composition of elements suggests the presence of FeS pyrrhotite, where, theoretically, the content of sulphur may reach 37.67% and the content of iron reaches 62.33% [21].

Based on the X-ray spectral microanalysis, also the presence of impurities was identified, namely the elements that occur in slags in low amounts, such as the rare earth elements. It has been found that the elements representing the lanthanides, such as La lanthanum, Ce cerium, Dy dysprosium as well as Ir iridium, considered to be a lanthanide, constitute substitutions in the internal structure of sulphides, mostly mullite.
Table 3. Chemical composition of Zn-Pb slag phases; points of analyzes according to figure 6.

| Element | 1       | 2       | 3       | 4       | 5       |
|---------|---------|---------|---------|---------|---------|
| O       | -       | -       | -       | 46.948  | 46.453  |
| Si      | -       | -       | -       | 12.238  | 11.892  |
| Al      | -       | -       | -       | 40.451  | 41.250  |
| Ca      | -       | -       | -       | 0.015   | 0.011   |
| Mg      | -       | -       | -       | 0.019   | -       |
| Fe      | 52.985  | 58.112  | 58.850  | 0.042   | 0.039   |
| Ti      | -       | -       | -       | 0.139   | 0.142   |
| Ni      | 6.777   | 4.088   | 3.372   | -       | 0.003   |
| As      | -       | -       | -       | 0.015   | -       |
| Cd      | 0.036   | -       | -       | 0.019   | 0.014   |
| Co      | 0.436   | 0.378   | 0.310   | -       | 0.004   |
| Cr      | 0.002   | -       | 0.002   | 0.009   | 0.022   |
| Zn      | 0.038   | -       | -       | -       | 0.027   |
| W       | -       | 0.014   | -       | -       | 0.006   |
| Tl      | 0.159   | 0.127   | 0.145   | -       | 0.014   |
| S       | 39.180  | 37.052  | 37.117  | -       | 0.002   |
| La      | 0.210   | 0.093   | 0.083   | -       | 0.073   |
| Ce      | -       | 0.079   | 0.069   | 0.023   | -       |
| Dy      | 0.134   | 0.050   | 0.023   | 0.044   | -       |
| Ir      | 0.041   | 0.005   | 0.029   | 0.037   | 0.046   |

Explanations: 1−3 iron sulphide, 4−5 mullite

4. Discussion
The identification of phase components using X-ray diffraction has proven to be one of the most precise techniques used in qualitative analysis of the phase composition of slags. Based on it, it was also possible to determine the percentage of each of the components in a given sample. The application of this technique also allowed for the identification of solid solutions of oxide phases and the identification of two kinds of polymorphous calcium carbonate – calcite and aragonite.

The identification of hydroxides, which may manifest in micro- or cryptocrystalline forms, usually poses a difficulty in the analysis of the phase composition of slags. Microscopic observations, i.e. in thin plates, do not provide the possibility to identify the individual hydroxides unequivocally. Their identification due to the presence of the OH groups by means of the X-ray spectral microanalysis, on the other hand, is not possible. Favourable conditions may thus be achieved using X-ray structural analysis – the presence of ferrihydrite was found in the analyzed slags. A good result was also obtained in earlier studies using Mössbauer spectroscopy to identify iron hydroxides. Depending on the type of tested Zn-Pb waste material different iron phases have been shown: in the weathered slag four different products of the iron oxidation were detected: divalent Fe(OH)$_2$, mixed valence magnetite, Fe$_3$O$_4$ and three valence Fe(OH)$_3$, α Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ compounds, in the vitrified material metallic forms of iron are dominated [22,23].

The tests using electron scanning microscopy and X-ray spectral microanalysis allowed for the determination of the chemical composition of the individual phases and the amorphous substance. The results were more precise and detailed, however, in case of tests conducted using the X-ray spectral microanalysis. These tests served the identification of lanthanide and platinum group elements substitutions in the sulphide phases. These elements are considered critical materials, which were defined in 2008 as „minerals that are subject to the risk of fluctuation or restriction of supply, the
deficit of which may have severe consequences to the entire economy” by the committee for Minerals Critical for the Economy of the United States [24,25].

The conducted analyses of the mineral composition of slags indicate the necessity to apply several complementary research methods. This may be exemplified by the inclusions of iron sulphides that were identified using the X-ray spectral microanalysis, but were not found using other methods, e.g. using the X-ray diffraction method. The microphotographs show that the iron sulphides are in the form of fine inclusions surrounded from all sides by the amorphous substance, which is the main component of slags. This is why the identification using the X-ray diffraction method could have been hindered. It may be assumed that the low peaks resulting from sulphides were overlapped by the reflections of other components. A similar situation was noted in observations using electron scanning microscopy – this technique, however, has identified the presence of forsterite.

All the examples provided above clearly show that conducting a mineralogical study of smelter slags requires the application of several complementary research methods. This is caused by the variable and differentiated phase composition of slags as well as the specific structure of the phase components, most often occurring as fine crystallites covered by the amorphous substance.

5. Conclusions
Based on the conducted research, the following conclusions have been made:

- It has been exhibited that the application of several complementary research techniques is necessary in the determination of the phase composition of slags, as only the application of the full spectrum of tests may provide reliable information regarding the presence of the individual phases in the slags. Some phases, e.g. iron sulphides, forsterite and ferrhydrite were found in the Zn-Pb slags using only one of the applied research methods.
- In case of the tested Zn-Pb slags and in view of obtaining qualitative characteristics of the components of slags, the phase identification tests by means of X-ray diffraction were found to be precise. Based on them, also the percentage of the individual crystalline phases and the percentage of the amorphous substance have been determined.
- Analyses using electron scanning microscopy and X-ray spectral microanalysis allowed for the determination of the chemical composition of the individual phases. In that case, the X-ray spectral microanalysis was found to be more precise and it allowed for the identification of substitutions of elements occurring in small amounts in the phase components, i.e. the rare earth elements.

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