LEACHING OF WASTE SLAGS FROM COPPER SMELTING PROCESSES

Jakub Zieliński[1], Patrycja Chodorowska[1], Dominik Nieweś[1], Mariusz Kowalski[2], Józef Hoffmann[1]

[1]*Department of Engineering and Technology of Chemical Processes*
Faculty of Chemistry, Wroclaw University of Science and Technology
27 Wybrzeże Wyspiańskiego St., 50-370 Wrocław, Poland, jakub.zielinski@pwr.edu.pl (J.Z.);
240366@student.pwr.edu.pl (P.C.); dominik.niewes@pwr.edu.pl (D.N.); jozef.hoffmann@pwr.edu.pl (J.H.)
[2]*KGHM Polska Miedź S.A. Huta Miedzi „Głogów"*
1 Żukowicka St., 67-200 Głogów, Poland, m.kowalski@kghm.com (M.K.)

Received 11 January 2024
Accepted 20 March 2024 *DOI: 10.59957/jctm.v60.i1.2025.14*

ABSTRACT

The experiments were carried out to examine the possibility of utilizing waste slags generated in fire smelting processes. Metallurgical slags - Fe-As Alloy, Lead Slag and Ground Pb Slag were subjected to leaching with nitric acid with varying concentrations, at 100°C for 1 h under atmospheric pressure. The possibility to recover iron, copper, lead, cadmium, cobalt and molybdenum was examined. Elements with high enough content in raw material can be successfully leached and the plateau of leaching efficiency is reached with 55 wt. % nitric acid in most cases and is recommended for this process. If iron is not targeted for leaching even as low as 30 wt. % nitric acid can be used while maintaining high leaching.

Keywords: waste slags, waste slags leaching, copper smelting processes.

INTRODUCTION

Metallurgy is an economic sector that produces a considerable amount of waste, mainly various types of slags. Waste is accumulated in heaps, although more and more often is being explored for economic use, especially in the production of aggregates [1].

Metallurgical slags, as a by-product of smelting, reflect the processed material, processing method and the conditions in the furnace [2]. They represent one of the most diverse groups of waste materials. Their chemical composition varies, depending on the type of raw materials used in the metallurgical process. The complex nature of the input affects the chemical composition of the final product, thereby also the chemical composition of waste material generated in parallel, which is mainly metallurgical slag [3].

The copper production begins in the mine, from where the ore undergoes an enrichment process. Ores with a copper content of about 1 wt. % are ground into particles sufficiently fine to separate valuable mineral grains from the waste rock by flotation. This stage results in a copper concentrate (copper content of 13 - 25 wt. %) that is then melted at 1200 - 1300°C forming blister copper and slurry slag [4]. The slurry slag is used to produce Cu-Pb-Fe alloy and de-copperized slag.

Produced slags might be either internal recycling streams or final waste products. In some cases, when the content of significant elements (copper, silver, lead) is sufficiently high, they are treated by slow cooling, grinding and froth-flotation. After granulation they can be recycled to production process. Other methods of processing slags include hydrometallurgical treatment, including direct leaching in sulphuric acid or ferric chloride as well as roasting of the slag with sulphuric acid and ammonium sulphate [5, 6]. Effects of varying parameters such as temperature, acid concentration, ferrous sulphate concentration, ultrasonic energy, and time on copper dissolution from Lead Slag were previously investigated [7].

The chemical composition of slags is one of the most important aspects to which attention should be paid during their economic exploitation. Research on the physical properties of slags showed that these materials often can be used in the construction industry. However, many other possibilities of slag utilisation also require research in terms of its heavy metals content as the release into the environment of material with such complex chemical composition as slag may be a potential source of pollution [2].

Slags are characterized by a diverse and abundant phase composition, which can change over time due to landfill disposal. It is possible to find components that have their analogues among naturally occurring minerals. In such cases the metallurgical process is often compared to a natural magma process in which individual phases crystallise at a specific temperature and in a specific sequence [8].

Considerable amounts of value metals, including cobalt, nickel, and copper, can be found in low-grade metallurgical wastes. Those wastes reach thousands of tons of annual volume in copper smelters. Currently, economic and environmental demands are forcing the development of efficient and cheap methods to recover valuable metals from secondary sources [5]. Attempts are made to recover metals from metallurgical wastes originating from on-going production [9]. Besides the economic benefits, the environmental requirements will increase the need for further product development to follow the principles of sustainability. Slag production and utilization are now one of the most important indicators for the sustainable industry [10].

Copper is the fifth most widely used metal with total global smelting production of around 24.5 million metric tons in 2020. Production of this valuable metal is not expected to decline in the future, given its wide application and unique characteristic. High demand for copper favours the extraction of primary raw materials, which causes many environmental issues [11].

Lead is usually present in copper ore in large amount. Consequently, its content in copper concentrates of KGHM Polska Miedź S.A. can reach up to 4 %, depending on the raw material used. Due to the specific properties of compounds, it forms, lead is mainly concentrated in by-products of the smelting processes - dust and sludge from the dedusting of smelter gases.

These materials have been the source of the recovery of this metal carried out at the Lead Division of the Głogów smelter since 1973, while for several years the main feedstock has been the post-reduction converter slag produced from converting the alloy from the electric furnace. The basis of the technology for recovering lead from the by-products of copper pyrometallurgical processes is reduction smelting in rotary furnaces called Dörschl furnaces. This is a batch process and consists of a stage of charging, drying, roasting, melting and smelting the metallic lead. The material from the furnace after the process is poured into vats where the raw lead is sedimented [12, 13].

Natural resources of metals available to humanity will soon not be enough to fulfil the demand. As an alternative source to meet the future demand for some metals, various secondary raw materials such as lead slag, zinc ash, flue dusts of an electric arc furnace, leaching residues, etc. may be considered. Lead slag can be considered an important secondary source because each year the industry discharges tons of slag containing 5 - 10 % Zn, 1 - 8 % Pb and other less valuable elements. These slags not only occupy valuable lands but also threaten the environment [14].

Removal of heaps and utilization of metallurgical slags, among others, for production of aggregates, combine both ecological and economical aspects. However, it should be considered that this material may contain considerable amounts of metals, including heavy metals. Therefore, it is important to know the chemical composition of slags to use them in an environmentally safe way [9].

Sustainable development is becoming an important objective for an increasing number of industries and governments. Consequently, the focus has shifted from the manufacturing process to the complete life cycle. Minimizing the impact on the environment, together with more efficient waste control is one of the most crucial goals of mining producers. There is growing pressure on the mining industry worldwide to minimize the ecological impact of mining operations [15]. The metallurgical industry, including copper smelters, generate thousands of tons of low-quality metallurgical waste each year, which contains considerable amounts of lead, nickel, and cobalt. The development of efficient and affordable methods for recovering metals from secondary sources is essential [5].

EXPERIMENTAL

Materials

For this research Fe-As Alloy, Lead Slag and Ground Pb Slag were obtained from the Lead Department of Głogów Copper Smelter KGHM Polska Miedź S.A. Content of selected elements in studied materials is presented in Table 1.

For leaching of tested materials nitric acid with varying concentration was used. This acid was chosen as the effect of different acids, i.e., sulphuric acid, nitric acid and hydrochloric acid, on leaching cobalt, cadmium and molybdenum from similar materials was investigated prior to this research. Results of this research is presented in Table 2. It was assumed that the use of nitric acid with no addition at different concentrations could give the best results for leaching of selected elements.

Research methodology

About 5 g of tested material was weighted to a reaction tube. Then about 50 cm^3 of nitric acid of selected concentration ranging from 30 wt. % to 65 wt. % was added to the flask. Samples were then heated for 1 hour at 100°C under atmospheric pressure in the KJELDATHERM Block Digestion Unit. After heating, samples were cooled and filtered. Solid phase filtered out was additionally rinsed several times with distilled water. Filtrate together with the rinsing distilled water were collected in volumetric flasks. Resulting samples were subjected to further examination by flame atomic absorption spectrometry (FAAS). The Thermo Scientific ICE 3000 Series instrument with a 50 mm universal burner was used to measure content of iron, copper, lead, cadmium, cobalt and molybdenum in the samples.

The research methodology is schematically presented in Fig. 1.

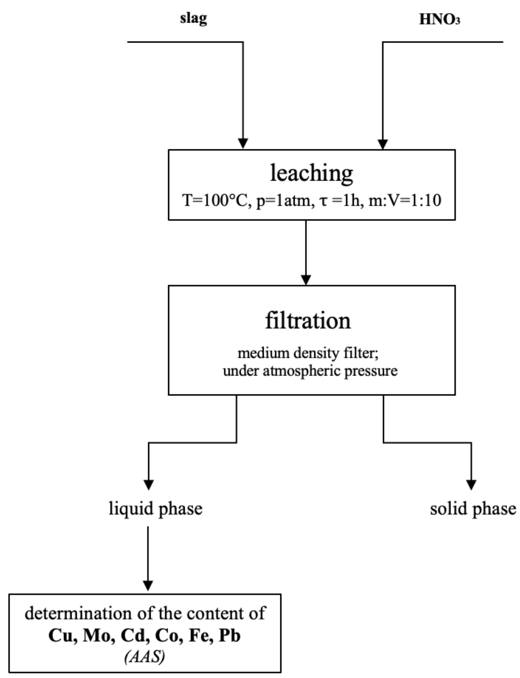

Fig. 1. Scheme of research methodology.

Table 1. Content of selected elements in the studied slags.

	Cu, wt. %	Mo, wt. %	Cd, wt. %	Co, wt. %	Fe, wt. %	Pb, wt. %
Fe-As alloy	9.22	0.33	0.53	0.78	44.45	4.96
Lead Slag	2.11	0.09	1.30	0.32	27.35	3.24
Ground Pb Slag	2.29	0.05	0.03	0.13	20.03	3.58

Table 2. Leaching efficiency of selected elements from two slag samples depending on the type of acid or mixture of acids used.

	Slag 1 leaching efficiency, %			Slag 2 leaching efficiency, %		
	Co	Cd	Mo	Co	Cd	Mo
H_2SO_4	33.16	26.91	-	1.55	15.59	-
HNO_3:HCl (1:1)	83.92	92.04	85.51	77.03	83.13	46.97
HNO_3:HCl (3:7)	83.14	96.67	63.46	94.69	81.95	40.49
HNO_3:HCl (7:3)	93.89	96.97	85.17	99.8	90.4	46.64

RESULTS AND DISCUSSION

Material balances for each experiment are presented in Table 3. Content of selected elements in liquid phase as obtained from AAS analysis and content in solid residue calculated from mass balance are presented in Table 4.

The leaching efficiency, Y for each element was calculated from the formula:

$$Y = \frac{m_{\mathrm{liquid}}}{m_0} \cdot 100\ \% = \frac{m_{\mathrm{liquid}}}{M_{\mathrm{slag}} \cdot \frac{c_0}{100}} \cdot 100\ \% \quad (1)$$

Where Y - leaching efficiency, %; m_{liquid} - mass of selected element in the liquid phase after leaching, mg; m_0 - mass of selected element in the slag used in the experiment, mg; M_{slag} - mass of slag added, mg; c_o - content of selected element in the slag used in the experiment, wt. %.

Leaching efficiencies for selected elements in studied slag samples are presented graphically in Fig. 2 - 4.

In liquid phases after leaching there is great amount of iron (500 - 2000 mg depending on slag used) which was to be expected due to its large content in raw materials (20 - 45 wt. %). Conducted experiments show that the concentration of iron in solid residue is very similar to the content in raw materials (20 - 45 wt. %). This corresponds to high leaching efficiencies for each studied slag. For Fe-As alloy leaching efficiency of iron is not affected by nitric acid concentration used for process and is about 85 %. For both Lead Slag and Ground Pb Slag leaching efficiency of iron is highest for nitric acid concentration

Table 3. Material balances of performed experiments.

Slag	Exp. no.	Nitric acid concentration, wt.%	Slag mass, g	Nitric acid mass, g	Rinsing water mass, g	Solid residue mass, g	Liquid phase mass, g
Fe-As alloy	1	30	4.9974	58.9675	23.9643	0.8476	85.3825
	2	35	5.0010	60.6613	20.2935	0.8249	83.4991
	3	40	4.9903	62.3489	21.2962	0.7965	86.1948
	4	45	5.0042	63.9366	18.5069	0.7619	85.1070
	5	50	4.9481	65.4868	23.5256	0.6597	91.9094
	6	55	4.9879	66.9643	24.5085	0.7205	94.2911
	7	60	5.0149	68.2789	30.5372	0.7488	101.5005
	8	65	5.0171	69.5704	22.9765	0.7156	95.4372
Lead Slag	9	30	5.0228	59.0102	36.2599	3.7402	89.1254
	10	35	5.0023	60.7228	37.2523	3.5360	92.4374
	11	40	5.0053	62.2854	44.1102	3.0962	102.1052
	12	45	4.9407	63.9481	33.5449	2.9496	93.5838
	13	50	4.9526	65.5252	21.0427	2.8842	82.8638
	14	55	4.9774	66.9604	29.5624	2.7698	93.2559
	15	60	5.0133	68.2957	31.4790	2.7360	96.6659
	16	65	5.0397	69.5774	29.3866	2.8013	95.6947
Ground Pb Slag	17	30	5.0301	59.0100	43.3763	2.7507	99.0884
	18	35	5.0479	60.6606	32.0287	2.2948	90.8909
	19	40	5.0233	62.3370	35.7101	1.8514	97.5961
	20	45	4.9771	63.8906	43.7110	1.6573	107.6557
	21	50	5.0142	65.5105	45.4791	1.5431	111.3746
	22	55	5.0204	66.9797	37.3315	1.4924	104.7935
	23	60	5.0111	68.3043	40.7269	1.5960	109.3372
	24	65	5.0285	69.5112	45.2903	1.7682	114.5504

Table 4. Content of selected elements in liquid phase and solid residue after leaching of studied slags with nitric acid.

Exp.	Content in liquid phase, mg						Content in solid residue, mg					
no.	Cu	Mo	Cd	Co	Fe	Pb	Cu	Mo	Cd	Co	Fe	Pb
1	426	14.6	0.630	15.7	1893	81.4	34.6	1.88	25.9	23.3	329	11.5
2	434	13.0	0.625	15.7	1901	81.8	27.4	3.51	25.9	23.3	322	11.2
3	439	12.3	0.609	15.7	1906	82.8	21.2	4.12	25.8	23.2	312	10.1
4	445	11.9	0.621	15.6	1924	83.5	16.0	4.62	25.9	23.4	300	9.54
5	444	11.3	0.612	15.7	1944	82.8	12.3	5.06	25.6	22.9	255	9.23
6	450	10.9	0.604	15.7	1931	83.5	10.1	5.56	25.8	23.2	287	9.32
7	453	10.8	0.600	15.7	1928	85.2	8.88	5.73	26.0	23.4	301	8.11
8	456	11.5	0.591	15.8	1939	86.0	6.42	5.08	26.0	23.4	291	7.30
9	14.3	1.07	0.473	1.58	426	41.3	91.7	3.45	64.8	14.5	948	121
10	16.8	1.09	0.528	1.66	478	41.9	88.7	3.41	64.5	14.3	890	120
11	19.3	1.36	0.652	2.03	609	55.7	86.3	3.14	64.4	14.0	760	106
12	21.0	1.33	0.693	2.07	634	59.0	83.2	3.11	63.5	13.7	717	101
13	21.8	1.17	0.704	2.14	656	59.9	82.7	3.28	63.7	13.7	699	101
14	22.2	1.53	0.717	2.17	699	64.7	82.8	2.95	64.0	13.8	662	96.5
15	23.1	1.30	0.755	2.20	719	67.2	82.7	3.21	64.4	13.8	652	95.2
16	23.7	0.973	0.738	2.10	710	64.2	82.6	3.56	64.8	14.0	668	99.0
17	49.3	1.41	0.984	4.45	448	123	65.9	1.11	0.525	2.08	559	57.5
18	48.8	1.39	1.14	5.16	544	144	66.8	1.13	0.377	1.40	467	36.3
19	48.2	2.03	1.32	5.84	622	170	66.8	0.480	0.189	0.695	384	9.79
20	47.7	2.05	1.35	5.94	655	173	66.3	0.441	0.139	0.531	342	5.43
21	47.5	1.94	1.39	6.01	691	175	67.3	0.572	0.115	0.505	313	4.40
22	47.2	1.95	1.40	6.05	704	176	67.8	0.556	0.104	0.473	301	3.27
23	46.8	1.67	1.35	5.83	677	178	67.9	0.836	0.153	0.686	327	1.70
24	46.0	2.12	1.25	5.61	637	180	69.1	0.395	0.255	0.930	370	0.180

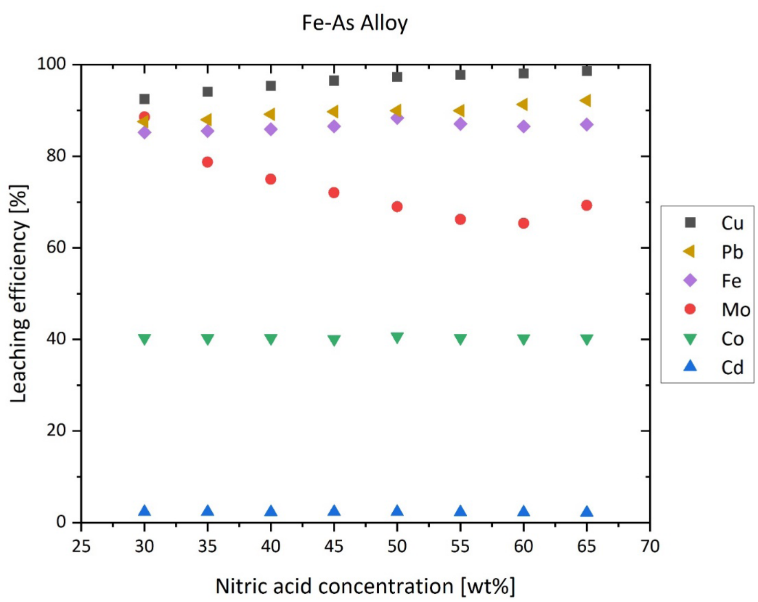

Fig. 2. Leaching efficiency of selected elements from Fe-As alloy versus nitric acid concentration used for leaching.

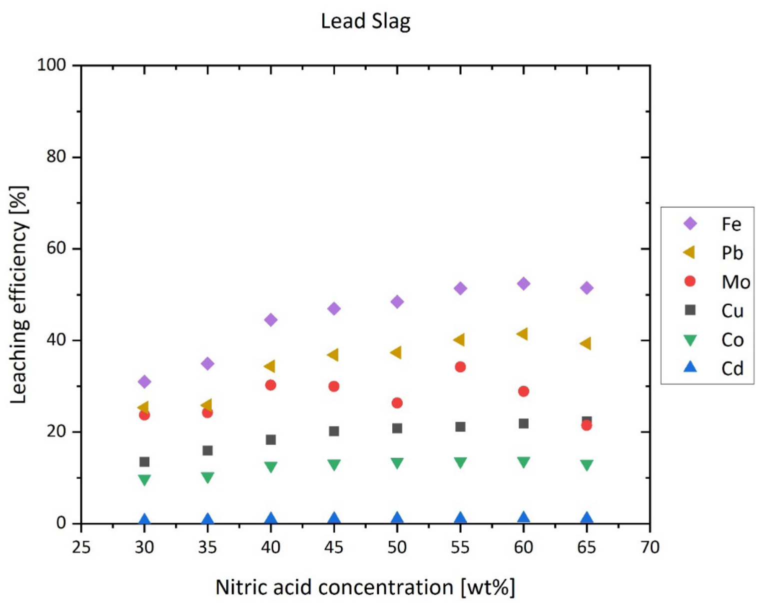

Fig. 3. Leaching efficiency of selected elements from Lead Slag versus nitric acid concentration used for leaching.

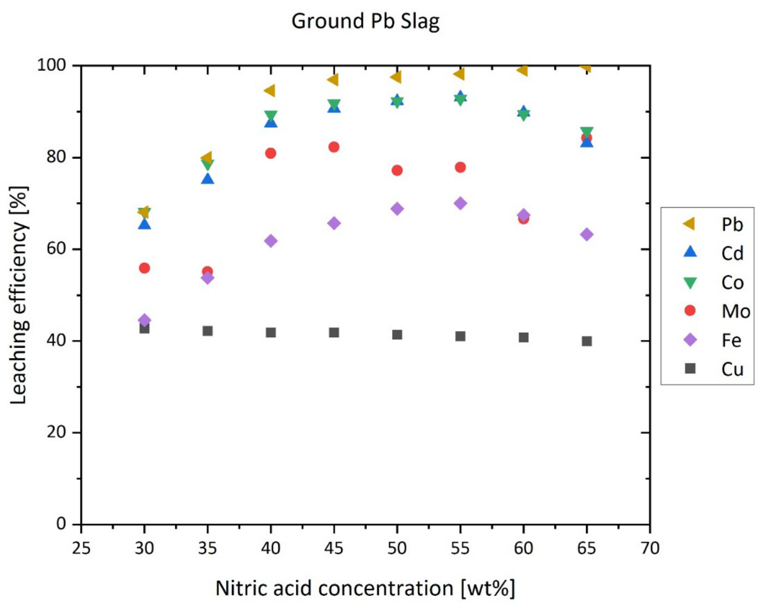

Fig. 4. Leaching efficiency of selected elements from Ground Pb Slag versus nitric acid concentration used for leaching.

of about 55 wt. % and amounts to about 50 % and 70 % respectively.

For copper leaching efficiency from Fe-As Alloy is the highest and increase for more concentrated nitric acid used for leaching up to 99 % for 65 wt. % nitric acid. For Lead Slag and Ground Pb Slag however, the leaching efficiency of copper is much lower - about 20 % and 40 % respectively. The effect of increasing nitric acid concentration in both cases is the same as for Fe-As alloy.

Lead can also be leached from each studied slag with high efficiency. For Ground Pb Slag a sharp increase in leaching efficiency is observed for 40 wt. % nitric acid and beyond. Up to 99 % leaching efficiency can be achieved. Similar trend is observed for Fe-As alloy, however the increase is not so sharp and about 90 %

efficiency is achieved even for 30 wt. % nitric acid. Leaching of Lead Slag is the least efficient from the three studied slags and amounts up to about 40 % for highest concentration of nitric acid used.

Leaching of other selected elements from studied slags is less efficient, however their content in raw materials is also significantly smaller. For cadmium in particular leaching from Fe-As Alloy and Lead Slag has 1 - 2 % efficiency. For Ground Pb Slag the efficiency is higher and amounts to about 90 % for 55 wt. % nitric acid. This can be due to small cadmium content in the raw material itself (0.03 wt. %). In every experiment only about 1 mg of cadmium was leached to liquid phase while the rest stayed within solid residue.

For cobalt leaching similar effect can be observed. For Fe-As alloy the leaching efficiency for each experiment is almost constant (about 40 %). For Lead Slag higher leaching efficiencies are observed for more concentrated nitric acid used for leaching (10 - 15 %). Ground Pb Slag can be leached from cobalt most efficiently (up to about 93%), however the cobalt content in this raw material was the smallest (0.13 wt. %).

Content of molybdenum in studied slags was the lowest - 0.33 wt. %, 0.09 wt. % and 0.05 wt. % for Fe-As Alloy, Lead Slag and Ground Pb Slag respectively. This corresponds to the least obvious trends in leaching efficiencies. It seems that for each material tested leaching efficiency is high, however the amounts of molybdenum in liquid phase are very small (0.5 - 15 mg).

CONCLUSIONS

Slags produced in copper concentrate smelting processes can have high content of several valuable elements that can be recovered. Currently those materials are most commonly stored in heaps and therefor have negative influence on environment as well as economical balance of the company. Consequently, producers look for methods of utilizing those materials. The most common processing method of slags present in the literature is chemical leaching. However, Głogów Copper Smelter KGHM Polska Miedź S.A. does not currently have a slag leaching technological process.

Nitric acid can be used as effective agent for leaching of smelter slags. Higher concentration of nitric acid used usually mean higher leaching efficiency. However, it may not be viable in every case to use highest available concentration of nitric acid from economical point of view.

Leaching efficiency of selected elements from materials studied in this research reached plateau with nitric acid concentration of about 55 wt. % and is recommended for leaching. If iron is not targeted for leaching even as low as 30 wt. % nitric acid can be used while maintaining high leaching efficiency of other elements.

Liquid phase after leaching and filtration of the solid residue can be then easily concentrated and used to recover selected elements from the concentrate.

Acknowledgments

This research was funded by the Ministry of Science and Higher Education of Poland within a frame of science subsidy for 2023 which was realized in the Department of Engineering and Technology of Chemical Processes, Wroclaw University of Science and Technology (no. 8211104160 - K24W03D05). Special thanks to KGHM Polska Miedź S.A. Huta Miedzi „Głogów" for providing materials for the research and expert opinion during preparation of the manuscript.

Authors' contributions: J.Z.: Methodology, Formal Analysis, Visualization, Writing - Original Draft Preparation; P.C.: Investigation, Writing - Original Draft Preparation; D.N.: Conceptualization, Validation; J.H.: Resources, Writing - Review, Editing; M.K.: Project Administration, Supervision.

REFERENCES

1. I. Jonczy, Charakterystyka mineralogiczno-chemiczna szkliw z żużli hutniczych, Gospodarka Surowcami Mineralnymi, 27, 1, 2011, 155-163, (in Polish).
2. M. Pearce, S. Merkel, A. Hauptmann, F. Nicolis, The smelting of copper in the third millennium cal BC Trentino, north-eastern Italy, Archaeological and Anthropological Sciences, 14, 10, 2022, 1-21.
3. I. Jonczy, L. Lata, Charakterystyka składu chemicznego żużli konwertorowych i wielkopiecowych, Górnictwo i Geologia, 8, 4, 2013, 51-61, (in Polish).
4. S. Mohaddes Khorassani, C. Siligardi, C. Mugoni, M. Pini, G.M. Cappucci, A.M. Ferrari, Life cycle

assessment of a ceramic glaze containing copper slags and its application on ceramic tile, Int. J. Appl. Ceram. Technol., 17, 1, 2020, 42-54.
5. E. Rudnik, L. Burzyńska, W. Gumowska, Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag, Minerals Engineering, 22, 1, 2009, 88-95.
6. R.T. Jones, D.A. Hayman, G.M. Denton, Recovery of cobalt, nickel, and copper from slags, using DC-arc furnace technology, International Symposium on Challenges of Process Intensification, 35th Annual Conference of Metallurgists, Montreal, Canada, 1996.
7. U. Yuksel, İ. Teğin, R. Ziyadanogullari, Recovery of Copper and Cobalt from Copper Slags as Selective, Journal of Environmental Science and Engineering A, 6, 8, 2017, 388-394.
8. I. Jonczy, M. Kamińska, K. Bilewska, Fazy siarczkowe i siarczanowe w żużlach hutniczych, Archiwum Gospodarki Odpadami i Ochrony Środowiska, 20, 1, 2018, 1-10, (in Polish).
9. I. Jonczy, Forms of Occurrence of Selected Metals in Metallurgical Slags in Comparison with their Geochemical Properties, Mineral Resources Management, 28, 1, 2012, 63-75.
10. M.H. Joulazadeh, F. Joulazadeh, Slag; Value added steel industry byproducts, Archives of Metallurgy and Materials, 55, 4, 2010, 1137-1145.
11. D. Oráč, J. Klimko, D. Klein, J. Pirošková, P. Liptai, T. Vindt, A. Miškufová, Hydrometallurgical Recycling of Copper Anode Furnace Dust for a Complete Recovery of Metal Values, Metals, 12, 1, 2022.
12. J. Stec, Monografia KGHM Polska Miedź S.A., CBPM „Cuprum" Sp. z o.o., Lubin, Poland, 2007, 801-802.
13. G. Schroeder, Środowisko I Przemysł, Poznań, Cursiva, 2013, (in Polish).
14. Y. Zheng, W. Liu, W. Qin, Y. Kong, H. Luo, J. Han, Mineralogical Reconstruction of Lead Smelter Slag for Zinc Recovery, Separation Science and Technology, 49, 5, 2014, 783-791.
15. M. Góralczyk, J. Kulczycka, LCC application in the Polish mining industry, Management of Environmental Quality, 16, 2, 2005, 119-129.