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## The assessment of heavy metal binding forms in foundry wastes used as raw materials in agrotechnics, construction and road construction

### Introduction

The assessment of forms of heavy metal in environmental samples is very complex and often difficult due to variations in the metal binding phases, the influence of environmental factors or the amorphous nature of metals. Most methods for assessing the physical and chemical forms of metals in the environment are based on leaching using selected eluents that simulate environmental conditions. Extraction with eluents can be performed in one step (sample + eluent), in which case we call it a single-step extraction. The second type involves many steps (sample + multiple eluents), and is called sequential/multi-step extraction or speciation. The term “speciation analysis” emerged in literature in 1954 to describe the circulation of trace elements in seawater, then in bottom sediments and soils (1958) (Głosińska et al. 2001). In the 1970s, extensive research on the occurrence of heavy metal

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compounds in other environmental samples started. The result was the development of the best known sequential procedure for the speciation of metals in bottom sediments proposed by Tessier et al. (Tessier et al. 1979). Speciation is not a chemical term, so IUPAC recommended the use of the substitute “fractionation”. However, in scientific literature, “speciation”, “sequential extraction” and “fractionation” are still used as synonyms. Currently, speciation techniques are used to assess metal fractions in bottom sediment, soil, sewage sludge, compost, ash, waste and others. Speciation analysis is important especially when assessing the suitability of waste for agrotechnological use (Förstner 1993; Świetlik and Trojanowska 2008). However, for wastes that are landfilled or destined for reuse, one-step extraction with the use of one eluent under controlled conditions is most commonly used (Rao et al. 2008). Analyses of the chemical speciation of heavy metals is useful for assessing most heavy metals and metalloids. One exception may be mercury, which is bound in a different way to other metals in the environment (Bloom et al. 2003; O’Connor et al. 2019). The low content of Hg in environmental samples, including foundry waste, is also important (Bożym and Kłojzy-Karczmarczyk 2020, 2021; Kłojzy-Karczmarczyk and Mazurek 2021). It may cause problems in assessing the speciation of this metal in the samples.

Two speciation procedures are the most popular and recognized: the Tessier procedure and the SM&T procedure (the Standards, Measurements and Testing Program, until 1993 BCR from the Community Bureau of Reference) (Ure et al. 1993). The history of the SM&T procedure began in 1987 during the implementation of the European Community Standards, Measurement and Testing Program. The aim of the program was to standardize procedures for the speciation of metals in environmental samples. The result was the standardization of metal separation techniques. The following fractions are distinguished in the Tessier’s procedure: exchangeable (F1), carbonate (F2), Fe-Mn oxides (F3), organic (F4) and residual (F5) oxides. By contrast, the SM&T procedure categorizes metals into four fractions by combining the exchangeable and carbonate fractions (F1). The other fractions, as in Tessier’s procedure, have consecutive numbers (F2–F4). The exchangeable fractions are poorly adsorbed metals retained on the surface of the solid with relatively weak electrostatic interactions. These metals can be mobilized as a result of ion exchange processes, sensitivity to adsorption-desorption processes or pH reduction. The metals which are bound with this fraction are highly mobile and bioavailable. In the Tessier procedure, this fraction is eluted with saline while the carbonate fraction is eluted with a mixture of sodium acetate and acetic acid. By contrast, in the SM&T procedure, the exchangeable and carbonate fractions are eluted with acetic acid. The metals that are exchangeable and bound to carbonates (fractions 1 and 2) are corresponded to be the most mobile, and therefore the fractions are leachable. The metals related to iron and manganese oxides and organic matter are also available, but their mobility is much slower (Ure 1995; Rao et al. 2008).

The one-step procedure recommended for evaluating the reuse of foundry waste is The Toxicity Characteristic Leaching Procedure (TCLP) (USEPA Test Method 1311) (Fahnline 1995; Bastian and Alleman 1998; Lindsay and Logan 2005; Dungan and Dees 2009; Siddique et al. 2010; Zhang et al. 2014; Bożym 2017). The TCLP procedure classifies wastes

and assesses their toxicity and impact on groundwater (Ji et al. 2001). The TCLP procedure may be used to assess the toxicity of various waste (Klojzy-Karczmarczyk et al. 2021). It is used to evaluate the leaching of pollutants from solid waste, solidified waste, monolithic waste, waste-based products and hazardous waste. The procedure relies on the use of acetic acid to simulate the effect of acid rain on the leaching of contaminants from waste. A single TCLP extraction can be compared to the first fraction of the SM&T procedure due to the use of acetic acid. Thus, the metals leached by both of these procedures may be mobile and potentially bioavailable metal fractions.

The final step of the evaluation of metal fractions present in the samples is to determine their total content. Neither the Tessier nor the SM&T procedure specifies the leaching conditions of the residual fraction. The content of metals associated with residual fraction is usually calculated on the basis of the difference between the total metal content and the sum of other fractions. Rao et al. (Rao et al. 2008) propose a separation of the term “total content” from the term “pseudo-total.” The authors suggest that the term “total” should only be used for metals contained in the sample, including those bound with the crystal lattice that are not bioavailable or mobile. Therefore, the authors propose using the term “pseudo-total content” for metals bound with potential mobile fractions in different environmental conditions.

The presented extraction procedures may be useful for evaluating foundry waste that is reused as raw materials in various industrial and agricultural sectors. Foundry waste is usually used for backfilling excavations, the production of asphalt, Portland and bituminous cement, and the manufacture of ceramic products (Bożym and Dąbrowska 2012; Bożym 2018). The grain composition of foundry waste based on spent foundry sands (SFS) is similar to soils; therefore, many countries use this waste for the production of Technosols and as artificial gardening substrates (AGS) (Bożym 2021). Foundry dust is used as a raw material and as a fuel in the foundry industry and as an additive to building materials due to the high proportion of silica or as an inert material, i.e. in inactive hard coal mines or as a covering for top heaps (Bożym and Zalejska 2014; Bożym 2018).

Many countries regulate the use of industrial by-products. The most stringent requirements have been developed for the agricultural use of waste (Bożym 2017, 2020, 2021). Foundry wastes can be used in agrotechnology provided that the level of contamination with heavy metals and organic pollutants is low (Dungan et al. 2006; Bożym 2021). There are no reports on heavy metal fractions in foundry waste (Bożym 2017). There are few reports on the use of speciation methods for the analysis of landfilled metallurgical waste and local soils, and coming from the study of iron and steel works area located in southern Italy and in the north-east of France (Venditti et al. 2000a, b; Adamo et al. 2002; Remon et al. 2005). To evaluate foundry waste used in road engineering, construction and agrotechnology or deposited in landfills, researchers most often use extraction with deionized water according to the ASTM or EN 12457 procedure (Dungan and Dees 2009; Dayton et al. 2010; Siddique et al. 2010; Bożym 2019, 2020) or extraction with acids according to the TCLP or SPLP procedures (Fahnlne 1995; Bastian and Alleman 1998; Lindsay and Logan 2005; Dungan and Dees 2009; Siddique et al. 2010; Zhang et al. 2014). So far, the chemical forms of heavy

metals in foundry waste used in agrotechnology have not been analyzed based on the speciation procedures.

The aim of this study was to analyze the fractions of heavy metals in foundry wastes based on one-step extraction according to the TCLP procedure and sequential extraction according to Tessier and SM&T. The first type of extraction is used to assess foundry waste reused in the construction and the road-building industries. It can also be useful for the classification of waste and for assessing its use in agrotechnology. Sequential extractions are mainly used to assess the suitability of waste in agrotechnology, and, to a lesser extent, in industrial applications or landfilling. Additionally, speciation analysis of heavy metals in local soils was carried out for comparison with the use of foundry waste as a raw material for the production of artificial soil substrates.

## 1. Research methodology

### 1.1. Description of the samples

Landfill foundry waste LFW and dust from one of the Polish iron and cast steel foundries were used in the research. The waste was landfilled in the heap in the years 1985–2017. The components of LFW were mainly spent foundry sands SFS (80–90% wt.), but also included slag, used refractory materials, dasts, and metallic inclusions. At present, the LFW are recovered and used for the production of road aggregates. LFW samples were taken from six piles of recovered material with a granulation size of <10 mm. The samples were collected in accordance with Polish standards (PN-EN 932–1.2). From each pile, 10–15 primary samples were taken. The samples were mixed and the volume was reduced by quartering. The samples were dried at room temperature ( $\approx 20^{\circ}\text{C}$ ), ground in a mortar and sieved through a sieve with a mesh size of 1 mm. The samples prepared in this way were analyzed.

Dust samples were collected from the same foundry in 2017 and 2018 from dust collectors of forming, shot blasting and steelworks units: shock grating dust (SGD), regeneration (of spent foundry sands) dust (RD), transport (of molding sands) dust (TD), electric arc furnace dust (EAFD) and pneumatic blast cabinet dust (PBCD). The foundry uses bag dedusting, which facilitated sampling. The dust from the foundry is reused outside the foundry, e.g. in the steel industry (EACD and PBCD) or as shaft filler in closed mines. RD can also be used as a combined fuel and raw material in the cement industry due to the high proportion of silica from the foundry sands and organic matter from the binders (Bożym 2018).

In order to assess the local background, soil samples were collected from twenty measurement points located at different distances from the landfill (Bożym et al. 2009; Bożym and Kłojzy-Karczmarczyk 2021). Soil samples were collected from arable lands, meadows, wastelands, allotment gardens and forest areas. The tested soil samples were classified as

sand and loamy sand according to the soil granulometric classification. Soil samples were taken at the same time as the waste. Soil samples were prepared as LFW.

For waste and soil samples, the loss on ignition LOI was determined in accordance with the PN-EN 15169 standard, and the pH was determined in accordance with the PN-ISO 10390 standard.

## 1.2. Extraction procedures

The Tessier (Tessier et al. 1979) and SM&T (Ure et al. 1993) procedures and single TCLP (USEPA Test Method 1311) extraction were used to analyze the forms of heavy metals. The extractions were carried out by shaking the samples with a sequence of extractants. The shaking was performed on a rotary shaker at a speed of 30 rpm. After each step, the suspension was centrifuged at 3500 rpm and the supernatant was decanted and analyzed. The sediment was washed with water, shaken for fifteen minutes and centrifuged again. The water after washing was removed. The sediment was subjected to the next extraction step.

## 1.3. Heavy-metal analysis

The samples of foundry wastes were digested in a mixture of concentrated acids HNO<sub>3</sub>, HCl and HF in the proportions 1 : 3 : 0.1 in accordance with the PN-EN 13656 standard. A Start D (Milestone) microwave mineralizer was used for digestion. The analysis of heavy metals in extracts and mineralizates was performed with the Solaar 6M (Thermo) atomic absorption spectrometer using two techniques: flame atomic absorption spectrometry FAAS and graphite furnace atomic absorption spectrometry GF-AAS (PN-ISO 11047). All analyses were performed in triplicate.

## 1.4. Quality control

All reagents used during extraction and mineralization were of high purity. For the quality control of heavy metals, the total content of certified reference materials (CRM) were analysed such as ‘metals in soil’ (SQC001, Merck), ‘urban particulate matter’ (SRM 1648a, Sigma Aldrich) and ‘fine dust PM10-LIKE’ (ERM®-CZ120, IRMM). Certified material was used to assess the quality of the extraction procedures SQC006 (CA WET Metals in Soil – QC; Sigma-Aldrich). A recovery of heavy-metal analysis in the CRM samples ranged from 80–110%. The analytical range control was based on the analysis of samples of the established standards and was performed for each measurement series. In order to check the correctness of the curve range, the standard checking the ICP-multi-element standard XI was analyzed each time (Merck, Lot: HC394644).

## 1.5. Results

Table 1 presents the content of heavy metals in the tested waste samples and soils. Due to the spread of the results for tested soils, the range (min–max) of heavy-metal content is presented.

Table 1. Physicochemical properties (pH, LOI) and total heavy-metal content in waste and soil samples (mean  $\pm$  SD)

Tabela 1. Właściwości fizykochemiczne (pH, LOI) i zawartość całkowita metali ciężkich w próbkach odpadów i gleb (średnia  $\pm$  SD)

Parameter	LFW (n = 6)	SGD (n = 2)	RD (n = 2)	TD (n = 2)	EAFD (n = 2)	PBCD (n = 10)	Soil* (n = 20)
pH	7.9 $\pm$ 0.4	5.1 $\pm$ 0.1	5.4 $\pm$ 0.5	6.0 $\pm$ 0.2	7.6 $\pm$ 1.5	8.2 $\pm$ 0.5	6.0–7.6
LOI (% wt.)	4.0 $\pm$ 2.0	7.0 $\pm$ 0.6	13.8 $\pm$ 3.2	7.9 $\pm$ 5.2	10.1 $\pm$ 0.7	2.5 $\pm$ 0.4	1.77–5.25
Cd (mg/kg DM)	0.25 $\pm$ 0.00	0.30 $\pm$ 0.00	1.45 $\pm$ 0.18	7.60 $\pm$ 1.20	33.55 $\pm$ 5.60	2.11 $\pm$ 0.67	0.33–0.98
Pb (mg/kg DM)	35.7 $\pm$ 4.3	111 $\pm$ 12	36.4 $\pm$ 4.5	75.9 $\pm$ 5.7	2 590 $\pm$ 121	14.2 $\pm$ 2.9	10.1–50.9
Cu (mg/kg DM)	81.2 $\pm$ 5.1	1 100 $\pm$ 25	659 $\pm$ 22	412 $\pm$ 12	1 345 $\pm$ 101	456 $\pm$ 27	3.2–33.5
Zn (mg/kg DM)	102 $\pm$ 9	1 655 $\pm$ 26	1 045 $\pm$ 13	712 $\pm$ 2	3 290 $\pm$ 218	6 598 $\pm$ 176	10.5–87.1
Cr (mg/kg DM)	125 $\pm$ 7	458 $\pm$ 25	298 $\pm$ 11	255 $\pm$ 11	228 $\pm$ 17	298 $\pm$ 11	3.4–12.4
Ni (mg/kg DM)	71 $\pm$ 5	178 $\pm$ 12	101 $\pm$ 7	75 $\pm$ 4	345 $\pm$ 22	629 $\pm$ 43	1.5–21.6
Mo (mg/kg DM)	29 $\pm$ 4	139 $\pm$ 22	84 $\pm$ 5	66 $\pm$ 5	176 $\pm$ 12	71 $\pm$ 9	1.5–2.7
Co (mg/kg DM)	25 $\pm$ 2	16 $\pm$ 1	15 $\pm$ 1	34 $\pm$ 2	42 $\pm$ 2	55 $\pm$ 3	1.5–3.2

\* For soil samples a range min–max was presented.

LFW – landfilled foundry waste; SGD – shock grating dust; RD – regeneration dust; TD – transport (of molding sands) dust; EAFD – electric arc furnace dust; PBCD – pneumatic blast cabinet dust.

Of the foundry waste samples tested, LFW had the lowest total content of heavy metals. This waste consisted mainly of SFS. Many authors propose the use of foundry waste based on SFS for agrotechnological purposes (Dungan et al. 2006; Dayton et al. 2010; Miguel et al. 2014). The condition for such application is a low content of heavy metals and organic

pollutants. Therefore, only SFS from steel and iron foundries containing mineral binders are used in agriculture and horticulture (EPA Report 2014). The total content of heavy metals in LFW was found to be higher than in local soils (Table 1). The content of heavy metals in LFW did not exceed the permissible values for arable soils in Poland (Journal of Law 2016, item 1395), which may suggest no contamination. The content of heavy metals in local soils did not differ from the average values for Polish soil (gios.gov.pl). No contamination with heavy metals was found in the soils according to the guidelines of Polish law (Journal of Laws 2016, item 1395), which may indicate that the foundry did not have a negative impact on local soils. Considering the possibility of using the studied LFW for agricultural purposes, it is necessary to assess the leachability of organic compounds and heavy-metal fractions. Previous studies have shown that formaldehyde and phenol from phenol-formaldehyde binders were leached from LFW. The phenol concentration in LFW water extracts exceeded the limit values specified for inert waste. Formaldehyde released in leachate from landfill waste in Poland is not regulated by law (Bożym 2020). For this reason, the use of LFW for agricultural purposes should not be considered.

## 2. Speciation analysis

Figures 1 and 2 show the results of the analysis of heavy-metal speciation according to the Tessier and SM&T procedure in waste samples and in soils. The results are shown as a percentage for each fraction compared to the total content.

In the environment, and especially in the soil, **cadmium** usually occurs as mobile divalent ions, complex ions ( $\text{CdOH}^+$ ,  $\text{CdHCO}_3^-$ ,  $\text{CdCl}^-$ ,  $\text{Cd}(\text{OH})_4^-$ ) and organic chelates. In acidic soils, Cd is very mobile and is mobilized at pH values as low as 6.5 (Kabata-Pendias and Pendias 1999; Kabata-Pendias 2010). In contaminated soils, Cd is associated with exchangeable and carbonate fractions, while the percentage of its organic and oxide forms is lower (Filipek and Domańska 2002). In the current study, the highest percentage of mobile fractions (F1 and F2 Tessier and F1 SM&T) was found in LFW (29 and 20%). A slightly lower percentage of these compounds was found in EAFD dust samples (23 and 22%). These dusts also revealed increased percentages of Fe-Mn oxides (F3 Tessier and F2 SM&T) and the organic form (F4 Tessier and F3 SM&T), which may be released into the environment under appropriate red-ox conditions or after the decomposition of organic compounds. It is conceivable that environmental contamination may occur due to the improper handling of this waste. Many authors report that EAFD is classified as hazardous waste due to the high leachability of heavy metals (Bożym 2020; Strobos and Friend 2004; Salihoglu and Pinarli 2008; Mymrin et al. 2016). Therefore, this dust should not be landfilled without processing, i.e. after it has solidified in concrete. This procedure entails high costs; therefore, foundries reuse it as a raw material in the casting process due to the high percentage of Fe. In this study, LFW samples had a higher percentage of the organic fraction (F4 Tessier and F3 SM&T) at 35 and 25%. This may indicate the strong bonding of cadmium to the remaining

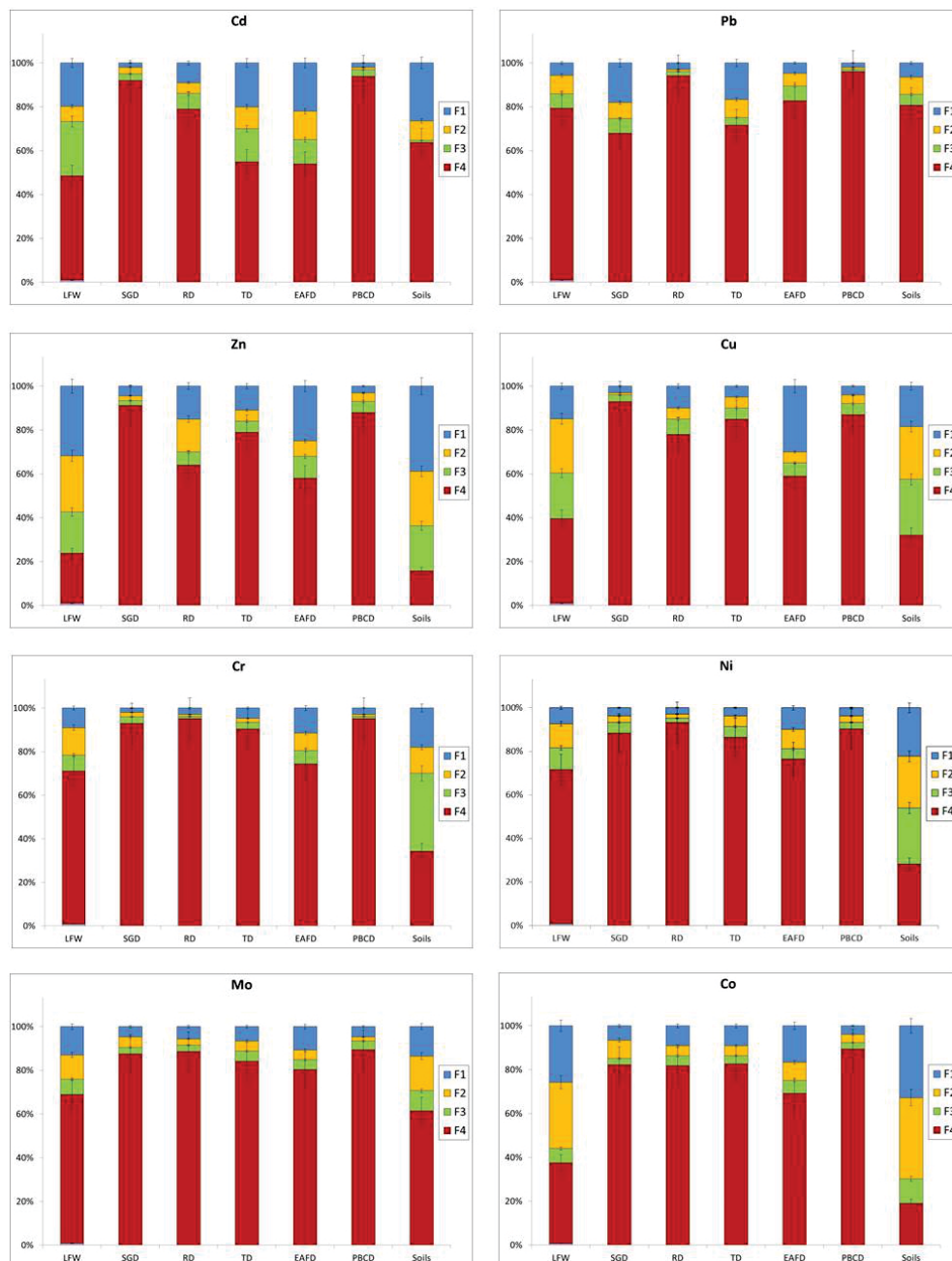


Fig. 1. Speciation analysis of waste and soil samples according to SM&T procedure

LFW – landfilled foundry waste; SGD – shock grating dust; RD – egeneration dust;

TD – transport (of molding sands) dust; EAFD – electric arc furnace dust; PBCD – pneumatic blast cabinet dust;

F1–F4 – fractions of SM&T procedure

Rys. 1. Analiza specyjacyjna badanych próbek odpadów i gleb według procedury SM&T



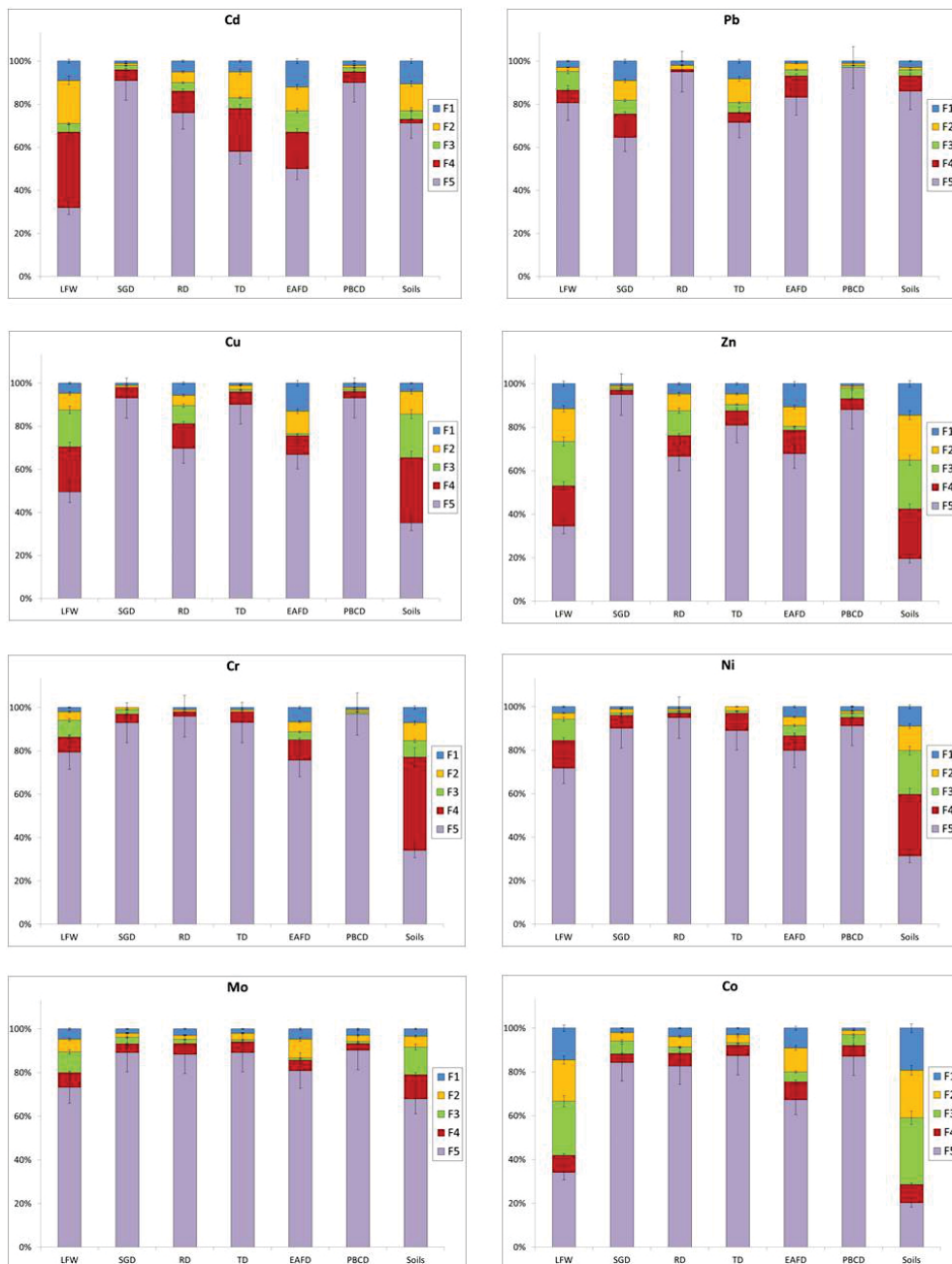


Fig. 2. Speciation analysis of waste and soil samples according to Tessier's procedure

LFW – landfilled foundry waste; SGD – shock grating dust; RD – egeneration dust; TD – transport (of molding sands) dust; EAFD – electric arc furnace dust; PBCD – pneumatic blast cabinet dust; F1–F5 – fractions of Tessier's procedure

Rys. 2. Analiza specyjacyjna badanych próbek odpadów i gleb według procedury Tessiera

organic binders in these wastes. The release of metal from this fraction is only possible after the decomposition of organic compounds (Rao et al. 2008). In the dust samples, there was no high proportion of Cd in the mobile, oxide and organic compounds. Cadmium in the dust was mainly associated with the residual fraction, which is not leachable. In the studied soils, cadmium was mainly present in the residual form (71% Tessier and 65% SM&T), and to a lesser extent in the mobile forms at the level of 23% (Tessier) and 27% (SM&T).

**Lead** is not very mobile in the environment: it usually forms complex ions ( $\text{PbOH}^+$  and  $\text{Pb}(\text{OH})_4^{2-}$ ). Under acidic conditions, it binds to organic matter, which can both increase and decrease its migration (Kabata-Pendias and Pendias 1999). In the analyzed waste and soil, lead was mainly present in the residual form. In RD and PBCD dust, this was a share of 97–98% (Tessier and SM&T). These dusts mainly contain residual organic binders and silica (RD) or steel grit – the metal used in the cleaning of castings (PBCD). Probably for this reason, the percentages of mobile and bioavailable fractions (F1 and F2) were low. The percentage of potentially mobile and bioavailable fractions (F1–F4 Tessier and F1–F3 SM&T) was higher in SGD and EACD as well as in LFW. This may indicate a potential environmental hazard. A high percentage of mobile and bioavailable Pb forms (49%) in EAFD was also confirmed by Laforest and Duchesne (2006). The percentage of lead forms in LFW was similar to that in soils.

The mobility of **copper** depends on the pH of the environment: it increases in an acidic environment. In soils, copper is strongly bound with organic matter and clay minerals. This is due to its affinity for the organic matter of the soil with which copper binds permanently to carboxyl groups. Cu precipitates in the form of sulfates, sulfides, and carbonates, etc., resulting in its less mobile forms. Thus, a small proportion of copper in soils occurs in mobile forms, i.e. in easily soluble and exchangeable fractions (Kabata-Pendias and Pendias 1999). This effect has been confirmed by soil studies. In the soils tested, copper was bound with organic matter (F4 30% Tessier and F3 25% SM&T) and to the Fe-Mn oxide fraction (F3 20% Tessier and F2 24% SM&T). The mobile fraction accounted for only 14% (F1 and F2 Tessier) and 18% (F1 SM&T). A similar fraction distribution was found for LFW. In dust, on the other hand, copper was mainly associated with the residual fraction. The exception was EAFD, for which a higher share of the mobile and bioavailable fraction was found: 27% (F1 and F2, Tessier) and 30% (F1, SM&T). As mentioned before, EAFD can contain significant amounts of heavy metals, also in soluble forms (Strobos and Friend 2004; Salihoglu and Pinarli 2008; Myrmin et al. 2016; Bożym 2020), which is also confirmed by the current research. The tested EAFDs has the highest total content of Cu of all dusts ( $1345 \pm 101$  mg/kg DM) (Table 1). Even with low percentages of mobile and bioavailable forms, the leachability of Cu may be significant. This may constitute a high threat to the natural environment.

**Zinc** in the environment usually occurs in mobile forms as a divalent ion or in complex compounds. The mobility of zinc depends on the pH: the lower the pH, the higher the mobility (Kicińska et al. 2022). The organic matter of the soil binds zinc permanently and therefore it accumulates in the surface layers of the soil. Zinc also strongly binds to Fe and Mn oxides, especially in contaminated soils (Kabata-Pendias and Pendias 1999). The proportion of

mobile and available zinc forms in the tested soils and LFW was high: 35% and 30% (F1 and F2, Tessier) and 39% and 32% (F1, SM&T). Therefore, there is a high risk of this metal leaching from LFW if it were used agrotechnologically. Zinc has a high environmental content compared to that of other metals and is easily absorbed by plants (Kicińska and Gruszecka-Kosowska 2016). Its increased leaching may be toxic to wildlife (Kabata-Pendias and Pendias 1999). In the tested dust samples, zinc was mainly bound with the residual fraction. It was also bound with mobile and bioavailable fractions in dusts, especially EAFD and RD. Due to the high total content of Zn in these dusts (Table 1), there is a high risk of environmental contamination during the use or landfilling of EAFD. The high proportion of mobile and bioavailable Zn forms (40%) in EAFD was also confirmed by Laforest and Duchesne (Laforest and Duchesne 2006).

**Chromium** usually occurs in forms that are not very mobile in the soil. It permanently binds to the organic or residual fractions which do not pose a threat to the environment (Kabata-Pendias and Pendias 1999). In the studied samples, only soils showed significant amounts of chromium bound with the organic fraction (43% Tessier, 36% SM&T) and less to other forms. The percentage of the residual Cr fraction in the soil was 34% (Tessier and SM&T). By contrast, in foundry waste, chromium was mainly associated with the residual fraction (81–98%). This indicates a low risk of the leaching of this metal from foundry waste. The low proportion of potential mobile Cr forms (3%) in EAFD was also observed by Laforest and Duchesne (Laforest and Duchesne 2006).

In soils, **nickel** is typically associated with all fractions. It occurs both in mobile and bioavailable forms and in the form associated with organic matter as mobile chelates. This metal is sorbed by Fe and Mn hydroxides, from which it can be activated when the pH changes (Kabata-Pendias and Pendias 1999). In the current research, nickel was bound with all fractions in the soil samples. Similar to chromium, nickel in foundry tailings was mainly associated with the residual fraction. A slightly higher percentage of the remaining fractions was found only for LFW and EAFD, not exceeding 25% in total. This suggests that the leaching of Ni from foundry waste is low during landfilling or reuse. For comparison, Laforest and Duchesne (Laforest and Duchesne 2006) found a lower percentage of potential mobile forms of Ni (6%) in EAFD.

Iron and aluminum compounds as well as clay minerals affect the bonding of **molybdenum** in the soil. At pH below 5.0, the molybdate anion may bind to hydrated iron and aluminum oxides (Fotyma and Mercik 1995). In acidic soils, Mo binds to aluminum, iron and manganese oxides and hydroxides, organic matter and clay minerals, which may reduce its bioavailability (Bożym and Rajmund 2014). In the current research, molybdenum in both foundry waste and soil samples was associated mainly with the residual fraction. In the dust samples, the percentage of Mo in the residual fraction was the highest and ranged from 85 to 93% (F5, Tessier) and from 90 to 94% (F4, SM&T). In the LFW samples, the percentages of other fractions were found to be 28% (F1–F4, Tessier) and 36% (F1–F3, SM&T). Slightly higher percentages were noted for all fractions in the soil samples: mobile and bioavailable fractions (F1 and F2 Tessier, F1 SM&T) were 8–14%; Fe–Mn oxides

(F3 Tessier, F2 SM&T) were 13–16%; while the share for organic matter was (F4 Tessier, F3 SM&T) 9–11%.

**Cobalt** occurs in various forms in soils. The mobility of cobalt is influenced not only by pH but also by its binding to organic substances and Fe-Mn oxides. Manganese reduces the mobility of Co (Bożym and Rajmund 2015). In the studied dusts, cobalt was associated with the residual fraction (74–90% Tessier, 83–93% SM&T). Only in EAFD were slightly higher amounts of Co associated with the other fractions and did not exceed 30%. A slightly higher percentage of potentially mobile and bioavailable forms of Co was found in EAFD. The only possibility of reducing metal leaching from EAFD is solidification in concrete or other binding materials. The proportion of potentially mobile fractions in LFW was similar to that in the soils. Due to the higher total content of this metal in LFW than in soils, the threat to the environment may be higher. In the tested soils, cobalt was bound with all fractions. In the Tessier procedure, Co was mainly bound with the oxide fraction, while in the SM&T procedure, it was mainly bound to the organic fraction.

The likely cause of the lower leachability of heavy metals from dust compared to from soils may be the high content of iron and manganese, which reduce leachability (Bożym 2020). Iron, manganese and their oxides reduce the leachability of heavy metals as a result of the sorption, precipitation and formation of oxide networks and minerals containing Fe and Mn (Davranche and Bollinger 2000; Schwertmann and Cornell 2000; O'Reilly and Hochella 2003; Kumpiene 2010). The current research has shown that some heavy metals were present in mobile and bioavailable forms in LFW, which may have negative consequences after agrotechnological use.

### 3. Comparison of two speciation procedures

The differences between the results obtained for the two procedures are shown in Figures 3 and 4. The differences in the proportions of the fractions (Tessier vs SM&T) related to the mean value were used. Because the share of metals in some fractions was small, the results were related to the mean values for each metal and each fraction. For Tessier's speciation, the exchangeable (F1) and carbonate (F2) fractions were totaled and compared with the exchangeable and carbonate (F1) fractions in the SM&T speciation procedure. The differences between the procedures may be due to the incomplete extraction of each fraction or specific properties of the samples (pH, organic matter). For example, organic matter in the soil is mainly humus, while in foundry waste, it is residues of organic binders or organic contaminants from thermal processes. Figure 3 shows the results of the comparison of both procedures for foundry waste, while Figure 4 shows the differences for soils. These two types of samples were separated due to their different composition and metal content.

The Tessier procedure was found to be more effective for organic (F3) and residual (F4) fractions, both in the soils and the foundry waste samples (Figure 4). The only exception was Co in the soil, where the Tessier procedure was more effective than SM&T for all fractions

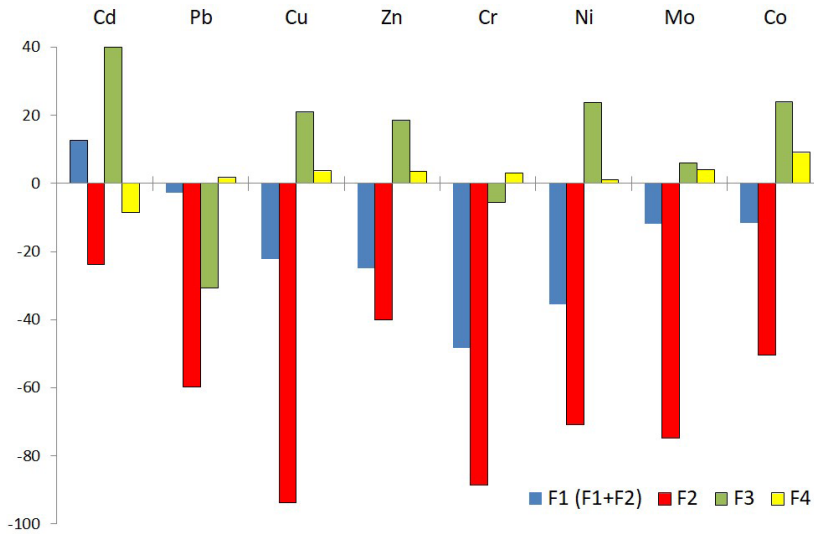


Fig. 3. Comparison of the effectiveness of the Tessier procedure with SM&T for waste samples. The differences in the proportions of the fractions (Tessier vs SM&T) related to the mean value

Rys. 3. Porównanie efektywności procedury Tessiera z SM&T dla próbek odpadów. Różnice udziałów frakcji w odniesieniu do wartości średniej (Tessier vs SM&T)

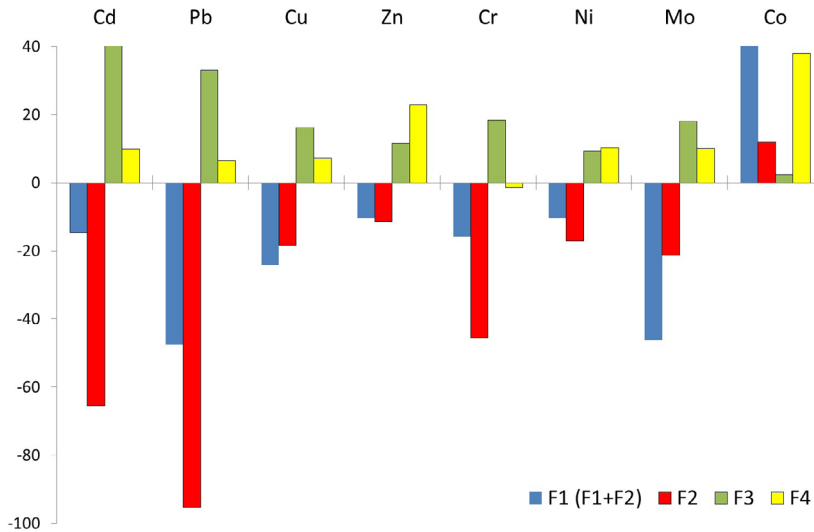


Fig. 4. Comparison of the effectiveness of the Tessier procedure with SM&T for soil samples. The differences in the proportions of the fractions (Tessier vs SM&T) related to the mean value

Rys. 4. Porównanie efektywności procedury Tessiera z SM&T dla próbek gleb. Różnice udziałów frakcji w odniesieniu do wartości średniej (Tessier vs SM&T)

(Figure 4). However, the Tessier procedure was less effective than SM&T for the exchangeable and carbonate fractions (F1), and also for the Fe-Mn oxide (F2) fractions in all samples. Slightly lower differences for these fractions were found for soils (Figure 4). Fernandez Alborez et al. (Fernandez Alborez et al. 2000) found a higher effectiveness of SM&T compared to the Tessier procedure for the extraction of metals bound with the Fe-Mn oxide fraction in sewage sludge samples.

Based on the results of the comparison of both procedures and the analysis of literature reports, the following conclusions have been drawn:

- ◆ In the Tessier procedure, the carbonate-bound fractions are not only in the carbonate form but also specifically absorbed by organic matter; furthermore, iron and manganese hydroxide forms are eluted. By contrast, the SM&T procedure uses acetic acid, which is less specific than the salts from the Tessier procedure. Acetic acid can also mobilize silicates (Rao et al. 2008). Therefore, it is recommended to use a different extractant for high carbonate content (> 16%), for example, EDTA, as both salts (Tessier) and acetic acid (SM&T) may not release all the metals bound with the carbonates. Consequently, metals may be extracted from carbonates only in the next step of extraction, which causes the overestimation of the results for this fraction (Rao et al. 2008, 2010).
- ◆ In the Tessier procedure, the oxide fraction is extracted at a higher temperature, which increases the amount of metals bound with the Fe-Mn oxide fraction but may also mobilize metals bound with organic matter and sulfides. This problem does not occur with the SM&T procedure where the extraction is performed at room temperature ( $\approx 20^{\circ}\text{C}$ ) (Rao et al. 2008, 2010; Świetlik and Trojanowska 2008).
- ◆ In both procedures, the organic fraction is extracted with the use of  $\text{H}_2\text{O}_2$ . While, in the speciation of Tessier, nitric acid is additionally used to prevent the precipitation of metal hydroxides with iron hydroxides. Thus, metal losses from this fraction are possible in the SM&T procedure.

#### 4. TCLP one-step procedure

One-step procedures, for example, TCLP, SPLP, and ASTM, are faster and less labor-intensive than speciation. Therefore, they are more popular for assessing the reuse or land-filling of foundry waste. In the USA, the USEPA soil screening levels (SSL) are used to interpret the leaching results of the TCLP procedure from foundry waste to soils (Dungan and Dees 2009; Lindsay and Logan 2009) or the toxicity threshold values (Siddique et al. 2010). Table 2 shows the results for the leachability of metals based on the TCLP procedure in comparison with the guidelines for foundry wastes used in construction and road building in the USA (TCLP and SSL toxicity). For TCLP toxicity, the threshold concentration (mg/l) was converted to mass units (mg/kg DM) according to soil guidelines. The degree of metal leaching using the TCLP procedure is shown in Table 2.

Table 2. Leachability of heavy metals from tested wastes using the TCLP procedure compared to the American requirements for agricultural (SSL) and industrial (TCLP toxicity level) use of foundry waste

Tabela 2. Wymawalność metali ciężkich z badanych odpadów przy wykorzystaniu procedury TCLP w porównaniu do wymagań amerykańskich określonych dla odpadów odlewniczych stosowanych w agrotechnice (SSL) oraz innych dziedzinach przemysłowych (TCLP toxicity level)

Description	LFW	SGD	RD	TD	EAFD	PBCD	SLL*	TCLP toxicity level**
Cd (mg/kg DM)	0.1	0.01	0.2	1.4	6.4	0.1	39.1	20
Cd (%)***	22	3	11	18	19	3	–	–
Pb (mg/kg DM)	3	28	2	14	155	1	ND	100
Pb (%)***	9	25	5	19	6	5	–	–
Cu (mg/kg DM)	11	55	59	25	363	23	ND	2,000
Cu (%)***	14	5	9	6	27	5	–	–
Zn (mg/kg DM)	36	50	178	71	954	330	23 500	10,000
Zn (%)***	35	3	17	10	29	5	–	–
Cr (mg/kg DM)	16	5	15	15	34	15	145 (Cr <sup>+6</sup> )	100
Cr (%)***	13	1	5	6	15	5	–	–
Ni (mg/kg DM)	8	11	5	4	41	38	1,560	NL
Ni (%)***	11	6	5	5	12	6	–	–
Mo (mg/kg DM)	5	10	7	3	16	6	391	NL
Mo (%)***	19	7	8	5	9	8	–	–
Co (mg/kg DM)	8	1	2	4	9	3	ND	NL
Co (%)***	30	8	12	12	22	5	–	–

\* According to: [Lindsay and Logan 2009](#).

\*\* According to: [Fahnline 1995](#); [Siddique et al. 2010](#).

\*\*\* Percentage of fractions compared to the total content of metal.

ND – no data; NL – not limited; LFW – landfilled foundry waste; SGD – shock grating dust; RD – egeneration dust; TD – transport (of molding sands) dust; EAFD – electric arc furnace dust; PBCD – pneumatic blast cabinet dust.

The tested waste did not exceed the limit of toxicity defined for waste in accordance with the TCLP procedure (Table 2). The leachability of heavy metals was well below the limits for agricultural foundry wastes (SSL) and other industrial sites (TCLP toxicity level) in the USA ([Fahnline 1995](#); [Bastian and Alleman 1998](#); [Lindsay and Logan 2005](#); [Dungan and Dees 2009](#); [Siddique et al. 2010](#); [Zhang et al. 2014](#)). Therefore, it can be concluded that according to US standards, the tested waste may be potentially used for these purposes. The leachability of heavy metals using the TCLP one-step procedure was significantly lower than

the permitted values for foundry wastes used in construction and road building. However, it should be taken into account that heavy metals are not the only contaminants in foundry waste as other inorganic pollutants such as cyanides, fluorides, chlorides and sulfates or organic pollutants (e.g. phenol and formaldehyde derived from organic binders in this waste) are also found (Bożym 2020). For this reason, many authors recommend the reuse of foundry waste only from iron foundries using mineral binders for agrotechnological applications (Lindsay and Logan 2005; Dungan et al. 2006; Dungan and Dees 2009; Zhang et al. 2014).

In Poland, water leaching according to the PN-EN 12457 norm is typically used to assess the toxicity and method of use of foundry wastes. Landfilled wastes are classified as inert, hazardous or other in Poland (Journal of Laws 2015, item. 1277). This waste classification is based on the degree of leaching of organic pollutants, inorganic pollutants, and heavy metals. Inert waste may be used in the construction and road-building industries. The results of foundry wastewater extracts have been discussed in previous articles (Bożym 2017, 2020, 2021). The water leaching of heavy metals from the LFW allowed their non-toxic character to be stated. However, the leaching of mobile and bioavailable fractions of heavy metals with water is much lower than with acetic acid (Bożym 2017). For this reason, both methods can be useful for assessing the reuse of foundry waste. The effectiveness of the TCLP procedure for evaluating foundry waste reuse in agrotechnology and industry has been confirmed by many authors (Fahnline 1995; Bastian and Alleman 1998; Lindsay and Logan 2005; Zhang et al. 2014). However, it would be better to use one of the speciation procedures for agrotechnological applications. The SM&T procedure has the advantage of being highly effective with regard to leaching the mobile and bioavailable fractions with acetic acid. The procedure enables the assessment of the mobilizing potential of metals in the environment and it is less time consuming than the Tessier procedure. In addition, the SM&T procedure is the reference method used in the EU.

## Conclusions

The total content of heavy metals in LFW was slightly higher than in local soils, but did not exceed the limits for arable soils. The percentage of mobile and bioavailable forms was the highest in LFW of all the analyzed foundry waste samples and was comparable with local soils. For this reason, the use of this waste for agricultural purposes should be limited. In addition, organic contaminants may be leached from LFW.

The proportion of potentially mobile and bioavailable forms in foundry dust was low, except for EAFD, but this does not guarantee environmental safety. The total content of pollutants leached from the dust may be significant due to the high total metal content. Foundry dust may be considered for reuse as a raw material in construction or road building, which will reduce leaching and dusting. Agrotechnological use of dusts should not be considered due to the high total metal content and the potential for the leaching of organic pollutants.



However, a small amount of uncontaminated dust may be suitable as an additive to artificial soil as a binding material. Additionally, EAFDs should not be used for any purpose except reuse in foundries or when landfilled after solidification. Reuse of EAFDs should be performed with extreme caution due to potential toxicity to wildlife and humans.

After comparing the two speciation procedures, Tessier extraction efficiency was found to be higher compared to SM&T for the organic and residual fractions and lower for the mobile and bioavailable fractions (exchangeable, carbonate and oxide). The differences in the effectiveness of the two procedures may result from the use of different reagents with different affinities for the metal fraction and process conditions, e.g. additional acidification or higher temperatures during extraction.

Based on the results of the single TCLP procedure, the leachability of metals was found to be well below the TCLP toxicity threshold (USEPA SSL) established in US law. Due to the fact that in Poland there are no tests to assess the reuse of foundry waste in the road-building or construction industries, it seems reasonable to use the TCLP method as an additional test in addition to the required water test according to the PN-EN 12457 norm used for waste classification.

Assessment of the potential impact of foundry waste used in agrotechnology should focus on the analysis of the total content of heavy metals and their fractions using the speciation procedures according to either Tessier or SM&T. The choice of the extraction method should depend on the composition and type of waste and the goal of its reuse. The problem may be the lack of national legal requirements for such application. In this case, landfill standards, soil guidelines or US guidelines may be used.

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**THE ASSESSMENT OF HEAVY METAL BINDING FORMS IN FOUNDRY WASTES USED AS RAW MATERIALS IN AGROTECHNICS, CONSTRUCTION AND ROAD CONSTRUCTION**

**Keywords**

heavy metals, speciation, foundry wastes, soils

**Abstract**

The aim of this study was to evaluate foundry waste used for various applications in terms of heavy metals quantity of fractions of their binding. The novelty of these studies is the use of speciation

procedures to assess the fraction of heavy metals in foundry waste. The two most popular speciation procedures, the Tessier method and the SM&T, and also the TCLP single extraction procedure were used to evaluate the use of foundry waste in agritech, road engineering and construction in this research. Additionally, local soils were analyzed and compared to landfill foundry waste (LFW). It was found that LFW may have a negative impact on the natural environment when used for agrotechnological applications due to the increased concentration of mobile and bioavailable fractions (mean 9–18%) of metals. Foundry dusts were characterized by a low percentage of mobile and bioavailable (mean 2–6%) forms, although this does not include electric arc furnace dust (EAFD) (mean 17%). The metal content in TCLP extracts was low in all foundry waste samples and allowed the use of the analyzed wastes in construction and road construction. The usefulness of both speciation procedures for the assessment of the leaching of heavy metal forms from foundry waste was confirmed. However, the SM&T procedure was more effective in leaching mobile and bioavailable forms of heavy metals in foundry waste and soil samples.

#### OCENA FORM WIĄZANIA METALI CIĘŻKICH W ODPADACH ODLEWNICZYCH STOSOWANYCH JAKO SUROWCE W AGROTECHNICE, BUDOWNICTWIE I DROGOWNICTWIE

##### Słowa kluczowe

metale ciężkie, specjacja, odpady odlewnicze, gleby

##### Streszczenie

Celem pracy była ocena zawartości frakcji związania metali ciężkich w odpadach odlewniczych wykorzystywanych do różnych zastosowań. Nowością tych badań jest wykorzystanie procedur specjacyjnych do oceny udziału form metali ciężkich w odpadach odlewniczych. Do badań wykorzystano dwie najpopularniejsze procedury specjacyjne, metodę Tessiera oraz SM&T, a także procedurę jednoetapowej ekstrakcji TCLP, do oceny wykorzystania odpadów odlewniczych w agrotechnice, drogownictwie i budownictwie. Dodatkowo przeanalizowano lokalne gleby i porównano je ze składowanymi odpadami odlewniczymi (LFW). Stwierdzono, że LFW mogą mieć negatywny wpływ na środowisko naturalne podczas zastosowań agrotechnicznych ze względu na zwiększoną koncentrację frakcji mobilnych i biodostępnych (średnio 9–18%) metali. Pyły odlewnicze charakteryzowały się niskim udziałem form mobilnych i biodostępnych (średnio 2–6%), z wyjątkiem pyłu z elektrycznych pieców łukowych (EAFD) (średnio 17%). Zawartość metali w ekstraktach TCLP była niska we wszystkich próbkach odpadów odlewniczych, co pozwala na wykorzystanie analizowanych odpadów w budownictwie i drogownictwie. W pracy potwierdzono przydatność obu procedur specjacyjnych do oceny ługowania form metali ciężkich z odpadów odlewniczych. Jednakże stwierdzono lepszą skuteczność procedury SM&T w zakresie wymywania mobilnych i biodostępnych form metali ciężkich zarówno dla odpadów odlewniczych, jak i gleby.

