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Trace elements in solid residues from the thermal treatment of municipal solid waste, sewage sludge and hazardous waste

Introduction

Continuous technological progress and economic development in the world is associated with the need to obtain and use natural resources. Limited amounts of some of them, their presence in widely dispersed locations, problems with obtaining them or the inability to replace them has resulted in the specification of rare earth elements (REEs). In 2011, the EU developed a list of raw materials classified as critical raw materials (CRMs). These are raw materials that are important to the EU economy and useful to industry. The list was updated in 2014, 2017 and 2020 (European Commission 2020). In 2023, a Proposal for a Regulation of the European Parliament concerning the list of critical raw materials (European Commission 2023) was published, which included thirty-four raw materials, including Be, Bi, Co, Ga, Ge, Hf, In, Li, Mg, Nb, P, Sb, Sc, Sr, Ta, Ti, V, W, LREE (light rare earth elements), HREE (light rare earth elements) and platinum group metals.

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CRMs are used in various industries including: aerospace, defense, electronics, digital, automotive, renewable energy, construction and healthcare. Humanity's attachment to and dependence on many of the technological solutions used in everyday life, increasingly indicates that the demand for raw materials will increase in the coming years. Both the extraction of ores and the availability of raw materials depend on a number of factors (economic, environmental, geopolitical) that increase the risk of shortages (Glöser et al. 2015; Zhou et al. 2017).

To date, more than 250 rare earth minerals have been identified, but most of the concentration of metals is low, ranging from 10 to 300 ppm. Of these, fluorocarbonate minerals like basanite, phosphate minerals like monazite and xenotime and ion-adsorbed clays are the most commonly used (Jha et al. 2016).

In recent years, other alternative sources of CRMs, such as secondary raw materials, have become increasingly important. In many countries, urban mining is practiced, involving the recovery of trace elements from end-of-life products, and landfill mining, involving the recovery of raw materials from landfills, which is becoming increasingly important (Viegas ed. 2019). In the case of metals classified as CRM and other valuable examples such as Al, Ag, Au, Cu, Sn, waste electrical and electronic equipment (WEEE) are currently and will continue to be a significant source in the future (Meshram et al. 2019; Arduin et al. 2020; Charles et al. 2020). Uncertainty in supply and, above all, an increase in the prices of raw materials on the global markets, means that methods of recovering metals from other wastes in which their concentration is low are becoming more and more profitable, although recovery for economic reasons has not been conducted on an industrial scale so far. In addition, the development of existing technologies and the creation of new alternatives to enable environmentally-friendly raw material acquisition are equally important. The changes taking place mean that the source of metals may become mineral waste, arising in the mining and processing industry of coal and ores, metallurgical and chemical such as phosphogypsum, metallurgical slags, mine tailings, red mud (Binnemans et al. 2015; Meshram et al. 2019), or energy burning solid fuels (Santos et al. 2022; Całus-Moszko and Białocka 2013; Adameczyk et al. 2023). These industries annually produce various types of waste which are either landfilled or recovered in construction, road building or reclamation. The recovery of waste in which valuable raw materials are accumulated, as mentioned above, is the most beneficial, as they are a substitute for natural resources; nevertheless, a potential source of metallic elements and other trace elements is irretrievably lost. One of the reasons for this is a lack of information on the amount of metals found in waste. Complete information will facilitate decisions on the recovery of elements from waste. It is important to note that these processes should be performed in such a way that they cause as little damage to the environment as possible while the residue remaining after useful components are recovered are economically exploited.

One of the sources of trace elements may be residues from thermal processes (combustion, gasification, pyrolysis) of various types of waste: municipal solid waste (MSW), medical waste (MW), hazardous waste (HW) and sewage sludge (SS). The thermal treatment

of waste is most often used for energy recovery and the production of electricity and heat or, to a lesser extent, for disposal. Installations in which thermal processes are performed are equipped with devices to protect the environment against the emission of harmful gases and dusts. As a result, the thermal treatment of waste generates other solid wastes, most commonly bottom ash (BA), fly ash (FA) and air pollution control residues (APCr). Bottom ash produced in boilers, based on the European Waste Catalogue (Decision 2000) – is classified under code 19 01 12. Fly ash is classified under code 19 01 14 (fly ash other than those types mentioned in 19 01 13) or as hazardous waste 19 01 13* (fly ash containing hazardous substances). These types of ash are captured in recovery boilers and removed from exhaust gases by multicyclones or electrostatic precipitators. The third type of waste is APCr – resulting from the purification of exhaust gases from gaseous impurities and mineral fraction residues, most often removed from exhaust gases in bag filters. Due to the content of heavy metals, soluble chloride and sulfate salts or dioxins and furans, this waste is classified as hazardous waste, code 19 01 07* (solid waste from gas treatment). Slag usually goes directly from the furnace to the wet slag remover, while the remaining waste can be combined together or collected in separate silos.

The properties of these types of waste depend on a number of factors, primarily on the type of waste incinerated – its chemical composition. From the point of view of chemical composition, the substances that are part of the incinerated waste can be divided into compounds: organic, inorganic, organometallic and their mixtures. Nowadays, a significant proportion of the thermal transformation of waste is organic substances, the useful properties of which have been achieved by introducing various inorganic compounds (polymers) during their production. Thus, in waste such as BA, FA and APCr there are metals that occur in fillers, stabilizers, pigments and plasticizers (Turner and Filella 2021). Therefore, they are found in incinerated paper, textile, plastic, petrochemical or metallurgical products. Other factors influencing the properties of residues after thermal processes include the type of thermal process, the type of furnace (grate, rotary, fluidized bed), the temperature of the thermal processes and the method of flue gas treatment used (Li et al. 2004; Vassilev et al. 2005).

There are many methods of managing this type of waste, they are used for the production of aggregates, glass-ceramics, cement, bricks, zeolites, in mining as backfill (Kępyś et al. 2014; Donatello and Cheeseman 2013; Smol et al. 2015; Cho et al. 2020). In addition, they are subjected to processes limiting the leachability of impurities, chemical or changing their form from fine-grained to larger agglomerates (washing, stabilization, solidification, vitrification, sintering) and storage (Quina et al. 2008). In recent years, they have become a source of recovery of metals such as Zn, Pb and Cd, more and more often recognized as a low grade stream of high-tech metals (Quina et al. 2018)

Metals are recovered from waste using various methods involved in ore processing, such as pyrometallurgy, hydrometallurgy and electrometallurgy. In addition to the above-mentioned “traditional” methods, biotechnological processes (bioleaching and biosorption), which are particularly beneficial to low grade ore, will play an increasingly important role

(Işıldar et al. 2019; Watling 2015). Therefore, due to the dispersed concentration of metals in fine-grained wastes, the development of microbial electro-metallurgy (Dominguez-Benetton et al. 2018) is envisaged, in which microorganisms such as fungi and bacteria will play an important role in the recovery of metals.

Importantly, from the point of view of the recovery of trace elements, the processes of burning coal or waste cause an increase in their concentration in ash compared to the content in the fuel (Santos et al. 2022). In the case of coal combustion, the amount of REE in the ash is much higher than in the coal, by up to twenty times (Zhao et al. 2008). In addition, studies of ash from coal combustion have shown that there is partitioning of trace elements associated with the boiling points of different phases occurring in ash. For this reason, depending on the accumulation of trace elements, it was proposed to divide the ash into four classes (Klein et al. 1975): Class I are trace elements with high boiling points (Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti) that do not escape in the combustion chamber – by melting, they are part of the bottom ash and form the basis of fly ash and, to a lesser extent, they also settle on their surface; Class II are trace elements such as As, Cd, Cu, Ga, Pb, Sb, Se, Zn, which evaporate during thermal processes and then condense on the surface of fly ash particles as a result of a decrease in the temperature of the gases; Class III are trace elements such as Hg, Cl and Br, which remain in the gas phase throughout the thermal process and do not condense; Class IV are trace elements like Cr, Cs, Na, Ni, U, V that behave like elements in Classes I and II.

The behavior of metals in the process of municipal waste incineration has been presented by Verhulst et al. (Verhulst et al. 1996) and Fernández et al. (Fernandez et al. 1992). Studies have shown that metal partitioning depends on the thermodynamic stability of their oxides and chlorides. If the oxide is more stable than the chloride, an element is transported mechanically and is found in the matrix of the fly ash particles. Metals for which the oxides and chlorides have similar stabilities are transported by both volatilization-condensation and mechanical mechanisms. A third situation occurs if the chloride is more stable than the oxide, then the metal chloride volatilizes and condenses on the surface of the fly ash particles. In addition, Zhang et al. (Zhang et al. 2012) performed partitioning studies depending on humidity during the combustion of the MSW. They showed that humidity has a significant impact on the behavior of metals, especially at temperatures ranging from 700 to 1,000°C.

Research on ash obtained from medical waste incineration (Zhao et al. 2008) shows that there were from four to eight times more REEs (Rare Earth Elements) in bottom ash than there were in fly ash. This is explained by the high boiling points of REEs. Research performed on ash obtained from municipal solid waste incineration (Funari et al. 2015) showed that the average concentration of REEs in bottom ash (104 mg/kg) was about twice as high it was in fly ash (54 mg/kg). Bogush et al. (Bogush et al. 2015) found that APC residues obtained from MSW incineration were enriched in more volatile elements than bottom ash. According to (Quina et al. 2018), MSW incineration residues have a total REE content ranging from 1 to 100 mg/kg, while medical waste ash has a total REE content ranging from 10 to 78 mg/kg (Zhao et al. 2008).

It is also important to note that the fine-grained form of ash, particularly that collected on filters from flue gases, is conducive to the recovery of trace elements from ash. This eliminates, or at least significantly reduces the need for crushing and grinding, which is important for the environment and reduces the cost of preparing ash for recovery.

Since the thermal treatment of waste plays a fundamental role in the waste management systems used in many countries in the world, while thermal processes are still being developed in other countries, the amount of residues generated will increase all over the world. It is also worth noting that, apart from residues from the thermal treatment of waste that are created on an ongoing basis, many other residues have not been used in the past; instead, they have been placed into landfill. Thus, they can also constitute anthropogenic deposits of raw materials. The variety of thermally transformed waste and their physico-chemical properties as well as methods of flue gas cleaning mean that the resulting residues will show different chemical compositions. Therefore, the article presents the results of research aimed at investigating the properties of ash formed in the processes of the thermal transformation of various types of waste (MSW, HW, SS) in terms of their selected trace element content. This is important for using residues from the thermal treatment of waste as secondary raw materials for environmental impact.

1. Materials and research methodology

1.1. Incinerator characterization

The tested ash came from three thermal waste treatment installations, in which municipal solid waste, hazardous waste and sewage sludge were incinerated. The relevant information on the installations affecting the types and properties of the waste generated is presented below.

The municipal solid waste incineration (MSWI) plant is equipped with a grate boiler (inclined reciprocating grate) in which mixed municipal solid waste (waste code 20 03 01) is burned, as well as residues from mechanical municipal waste processing (waste code 19 12 12). The plant has a capacity of approximately 220,000 t/a (two lines of 110,000 t/a each) and operates at temperatures between 850°C and 1,100°C (typically >950°C). The calorific value of the waste received is within the range of 7 to 14 MJ/kg. The resulting flue gases pass through the afterburning chamber (min. temperature: 850°C for 2 sec.), and urea is injected into the chamber to reduce the nitrogen oxides (selective, non-catalytic reduction of nitrogen oxides – SNCR). In the recovery boiler, the flue gases are cooled to a temperature of approx. 180°C, and steam is produced for the production of electricity and heat. Fly ash (waste code 19 01 13*) is collected from the recovery boiler. In the next stage of flue gas treatment, the semi-dry method using lime milk and activated carbon removes acidic impurities (HCl, HF, SO₂), heavy metals, dioxins and furans. The remnants of fly ash together with flue gas cleaning products (waste code 19 01 07*) are caught on bag filters.

Sewage sludge incineration (SSI) plants are often referred to as mono-combustion plants because only one type of waste (sewage sludge) is incinerated in them. The incineration of municipal sewage sludge (waste code 19 08 05) takes place in a fluidized bed boiler with a capacity of approx. 20,000 t d.m./a. To ensure that the process remains autothermal, the sewage sludge is dried before combustion at a humidity rate of approx. 36% d.m. (heat for drying is recovered from the flue gases) with a calorific value of approx. 10.5 MJ/kg. After drying, the sludge is introduced into the furnace, where it is burned at a temperature of approx. 750°C. The thermal process continues in the combustion chamber. The temperature of the flue gases in the chamber exceeds 850°C and their stopping time is longer than two seconds. Where necessary, selective non-catalytic NOx reduction (SNCR) by injecting ammonia water is used. The flue gases are directed towards heat exchangers and cleaned of gaseous and dust impurities (using the dry technique). First, the fly ash is removed using a multicyclone and an electrostatic precipitator and is sent to a silo (waste code 19 01 14). The next step is the removal of acidic impurities and heavy metals by adding acidic sodium hydroxide and activated carbon to the flue gases. Flue gas cleaning products and previously uncollected fly ash are removed by bag filters (waste code 19 01 07*).

The hazardous waste (e.g. medical waste, tar sludge, plastics, expired and used petroleum derivatives, used chemical packaging) is incinerated in a rotary kiln. The capacity of the plant is approx. 50,000 t/a. The amount of waste fed into the kiln for incineration is selected in such a way that the energy value of the charge is approx. 16 MJ/kg. After passing through the afterburning chamber, the flue gases are cooled in a recovery boiler and then cleaned of solid particles in the electrostatic precipitator. After passing through the electrostatic precipitator, Na₂S₄ is added to the flue gas to bind the mercury. They are then directed towards the spray dryer and bag filter. Next, the flue gases are cleansed of acidic gaseous impurities such as SO₂ and HCl in scrubbers, while the liquid from the scrubbers is returned to the spray dryer. In the final stage, the flue gases are cleaned on activated carbon and on an SCR catalyst. The fly ash with flue gas cleaning products from gaseous pollutants (from the last section of the recovery boiler, electrostatic precipitator and bag filter) goes to one silo (waste code 19 01 13*).

1.2. Sampling and marking of solid residues

Samples of fly ash (FA), depending on the type of installation, were caught in recovery boilers (MSWI) or multicyclones and electrostatic precipitators (SSI). As a result of flue gas treatment (FGT), the bag filters were collected with the remnants of fly ash along with products of flue gas cleaning from gaseous pollutants (MSWI and SSI). In the hazardous waste incinerator (HWI), the fly ash with flue gas cleaning products from gaseous pollutants (from the last section of the recovery boiler, electrostatic precipitator and bag filter) goes to one silo.

In the labelling of the solid residues tested, the abbreviation FA (fly ash) or FGT (flue gas treatment products) was preceded by a letter indicating the source; from municipal solid waste – the letter M, from hazardous waste – the letter H, from sewage sludge – the letter S. The solid residues tested were determined as follows:

- ◆ MFA – fly ash from municipal solid waste incineration plant;
- ◆ MFGT – flue gas treatment products from municipal solid waste incineration plant;
- ◆ SFA – fly ash from sewage sludge incineration plant;
- ◆ SFGT – flue gas treatment products from sewage sludge incineration plant;
- ◆ HFGT – flue gas treatment products from hazardous waste incinerator plant.

1.3. Analytical methods

Each solid residue was sampled three times (approximately 10 kg each time) from the feed pipe to the silo. Representative samples were obtained by coning and quartering and the results of the analyses were averaged. Grain composition was determined by a laser diffraction method using the Analysette 22 by Fritsch. Phase composition was determined using the Philips APD PW 3020 X'Pert diffractometer. This diffractometer was equipped with a copper lamp with a nickel filter (Cu/Ni) under conditions of 35 kV, 29 mA; measurements were made in the range 5–65° 2 θ with a resolution of 0.05° at a recording time of 3 seconds per position. Phases were identified by search-matching to the International Centre for Diffraction Data (ICDD). For chemical composition analysis, solid residues were digested with a mixture of HNO₃/HCl in a microwave oven. The solution obtained was analyzed after dilution by inductively coupled plasma spectrometry/atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The content of basic ingredients such as SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, SO₃ was determined, and trace elements classified as CRM (Be, Co, Li, Mg, Ni, Sb, Sr, Ti, V, W), some metals of high economic importance (Ag, Al, Cu, Zn) and others used in industry, but also some environmental pollutants (Cd, Cr, Hg, Pb).

2. Results and discussion

2.1. Grain composition

The grain composition is shown in Figure 1. The vast majority of the residues studied were characterized by grain sizes of less than 100 μm , with only a small number (4.5%) of larger grains of up to 200 μm occurring in HFAT. The difference in the grain sizes of fly ash (FA) and residues from the gas cleaning of gaseous contaminants (FGT) from the same installation is noteworthy. The FGT residue grains are significantly smaller than the FA grains.

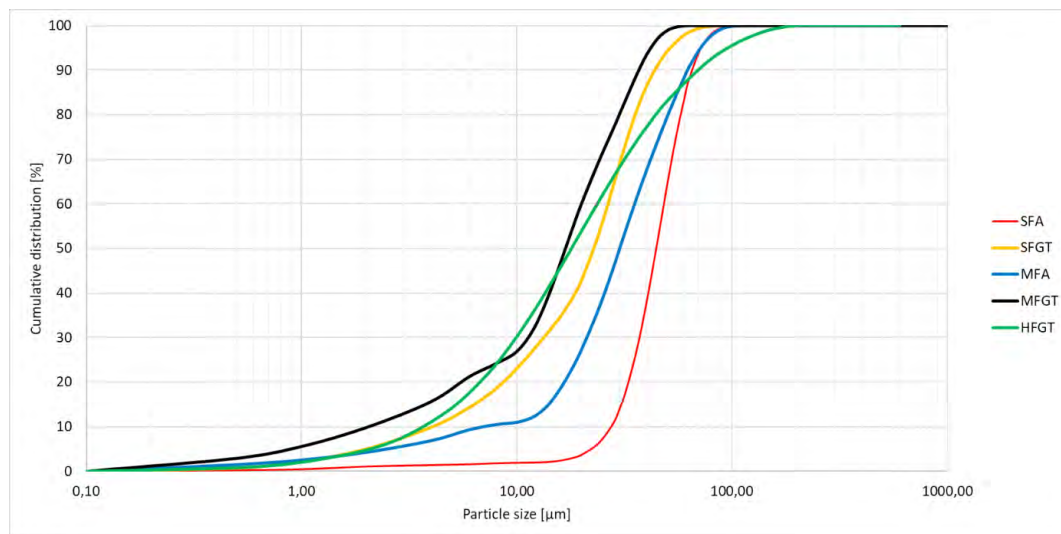


Fig. 1. Grain size composition of solid residues from thermal waste treatment

Rys. 1. Skład ziarnowy stałych pozostałości z instalacji termicznego przekształcania odpadów

The largest grains for SFA were 100 µm and SFGT 71 µm, while the maximum grain size for MFA was also 100 µm and for MFGT, it was decidedly less at 60 µm. This was due to the occurrence of the flue gas leaning process in the first instance and the capture of the largest particles, followed by the removal of the gaseous pollutants with sorbents.

2.2. Phase composition

The phase composition of the residues tested varies due to the type of waste incinerated, the method of flue gas treatment and the sampling location for testing. Significant amounts of quartz and iron sulfate are present in FA, while these phases are practically absent in FGT. In both samples of residues from sludge incineration, the potassium sulfate content stands out; in addition, sodium sulfate is present in SFGT, resulting from the use of sodium hydroxide for flue gas treatment. By contrast, the predominant constituents of residues from municipal waste incineration plants are calcium sulfate (anhydrite) and iron and potassium sulfate (yavapaiite) in addition to the calcium compounds calcium hydroxide and calcite. By contrast, the residues from hazardous waste incineration are dominated by chlorine-containing phases – $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, magnesium – $\text{Mg}_3(\text{PO}_4)_2$ and magnesium and chromium – MgCrO_4 . Most of these mineralogical phases have been identified in solid residues from the incineration of SS (Nowak et al. 2013), HW (Anastasiadou et al. 2012) and MSW (Sabbas et al. 2003; Bodenand and Deniard 2003; Chiang et al. 2009).

acid leaching processes (Fang et al. 2018). In SFGT, the P_2O_5 content is on average 10% (43 g/kg), which is much lower than it is in SFA, but still of considerable significance for treating ash as an alternative source of phosphorus. In other solid residues from the incineration of MSW and HW, the P_2O_5 contents are considerably lower (3.4% in MFA, 1.9 in MFGT and 0.3 in HFGT). As acidic sodium carbonate is added in the flue gas treatment process, Na_2O (30.9%) and SO_3 (34.4%) are found in SFGT.

Table 1. Content of major elements in test solid residues compared with literature ranges: average upper continental crust, (% by weight)

Tabela 1. Zawartość składników głównych w stałych pozostałościach z termicznego przekształcania odpadów, (% wag.)

Elements	SFA	SFGT	MFA	MFGT	HFGT	Average upper continental crust (Funari et al. 2015)
SiO_2	38.5	5.4	42.1	44.2	22.7	66.6
Al_2O_3	4.5	1.3	16.5	16.8	2.4	15.4
Fe_2O_3	3.4	2.3	2.8	2.5	1.9	5.04
MgO	3.7	0.9	2.7	1.8	1.3	2.48
CaO	18.4	4.7	22.0	22.5	32.6	3.59
Na_2O	0.5	30.9	1.7	2.0	4.9	3.27
K_2O	1.3	0.4	1.8	2.2	3.0	2.8
TiO_2	0.2	0.1	0.1	0.2	0.1	0.64
P_2O_5	26.9	10.0	3.4	1.9	0.3	0.15
MnO	0.1	0.1	0.1	0.1	0.1	0.1
SO_3	1.7	34.4	5.0	5.1	14.2	n.d.

n.d. – not data in the cited references.

In the MFA and MFGT incineration residues, the dominant constituents are SiO_2 at 42.1 and 44.2%, respectively, and Al_2O_3 at 16.5 and 16.8%, respectively. The use of limestone sorbent in flue gas treatment results in high amounts of CaO in MFA and MFGT, at 22.0 and 22.5%, respectively, while the amounts of SO_3 were 5.0 and 5.1%, respectively. Furthermore, it is noteworthy that there is little difference in the content of the main components in the MFA and MFGT residues from MSW combustion.

In addition, HFGT samples, which are a mixture of fly ash and flue gas cleaning products, contained mainly CaO (32.6%) and SO_3 (14.2%) as a result of using a lime sorbent for flue gas treatment. These ashes also contained SiO_2 (22.7%).

Considering the different sources of the tested ashes, the different specificities of the waste incineration plants together with the flue gas cleaning system, similarities in the occurrence of trace elements can be noted, although they are far fewer in number than the differences.

Among the constituents included in the CRM, the content of Sb in the residues from installations incinerating municipal and hazardous waste is noteworthy. The amount of Sb in MFA was 268, in MFGT 276 and 267 mg/kg in HFGT. In comparison, the Sb content in ACP residues from the UK ranged from 170 to 510 mg/kg (Bogush et al. 2015). The recorded amounts exceed the average content in the earth's crust by more than 1,300 times, nevertheless in amounts much lower than the content in the ore (Figure 1). Other constituents included in the CRM such as Co (in MFA, MFGT, HFGT), Ni (in SFA), Sr (in SFA, MFA,

Table 2. Concentration trace elements of FA and FGT from MSW, SS, HW, (mg/kg)

Tabela 2. Zawartość pierwiastków śladowych w stałych pozostałościach ze spalania odpadów komunalnych, niebezpiecznych i osadów ściekowych, (mg/kg)

Trace elements	Sewage sludge incinerator		Municipal solid waste incinerator		Hazardous waste incinerator	Abundance in the Earth's crust ^a	Ore concentration ^b
	SFA	SFGT	MFA	MFGT	HFGT		
Ag	8.34	2.52	1.62	0.62	16.37	0.07	n.d.
Be	0.76	0.31	1.71	1.48	1.13	2.8	3,000–50,000
Cd	4.20	1.46	13.46	34.23	293.53	0.15	1,000–10,000
Co	16.39	5.02	22.89	23.10	47.19	25	500–3,000
Cr	469.76	127.50	305.52	174.46	704.50	102	310,000
Cu	698.27	199.09	337.91	368.11	2,827.54	60	5,000–20,000
Hg	0.16	17.45	0.05	0.02	73.78	0.08	n.d.
Ni	83.16	23.17	54.33	51.77	464.95	84	15,000–30,000
Pb	91.68	25.35	415.64	881.21	7,549.92	14	300,000–400,000
Sb	18.73	16.53	268.47	276.37	267.33	0.2	27,000
Sr	479.23	146.06	424.53	313.81	496.25	370	n.d.
W	0.83	1.92	0.11	0.16	195.40	1.25	<15,000
V	53.82	17.24	39.57	33.48	59.75	120	500–13,000
Zn	3,461.31	1,031.82	6,523.68	3,023.36	19,272.62	70	50,000–150,000

n.d. – not data in the cited references.

^a Abundance of elements in earth's crust values from (Helmenstine 2023).

^b Ore concentration from (Allegrini et al. 2014).

HFGT) are in comparable amounts as found in the earth's crust. In addition, the amount of a valuable metal like silver was 8.3 mg/kg in the SFA and 16.37 mg/kg in the HFGT, which exceeds the average crustal abundance by 130 and 233 times, respectively. When analyzing the content of other base metals, Zn is present in the highest amounts, at about 19 g/kg in HFGT, about 6.5 g/kg in MFA, about 3.5 g/kg in SFA, 3.0 g/kg in MFGT, and about 1.0 g/kg in SFGT. This is due to the presence of plastics and paper products in the incinerated waste (Yen et al. 2020).

In terms of the possible harmfulness of the ash, it is important to note the mercury content of the HFGT and SFGT caught after the flue gases have been cooled by activated carbon on a bag filter. The presence of other heavy metals such as Cd, Cr, Pb in ACP residues is a consequence of their volatility, evaporation during the combustion process and their transformation, most often in the form of oxides or chlorides, which are removed during the flue gas cleaning process. Thus, the presence of heavy metals in ACP residues is also confirmed by studies by Bogush et al. (Bogush et al. 2015) or others (Jung et al. 2004; Thipse and Dreizin 2002)

The highest heavy metal content in HFGT is due to the fact that a variety of hazardous wastes are incinerated, for example, as metallic objects, packaging, medical tools, chemicals

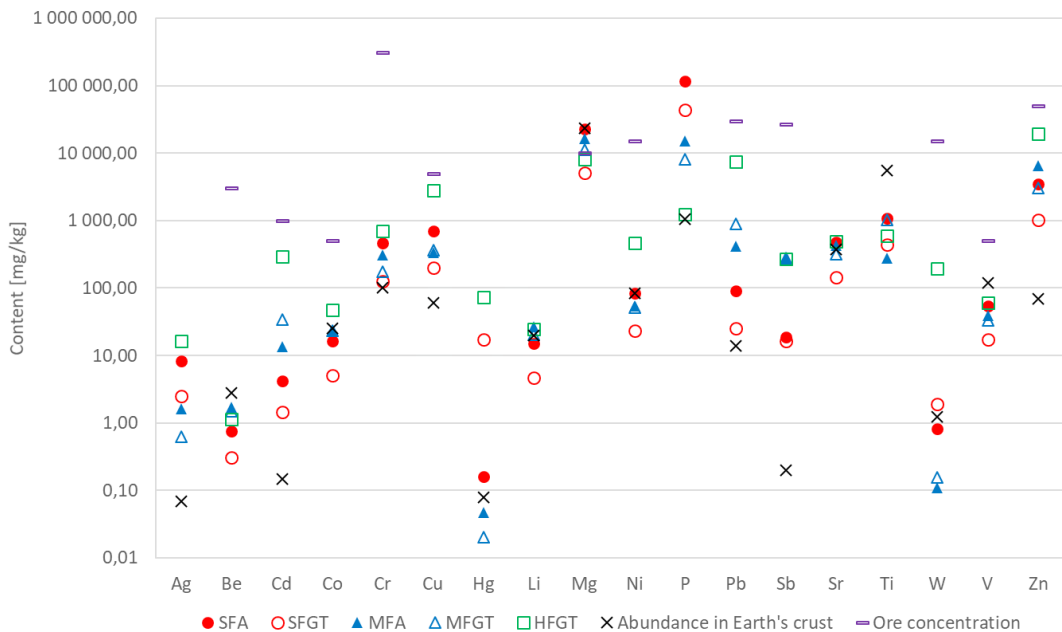


Fig. 3. Concentration trace elements of FA and FGT from MSW, SS, HW compared with literature ranges: abundance in earth's crust and ore concentration

Rys. 3. Zawartość pierwiastków śladowych w stałych pozostałościach ze spalania odpadów komunalnych, niebezpiecznych i osadów ściekowych w porównaniu z zawartością w skorupie ziemskiej i rudach

and petroleum substances. According to literature data (Sabiha-Javied et al. 2008; Bakoglu et al. 2003) HFGT is characterized by high amounts of Cd and Hg, which may pose a risk to the environment, thus the ash is classified as hazardous waste. The variability of metal concentrations in ash was presented by Zhao et al. (Zhao et al. 2008); zinc content in FA medical waste was found to be as high as 121 g/kg. When considering the partitioning of other trace elements it is apparent, 2–3 times higher amounts of Co, Cr, Cu, Ni, Sr in bottom ash than ash from flue gas treatment.

Of the fourteen trace elements, twelve are present in the HFGT in the highest quantities, in particular metals included in the CRMs such as Co, W, V, noble metals such as Ag, but also the harmful metals Cd, Cu, Hg, Pb. By contrast, Be (in all analyzed solid residues), and W (except HFGT) were present in the lowest amounts from the CRM list (Table 3).

Table 3. Occurrence of trace elements in tested solid residues

Tabela 3. Występowanie pierwiastków śladowych w badanych pozostałościach stałych ze spalania odpadów

Amount (mg/kg)	Solid residues				
	SFA	SFGT	MFA	MFGT	HFGT
>100,000	P	–	–	–	–
100,000–10,000	Mg	P	Mg, P	Mg	Zn
10,000–1,000	Ti, Zn	Mg, Zn	Zn	P, Ti, Zn	Cu, Mg, P, Pb
1,000–100	Cr, Cu, Sr	Cr, Cu, Sr, Ti	Cr, Cu, Pb, Sb, Sr, Ti	Cr, Cu, Pb, Sb, Sr	Cd, Cr, Ni, Sb, Sr, Ti, W
100–10	Co, Li, Ni, Pb, Sb, V	Hg, Ni, Pb, Sb, V	Cd, Co, Li, Ni, V	Cd, Co, Li, Ni, V	Ag, Co, Hg, Li, V
10–1	Ag, Cd	Ag, Cd, Co, Li, W	Ag, Be	Be	Be
<1	Be, Hg, W	Be	Hg, W	Ag, Hg, W	–

Conclusions

Samples of solid residues (fly ash and flue gas treatment products) collected from the incineration of municipal solid waste, hazardous waste and sewage sludge, were characterized into the trace element content. The properties depend on the type of waste incinerated, the type of installation and the flue gas cleaning method. The particle size of the flue gas treatment products is significantly smaller than that of the fly ash. The main component of the solid residues is SiO₂, which is related to the content of the mineral fraction of the

incinerated waste, in particular to solid residues from municipal solid waste and fly ash from sewage sludge. In addition, the influence of sorbents during the removal of gaseous pollutants from the flue gas is evident, in particular with regard to the contents of Na_2O , CaO in flue gas products from sewage sludge or CaO and SO_3 in solid residues from municipal solid waste and hazardous waste incinerators. Additional influences are the properties of the metals and their compounds, which cause partitioning between the individual types of solid residues. This particularly applies to Cd, Cr, Cu, Hg, Ni, Pb and Zn. Most of the analyzed trace elements were present in the highest quantities in the flue gas treatment products from hazardous waste, especially metals included in the critical raw materials such as Co, Cu, Ni, W and V. Due to the presence of phosphorus in waste water, it was also detected in the solid residues from sewage sludge. Phosphorus is also classified as a critical raw material and significant amounts of phosphorus (117 g/kg) were found in fly ash from sewage sludge, which is important in the search for alternative sources. Also noteworthy is the presence in solid residues of valuable metals such as Ag, Zn and Sb in amounts well above the average crustal abundance.

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TRACE ELEMENTS IN SOLID RESIDUES FROM THE THERMAL TREATMENT OF MUNICIPAL SOLID WASTE, SEWAGE SLUDGE AND HAZARDOUS WASTE

Key words

waste thermal treatment, fly ash, air pollution control residues,
trace elements, secondary raw materials

Abstract

In many countries around the world, the thermal treatment of waste plays an important role in the waste-management system. As a result, electricity and heat are produced. However, solid residues are produced in the form of bottom ash, fly ash (FA) and air pollution control (APC) residues. Alternative raw material resources are currently being sought, one of which may be anthropogenic materials from waste thermal treatment processes. This paper presents the results of a study on the trace element content of FA and APC residues from three different installations: municipal solid waste incineration (grate boiler), sewage sludge (fluidized bed boiler) and hazardous waste (rotary kiln). Research methods such as ICP-MS (inductively coupled plasma mass spectrometry), ICP-AES (inductively coupled plasma/atomic emission spectroscopy) and XRD (X-ray diffraction) were used. The results obtained indicate that the chemical composition of FA and APC residues depends mainly on the type of waste being converted, the thermal process and the flue gas treatment method. Ash from sewage sludge incineration in particular contains significant amounts of P and Sb – elements classified as critical raw materials (CRM). In addition, they also contain other valuable metals such as Ag and Zn, in amounts far exceeding the average crustal abundance. In addition, residues from the incineration of hazardous waste may pose a potential risk to the environment due to the presence of significant amounts of heavy metals such as Pb, Cd and Hg.

**PIERWIĄSTKI ŚLADOWE W POZOSTAŁOŚCIACH Z TERMICZNEGO PRZEKSZTAŁCANIA
ODPADÓW KOMUNALNYCH, OSADÓW ŚCIEKOWYCH I ODPADÓW NIEBEZPIECZNYCH**

Słowa kluczowe

termiczne przekształcanie odpadów, popiół lotny,
stałe pozostałości z oczyszczania spalin, pierwiastki śladowe, surowce wtórne

Streszczenie

W wielu krajach na świecie termiczne przekształcanie odpadów odgrywa istotną rolę w systemie gospodarki odpadami. W efekcie produkowana jest energia elektryczna oraz ciepła. Z drugiej strony powstają także stałe pozostałości w postaci popiołów dennych, popiołów lotnych oraz produktów oczyszczania spalin z gazowych zanieczyszczeń. Obecnie poszukiwane są alternatywne źródła surowców, jednym z nich mogą być pozostałości z procesów termicznego przekształcania odpadów. W artykule przedstawiono wyniki badań zawartości pierwiastków śladowych w popiołach lotnych (FA) i produktach oczyszczania spalin z gazowych zanieczyszczeń (APC), pochodzących z trzech różnych instalacji: spalających odpady komunalne (kocioł rusztowy), osady ściekowe (kocioł fluidalny) i odpady niebezpieczne (piec obrotowy). Zastosowano metody badawcze takie jak ICP-MS (spektrometria mas ze wzbudzeniem w plazmie indukcyjnie sprzężonej), ICP-AES (spektrometria plazmy sprzężonej indukcyjnie, atomowa spektroskopia emisyjna) i XRD (dyfrakcja rentgenowska). Uzyskane wyniki wskazują, że skład chemiczny FA i APC jest zależy przede wszystkim od rodzaju przekształcanych odpadów, procesu termicznego oraz sposobu oczyszczania spalin. Popioły, w szczególności ze spalania osadów ściekowych, zawierają znaczne ilości P oraz Sb – pierwiastków zaliczanych do surowców krytycznych (CRM). Ponadto zawierają także inne cenne metale jak Ag czy Zn, w ilości znacznie przewyższającej średnią zasobność skorupy ziemskiej. Z drugiej strony pozostałości ze spalania odpadów niebezpiecznych mogą stanowić potencjalne zagrożenie dla środowiska z powodu obecności w nich znacznych ilości metali ciężkich jak Pb, Cd i Hg.