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LEACHING OF HEAVY METALS FROM MONOLITHIC WASTE

Leaching of heavy metals (Zn, Pb, Cu, Ni and Cr) from hazardous waste originating from steel works (slag) has been investigated. Contaminant leaching behavior from monolithic waste materials in the function of time was examined. There was established the cumulative leaching of elements per surface area of waste material and the impact of the duration of the leachant contact with the waste on the leachability. The types of processes accompanying the release of heavy metals were determined as well. Surface wash-off and dissolution were dominant processes during the leaching of the analyzed elements. Chromium was the only element whose release from the sample was controlled by diffusion when subjected to leaching in a liquid of pH 7. Due to the low levels of heavy metal leaching in relation to their concentrations in the samples, it seems that longer duration of the tank test can contribute to the release of additional amounts of the heavy metals.

1. INTRODUCTION

The extraction of minerals and their processing is directly associated with the production of waste. Waste from steel works forms one of the most diverse groups of industrial waste. The main types of waste generated in the metallurgical industry are as follows: slag and dust from blast furnace processes and steel production in electric arc furnaces, dust and sludge from the sintering and steel production in converters, fine metal-bearing wastes, grinding dust and ceramic debris [1]. Production of metallurgical slag is a huge load for environment from a viewpoint of their quantity. Sitko [2] reports that slag is the waste produced in the largest amount by the steel and iron industry. Currently, average slag weight produced by the steel and iron industry globally is about 300 kg/Mg of crude iron, and for individual steel plants it varies from ca. 180 kg/Mg to over 400 kg/Mg. In Poland, up till 1980 this value was ca. 700 kg/Mg, while today it is somewhere between 300 and 400 kg/Mg of crude iron.

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Chemical composition of metallurgical slag is variable and depends on chemical composition of the charging materials and a melting technology [3]. Slag from electric arc furnace is characterized by a high level of the total Fe content (at a level of 31–40% in dry mass) and FeO in the range of 28–43% in dry mass, depending on the applied manufacturing technology. This type of waste also contains considerable amounts of CaO (23–38% in dry mass). Blast furnace slags are also rich in CaO (34–43% in dry mass). These slags also contain considerable amounts of SiO₂ (27–40% in dry mass) [4–6]. In the chemical composition of blast furnace slags, some of the most common elements include metals (Zn, Pb, Cu, Mn, Cd, Cr, Ni, V, Mo, Ag, Au). They can form phases specific to them (such as oxides) as well as occur in the dispersed form as glaze and amorphous solids, as well as in the form of substitutions in the silicate phases and forming single droplets present in alloys. The awareness regarding the phase composition and metal forms can be applied in the popular attempts to recover metals from blast furnace slags throughout the phase of selecting an adequate technology of recovering them [7].

For years, metallurgical slag has been deposited at landfills. An increase in the awareness regarding the hazard posed by the industrial waste resulted in the gradual liquidation of landfills and heaps as well as the application of waste in the form of raw material in a number of industrial branches. Increasing emphasis is placed on re-utilisation of waste due to rising cost of disposal and stringent environmental regulation [8]. Chemical similarity of metallurgical slag with some natural gravels enables its utilization mainly in highway engineering and in production of expanded building materials [4]. However, the steel industry also produces slag, whose reuse is impossible due to the considerable level of heavy metal contamination. This type of waste is deposited on adequately prepared and safe landfills for hazardous waste. If it is necessary to deposit of waste, its negative impact on the environment and human health has to be reduced. Such actions should comply with the waste management hierarchy set out in the Waste Framework Directive [9]. The function of assessing the hazard posed by the waste to the environment and determination of an adequate manner of its processing involves a test performed with regard to the leachability of heavy metals. Each test forms a source of important information regarding the potential of leaching heavy metals and their migration into the environment. The assessment of leached pollutants from landfilled waste is relevant in the context of maintaining the quality and safety of the ground and water environment.

The waste landfilled in the environment is exposed to the action of various physical and chemical factors, which play a significant role on the level of pollutant release. In the last 20 years, various efforts were taken with the aim of assessing the behavior of leaching particular heavy metals from various types of materials. As a result of such studies, the factors and processes determining the leaching of heavy metals from a variety of waste and construction materials are well researched and established [10, 11]. The shape and the waste form are the principal factors, which determine the level of pollutant leaching. However, this process is also affected by the ambient temperature, duration of contact with water and

pH of the surrounding environment [11]. Various leaching tests are available with the purpose of testing the impact of atmospheric conditions on the level of heavy metal leaching [12]. One of the objectives of the comprehensive and adequate assessment of heavy metal leaching from waste materials in direct contact with the natural environment involves the use of leaching tests that account for the impact of the atmospheric conditions as well as simulations of such conditions in a laboratory environment [13, 14].

In recent years, special attention was paid to the topics associated with pollutant removal from industrial waste, including blast furnace slag. Table 1 contains the results of leaching of selected heavy metals from blast furnace slag, gained by various authors [3, 15–17]. The results, presented for illustrative purposes only, are compared with the purpose of assessing the leachability of heavy metals from various branches of the smelting industry. The release of heavy metals varies depending on the applied technology in which waste is derived, form of waste, duration of its storage, and the approach taken to the production of water extracts.

Table 1

Heavy metals leachability from various types of metallurgical slags [3, 15–17]

Type of waste	Concentrations of heavy metals in water extracts [mg/dm ³]					
	Cd	Cr	Ni	Cu	Zn	Pb
Blast furnace slag [3]		0.004		b.d.l.		b.d.l.
Basic oxygen furnace slag [3]	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.027
Electric arc furnace slag [3]		0.066		0.005		0.018
Slag from closed steel plant landfill [15]	n.d.	0.003–0.015	0.008–0.019	0.008–0.014	n.d.	
Vitrified metallurgical slag (Zn and Pb metallurgy) [16]	b.d.l.	b.d.l.	b.d.l.	0.006–0.055	0.009–0.017	b.d.l.
Sodium lead slag [17]		0.01		b.d.l.	0.01	2.16

b.d.l. – below detection limit (0.005 mg/dm³), n.d. – no data available.

The first three waste samples are slags from the steel industry [3]. Blast furnaces are applied for iron production, whereas electric arc furnaces and basic oxygen furnaces are used for steel production. The leachability of slags derived from these furnaces is negligible; hence, they are commonly used. When they are applied as engineering materials in construction, they do not pose a hazard to the environment. The second type of waste used in this study was also obtained from the steel industry, yet the sample of the slag used in the study was derived from an inactive landfill. The authors [15] analyzed the leaching of heavy metals from three slag samples taken in various places from a waste dump. Jonczy et al. [16] analyzed the leachability of heavy metals from vitrified blast furnace slags derived from an old, unused dump for waste storage from zinc and lead production. This waste originated as a result of fast thickening of liquid slag. This slag was characterized by extremely low level of heavy metal leaching. However, due

to the fact that the waste accumulated over the turn of 19th and 20th centuries, throughout the long years the maximum levels of contaminants could have been released. In addition, the compact and solidified waste structure could limit the leaching of heavy metal into the environment. Sodium lead slag, generated during secondary lead production, was characterized as hazardous waste (due to the high release of lead) [17]. Slag was an inevitable waste from secondary lead smelting process.

The results of leaching of selected heavy metals from metallurgical slag obtained on the basis of the EA NEN 7375 procedure (tank test) [18] have been presented in the paper. An emphasis was placed on the release of Zn, Pb, Cu, Ni and total Cr due to their high mass concentration in the waste as well as the potential environmental hazard during leaching. The total leachability of heavy metals is assessed as well as the mechanisms of their leaching from the surface of waste materials.

2. MATERIALS AND METHODS

Materials. The material applied consisted of furnace slag from a rotational kiln originating from lead refinery section in a zinc works. The waste took the form of crushed irregular lumps. In the leaching test, two such lumps (samples A and B) were used (Fig. 1). Each sample was weighed and measured by the print paper method. Weights of samples were as follows: A – 3374 g, and B – 975 g. The surface areas of samples were 0.0509 m² (sample A) and 0.0216 m² (sample B). The volume of each sample was calculated in order to ensure that adequate volume of leachant (2–5 volumes of the sample) used in the test.



Fig. 1. Pieces of waste materials prepared for the tank test

The analysis of the chemical composition of the slag was carried out (Table 2). The loss on ignition (2.68 wt. %) was determined by the weight method in accordance with EN 15935 [19], and element oxidation forms by the ICP-OES method in accordance with EN 196-2

[20]. The main composites were: Fe_2O_3 (41.86 wt. %) and Al_2O_3 (15.33 wt. %). The content of crystalline silica was 10.02%. Subsequently, the test involved determination of the ratio of SO_3 and the alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$). The slag was characterized with the lowest concentration of CaO and MgO .

Table 2

Chemical composition of metallurgical waste

Component	Loss on ignition	SO_3	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Content, wt. %	2.68	7.61	10.02	15.33	41.86	2.10	0.98	3.38	0.27

Table 3 contains the total contents of heavy metals in the waste. The total concentrations were determined after mineralization process of the waste using aqua regia. The test material was characterized by a very high contents of heavy metals with the highest content of copper (101 023 mg/kg). The table also contains the results regarding the leaching of heavy metal determined on the basis of EN 12457-2 [21]. The analysis of the concentrations in the water extracts from waste is required with the purpose of determining the possibility of storing waste in a given type of landfill, and additionally, for the assessment of the contamination level of a given waste. The results of analysis for Zn, Pb, Cu, Ni and Cr were compared with the admissible values of leaching for landfills designed for non-hazardous waste and hazardous waste [22] (Table 3). Due to the fact that the admissible levels for non-hazardous waste for Zn, Pb and Ni are exceeded in the analyzed waste, the slag was classified as hazardous for storage. The waste is sent for storage in an in-house hazardous waste landfill. The degree of hazard is also indicated by the zinc concentration 5 times exceeding that for hazardous waste landfills. The concentration of Ni was also exceeded in this type of waste.

Table 1

Contents of heavy metals and their concentrations [mg/kg] in water extracts compared with criteria for landfills for non-hazardous and hazardous waste [22]

Element	Zn	Pb	Cu	Ni	Cr
Total content, mg/kg	61 076	87 410	101 023	2402	5040
Concentration, mg/kg	1112	35.05	13.17	44.11	0.15
Limit value for non-hazardous waste [28]	50	10	50	10	10
Limit value for hazardous waste [22]	200	50	100	40	70

Methods. The assessment of inorganic component leaching from waste materials in the solidified, monolithic form applies tank tests, often referred to as diffusion tests. Netherlands Standardization Institute (NEN), European Committee for Standardization (CEN) and Environmental Protection Agency (EPA) have created a leaching test for different types of waste materials (building materials, stabilized waste, compacted granular

materials) [18, 23–25]. The most common test is based on the EA NEN 7375 standard [18]. In the test procedure, a sample of a given capacity is placed in a vessel filled with demineralized water. Its volume should be 2–5 times greater than the volume of the sample. It is also important to place the sample at the distance of at least 2 cm from the vessel walls and to ensure that it is completely immersed in the leachant. The materials are then subjected to leaching over the period of 64 days. The tank test is applied with regard to construction materials and waste solidifying materials as well as to waste itself [17, 26]. The tank test [18] enables assessing the impact of the duration of contact between the leachant and the material on the leaching of pollutants, as well as to the analysis of cumulative leachability of a given component per specific unit of waste surface. It can also enable forecasting the leaching rate a given component, which cannot be determined in short-term tests, e.g., batch tests (EN 12457-2 [21]). It is also possible to recognize the nature of the leaching, i.e., whether it is dominated by diffusion, surface wash-off, depletion or dissolution.

In the tank test, all reagents were at least p.a. grade. The samples with a given mass, surface and volume were placed in separate vessels presented on supports in such a way that the liquid is in contact with all sample surfaces. The lumps were immersed in demineralized water (pH 7 (sample A), and pH 4 (sample B)). The water was acidified with 1 M HNO₃. 1.8 dm³ of leachant was used for sample A, and 0.6 dm³ for sample B. The tests were performed at the temperature range of 19–21 °C. The eluates were collected after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days of leaching. After each sampling, the liquids were replaced with new ones. The eluates were filtered through the membrane filters with the pore size of 0.45 μm, and pH and electrical conductivity were measured. The concentration of heavy metals in each eluate fraction was determined by the flame atomic absorption spectrometry (FAAS).

Calculation of the results. Measured cumulative leaching ε_n^* of a component was calculated according to the formula [18]:

$$\varepsilon_n^* = \sum_{i=1}^n E_i^*, \quad i = 1, \dots, N \quad (1)$$

where the measured cumulative leaching ε_n^* of a component refers to period n comprising fractions from $i = 1$ to n , mg/m² of the sample surface area, E_i^* is the measured leaching of the component in fraction i , mg/m², and N is the total number of leachant replenishment periods.

Derived cumulative leaching ε_n of a component was calculated using the formula [18]:

$$\varepsilon_n + E_i^* \frac{\sqrt{t_i}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \quad (2)$$

where ε_n is the derived cumulative leaching of a component for period n comprising fractions from $i=1$ to n , mg/m^2 of the sample surface area, E_i^* is the measured leaching of the component in fraction i , mg/m^2 , t_i is the replenishment time of fraction i , s , and t_{i-1} is the replenishment time of fraction $i-1$, s .

Derived cumulative leaching ε_{64} for each component over 64 days was calculated according to the formula [18]:

$$\varepsilon_{64} = \sqrt{64} \left(\prod_{i=a}^b \frac{E_i^*}{\sqrt{t_i} - \sqrt{t_{i-1}}} \right)^{1/(1+b-a)} \quad (3)$$

where ε_{64} is the derived cumulative leaching for a component over 64 days, mg/m^2 , E_i^* is the measured leaching of the component in fraction i , mg/m^2 , t_i is end time of fraction i for which diffusion has been established, in days and t_{i-1} is the start time of fraction i for which diffusion has been established, days.

The diffusion coefficient of a component was calculated from [18]:

$$D_e = f \left(\frac{\varepsilon_{64}}{2653 \rho U_{\text{avail}}} \right)^2 \quad (4)$$

where D_e is the average effective diffusion coefficient for a given component, m^2/s , ρ is the density of the test piece, kg/m^3 , U_{avail} is the leachable available quantity of a component derived according to EA NEN 7371 [27], mg/kg (Table 9) and f is a factor equal to 1 s^{-1} .

Leached quantity of a component per unit mass over 64 days was calculated using the formula [18]:

$$U_{\text{dif}, 64} = \frac{2A\rho U_{\text{avail}} \sqrt{\frac{D_e t}{\pi}}}{m} \quad (5)$$

where $U_{\text{dif}, 64}$ is the quantity of a component leached out in the diffusion test, mg/kg , t is the duration of the leaching, s , A is the surface area of the test piece, m^2 , m is the weight of the test piece, kg .

The percentage of the leached component with respect to its available content was calculated according to the formula [18]:

$$UP_{\text{dif}, 64} = \frac{U_{\text{dif}, 64}}{U_{\text{avail}}} \times 100\% \quad (6)$$

3. RESULTS AND DISCUSSION

Table 4 contains the values of pH and electrical conductivity of particular eluate fractions obtained in the tank test. The alkaline nature of the waste changed the level of the eluate pH. pH of the eluates from sample A was in the range 12.76–13.24, whereas for sample B, pH it was 12.69–12.95. A high electrical conductivity of the eluates was observed, which could indicate high mobility of ions from the monoliths into the water phase. For sample A, the conductivity increased in the first 5 fractions of the eluates reaching 37.40 mS/cm after 9 days, then it decreased to 22.60 mS/cm at the end of the test. For eluates from sample B the lowest value (15.08 mS/cm) was observed after 0.25 days of the test duration, whereas the highest (26.20 mS/cm) after 1 day.

Table 4

pH and electrical conductivity (*EC*) obtained during 64 days of the tank test

Eluate fraction	Period [days]	Sample A		Sample B	
		pH	<i>EC</i> [mS/cm]	pH	<i>EC</i> [mS/cm]
1	0.25	12.76	19.94	12.69	15.08
2	1	12.83	19.50	12.93	26.20
3	2.25	12.89	21.90	12.83	17.29
4	4	13.15	22.70	12.81	15.40
5	9	13.24	37.40	12.95	25.00
6	16	13.00	29.50	12.81	16.65
7	36	13.07	35.30	12.92	21.90
8	64	13.00	22.60	12.86	16.40

Table 5

Measured cumulative leaching (ϵ_n^*) of heavy metals [mg/m²]

Element	Zn	Pb	Cu	Ni	Cr
Sample A	6630	2834	200	37.35	5.32
Sample B	2605	1099	120	b.d.l.	7.31
Limit value for hazardous waste [28] [mg/m ²]	100	20	60	15	25

b.d.l. – below detection limit.

The data regarding measured cumulative leaching of heavy metals after 64 days of the test duration are presented in Table 5. The assessment of the potential environmental hazard during the waste storage in the monolithic form delivers a comparison between

this data and admissible levels for storing hazardous waste contained in Landfill Regulations [28]. The tested slag was characterized by a high concentration of elements released into the water phase, i.e., Zn, Pb, Cu and Ni. This is demonstrated by several times exceeded admissible contents of Zn and Pb. The admissible copper concentration three times (sample A). The concentration of chromium did not exceed the admissible level. This waste was considered as hazardous.

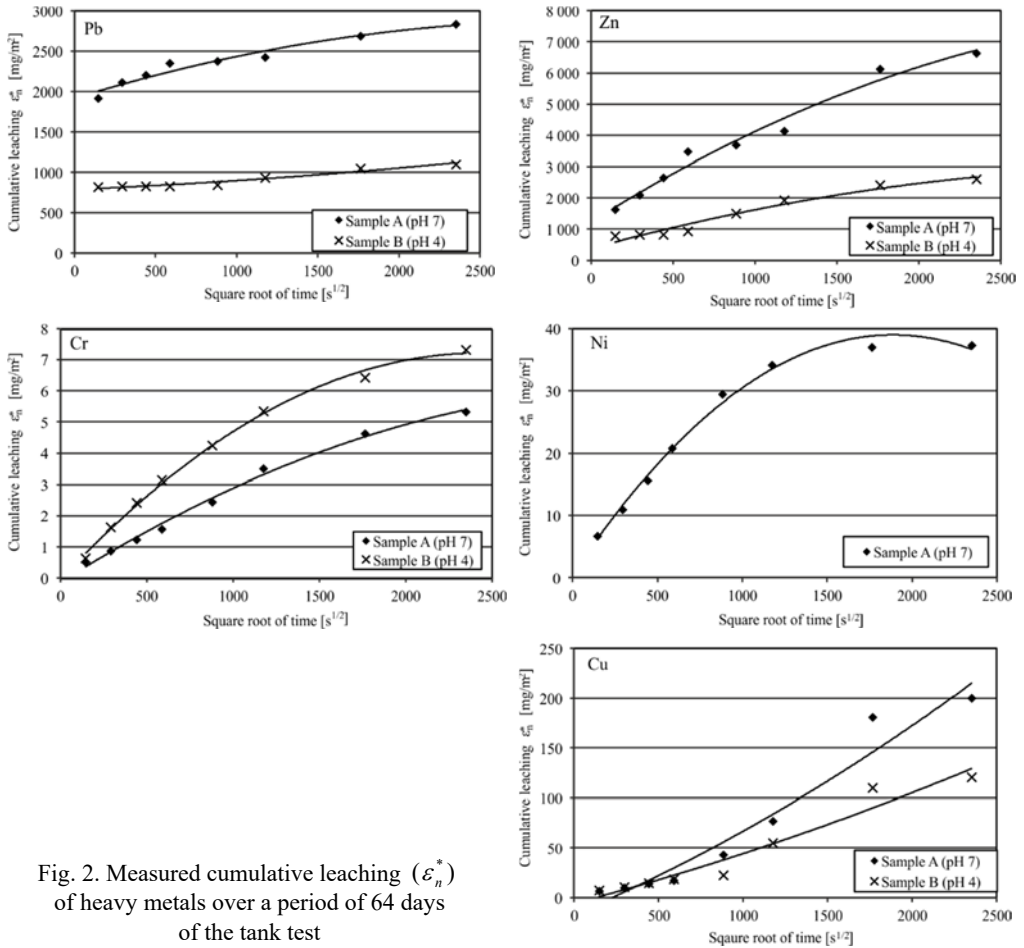


Fig. 2. Measured cumulative leaching (ε_n^*) of heavy metals over a period of 64 days of the tank test

Figure 2 presents time dependences of the cumulative concentrations of heavy metals (ε_n^* vs. \sqrt{t}). Heavy metal cations are characterized by a higher level of leaching in the acidic environment than in the alkaline one [11]. However, in this study the authors found that lower concentrations of heavy metals were determined in the eluates obtained from sample B throughout the entire duration of the test (with the only exception of Cr). Despite the fact that the lumps of waste were representative of the tested

material, various metals were released into the environment to a different degree. This can demonstrate both the heterogeneity of the tested material as well as small impact of the lower pH of the leachant used in the test. After each liquid draining, fast neutralization of the acid occurred under the effect of the waste.

The level of zinc leaching from sample A was high. The greatest increase of the concentration of this element could be noted after 36 days of leaching (Fig. 2). The zinc contained in sample B was characterized by low leachability in extractions 2–4. Throughout the 5th phase of the research, its concentration increased. 65% of total leached amount of zinc was released in the final four phases. The highest lead levels, equal to 83%, were recorded in the first 4 days of leaching. 75% of Pb was leached after only 0.25 day. In contrast, during the first four phases of the test, only 5.5% (sample A) and 15% (sample B) of its concentration was released from the sample. The highest concentration was recorded in extract No. 7. The curves representing the tendencies of the total leachability of Zn, Pb, Cu and Cr demonstrate that over the period of 64 days, complete leaching of the elements from the waste did not occur in practice. The curve representing nickel leaching takes on a different shape than the curves for other heavy metals. It assumes a rounded shape at the end of the test, which indicates that nickel ions available for leaching have depleted. This fact is also confirmed by the decrease of nickel concentrations in the final three eluate fractions. 23% of nickel was released in this eluates. Chromium at pH 7 was leached in lower concentrations than at pH 4. The curve of chromium leaching from sample B is also partly rounded at the end of the test procedure. Hence, the results demonstrate that if the test had a slightly longer duration, this element would be completely released from the samples as well.

The results of calculations of the cumulative leaching ε_n obtained from Eq. (2) in function of time are presented in Fig. 3 in the form of log–log plots. In order to demonstrate the differences in leaching in the function of the test duration, the points are connected by a dotted line. In accordance with EA NEN 7375 [18], the slope of the linear regression line in the log–log plots indicates the dominant mechanism of leaching in a given time range. This mechanism was evaluated for the following time increments: 2–7, 5–8, 4–7, 3–6, 2–5 and 1–4. The presentation of the results in each increment includes: the concentration factor, slope of regression line as well as standard deviation. If the slope is greater than 0.65, leaching is accompanied by dissolution. The values below 0.35 indicate surface wash-off or depletion. If leaching is controlled by diffusion, the slope should be in the range between 0.35 and 0.65. In addition, the concentration factor should be greater or equal to 1.5, and the standard deviation smaller or equal to 0.5.

The increments 2–7 (from 1 to 36 days) are considered to represent the entire duration of the diffusion test [18]. This increment does not include the initial and the final eluate fractions with the purpose of avoiding interpretation errors. The first increment is disregarded due the effect of the wash-off process, whereas the other due to the possible avoidance of the fact of a given component depletion during the test. For these

reasons, the data in Table 6 can demonstrate the dominant leaching mechanisms assessed as the total increment. The value of the concentration factor is also given there, calculated as the quotient of the mean concentration of a component in a given increment and the lower detection limit for this component along with the regression lines (i.e., slope and standard deviation).

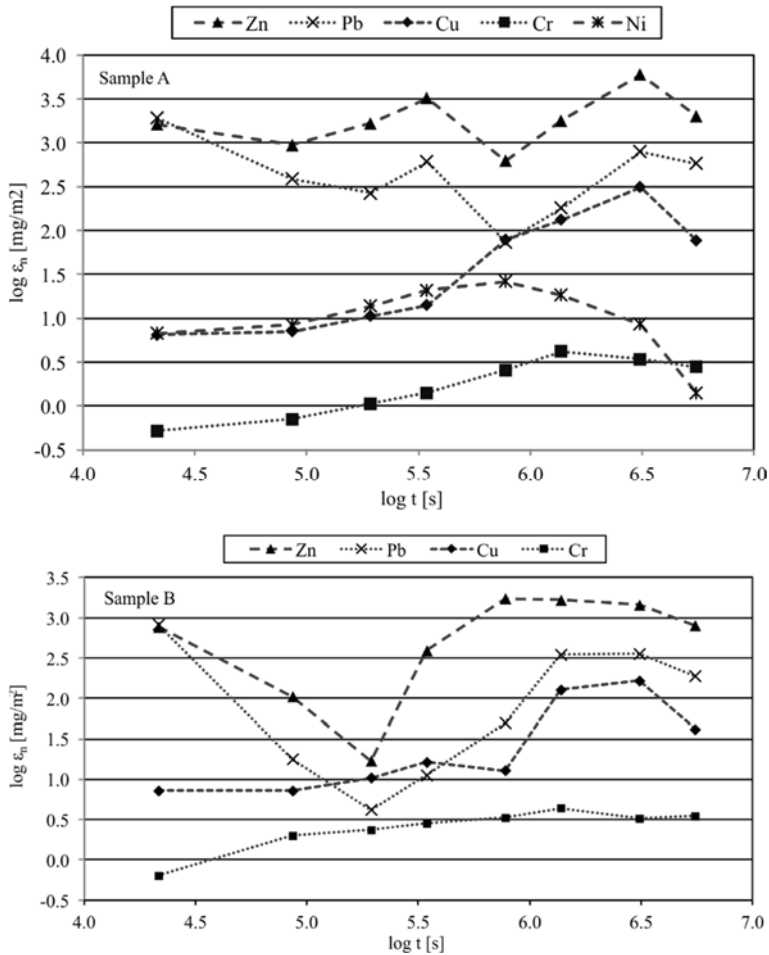


Fig. 3. Time dependences of the derived cumulative leaching (ϵ_n^*) of heavy metals in a logarithmic scale

We can note that the leaching of heavy metals from the two waste samples was controlled by different mechanisms. Chromium was the only element in sample A, whose leaching was controlled by diffusion. Surface wash-off into water phase formed was the key mechanism of releasing Zn, Pb and Ni from sample A and Cr from sample B.

Hence, the low pH during leaching can be considered the factor responsible for the domination of dissolution. However, in accordance with EA NEN 7375 [18], the waste lumps were considered insoluble (i.e., the criteria for matrix insolubility are fulfilled). In this case, the solution of particular components is not permanent, and occurs from the outer layer of the sample lumps. The possible depletion of the components at the end of the test procedure is visible by analyzing the curves of the cumulative nickel leaching from sample A and chromium from sample B. This is confirmed by the slope of the regression lines, whose values are lower than 0.35 for the time increments 5–8 (from 9 to 64 days).

Table 6

Dominant leaching mechanism in “total increment” (2–7)
according to the tank test and parameters of regressions line

Sample	Element	Leaching mechanism	Concentration factor	Regression line	
				Slope	Standard deviation
A	Zn	surface wash-off	212	0.31	0.36
	Pb		72.60	0.008	0.38
	Cu	dissolution	7.90	1.15	0.67
	Ni	surface wash-off	14.27	0.05	0.21
	Cr	diffusion	1.57	0.51	0.31
B	Zn	dissolution	97.94	1.13	0.82
	Pb		28.09	1.19	0.78
	Cu		6.15	0.92	0.59
	Cr	surface wash-off	3.47	0.18	0.12

Table 7 contains only the data for the increments, in which diffusion was the dominant leaching mechanism. This table does not contain data for Pb and Cu from sample A, while for the case of sample B, diffusion accompanied the release of these elements in the final increments (5–8). The leaching of zinc was dominated by diffusion during the increments 4. The increments numbered 2–7 (from 1 to 36 days) are considered to represent the “total increment” representing the entire duration of the diffusion test [18]. This increment does not include the initial and the final eluate fractions with the purpose of avoiding interpretation errors. The first increment is disregarded due the effect of the wash-off process, whereas the other due to the possible avoidance of the fact of a given component depletion during the test. For these reasons, the data in Table 6 can demonstrate the dominant leaching mechanisms assessed as the “total increment”. The value of the concentration factor is also given there, and it is calculated as the quotient of the mean concentration of a component in a given increment and the lower detection limit for this component along with the regression lines (i.e., slope and standard deviation), i.e., between days 4 and 36 of the experiment. Apart from the increments numbered 2–7, the leaching of chromium from sample A was controlled by diffusion during the increments 4–7 as well. With regard to the leaching of nickel from sample A and chromium

from sample B, this process could only be observed over the initial period of the test duration (throughout the 1–4 increments). If the leaching of the given component is dominated by diffusion in a given increment, it is possible to calculate the estimated value of 64 day release (ε_{64} , Eq. (3)) [18]. The results of the estimated cumulative leaching can be compared with the measured cumulative leaching ε_n^* (in Table 5). The best agreement of both values was observed for Zn and Cu for in sample B and Cr in sample A.

Table 7

Diffusion controlled increment according to the tank test, parameters of regressions line and derived cumulative leaching over 64 days (ε_{64})

Sample	Element	Diffusion controlled increment	Concentration factor	Regression line		ε_{64} [mg/m ²]
				Slope	Standard deviation	
A	Zn	4–7	246	0.38	0.42	4990
	Ni	1–4	14.70	0.40	0.22	75.40
		2–5	16.13	0.53	0.22	
	Cr	2–7	1.57	0.51	0.31	4.57
		4–7	2.35	0.43	0.21	
B	Zn	4–7	142	0.55	0.31	2617
	Pb	5–8	48.52	0.59	0.40	302
	Cu	5–8	9.16	0.56	0.51	94.80
	Cr	1–4	2.80	0.54	0.29	10.39

Table 8

Parameters of diffusion of leached elements after 64 days

Sample	Metal	D_e [m ² /s]	pD_e [m ² /s]	$U_{\text{dif}, 64}$ [mg/kg]	$UP_{\text{dif}, 64}$ [%]
A	Zn	$4.12 \cdot 10^{-16}$	15.39	61.56	0.31
	Ni	$5.39 \cdot 10^{-15}$	14.27	0.93	1.11
	Cr	$1.18 \cdot 10^{-13}$	12.93	0.06	5.19
B	Zn	$1.58 \cdot 10^{-16}$	15.80	57.90	0.29
	Pb	$4.17 \cdot 10^{-16}$	15.38	6.67	0.47
	Cu	$1.74 \cdot 10^{-19}$	18.76	2.10	0.01
	Cr	$8.53 \cdot 10^{-13}$	12.07	0.23	21.15

The values of ε_{64} were used to determine the diffusion coefficients (D_e) of individual metals which may serve for the determination of their leaching rates. Table 8 contains the diffusion coefficients (D_e) and the values of pD_e ($-\log D_e$) for Zn, Pb, Cu and Cr. The table also contains the leaching levels of these elements calculated per specific mass unit during the 64 days of the test ($U_{\text{dif}, 64}$, Eq. (5) [18]) and the leaching percentage ($UP_{\text{dif}, 64}$, Eq. (6) [24]).

It is also possible to assess the leaching rate of a given component for its constant availability (U_{avail}) in accordance with EA NEN 7375 [18] based on the pD_e . If $pD_e > 12.5$, the element is said to have a low mobility; for $12.5 > pD_e > 11.0$, it has an average mobility, and for $pD_e < 11.0$ – a high mobility. As is seen in Table 8, all elements with the exception of Cr in sample B have low mobility. Chromium was characterized by the highest level of leaching during the test ($UP_{dif, 64} = 21.15\%$ in sample B, and 5.19% in sample A) of its available content for leaching (as presented in Table 9). Since the level of leaching with regard to the remaining heavy metals was small, we can conclude that the longer duration of the tank test would lead to the release of additional amounts of these metals. Apparently, this tendency is not confirmed with regard to nickel. Despite the fact that the level of its leaching was only 1.11% (and only in sample A), the monolithic form of the waste could prevent its further leaching. Hence, the depletion of this element was recorded in the final phases of the experiment.

Table 9

Available content of a heavy metals determined according to EA NEN 7371 [27]

Element	Zn	Pb	Cu	Ni	Cr
U_{avail} [mg/kg]	20137	1427	21938	84.10	1.09

The leachability of heavy metals differs depending on the physical form of the waste. The leaching of waste in a shredded form is different from the leaching properties of solidified forms. Hence, the assessment of heavy metal leaching from monolithic forms deposited in landfills is relevant in the context of the quality and safety of the ground and water environment. As a result of using diffusion test, such as tank test [18], it is possible to identify the processes accompanying leaching as well as to determine the rate of release of particular elements in addition to the determination of the level of cumulative heavy metal leaching.

4. CONCLUSIONS

The slag from steelworks is considered to be highly hazardous waste due to significant level of Zn, Pb, Cu and Ni leaching during its storage in a landfill, exceeding the admissible values. Heavy metals were leached in lower concentrations with the use of leachants of pH of 4 and 7 (with the exception of chromium). This indicates a heterogeneous content of heavy metals in the waste as well as the small impact of the acidic environment on the leaching of contaminants from the waste in a monolithic form. The waste was characterized by ambiguous leaching mechanism of heavy metals over the entire duration of the test procedure. Surface wash-off and dissolution were the dominant processes during the first 36 of the experiment. Despite the fact that the waste was

considered insoluble, the dissolution could occur from the outer layer of the waste lumps. Chromium was the only element, whose release from the sample subjected to leaching at pH 7 was controlled by diffusion. This process was also observed during some of the increment for the entire duration of the experiment. However, it was not the dominant mechanism noted during the leaching of Zn, Pb, Cu and Ni. On the basis of the calculated diffusion coefficients in the analyzed increments, we recorded low mobilities of all heavy metals except chromium leached at pH 4. Cr was characterized by average mobility. The longer duration of the tank test would lead to the release of additional volumes of heavy metals. This is confirmed by the low level of the leaching of elements in relation to their available content.

In the legislation in Poland, the explicit standard regarding waste characterization concerning the leaching of heavy metals is procedure based on the standard EN 12457-2 (batch test). The requirement for the waste to be deposited in a designated type of a landfill (inert, hazardous or non-hazardous) is fulfilling relevant criteria on the leaching of contaminants presented in the Regulation of the Ministry of Economy on the acceptance of waste for landfill [22]. Nevertheless, the batch test is designed for use with regard to waste in a granulated form, not the waste in the monolithic, solidified form such as waste deposited on dumps and landfills. For this reason, in this paper attention was drawn to the issue associated with leaching of contaminants from monolithic waste. There is a need to establish the leachability criteria to specify the admission conditions of such waste to specific types of landfills.

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