

## Fractions of Zinc, Chromium and Cobalt in Municipal Solid Waste Incineration Bottom Ash

Adam Łukowski<sup>1</sup>

<sup>1</sup> Institute of Environmental Engineering and Energy Production, Department of Technology in Environmental Engineering, Białystok University of Technology, ul. Wiejska 45A, 15-351 Białystok, Poland  
e-mail: a.lukowski@pb.edu.pl

### ABSTRACT

In the fresh samples of municipal solid waste incineration (MSWI) bottom ash, the fractional composition of Zn, Cr and Co was investigated. The BCR method was utilised to evaluate the acid soluble and exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4). Physico-chemical parameters such as pH, dry mass, and pseudo-total metal content were also determined. The percentage of zinc in fractions was in the following order: F3 (31.8%) > F1 (30.6%) > F2 (27.8%) > F4 (9.8%), for chromium F4 (88.7%) > F3 (5.4%) > F1 (3.2%) > F2 (2.7%), and in the case of cobalt F4 (59.8%) > F1 (14.3%) > F2 (13.6%) > F3 (12.3%). Mobile metal pool (F1–F3) gathered the most of zinc (90.2%) and the least of chromium (11.3%).

**Keywords:** MSWI bottom ash, BCR method, heavy metal, metal fraction.

### INTRODUCTION

The amount of municipal solid waste will be increasing in the coming years, mainly due to the progressive urbanization and living standards. Therefore, the waste disposal problems will be also aggravated (Vishnu and Singh 2021).

One of the widely used procedures of disposal is incineration, which reduces the solid waste volume by approx. 90%, which translates into the mass reduction by 70% (Vaitkus et al. 2019). This process is currently the main approach to municipal solid waste management in Europe (Minane et al. 2017). MSWI bottom ash is the main solid residue from the waste incineration. It comprises even 20–25% of the waste introduced into the incinerator (Huber et al. 2021). It is a potential source of environmental threat, due to the content of heavy metals and other harmful pollutants (Huang et al. 2020). MSWI bottom ash is utilized as concrete or loose aggregates and raw material in the production of cement and ceramic materials (Verbinnen et al. 2017). Nowadays, in Europe about 50% of countries are utilizing the processed bottom ash as a construction material (Vateva and Laner 2020).

The aim of this study was determination of fractional composition of zinc, chromium and cobalt in particle size fraction  $\leq 2$ mm, since this fraction accumulates the most of heavy metals contained in MSWI bottom ash (Chimenes et al., 1999). In order to evaluate the fractional composition of metals in bottom ash, the sequential extraction method is widely used (Bruder-Hubscher et al., 2002; Kuokkanen et al., 2006; Haberl and Schuster, 2019). The main advantage of the BCR method used in this study is harmonization (Salam et al. 2019), which has a major impact on the comparability of results at international level. This extraction scheme illustrates the processes which occur in the environment, related to metal fractionation and thus its solubility (Rodgers et al. 2015).

### MATERIALS AND METHODS

#### Sample collection

Twenty samples of the fresh bottom ash, approx. 1 kg each, were derived from MSWI plant in Białystok, Poland (53°09'30" N, 23°10'07" E).

E). They were collected during 7 weeks in 2016, when 11650t of waste with average heating value of  $8.95 \text{ MJ}\cdot\text{kg}^{-1}$  were incinerated. Incineration of mixed MSW and sorted waste ran in the stoker-fired furnace at  $700 \text{ }^\circ\text{C}$  on the grate.

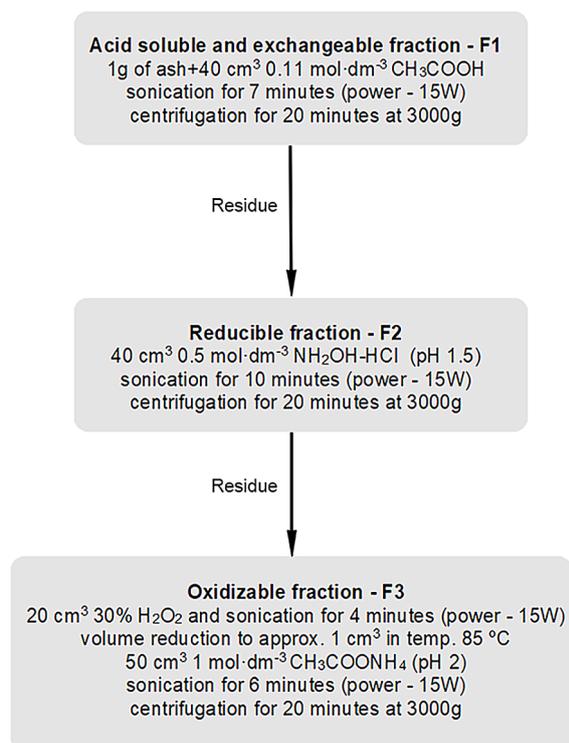
Water was used to cool down the bottom ash. Ferrous metals were magnetically recovered before sampling. The samples were ground in an agate mortar, after previous sifting through a 2 mm sieve.

### Physico-chemical properties

Dry mass was determined by drying at  $105 \text{ }^\circ\text{C}$  to the constant mass. Flame atomic absorption spectrometry (FAAS) was used to evaluate the pseudo-total Zn, Cr and Co content, after closed vessel microwave digestion (0.5 g sample with  $3 \text{ cm}^3 \text{ HClO}_4$  and  $10 \text{ cm}^3 \text{ HNO}_3$ ). The pH was measured in suspension (5 g of ash +  $25 \text{ cm}^3$  of deionized water), after 24 hours using the potentiometric method.

### Assessment of metal fractions

In the dry MSWI bottom ash, the fractional composition of zinc, chromium and cobalt was evaluated by the ultrasound accelerated BCR method. The extraction comprised three stages (Figure 1).



**Figure 1.** The BCR sequential extraction scheme

The content of Zn, Cr and Co in fractions was determined by flame atomic absorption spectrometry (FAAS). The percentage of zinc, chromium and cobalt in fractions and the mobile pool (F1–F3) were computed. The amount of studied metals in the residual fraction (F4) was calculated as a difference between pseudo-total content and content in fractions F1–F3.

## RESULTS AND DISCUSSION

### Physico-chemical properties of MSWI bottom ash

The dry mass content and pH of the investigated MSWI bottom ash were described in the previous paper (Łukowski and Olejniczak, 2020).

The studied samples contained the most of pseudo-total zinc ( $669.6 \text{ mg}\cdot\text{kg}^{-1}$ ) and the least of cobalt ( $14.72 \text{ mg}\cdot\text{kg}^{-1}$  DM on average) (Table 1). Zinc content was in good accordance with the results presented by Yao et al. (2010), who noted  $304.5\text{--}1922 \text{ mg}\cdot\text{kg}^{-1}$  of Zn in bottom ash from six incinerators. The amount of cobalt was a little higher ( $17.4\text{--}28.07 \text{ mg}\cdot\text{kg}^{-1}$ ) than in the present study. Vateva and Laner (2020) emphasized that the mineral part of fine fraction, which was predominant, contained  $13047 \text{ mg}\cdot\text{kg}^{-1}$  of Zn and  $815 \text{ mg}\cdot\text{kg}^{-1}$  of Cr, while the Co content was below the limit of determination. Chimenos et al. (2003) found  $11096 \text{ mg}\cdot\text{kg}^{-1}$  (48.3%) of Zn and  $332 \text{ mg}\cdot\text{kg}^{-1}$  (46.5%) of Cr in the discussed grain size fraction. Dou et al. (2017) reported, according to the results from many regions in the world, that the content of Zn as well as Cr and Co in the MSWI bottom ash is in approximate range 100–10000 and 10–1000  $\text{mg}\cdot\text{kg}^{-1}$ , respectively.

### Fractionation of metals in MSWI bottom ash

The most of zinc,  $215.6 \text{ mg}\cdot\text{kg}^{-1}$  on average, was found in F3 fraction (Table 1). It was 31.8% of pseudo-total content (Figure 2), in the range of 8.0 to 43.8%. Comparable result was achieved by Yao et al. (2013), since the authors noted about 28% of zinc in the oxidizable fraction. The metals in this fraction are bound to organic matter and/or sulfides (Pöykiö et al., 2016) and can be released under oxidizing conditions. Microbial activity could lead to such a process as well, because biodegradation of organic matter is a source of organic acids and carbon dioxide. These compounds

are able to react with the alkaline constituents of bottom ash, thus decreasing its pH value (Zhang et al., 2004). The F1 fraction gathered 30.6% of pseudo-total Zn content on average, at the range from 17.4 to 43.9%. Similar result, about 25% of zinc in the exchangeable and carbonate fractions, stated Yao et al. (2013). The metals contained in the discussed fraction are the most mobile and available; thus, they represent the highest threat to the environment and human health. They can be released very easily under acidic and even neutral conditions (Pöykiö et al., 2016). Despite zinc is considered as an essential element for the proper plant growth and development, in excess is phytotoxic (Guarino et al. 2020). The F2 fraction accumulated 27.8% of zinc. It was the highest percentage in this fraction, similarly to F1 and F2, as compared to the rest of investigated metals. Yao et al. (2012) noted a similar share of zinc (around 20%) in the fresh bottom ash, in the fraction bound to Fe/Mn oxides. The metals from this fraction can be released under reductive conditions, but the probability of such a process is lower, than in the case of acid soluble and exchangeable fraction (Zhao et al. 2021). The least of zinc (9.8%) was found in F4 fraction. It was also the lowest share among all the studied elements, which probably arose from its volatility. It seems that this attribute also influenced the near-even Zn distribution in F1–F3 fractions. Zinc is regarded as semi-volatile element, whereas Cr and Co are non-volatile (Yang et al., 2016), which is confirmed in the present study by

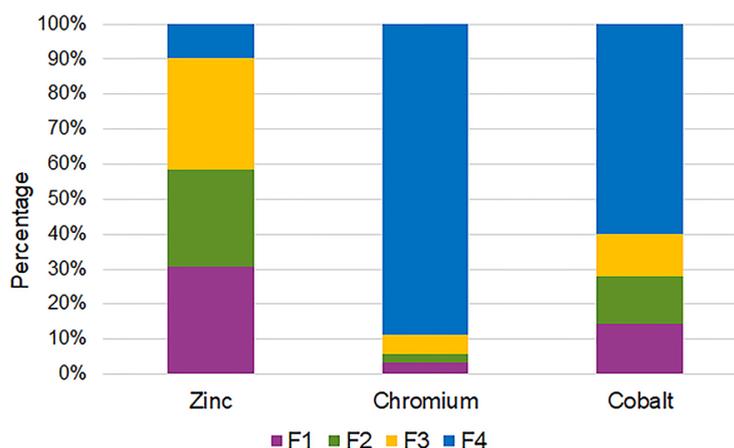
their high content in residual fraction. Zn mobile pool, 90.2% at the range from 74 to 98%, was the highest among studied metals, which means that almost entire metal can be potentially mobilized, as a result of changing environmental conditions.

The highest amount of chromium, 300.1 mg·kg<sup>-1</sup> on average, was found in the F4 fraction. It constituted 88.7% of pseudo-total content on average, at the range from 83 to 95%. This was the largest percentage among investigated elements. It means that Cr was mainly bound to the vitreous and silicate phases (Gonzales et al., 2019) and indicates its very low leachability. Similar result, about 96% in residual fraction, was stated by Gonzales et al. (2019). According to the authors, such a high share is obvious, since this element is a glass component. They also emphasised that only small part of chromium (4%), bound to oxyhydroxides and organic matter, was mobilized under redox conditions. The present investigations confirmed such a claim, because F2 and F3 fractions gathered merely 8.1% of Cr. Additionally, the entire Cr mobile pool amounted to 11.3%, within the range of 5–17%, and was the lowest among studied metals. Thus, potential chromium release to the environment was also the lowest. It should be borne in mind that chromium is considered as very harmful and even small amounts pose a significant hazard for the ecosystem (Nilanjana and Lazar 2011; Coetzee et al., 2020).

Cobalt, similarly to Cr, was accumulated mainly in F4 fraction (14.72 mg·kg<sup>-1</sup> on average). It was 59.8% of pseudo-total content,

**Table 1.** The pseudo-total Zn, Cr and Co and content in the fractions in bottom ash

Metal	Fractions	Min - Max	Mean ± SD, n=20
Zn (mg·kg <sup>-1</sup> DM)	Pseudo-total content	557.7–862.9	669.6±64.6
	F1	142.5–285.4	203.8±47.8
	F2	105.2–247.9	186.9±37.7
	F3	48.8–309.6	215.6±63.4
	F4	9.4 -174.2	67.1±48.3
Cr (mg·kg <sup>-1</sup> DM)	Pseudo-total content	159.6-849.2	335.1±174.0
	F1	1.5–11.9	9.0±2.2
	F2	2.6 -17.7	8.5±3.5
	F3	2.5–50.2	17.5±11.6
	F4	132.2–778.7	300.1±164.5
Co (mg·kg <sup>-1</sup> DM)	Pseudo-total content	8.03-38.75	14.72±8.87
	F1	0.64–3.67	1.81±0.71
	F2	0.5–7.5	2.00±1.65
	F3	0.17–4.94	1.75±0.95
	F4	2.2–28.3	8.88±5.49



**Figure 2.** Fractional composition of Zn, Cr and Co in MSWI bottom ash

in the range from 21 to 77%. As stated by Wielgosiński et al. (2014), residual fraction is not hazardous for the environment, since it is almost immobile. Even more cobalt in this fraction, about 90%, stated Yao et al. (2010) in the MSWI bottom ash samples that came from six incinerators. Additionally, the authors found in exchangeable and carbonate bound fraction about 1% of Co on average, in fraction Fe/Mn oxides about 7% and in organic matter bound fraction about 2%. On the contrary, in current investigations the share of Co in F1, F2 and F3 fractions amounted 14.3, 13.6 and 12.3%, respectively. The percentage of cobalt in mobile pool was 40.2 and ranged from 23 to 79%.

## CONCLUSIONS

The most mobile fraction, acid soluble and exchangeable, gathered the highest amount of zinc. The share of zinc in fractions followed the sequence: F3 (31.8%) > F1 (30.6%) > F2 (27.8%) > F4 (9.8%), for chromium: F4 (88.7%) > F3 (5.4%) > F1 (3.2%) > F2 (2.7%) and for cobalt: F4 (59.8%) > F1 (14.3%) > F2 (13.6%) > F3 (12.3%). Zinc was the most soluble and chromium the least soluble, assuming the percentage in fractions F1–F3 as the solubility criterion.

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