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Metal potential in copper smelting slags from Polkowice tailings dump – preliminary studies

Introduction

A closed-loop economy is a technological and civilization challenge for the contemporary world. The scale of anthropogenic mineral substances accumulated throughout centuries creates, on the one hand, environmental and urbanization threats and, on the other hand, reveals opportunities and possibilities of utilizing useful elements contained therein (Zn, Pb, Cu, Cr, Rare Earth Elements-REE and others). The current stream of waste from the mineral sector is constantly growing and expanding the base of secondary deposits (Lottermoser 2010). According to forecasts, total global mineral consumption could rise to 190 billion tons

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by 2060, up from about 92 billion tons currently consumed (Global Resource Outlook 2019). This will result in a significant stream of waste mineral anthropogenic deposits. This large increase in mineral wastes is the result of increased extraction of raw materials from mineral deposits, as well as the exploitation and processing of increasingly lesser-grade ores. It is estimated that about 14 billion tons of tailings are generated annually in the world (Jones and Boger 2012), which is generated as a result of mining and processing of, among others: copper ores, cassiterite, zinc and lead ores and other minerals (Cuesta-Lopez et al. 2016). In Poland, the mineral sector generates 110–130 million tons of wastes annually (in the last 20 years), and metal ore mining alone was responsible for 31.2 million tons of wastes in 2017 (Galos 2019; Domańska 2020). The problem of managing waste from the mining sector is an important economic, environmental, technological, as well as a legal challenge (Uberman 2021).

The discovery of rich deposits of copper and silver in the Fore-Sudetic Monocline in the 1950s (Poland), contributed to the construction of a huge mining and smelting complex (Kombinat Górniczo-Hutniczy Miedzi – KGHM) (Butra et al. 2005). The increased production capacity of the "New Copper Belt" led to a significant amount of waste generated at each stage of the mining and production process. Waste material (waste-rocks, smelter slags) in the initial years of production was deposited at mine waste dumps located near shaft sites and at waste disposal facilities (e.g. Gilów tailings pond, where about 92 million Mg of industrial waste was deposited) (Żylińska-Dusza et al. 1996).

The smelter slags produced en masse during the initial years of production at KGHM contained significant amounts of metals (Zn, Pb, Cu, Cr). The waste material deposited at the Polkowice tailings pond has not been utilized to date. The application of modern hydrometallurgical methods could contribute to the recovery of valuable metals from slag and bring economic gain. Due to increasing environmental awareness, more and more branches of the mining industry are turning to closed-loop production cycles (circular economy) (Kotarska and Mizera 2019; Krukowski 2020; Kinnunen et al. 2021).

The growing demand for metals, including critical raw materials (e.g. REE, Co, Li, Nb, Ta), combined with depletion of high-quality mineral ore deposits, creates a need to verify the deposit potential of mining and tailings wastes. Recycled waste can be a source of metals not yet taken into account during the documentation and processing of mineral ores for economic and technological reasons. The development of the global COVID-19 pandemic has contributed to the disruption of the global supply chains of many mineral resources. A discontinuity of supply poses a threat to the raw material security and economic security of the countries of the European Union (EU). The reduction of imports of raw materials creates the need to search for their alternative sources, among others: through the inventory of old tailings dumps and mining pits (Sroga et al. 2018), the intensification of activities in marine areas (Zglinicki et al. 2021) and hard-to-reach areas (e.g. Greenland) (Goodenough et al. 2018), as well as the development of modern recycling technologies and metal substitution (Grilli et al. 2017). These activities are undertaken among others by Horizon 2020 projects, EIT Raw Materials, the European Commission (EC),the association of geological surveys – EuroGeoSurveys (www.eurogeosurveys.org), state-owned institutions, and think tanks.

The European Commission's long-term strategies (European Commission 2018, 2019) and sustainable development agendas indicate the need to reuse waste. These policies aim to reduce the amount of waste generated, promote higher levels of recycling, safe waste disposal, and extract metals and energy from waste. The policies adopted are in line with the philosophy of zero-waste and circular economy (European Commission 2020).

The transformation towards a closed-loop economy is also being carried out in Poland and is presented in the *Roadmap for the Transformation towards a Closed-Loop Economy – GOZ* (2019) (*Mapa drogowa. Transformacja w kierunku gospodarki o obiegu zamkniętym, GOZ, 2019*). It is one of the projects of the Strategy for Responsible Development until 2020 (with an outlook until 2030) (*Strategia na rzecz odpowiedzialnego rozwoju do roku 2020 z perspektywą do 2030 r.*). Pro-environmental activities based on the closed-loop economy are also undertaken by private companies, e.g. the zinc smelter "ZGH Bolesław" S.A. in Bukowno, where a significant part of the input is recycled material (www.zghboleslaw.pl).

For several years, the Polish Geological Institute (PIG-PIB) has been carrying out tasks aimed at inventorying tailings dumps and waste from the current stream of metal ore mining and processing (Sroga et al. 2018). As part of the undertaken activities, the raw materials' potential of post-copper slag generated in the 1980s was assessed. The research covered waste initially stored in the mine's landfill and then transferred to a private property in Polkowice. This waste may be a potential source of many valuable metals (Zn, Pb, Cu, Sb, Sn, Se). During field work an inventory of the tailings dump in Polkowice was made and samples of slag were taken from for laboratory tests. Mineralogical and chemical analyses were made. On the basis of archival data and new data obtained the potential usefulness of the material was determined. During research special attention was paid to the presence of zinc and lead phases.

1. Materials and methods

1.1. Materials

The material for analysis was collected from a tailings dump (Figure 1), originally located in the Legnica-Głogów Copper Belt (Legnicko-Głogowski Okręg Miedziowy). The waste was generated from copper ore smelting at the Głogów smelter in the 1980s and transported to its present location in Polkowice at Zawilcowa Street. It is estimated that the tailings dump (Waste code in Poland 01 03 04*, Rozporządzenie Ministra Klimatu, Dz.U. 2020 poz. 10) contains approximately 80 000 tonnes of unused slag (Figure 2). The material is deposited on an area of approximately 2 ha.

During field work, 10 slag samples weighing approximately 2 kg each were collected from randomly selected locations. The samples were taken in accordance with the

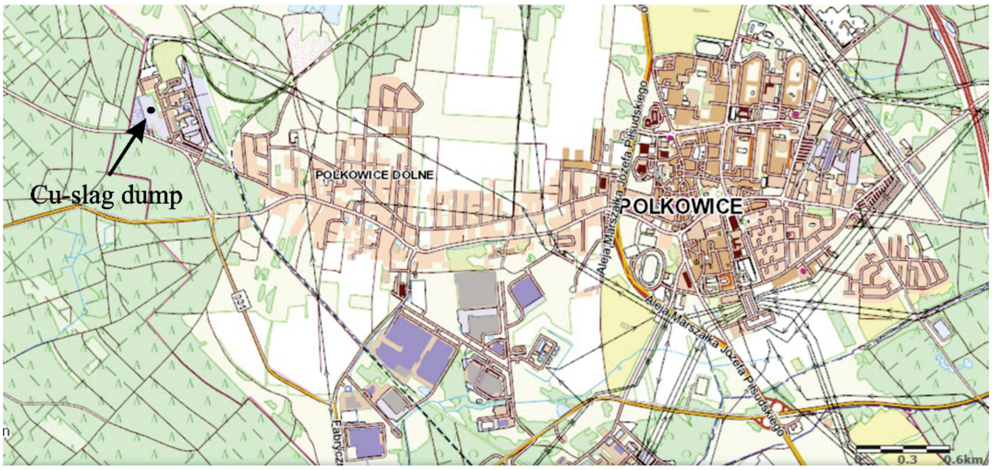

Fig. 1. Location of post-industrial slag heap in Polkowice on the background of topographic map (geoportal.gov.pl)

Rys. 1. Lokalizacja hałdy zgaru pohutniczego na tle mapy topograficznej

Fig. 2. The tailings dump in Polkowice (Photo: F. Owczarek 2021)

Rys. 2. Hałda zgaru pohutniczego w Polkowicach (foto: F. Owczarek 2021)

PN-EN 932-1:1999 standard, from trenches approximately 30–40 cm deep so that the samples would be free from compositional changes due to surface weathering.

2. Methods

2.1. X-Ray Diffraction

The mineral composition of the samples was analyzed at the Institute of Ceramics and Building Materials, Warsaw, using a X-ray diffraction on a Bruker AXS D8 Advance Davinci diffractometer in the Bragg-Brentatno system. The analyses were carried out in the angular range of 5–100° 2θ using a lamp with a copper anode and a nickel filter. A divergence gap of 0.30, a soller gap of 2.5, a detector gap of 2.50, and a Lynx Eye solid-state detector were used. Recording was performed with a measurement step of 0.02°, at 2.5 s/step. EVA software with access to the ICDD pattern database PDF-2 version 2007 and PDF-4 version 2011 was used to identify crystalline phases. Quantitative phase analysis was performed in TOPAS v 4.2 software using the Rietveld method (Rietveld 1968). The zero shift of the diffractometer was determined using NIST standard LaB6 No. 660b.

2.2. Optical and Scanning Electron Microscopy

Standard thin plates were made of the metallurgical waste samples for microscopic observations. A NIKON ECLIPSE E600 POL polarizing microscope was used to determine the mineral composition. Observations were made in transmitted and reflected light using LU Plan Fluor objective from x2.5 to x50. SEM-BSE observations were carried out using a FE-SIGMA VP scanning microscope (Carl Zeiss Microscopy Ltd., Cambridge, UK) equipped with two EDS detectors (SDD XFlash| 10) (Bruker, Germany). Analytical conditions were an accelerating voltage of 25 kV in a high vacuum. The samples were sputtered with a thin layer of carbon. The research was conducted at the Faculty of Geology, University of Warsaw.

2.3. Electron probe micro-analyzer (EPMA)

Chemical composition studies of the mineral phases present in the samples were performed using an electron microprobe (EPMA) CAMECA SX-100 (Cameca, Cedex, France) equipped with wave dispersive spectrometers (WDS). Analyses were performed at 15 keV and 10 nA beam current and using PET, LIF, TAP, LPET crystals (Table 1). EPMA calibration was performed using standards included in the equipment of the Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances of the Faculty of Geology of the University of Warsaw. Results were corrected based on the CAMECA PAP algorithm by Pouchou and Pichoir (Pouchou and Pichoir 1985).

Table 1. Conditions of EPM (Electro Probe Microanalysis) analyses

Tabela 1. Warunki analizy mikrosondy elektronowej (EPM)

Element	Standard	Analytical line	Crystal	Detection limit (wt%)
Si	Diopside	Kα	TAP	0.03–0.04
Al	Orthoclase	Kα	TAP	0.03–0.04
K	Orthoclase	Kα	PET	0.04–0.06
Na	Albite	Kα	TAP	0.07–1.00
Mg	Diopside	Kα	TAP	0.03–0.04
P	YPO_4	Kα	PET	0.05–0.07
Fe	Fe_2O_3	Kα	LIF	0.10–0.15
Mn	Rhodonite	Kα	LIF	0.08–0.10
Ca	Diopside	Kα	PET	0.04–0.05
Cu	Metallic Cu	Kα	LIF	0.13–0.16
Zn	Sphalerite	Kα	LIF	0.17–0.21
Ni	NiO	Kα	LIF	0.20
Co	CoO	Kα	LIF	0.18
Sb	InSb	Lα	LPET	0.05–0.09
Sn	Cassiterite	Lα	LPET	0.06–0.07
Pb	Crocoite	Mα	LPET	0.12–0.17
As	GaAs	Lα	TAP	0.09–0.14
Cd	CdS	Lα	LPET	0.08–0.09
Se	Bi_2Se_3	Lα	TAP	0.20
S	Barite	Kα	LPET	0.02
Cl	Tugtupite	Kα	LPET	0.02

2.4. Geochemical method

Chemical composition studies of selected samples were performed in a certified laboratory (ISO 9001:2008) ACME Labs in Vancouver (Canada). Two analytical programs (www.acmelabs.com) were used to determine the chemical composition:

- LF725 – analysis using the X-ray fluorescence method (WDS-XRF),
- MA270 – analysis using plasma coupled mass spectroscopy (ICP-MS) and inductively coupled plasma emission spectroscopy (ICP-ES).

Additionally, loss on ignition (LOI) was determined for the samples. The level of analytical accuracy and precision is available at www.acmelab.com. Additionally, for selected samples, precious metals content tests were performed by ICP-ES method. Samples for testing were prepared according to the procedure adopted by the laboratory for the analytical method used.

3. Results

3.1. Mineralogy

Slags from pyrometallurgical processes are petrographically equivalent to magmatic rocks and resemble them in texture and mineral composition (Muszer 1996). According to the definition of mineral, phases formed during metallurgical processes are not minerals (Nickel 1995). In presented publication, the authors adopt mineral names for their synthetic equivalents.

A study by Żyłka (Żyłka 2021) showed that the size of the slag fragments deposited in the tailings dumps ranges from a few to several cm. Fractions in the range of 1 to 2 cm are pre-

Table 2. Rietveld quantitative phase analysis for selected samples

Tabela 2. Ilościowa analiza fazowa metodą Rietvelda wybranych próbek

Minerals	Sample in wt%				
	1	2	3	4	9
Sphalerite	36.3	5.5	21.9	35.0	23.6
Bassanite	4.4	32.8	6.1	–	7.8
Quartz	7.3	41.5	8.0	5.3	9.7
Palmierite	13.2	5.0	16.5	4.1	12.7
Beaverite-(Zn)	3.8	1.0	5.7	15.3	3.9
Magnetite	2.9	1.2	6.6	3.5	4.7
Wurtzite	1.2	0.9	1.5	1.5	3.6
Goethite	8.3	3.5	10.4	5.8	9.7
Hematite	1.8	0.8	0.8	–	1.7
Microcline	9.5	4.1	8.6	6.8	9.7
Wüestite	1.2	0.1	2.5	–	3.2
Petedunnite	10.0	3.5	11.3	11.4	9.5
Jarosite	–	–	–	11.3	–

dominant. In the complex material there are also blocks up to 0.5 m in diameter and volume of several dm^3. The examined material is of brown-grey color with metallic sheen in places. Sulfide mineralization and glass are visible on the surface of the samples. Macroscopic observation reveals varied slag texture, from compact, densely packed to coarsely porous. The diameter of individual pores is in the range of 0.5 to 2.5 mm. Most of the pores have been refilled, mainly with jarosite.

X-ray diffraction (XRD) analysis, microscopic observations (optical microscope, SEM-BSE) revealed the complex composition of the slag samples (Figure 3A, B). The results are presented in Table 2. The material contains primary phases (Figure 4A) formed by

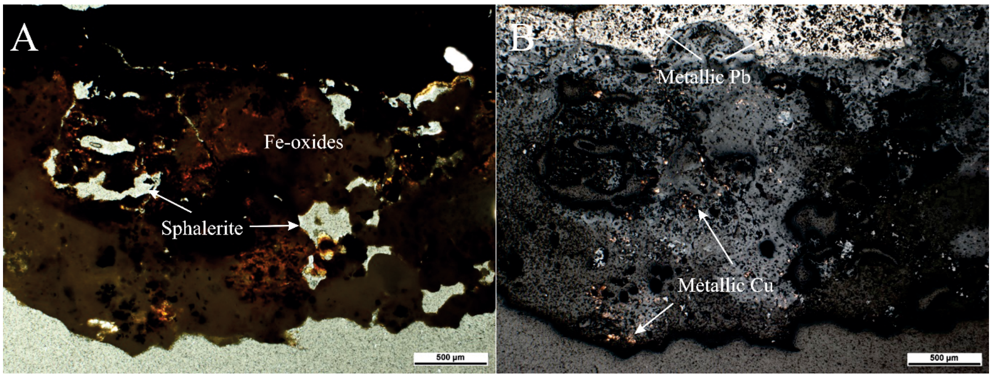

Fig. 3. Slag samples photos from under an optical microscope
A) transmitted light; B) reflected light. Magnification ×2.5

Rys. 3. Zdjęcia próbek żużlu pod mikroskopem optycznym
A) światło przechodzące; B) światło odbite. Powiększenie 2,5×

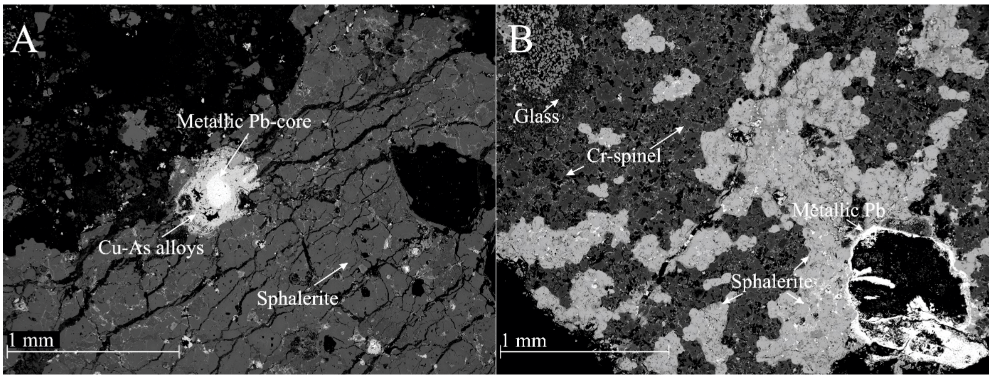

Fig. 4. Variation in the form of occurrence of synthetic phases in the samples
A) Cu metallic nucleus with Cu-As weathering, sample No. 1;
B) speckled sphalerite in the vitreous mass, sample No. 10. SEM-BSE observations

Rys. 4. Forma występowania zróżnicowanych faz syntetycznych w próbkach
A) jądro metalicznej Cu z otoczką wietrzeniową Cu-As, próbka 1;
B) wtrącenia sfalerytu w masie szklistej, próbka nr 10. Obserwacje SEM-BSE

pyrometallurgical processes and secondary phases, which are the result of transformation of primary components. The primary phases are represented by **sulfides**: sphalerite [ZnS]; wurtzite [(Zn,Fe)S]; pyrite [FeS_2]; **sulfates:** beaverite-(Zn) [$Pb(Fe^{3+}{}_2Zn)(SO_4)_2(OH)_6$]; palmierite [$(K,Na)_2Pb(SO_4)_2$]; **oxides and hydroxides:** goethite [$Fe^{3+}O(OH)$]; wüestite [FeO]; hematite [Fe_2O_3]; magnetite [$Fe^{2+}Fe^{3+}{}_2O_4$]; chromian spinel [$Fe^{2+}Cr^{3+}{}_2O_4$]; **silicates:** petedunnite [$Ca(Zn,Mn^{2+},Mg,Fe^{2+})Si_2O_6$]; quartz [$SiO_2$]; and microcline [$KAlSi_3O_8$]. Additionally, SEM-BSE observations revealed that oxidized native metals (Cu, Pb, As) and metal alloys and semi-metals appear in the slag to varying degrees: Cu-As; Cu-Sb-Sn; PbO-As_2O_3; FeO-As_2O_3; PbO-SO_3; PbO-SiO_2-FeO (Figure 4B).

Crystalline phases are usually found in the form of clusters, nuclei, irregular plates, columns and laths. The variation in the occurrence of individual phases and their distribution is due to segregation during solidification of the alloy.

Sphalerite is the major phase (5.50–36.30 wt%) found in slag (Figure 4A, B). Depending on the sample, it forms irregular platelets, clusters and scattered larger clusters in the vitreous mass. Chemical composition studies (Table 3) indicate that sphalerite consists of Zn (51.13–58.88 wt%) and Fe (6.45–14.55 wt%), with subordinate amounts formed by Cu (0.02–0.22 wt%), Mn (0.33–0.53 wt%), Cd (0.16–0.36 wt%). Sphalerite is accompanied by synthetic equivalents of zinc-lead minerals: palmierite (up to 16.5 wt%), beaverite-(Zn) (up to 15.3 wt%), petedunnite (up to 11.4 wt%). The composition of these phases varies greatly depending on the sample and the point of analysis performed (Table 4). These phases are characterized by a significant degree of oxidation.

A characteristic feature of some of the samples is the presence of metallic nuclei (Figure 4A; Table 5) composed of Pb (98.14–99.07 wt%) and subordinately of Sb (0.08–1.01 wt%), Zn (0.03–0.18 wt%), Fe (up to 0.13 wt%), As (up to 0.01 wt%) and S (0.05–0.18 wt%).

Table 3. Chemical composition of sphalerite. EPM analysis in wt%

Tabela 3. Skład chemiczny sfalerytu. Analizy EPM w % wag.

Sample	2		3		4		6		8		10	
Point of analysis	1/1	2/1	3/1	4/2	5/4	6/7	7/1	8/2	9/4	10/6	11/2	12/4
Element	wt%											
Zn	51.67	51.53	52.23	57.82	57.03	57.51	56.57	56.47	52.47	51.13	57.86	57.64
Fe	13.80	14.28	13.66	7.90	8.20	7.91	8.61	9.05	13.90	14.55	7.02	6.80
Cu	0.12	0.09	0.10	0.00	0.06	0.05	0.04	0.00	0.22	0.08	0.09	0.02
Mn	0.45	0.35	0.39	0.42	0.49	0.50	0.49	0.48	0.37	0.39	0.41	0.38
Cd	0.23	0.20	0.30	0.27	0.18	0.27	0.22	0.18	0.16	0.33	0.36	0.33
S	33.24	33.29	33.17	32.91	33.01	33.94	32.72	32.93	33.19	33.03	33.07	33.20
Total	99.51	99.74	99.84	99.31	98.96	99.17	98.54	99.11	100.30	99.51	98.80	98.36

Table 4. Chemical composition of beaverite-(Zn) and palmierite. EPM analysis in wt%

Tabela 4. Skład chemiczny beaverytu-(Zn) oraz palmierytu. Analizy EPM w % wag.

Sample	1		3		4		6		7		9	
Point of analysis	1/2	2/3	3/2	4/3	5/2	6/5	7/1	8/2	9/6	10/8	11/2	12/3
Element	wt%											
Si	0.16	0.54	0.33	0.11	0.04	0.05	6.27	7.60	6.71	6.28	6.42	6.21
Al	0.00	0.02	0.00	0.01	0.00	0.00	0.33	0.73	0.49	0.41	0.46	0.42
Fe	26.25	19.70	22.78	26.21	26.74	27.60	25.99	20.64	22.71	22.19	25.09	24.64
Mn	0.09	0.08	0.07	0.04	0.11	0.12	0.09	0.11	0.21	0.15	0.10	0.10
K	0.23	0.33	0.29	0.25	0.06	0.02	0.16	0.33	0.22	0.22	0.19	0.23
Ca	0.88	0.51	0.94	0.44	0.00	0.00	0.19	0.17	0.15	0.13	0.31	0.42
Pb	4.95	10.10	4.52	2.05	2.29	1.82	12.34	10.80	12.95	13.00	12.25	13.70
Zn	0.44	4.40	5.20	3.00	0.45	1.13	4.23	5.77	5.85	4.63	6.89	7.63
As	20.34	13.51	18.05	18.47	26.26	27.36	0.19	0.06	0.16	0.19	0.20	0.10
Cu	4.39	7.68	5.15	1.93	11.74	9.63	9.45	7.58	6.70	7.91	4.21	3.53
Ni	0.66	0.28	0.25	0.13	2.11	2.13	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.11	0.10	0.05	0.04	0.33	0.42	0.07	0.07	0.09	0.09	0.05	0.03
Sb	1.81	0.99	1.07	2.91	3.87	3.85	0.59	0.53	0.61	0.59	0.43	0.58
Sn	0.21	0.37	0.20	0.79	0.11	0.13	0.00	0.00	0.00	0.00	0.00	0.00
Se	0.13	0.13	0.19	0.25	0.38	0.31	0.00	0.00	0.00	0.00	0.00	0.00
S	2.67	2.92	2.58	1.09	9.55	8.49	1.90	1.98	1.25	1.82	0.64	0.77
Cl	0.08	0.12	0.06	0.06	0.01	0.06	0.25	0.37	0.35	0.27	0.54	0.65
Total	63.65	61.94	62.00	58.03	84.05	83.12	62.50	57.57	59.20	58.35	58.53	59.01

1–6 – Beaverite-(Zn).
7–12 – Palmierite.

The nuclei show oxidation features occurring from the center to the outer zone. The result of this process is a change in chemical composition: Pb (58.41–77.07 wt.%), Sb (0.01–0.61 wt%), Zn (0.17–1.00 wt%), Fe (0.28–3.57 wt%), As (0.21–11.13 wt%), S (0.80–11.78 wt%).

The vitreous (silicate) mass is the filling between the crystallized phases. The glass in all samples is porous and heterogeneous. Silicates are characterized by varying degrees of substitution of metallic elements (As, Cu, Pb, Zn, Cr). Microscopic observations of the glass revealed the presence of oxidized iron in the form of a rusty film. The glass in terms of chemical composition is extremely diverse (Table 6). Its complex chemical composition

Table 5. Chemical composition of metallic core (1–6) and its weathering changes (7–12). EPM analysis in wt%.

Tabela 5. Skład chemiczny metalicznego jądra (1–6) oraz zmian wietrzeniowych (7–12). Analiza EPM w % wag.

Sample	2		3		4		6		7		8	
Point of analysis	1/6	2/8	3/2	4/4	5/6	6/2	7/1	8/3	9/2	10/3	11/1	12/2
Element	wt%											
Si	0.02	0.01	0.04	0.02	0.04	0.02	0.08	0.03	0.04	0.03	0.06	0.11
K	0.02	0.02	0.01	0.01	0.00	0.00	0.11	0.10	0.25	0.24	0.06	0.03
Pb	98.14	99.07	98.46	98.15	98.16	98.83	64.92	65.44	63.60	65.91	58.41	77.07
Zn	0.14	0.03	0.18	0.16	0.16	0.07	0.17	0.46	0.65	0.58	0.47	1.00
As	0.00	0.01	0.00	0.00	0.00	0.00	0.25	1.45	11.13	10.78	0.21	0.81
Fe	0.00	0.12	0.13	0.07	0.05	0.01	0.28	0.54	0.47	0.41	0.67	3.57
Mn	0.01	0.03	0.03	0.05	0.00	0.01	0.03	0.04	0.01	0.03	0.01	0.05
Sb	0.31	0.57	0.08	1.00	1.01	0.21	0.02	0.01	0.04	0.07	0.22	0.61
S	0.08	0.05	0.06	0.07	0.08	0.07	7.48	6.67	0.80	1.14	1.71	11.78
Cl	0.06	0.06	0.15	0.09	0.09	0.08	0.10	0.43	0.29	3.06	0.43	0.37
Total	98.77	99.69	99.13	99.62	99.59	99.31	73.43	75.17	79.94	82.24	62.24	95.37

is due to the conditions of its formation, which do not correspond to conditions occurring naturally in nature.

Secondary phases are the result of hypogene processes. They are formed as a result of the transformation of primary phases, forming efflorescence on the slag surface, poorly cemented crusts and pore-filling hypertrophies. These phases are represented by bassanite $Ca(SO4)^{-0.5}H_2O$ and jarosite $KFe_3{}^{+3}(SO_4)_2(OH)_6$.

3.2. Geochemistry

The chemical composition of the samples is presented in Table 7. The smelter slag consists mainly of SiO_2 (13.70–20.60 wt%) and Fe_2O_3 (24.90–39.62 wt%). Smaller amounts of Al_2O_3 (1.80–3.15 wt%), CaO (2.71–6.94 wt%), MgO (1.34–4.68 wt%). Analyses reveal very high contents of Zn (9.42–17.38 wt%), Pb (5.13–13.74 wt%) and Cu (1.29–2.88 wt%). Elevated contents are formed by trace elements Mo (487.4–980.1 ppm), Ni (245.3–530.7 ppm), Sn (2380.0–4441.5 ppm), Sb (2462.8–4446.0 ppm), Se (168.0–293.0 ppm). High concentrations are formed by As (13100–22600 ppm) and Cd (190.5–893.1 ppm). The loss on ignition (LOI) is high at 3.90–10.60 wt%. This is due to the presence of OH and H_2O groups in the

Table 6. Chemical composition of silicates. EPM analysis in wt%

Tabela 6. Skład chemiczny krzemianów. Analiza EPM w % wag.

Sample	1		2		3		4		6		10	
Point of analysis	1/1	2/3	3/8	4/2	5/11	6/2	7/4	8/2	9/5	10/6	11/2	12/5
Element	wt%											
Si	19.18	20.97	18.64	17.92	19.20	18.64	18.97	18.89	18.98	18.39	18.50	17.77
Al	7.37	1.01	5.07	5.00	9.16	6.20	8.21	8.85	8.55	16.06	16.25	0.05
Na	10.22	12.21	9.10	11.45	12.22	11.71	11.22	12.38	11.55	0.00	0.00	0.00
K	1.35	5.67	0.70	0.91	1.27	1.05	1.07	1.14	1.35	23.05	23.15	0.01
Mg	2.15	2.40	2.28	2.12	2.09	2.33	2.13	2.04	2.05	0.05	0.05	19.49
Ca	0.07	0.77	0.09	0.10	0.04	0.10	0.04	0.05	0.00	0.01	0.03	2.16
Mn	0.97	1.82	1.15	1.13	0.85	1.06	0.98	1.15	0.95	0.04	0.05	1.20
Fe	12.04	14.01	15.10	13.26	9.39	13.31	10.64	9.78	10.63	0.90	0.99	16.13
Pb	0.00	0.00	0.04	0.03	0.08	0.00	0.09	0.08	0.02	0.00	0.00	0.00
Cu	0.05	0.08	0.09	0.01	0.00	0.00	0.14	0.05	0.00	0.01	0.05	0.04
Zn	5.83	3.30	6.73	7.44	5.17	6.01	5.28	5.10	5.23	0.23	0.24	2.79
As	0.02	0.05	0.03	0.00	0.00	0.00	0.05	0.02	0.00	0.00	0.00	0.00
S	0.01	0.45	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.02
Cl	0.01	0.67	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02
Total	59.27	63.42	59.04	59.36	59.47	60.42	58.81	59.53	59.32	58.78	59.36	59.69

structure of the synthetic and secondary phases. The precious metals content varies among the samples. Anomalous amounts of precious metals were found in sample 4: Au 229 ppb, Pt 85 ppb and Pd 247 ppb. The average contents of these metals for the slag samples (n = 10) are Au 58 ppb, Pt 24.9 ppb, Pd 38.5 ppb and Ag 47.9 ppm (n = 5).

Preliminary resource estimates indicate that approximately 10,000 t Zn, approximately 6,700 t Pb, and 1,500 t Cu have been deposited in the tailings dump. The high metal contents indicate potential for development.

Table 7. Chemical composition of Cu-slag

Tabela 7. Skład chemiczny żużlu pomiedziowego

Sample	1	2	3	4	5	6	7	8	9	10
Oxide	wt%									
SiO_2	12.90	20.60	13.80	13.70	n.a	n.a	n.a	n.a	n.a	16.30
Al_2O_3	2.46	2.39	2.69	2.49	2.29	1.97	2.06	1.80	2.04	3.15
Fe_2O_3	29.10	25.60	27.50	25.00	34.66	29.07	38.93	39.62	29.54	24.90
CaO	3.56	6.94	3.99	3.29	5.55	2.71	4.27	3.82	3.30	3.70
MgO	4.68	2.16	1.72	2.06	2.87	1.64	2.19	1.69	1.34	4.38
K_2O	2.11	1.50	2.58	1.70	1.88	1.88	1.61	1.13	2.88	2.40
MnO	0.58	0.62	0.66	0.47	0.77	0.59	0.61	0.62	0.52	0.54
TiO_2	0.11	0.12	0.13	0.18	0.16	0.10	0.14	0.11	0.11	0.12
P_2O_5	0.11	0.12	0.14	0.13	0.14	0.11	0.11	0.09	0.11	0.17
Cr_2O_3	0.51	0.27	0.19	0.26	0.57	0.26	0.31	0.23	0.19	1.23
Ba	0.08	0.05	0.11	0.07	0.03	0.02	0.03	0.02	0.02	0.10
Cu	1.65	1.29	1.75	2.88	1.70	2.74	1.41	2.08	1.99	2.20
Pb	7.39	5.13	6.72	13.74	6.46	9.18	7.03	8.39	8.33	5.93
Zn	12.21	10.76	13.33	11.81	10.62	17.38	9.42	9.65	13.28	14.14
LOI	9.50	10.60	9.00	7.00	n.a	n.a	n.a	n.a	n.a	3.90
Total	92.69	93.00	90.54	91.07	n.a	n.a	n.a	n.a	n.a	90.92
Element	ppm									
Mo	n.a	n.a	n.a	n.a	618.1	706.3	487.4	980.1	823.8	n.a
Ni	n.a	n.a	n.a	n.a	263.2	336.9	237.4	530.7	245.3	n.a
Co	n.a	n.a	n.a	n.a	124.0	115.0	96.0	175.0	97.0	n.a
Sr	n.a	n.a	n.a	n.a	94.0	77.0	91.0	85.0	99.0	n.a
As	n.a	n.a	n.a	n.a	17200.0	13400.0	12700.0	22600.0	13100.0	n.a
Cd	n.a	n.a	n.a	n.a	190.5	893.1	243.1	301.3	293.8	n.a
Sb	n.a	n.a	n.a	n.a	2904.9	3429.3	2462.8	4446.0	3278.9	n.a
Bi	n.a	n.a	n.a	n.a	32.5	23.1	32.7	32.7	26.8	n.a
V	n.a	n.a	n.a	n.a	178.0	99.0	115.0	164.0	117.0	n.a
W	n.a	n.a	n.a	n.a	14.4	28.2	18.2	16.3	25.9	n.a
Sn	n.a	n.a	n.a	n.a	2418.1	4441.5	2380.0	3222.2	2848.7	n.a
Rb	n.a	n.a	n.a	n.a	87.4	113.2	72.6	56.8	117.6	n.a
Se	n.a	n.a	n.a	n.a	182.0	293.0	168.0	215.0	262.0	n.a
Precious metals	ppb									
Ag (ppm)	n.a	n.a	n.a	n.a	55.4	44.5	40.7	55.5	43.2	n.a
Au	42	21	9	229	140	30	29	53	13	15
Pt	9	17	7	85	62	13	17	17	9	13
Pd	13	7	8	247	57	15	9	19	4	6

n.a – no analysis.

4. Disscusion

4.1. Processing

The discovery of such a large polymetallic deposit of copper and silver ore in the Fore--Sudetic Monocline contributed to the construction of the entire infrastructure necessary for the processing and refining of the extracted mineral. The ore mined, consisting of copper sulphides (mainly chalcocite, bornite and covellite), is the starting material for hydro and pyrometallurgical processes. A detailed scheme of the technological sequence for processing of sulphide ores was presented by (Spalińska et al. 1996; Śmieszek et al. 2002; Staszak et al. 2006; www.copperalliance.pl).

During the early years (1970's) of the Głogów I smelter the copper production technology was based on three shaft furnaces. Głogów II smelter, from the beginning of its operation in the late 1970's, used a flash furnace and the single-shaft Outokumpu technology (Moskalyk and Alfantazi 2003). The differences between the technologies used, which are related to the amount of oxygen dosed, can affect the slag composition. In the case of slurry technology and copper matte converting, the processes take place in an oxidizing atmosphere, while in the case of shaft furnace technology and slurry slag decopperization in a reducing atmosphere. The input for the shaft furnace was a briquette produced from concentrate, converter slag, coke bonded with a polysulfide lye binder. In the upper part of the shaft furnace, at temperatures ranging between 500–700°C, partial transformation of chalcopyrite oxidation to iron oxides and copper sulfides occurred with simultaneous emission of sulfur dioxide according to equation (1):

$$2CuFeS_2(s) + 3O_2(g) \rightarrow 2FeO(s) +) 2CuS(s) + 2SO_2(g) \quad (1)$$

In the lower part of the furnace at 700–1000°C, complete oxidation of chalcopyrite and thermal decomposition of carbonates occurs. At temperatures of 1000–1300°C in the zone of oxygen supply nozzles, briquettes are burned; copper scale is formed due to melting of copper sulfide with flux. In addition, fayalite slag is formed according to equation (2):

$$2FeO + SiO_2 = Fe_2SiO_4 \quad (2)$$

The separation of copper scale from slag depends on the pressure of the oxygen feed, which should be low enough to prevent oxidation of the copper and its loss to the slag and on the temperature affecting the slag viscosity decrease. In addition, the separation of scale from slag is dependent on the chemical composition of the input, the addition of SiO_2 at a level of less than 5%, remaining in equilibrium with the slag, allows effective separation of scale from the fayalite phases. At the temperature of copper scale formation in the Cu-Fe-S stability system, iron is present in solid form, sulphur in gaseous form, while copper forms an alloy. A characteristic feature of Polish copper concentrates is the presence of Pb (1.5–3.0 wt%) and As (0.05–0.4 wt%) impurities (Śmieszek et al. 2017), which is introduced into the concentrate with ore minerals such as arsenopyrite or enargite. As a result of the success of the shaft furnace melting process and the subsequent conversion of the copper matte, a significant amount of As contained in the concentrate is transferred to waste in the form of dust that can provide material for Pb recovery.

Smelting of ore to recover valuable metals leads to generation of significant amounts of waste in the form of ash, sludge and slag. Slags produced at the initial stage of development of the "Legnica-Głogów Copper Belt" contain significant amounts of elements and other pollutants. Application of appropriate hydrometallurgical methods can bring potential economic benefits as part of the concept of sustainable development.

4.2. Environmental impact

Contemporary metallurgical slags are classified as potentially hazardous material. In the past they were considered as environmentally neutral waste. Hence, in many industrial regions slag tailings dumps were abandoned without proper environmental monitoring.

The post-copper slag tailings dump in Polkowice may pose a threat to the local ecosystem. In the studied material the occurrence of metal compounds was found in the form of sulphides, oxides and metallic phases which are not stable under hypogene conditions at appropriate pH and Eh. Synthetic phases are transformed into sulfates, hydroxides, or phosphates (Muszer 1996; Kądziołka et al. 2019), whose solutions can infiltrate into soils, surface water, and groundwater. This can result in local mobilization of toxic elements leading to a local ecological disaster.

Physical weathering, which results in disintegration of the composite material, also poses a threat. Dusting and transport of the dangerous material by the wind may result in the necessity of reclamation of the surrounding land by liming it with dolomitic material (Karczewska and Kabała 2010). In the reports on the condition of the environment of the Lower Silesian Voivodship for the years 2002–2020, a systematic decrease in the number of points for the administrative districts of Głogów and Polkowice, where standards of copper, lead and arsenic contents in soil were exceeded, was observed. None of the reports included the areas located close to the studied tailings dump in the sampling grid. There is no information about the magnitude of its impact on local ecosystem.

Tailings dumps developed over a similar time period in LGOM have been reclamated through the planting of tree. Inactive tailings dumps have undergone only partial reclamation due to difficult air and water conditions, high salinity, and a lack of organic matter to facilitate effective plantings (Kotarska 2012).

Currently, the waste rock and tailings repositories under construction at LGOM are secured according to BAT guidelines and are subject to continuous monitoring. Piwowońska and Pietrzyk (Piwowońska and Pietrzyk 2018) indicated a number of chemical methods applicable in hydrometallurgy, such as ion exchange or precipitation, which can potentially solve the problem of As derivation from Cu ore to avoid the threat of environmental degradation. The dominant direction in the utilization of post-copper slag currently produced by the smelters at KGHM is its processing into aggregates characterized by high hardness, strength and abrasion resistance (www.metraco.pl). These can find application as concrete additives or as abrasives (Gorai and Jana 2003; Kua 2013). The favorable geotechnical parameters of aggregate produced from slag allow it to be used in embankment construction (Machowski et al. 2014; Murari et al. 2015). In recent years, work has been carried out on the application of slags for the production of ceramic glaze (Mohaddes Khorassani et al. 2020). All of the ongoing studies assume the usefulness of slag, in which the concentration of Pb, Zn, Cu and As is at lower levels than in tailings dump samples, and the useful material is fayalite (de Rojas et al. 2008). The post-copper slag is characterized by a different chemical composition when compared to currently generated waste, due to changes in copper ore processing technology that have been introduced at the Głogów smelter after the material was deposited (Knop and Urbańczyk 2006).

4.3. Economic potential

According to the Balance of mineral deposit resources in Poland as at 31 December 2019, published by the Polish Geological Institute – National Research Institute (2020), there are 21 deposits of zinc and lead in Poland. They occur in the Silesian-Cracow region in Triassic metal-bearing dolomites. In Poland, only three deposits (Klucze I, Olkusz and Pomorzany) in the Olkusz region have been exploited until 2020 (Balance... 2020). However, the potential of Zn-Pb ores in Poland is high. Mikulski and Retman (2020) list several deposit--interesting locations such as: Klucze, Chechło, Laski, Sikorka and Jaroszowiec-Pazurek. Currently, zinc-lead ores are not being mined in Poland. During its mining period, the zinc content of the ore ranged from 4.0 to 4.5 wt%. However, in 2019, the zinc content in the ore was only 2.6 wt%. The COVID-19 pandemic and the decline in the percentage of zinc in the ore contributed to the lack of profitability of further mining of the deposit (Jajszczok 2020). However, the closure of the mine did not cause the decommissioning of the Boleslaw smelter. A large part of the input in the smelter is recycled material. In the coming years, ZGH "Bolesław" plans to use 50% of the recycled material in metallurgical production.

The cessation of exploitation of zinc-lead ore in Poland and possession of necessary infrastructure for processing the raw material makes it desirable to search for alternative sources of metals. The post-copper slag tailings dump deposited at the Polkowice landfill may be of potential importance for the acquisition of zinc and lead. High concentrations of Zn (up to 17.38 wt%) and Pb (13.74 wt%), as well as accompanying metals Cu, Ni, Mo and others, may be valuable raw material for their secondary use. Taking into account that there are ca.80,000 tons of slag on the Polkowice tailings dump, it could be used as a secondary material for production of zinc and lead concentrates and semi-concentrates.

Zinc and lead are traded on the London Metal Exchange. Metal prices have fluctuated quite a bit over the past 12 months. The reason for the changes was the development of the global COVID-19 pandemic. This is reflected in the price drop in March 2020. The zinc price was USD 1,173/t. It was then that ZGH "Bolesław" S.A. decided to stop mining the deposits due to lack of profitability. The current price (as of 08.04.2021) per tonne of zinc is USD 2.827. Similar changes can be observed in the prices of lead, which is rising on the London Metal Exchange and currently amounts to USD 1.969 per tonne (as at 08.04.2021) (www.lme.com).

Zinc is a metal used primarily in electroplating and the chemical industry. Technological advancements in medicine make zinc one of the metals that can be used for cancer imaging and diagnosis. According to MordorIntelligence (2021), growth in the automotive industry after a slump in 2018 will drive the zinc market globally.

The need to manage the post-copper slag tailings dump seems to be justified and profitable. The recovery of metals can bring economic and environmental benefits, and this activity will fit into the model of a closed-cycle economy. For this purpose, it is necessary to carry out technological works, which would allow for the possibility of recovering valuable metals contained in the slag.

Conclusion

Geological reconnaissance of a slag tailings dump deposited on private property in Polkowice was carried out during field work. The slag originated from pyrometallurgical processes at the Głogów II smelter. Examination of the mineral composition revealed the presence of primary and secondary phases resulting from weathering processes. Depending on the location of sampling and analyses, the mineral composition of slag is not homogeneous. The dominant group are synthetic zinc-lead phases sphalerite (5.50–36.30 wt%), palmierite (up to 16.5 wt%), beaverite-(Zn) (up to 15.3 wt%), petedunnite (up to 11.4 wt%). Chemical analyses of the slag show that it consists mainly of SiO_2 (13.70–20.60 wt%), Fe_2O_3 (24.90–39.62 wt%) and subordinately of CaO (2.71–6.94 wt%) and MgO (1.34–4.68 wt%). High contents are formed by Zn (9.42–17.38 wt%), Pb (5.13–13.74 wt%) and Cu (1.29–2.88 wt%). The slag contains trace elements Mo (487.4–980.1 ppm), Ni (245.3–530.7 ppm), Sn (2380.0––4441.5 ppm), Sb (2462.8–4446.0 ppm), Se (168.0–293.0 ppm). High concentrations are formed by toxic elements, such as As (13100–22600 ppm) and Cd (190.5–893.1 ppm). The unprotected slag tailings dump has a negative impact on the local ecosystem. Long-term exposure to slag chemical weathering agents may contribute to environmental pollution. It is necessary to conduct stability studies of the phases deposited in the tailings dump to determine the directions of migration of contaminants and adequate methods to secure the tailings dump until it is removed. It is estimated that the tailings dump has accumulated about 80,000 t of slag, which may contain about 10 000 t of Zn, about 6,700 t of Pb, and 1,500 t of Cu. Application of appropriate pyro-hydro-biometallurgical methods could enable recovery of valuable metals (Zn, Cu, Pb,) contained in the waste. The recovery of metals fits into the concept of sustainable closed-cycle economy.

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METAL POTENTIAL IN COPPER SMELTING SLAGS FROM POLKOWICE TAILINGS DUMP – PRELIMINARY STUDIES

Keywords

copper melting slag, circular economy, secondary mineral resources

Abstract

In Poland, the mineral sector generates 110–130 million tons of wastes annually (in the last 20 years), and metal ore mining alone was responsible for 31.2 million tons of wastes in 2017. The slags deposited at the Polkowice were investigated. This waste may be a potential source of many valuable metals (Zn, Pb, Cu, Sb, Sn, Se). The tailings dump in Polkowice contains approximately 80,000 tons of slag. The material contains primary phases formed by pyrometallurgical processes and secondary phases, which are the result of transformation of primary components. The primary phases are represented by sulfides: sphalerite [ZnS]; wurtzite [(Zn,Fe)S]; pyrite [FeS_2]; sulfates: beaverite-(Zn) [$Pb(Fe^{3+}{}_2Zn)(SO_4)_2(OH)_6$]; palmierite [$(K,Na)_2Pb(SO_4)_2$]; oxides and hydroxides: goethite [$Fe^{3+}O(OH)$]; wüestite [FeO]; hematite [Fe_2O_3]; magnetite [$Fe^{2+}Fe^{3+}{}_2O_4$]; chromian spinel [$Fe^{2+}Cr^{3+}{}_2O_4$]; silicates: petedunnite [$Ca(Zn,Mn^{2+},Mg,Fe^{2+})Si_2O_6$]; quartz [$SiO_2$]; and microcline [$KAlSi_3O_8$]. Additionally, SEM-BSE observations revealed that oxidized native metals (Cu, Pb, As) and metal alloys and semi-metals appear. The slag consists mainly of SiO_2 (13.70–20.60 wt%), Fe_2O_3 (24.90–39.62 wt%) and subordinately of CaO (2.71–6.94 wt%) and MgO (1.34–4.68 wt%). High contents are formed by Zn (9.42–17.38 wt%), Pb (5.13–13.74 wt%) and Cu (1.29–2.88 wt%). The slag contains trace elements Mo (487.4–980.1 ppm), Ni (245.3–530.7 ppm), Sn (2380.0–4441.5 ppm), Sb (2462.8–4446.0 ppm), Se (168.0–293.0 ppm). High concentrations are formed by toxic elements, such as e.g. As (13 100–22 600 ppm) and Cd (190.5–893.1 ppm). It is estimated that the tailings dump has accumulated about 80,000 t of slag, which may contain about 10,000 t of Zn, about 6,700 t of Pb, and 1,500 t of Cu.

POTENCJAŁ METALI W ŻUŻLACH POMIEDZIOWYCH ZE SKŁADOWISKA ODPADÓW POHUTNICZYCH W POLKOWICACH – BADANIA WSTĘPNE

Słowa kluczowe

hutnicze żużle pomiedziowe, gospodarka o obiegu zamkniętym, stare hałdy, wtórne źródła mineralne

Streszczenie

Sektor mineralny wytwarza w Polsce około 110–130 mln odpadów rocznie (w ostatnich 20 latach), a górnictwo metali odpowiedzialne jest za wyprodukowanie 31,2 mln t odpadów w 2017 r. Odpady hutnicze powstałe w KGHM zawierają istotne ilości metali (Zn, Pb, Cu, Cr). Przedmiotem badań były hutnicze odpady pomiedziowe z hałdy w Polkowicach. Odpady te mogą być potencjalnym źródłem kilku metali (Zn, Pb, Cu, Sb, Sn, Se). Hałda w Polkowicach zawiera około 80 000 ton żużli pohutniczych. Badany materiał mieści fazy pierwotne powstałe w pirometalurgicznym procesie i fazy wtórne, które są rezultatem przemian faz pierwotnych. Fazy pierwotne reprezentowane są przez siarczki: sfaleryt [ZnS]; wurcyt [(Zn,Fe)S]; piryt [FeS_2]; siarczany: beaveryt-(Zn)[$Pb(Fe^{3+}{}_2Zn)(SO_4)_2(OH)_6$]; palmieryt [$(K,Na)_2Pb(SO_4)_2$]; tlenki i wodorotlenki: goethyt [$Fe^{3+}O(OH)$]; wüstyt [FeO]; hematyt [Fe_2O_3]; magnetyt [$Fe^{2+}Fe^{3+}{}_2O_4$]; spinel chromowy [$Fe^{2+}Cr^{3+}{}_2O_4$]; krzemiany: petedunnit [$Ca(Zn,Mn^{2+},Mg,Fe^{2+})Si_2O_6$]; kwarc [$SiO_2$]; i mikroklin [$KAlSi_3O_8$]. Ponadto obserwacje SEM-BSE ujawniły obecność utlenionych metali rodzimych (Cu, Pb, As), stopów metali i półmetali. Żużle zawierają głównie SiO_2 (13,70–20,60% wag.), Fe_2O_3 (24,90–39,62% wag.) i pobocznie CaO (2,71–6,94% wag.), MgO (1,34–4,68% wag.). Wysoka jest zawartość Zn (9,42–17,38% wag.), Pb (5,13–13,74% wag.) i Cu (1,29–2,88% wag.). Ponadto żużel zawiera pierwiastki śladowe Mo (487,4–980,1 ppm), Ni (245,3–530,7 ppm), Sn (2380,0–4441,5 ppm), Sb (2462,8–4446,0 ppm), Se (168,0–293,0 ppm). Zawartość pierwiastków toksycznych jest wysoka: As (13 100–22 600 ppm), Cd (190,5–893,1 ppm). Oszacowano, że hałda żużla o masie 80 000 t może zawierać około 10 000 t cynku, około 6700 t ołowiu i około 1500 t miedzi.