Phase composition of Katowice – Wełnowiec pytometallurgical slags: preliminary SEM study

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Abstract

Exploitation on Zn-Pb ores in Upper Silesia region dates back to the XIII century. Analyzed slags are associated with Hohenlohe smelting plant which started its work in 1804 as an iron smelter, and continued as zinc smelter since 1873. Waste material from smelting plant production was stored in Katowice – Wełnowiec, although nowadays most of it has been used for commercial purposes. Slags are composed of silicates and aluminosilicates, e.g. willemite, pyroxene- and melilite-group, K-feldspar accompanied by silico-phosphates close to perhamite, harrisonite and arsenate-chloride with composition similar to nealite. Chemical composition of most phases is simple with some unique substitutions in case of Sr and Ce.

Key words: Katowice, Wełnowiec, Zn-Pb, slags, willemite, melilite-group

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Introduction

Location

Katowice – Wełnowiec is a part of Upper Silesian Industry District, covering around 2700 km^2, with extreme concentration of smelting and mining industry. As a result it is an area where an extreme environment degradation is observed, including health risks for inhabitants. Wełnowiec slag dump, here described, is located in a district center (fig.1), near an old smelting plant production halls. Currently most of the stored material has been used for commercial purposes (e.g., road substructures). The only evidence of slag heaps that used to be here is a monadnock (fig.2), left as a monument for smelting plant history.

Historical background

Analyzed slags are a result of Hohenlohe (later Silesia) smelting plant activity. Industry dates back to 1804 when Fryderyk Hohenlohe - Ingelfingen – Oehringen started construction of iron smelter in Katowice – Wełnowiec. In 1873 it was turned into zinc smelting plant associated with rolling mill, working since 1889. In 1961 the industry was combined with smelting plant in Świętochłowice-Lipniki as Zinc Industries "Silesia". In 2000 production of rectified zinc was stopped and a part of industry buildings were adapted for offices and other commercial purposes (http://www.silesiasa.pl/).

Geological setting

The ores used in metallurgy were Mississippi Valley-type lead-zinc ores from Cracow-Silesia zinc-lead district in Poland, which are composed of mainly sphalerite, pyrite, marcasite and galena, hosted in dolomite rocks (Heijlen, Muchez et al. 2003).

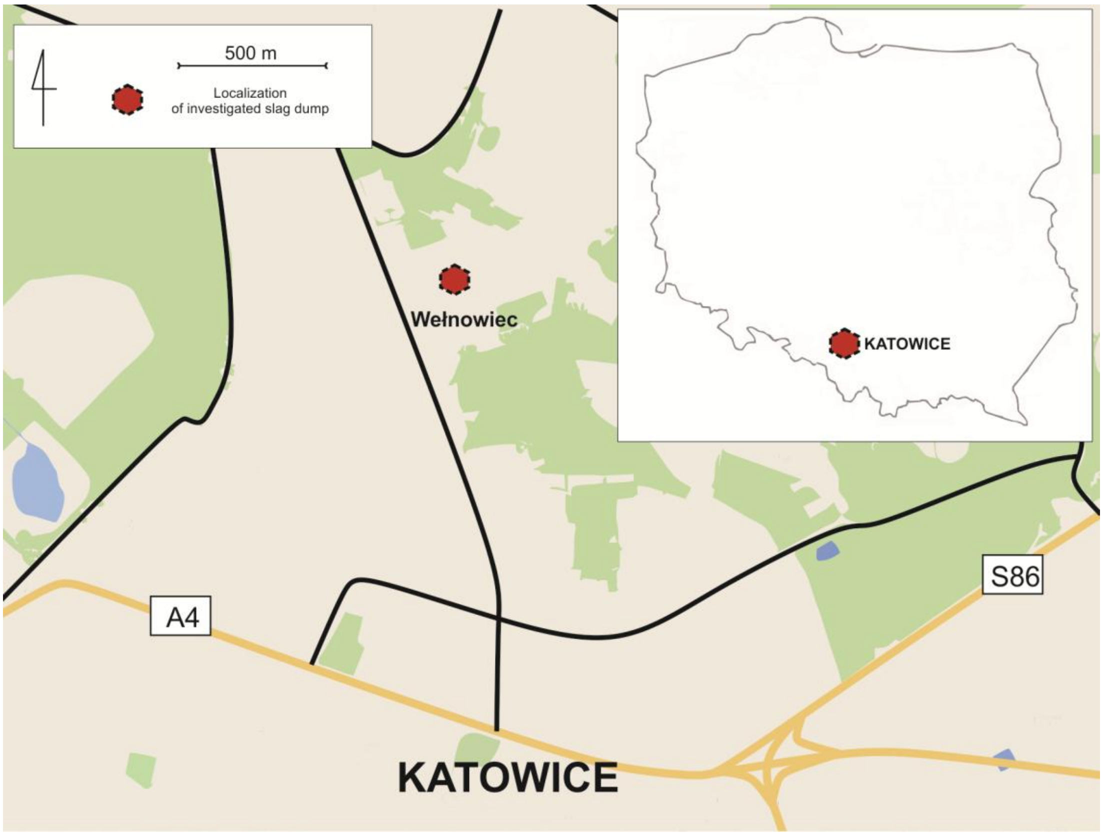

Fig.1. Location of the investigated slag dump

Methods

The aim of this paper is to present preliminary, SEM-based study on phase composition of slags from one of slag dumps located in Katowice – Wełnowiec. To accomplish this goal following methodology was applied: 15 representative samples (0,5 – 6 kg in weight) were collected during the macroscopic examination in the dump. Thin sections from samples were examined for the texture, structure and phase composition using polarizing Olympus BX-51 microscope. Additional observations for obtaining the phase chemistry data were performed on thin sections and separates using scanning electron microscope (SEM; FET Philips XL30) with an energy-dispersive spectrometer (EDS) at the Faculty of Earth Sciences, University of Silesia, Sosnowiec, Poland. It is necessary to underline that due to applied methodology results are preliminary and phase determination are approximate.

Results

The studied material is composed of mainly willemite, pyroxene- and melilite-group phases. Phase relations suggest that melilite was the first phase to crystalize and other crystals grow on the melilite base. Slags are highly porous. Wastes from Katowice – Wełnowiec are chemically active as a result of weathering process, so the secondary phases are commonly observed on the slag surface and inside the voids.

Willemite (fig.3A) represents different morphological varieties from needle radial aggregates up to 50 µm across to polygonal aggregates up to 1mm in diameter. It has simple chemical composition with some Mg addition.

Pyroxene in slags from Katowice-Wełnowiec forms euhedral to subhedral crystals up to 800 µm long, growing usually on laths of melilite. According to EDS analyses pyroxene crystals in studied slags show the composition close to augite – diopside - hedenbergite (fig.3B).

Fig.2. Leftover waste material in the Wełnowiec slag dump

Melilite-group species usually forms laths up to 10 mm across, with well visible cleavage {001} and {110} faces (fig.3C), in some cases tetragonal-prism melilite is present. Melilite crystals may have composition between åkermanite-gehlenite-ferrigehlenite.

SEM – EDS observations proved also the presence of additional phases, not determined macroscopically. This includes Celsian, that seems to be a rare phase in slags from Katowice-Wełnowiec. It forms massive laths up to 200 μm along and present complex chemical composition, where potassium and cerium substitutions are common (fig.3D).

Possible monticellite-kirschsteinite is accompanied by Zn-sulphide. This sulphide is probably wurtzite due to temperature relations in Zn-S system, and technological process at site: temperature at least 1000 °C during smelting and rapid cooling of melt. Phase relations suggests exsolution of sulphide – it is present as droplets usually of few micrometers across within monticellite-kirschsteinite crystal about 1 mm across (fig.3E). Both phases show simple chemical composition with no or minor substitutions.

Zincite is common phase in studied slags, usually present as rose aggregates of anhedral laths, in some cases these aggregates form zincite-rich pipes with overgrowing calcite crystals (fig. 3F). Analyzed zincite crystals show simple chemistry with no substitutions.

Olivine (close to fayalite end-member) seems to be uncommon phase in studied slags, analyzed olivine-group crystal, 50 μm across, has anhedral morphology and is overgrown by willemite. Willemite, on the other hand, is often accompanied by two phases: a lath-like lead oxide and needle shaped aggregates of crystals showing complex-composition, close to mimetite ($Pb_5[AsO_4]_3Cl$; fig.3G; Si and Zn peaks are probably caused by willemite, although some mimetite varieties may have Si in composition. Laths of the first phase are up to 20 μm across and have some strontium in chemical composition. In the analyzed material several other phases were determined: silicocarnotite-like phase, possibly ($Ca_5[PO_4]_2[SiO_4]$) with essential As admixture (fig.3H), in lath-like crystals arranged in aggregates up to 250 μm long; harrisonite-like one, possibly ($Ca(Fe^{2+},Mg)_6(PO_4)_2(SiO_4)_2$), enriched in Zn, as an aggregate of column crystals up to 250 μm long (fig.3I).

Barite in studied material forms anhedral laths up to 100 μm across, growing on the surface of other phases and showing complicated substitutions – calcium and possibly cerium are present in most analyzed crystals, while some of them present also strontium concentrations (fig.3J), approaching it to barian celestine.

Discussion

On the base of this study it is possible to determine the approximate sequence of crystallization in the slag. At the beginning the first generation of the melilite-group phase, of lath-like habit, crystallized. Pyroxene, K-feldspar and olivine are later as their crystals grow on the melilite. The second-generation of melilite crystallizes as prisms, together with supposed monticellite-kirschsteinite. Willemite overgrows other phases, e.g., monticellite-kirschteinite, or occurs as stand-alone polygon aggregates on the slag surface, probably caused by undercooling conditions. Other phases are the result of late stage crystallization and weathering process. Most of distinguished phases are common in pyrometallurgical slags and have been described before in material from Poland (Puziewicz et al. 2007; Warchulski, Szopa 2013) and from around the world (Ettler et al. 2009; Piatak, Seal II 2010), although some of them seems to be unique in such assemblages. The presence of a number of silico-phosphates and arsenate-chlorides seems to be rare in pyrometallurgical slags, although mimetite and johnbaumite have been described before in slags from Świętochłowice, Poland (Puziewicz et al. 2007). It poses the question about the source and activity of Cl in slags from Poland. Due to lack of preserved documentation from smelting plant it is impossible to determine precise conditions of smelting process, especially cooling of slag melt. Described silico-phosphates are associated with pegmatitic conditions (Dunn, Appleman 1977), oxidation zones of ores or granulite facies (Roberts et al., 1993) or metacarbonate slags from Upper Silesian coal-mining burning dumps (Ciesielczuk 2008; Kruszewski 2008). According to the historical data (Kotucha 2008) and petrological observations at similar sites (Piatak, Seal II 2010) such or similar conditions could occur during smelting process or during solidification of slag melt in the dump. Phase chemistry in most crystals is rather simple and do not differ for that of crystals from other Zn-Pb slags. Although, as it was mentioned before, the presence of phases with high chloride concentrations is uncommon in pyrometallurgical slags from Poland due to lack of significant amount of Cl in used ores and smelting process, thus further investigations are necessary to determine the source of Cl. Similar situation applies for a few other elements like Ba or Sr. The presence of cerium in studied material also pose the question about the REE source and behaviour in smelting slags, especially as it seems to be common element in many phases e.g. barite and celsian. Cerium has never been reported as addition in sulphates and aluminosilicates from pyrometallurgical slags, although presence of rare monazite was determined in wastes from Świętochłowice, Poland (Puziewicz et al. 2007).

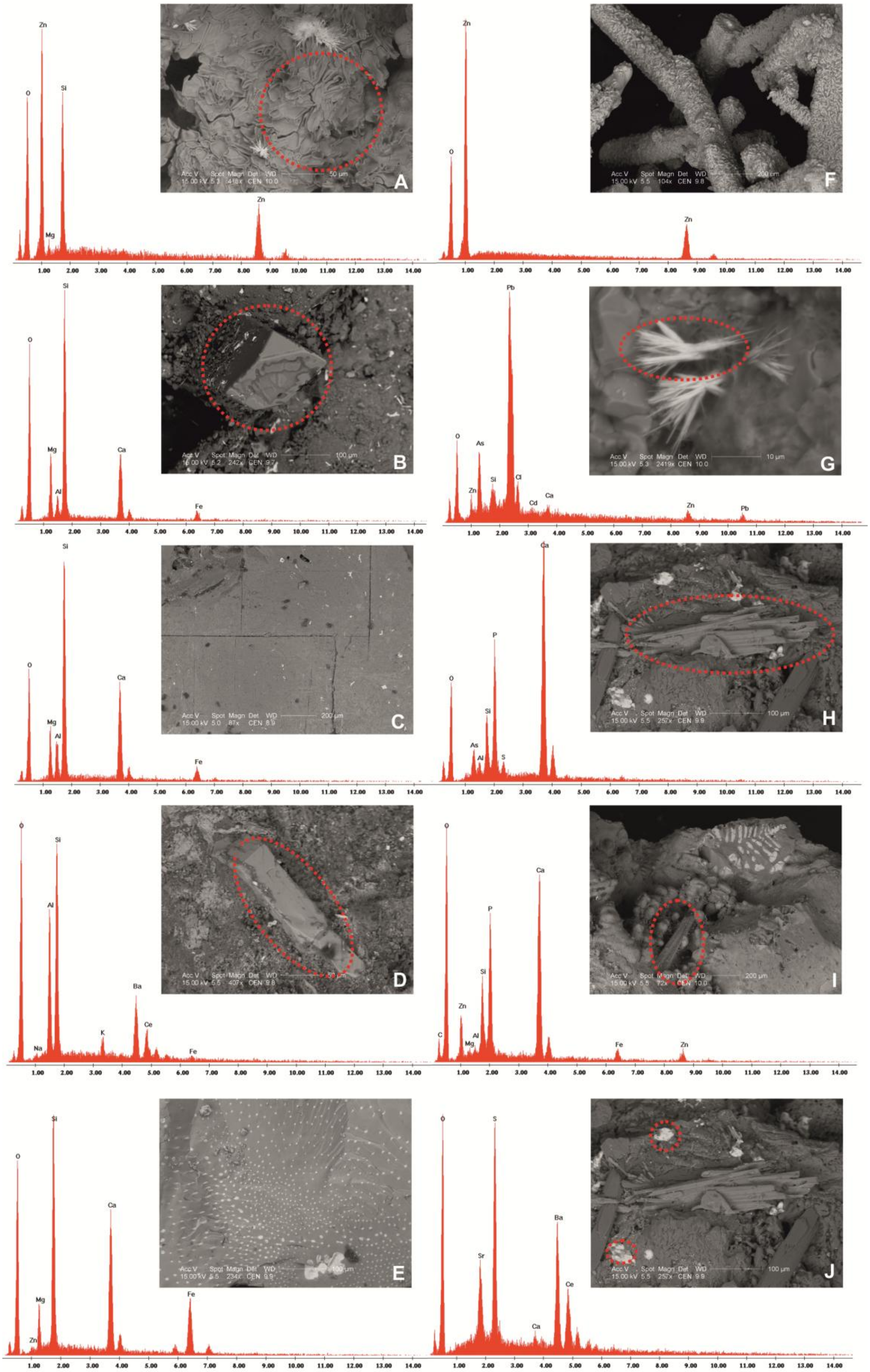
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Fig.3. SEM images with EDS spectra of the particular recorded phases from Zn-Pb Katowice – Wełnowiec slags. **A)** Polygonal aggregates of willemite (circled); **B)** Pyroxene crystal (circled); **C)** Melilite-group phase with visible cleavage; **D)** Celsian lath (circled) showing Ce concentrations; **E)** Supposed monticellite – kirschsteinite with droplets of a Zn sulphide; **F)** Pipe-like aggregates of zincite laths; **G)** Needles of an arsenate-chloride phase (circled); **H)** Silico-phosphate lath (circled) with composition close to silicocarnotite; **I)** Lath-like crystal aggregate of a silico-phosphate (circled) chemically close to harrisonite; **J)** Crystals of barian celestine (circled) showing cerium concentrations.

Conclusions

Slags from Katowice – Wełnowiec are, in general, close to the ones from other locations, although some differences were determined. Main phases belong to pyroxene and melilite groups and are associated with olivine, supposed monticellite-kirschsteinite, and celsian. In studied material also presence of uncommon phases was determined, e.g., silico-phosphates and arsenate-chloride. The chemical composition of the analyzed crystals in most cases show no or minor substitutions, except for the mentioned rare phases. Also the presence of Cl, Sr and Ce is unique and need further investigations.

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References

Ciesielczuk J. (2008) Ellestadite-(F) – a mineral formed in the overburned coal dump (Upper Silesian Coal Basin). Mineralogia – Special Papers 32, 53.

Dunn P. J., Appleman D. (1977) Perhamite, a new calcium aluminum silico-phosphate mineral and a re-examination of viseite. Mineralogical Magazine 41, 437-442.

Ettler V., Johan Z., Kribek B., Šebek O., Mihaljevic M. (2009) Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Applied Geochemistry 24, 1-15.

Heijlen W., Muchez P., Banks D. A., Schneider J., Kucha H., Keppens. E. (2003) Carbonate-Hosted Zn-Pb Deposits in Upper Silesia, Poland: Origin and Evolution of Mineralizing Fluids and Constraints on Genetic Models. Economic Geology 98, 911-932.

Kotucha W. (2008) Brzeziny Śląskie – historical sketch (Brzeziny Śląskie -rys historyczny). Wydawnictwo Kubajak, Krzeszowice (in Polish).

Kruszewski Ł. (2008) Apatite-ellestadite solid solution and associated minerals of metacarbonate slags from burning coal dump in Rydułtowy (Upper Silesia). Mineralogia – Special Papers 32, 100.

Piatak N. M., Seal II R. R. (2010) Mineralogy and the release of trace elements from slag from the Hegelr Zinc smelter, Illinois (USA). Applied Geochemistry 25, 302-320.

Puziewicz J., Zainoun K., Bril H. (2007) Primary phases in pyrometallurgical slags from a zinc-smelting waste dump, Świętochłowice, Upper Silesia, Poland. Canadian Mineralogist 45, 1189-1200.

Roberts A. C., Stirling J. A. R., Grice J. D., Frisch T., Herd R. K., Jambor J. L. (1993) Harrisonite, a new calcium iron silicate-phosphate from Arcedeckne Island, District of Franklin, Arctic Canada. Canadian Mineralogist 31, 775-780.

Warchulski R., Szopa K. (2013) Fractional crystallization recorded in the Zn-Pb slags from Piekary Śląskie-Bytom area. Mineralogia – Special Papers 41, 89-90.

http://www.silesiasa.pl, accessed on 26 may 2014