

Phase and chemical composition of historical Zn-Pb slag from the dump in Ruda Śląska (Silesian Province, southern Poland)

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Abstract

The locations and structures testifying the historic Zn-Pb ore exploitation and processing are found in numerous southern Poland regions, especially Silesian Province. The Zn-Pb slag dump in Ruda Śląska, which is over one hundred years old, is an example of such a location. Chemical composition tests have exhibited that the slag is characterized by a relatively rich mineral composition with Si and Fe's dominant content. Impurities in the form of heavy metals, i.a. Zn, Pb, Cd, As, and rare earth metals: La, Dy, and Y, have also been identified. The components of which the slags are comprised include near-equal amounts of silica glass and crystalline phases represented by oxides (hematite, spinel, magnetite, and hercynite) and by silicates (fayalite, forsterite, augite, anorthite, mullite, and quartz). The crystalline phases rarely form euhedral shapes and are mostly found in fine glass-surrounded crystallites. Based on the conducted mineralogical and chemical analyses, it has been established that the tested slags are a waste material resulting from the processing of locally found oxidized Zn-Pb ores – so-called calamine – rich in iron impurities.

Keywords

Zn-Pb slag, phase and chemical composition, historic exploitation index



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Introduction

Mining and steel industries are inseparable, as the processing of mined minerals always accompanied the mining industry. A natural consequence of that was also the development of the culture of the societies inhabiting these areas, related to the possibility of using these resources. It is partially reflected in the scientific division of the history of cultural development in the Stone, Bronze, and Iron Age. Based on the remains of ancient civilizations, or rather based on the material of which these were made, the above division was first proposed in 1836 by Christian Jürgensen Thomsen, one of the first archaeologists (Fagan, 2002).

The locations of historical exploitation and processing of ores are known and still found all over the world, for example, East Belgium (Cappuyns et al., 2006), mid-Wales in the UK (Mighall et al., 2002), Bohutín – Příbram District in the Czech republic – the place of lead and silver smelting (Ettler et al., 2009 a), Tsumeb District in Namibia, where tests were carried out on lead-copper slags (Ettler et al., 2009 b; Ettler et al., 2009 c), historical zinc smelting in New Jersey, Pennsylvania, Virginia, West Virginia, and Washington in the USA (Bleiwas and DiFrancesco, 2010) zinc smelting in China and India (Deshpande, 1996; Lin et al., 2015), as also unnamed mine site in western Okayama, southwest Japan, were was conducted smelting of Au, Ag, Cu, Pb, Zn, and As (Sueoka and Sakakibara, 2013). In Pennsylvania (Baltimore, Maryland, and Philadelphia), historical processing sites are associated with the production of batteries. There are over 400 sites, dated to 1931– 1964, of recycled lead-acid batteries or production of lead alloys (Eckel et al., 2002) and in the Blue Mountains National Park (New South Wales, Australia) core and surface sediments from the Tonalli River were studied because of the pollutants from the Yerranderie silver–lead–zinc mine site, abandoned in the late 1920s (Harrison et al., 2003). The area of Wiesloch near Heidelberg (SW-Germany) has seen mining activity for at least 2,000 years as the oxidation zone of the carbonate-hosted lead-zinc deposit of the Mississippi Valley-type was exploited for lead and silver ores since Roman times (Ströbele et al., 2010).

In Poland, the area of Silesian Province, in the south part of the country, is an example of a particularly developed region in terms of economy. This is related to its rich deposits, including iron, zinc, and lead ores, as well as the presence of hard coal (Cabała et al., 2008). The exploitation of the resources, and the processing activity, were conducted in Silesian Province since the early Middle Ages. However, the most extensive development of the mining and steel production industries occurred in the 19th and 20th centuries. To this day, the remains of old mines and steelworks may be found in this region of Poland. These include buildings related to their former activities, old exploitation locations, and equipment for mining and processing the ore found in museums. Waste dumps, especially metallurgical slag dumps, are special evidence of human activity related to using ores (Jonczy and Gawor, 2017). On the other hand, such waste dumps also constitute an issue because of environmental protection. Due to weathering, the waste may release certain elements, including metals. Their migration, along with their solutions, may constitute a potential source of pollution (Ettler et al., 2001; Schneider et al., 2016). In France, The Lot River watershed, tributary of the Gironde River, is known for its chronic Cd pollution resulting from mining and smelting activities since the late 19th century (Audry et al., 2004).

Old metallurgical waste dumps pose a particular threat. For many years, the wastes deposited in the dumps are subject to physical weathering, which is the cause of the disintegration of the waste material and the formation of dust fractions that are susceptible to deflation and chemical weathering leading to transformations of slag components and the migration of the elements found in the slag. The long-term deposition also results in the fading of the contours of the dumps and leveling of the dumps to the ground level. The same is also applicable to the historic exploitation locations – the shallow open-cast mines become less and less distinct with time. Natural vegetal succession and urban expansion cause the signs of the former mining and steel industries to become seemingly invisible. The research conducted in the areas of the historical exploitation and processing of ores, however, exhibit that even centuries later, these areas are a source of metal ion migration and concentration (Merrington and Alloway, 1994; Eckel et al., 2001). Thus, it is necessary to keep track and monitor such areas, as this is crucial for the correct designing and conducting of environmental studies – especially if an agricultural activity is planned in a given area. Such activities are aimed to prevent hazards posed to human health; in Santo Amaro (Brazil), for example, large amounts of Pb and Cd have been documented since 1970 in the blood and hair of the people living nearby the steelworks (De Andrade Lima and Bernardez, 2011). To prevent environmental pollution and make decisions regarding the management of the slag, it is necessary to conduct multidimensional studies of the slag, especially mineralogical and chemical analyses. In terms of their phase composition, smelter slags constitute one of the most diverse groups among the waste materials. Their phase composition changes depending on the type of the furnace charge material as well as the use of additives and fluxing agents.

The phases that are subject to crystallization in furnace conditions are identified with minerals forming as a result of natural geological processes. Their form, however, is often different, and it results from the changing crystallization conditions. The intensity of the slag cooling process has an impact on the size and form of the crystals. Well-developed phases may be observed in the slags where the crystallization proceeded in slow setting conditions, while fine crystallites surrounded by glass may be found in case of the crystallization process being

interrupted due to the rapid cooling of the slag. This also impacts the distribution of elements among the crystalline phases and the glass (Ettler et al., 2000).

The chemical composition of the phases comprising the slags is, in most cases, much richer than the chemical composition of their natural counterparts. The impurities of different elements may occur as substitutions in the internal structure of the crystalline phases, may be dispersed in the glass, or may constitute a component of metallic precipitates. Due to the above, slags are increasingly considered in terms of the recovery of elements.

The purpose of the study was to provide characteristics of the phase, and chemical composition of two types of slags resulting from Zn-Pb ore processing found at one of the old waste dumps located in Ruda Śląska in the Silesian Province (southern Poland).

Materials and methods

Slag samples characterized by variable macroscopic features, that is: color, structure, and texture, were acquired for the tests. Before commencing laboratory analyses, the samples were described in terms of their macroscopic characteristics, dried, and reduced by quartering. A part of each of the samples was ground in an agate grinder to reach the grain size below 63 μm and was subsequently dried at the temperature of 105 $^{\circ}\text{C}$ for 2 h. The other part served as preparations for microscopic analyses.

The following research techniques were used:

- Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES),
- Identification of phases by X-ray diffraction,
- X-ray spectral microanalysis,
- Scanning Electron Microscopy.

To establish the chemical composition of the analyzed wastes, sample solutions were prepared; approximately 0.5 g of a sample was poured with a mixture of acids: 15 ml of HCl and 5 ml of HNO₃. The samples were subject to mineralization using a UniClever II microwave mineralizer.

Following the mineralization, the samples were transferred to 50 ml measuring flasks. The selected elements were identified using inductively coupled plasma – optical emission spectrometry (ICP-OES) using an ICPE 9800 emissive spectrometer manufactured by Shimadzu with a Teflon sample introduction system allowing for work with hydrofluoric acid. The elements: Al, Ca, Fe, Mg, Mn, and S were identified in the solutions after a 40-fold dilution. The content of SiO₂ in slags was determined by means of an alkaline flux in the form of Na₂CO₃. The obtained results were converted to the Si concentration.

The X-ray diffraction analysis (XRD) was conducted using a Panalytical XPERT PRO MPD powder diffractometer. The diffractometer was equipped 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. For the range of angles of 5-80° 2 θ at operational lamp parameters of 35 mA and 45 kV, the X-ray diffractograms were prepared. HighScore software by Pananalytical as well as the ICDD PDF-4+ (2011 issue) database were used to identify the phase composition of slags, while the quantitative analysis was performed using the Rietveld Method with the SIROQUANT software. Two corrections were applied during the measurements: the effect of anomalous X-ray scattering and the micro absorption.

The X-ray spectral microanalysis was conducted using an X-ray JXA 8230 microanalyzer 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.

The tests using electron scanning microscopy were conducted with the use of a microscope equipped with an electron gun in the form of a Schottky emitter (accelerating voltage of 200V-30kV) 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 a high-vacuum mode, LVSTD low vacuum secondary electron detector (1.5 nm), and a CL cathodoluminescence detector (radiation range of 350-650 nm).

Research area

The tests were conducted using slag samples obtained from a dump located in the city of Ruda Śląska in the central part of Silesian Province – southern Poland (Fig. 1).

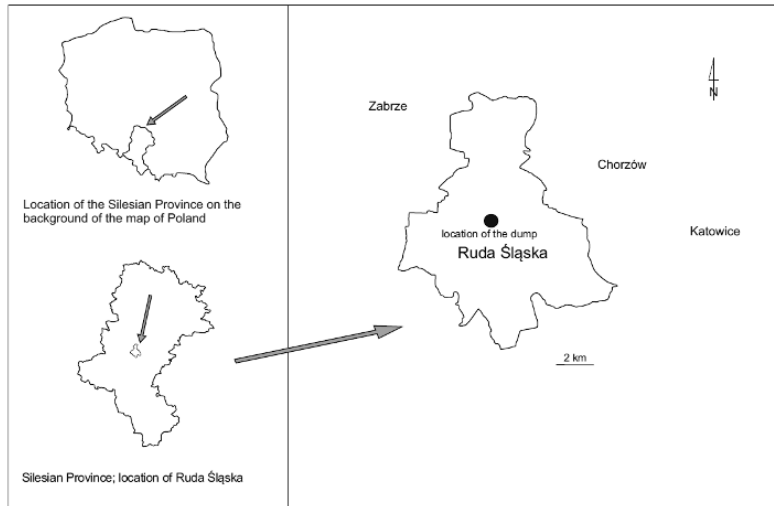


Fig. 1. Schematic sketch of the dump location

The dump in concern constitutes an example of an object testifying of the history of the ore industries in this area. It is a remnant of a small smelter plant activity, which operated as a production facility in the years from 1812 to 1932. During over 100 years of its existence, the plant accumulated 1,860,000 cubic meters of wastes at an area of 8.5 ha (Fig. 2).



Fig. 2. Part of a metallurgical furnace housing on the Zn-Pb slag dump

In subsequent years, the wastes – among which smelter slags are dominant – were not the subject of any utilization. The currently increasing environmental awareness caused both the impact of this dump, over a century old, on the environment and the possibility of reusing the deposited wastes became a subject of interest.

In general, two types of slags may be distinguished in the dump, characterized by different colors: red-brown or dark-grey (Fig. 3). The structure of both types of slags is medium-grained; the texture is dense and sometimes porous. A white, fine-crystalline bloom may be noted at the surface of slags that are deposited in the dump areas that are particularly exposed to external factors (Fig. 4).



Fig. 3. Two kinds of Zn-Pb metallurgical slag



Fig. 4. White bloom of secondary phases

Results

Chemical composition of slags. The results of the analysis of the chemical composition of the slags have been presented in Table 1.

Tab. 1. Chemical composition of Zn-Pb slags

Element	Unit	No. of sample	
		Slag No. 1	Slag No. 2
Si	[% wt]	9.07	9.03
Ti	[mg/kg]	1131	3461
Al	[% wt]	7.63	7.67
Fe	[% wt]	8.99	9.23
Mn	[mg/kg]	1114.3	835.0
Mg	[% wt]	1.49	0.83
Ca	[% wt]	4.89	4.29
Na	[mg/kg]	2378.3	4807.6
K	[mg/kg]	7889.2	5300.9
P	[mg/kg]	1887.8	4423.8
S	[% wt]	0.44	0.94
Ba	[mg/kg]	950.9	2558.2
Cr	[mg/kg]	24.17	34.47
Pb	[mg/kg]	36.2	555.8
Zn	[mg/kg]	207.0	2050.6
Cd	[mg/kg]	310.2	< 3.0
As	[mg/kg]	816.5	< 57.8
Sc	[mg/kg]	18.3	19.3
La	[mg/kg]	35.6	46.2
Dy	[mg/kg]	86.0	91.6
Y	[mg/kg]	28.1	25.5

The presence of Si, Al, Ca, Mg, as well as S, K, Na, P, and Ba has been identified in the chemical composition; heavy metals have also been found: Fe, Ti, Mn, As, Zn, Cr, and Pb. Moreover, the presence of rare-earth elements has been confirmed: La, Dy, Y, as well as Sc.

Mineralogy of slags. Among the components of the slags in concern, glass is dominant. This also applies to other types of slags, for example, blast-furnaces slags, steel slags (Fredericci et al., 2000; Jonczy, 2014; Jonczy, 2016). Its part in slag No. 1 reaches 51.3% and 55.9% in slag No. 2 (Tab. 2). Glass, however, is rarely found in the entire volume of the slag and often coincides with a crystalline phase. In such substances, domains of the crystalline phase appear (crystallites), mixed with the domains of the amorphous phase. Changing the conditions of liquid cooling makes it possible to change the proportions of one phase to another in a relatively wide range. However, in the case of smelter slags, the crystallites usually constitute a small percentage among other components surrounding them. The crystallization commences already in the furnace's conditions, but the process is suddenly interrupted during the cooling of the slag melt, which results in the formation of fine crystals surrounded by glass. Their identification is often hindered, and the application of at least two supplementary research techniques is thus necessary for the analysis. In case of the slags in concern, phase identification using X-ray diffraction was used, which allowed for the qualitative and quantitative determination of the dominant components, as well as X-ray spectral microanalysis, which allowed for the determination of the chemical composition of individual crystallites and the glass.

Based on the phase identification using X-ray diffraction, crystallites and sporadic well-developed crystals are represented by oxides (magnetite, hematite, spinel, hercynite), silicates (fayalite, forsterite, enstatite, anorthite, mullite, and quartz) was found. Recrystallized gypsum was also identified among the dump materials (Figs. 5-8, Tabs. 3-6).

Tab. 2. Components of Zn-Pb slags determined based on X-ray diffraction

Component	Chemistry	Content [wt %]	
		Slag No. 1	Slag No. 2
Glass	-	51.3	55.9
Hematite	Fe ₂ O ₃	6.6	1.1
Magnetite	Fe ₃ O ₄	-	2.9
Hercynite	Fe ²⁺ Al ₂ O ₄	5.0	8.5
Spinel	MgAl ₂ O ₄	2.3	-
Fayalite	Fe ₂ [SiO ₄]	-	2.8
Forsterite	Mg ₂ [SiO ₄]	4.4	-
Enstatite	Mg ₂ [Si ₂ O ₆]	4.5	0.5
Anorthite	Ca[Al ₂ Si ₂ O ₈]	22.0	21.7
Mullite	Al _(4+2x) Si _(2-2x) O _(10-x) where x = 0,17-0,59	3.1	2.9
Quartz	SiO ₂	0.9	0.5
Gypsum	CaSO ₄ ·2H ₂ O	-	3.7

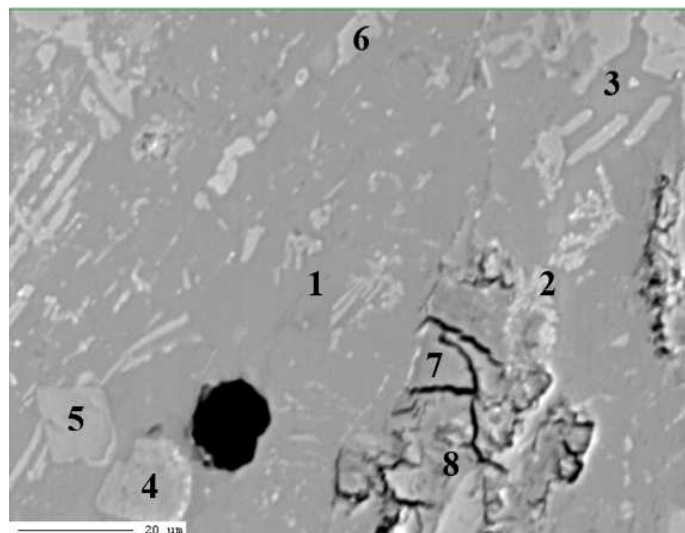


Fig. 5. Microphotography of slag No. 1 – example No. 1

Tab. 3. Chemical composition of components of slag No. 1; according to Fig. 5

Element	No. of analysis / Content [wt %]							
	1	2	3	4	5	6	7	8
O	51.59	49.82	52.43	48.53	46.95	49.63	57.21	58.41
Si	19.89	19.56	26.40	0.47	0.43	19.66	36.03	35.75
Ti	0.053	1.27	0.99	0.14	0.13	0.25	0.01	0.007
Al	16.19	7.24	8.17	34.39	31.59	4.86	2.62	2.08
Fe	0.78	16.39	6.78	11.51	12.28	13.47	0.60	0.56
Mn	0.02	0.29	0.17	0.093	0.12	0.26	0.07	0.03
Mg	0.13	2.79	0.61	3.37	6.75	11.34	0.38	0.34
Ca	10.53	2.57	1.96	0.07	0.07	0.34	0.26	0.82
Na	0.15	-	0.02	0.02	-	-	-	0.02
K	0.56	-	1.19	0.07	0.01	-	0.26	0.30
P	0.03	-	0.64	0.005	0.002	-	0.04	0.05
S	0.02	-	0.05	0.11	0.006	-	1.54	0.57
Ba	-	-	0.53	0.05	-	-	0.09	0.002
Cr	0.01	-	0.02	0.99	1.43	-	-	-
Zn	-	0.03	-	0.03	0.02	0.04	0.14	0.24
Cd	0.03	-	-	0.15	-	-	0.60	0.73
As	-	0.04	0.02	0.37	0.22	0.17	0.15	0.06

Explanations:

1, 3 – silica glass; 2 – silica phase: augite (Tab. 7, point 1); 4, 5 – oxide phase: hercynite; 6 – silica phase: augite (Tab. 7, point 2); 7, 8 – quartz

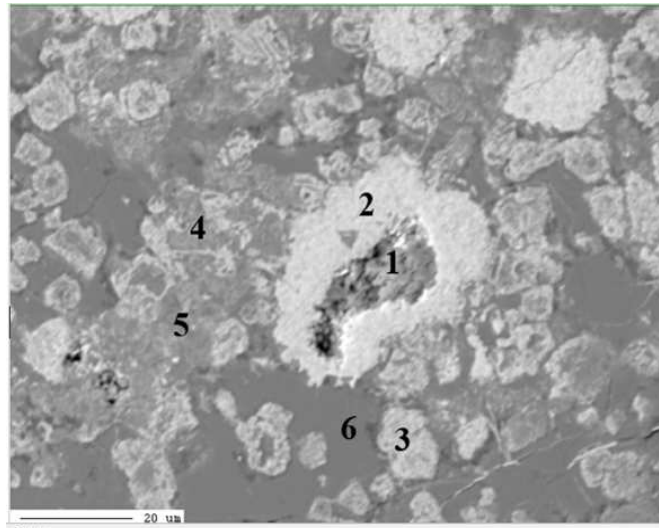


Fig. 6. Microphotography of slag No. 1 – example No. 2

Tab. 4. Chemical composition of components of slag No. 1; according to Fig. 6

Element	No. of analysis / Content [wt %]					
	1	2	3	4	5	6
O	28.40	29.67	32.19	41.95	42.45	53.08
Si	0.06	0.15	1.17	17.20	18.10	17.83
Ti	0.12	0.08	1.98	0.39	0.31	-
Al	26.42	0.39	12.39	4.88	5.20	15.46
Fe	16.02	67.50	47.54	19.33	17.89	1.74
Mn	0.35	0.05	0.12	0.14	0.11	-
Mg	0.56	0.11	2.20	3.87	3.39	0.15
Ca	0.81	0.63	0.31	9.05	7.48	10.90
Na	0.09	-	-	-	-	0.33
K	2.09	0.07	0.20	-	-	0.48
P	0.95	0.02	0.16	-	-	-
S	17.27	0.26	0.19	-	-	0.003
Cr	0.01	0.01	0.02	-	0.02	0.01
Pb	2.21	-	0.15	0.12	0.05	0.02
Zn	0.92	0.05	0.12	0.03	-	-
Cd	0.70	0.72	0.60	1.82	2.06	0.01
As	3.52	0.31	0.65	0.07	0.40	-

Explanations:

1 – sulfate phase; 2 – iron oxide; 3 – oxide phase: hercynite; 4 – silica phase: augite (Tab. 7, point 3); 5 – silica phase: augite (Tab. 7, point 4); 6 – silica glass

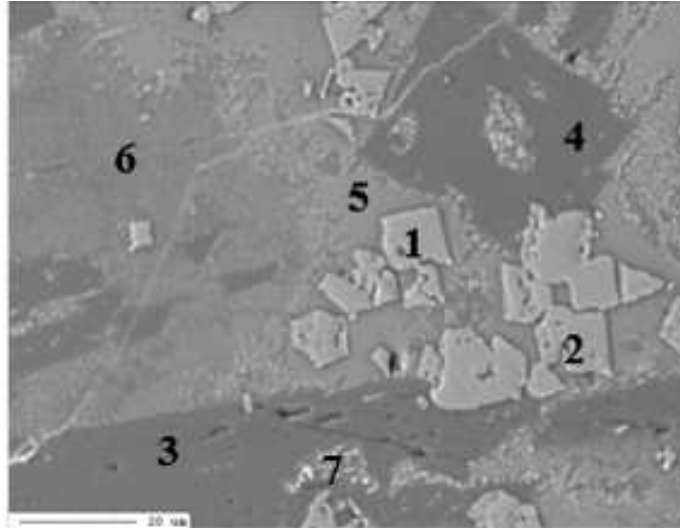


Fig. 7. Microphotography of slag No. 2 – example No. 1

Tab. 5. Chemical composition of components of slag No. 2; according to Fig. 7

Element	No. of analysis / Content [wt %]						
	1	2	3	4	5	6	7
O	48.06	51.26	54.90	55.45	54.73	55.78	51.31
Si	-	-	19.20	19.304	21.96	21.70	17.27
Ti	0.27	0.18	0.01	-	0.94	1.42	1.97
Al	26.64	24.96	14.72	14.932	6.71	8.02	5.10
Fe	21.01	19.57	0.53	0.628	10.91	9.47	21.67
Mn	0.07	0.09	0.01	-	0.09	0.03	0.15
Mg	3.71	3.68	0.04	-	0.10	0.33	1.72
Ca	-	-	9.12	9.212	1.00	1.04	0.45
Na	-	-	0.93	0.476	0.06	0.05	-
K	-	-	0.41	-	2.27	1.73	-
P	-	-	0.04	-	0.22	0.12	-
S	-	-	0.003	-	0.09	0.20	-
Cr	0.20	0.10	-	-	0.004	-	-
Zn	0.007	0.09	0.05	-	-	0.09	-
Cd	-	0.02	0.008	-	-	-	-
As	0.03	0.04	-	-	0.006	0.01	0.05

Explanations:

1, 2 – oxide phase: hercynite; 3, 5, 6 – silica glass; 4 – silica phase: anorthite (Tab. 7, point 5); 7 – silica phase: augite (Tab. 7, point 6)

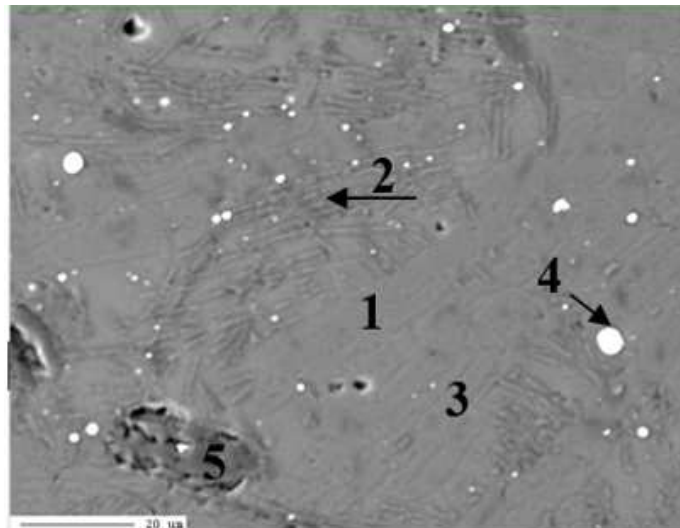


Fig. 8. Microphotography of slag No. 2 – example 2

Tab. 6. Chemical composition of components of slag No. 2; according to Fig. 8

Element	No. of analysis / Content [wt %]				
	1	2	3	4	5
O	54.72	56.97	55.19	1.35	54.78
Si	119.57	16.64	26.95	-	0.05
Ti	0.05	0.97	0.77	0.08	0.04
Al	15.03	16.59	9.41	-	44.93
Fe	0.13	2.35	1.22	98.56	0.09
Mn	0.01	-	0.09	-	0.002
Mg	0.14	5.98	2.19	-	0.03
Ca	8.81	0.50	0.94	-	0.02
Na	1.13	-	0.14	-	-
K	0.37	-	3.03	-	-
P	0.008	-	0.008	-	-
S	-	-	0.01	-	0.006
Cr	-	-	0.003	-	-
Zn	0.02	-	-	0.008	0.04
Cd	-	-	0.009	0.007	-
As	-	-	0.03	-	-

Explanations:

1, 3 – silica glass; 2 – mullite; 4 – iron precipitation; 5 – corundum

Tab. 7. Composition of selected silicate phases; structural formulae were calculated on the basis of 6 (pyroxenes) and 8 (feldspars) oxygens

Element	No. of analysis / Content [wt %]					
	1	2	3	4	5	6
O	49.82	49.63	41.95	42.45	55.45	51.31
Si	19.56	19.65	17.20	18.10	19.30	17.27
Ti	1.27	0.25	0.39	0.31	-	1.97
Al	7.24	4.86	4.88	5.20	14.93	5.40
Fe	16.39	13.47	19.33	17.89	0.63	21.67
Mn	0.29	0.26	0.14	0.11	-	0.15
Mg	2.79	11.34	3.87	3.39	-	1.72
Ca	2.57	0.34	9.05	7.48	9.21	0.45
Na	-	-	-	-	0.48	-
Cr	-	-	-	0.02	-	-
Pb	-	-	0.12	0.05	-	-
Zn	0.03	0.04	0.03	-	-	-
Cd	-	-	1.82	2.06	-	-
As	0.04	0.17	0.07	0.40	-	0.05
wt. %						
SiO ₂	47.90	47.30	39.53	42.42	49.29	45.07
TiO ₂	2.42	0.47	0.70	0.57	-	4.00
Al ₂ O ₃	15.63	10.31	9.89	10.74	33.61	12.42
FeO	24.08	19.44	26.66	25.15	0.97	33.93
MnO	0.43	0.38	0.19	0.16	-	0.24
MgO	5.31	21.22	6.92	6.18	-	3.49
CaO	4.11	0.53	13.59	11.45	15.37	0.77
Na ₂ O	-	-	-	-	0.77	-
Cr ₂ O ₃	-	-	-	0.03	-	-
PbO	-	-	0.14	0.06	-	-
ZnO	0.04	0.06	0.04	-	-	-
CdO	-	-	2.23	2.57	-	-
As ₂ O ₅	0.07	0.29	0.12	0.67	-	0.09
apfu						
Si	1.8	1.77	1.69	1.70	2.24	1.77
Ti	-	0.12	0.02	0.02	-	0.01
Al	0.70	0.7	0.75	0.49	1.80	0.57
Fe	0.7	1.11	0.95	0.84	0.04	1.11
Mn	-	0.007	0.007	0.006	-	0.008
Mg	0.3	0.2	0.44	0.37	-	0.21
Ca	0.2	0.03	0.62	0.49	0.75	0.03
Na	-	-	-	-	0.07	-
Cr	-	-	-	0.001	-	-
Pb	-	-	0.001	0.0007	-	-
Zn	0.001	-	0.001	-	-	-
Cd	-	-	0.04	0.05	-	-
As	-	0.002	0.003	0.001	-	0.002

Explanations:

1 – augite (Al_{0.5}Fe_{0.7}Ca_{0.2}Mg_{0.3}Zn_{0.001})(Si_{1.80}Al_{0.20}O₆) (Fig. 5, Tab. 3, point 2)2 – augite (Al_{0.52}Fe_{0.62}Ca_{0.02}Mg_{1.22}Zn_{0.002}Ti_{0.03}Mn_{0.01}As_{0.01})(Si_{1.82}Al_{0.18}O₆) (Fig. 5, Tab. 3, point 6)3 – augite (Fe_{0.95}Ca_{0.62}Al_{0.44}Mg_{0.44}Cd_{0.04}Ti_{0.02}Mn_{0.007}As_{0.003}Pb_{0.001}Zn_{0.001})(Si_{1.69}Al_{0.31}O₆) (Fig. 6, Tab. 4, point 4)4 – augite (Fe_{0.84}Ca_{0.49}Mg_{0.37}Al_{0.19}Cd_{0.05}Ti_{0.02}Pb_{0.0007}Mn_{0.006}Cr_{0.001}As_{0.001})(Si_{1.70}Al_{0.30}O₆) (Fig. 6, Tab. 4, point 5)5 – anorthite (Ca_{0.75}Na_{0.07}Fe_{0.04})(Al_{1.80}Si_{2.24}O₈) (Fig. 7, Tab. 5, point 4)6 – augite (Al_{0.34}Fe_{1.11}Ca_{0.03}Mg_{0.21}Ti_{0.01}Mn_{0.008}As_{0.002})(Si_{1.77}Al_{0.23}O₆) (Fig. 7, Tab. 5, point 7)

Characteristic of slag components. Among the oxides, hematite was identified in both types of slags; the content in slag No. 1 was 6.6% and 1.1% in slag No. 2 (Tab. 2). Hematite was present in the form of very fine cryptocrystalline grains dispersed among other components of the slags. Their presence results in the red color of the slags, which was already noted in macroscopic observations. Along with the recrystallized sulfates, hematite also forms larger agglomerations, which fill the pores and fissures resulting from the rapid cooling of the slag melt (Fig. 6, Tab. 4, point 2).

Hercynite occurs in slag No. 1 and No. 2 in the amounts of 5.0% and 8.5%, respectively (Tab. 2). In the slags, hercynite crystallized in the form of euhedral grains with variable dimensions. Theoretically, besides the dominating aluminum (23-26%) and iron (18-20%), hercynite's chemical composition comprises also of impurities of other elements, including mostly heavy metals: As, Cd, Cr, Ti, Zn, as well as Mg and Mn. Very often, hercynite forms a solid solution with magnetite, which may be noted as distinct zones within a single grain in the microscopic image.

Magnetite only occurs in slag No. 2, and the presence of spinel (slag No. 1) and corundum (slag No. 2) was also identified.

Plagioclases represented by anorthite were found among the silicate minerals in the largest amounts in both of the slag types. Its content in slag No. 1 reaches 22.0%, and it amounts to 21.7% in slag No. 2 (Tab. 2). Anorthite is found in the form of large euhedral grains with a platy habit, the size of which reaches 20 μm (Fig. 7, Tab. 5, point 4). During microanalysis, it was noted that most of the anorthite grains contain numerous inclusions. Moreover, Na and Fe substitutions were found in their internal structures.

Olivines in the slags are represented by forsterite, the content of which – reaching 4.4% – was found in slag No. 1 and by fayalite, the content of which was found in slag No. 2 and was slightly smaller, reaching 2.8% (Tab. 2). As in natural conditions, the phase is one of the first ones to be crystallized from liquid slag. Olivines have been identified in the slags only in the identification using X-ray diffraction. Their presence was not confirmed during the microanalysis. This may testify of the micro- or cryptocrystalline form of the olivine grains, as their identification in microscopic observations is hindered.

In the analyzed slags, pyroxenes form fine crystallites surrounded by glass (Fig. 5, Tab. 3, points 2 and 6). For that reason, the identification using X-ray diffraction does not always provide satisfactory results. Moreover, the small peaks of pyroxenes overlap with peaks of other components. The identification of phases using X-ray diffraction has exhibited the presence of enstatite, while the chemical analysis of the fine crystallites found within the amorphous substance has exhibited the presence of pyroxenes represented by augite-structured phases characterized by highly variable chemical composition (Tab. 7). Numerous element impurities, including Zn, have been found in their internal structure. The presence of this type of pyroxenes was exhibited in both the analyzed slag types. In natural conditions, pyroxenes with zinc substitutions are rare; one of the few examples of its occurrence is the zinc deposit in Franklin, New Jersey (Essene and Peacor, 1987).

Among silicate phases of the slags, also the presence of mullite in the form of fine crystallites with needle-like habit was identified (Fig. 8, Tab. 6, point 2). Mullite is crystallized at the temperature of 1000°C as one of the kaolinite transformation products, which, along with other clay minerals, often constitutes an impurity in carbonate rocks added to the alloy as a fluxing agent. In higher temperatures, its structure is ordered, and the crystal dimensions increase. This process is ended at the temperature of 1300–1400°C.

The presence of quartz was found in both types of slag. In slag No. 1, the amount was 0.9%, while the content reached 0.5% in the case of slag No. 2 (Tab. 2). The quartz grains were in various dimensions; their surface was fissured and uneven; quartz grains usually form aggregates consisting of interpenetrating grains (Fig. 5, Tab. 3, points 7 and 8).

The presence of metallic precipitates in fine drops of metal that was not separated from the slag in the process was identified in slag No. 2 (Fig. 8, Tab. 6, point 4). In terms of the chemical composition, the precipitates mostly contain metallic iron, the content of which usually exceeds 98%; the impurities are constituted by Cd, Ti, and Zn.

The tests conducted using X-ray spectral microanalysis also allowed for determining the chemical composition of the glass (Fig. 5-8, Tab. 3-6). In all the analytic points in both types of slags, silicon was the glass's dominant component. Its content reached 26.90% in slag No. 2, and it varied between 19.89% and 26.83% in the case of slag No. 1. Moreover, the glass contained: Al, Ba, Ca, K, Mg, Mn, Na, P, as well as heavy metals: Cd, Cr, Fe, Ti, As, Pb, and Zn. Sulfur was also found to be dispersed in the glass. The devitrification of glass may lead to the release of sulfide ions, which are easily oxidized to SO^+ in the weathering processes. The sulfides that are formed in this way, migrating along with their solutions, may contribute to the acidification of the environment. As an effect, crystallization of sulfate minerals proceeds in the pores and at the surface of the slags, predominantly gypsum, which was identified during the XRD analysis (Tab. 2) – it is the main component of the "white bloom" which was observed macroscopically. Besides gypsum, the sporadic presence of Al-Fe sulfates was identified in the X-ray spectral microanalysis (Fig. 6, Tab. 4, point 1).

Discussion

The conducted tests have exhibited the diversity of the chemical and phase composition of Zn-Pb slags. It has also been established that it is necessary to select a correct research technique in such analyses. Smelter slags, due to the variability of their chemical and phase composition, are a material that is difficult in terms of testing and may not be subject to too many generalizations (Smirnov et al., 2015; Jonczy, 2018). Therefore, the phase composition of slags can change; Muszer (2006) proves that the phase composition of lead metallurgical slag from the Dörschl furnace from the Głogów Foundry depends on the share of individual components in the furnace charge. The differences in the mineralogical composition of the slags can also be related to the initial composition and the cooling regime of the melt (Ettler et al., 2009 b).

The tested slags' chemical composition reflects the chemical composition of the input material constituted by the locally found Zn-Pb ores. As compared to slag No. 2, the content of zinc Zn and lead Pb in slag No. 1 is much lower and reaches 207.0 mg/kg and 36.2 mg/kg, respectively. In slag No. 2, the concentration of these elements increases – the amount of Zn is 2056.6 mg/kg, while in the case of Pb, the value reaches 555.8 mg/kg.

On the other hand, in slag No. 1, the amount of Cd increases, reaching the concentration of 310.2 mg/kg, while this value for As reaches 816.5 mg/kg. In slag 2, the content of these elements was much smaller, and the concentrations of Cd and As were around the limit of detection. The source of Cd in the ore is constituted by its sulfide–greenockite CdS, while the concentration of As is related to the Ta-rich As-Pb sulfosalts and the tendency to accumulate this element in iron sulfides.

In both types of slags, the presence of considerable amounts of i.a. Ba, K, Na, and Mn, was identified. Barium is an element that accompanies metal sulfides in the ore while forming its own phase – the BaSO₄ barite. The content of K and Na, on the other hand, is related to barren rock mostly constituted by clay minerals (montmorillonite, illite, and kaolinite). Mn forms substitutions in the internal structure of the ankerite Ca(Fe, Mg, Mn)(CO₃)₂, which is also classified as a barren rock. Presence of sulfur was also found in the slags. Its content in slag No. 1 reached 0.44%, while in the case of slag No. 2, it reached nearly 1%.

Piatak and Seal (2010) confirm that in Zn-Pb smelter slag, Zn is the dominant metal; for example, its concentration in the slags from the former Hegeler Zn-smelting facility in Illinois (USA) reaches Zn with >28.4 wt.% in the Zn-rich material and between 212 and 14,900 mg/kg in the other slags. In addition to zinc, the other trace elements: As – 45 mg/kg, Ba – 1170 mg/kg, Cd – 191 mg/kg, Co – 242 mg/kg, Cr – 103 mg/kg, Cu – 6360 mg/kg, Ni – 107 mg/kg, and Pb – 711 mg/kg were also marked. A similar set of elements was found by De Andrade Lima and Bernardez (2011) in lead smelter slag; the conducted chemical analyses showed that the main constituents of the slag were Fe, Ca, Si, Zn, Mg, Pb, Al, C, and Mn. Among the trace elements found most abundantly were Ti, Sr, As, and Cu, as also low content of Cd (57.3 mg/kg).

While analyzing the chemical composition of tested slags, it may be assumed that the feed material used in the plant comprised mostly of weathered Zn-Pb ores as well as sulfide ores. During more than a century of the plant's operation, however, the type of the feed material could have been changing along with the mining technology development. Historical sources indicate that initially, calamine – which is a historical name for zinc ore – found at the surface, oxidized and causing little problems in terms of exploitation, was used. The chemical composition of calamine includes smithsonite ZnCO₃ and hemimorphite Zn₄Si₂O₇(OH)₂·H₂O and clay minerals, oxides, and iron hydroxides. The iron compounds result in the red color of the calamine. These types of oxidized ores are found near the area subject to the research. The previously conducted research based on Mössbauer spectroscopy has exhibited that hematite is dominant among the iron compounds, and it is accompanied by iron hydroxides (Jonczy et al., 2015). The increased content of Zn, Pb, and S in the wastes, on the other hand, indicates that besides calamine, the exploitation and processing must have also encompassed sulphidic deposits rich in Zn blende. The phase composition of the slags has not been found to contain sulfides, which were oxidized due to the long-term deposition of the slags and the weathering activity. The sulfates that were formed due to the oxidation, mostly gypsum CaSO₄·2H₂O, are crystallized in the dump and cover the slag with a white bloom. The secondary crystallization of gypsum is the most popular weathering process observed in the dumps of Zn wastes (Piatak and Seal, 2010).

On the other hand, the chemical composition analysis exhibited that the Zn and Pb acquisition methods developing at the end of the 19th century still required improvement if such a significant amount of metals reached the wastes. It is also possible that the processed ore has changed within approximately two hundred years of the plant's operation. Information that this type of practice was rather common in the past centuries can be found in many historical sources. Smelters were changed into plants processing the ore that was available at a given time. For these reasons, old dumps often contain material that is a mixture of different types of smelter slags and mining wastes.

In general, the presence of glass and crystallites may be distinguished among the components comprising the slags. In the mineral composition of studied slag, the following phases were distinguished: magnetite, hercynite, spinel, corundum, plagioclases (anorthite), olivines (fayalite), pyroxenes (enstatite, augite-structured phases), mullite, quartz, and secondary phases: hematite and gypsum. Piatak and Seal (2010) described a similar

phase composition in the slag from the former Hegeler Zn-smelting facility in Illinois (USA). This slag contains Ca-rich plagioclase, clinopyroxenes, spinels, fayalitic olivine, mullite, and quartz, as also secondary phases such as goethite, hematite, and gypsum, which reflect surficial weathering of the dump piles or represent byproducts of roasting. This material is less weathered and contains well-preserved spherical blebs of Fe sulfides in comparison to studied slag. In turn, slag from the Plombières (Belgium) dumps is characterized by a slightly different composition; a lot of metallic Fe, Pb, Cu, Zn, Fe-Zn alloys, carbides, phosphides, sulfides of Fe, Zn, Pb, Cu, Mn (alabandite), and FeAs were found in it (Kucha et al., 1996). Another zinc-lead smelter slag from Santo Amaro, Bahia (Brazil), described by De Andrade Lima and Bernardez (2011), is composed of wustite, olivine, kirschsteinite, franklinite, and metallic Pb. Ettler et al. (2009 b, 2009 c) describe the 100-year old slags from smelters in the Tsumeb district (Namibia) which is mainly composed of Pb-bearing feldspars Cu-rich spinels, delafossite-like phases, and complex Ca-Pb arsenates. In contrast, 30-40-year-old and recent granulated slags are mainly composed of high-temperature phases: Ca-Fe aluminosilicates (olivines, melilite), Pb- and Zn-bearing silicate glass, spinel oxides, and metallic/sulfide inclusions within a glass.

In the tested slag from the dump in Ruda Śląska, zinc mainly occurs in the form of substitutions in other phases or is dispersed in silica glass. The presence of ZnO in the glass was also observed by Ettler et al. (2001, 2009 a) in the lead-zinc metallurgical slags from the Příbram district in the Czech Republic. Zinc phases were described in slag from the other old dump also located in Upper Silesia (Poland) in Świętochłowice by Vanaecker et al. (2014) and Tyszka et al. (2014). The primary assemblages in this slag are composed of willemite, hardystonite, zincite, wurtzite, petedunnite, and franklinite. Some of these phases are sensitive to weathering processes, and, as a result, goslarite, smithsonite, and hemimorphite have been identified as secondary products. Similar phases were also found in the weathered slags from the Decazeville Basin (France), where the pyrometallurgical extraction of Zn ore remained active until 1922 and in slag samples collected in the Pontgibaud mining district (Massif Central, France), which is well known for lead and silver extraction and metallurgical processes that lasted centuries (Vanaecker et al., 2014).

The glass surrounds both the crystallites of oxide and silicate phases, and the presence of well-developed euhedral crystals is rare in slags. In the case of the slags that were subject to testing, this type of crystals was developed by hercynite and anorthite. A common characteristic of all the identified phase components was their diverse chemical composition. None of the analyses has exhibited the presence of phase components without impurities in the form of other elements.

It has been found that glass is characterized by rather complex chemical composition, and the heavy metals and sulfur contained in the glass may constitute a potential hazard in terms of environmental protection. Although these elements' values reach maximally 1% in each of the analytical points, one should consider the fact that glass is one of the components that is the most prone to the weathering processes and that it constitutes the main component of the slags. Thus, it will also constitute the main source of migration of the elements to the environment. The glass devitrification processes had been observed in the previously conducted studies; firstly, the surface of the glass is subject to cracking; the cracks increase in size, causing the disintegration of the glass to smaller fragments along with the progress of the devitrification process. In the final stage, the metals in the glass are precipitated and cover the glass's surface or are accumulated in the fissures. It should also be noted that the slag components' stability will depend on two main parameters: slag porosity and the intrinsic properties of the considered phases. The less stable slag is either powdery or the most porous, thereby facilitating contact with the solution (Vanaecker et al., 2014). In the Nord-Pas-de-Calais (France) industrial basin, blast, and smelting furnaces The Noyelles-Godault produces slag, which contains Pb-Zn-rich vitreous material with a CaO-SiO₂-FeO-rich glass matrix with metallic lead droplets and Fe oxides. As a result, a dump of this slag exposed to weathering processes can be a source of chemical pollution (Seigneur et al., 2006).

The problem of environmental pollution near the historical zinc-lead smelting sites is extremely important and still valid. The study in the area located at Magu, Hezhang County, Guizhou Province, southwest China indicates that more Cd was migrated into the surrounding environment than Pb and Zn during smelting. There existed higher percentages of weak acid extracted Pb, Zn, and Cd in contaminated soil than in smelting slag, but the concentrations of the weak acid extracted Pb, Zn, and Cd in smelting slag were higher than those in contaminated soil, causing a long-term risk to the surrounding environment (Lin et al., 2015). So that is why the proper disposal of lead-zinc smelting slag having toxic metals is a great challenge for a sustainable environment (Mao et al., 2019).

Conclusions

The following conclusions were made based on the conducted research:

- The tested slags are characterized by diversified chemical composition; besides the dominant contents of Si and Fe, they contain impurities in the form of numerous elements, including heavy metals, i.a. Zn, Pb, Cd, As, as well as rare earth elements: La, Dy, and Y.

- In general, two groups may be distinguished among the slag components: the silicate glass and the crystalline phases represented by oxides and silicates.
- The phase components are most of all comprised of fine crystallites occurring within the glass, while only some of them, for example, hercynite and anorthite, have been crystallized in the form of large euhedral grains.
- The chemical composition of each of the phases is complex. In their internal structures, they contain impurities in the form of elements, the substitutions of which are not characteristic to the same minerals crystallized in natural conditions.
- The analysis of slags' chemical and phase composition indicates that the input material mostly processed in the smelter were the locally occurring weathered Zn-Pb ores, the so-called calamines, rich in iron compound impurities.

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