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Quantitative and qualitative analysis of slags from zinc and lead metallurgy

Milena Nocoń*, Irena Korus, Krzysztof Loska

Silesian University of Technology, Faculty of Environmental Engineering and Energy,
Department of Water and Wastewater Engineering, Poland

*Corresponding author's e-mail: milena.nocon@polsl.pl

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Abstract: The zinc and lead industry generates substantial quantities of waste. Among the many types of wastes, such as dust or liquid, a large proportion are solid waste such as slags. The purpose of the study was the qualitative and quantitative assessment of the short rotary kiln slags and slags deposited in a hazardous waste landfill originating from zinc and lead metallurgy. This assessment represents the primary step in evaluating materials such as slags concerning their potential for substantial applications, such as process for metal separation. Additionally, this evaluation forms the basis for a comprehensive environmental study. The concentrations of the four predominant metals – Fe>Pb>Zn>Cu – and accompanying elements – Na>Ca>K>Ni>Mn>Cr – were determined using atomic absorption spectroscopy (AAS) after aqua regia digestion. A large variation was found in the phase analysis of the studied materials based on SEM, XRD, X-ray microanalysis, and BCR sequential extraction. The BCR analysis revealed the occurrence of major metals in four different fractions: acid-soluble, reducible, oxidizable, and residual. Pb was mainly present in the acid-soluble fraction, while Fe, Cu, and Zn were present in the residual fraction.

Introduction

Slags from zinc and lead metallurgy are a source of many chemical elements, especially transition metals (Xu et al. 2021). Despite all safety measures, slags deposited in hazardous waste landfills remain susceptible to the influence of atmospheric conditions. Metals can exist in a stable form (bound in the crystal structures of minerals) or a mobile form (present in ion-exchange positions in the structures or on the surfaces of the grains). The stability or mobility of an element depends mainly on the environmental conditions, because even though an element is present in a stable form, the mineral may decompose and release the element into the environment (Róžański 2013). Heavy metals that enter the environment have a toxic effect on biota. They can enter the food chain and affect living organisms. These metals can accumulate in the human or animal body, and long-term exposure can cause chronic poisoning, which may lead to various types of damage to the nervous and circulatory systems, as well as the kidneys, and the digestive system (Patle et al. 2022). It is important to have a thorough understanding regarding the presence of harmful elements in landfill materials. Knowledge of the overall content of heavy metals in waste is not sufficient: in order to establish the environmental impact of heavy metals, their potential bioavailability and mobility must be determined. The most precise method for determining the chemical forms of metals is the use of sequential extraction

techniques, which involve leaching with a series of extractants of increasing aggressiveness. Sequential extractions are used to define the forms of metals, their origin, how they bind with the matrix components, and how they can be transported into the environment (Tlustos et al. 2005). However, the sequential extraction has the operational nature what limits the possibility of comparing results carried out by different protocols. Knowledge of the composition of waste materials may also result in their reuse in the production process or their reprocessing in order to separate valuable components, which may be profitable for the plant.

Smelters generate a wide range of wastes such as slags, sludges, dusts etc. All of these wastes are found to be a source of many heavy metals (Chao-Yin et al. 2005, Nowińska and Adamczyk 2013, Dan Chen et al. 2021). Slags of metallurgy origin are subjected to plenty of analysis such as: Scanning Electron Microscopy (SEM), X-ray microanalysis with EDS, and X-ray diffraction (XRD) (Ettler et al. 2001, Warchulski and Szopa 2014, Król et al. 2020). A BCR (Community Bureau of Reference) three-step sequential extraction analysis has been widely used to determine the forms of metals present in soils and sediments (Rauret et al. 1999, Róžański 2013, Wali et al. 2014, Lestari et al. 2018). This technique is relatively simple and has been shown to be useful in assessing the potential mobility of metals in solid samples.

The purpose of the research was to carry the qualitative and quantitative analysis of the metallurgical slags by using

various analytical methods. It was anticipated that the tested materials would contain numerous heavy metals in various forms. The primary objective of this study was to achieve a comprehensive understanding of the composition of the materials under study including their metal content and forms of occurrence. Such a study represents the initial step in evaluating materials such as slags for potential subsequent utilization and serves as the foundation for comprehensive environmental assessments. The results of the analysis offer highly promising possibilities for further utilization of these materials, including the separation of selected metals through extraction methods followed by subsequent concentration. The separation of metals from waste materials using cheap and effective methods is highly desirable, not only for economic considerations but also for environmental concerns. As heavy metals become increasingly expensive as raw materials in today's context, the prospect of separating and reusing them is highly desirable. Furthermore, the early separation of metals makes it possible to decrease the extent of soil contamination in the vicinity of smelter waste landfills, a widely recognized phenomenon. The possibility of separation is still inaccurately recognized by researchers and the materials studied are not often the subject of research. The studied slags pose a distinct and localized issue, being residues from lead and zinc metallurgy generated through the ISP method. Therefore, the comprehensive characterization of these materials, as outlined in the article, can also be very useful for researchers exploring methods of metal separation from similar materials. This article offers potential insights and essential information for other researchers addressing the same issue, serving as both reference point and comparative material.

Materials and methods

Two different slags from the zinc-lead smelter were investigated. One originated from a short rotary kiln (SRK) in the Lead Refinery Department, and the other from the on-site hazardous waste landfill (SRK HWL). The SRK (Kruk 2022) sample was collected directly from the short rotary kiln during an oxides campaign. The reduction processes carried out in the smelter are categorized into two types, oxides and sulfides, depending on the charge mixture used, which mainly consists of either metal oxides or metal sulfides. These processes were typically conducted alternately. The SRK HWL material was periodically deposited into the landfill following slag accumulation during the production process, allowing for the potential presence of slags from both campaigns. Samples were collected from various locations, with each sample weighing approximately 30 kg. For analytical testing, the sample underwent preliminary preparation, including crushing, drying, and grinding. Afterward, homogenization was achieved through thorough mixing, and then a representative sample was obtained using the quartering method. To ensure reproducibility of the tests, triplicate samples were prepared and used for sequential analysis. Both samples were in the form of hard, dark materials resistant to manual crushing. The SRK sample displayed a dark black color, with a metallic sheen, while the SRK HWL material exhibited a dark grey color with a matt surface and brown inclusions.

Preliminary sample preparation

The SRK and SRK HWL materials were delivered as particles with sizes reaching up to 10 cm. To reduce the particle size, the slags were crushed to less than 4 mm using an LJI crusher, dried to achieve a constant mass at 105°C, and ground to reduce the particle size to less than 2 mm. The obtained materials were air-dried and oven-dried at 105°C to determine their moisture content.

In order to characterize the particle sizes of the ground slags, the material was separated by size fraction. An analysis of the percentage composition concerning grain size was performed according to PN-EN 933-1:2012 including sieve methods. A representative 500 g sample of the dried and milled slag was obtained using the quartering method. For a comprehensive sieve analysis, a series of sieves were used with the dimension range of 2 mm, 1.6 mm, 1 mm, 0.8 mm, 0.6 mm, 0.5 mm, 0.43 mm, 0.3 mm, 0.25 mm, 0.2 mm, and 0.102 mm (Singh et al. 2015).

The size fraction separation of the tested materials gave information on the amount and percentage composition of each size fraction. Consequently, the slags were divided into six fractions, determined by the grains composition percentage within distinct size ranges. The following fraction was separated (the percentage of the corresponding fraction for both samples is given in brackets): >2 mm (3–5%), 2–1.6 mm (24–30%), 1.6–1.0 mm (22%), 1.0–0.6 mm (13–14%), 0.6–0.25 mm (12–15%), and <0.25 mm (15–19%).

The samples of the SRK and SRK HWL materials, as well as the sample residues after sequential extraction, were digested in a closed system with microwave assistance using aqua regia, following EN-13657:2006 standard. This acidic mixture had been previously used to successfully digest slags (Li et al. 2008, Król et al. 2020). The digestion process was conducted using a Milestone MLS 1200 MEGA microwave system equipped with a ventilation unit, in 100 ml Teflon vessels. Approximately 100 mg of the dry material was ground using a Retsch S 1000 centrifugal ball mill to achieve a suitable grain size for analysis. The weighed samples were placed into Teflon vessels and treated with 6 ml of aqua regia. Complete degradation of the samples was achieved after a digestion time of 6–7.5 min, employing a fixed power of 1000 W. The selection of aqua regia as the digestion agent was based on the results from previous digestion tests involving various mixtures (aqua regia, reverse aqua regia, HNO₃+HF).

An ANOVA test was used to assess the reliability of the method, and the results were checked by comparison with certified reference materials (CPB-1 (Lead Concentrate) and CZN-3 (Zinc Concentrate) from CANMET (Kruk 2022)). In this context, the application of microwave-assisted aqua regia digestion to the CRMs samples, yielded values in line with certification for Pb and Zn. In addition, the use of certified reference materials enabled the validation of analytical methods used to quantify metal concentrations in samples (as described in the Section 2.6.). These materials, originally metal concentrates used as input products in metallurgical processes, serve as sources of heavy metals. Their usage as certified comparison materials allows us to evaluate the possibility of metal recovery from various forms of source materials, including slags. However, slags, being waste materials from metallurgical processes, may contain vitrified components, while still harboring heavy metals.

Consequently, direct comparison results could entail some degree of error. Nonetheless, such a comparison offers valuable insights into evaluating the efficacy of metal recovery using a specific digestion method.

Scanning Electron Microscope analysis

Sample characterization was performed using a JEOL JXA-8230 scanning electron microscope (SEM). An accelerating voltage of 15 kV was used. The tests were carried out on the surface of the SRK and SRK HWL samples. Electron images were taken using secondary electrons (SEI – the contrast depended mainly on the surface topography) and backscattered electrons (COMPO – revealed differences in the chemical composition).

X-ray spectral analysis

X-ray spectral analyses were performed using the JEOL JXA-8230 X-ray microprobe. The analyses were carried out on SRK and SRK HWL samples that had been sputtered with a conductive gold film. Quantitative analyses of selected grains were performed at various points using the wave-dispersion method (WDS) at a voltage of 15 kV. Multiple micro-areas were examined for each sample, providing an average analysis for each grain. The visible contrast in these areas depended solely on the differences in chemical composition. Elemental distribution maps were produced using EDS, and qualitative and quantitative analyses of the chemical composition were also performed. The elemental distribution maps were generated for each of the previously indicated micro-areas. On these maps, changes in concentration are represented by colors ranging from red (indicating maximum concentration) to yellow, green, and blue, to black (indicating minimum content) (Jonczy et al. 2017). This article presents two photographed micro-areas for both samples, with each sample showcasing an example of an elemental distribution map based on single micro-area.

XRD analysis

To determine the mineralogical composition of the tested SRK and SRK HWL samples, XRD analysis was performed (Król et al. 2020). Phase identification and composition were examined by XRD according to PN-EN 13925-1:2007, using a PANanalytical, X'PERT PRO diffractometer (Cu radiation at 30 kV and 40 mA).

Sequential extraction

Speciation analyses of selected metals in both materials were performed using a modified three-step sequential extraction procedure (Rauret et al. 1999, Rauret et al. 2001, Li et al. 2008, Alan and Kara 2019).

For analysis, SRK and SRK HWL samples were collected based on size fractions: >2 mm, 2–1.6 mm, 1.6–1.0 mm, 1.0–0.6 mm, 0.6–0.25 mm, and <0.25 mm for analysis. The leaching process for individual metal fractions in the 1st, 2nd, and 3rd steps was conducted in centrifuge tubes placed on a Ohaus Orbital Shaker (250 rpm, 16 h). Subsequently, separation of sediment from liquid was performed using an MPW-380 centrifuge (3000 rpm, 20 min). Between steps, sediment rinsing was accomplished adding 20 ml of demineralized water, shaking the solution on a shaker (250 rpm, 20 min), and

centrifuging (3000 rpm, 20 min). The residue from the 3rd step underwent digestion with microwave assistance using aqua regia solution, maintaining a constant power of 1000 W for 8.5 min. The obtained solutions were then analyzed for concentrations of Zn, Pb, Cu, and Fe using AAS.

The total sum of the four metals (Pb, Zn, Cu and Fe) in the individual fractions was adjusted to 100%, based on the relative proportions for each of these metals. Reliability of the method was calculated in reference to the total amount of metals in tested materials. Reliability of the method for Pb was as follows: SRK – 93.1%, SRK HWL – 81.7%, Zn: SRK – 93.8%, SRK HWL – 100.5%, Fe: SRK and SRK HWL – 89.4%, Cu: SRK – 102.8%, SRK HWL – 98.1%.

Metal analysis

SRK and SRK HWL slag samples, along with the sample residues after sequential extraction, were digested using aqua regia.

After digestion, the samples were quantitatively transferred to 100 ml volumetric flasks. Subsequently, the concentrations of the following metals were determined: Pb, Zn, Cu, Fe, Ni, Mn, Cr, Na, K, and Ca. This was achieved through flame atomic absorption spectroscopy (AAS), using a Varian SpectrAA-880 spectrophotometer. The instrument was equipped with a SIPS system, enabling precise dilution of samples when dealing with elevated concentrations of the target metals. Flame generation was facilitated by using acetylene-air as the combustible gas. Calibration curves were prepared using standard metal solutions (MERCK).

Results and discussion

Moisture content

The moisture contents of both samples were determined. The moisture values did not exceed 0.04% for the SRK material and 1.22% for the SRK HWL, and there was no significant difference between the moisture content of the oven-dried and air-dried samples. This large difference in moisture content between the two materials may be caused by their origin. The SRK sample was collected directly from the short rotary kiln, which, due to the process conditions, significantly contributed to the low moisture content of the material. The SRK HWL sample collected from the landfill exhibited nearly 30 times more moisture content, likely attributed to an extended period of exposure to the atmosphere in contrast to the SRK sample. This substantial difference in moisture content between the two samples may be attributed to differing material storage conditions.

Separation by fraction size

The separation of the dried and ground slag based on fraction size revealed a notable distinction with the tested samples. Table 1 presents the results of the analysis for the SRK and SRK HWL samples.

While the samples exhibited some similarities, the SRK HWL slag featured a greater abundance of intermediate size fractions after grinding. The SRK slag demonstrated a higher prevalence of larger size fractions, particularly those >2 mm. These disparities suggest some differences in material hardness and homogeneity. Despite the >2 mm fraction contributing less

to the SRK HWL slag compared to the SRK, achieving material homogeneity necessitated a lengthier grinding duration for the SRK HWL slag (60 min) in contrast to the SRK (40 min).

Total content of metals in the SRK and SRK HWL samples

Among the analyzed metals, Fe, Cu, Pb, and Zn were found to be present in higher amounts, and their concentrations are presented in Figure 1. Other metals, such as Ni, Mn, Cr, Na, K, and Ca, were present in lower amounts. The quantitative distribution of metals identified in the tested materials has been confirmed by other studies concerning wastes produced during ISP process (Bernasowski et al. 2017, Nowińska and Adamczyk 2017). Lead is often a prominent component in lead-zinc slags, frequently occurring in substantial percentages. Luo et al. found elevated concentrations in such materials. The metal content essentially depends on fractions like the origin of the research samples, the ores used in the process, and the conditions under which the metallurgical process is conducted (Li et al. 2008, Jin et al. 2014, Pan et al. 2019, Xu et al. 2021). The variation in metal content within individual samples was characterized using two basic statistical parameters: the arithmetic mean and standard deviation (SD). The analysis was performed using six size fractions extracted from the samples, alongside an unfractionated material for reference, yielding the following categories: NF (not fractionated), >2 mm, 2–1.6 mm, 1.6–1.0 mm, 0.6–1.0 mm, 0.25–0.6 mm, and <0.25 mm.

The zinc content in the SRK sample remained relatively stable around 14%, whereas in the SRK HWL sample, it ranged from 3% to 4%. The zinc content did not show significant variation across the individual fractions. In the case of lead, the SRK sample oscillated around 5% and did not vary significantly between fractions. However, in the SRK HWL

sample, the lead content increased noticeably as the fraction size decreased. For instance, it reached its minimum (5.5%) in fractions larger than 2 mm and its maximum (12.5%) in fractions smaller than 0.25 mm, which was more than twice the content in the largest fraction.

In the SRK sample, copper content ranged 1.6% to 2.8% across all fractions. The content exhibited an upward trend as particle size decreased, with more substantial changes observed for the landfill slag. The lowest copper content (3.8%) was found in fraction larger than 2 mm, while the highest (7.4%) occurred in fraction smaller than 0.25 mm, nearly twice the content of the larger fraction. For iron, the SRK sample had a content close to 30%, while the SRK HWL sample had

Table 1. Sieve analysis of the SRK and SRK HWL sample

Sieve sizes	Remaining material on the sieve	
	mm	%
		%
	SRK	SRK HWL
2	16.9	3.8
1.6	27.1	26.4
1	16.2	22.8
0.8	6.9	9.4
0.6	3.1	4.8
0.5	3.5	4.8
0.43	2.1	3.3
0.3	2.6	3.4
0.25	2.2	3.0
0.2	1.8	2.3
0.102	5.1	5.9

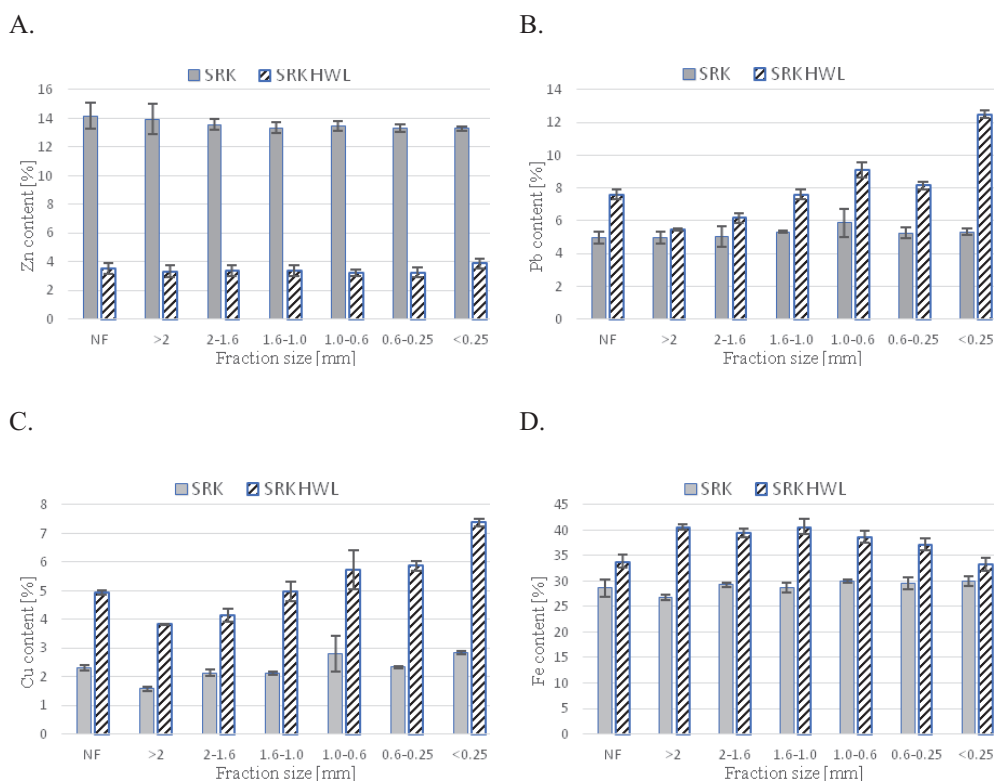


Fig. 1. The average content of A – Zn, B – Pb, C – Cu, D – Fe

a higher content, nearing 40%. In the case of SRK, the iron content remained relatively consistent across individual fractions. However, in the SRK HWL case, there was a clear trend of decreasing iron content as the fraction size decreased.

The content of other elements did not exceed 3.32% for Na, 2.90% for Ca, 0.25% for K, and 0.25% for Ni in both materials. The content of Mn in the SRK reached no more than 0.08%, while in the SRK HWL, it was twice as high (0.16%). The Cr content reached 0.02% in the SRK and 0.01% in the SRK HWL sample. Moreover, no differences were found in the content of these metals in the fractions used.

Both slags show relatively high concentrations of key elements, such as lead and zinc, which are byproducts of the process and thus end up in the wastes in varying quantities. The difference in lead or zinc content between the two slags could potentially be attributed to the source of the samples. Additionally, the slags also showed a significant diversity in copper and iron content, as well as other accompanying elements. This diversity is influenced by the variability in input materials and the course of the technological process.

Scanning electron microscopy

SEM analysis proved to be an effective technique for examining the morphology of the samples. Fig. 2 displays SEM images of surfaces of the SRK and SRK HWL at three different magnifications – 100×, 500×, and 1000×. The images reveal a compact, plate-like grain structure for both materials, characterized by the absence of visible pores or channels. The material also exhibits noticeable heterogeneity, with varying grains sizes. Similar observations were reported by Xu (2021) and Luo (2022), suggesting that these characteristics could result from the technological process and uncontrolled slag formation. The color of these grains did not differ between the two tested samples. In addition, a disparity in grain edge sharpness can be observed from the images. The SRK sample displays very sharp grain edges, while the SRK HWL sample shows less sharp edges. This distinction could potentially signify the influence of slag ageing in the landfill. Moreover, areas of significant brightening are evident, possibly indicating the presence of distinct metallic inclusions.

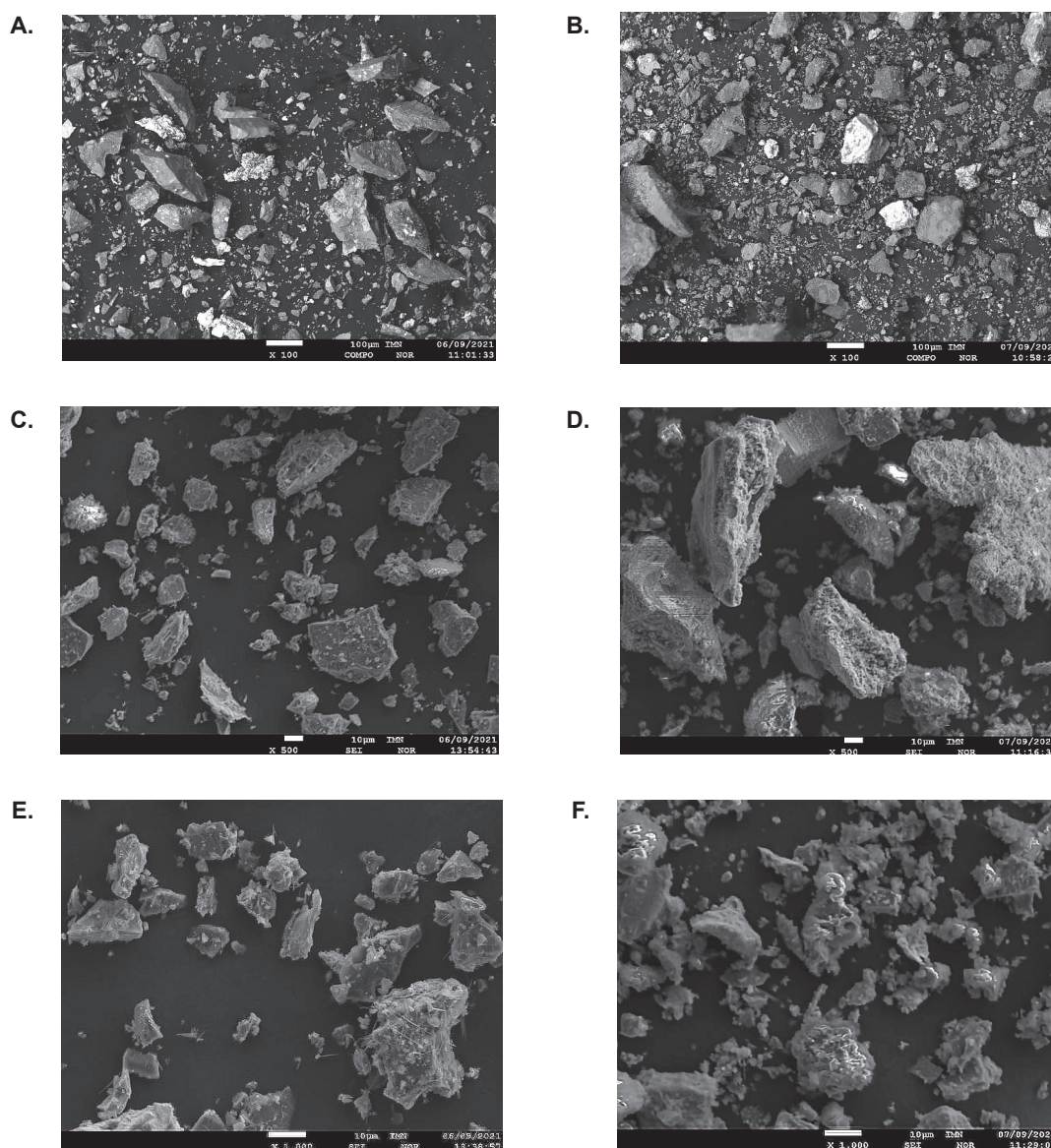


Fig. 2. SEM images of A – SRK (100× zoom), B – SRK HWL (100× zoom), C – SRK (500× zoom), D – SRK HWL (500× zoom), E – SRK (1000× zoom), F – SRK HWL (1000× zoom)

No significant differences can be seen in the photographs captured from the two tested slags. It can therefore be assumed that the phenomenon the storage and exposure of slag to changing weather conditions does not change the slag structure. The SEM method allows for more detailed insights, such as assessing the specific surface area development, porosity, and surface homogeneity. In the case of tested samples, a noticeable observation is that both samples exhibit a relatively compact and uniform structure, featuring only a limited number of pores. This information is necessary to accurately describe the samples and, in some cases, also to understand their behavior during testing or choosing an appropriate methodology.

X-ray microanalysis

X-ray microanalysis of the SRK and SRK HWL samples showed considerable variability in the content of metals and other accompanying elements. Apart from the primary metals of interest – Pb, Cu, Zn, and Fe – other metals were detected, including Na, Mg, Al, Ca, Cr, Mn, K, and Sn. Comparatively, the presence of metals in both tested materials did not exhibit significant divergence. However, their content displayed considerable variability depending on the measurement point.

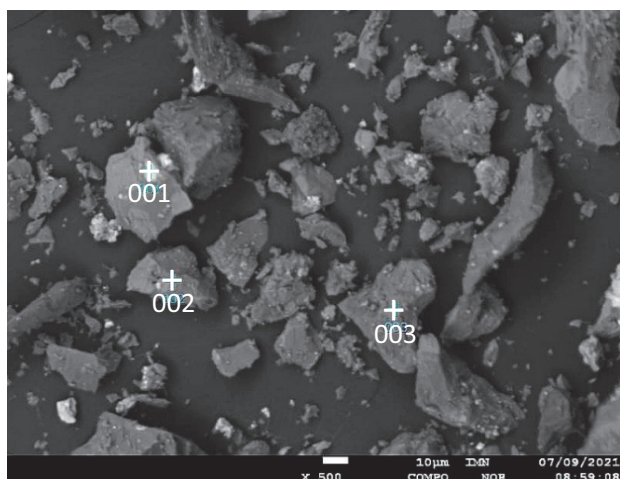
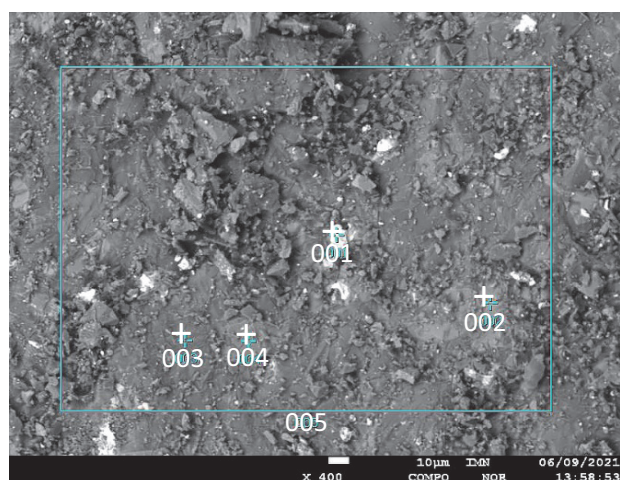
The observation of aluminum and silicon may suggest the presence of aluminosilicate species of metals, while elements like carbon, oxygen, and sulfur may indicate the presence of metal carbonate, sulfide, and sulfate phases. Fig. 3 and Fig. 4 show two examples of photomicrographs along with EDS analysis for the SRK and SRK HWL samples, respectively.

In all minerals detected in the samples, the identified elements are dispersed unequally, as evidenced by the quantitative determinations of elements in each micro-area. This fact was confirmed by many researchers studying slags of non-ferrous metallurgy (Jonczy et al. 2017, Zhang et al. 2022).

Element distribution maps

Element distribution maps were defined for each photomicrographed area. Fig. 5 and 6 present examples of distribution maps determined in the defined micro areas for the SRK and SRK HWL samples, respectively.

The elemental distribution maps of the SRK and SRK HWL samples showed the common areas for individual elements. By examining these maps and considering color intensity, it becomes plausible that some elements coexist in chemical compounds. The deeper colors, which are indicative



Element content at the measuring point

	%				
	001	002	003	004	005
O	3.08	16.97	26.43	16.21	25.35
Na	1		1.97		8.5
Mg		1.58	2.92	1.37	1.16
Al		0.28	0.56	0.26	1.38
Si		0.23	16.08	0.11	10.55
S					0.88
K					0.4
Ca		0.13	14.06	0.16	4.05
Fe	2.84	68.44	28.7	68.87	27.2
Ni	1.99				
Cu	2.86				0.94
Zn	1.76	11.85	9.29	12.39	13.62
Sn	7.05	0.53		0.64	2.02
Pb	79.41				3.95
C	6.89				
O	10.07	28.65	34.2		
Na			8.2		
Mg	0.37	2.38	0.4		
Al	0.41	1.53	2.06		
Si	2.64	14.24	15.71		
S	9.5	4.19	0.36		
K		0.23	0.47		
Ca	0.95		1.69		
Fe	8.18	28.39	11.22		
Cu	1.66	1.01	1.04		
Zn	25.1	13.59	20.38		
Sn	0.34		1.85		
Pb	33.89	0.85	2.85		

Fig. 3. Photomicrographs of SRK sample with total element content in the measured points

of maximum element concentration, were identified in corresponding areas for sulfur (red) and lead (green for SRK, red for SRK HWL). This occurrence potentially suggests a shared presence of both elements in high concentrations, possibly in the form of PbS (lead sulfide). The distribution map for aluminum and silicon showed very similar patterns. Although silicon (blue) held a slightly higher concentration in comparison to aluminum (purple), this alignment suggests the presence of aluminosilicate forms of metals. Moreover, the distribution maps for magnesium, calcium, sodium, silicon, aluminum, and oxygen showed the potential existence of more complex forms of aluminosilicates in the material.

XRD Analysis

The XRD pattern of the tested slags is presented in Fig. 7. The analysis revealed the presence of various metal oxide minerals in both analyzed materials. These included wüstite (FeO), magnetite (Fe₂O₃), zincite (ZnO), and FeZnO. Wüstite and magnetite, as forms of Fe binding, are commonly found in many metallurgical slags samples, while the presence of hematite is less often detected in these materials (Seigneur et al. 2006, Sobanska et al. 2016). Metal silicate compounds were also identified in both materials, such as fayalite (Fe₂SiO₄),

monticellite (CaMgSiO₄), and nepheline (NaAlSiO₄). Furthermore, the SRK slag displayed forms such as melilite (Ca,Na)₂(Al,Mg)[(Si,Al)₂O₇] and wurtzite (ZnS), along with non-stoichiometric forms such as CaFe₅O₇ and KMgSn₃O₈. A non-stoichiometric form of NaFeSiO₂ was found in the SRK HWL slag. Both slags contained inclusions of pure metal Pb. Similar observations were described by many researchers who studied similar slag samples (Ettler et al. 2001, Seigneur et al. 2006, Sobanska et al. 2016, Yin et al. 2016). In the case of SRK HWL, components like litharge (PbO) were observed, a presence not noted in SRK. This could indicate that PbO is a secondary mineral arising from material storage processes, specifically Pb oxidation.

Quantitative analyses were not performed on the slag samples due to incomplete structural data for certain identified phases. It is not uncommon for certain identified minerals to have uncertain phase identifications. These aspects demonstrate the great diversity and heterogeneity inherent in the two materials in question. However, the two examined slags showed a substantial phase similarity, albeit with minor differences, primarily attributed to the presence of non-stoichiometric compounds.

The complexity of the chemical structure in metallurgical wastes is a commonplace occurrence, often depending on

Element content at the measuring point
%

	001	002	003	004	005
C		2.07		0.8	1.78
O	28.91	14.21	26.21	17.4	20.17
Na	4.85	4.49	4.49	17.28	12.06
Mg	3.17	1.24	2.24	0.51	1.16
Al	3.43	1.55	3.4	0.89	1.37
Si	14.2	6.62	11.13	2.55	4.78
S	0.21			2.37	0.14
K	0.19	0.32	0.19		0.49
Ca	10.08	4.98	6.23	2.4	3.27
Fe	17.58	22.85	34.36	23.77	29.43
Cu	0.67	1.14	0.65	13.09	3.37
Zn	3.64	2.32	3.53	7.56	2.49
Sn		2.84	0.87	1.1	1.03
Pb	13.07	35.36	6.7	10.29	18.47
O	5.58	20.6	7.33	21.39	
Na	1.32	1.33	1.41	2.64	
Mg	0.34	1.38	0.16	1.08	
Al	0.51	0.15	0.34	0.39	
Si	1.11	0.13	1.05	0.55	
Ca	0.44		0.84	0.41	
Fe	80.37	72.41	3.11	56.37	
Cu	1.29	0.44	2.7	1.31	
Zn	0.87	1.94	2.15	6.73	
Pb	7.11	1.61	80.92	9.12	
Cr	0.42				
Mn	0.64				

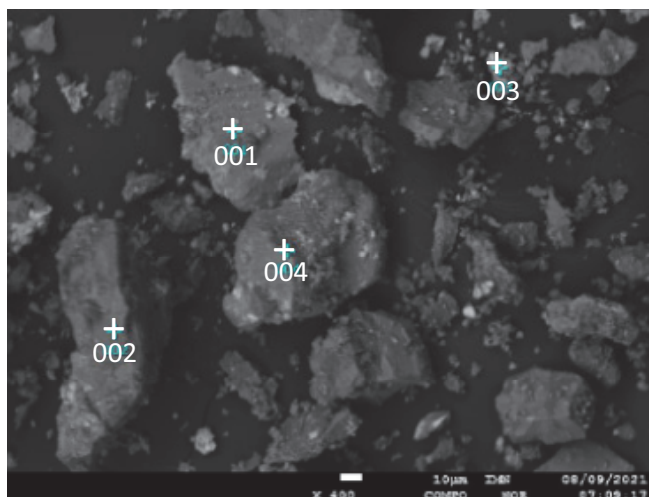
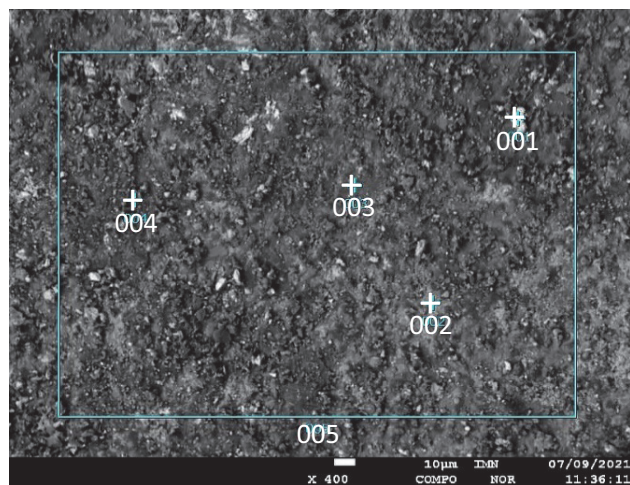


Fig. 4. Photomicrographs of SRK HWL sample with total element content in the measured points

the input material for the production process and the specific process conditions. Primary minerals are often found in waste materials, alongside numerous minerals generated in the furnace during smelting processes. The group of synthetic minerals formed during the production process can include, for example: melilite, monticellite, magnetite and metallic Pb (Cabała 2009, Warchulski and Szopa 2014, Król et al. 2020). However, certain minerals found in the tested material, such as non-stoichiometric forms, appear to be unique to these specific types of SRK and SRK HWL slags.

Sequential extraction analysis

The BCR sequential extraction analysis allowed for the separation of four metal fractions: acid-soluble associated with iron and manganese oxides (also called reducible), oxidizable, and residual. The acid-soluble fraction (F1) of heavy metals is a mobile fraction that tends to exhibit ready bioavailable. The reducible (F2) and oxidizable (F3) fractions, referred to

as potentially bioavailable, are typically accessible only under highly reducing and oxidizing conditions. In contrast, the residual fraction (F4) is the non-mobile and biologically unavailable fraction that is firmly bound to the mineral matrix (Singh and Chandel 2022). The presence of an element in a mobile form can contribute to its release into the environment. It should be also noted, that the stability or mobility of an element is primarily determined by environmental factors such as pH, Eh, and solubility equilibrium. This is crucial because even if an element is present in a stable form, the mineral component may decompose in the environment (Briffa et al. 2020).

Soil contamination with heavy metals in the vicinity of metal smelters is a frequent and well-recognized issue (Li et al. 2020, Gao et al. 2022). In addition, it has been observed that the concentration of these toxic metals remains dependent on the distance from the smelter and associated landfills (Baczewska et al. 2016, Ke et al. 2022). However, soil contamination is not the only concern, as the presence of toxic heavy metals has

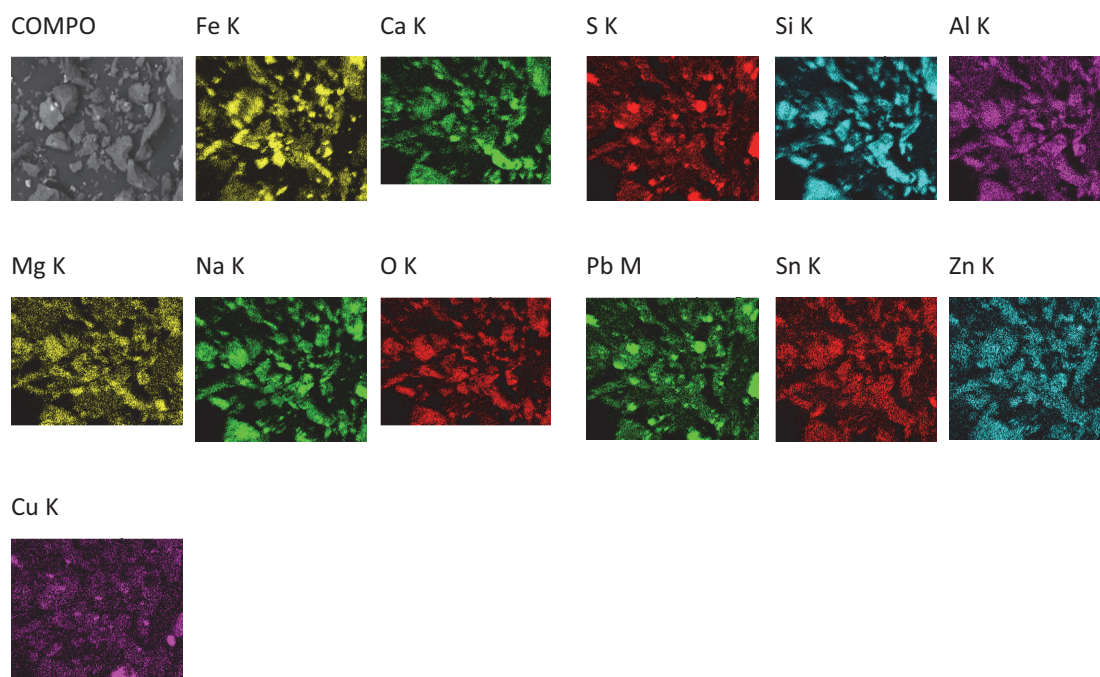


Fig. 5. Element distribution map of SRK sample

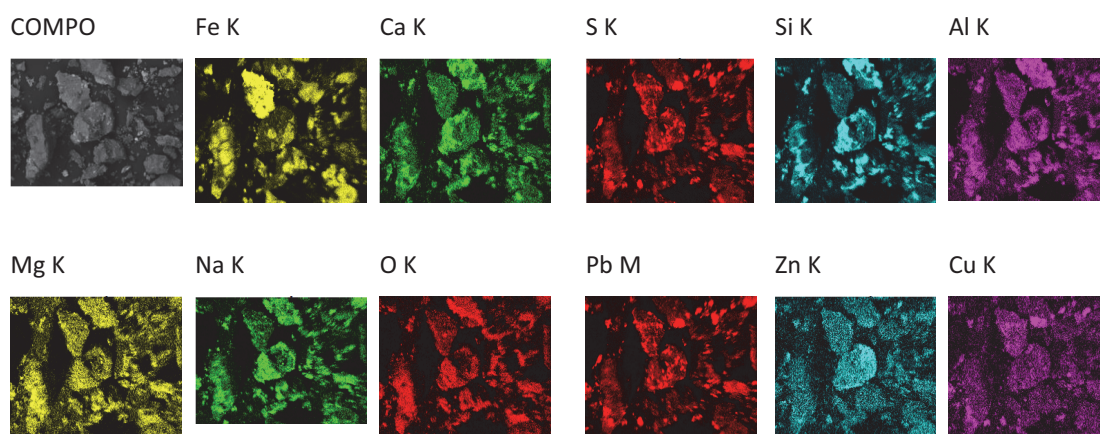


Fig. 6. Element distribution map of SRK HWL sample

been found in other environmental components, including air, water, and bottom sediments near smelting facilities (Wang et al. 2020, Izydorczyk et al. 2021). This correlation may clearly indicate that the activities of the smelter, coupled with the presence of mobile forms of toxic heavy metals in wastes, play a pivotal role in their migration to the environment and ensuing pollution.

The results of the speciation analysis performed on the SRK and SRK HWL samples for the four predominant metals, Pb, Cu, Zn, and Fe are shown in Fig. 7.

In general, both materials showed similar percentage distribution across each fraction of the sequential analysis for each of the tested metals. The absence of significant variations in the metal content between these materials shows

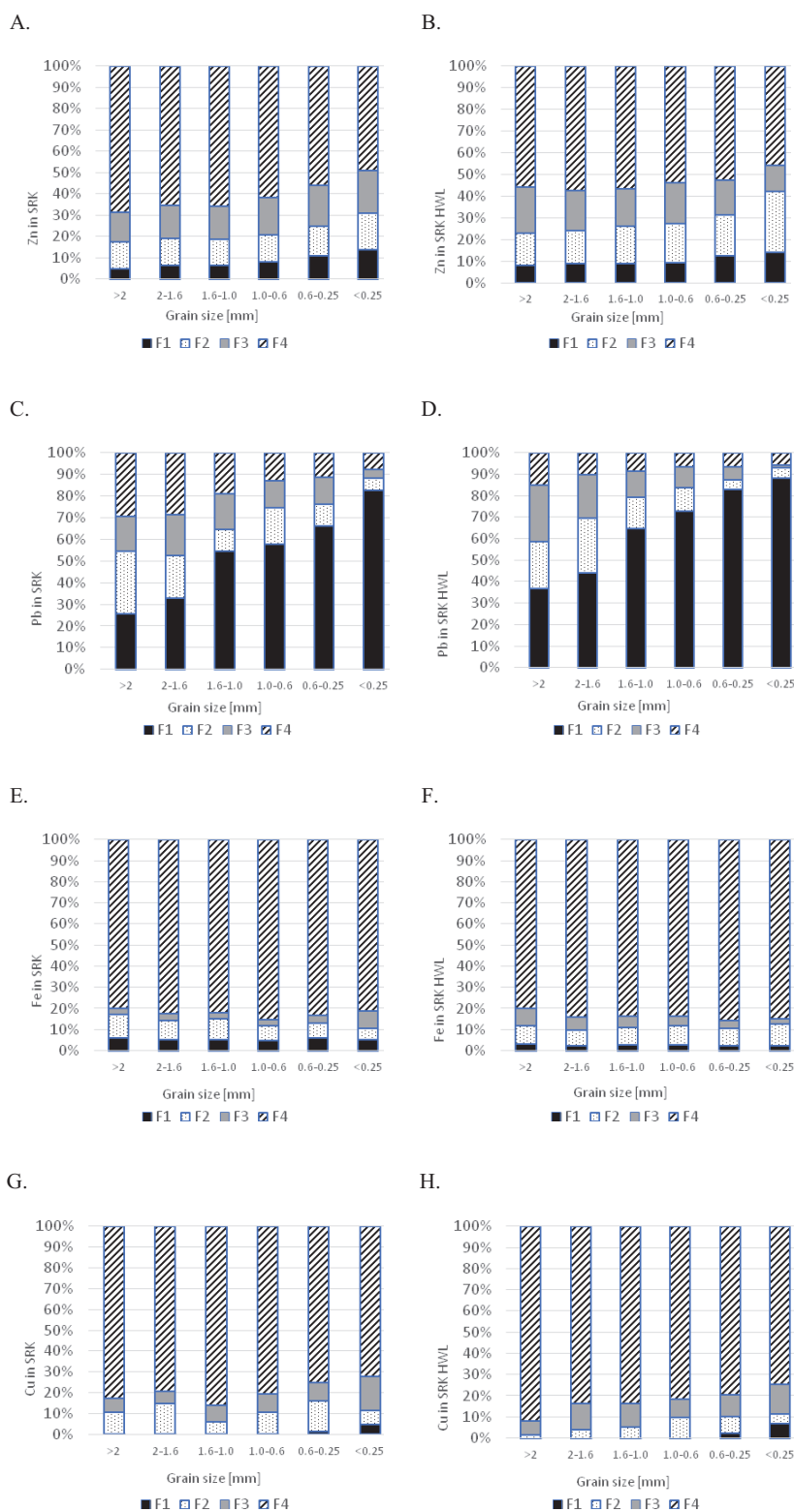


Fig. 7. Concentration of metals in the individual fractions of the SRK sample (A – Zn C – Pb E – Fe G – Cu) and the SRK HWL sample (B – Zn D – Pb F – Fe H – Cu). F1 – acid-soluble fraction, F2 – reducible fraction, F3 – oxidizable fraction, F4 – residual fraction

the negligible impact of slag disposal in a hazardous waste landfill. Nevertheless, differences in chemical composition between stored slag and production slag do appear. Such situation occurs in the case of slags that have been stored on the landfill for a prolonged period, often for a couple of years. (Jin et al. 2014).

The investigations of the slag samples revealed that Pb displayed the highest association with the mobile fractions. Notably, in the finest grain fraction, Pb in the mobile form constituted over 80% of the total metal content. The mobility of Pb in the material exhibited a strong dependence on grain size, with the proportion of the mobile form escalating as grain size decreased across both tested slags. Parallel findings from tests on Pb/Zn smelting slags, encompassing fractions < 0.75 mm, 0.075–0.15 mm, 0.15–0.25 mm, 0.25–2 mm, corroborated this observation, revealing Pb to be predominantly present in the mobile form (acid-soluble) (F1) (Xu et al. 2021). In contrast, distinct results emerged from soil samples near smelters, where Pb was predominantly found in the F2 (reducible form) (Herreweghe et al. 2003, Margui et al. 2004, Zemberyova et al. 2006). This discrepancy suggests that Pb, initially present in an acid-soluble form in smelter waste, easily transitions to the environment. Subsequently, as observed in soils, it transforms into a reducible form.

In the case of copper, the tested samples revealed that this metal is present mostly in the residual form (this fraction represents approximately 80% of the total amount in each examined size range for the SRK and SRK HWL samples). It means that a small amount of mobile form of copper found in the material or residual form under certain environmental conditions may be transferred to the environment. Many research studies show that Cu is primarily associated with the residual form (Xu et al. 2021, Luo et al. 2022).

The presence of zinc within fraction 1 (F1) did not account for a substantial proportion, remaining below 14% for both materials. There was an increase in zinc concentration in the F1 fraction as a consequence of sample grinding. Moreover, on comparison of corresponding grain sizes, the SRK HWL slag exhibited a higher zinc concentration within F1 compared to the SRK slag. Conversely, zinc associated with fraction 2 (F2) showed a markedly higher concentration in the SRK HWL slag. Fraction 3-bound zinc (F3) exhibited similar levels for both tested materials (Figure 7A,B). Such a distribution of zinc forms identified in the study is relatively infrequent in the literature. While in most cases, zinc in similar materials is primarily associated with the acid-soluble fraction (Luo et al. 2022), there are instances where research indicates zinc to be predominantly associated with residual form (Zhang et al. 2022).

While iron is not commonly a focus of sequential extraction analysis in the literature, its significance as the element with the highest percentage share in the studied material is undeniable. Notably, iron was found to predominantly exist within the residual fraction.

Conclusions

The primary conclusions can be summarized as follows:

- (1) The analyzed samples from the tested SRK and SRK HWL materials showed a wide variety of metals present, occurring in various forms. AAS

analysis of the samples after aqua regia digestion revealed four metals present in higher concentrations, with total concentrations ranked in the order Fe>Pb>Zn>Cu. In addition, other metals were detected at lower concentrations, with their prevalence following the order Na>Ca>K>Ni>Mn>Cr. X-ray photomicrography also revealed the great variability in metal concentrations across different regions of the sample.

- (2) The materials necessitated preparatory measures such as crushing, milling, sieving before processing and analysis, due to their challenging characteristics.
- (3) The sequential analysis revealed the distribution of metals across four distinct fractions: acid-soluble, reducible, oxidizable, and residual. Notably, lead exhibited a significant presence within F1 (acid-soluble), whereas iron, copper, and zinc predominantly occurred within F4 (residual) fractions.
- (4) Interpreting the results of BCR analysis across all grain size fractions posed challenges. Significant discrepancies were observed in the results of metal concentrations in the extracts, especially noticeable for the larger fractions (>2 mm, 2–1.6 mm and 1.6–1.0 mm).
- (5) The SRK and SRK HWL samples showed differences in the physical properties such as color, shine, and hardness, and in their chemical composition. The tested materials did not show a high moisture content, which was no more than 0.04% for the SRK sample and 1.22% for SRK HWL. This fact was also supported by SEM tests, which revealed the structure of the sample, such as the lack of pores and compact structure, which may prevent water retention.
- (6) The studied materials are a rich source of metals occurring in various forms. On the basis of sequential extraction, but also XRD analysis, it can be concluded that materials contain numerous mobile but also immobile forms with complex structures. However, quantification of the content of these forms is impossible for this type of materials.
- (7) The discrepancies in the properties of the two materials could be attributed to differences in production campaigns, the evolving composition of processed raw materials, and the distinct origins of the samples (one directly collected from production, the other seasoned on the landfill).

The results of the conducted study focusing on the analysis of metallurgical slags bear relevance for subsequent investigations into the presented materials. The acquired data serve as a foundational resource for exploring the viable separation of metals from these materials, a pursuit that can yield substantial economic benefits for metallurgical establishments.

This type of research concerning slags offers a comprehensive overview of landfill-stored materials, encompassing heavy metals content, their various forms of occurrence or mobility, and even potential soil contamination. The study results offer valuable insights for personnel within metallurgical plants, fostering the formulation of novel technologies for extracting valuable components like heavy metals from wastes.

Beyond the metallurgical context, these results carry significance for environmental protection and engineering fields. The study's contribution lies in the elucidation of metal mobility and, consequently, the likelihood of their introduction into the environment – an issue of widespread concern, particularly in the vicinity of smelters.

Statements and declarations

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References

- Alan, M., Kara, D. (2019). Comparison of a new sequential extraction method and the BCR sequential extraction method for mobility assessment of elements around boron mines in Turkey, *Talanta*, 194, pp. 189–198, DOI: 10.1016/j.talanta.2018.10.030.
- Baczewska, A.H., Dmochowski, W., Gworek, B., Dąbrowski, P., Brągoszewska, P. (2016). Comparison of bioindication methods for assessing the level of air pollution with heavy metals in Warsaw, *Przemysł Chemiczny*, 95/3, pp. 334–338, DOI: 10.15199/62.2016.3.1.
- Bernasowski, M., Klimczyk, A., Stachura, R. (2017). Overview of Zinc Production in Imperial Smelting Process. Iron and Steelmaking Conference 4–6.10.2017, Horní Bečva, Česká republika.
- Briffa, J., Sinagra, E., Blundell, R. (2020). Heavy metal pollution in the environment and their toxicological effects on humans, *Heliyon*, 6, 9, pp. 1–26, DOI: 10.1016/j.heliyon.2020.e04691.
- Cabała, J. (2009). Heavy metals in the soil environment of Olkusz Zn-Pb ore mining regions. Wydawnictwo Uniwersytetu Śląskiego Katowice 2009 (in Polish)
- Chao-Yin, K., Chung-Hsin, W., Shang-Lien, L. (2005). Removal of copper from industrial sludge by traditional and microwave acid extraction, *Journal of Hazardous Materials*, 120, 1–3, pp. 249–256, DOI: 10.1016/j.jhazmat.2005.01.013.
- Dan Chen, Wing Yin Aua, Stijn, A.R. van Ewijk, Stegemann, J. (2021). Elemental and mineralogical composition of metal-bearing neutralisation sludges and zinc speciation – A review, *Journal of Hazardous Materials*, 416, 2, DOI: 10.1016/j.jhazmat.2021.125676.
- Ettler, V., Bodenán, F., Legendre, O. (2001). Primary phases and natural weathering of old lead-zinc pyrometallurgical slag from Příbram, Czech Republic, *The Canadian Mineralogist*, 39, pp. 873–888, DOI: 10.2113/gscanmin.39.3.873.
- Gao, H., Koopmans, G.F. Song, J., Groenenberg, J.E., Liu, X., Comans, R.N.J., Weng, L. (2022). Evaluation of heavy metal availability in soils near former zinc smelters by chemical extractions and geochemical modelling, *Geoderma*, 423, DOI: 10.1016/j.geoderma.2022.115970.
- Herreweghe, S.V., Swennen, R., Vandecasteele, C., Cappuyns, V. (2003). Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples, *Environmental Pollution*, 122, pp. 323–342, DOI: 10.1016/S0269-7491(02)00332-9.
- Izidorczyk, G., Mikula, K., Skrzypczak, D., Moustakas, K., Witek-Krowiak, A., Chojnacka, K. (2021). Potential environmental pollution from copper metallurgy and methods of management, *Environmental Research*, 197, pp. 1–11, DOI: 10.1016/j.envres.2021.111050.
- Jin, Z., Liu, T., Yang, Y., Jackson, D. (2014). Leaching of cadmium, chromium, copper, lead, and zinc from two slag dumps with different environmental exposure periods under dynamic acidic condition, *Ecotoxicology and Environmental Safety*, 104, pp. 43–50, DOI: 10.1016/j.ecoenv.2014.02.003.
- Jonczy, I., Kamińska, M., Chwedorowicz, B., Kowalski, B. (2017). The use of X-ray Spectral Analysis in Microareas in the determination of elements accompanying minerals of Zinc-Lead Ores from the Klucze I deposit. Systemy Wspomagania w Inżynierii Produkcji Górnictwo Zrównoważonego Rozwoju 2016, P.A. Nova. (in Polish)
- Ke, W., Zeng, J., Zhu, F., Luo, X., Feng, J., He, J., Xue, S. (2022). Geochemical partitioning and spatial distribution of heavy metals in soils contaminated by lead smelting, *Environmental Pollution*, 307, pp. 1–11, DOI: 10.1016/j.envpol.2022.119586.
- Król, A., Mizerna, K., Bożym, M. (2020). An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag, *Journal of Hazardous Materials*, 384, 121502, pp. 1–9, DOI: 10.1016/j.jhazmat.2019.121502.
- Kruk, M. (2022). Comparison of digestion methods of slag samples from zinc and lead industry to identify the content of selected metals. *ArchaeGraph. Łódź 2022* (in Polish)
- Lestari, F. Budiyo, Hindarti, D. (2018). Speciation of heavy metals Cu, Ni and Zn by modified BCR sequential extraction procedure in sediments from Banten Bay, Banten Province, Indonesia, *IOP Conference Series: Earth and Environmental Science*, 118, 1, pp. 1–7, DOI: 10.1088/1755-1315/118/1/012059.
- Li, L., Zhang, Y., Ippolito, J.A., Xing, W., Qiu, K., Yang, H. (2020). Lead smelting effects heavy metal concentrations in soils, wheat, and potentially humans, *Environmental Pollution*, 257, pp. 1–7, DOI: 10.1016/j.envpol.2019.11361.
- Li, Y., Perederiy, I., Papangelakis, V.G. (2008). Cleaning of waste smelter slags and recovery of valuable metals by pressure oxidative leaching, *Journal of Hazardous Materials*, 152, pp. 607–615, DOI: 10.1016/j.jhazmat.2007.07.052.
- Luo, S., Zhao, S., Zhang, P., Li, J., Huang, X., Jiao, B., Li, D. (2022). Co-disposal of MSWI fly ash and lead-zinc smelting slag through alkali-activation technology, *Construction and Building Materials*, 327, pp. 1–10, DOI: 10.1016/j.conbuildmat.2022.127006.
- Margui, V. Salvado, Queralt, I., Hidalgo, M. (2004). Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes, *Analytica Chimica Acta*, 524, pp. 151–159, DOI: 10.1016/j.aca.2004.05.043.
- Nowińska, K., Adamczyk, Z. (2013). The mobility of accompanying elements to wastes from metallurgy of the zinc and the lead in the environment, *Górnictwo i Geologia*, T. 8, z. 1, pp. 77–87. (in Polish)
- Nowińska, K., Adamczyk, Z. (2017). Slags of the Imperial Smelting Process for Zn and Pb production, *Reference Module in Materials Science and Materials Engineering*, pp. 1–5, DOI: 10.1016/B978-0-12-803581-8.03607-9.
- Pan, D. a., Li, L., Tian, X., Wu, Y., Cheng, N., Yu, H. (2019). A review on lead slag generation, characteristic, and utilization, *Resources, Conservation & Recycling*, 146, pp. 140–155, DOI: 10.1016/j.resconrec.2019.03.036.
- Patle, A.R., Kurrey, M.K. Deb, Patle, T.K., Sinha, D., Shrivastava, K. (2022). Analytical approaches on some selected toxic heavy metals in the environment and their socio-environmental impacts: A meticulous review, *Journal of the Indian Chemical Society*, 99, pp. 1–12, DOI: 10.1016/j.jics.2022.100545.
- Rauret, G., Lopez-Sanchez, J., Luck, D., Yli-Haila, M., Muntau, H., Quevauviller, P. (2001). EUR 19775 EN. E. Commission. Belgium.

- Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P. (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, *Journal of Environmental Monitoring*, 1, pp. 57–61. DOI: 10.1039/a807854h
- Róžański, S. (2013). Fractionation of selected heavy metals in agricultural soils, *Ecological Chemistry and Engineering S*, 20, 1, pp. 117–125, DOI: 10.2478/eces-2013-0009.
- Seigneur, N., Bulteel, D., Damidot, D., Gauthier, A., Potdevin, J.-L. (2006). Weathering of metallurgical slag heaps: multi-experimental approach of the chemical behaviours of lead and zinc, *Waste Management and the Environment III*, 92, pp. 31–40, DOI: 10.2495/WM060041.
- Singh, A. and Chandel, M.K. (2022). Mobility and environmental fate of heavy metals in fine fraction of dumped legacy waste: Implications on reclamation and ecological risk, *Journal of Environmental Management*, 304, pp. 1–11, DOI: 10.1016/j.jenvman.2021.114206.
- Singh, G., Das, S., Ahmed, A.A., Saha, S., Karmakar, S. (2015). Study of Granulated Blast Furnace Slag as Fine Aggregates in Concrete for Sustainable Infrastructure, *Procedia – Social and Behavioral Sciences*, 195, pp. 2272–2279, DOI: 10.1016/j.sbspro.2015.06.316.
- Sobanska, S., Deneele, D., Barbillat, J., Ledesert, B.A. (2016). Natural weathering of slags from primary Pb-Zn smelting as evidenced by Raman microspectroscopy, *Applied Geochemistry*, 64, pp. 107–117, DOI: 10.1016/j.apgeochem.2015.09.011.
- Tlustos, P., Szakova, J., Starkova, A., Pavlikova, D. (2005). A comparison of sequential extraction procedures for fractionation of arsenic, cadmium, lead, and zinc in soil, *Central European Journal of Chemistry*, 3, 4, pp. 830–851, DOI: 10.2478/BF02475207.
- Wali, A., Colinet, G., Ksibi, M. (2014). Speciation of Heavy Metals by Modified BCR Sequential Extraction in Soils Contaminated by Phosphogypsum in Sfax, Tunisia, *Environmental Research, Engineering and Management*, 4, 70, pp. 14–26, DOI: 10.5755/j01.erem.70.4.7807.
- Wang, J., Jiang, Y., Sun, J., She, J., Yin, M., Fang, F., Xiao, T., Song, G., Liu, J. (2020). Geochemical transfer of cadmium in river sediments near a lead-zinc smelter, *Ecotoxicology and Environmental Safety*, 196, pp. 1–10, DOI: 10.1016/j.ecoenv.2020.110529.
- Warchulski, R., Szopa, K. (2014). Phase composition of Katowice – Wełnowiec pyrometallurgical slags: preliminary SEM study, *Contemporary Trends in Geoscience*, 3, pp. 76–81, DOI: 10.2478/ctg-2014-0025.
- Xu, D.-M., Fu, R.-B., Tong, Y.-H., Shen, D.-L., Guo, X.-P. (2021). The potential environment risk implications of heavy metals based on their geochemical and mineralogical characteristic in the size-segregated zinc smelting slags, *Journal of Cleaner Production*, 315, pp. 1–13, DOI: 10.1016/j.jclepro.2021.128199.
- Yin, N.-H., Sivry, Y., Guyou, F., Lens, P.N.L., v. Hullebusch, E.D. (2016). Evaluation on chemical stability of lead blast furnace (LBF) and imperial smelting furnace (ISF) slags, *Journal of Environmental Management*, 180, pp. 310–323, DOI: 10.1016/j.jenvman.2016.05.052.
- Zemberyova, M., Bartekova, J., Hagarova, I. (2006). The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins, *Talanta*, 70, pp. 973–978. DOI: 10.1016/j.talanta.2006.05.057.
- Zhang, S., Zhu, N., Shen, W., Wei, X., Li, F., Ma, W., Mao, F. and Wu, P. (2022). Relationship between mineralogical phase and bound heavy metals in copper smelting slags, *Resources, Conservation & Recycling*, 178, pp. 1–7, DOI: 10.1016/j.resconrec.2021.106098.