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THE RELEASE OF LEACHABLE CONSTITUENTS FROM COPPER SLAG DEPENDING ON CONDITIONS OF THE LEACHING PROCESS

UWALNIANIE WYMYWALNYCH SKŁADNIKÓW Z ŻUŻLA POMIEDZIOWEGO W ZALEŻNOŚCI OD WARUNKÓW PROCESU WYMYWANIA

Abstract: The research on leaching of waste components is one of the methods for assessing the level of their contamination by soluble forms of heavy metals. The process of leaching depends on several factors, which change can cause a release of contaminants at different levels. The study presents the results on leaching of Cl^-, SO_4^{2-}, Fe, Na, K and heavy metals (Pb, Cd, Ni, Zn, Cu, Cr) from copper slag, which depends on the pH level of the eluent being used in the research. The research on leaching of heavy metals was also performed at various ratio of liquid to solid (L/S = 10 and 100 dm^3/kg) and with using a waste with different sizes of the fraction. There was also analysed the total content of heavy metals in the waste. The highest leaching of Cl^-, Cr, Ni, Cu, Pb and Zn was observed with the eluent pH level of 13. Waste grain reduction to the size of < 0.125 mm has caused an increase in the release of copper and zinc into the aqueous phase.

Keywords: cooper slag, leaching, heavy metals

Introduction

Mining of copper ore and its processing are inseparably associated with the impact on the natural environment. Copper metallurgy is a branch of industry, producing a diverse range of wastes. There can be included, among others, flotation tailings wastes, smelter slags, dusts from dedusting dust-containing gases and sludge from wastewater treatments. Certain wastes are reused in a production process, and some of

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them are used in various sectors of the economy. The waste, which cannot be reused in any other manner is deposited in waste landfills, which are specially designated for this purpose. Such action is within the line of the concept of sustainable development, and safety for environment is one of the principles for rational management of industrial wastes.

During copper smelting in electric or shaft kilns, the so-called (lump or granulated) copper slag is formed. For more than 40 years, the lump copper slag is used for production of road aggregates. This waste is poured on heaps, where after crystallization is processed into aggregate that is used for substructures and grits for upper layers of roads. Granulated copper slag is used as an abrasive to clean metal parts and as a material for backfilling former mine excavations. Due to the works, leading to introduce technologies of (electric) suspension roasters instead of shaft kilns, undertaken by the Polish steel industry, there will cause a raise in copper production, and thus, an increase of the quantity of slag being produced from electric furnace [1, 2]. Therefore, some attempts were made to use this waste as a raw material for production of hydraulic binders [3, 4].

Industrial waste placed in slag heaps or landfills can affect the soil-water environment. Contaminants contained therein can be leached into the soil and then get into the surface and underground waters. Leaching of constituent from waste may depend on the influence of different weather conditions [5]. The mobility of harmful substances is most frequently determined by the fundamental leaching test comprising of a single 24-hour extraction with a ration of liquid to solid applied in the test, amounting to L/S = 10 dm^3/kg [6]. This method is utilized in Poland, inter alia, for the purpose of identifying the possibilities of disposing wastes in landfills of a given type. The criteria for waste acceptance at landfills are governed by the Council Decision of 19 December 2002 (2003/33/EC) [7]. This document specifies admissible limit values of leaching particular waste components. When performing the test on leaching contaminants from waste materials, the conditions in which the process is carried out are of special meaning. A change made in the laboratory conditions can impact on the level of contaminants' release. In case of heavy metals, their solubility depends on the pH of the eluent with which the waste is in contact [8]. Zink, nickel and lead are generally characterized by the lowest leachability at the pH ranging from 7 to 10, depending on the test material. Chromium occurring in the form of anion has the lowest leachability at the pH within the range of 5–7. This is caused by the fact that the test materials have varying capacities to neutralize the acids or alkalis.

The paper presents test results on the leachability of contaminants from lump copper slag in terms of its impact on the environment. There were implemented changes in conditions for performing the process of leaching, involving the application of leachant having various pH levels. Additionally, there was performed analysis of concentrations of selected heavy metals (Pb, Cd, Ni, Zn, Cu, and Cr) in the waste and in water extracts prepared from two slag fractions with grain size of < 10 mm and < 0.125 mm and at the ratio of L/S = 10 and 100 dm^3/kg.

Material and methods

As the research material was used lump copper slag from smelting copper with code 10 06 80 (lump and granular copper slags) [9]. Lump copper slag extracted for the research tests was as fraction (lumps of irregular shapes and sizes). This slag is obtained in the process of smelting briquetted copper concentrates in a shaft kiln. Due to its low copper content, it constitutes the final waste in the smelting process. In the liquid state and at a temperature of approx. 1200°C, it is transported to the place of deposition – on a heap, where after being poured out, the process of solidification and slow cooling are taking place under atmospheric conditions. Chemical and mineral compositions of the tested slag are demonstrated in Table 1 and in Fig. 1.

Table 1

Chemical composition of copper slag

Properties	Content [wt.%]
Loss on ignition*	0.00
Fe_2O_3	17.38
Al_2O_3	15.56
Total SiO_2	42.76
CaO	11.88
MgO	7.29
SO_3	0.12
Cl^-	0.015
Na_2O	1.09
K_2O	3.38

* With the correction associated to the oxidation of sulfides.

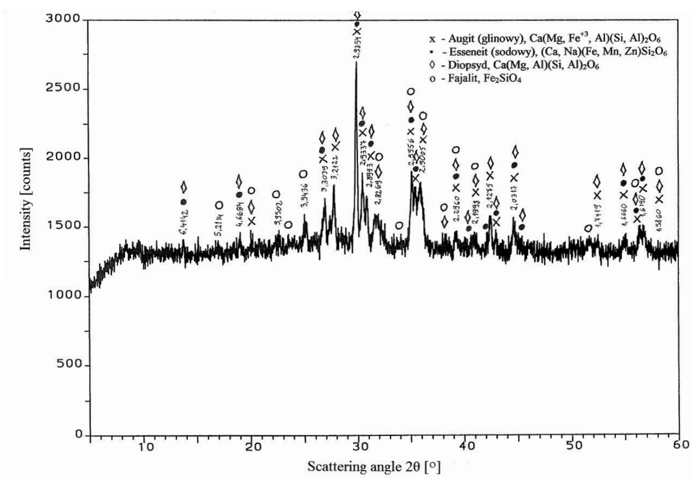

Fig. 1. XRD pattern of lump copper slag

The tested slag was characterized by the highest percentage content of SiO_2, and the lowest content of Cl^-. On the diffractogram characterizing the lump copper slag (Fig. 1) can be observed peaks demonstrating the contents of its crystalline phases. These are mainly augite, diopside and esseneit – minerals included in the pyroxene group. Table 2 presents results determining the total content of heavy metals in the waste. The tested slag contains mostly: zinc (7833 mg/kg d.m.), copper (4679 mg/kg d.m.) and lead (2364 mg/kg d.m.). The lowest concentration was observed for nickel – 41.5 mg/kg d.m..

Table 2

Total content of heavy metals in the waste

Heavy metal	Total content [mg/kg d.m.]
Cu	4679
Pb	2364
Zn	7833
Cd	68.6
Ni	41.5
Cr	595

Chemical composition was designated according to the procedures outlined in European Standard EN 196-2:2013 [10]. Designation of the mineral composition was performed by using X-ray power diffraction (XRD). In order to tailor water extracts from waste, a laboratory sample was prepared with grain size of < 10 mm in accordance to requirements specified in EN 12457-4:2002 [6]. The research test on leaching contaminants was performed under the impact of eluent with different pH levels of: 4, 7 and 13. This liquid consisted of deionized water, the pH level of which was reduced by adding nitric acid(V) and raised by applying sodium hydroxide. The course of the study on leaching contaminants involved 24-hour extraction [6]. The test on leaching heavy metals from waste fraction of < 10 mm was also performed at the liquid to solid ratio of L/S = 100. Additionally, the waste was shredded into the fraction size of < 0.125 mm and it was checked to what extent the reduction of waste grain size impacts the leachability of selected heavy metals. The waste sample were also subjected to mineralization to determine the total content of heavy metals. Waste digestion was performed using aqua regina by mineralization in a closed system. Concentrations of individual components of eluents after being filtrated were determined by the method of atomic absorption spectrometry.

Results and discussion

The concentrations of leachable forms of waste components in water extracts are presented in Figs. 2–5. The obtained research test results demonstrate the release of such parameters as: chlorides (Cl^-), sulphates (SO_4^{2-}), iron (Fe), potassium (K), sodium (Na), heavy metals, including: cadmium (Cd), general chrome (Cr), nickel (Ni), copper

(Cu), lead (Pb), zinc (Zn), caused by changes in the pH level of the eluent. Analysis of concentrations of selected contaminants in water extracts from wastes is required to be performed for the purpose of determining the feasibility of storing wastes at landfills of a given type, and at the same time, to assess the degree of contamination of the waste. Therefore, the results of analyses of individual parameters were compared with the permissible leaching limit values for inert waste landfills [7] (Figs. 2–4).

On the basis of the test results, the dependency between the release level of particular components and the pH of the eluent was observed. The concentrations of chlorides with the pH of 4 were designated at the same level. While, this indicator was characterized by 15 times higher leachability then it has in an alkaline environment. The leachability of sulphates was characterized differently. The lowest concentration was determined at the pH of 4, and the highest one at the pH of 7. For chlorides and sulphates the leaching limit values were not exceeded. This indicates a low rate of contamination of the water extracts by these compounds, and thus on their negligible salinity.

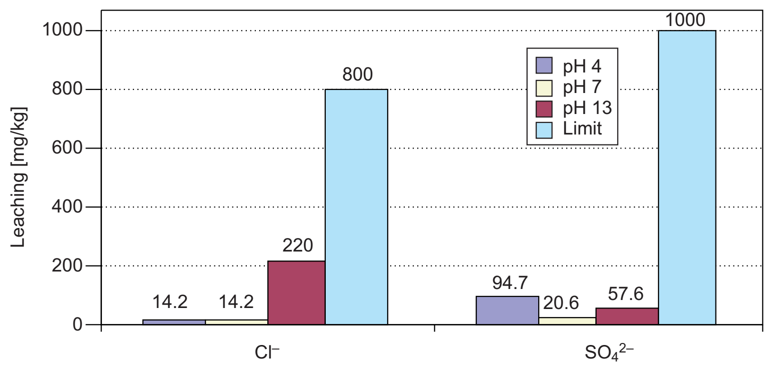

Fig. 2. Leaching of Cl^- and SO_4^{2-} depending on the pH of the eluent, compared to the permissible limit value for inert waste landfills

Water extracts collected from the test waste were characterized by a low content of leachable forms of heavy metals. However, the effect of changes in the pH of the eluent on the derived values of concentrations can be observed. The slag being subject of the study was characterized by a higher tendency for the release of Cr, Ni, Cu, Pb, and Zn under the impact of the acting liquid with the pH of 13 (Figs. 3, 4). In all of the samples, concentrations of cadmium and manganese were below the limit of quantification. Chromium and nickel are being leached above the limit of quantification solely under the alkaline conditions. The lowest leaching of Cu, Pb and Zn was observed in the pH-neutral environment. As the acidity of the eluent increased, the content of these elements in the water extracts increased. The greatest difference in the eluent's pH-dependent release rate can be observed for lead. Concentration of this element was almost three times higher at the pH of 3 and thirteen times higher at the pH of 13, when compared to the value obtained at neutral pH of the eluent.

The dependency between the leachability of heavy metals from waste materials and the pH of the eluent are also confirmed by research tests performed on the basis of other

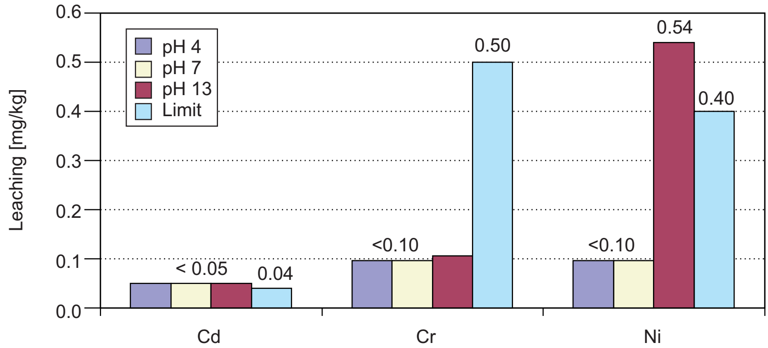

Fig. 3. Leaching of Cd, Cr, Ni depending on the pH of the eluent, compared to the permissible limit value for inert waste landfills

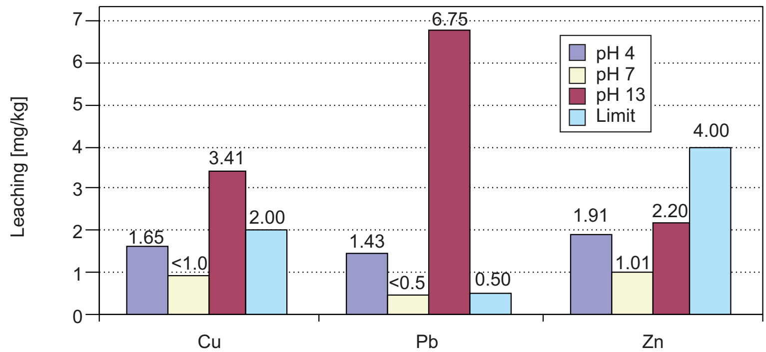

Fig. 4. Leaching of Cu, Pb, Zn depending on the pH of the eluent, compared to the permissible limit value for inert waste landfills

industrial waste [11] and conducted by other authors [12–13]. Due to changes in the pH of the environment, where the waste is placed, heavy metals are characterized by a raised tendency to release. This is significant, when waste are deposited in landfills and under the impact of the weather conditions. At such situation, it can lead to an increase in the release of leachable forms of contaminants from wastes. In accordance to legal regulations being in force in Poland, the permissible leaching limit values are being compared with results on concentrations of contaminants determined in the standard leaching test. This test is based on pouring the waste with water having a neutral pH in the proportion of 10 : 1 (water : waste).

Based on the obtained test results, it can be observed that none of these parameters at a pH of 7 does not exceed the limit concentration for inert waste landfills. However, in the case of leaching of Ni, Cu and Pb at a pH of 13, and for Pb at a pH of 4, the permissible leaching limits for this type of landfills have been exceeded. As a consequence, this can lead to pollution of the natural environment caused by heavy metals.

In the water extracts from waste the contents of Fe, K and Na (Fig. 5) were also determined. Potassium and sodium as alkali metals were characterized by another

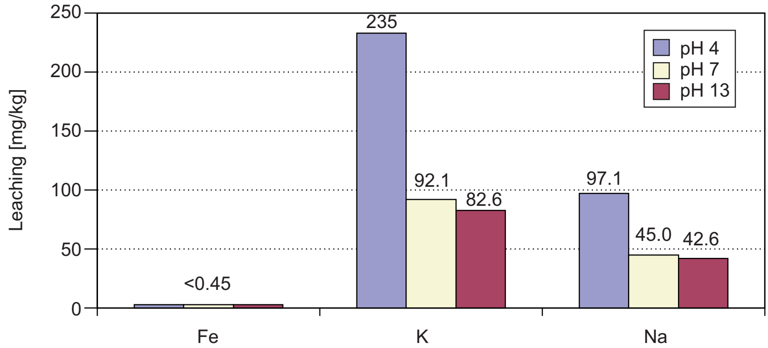

Fig. 5. Leaching of Fe, K, Na depending on the pH of the eluent

leaching tendency. The highest concentrations of these elements were designated in an acid environment, and the lowest ones in strongly alkaline environment. Concentrations of Fe in all specimens were determined below the limit of quantification.

In the study was also performed an analysis on the level of leaching of heavy metals from the waste. For this purpose, the overall content of heavy metals in digest solutions prepared from the waste specimens was determined (Table 3). The slag was characterized by marginal leaching level of heavy metals (within the limits ranging from 0.01 to 1.3%). The lowest leachability demonstrated chromium and also copper, zinc and lead, when the liquid with the pH of 7 was applied. Nickel, despite the fact that it had the lowest leachability in acidic and neutral environments, was characterized by an increased level of leaching in strongly alkaline environment.

Table 3

Percentage level of heavy metals leaching

Heavy metal	Total content [mg/kg d.m.]	Level of leaching [%]		
		pH 4	pH 7	pH 13
Cu	4679	0.04	0.01	0.07
Pb	2364	0.06	< 0.02	0.29
Zn	7833	0.02	0.01	0.03
Cd	68.6	< 0.07	< 0.07	< 0.07
Ni	41.5	< 0.24	< 0.24	1.30
Cr	595	< 0.02	< 0.02	0.02

The process of leaching contaminants also depends on the form in which the waste is available. In Table 4 are summarized results of leaching heavy metals from the waste with a grain size of < 10 mm (unground waste) and after its particles are grinded to the size of < 0.125 mm. The analysis of heavy metals leaching from waste with grinded particles was performed by applying an eluent with the pH levels of 4 and 7.

Table 4

Leaching of heavy metals depending on the particle size of the waste

Heavy metal	Leaching at pH 4 [mg/kg d.m.]		Leaching at pH 7 [mg/kg d.m.]	
	particle size < 0.125 mm	particle size < 10 mm	particle size < 0.125 mm	particle size < 10 mm
Cu	1.74	1.65	< 1.00	< 1.00
Pb	1.18	1.43	< 0.50	< 0.50
Zn	3.72	1.91	1.95	1.01
Cr	0.14	< 0.10	< 0.10	< 0.10
Cd	< 0.05	< 0.05	< 0.05	< 0.05
Ni	< 0.10	< 0.10	< 0.10	< 0.10

Reduction of waste particle size caused a slight increase in the release rate of Cu, Zn and Cr during the leaching by using a liquid having a pH of 4. If case of liquid with a pH of 7, higher concentrations in water extracts were observed for zinc. Designated concentrations of this metal in ground waste were almost doubled (both, for the pH levels of 4 and 7). Lead was the only element characterized by higher leaching from uncrushed faction of the waste. On the basis of results listed in the table, it can be noted that an acidic pH of the eluent caused a rise in the release rate of Cu, Pb and Zn from each fraction of the waste under tests.

The leaching of heavy metals is also affected by the ratio of liquid volume to the mass of a solid that is used in the test (L/S) and by the period for which the waste is shaken. Results of the analysed heavy metal concentrations derived in the test at L/S = 10 (fundamental test) and L/S = 100 dm^3/kg are presented in Table 5. The values expressed there are in mg/dm^3 and also calculated per kg dry mass, obtained in the test at the pH level of 4 for the eluent. For the sample with the ratio of L/S = 100, the test was also performed based on EN 12457-4:2002 standard, except that the period during which the waste was shaken amounted to 5 h.

Table 5

Concentration of heavy metals obtained with L/S = 10 and 100 dm^3/kg

Heavy metal	Leaching at pH 4			
	L/S = 10 24 hours shaking		L/S = 100 5 hours shaking	
	[mg/dm^3]	[mg/kg d.m.]	[mg/dm^3]	[mg/kg d.m.]
Cu	0.18	1.65	0.45	43.6
Pb	0.15	1.43	0.17	16.5
Zn	0.21	1.91	1.05	102
Cr	< 0.01	< 0.10	< 0.01	< 0.10
Cd	< 0.005	< 0.05	< 0.005	< 0.05
Ni	< 0.01	< 0.10	0.02	1.94

Adding a larger volume of water during the test (L/S = 100), despite the fact that the sample was shaken for a shorter period of time, caused an incensement in the release level of Cu, Pb, Zn, and Ni into the aqueous phase, greater than for the ratio of L/S = 10. The largest difference could be observed in a concentration of zinc, which in the water extract at L/S = 100 was 5 times higher than at L/S = 10. There were also observed higher concentrations for nickel (above the limit of quantification). During the test, at L/S = 100 heavy metals were also characterized by a higher leachability than at lower ratio of L/S, per one kg waste dry weight. This leads to this that in the test 10 times higher volume of water was used at the same weight of the waste sample. However, the impact of the ratio of liquid to the waste mass on the degree of leaching of cadmium and chromium was not observed. These metals, despite their high content in the waste do not exhibited the tendency to release.

Conclusions

The copper slag was characterized by a very low release of contaminants. According to the results of leaching being performed on the basis of the fundamental test, it was classified to the category of inert wastes. As it was presented in the study, the slag was characterized by various tendency to leaching contaminants due to changes in leaching conditions and in the waste grain size. Application of eluent at pH level of 13 caused an increase in the rate of leaching of Cl^-, Cr, Ni, Cu, Pb, and Zn. Heavy metals, such as Cu, Pb and Zn are also characterized by a higher leachability, when the pH of the liquid is at the level of 4, rather than in an inert environment. However, due to an extensive application of copper slag in road construction and cement industry, this waste is temporarily disposed in heaps. Therefore, it does not pose a high risk to the ground-water environment. Solely in the case, when the environment is strongly alkaline, the amount of leaching of certain heavy metals can exceed the acceptable levels. Mineral construction materials used in road construction can contribute to increasing the pH of the surrounding environment. Therefore, the research on level of contaminants release from cooper slag should be continued in the context of their safe use to the substructure roads in order to reduce the possible leaching of heavy metals.

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UWALNIANIE WYMYWALNYCH SKŁADNIKÓW Z ŻUŻLA POMIEDZIOWEGO W ZALEŻNOŚCI OD WARUNKÓW PROCESU WYMYWANIA

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Abstrakt: Badanie wymywalności składników odpadów jest jedną z metod oceny poziomu ich zanieczyszczenia rozpuszczalnymi formami metali ciężkich. Przebieg procesu wymywania uzależniony jest od kilku czynników, których zmiana może powodować uwalnianie zanieczyszczeń na różnych poziomach. W pracy przedstawiono wyniki wymywalności Cl^{-}, SO_4^{2-}, Fe, Na, K oraz metali ciężkich (Pb, Cd, Ni, Zn, Cu, Cr) z żużla pomiedziowego w zależności od pH cieczy wymywającej użytej w badaniu. Badanie wymywalności metali ciężkich przeprowadzono także przy różnym stosunku cieczy do ciała stałego (L/S = 10 i 100 dm^3/kg) oraz z wykorzystaniem odpadu o różnej wielkości frakcji. Dokonano także analizy zawartości ogólnej metali ciężkich w odpadzie. Zaobserwowano najwyższą wymywalność Cl^{-}, Cr, Ni, Cu, Pb i Zn przy pH cieczy wymywającej na poziomie 13. Redukcja ziaren odpadu do wartości < 0,125 mm spowodowała wzrost uwalniania miedzi i cynku do fazy wodnej.

Słowa kluczowe: żużel pomiedziowy, wymywalność, metale ciężkie