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Original Research

Assessment of Leaching of Heavy Metals from Landfilled Foundry Waste During Exploitation of the Heaps

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Abstract

This article presents the results of heavy metals leaching from foundry waste deposited on two heaps from a Polish foundry. The foundry waste was stored there until the end of the 20th century. The main components of the heaps included stored waste from molding and core sands, dust and sludge from dust collectors, refractory materials, parts from furnace linings, scrap, parts of graphite electrodes and other items. For several years, a portion of the stored waste was recovered and used for the production of road aggregate. Due to the fact that the exploitation of waste heaps and the disturbance of their structure could have a negative impact on the environment, research on the leachability of pollutants from stored waste was undertaken. In 2012-2017 waste samples from both heaps were regularly collected in order to assess the degree of leaching of heavy metals from wastes deposited at various periods. From the samples, the total content of heavy metals and their leachability were determined in accordance with the Polish standard. The research results showed that foundry waste does not have a negative impact on the environment, as the degree of metal leaching was low, and in most cases the permissible standards have not been exceeded.

Keywords: heavy metals, leaching, foundry waste, heap, environment

Introduction

The foundry industry generates various types of waste, depending on the applied technology. This waste includes: spent foundry sands (SFS), molding compounds, furnace slag, sludge or dust from dust collectors as well as other types of waste, e.g., chips, milling and casting scale. It is estimated that the mass of waste generated during foundry production conforms to the total weight of the castings. This means that approximately one ton of molding sand is required to produce each ton of iron or steel casting. According to the Polish classification of waste, foundry waste is listed among several categories of waste, including hazardous waste. In accordance with Polish legislation, more than 75 codes have been attributed to waste derived from foundry production [1, 2]. Some metallurgical waste is a valuable resource for industry, for example, granulated blast furnace slag, due to its high iron content, is used as a mineral additive for cement [3]. The metallic iron from the slag may be used as a raw material for steelmaking or in other technological processes [4-6].

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Spent foundry sands (SFS) are generated in the foundry industry, and they may form up to 90% of all waste mass. The main sources of SFS include byproducts of the molding process, shaking-out and fettling of casting. For this reason, the main direction of waste management of the foundry industry with regard to environmental protection requirements is associated with minimizing the amount of waste generated and providing arrangements for its reuse. Due to the high costs of waste storage, many foundries now use installations for the recovery of SFS. However, not all types of those sands are suitable for recovery and further application in foundries. One positive aspect is that SFS can be used in a variety of industrial branches. The demand for this type of resource is very high. At present, even in Poland waste that was stored for many years can be recycled and re-used. The economic aspects of re-using foundry waste depend on many factors, such as the type of waste, its composition (including the content of the contamination) and physical properties, as well as its accessibility and carriage costs [7]. Waste derived from foundries is usually used in the road building and construction sectors. For example, it is used in the production of concrete mortars, in the production of Portland cement, in filling road bedding, in building road embankments and industrial platforms, as well as in asphalt production and excavations [8-11]. When foundry waste is assigned for further application, it is necessary to carry out adequate tests concerned with contamination leaching. The usual tests offer a variety of measures to assess the toxicity of the investigated wastes and provide classification criteria to determine its further reuse. In 2003 a legal act was issued that unified the criteria for the waste acceptable at landfills in EU countries. Most of the 15 countries of the European Union adopted limits for the pollutants leached from landfill waste according to Waste Acceptance Criteria (WAC) with Decision 2003/33/EC [12]. The countries that have adopted the legislation without amendment CD 2003/33/EC are: the Netherlands, Portugal and the UK (except Northern Ireland), whereas France and Germany have adopted WAC guidelines with changes, mainly regarding limits for non-waste landfill. Within the regulations of the European Union countries, differences in limit values are mainly concerned with the content of organic compounds in eluates from landfilled waste. Most of the Nordic Countries have adopted the WAC directly (CD 2003/33/EC) [12-15]. Denmark adopted the WAC guidelines for inert waste, non-hazardous landfills receiving stable, non-reactive hazardous waste and for hazardous waste. While for landfilled mineral waste, other guidelines apply in Denmark, which are more restrictive than those applied elsewhere in the EU (Table 1). The criteria for waste acceptable at landfills according to Council Decision annex 2003/33/EC for inert, non-hazardous and hazardous waste compared to Danish guidelines are presented in Table 1.

Regarding the acceptance criteria, implementation by national legislation has largely been achieved in most EU-12 member states. Out of the EU-12 countries, only Malta did not accept the WAC guidelines (data from 2010). Poland has adopted the WAC guidelines without major changes; the number of divergences is small in Polish regulation [16]. In contrast, in non-European countries different methods were used to assess the quality of landfilled waste and their impact on the environment. For example, in the USA, more aggressive reagents are used for leaching contaminants from waste, e.g., using the method termed the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP). The most commonly used method in the spent foundry sands quality batch leaching test are also TCLP with liquid solution pH 2.88 or 4.93 (shaking for 18h, ratio 20:1 L/S), SPLP with H_2SO_4 and HNO_3 solution with pH 4.2 (shaking for 18h, ratio 20:1 L/S) or Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM D3987) with water solution [15]. According to Siddique

Table. 1. Criteria for waste acceptable at landfills according to Council Decision annex 2003/33/EC (mg/kg, for liquid to solid ratio of 10/1) for heavy metals (Cd, Pb, Cu, Zn, Cr, Ni, mg/kg) in comparison with exemplary differences in Denmark (for mineral waste).

Metal	Waste Acceptance Criteria (Council Direction 2003/33/EC) [11]			Danish criteria for landfilled mineral waste [13]	
	1	2	3	2	3
Cd	0.04	1	5	0.11	0.14
Pb	0.5	10	50	0.6	0.72
Cu	2	50	100	13	15
Zn	4	50	200	5	5.3
Cr	0.5	10	70	1	1.1
Ni	0.4	10	40	0.5	0.53

1 – limit values for inert waste; in Denmark the criteria were adopted directly from the WAC

2 – limit values for stable, non-reactive hazardous waste and to non-hazardous waste co-disposed, in Denmark for mineral non-hazardous waste

3 – limit values for landfilled hazardous waste, in Denmark for mineral hazardous waste

Table 2. Limit values for heavy metals in eluates from landfilled, industrial or hazardous waste in the USA, Australia, Taiwan and China according to TCLP test or equivalent (mg/L).

Metal	Industrial waste Australia and USA (EPA 2009) [16]	Landfill waste China (Ministry of Environmental Protection, 2008) [14]	Hazardous waste USA (U.S.Government Publishing Office, 2011) [14]	Hazardous waste Taiwan (Taiwan EPA, 2006) [14]	Hazardous waste China (Ministry of Environmental Protection of the People's Republic of China, 2007) [14]
Cd	No limit	0.15	1	1	1
Pb	0.5	0.25	5.0	5	5
Cu	100	40	No limit	15	100
Zn	150	100	No limit	No limit	100
Ni	1	0.5	No limit	No limit	5
Cr	2.5	4.5	5.0	5.0	5

et al. [10], leachate from spent foundry sands may be analyzed, in addition to these three methods, by various leaching methods, i.e., NEN 7343 (Dutch standard column test), NORD TEST 1995 (Nordtest column method) or NEN 7341 (sequential batch availability test). In many countries, including the USA, Australia, China and Taiwan, the amount of leached pollutants is expressed in concentration units (mg/L). According to Arulrajah et al. [17] the U.S. Environmental Protection Agency classifies a material as hazardous if any metal is present in concentrations greater than 100 times that of the drinking water standards. For example, according to Brazilian standards, spent foundry sands are classified as a non-inert residue due to the potential leaching of toxic metal ions [18]. The limits for the concentrations of heavy metals in eluates using the TCLP or an equivalent test in non-European countries are presented in Table 2.

In the USA, Cu, Zn and Ni are not limited in the eluates from hazardous waste, and in Taiwan there is no limitation placed on Zn and Ni concentrations. In China, however, all metals are limited in order to classify waste as hazardous. The Chinese limits for landfilled wastes are more restrictive (with the exception of Cr) than Australia's limit values for industrial waste. The degree of potential contamination caused by waste derived from foundries is related to the composition of the SFS, as well as to the types of binders and hardening substances applied in a specific application. The greatest hazard to the environment is associated mainly with the SFS and dust from dust collectors [10, 19-22]. Wastes with a high content of heavy metals may be solidified in concrete. This process allows for the physico-chemical properties of the waste to be altered; furthermore, this reduces both solubility and leaching [3, 23-25]. The water extraction method is most often used to assess the leaching of pollutants from waste in Europe [12, 26]. In order to increase the effectiveness of the landfilled waste, environmental impact assessments of the leaching tests are carried out using a range of available eluents [10, 15, 27, 28]. The structure and granulometric composition of SFS are similar to soil, and for this reason a mobility of metals analysis may be carried out using tests dedicated to soil and other environmental samples [18, 20]. For this purpose, many types of eluents are used for single versus sequential extractions, and the procedure is designed to provide an analysis of the mobility and bioavailability of metals in the environment, and also for by-products such as SFS [4, 20, 29-32]. The analysis of heavy metals mobility in waste measures their impact on the environment and the determination of the potential for their further application.

The foundry described herein was established in the 18th century, and the manufacture of steel and iron castings forms its market specialty. The molding production process includes the following steps: preparation of molds, smelting of metal, filling molds with liquid metal, separating moldings from molds, cleaning, machining and assembling the elements. For the recovery of sand from used foundry molds, the process of reclamation is used. Molding sands, mainly quartz sands and organic or inorganic binders (self-curing or chemically curing), are used for the production of molds. The process of smelting and casting of metal takes place in two independent production lines. In the first line, single casts are produced with the manual forming of molds. In the second line, molds are formed automatically and machine-made for higher production numbers. The foundry uses induction and arc furnaces. The main component of the waste produced by the foundry at present is spent foundry sands (SFS), which are not reclaimed. In previous years, landfilled waste also included dust from dust collectors (from furnaces, separation, cleaning and the SFS reclamation installation) as well as other waste (scrap, filters, refractory materials, electrodes etc.). In the 1990s, the site of the foundry comprised two heaps in which waste from foundry production was accumulated. Initially, the waste generated during production was landfilled directly on the ground located near the foundry. The first, industrial landfill dedicated to waste from this type of production was established in the 1950s. Waste was collected there on a heap until the 1980s. The second heap (h2) has been expanded twice and it was also recently modernized. SFS are the basic components of the waste collected in the heaps. Other types of waste landfilled in both heaps include foundry slags, refractory materials and dust, as well as other types of waste. Over the years, this waste accumulated in a non-selective manner. In 1995, several companies became interested in the utilization of the waste landfilled on both heaps. In 1997, the foundry signed an agreement with a company operating in the field of the production of road aggregates. The intensive exploitation and recovery of waste landfilled in both heaps began at the beginning of the 21st century. In 2005, the company, which specializes in waste treatment, took over one of the heaps. At the same time, exploitation activities were initiated on the second heap, owned by the foundry. As a result, the volume of the second heap has significantly decreased. After the waste was removed, part of the landfill area was transferred to the ownership of the local government. Recently, the area was divided into investment plots. Currently, a part of the landfill, owned by the foundry, was modernized and adapted to the provisions set out in the environmental protection requirements. As a part of the modernization process of the landfill, various procedures were implemented, including the building of a surrounding collector trench that was used to collect rainwater as well as the installation of piezometers used in the monitoring of the quality of groundwater in the areas surrounding the landfill site. Throughout the period of the exploitation of both heaps, various types of waste were recovered, because they were landfilled at different periods of time. Hence, the composition of the waste depends on the type of foundry production in a given period as well as on the technology applied at that time.

The aim of this study was to assess the level of heavy metal leaching from the foundry waste collected in two heaps belonging to one Polish foundry, during the exploitation of the heaps in 2012-2017. During this period, waste was recovered and used for the production of road aggregates.

Material and Methods

The waste samples were collected from two heaps located next to the foundry in southwestern Poland. The heap (h1) was characterized by an irregular form, approximately 1 km in length, 30-40 m in height and 10-30 m in width (on the top) with a slope of 35-45°. This landfill (h1) was closed in the 1980s and biologically reclaimed. At present, the foundry uses a second landfill, heap (h2), located closer to the foundry and characterized by a lower capacity than h1. The heap (h2) was characterized by a more regular form, 40 m in height. The bottom of heap h1 was characterized by a longitudinal shape, while heap h2 was more regular (Fig. 1).

The area of heap h1 was 7.3 ha, whereas heap h2 was 8.9 ha (from 2016-4.7 ha). It was estimated that before exploitation (2003), the mass of waste collected at both heaps was 3.5 million tons [33]. During the exploitation of heaps, deeper waste layers are often disturbed. For this reason, waste samples were collected over several years during the recovery of waste material from heaps. Samples were taken from a sieve fraction with a diameter of φ <10 mm, in a process designed for the production of aggregates (Fig. 2).

Samples were also taken from the area of the landfill that belongs to the local government at present. Sampling procedures were followed once or twice a year in the period from 2012 to 2017. Samples were derived from several places where specific types of waste are stored, creating a so-called incremental sample with a weight of approximately 25 kg. By application of

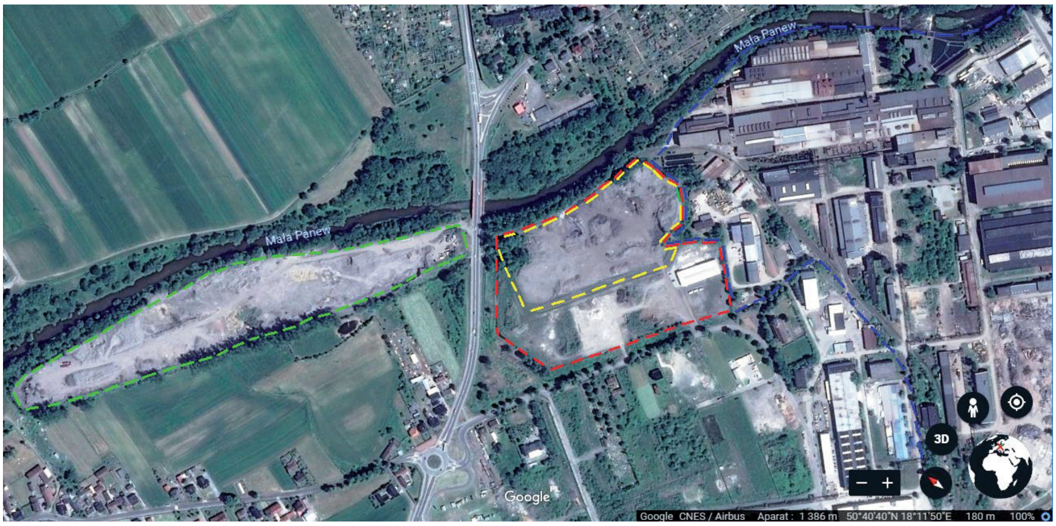

Fig. 1. Location of both heaps and the foundry, with borders marked with a dashed line in the appropriate color: green - heap h1, red - heap h2 until 2015, yellow - heap h2 ("new" after 2015), blue - foundry area.
Image source: Google Earth

Fig. 2. Exploitation of heap h1, sorting-screening machine (Powerscreen-Chieftain 1800), excavator and loader during work.

the quartering procedure, the mass of the incremental sample was reduced to about 5 kg, and a laboratory sample was created. Between 5 and 10 laboratory samples were taken from each heap. In 2012 and 2013, two samples per year (in spring and autumn) were collected. In the remaining years, samples were taken once per year, usually in the spring. During this time at landfill (h2) belonging to the foundry, renovation work was carried out, therefore there were difficulties with taking samples. In the laboratory, the samples were dried at room temperature, sieved (φ <4 mm) and crushed in a mortar to particle size φ <1 mm.

A leaching test was made according to PN–EN 12457–2:2006 [34]. The total content of heavy metals in samples after microwave mineralization (Start D, Millestone) in aqua regia, according to PN-ISO 11047:2001 [35] were determined. In water extracts the content of heavy metals and pH were analyzed. The contents of heavy metals (Cd, Pb, Cu, Zn, Cr, Ni) in digests and water extracts were determined by spectrometer Solaar 6M (Thermo) using the FAAS technique. In addition, the content of organic matter in the waste samples was analyzed at 550ºC according to PN-EN 15935:2013-02 [36]. The pH was measured in an aqueous extract (1/4, m/v) using a glass electrode with pH–conductometer CPC 501 (Elmetron). All samples were carried out and analyzed in triplicate.

For quality control of total metal content determination in the samples, certified reference materials (CRM) were also analyzed after digestion in aqua regia. Two CRM materials were analyzed: 1) ‘metals in soil’ SQC001 (Merck) and 2) rock NCS DC73303. The recovery of metals contents were: 1) Cd 112%, Pb 103%, Cu 106%, Zn 104%, Cr 94%, Ni 107% and 2) Cd 91%, Pb 90%, Cu 94%, Zn 96%, Cr 91%, and Ni 93%.

Table 3. Physicochemical characteristics of waste landfilled in both heaps.

Fractionation*	Percentage [%]	Basic mineral composition**	Percentage [%]	Others**	Value
Fraction 0-10 mm		SiO_2	31-67	Radioactivity [Bq/kg] (+natural radioactivity)	119-152 (100-700)
		Al_2O_3	6-7	^{40}K	24 (10-50)
<10.0-5.6 mm	6-23	Fe_2O_3	2-21	^{226}Ra	13-43 (7-50)
>4.0 mm	3-5	CaO	9-28	^{228}Ra	
>2.8 mm	4-5	MgO	3-9		
>2.0 mm	3-5	Na_2O	0.1-0.4		
>1.6 mm	2-3	K_2O	0.2-1.5		
>1.4 mm	1-2	Mn_3O_4	2-4		
>1.0 mm	4-8	SO_3	0.3-0.5		
>0.8 mm	3-7	P_2O_5	0.1-0.5		
>0.6 mm	10-39	BaO	0.04-0.05		
>0.4 mm	11-19	TiO_2	0.3-0.4		
>0.2 mm	11-24	Cr_2O_3	1.1-2.3		
<0.2 mm	3-10	SrO	0.04-0.05		

* - Own study (2012-2017)

** - the results of the analysis (1987-2006) made by commercial laboratories were presented in Table 3. The results were obtained from foundry materials and have been made available to present the composition of the waste in this article according to [37]

Results and Discussion

The physicochemical characteristics of the foundry waste are presented in Table 3.

In Table 4 the total metal content, organic matter content and pH of the foundry waste (SFS) samples collected from two heaps in the time range 2012-2017 are summarized.

On the basis of commercial expertise, it was found that the main component of landfilled waste is spent foundry sand (90% of waste mass). Other wastes are foundry slag and refractory materials. The waste was characterized by a dark-brown color. The waste did not emit odors. The highest percentage fractions were fine-grain (<0.8 mm) and coarse-grain fractions (10-5.6 mm). The landfilled waste from both heaps was classified as a mineral material. The main component of the waste is silica (Table 3). The waste also contains a high percentage of iron and calcium oxides. The radioactivity of the waste is at a natural level [38].

The foundry waste was characterized by a weakly alkaline pH, within the range of pH 8.0 (Table 4). The alkalinity of the analyzed waste may have an impact on the reduced leachability of heavy metals. Organic matter content, calculated as a loss of ignition, was low (up to 3%). The results of the analysis showed a very wide range of heavy metals concentrations in the tested foundry waste (Table 4). The waste samples were characterized by a low cadmium content (0.6-4.1 (h1) and <0.2-0.8 (h2) mg/kg. The lower cadmium content results were also obtained by Dayton et al. (2010) in spent foundry sands from 39 U.S. foundries at the level of <0.04-0.360 mg/kg. The authors investigated the green sands – the term for original sand being treated with a bonding agent (e.g., bentonite and clay) in the molding process. They obtained the content of other metals in a wide range: Pb 1-22.9 mg/kg, Cu 0.5-137 mg/kg, Zn 10-245 mg/kg, Cr 0.5-115 mg/kg and Ni 1.11-117 mg/kg. In the current study, the highest content of chromium was found in the tested waste (239-677 (h1) and 109-254 (h2) mg/kg). The source of this metal in the tested foundry waste may be residuals of metal scrap containing steel with the addition of chromium, nickel and zinc, which are alloy additives in steel. Therefore, in foundry waste, the Cr, Ni and Zn content may be high. In addition, chromite sand is used in the foundry for the production of some castings. The sand contains about 45% Cr_2O_3. Although it is a form of chromium bound in the crystalline structure of the sand, it may be a potential source of chromium in the investigated waste. As a result of thermal and chemical factors or the grinding of sand, the Cr could be leached or the raw sand may be contaminated with this metal [38, 39]. The total heavy metal content in the spent foundry sands is present in the following order: Cd (<0.2-4.1 mg/kg)<Pb (15-50 mg/kg)<Cu (22-106 mg/kg)<Ni (38-117)<Zn (60-284 mg/kg)<Cr (109-677 mg/kg). Dungan and Dees [27] examined the total content of metals from spent foundry sand samples taken from 43 foundries in the USA, which mainly use green sands for casting production. In the [27] study the total metal content was varied, within a wide range, respectively: Cd<5.9 mg/kg, Pb<7.7-25.7 mg/kg, Cu <23.1-3318 mg/kg, Zn<33.41-1640 mg/kg, Ni<1.21-2328 mg/kg, Cr<1-149 mg/kg.

The source of heavy metals in SFS could be raw foundry sand and the binding used for the production of molds. However, the main source of metals are the metallic residues from the cast [10, 27, 41]. The chemical composition of steel castings, especially metal additives that improves its properties also affects the total metal content in SFS. According to Dungan and Dees [27] trace metals may accumulate in the SFS during casting operations. It has been proven that the residual of metals of the cast in SFS are usually non-mobile (non-leached). However, it has been reported that some spent foundry sands may be corrosive to metals due to the presence of phenols in the foundry sand [10]. It turns out that SFS from the iron and steel foundry contain less heavy metals than those from the foundry of non-ferrous metals, especially Cd, Pb, Cu, Ni and Zn [10]. The EPA does not recommend the use of non-ferrous foundry sand because of concerns over the potential leaching of those metals. The most commonly used spent foundry sand is green sand. It has been proven that the leachability of organic contaminants and heavy metals from green sands is low. Therefore, this waste is most often used in road construction, construction and even in soil-related applications [41]. Spent foundry sands often demonstrate soil-like qualities, making them potentially attractive components in agriculture and horticulture [10, 27]. The Dungan and Dees [27] study concluded that the total metal concentrations in the majority of SFS were lower than the range measured in U.S. agricultural soils. The source of metals in foundry waste may be due to waste (dust, slags, scrap metal, etc.) other than spent foundry sands. In particular, dust from dust collectors that removes dust from foundry furnaces may contain organic pollutants and heavy metals from contaminated scrap. Scrap used in steel production may be contaminated by varnishes, greases and paints, which are a source of metals in the dust [19]. Contaminants from scrap may also be found in steel slags. Siddique et al. [10] concluded that dust and slag are more contaminated with heavy metals (e.g., Cd, Cu, Fe, Pb, and Zn) than sand. An important environmental aspect of using foundry waste is the leachability of pollutants. SFS leachate may be characterized as a water-based solution of different groups of contaminants, e.g., water-soluble organic substances, macronutrients inorganic cations and anions, heavy metals and xenobiotic organic compounds [10]. Some authors have obtained results that indicate that metal leaching from SFS is similar to that in soils [10, 27, 30]. This may suggest that metals in SFS are in non-mobile forms or that metal cations are bound with the structure of the sand as in soils, due to the content of organic matter, iron, manganese, aluminum and clay materials in the waste. According to a U.S. EPA

Table 4. The characteristic of foundry waste samples taken in the range 2012-2017 from two heaps during exploitation (fraction <4mm): mean±SD (min-max).

Year	n	pH	OM [%]	Total content of heavy metals [mg/kg]					
				Cd	Pb	Cu	Zn	Cr	Ni
h1									
2012	10	8.0±0.2(7.7-8.3)	1.9±0.5(1.3-3.0)	4.1±1.6(1.9-6.8)	37±10(21-54)	60±32(25-112)	130±39(76-189)	677±232(298-1090)	113±30(74-167)
2013	10	8.0±0.2(7.8-8.2)	1.8±0.2(1.7-2.1)	2.4±1.3(1.1-5.4)	50±15(29-70)	102±32(59-167)	234±102(110-450)	425±167(129-672)	106±24(76-145)
2014	5	8.1±0.2(7.8-8.3)	1.5±0.2(1.3-1.9)	1.8±0.9(1.1-2.9)	35±14(22-56)	106±19(86-132)	284±50(213-345)	305±105(189-459)	113±28(74-145)
2015	5	8.1±0.3(7.8-8.4)	1.5±0.2(1.2-1.7)	2.6±0.9(2.0-3.9)	34±13(20-56)	92±26(59-123)	235±73(154-349)	313±120(129-459)	117±30(70-149)
2016	5	8.3±0.1(8.2-8.4)	1.6±0.4(1.2-2.1)	2.0±1.0(1.1-3.1)	43±15(31-67)	85±19(56-102)	236±45(197-301)	316±106(198-460))	88±33(50-120)
2017	5	8.2±0.3(7.8-8.5)	1.5±0.2(1.2-1.8)	0.6±0.3(0.3-1.0)	50±24(23-82)	99±14(76-112)	228±54(156-302)	239±120(104-433)	115±36(76-167)
h2									
2012	10	7.6±0.6(6.4-8.1)	2.4±0.4(1.9-3.0)	0.7±0.2(0.2-1.0)	15±15(2.46)	22±16(6-56)	60±52(10-166)	109±98(43-311)	38±29(10-82)
2013	10	7.8±0.2(7.5-8.1)	2.4±0.4(2.1-3.0)	0.8±0.3(0.4-1.2)	37±16(10-57)	97±42(29-167)	97±48(42-178)	183±125(64-432)	79±39(20-129)
2014	5	7.8±0.1(7.6-8.0)	2.0±0.3(1.6-2.4)	0.5±0.3(0.2-0.8)	28±17(12-56)	59±36(29-120)	70±30(45-119)	114±30(78-154)	65±22(41-89)
2015	5	7.7±0.1(7.5-7.8)	2.1±0.3(1.8-2.6)	0.7±0.4(0.2-1.0)	42±15(24-56)	59±40(36-129)	97±48(35-157)	152±67(65-239)	71±23(48-107)
2016	5	7.8±0.2(7.5-8.1)	2.7±0.4(2.1-3.0)	0.7±0.5(0.2-1.3)	32±21(12-65)	38±12(25-56)	68±30(47-119)	144±51(65-189)	67±30(45-118)
2017	6	7.9±0.4(7.3-8.5)	2.9±0.4(2.2-3.3)	<0.2	33±13(16-46)	78±59(27-192)	98±25(55-121)	254±321(65-902)	63±29(34-98)

n – number of samples OM – organic matter report, the content of metals does not indicate whether SFS is similar to soil with respect to how those metals behave [42]. It has not yet been established whether the forms of metals in SFS are more mobile, bioavailable, or toxic than those same metals in native soils. It was found that metals in SFS will probably behave in a very similar manner to metals in native soils. According to Dungan and Dees [27], water leaching eluates measured using the ASTM test were below the limits of quantification for most samples, respectively: Cd<0.01, Pb<0.05, Cu<0.07 (to 1.1), Zn<0.22 (to 1.3), Ni<0.05, Cr<0.01 (to 0.04) mg/L. However, using more aggressive tests (SPLP and TCLP), the authors [27] found a slightly higher percentage of metal leaching. The conclusion of the authors was that the SFS have a low metal leaching potential under the specified test conditions [27]. Similarly, Arulrajah et al. [17] have determined that the concentrations of most metals in aqueous eluates from spent foundry sands (ASTM test) are below the limit of quantification: Pb, Cu, Ni, Cr<0.1 and Zn 1.067 mg/L. In the current study, the concentration of heavy metals in tested foundry waste water extracts [mg/kg] are presented in Table 5. The results were compared with Polish regulations concerning the storage of inert waste [42].

The leachability of metals from foundry waste was minimal, despite the high total content of these metals in the waste. The content of cadmium, lead and nickel was below the limit of quantification in all samples. Zinc was characterized by the highest level of leaching. Nevertheless, the concentration of this metal in water extracts was low (<0.5-1.2 mg/kg). The chromium was leached from waste landfilled on the h1 heap (<0.5-0.7 mg/kg). However, chromium toxicity is higher than that of zinc, so the soil and groundwater quality around the landfill should be analyzed regularly. For most samples, the content of metals in water extracts did not exceed the limit values for landfilled inert waste in Poland. Similar results were obtained by Żmudzińska and Latała-Holtzer [43], who analyzed the leachability of contaminants from typical Polish SFS. The authors observed the lower leachability of most metals compared with the limit values for inert waste, which allows for the use of this waste in road engineering. The results of heavy metals content in water extracts from SFS according to [43] were: Zn 0.508; Cu<LOQ; Cr 0.038; and Ni 0.099 mg/kg respectively. A significantly higher content of heavy metals in water extracts from metallurgical waste was presented by Iluțiu-Varvara [26]. The author analyzed the leachability of heavy metals from landfilled metallurgical waste from the Păgida metallurgical slag dump in Alba County, Romania. In Romania, landfilled wastes are classified as inert, non-hazardous or hazardous on the basis of water extracts (2 L/kg), whereas in Poland this type of test (2 L/kg) is an additional test. The main test is based on the ratio 10L/kg (liquid/solid phase), and the results are converted to mg/kg d.m. The author [26] obtained a very wide range of heavy metal concentrations leached

Table 5. Range (min-max) of heavy metals content in water extracts from spent foundry sands and limit values for landfilled inert waste in Poland [39].

Year /metal	Leachability of heavy metals [mg/kg]												Limit value from inert waste (liquid to solid ratio of 10/1)
	2012		2013		2014		2015		2016		2017		
	h1	h2	h1	h2	h1	h2	h1	h2	h1	h2	h1	h2	
Cd	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.04
Pb	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5
Cu	<0.5-1.0	<0.5-0.6	0.5-0.7	<0.5-0.6	<0.5	0.5-0.6	0.5-0.8	0.5-0.7	0.5-0.8	<0.5	<0.5	0.5-0.8	2
Zn	<0.5-0.8	<0.5-0.6	0.5-1.0	<0.5-0.7	0.5-0.6	0.5-1.2	<0.5-0.5	<0.5-0.5	<0.5-0.9	<0.5	<0.5-0.6	<0.5	4
Cr	<0.5-0.7	<0.5	<0.5-0.6	<0.5	<0.5-0.6	<0.5	<0.5-0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5
Ni	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5-0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.4

Limit of quantitation (LO
Q): Cd 0.05; Pb, Cu, Zn, Ni, Cr 0.5 mg/kg d.m.

from metallurgical wastes, especially in the case of chromium, nickel and zinc: Cd (0.104-0.479 mg/L), Pb (0.112-0.869 mg/L), Ni (0.112-3.212 mg/L), and Cr (0.192-2.514 mg/L, Zn (0.173-3.313 mg/L). The author [26] concluded that a metallurgical solid waste may have a hazardous potential for the environment due to the leaching of heavy metals. Moreover, the author [26] recommends an investigation of the degree of contamination of the soil, air, and water environmental factors in the slag dump and in its surrounding area.

Based on the results obtained, it may be concluded that the heavy metals present in the foundry waste landfilled on both heaps were strongly associated with the matrix, so that they were not leached. The exploitation of waste heaps and the recovery of waste did not have a negative impact on groundwater pollution and soil in the immediate surroundings of landfills, due to low metal leachability. However, the waste treatment process during exploitation, such as crushing, screening and sorting, may cause significant dust emissions. Therefore, in order to assess the environmental impact of operations carried out during exploitation, the quality of the environment (soil, water, air) after heap liquidation should be analyzed.

Conclusions

The tested wastes were characterized for total heavy metals content. This is related to the diversity of accumulated waste, mainly from the composition of the waste layer being sampled at a given time. Their composition was affected by the type of production and technology used in a given period. A high concentration of heavy metals, especially Cr, was found in some samples. Nevertheless, the leachability of metals was low. In many cases, the concentration of metals in aqueous extracts was below the limit of quantification. This is important, especially in the case of toxic metals (Cd, Pb, Ni), because their penetration into soil and groundwater may have a negative impact on the environment. The study showed that the heavy metals present in the tested foundry waste were mainly in non-mobile forms, strongly associated with the matrix. The waste landfilled in two heaps does not pose a considerable threat to the environment, in terms of heavy metal leaching. The main study showed a leaching of most commonly measured metals (Cd, Pb, Cu, Zn, Ni, Cr) in environmental samples. Foundry waste may also contain other heavy metals. Some metals are used as additives to cast steel or cast iron applied to adapt material properties to specific requirements. Therefore, in order to assess the environmental impact of the investigated waste, further metals analysis and the leaching of other inorganic and organic pollutants should be considered. The results of these analyses will be presented in the other article.

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