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Archives of Environmental Protection
Vol. 52 no. 1 pp. 96–109

PL ISSN 2083-4772
DOI: 10.24425/aep.2026.158386

Assessment of heavy metal immobilization in self-hardening slurries with the addition of ashes from municipal solid waste incineration and coal combustion in the context of hydraulic engineering applications

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Keywords: cut-off wall, self-hardening slurry, municipal solid waste fly ash, conventional fly ash, heavy metal immobilization

Abstract: This study aimed to assess the immobilization of heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn) in hardened self-hardening slurries (SHS) made with municipal solid waste fly ash (MSWFA) and conventional coal fly ash (CCFA) intended for cut-off wall construction. Five SHS mixtures were prepared using tap water, Portland cement, sodium bentonite, CCFA, and MSWFA. The microstructure and phase composition were analyzed by SEM and XRD. After 28 and 90 days of curing, samples were leached according to PN-EN 12457-4:2006, and metal concentrations in eluates and digested components were determined by flame AAS. The results were compared with regulatory limits for heavy metal content in leachate and soil. CCFA exhibited the highest Cd, Cu, Pb, and Zn contents, while MSWFA showed the lowest total heavy metal content. The eluates displayed an alkaline pH (≈12.5) and high salinity. Pb and Cd releases exceeded non-hazardous waste limits, while other metals remained below these limits. All tested metals demonstrated high immobilization levels (≥99.99%) regardless of recipe or curing time. Dense C-S-H matrix formation with hydrocalumite contributed to metal immobilization. SHS could potentially be a safe and environmentally friendly method for stabilizing and solidifying fly ash in its raw form. Heavy metals were strongly bound within the slurry structure, however, further research is needed.

Introduction

The introduction of the Waste Framework Directive (WFD) 2008/98/EC in the European Union, which is based on the waste hierarchy (reuse and recycling over recovery), has contributed to improvements of municipal solid waste (MSW) management. Following the implementation of the WFD, an initial linear decline in MSW generation was observed in the EU-27, probably mainly due to the financial crisis (Abis et al. 2020). In 2013, a minimum of 211,501,000 Mg was reached, after which a renewed increase in MSW production occurred. MSW generation reached 232,222,000 Mg (Eurostat 2024), corresponding to 510 kg per capita, in 2020, and 237,531,000 Mg, or 532 kg per capita, in 2021. In 2022, it amounted to 229,482,000 Mg, corresponding to 513 kg per capita in EU-27 and 364 kg in Poland.

Managing such vast amounts of MSW poses a significant challenge. One of the methods of MSW management is thermal treatment, particularly incineration. In the EU-27, in 2020, approximately 26.5% of the MSW generated was thermally treated, of which over 98% was used for energy recovery (Eurostat 2024); in 2022, these values were 25.9% and 98%, respectively. In Poland, in 2022, 21.1% of waste was subjected for thermal treatment, of which 96.0% was with energy recovery.

The thermal treatment of MSW most often takes place in grate furnaces. The calorific value of MSW ranges from 6.2 to 23.7 MJ/kg of dry mass (Ozbay and Durmusoglu 2013, Nzioka et al. 2017, O. A. Adeleke et al. 2021). It depends on its composition, which is influenced by factors such as the level of economic development of the region, residents' consumption patterns, seasonality, and the level of selective collection.

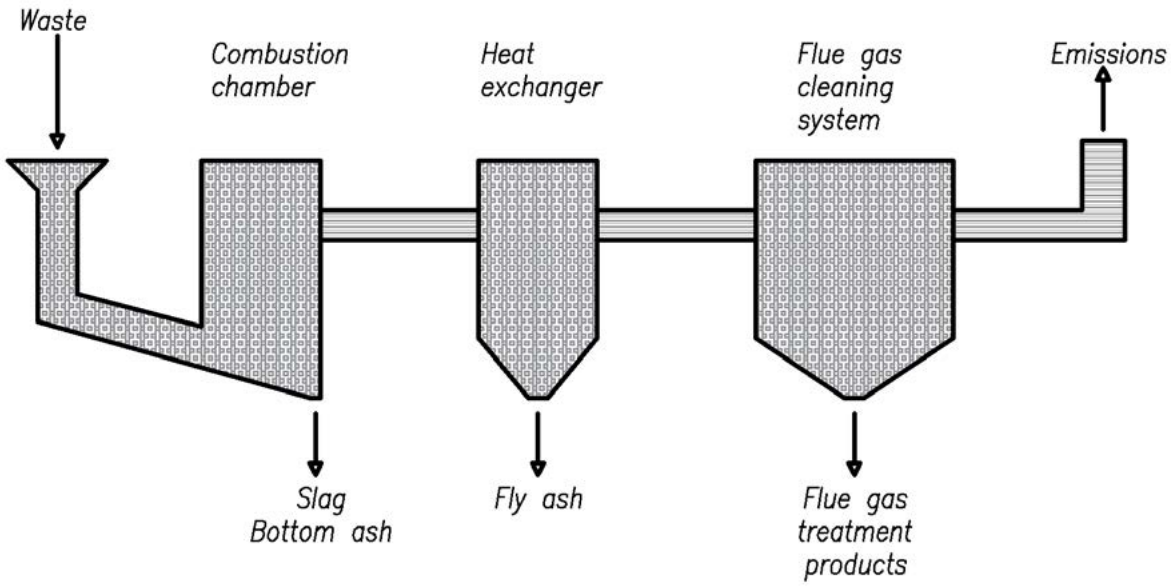

Fig. 1. Products of MSW incineration process.

As a result of MSW incineration, the overall volume of waste is significantly reduced, which leads to an increased concentration of heavy metals in the combustion residues. Incineration produces different types of ash (Fig. 1), depending on the technology used and the applied nomenclature, including bottom ash (BA) and fly ash (FA). Fly ash can be further subdivided into boiler ash, electrostatic precipitator ash (ESP ash), flue gas desulfurization ash, and solid flue gas treatment residues. Morf et al. investigated a full-scale MSW incineration plant equipped with a grate furnace operated by an automated control system. They reported the following average distribution of the total waste mass among the incineration residues: flue gas (including water vapor) - 68.9%, spent activated carbon - <1%, ESP ash - 1.1%, boiler ash - 2.2%, wastewater - <1%, scrap metal - 1.1%, and BA - 26.8% ((Morf et al. 2000, Rosik-Dulewska at al. 2008).

According to the concept of circular economy, FA from MSW incineration (MSWFA) should be regarded as a raw material rather than a waste. However, its often high content of heavy metals may limit its reuse potential. Various applications of MSWFA are currently being investigated, including road construction (He and Kasina 2023), reinforced borosilicate glass (Abou Hussein et al. 2024), fire-resistant boards (Peceño et al. 2024), cement-bound mixtures (Węgliński and Martysz 2024), steel fiber reinforced concrete (Wan et al. 2024), cement mortars (Loginova et al. 2023), and cut-off walls (Falaciński et al. 2023) are currently being investigated.

Another significant source of waste, especially in Poland, is coal combustion. Despite the reduction in the share of coal-fired power generation associated with the ongoing energy transition, more than 60% of electricity was still generated from coal combustion in 2023 (IEA 2025). Hard coal consumption in Europe was estimated to have reached 128 million tons in 2023, with Poland accounting for 42% of this amount (Eurostat 2024). Approximately 150 million tons of coal combustion by-products are produced annually by the European power industry, more than 100 million tons of which originate from the 28 EU Member States, including over 20 million tons in Poland (Szczygielski 2016).

Two main types of boilers are currently used in condensing and cogeneration plants: conventional pulverized fuel boilers and fluidized bed boilers. In both cases, the flue gases and entrained ash undergo dust removal, usually by electrostatic precipitators. In power plants equipped with pulverized fuel boilers, two types of fly ash are produced: conventional coal fly ash (CCFA) and fly ash containing flue gas desulfurization (FGD) products (in the case of dry or semi-dry FGD processes) (Szponder 2012). CCFA is mineral in character and exhibits pozzolanic properties. Detailed information on the properties, chemistry, and applications of CCFA can be found in review papers (Uliasz-Bochenczyk and Mokrzycki 2006, Ahmaruzzaman 2010, Izquierdo and Querol 2012; Yao et al. 2015, Bhatt et al. 2019).

One of the possible applications of MSWFA and CCFA is in self-hardening slurries (SHS). SHS are thixotropic mixtures of water, clay material, binders, and other additives, often combustion by-products. They are used in the construction of cut-off walls, which serve in hydraulic engineering to seal embankments, dams, and landfills, among other applications. Due to their nature and working conditions, cut-off walls are exposed to contact with groundwater, which can lead to the leaching of various substances. Therefore, given the frequent use of combustion by-products in their composition, often carrying a load of heavy metals, it is crucial to assess the immobilization of heavy metals in hardened SHS. A synthetic overview of the leaching behavior of heavy metals from cement-based materials is provided by (Szarek 2024), while more detailed discussions can be found in Malviya and Chaudhary (2006), van der Sloot and Dijkstra (2004), Dijkstra et al. (2005), and Król (2011).

This work aimed to determine the degree of heavy metal immobilization in hardened SHS based on MSWFA and CCFA intended for cut-off wall applications. The study introduces an innovative aspect to slurry formulation, namely the simultaneous use of two combustion by-products differing in origin and properties. In addition, selected chemical and physical properties of the ashes were determined.

Materials

The following materials were used to prepare the hardening slurries:

- tap water;
- Portland cement CEM I 42.5R, with high early strength, in accordance with (PN-EN 197-1:2012 2012);
- Sodium bentonite;
- CCFA produced in a cogeneration plant located in a large provincial city and equipped with a conventional pulverized fuel boiler.
- MSWFA, a solid waste from waste gas treatment. According to the *Journal of Laws* (2020, item 10), this ash is classified as hazardous waste under code 19 01 07*. The ash originates from an MSW incinerator in a large provincial city equipped with a grate furnace. The incinerated material consisted of mixed (unsegregated) waste in its raw form and was not subjected to prior drying or valorization (crushing). The ash was obtained using a dry flue-gas-cleaning method. Table 1 presents the compositions of the five tested SHS recipes.

Table 1. Content of dry ingredients in SHS per 1000 dm^3 of water. Source: author's own elaboration

Recipe	Bentonite	Cement	CCFA	MSW FA
	[kg/1000 dm^3 of water]			
R1	10	125	250	300
R2	10	175	250	300
R3	15	150	200	324
R4	15	150	200	250
R5	10	150	200	350

Methodology

Testing the metal content in SHS components and aqueous extracts

Samples of Portland cement, sodium bentonite, CCFA, and MSWFA (approximately 1.00 g each, prepared by quartering) were digested separately using microwave-assisted digestion in a Titan MPS system (PerkinElmer, Waltham, MA, USA) with aqua regia (HNO_3 + HCl mixed at a volume ratio of 1 : 3). The concentrations of selected heavy metals (Cd, Co, Cr, Cu, Ni, Pb, and Zn) were determined in the resulting digests and in aqueous extracts from the SHS samples by flame atomic absorption spectrometry (FAAS), according to PN-ISO 11047:2001 using a PinAAcle 900F FAAS (PerkinElmer, Waltham, MA, USA). Table 2 presents the limits of quantification of the testing method.

SEM examination of SHS samples

Microstructural observations of the SHS samples were performed using a ZEISS LEO 1430 scanning electron microscope equipped with an Oxford ISIS 300 energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments). Prior to examination, the samples were dried, mounted on specimen holders, and sputter-coated with a thin layer of gold. Observations were conducted under low-vacuum conditions ($6 \cdot 10^{-5} \div 7 \cdot 10^{-6}$ Torr) at an accelerating voltage of 20 kV (80μA).

Table 2. Thelimits of quantification of the testing method

Heavy metal	Wavelength	Limit of quantification
	λ [nm]	[mg/dm^3]
Cadmium (Cd)	228.8	0.01
Cobalt (Co)	240.7	0.01
Chromium (Cr)	357.9	0.01
Copper (Cu)	324.8	0.01
Nickel (Ni)	232.0	0.01
Lead (Pb)	283.3	0.01
Zinc (Zn)	213.9	0.01

XRD examination of SHS samples

Qualitative analysis of the mineral composition of SHS samples was performed using a Bruker D8 Advance apparatus (Bruker, Billerica, MA, USA) equipped with a position-sensitive LYNXEYE detector. Measurements were carried out in Bragg-Brentano geometry using Cu Kα radiation (λ = 0.15418 nm) with a nickel filter. The measurements were recorded over an angular range of 2θ = 8° - 75°, with a step size of 0.03° and a counting time of 960 s/step. Samples with a grain size greater than 0.1 mm were prepared by grinding approximately 5 g of material in an agate mortar. The tested samples were applied as a thin layer (~1 mm thick, 30 mm in diameter) onto crystalline silicon plates with <7 1 1> orientation.

Preparation of aqueous extracts from SHS samples

Aqueous extracts from SHS samples were prepared using a batch leaching test in accordance with PN-EN 12457-4:2006 2006. The test was performed on two time points, after 28 and 90 days of sample curing in tap water. The material was brought into contact with the leaching liquid (distilled water) under controlled conditions by mixing on a roller table for 24 hours, using a liquid-to-solid ratio of L/S = 10 dm^3/kg d. m. (dry matter). After leaching, the aqueous extracts were vacuum-filtered through a hydrophobic polytetrafluoroethylene membrane filter with a pore diameter of φ = 0,45 μm. Prior to filtration, the filters were moistened with ethanol. The pH and electrical conductivity of the filtrates were measured immediately after filtration using a CPC-511 device (Elmetron, Poland) equipped with an IJ-44C complex electrode (IONODE, Australia), an ECF-1 conductivity cell (Elmetron, Poland), and a temperature sensor. To prevent precipitation of dissolved compounds, the filtrates were preserved by adding approximately 1 ml of concentrated nitric acid per 100 ml of the filtrate. The applied test is not intended to determine the leaching mechanism; therefore, the pH of the filtrate is governed by the properties of the tested material.

The results of heavy metal analysis in the filtrates, expressed in mg/dm^3, were converted into the amount of each component relative to the total sample mass according to Equation (1), in accordance with PN-EN 12457-4:2006 2006.

$$A = C \cdot \left[\left(\frac{L}{M_D} \right) + \left(\frac{MC}{100} \right) \right] \quad (1)$$

where:

A – amount of component released at L/S = 10 dm^3/kg.d.m. [mg/kg d.m.],

C – component concentration in the filtrate [mg/dm^3],
L – volume of leaching liquid [dm3],
M_D – mass of the dried analytical sample [kg],
MC – moisture ratio [%].

Determination of the degree of immobilization of heavy metals in SHS

The content of heavy metals in the individual components of the hardening slurries was calculated according to Equation (2):

$$X_i = \frac{A_i \cdot V_m}{m_s} \tag{2}$$

where:
X_i – content of the i-th heavy metal in the component [mg/kg d.m.],
A_i – concentration of the i-th heavy metal in the mineralizate [mg/dm^3],
V_m – volume of the mineralizate [dm^3],
m_s – dry mass of the sample subjected to mineralization [kg d.m.].

The total content of selected heavy metals in the SHS was determined analytically using Equation (3). It was assumed that the mixing water does not contribute to the heavy metal load.

$$Z_i = \frac{\sum m_{sj} \cdot X_{ji}}{m_{sz}} \tag{3}$$

where:
Z_i – content of the i-th heavy metal in the SHS [mg/kg d.m.],
m_{sj} – dry mass of the j-th SHS component [kg d.m.],
m_{sz} – total dry mass of slurry [mg/kg d.m.],
X_{ji} – content of i-th heavy metal in the j-th SHS component [mg/kg d.m.].

It is impossible to precisely determine the heavy metal content in SHS before leachability tests. During slurry preparation and curing, part of the heavy metals present in the dry components may be transferred to the mixing water and subsequently removed with water released during sedimentation, or may be lost due to surface leaching or diffusion processes. Therefore, the reported content of selected heavy metals (calculated as the sum of their contents in the individual slurry components) should be regarded as the maximum possible values in the SHS samples.

In order to determine the degree of immobilization of heavy metals in the hardened slurry matrix, the following relationships given in Equation (4) and (5) were applied (Król, 2012):

$$I_i = 100 - W_i \tag{4}$$

$$W_i = \frac{m_{i,e}}{m_{i,m}} \cdot 100\% \tag{5}$$

where:
W_i – leachability of the i-th heavy metal [%],
$m_{(i,e)}$ – mass of the i-th heavy metal in the eluate [mg],
$m_{(i,m)}$ – mass of the i-th heavy metal in the material subjected to leaching [mg],
I_i – immobilization degree of the i-th heavy metal [%].

Results and discussion

Heavy metal content in dry SHS components

Table 3 shows the content of heavy metals in the components of SHS.

Table 3 shows that bentonite, a natural material activated during production, exhibited the lowest concentrations of all heavy metals. The highest contents of cadmium, copper, lead, and zinc were observed in CCFA. In the case of cobalt and nickel, comparable concentrations were found in ash and cement, with the highest values recorded in MSWFA. Cement was characterized by the highest total chromium, whereas chromium concentrations in both tested ashes were similar and significantly lower than in cement. MSWFA contained lower amounts of cadmium, copper, lead, and zinc than cement; moreover, its cadmium content was lower than that of bentonite. It should be noted that MSWFA exhibited the lowest total concentration of the analyzed heavy metals among the anthropogenic materials used in the experiment. Interestingly, the concentrations of the analyzed metals in MSWFA were lower than those reported for ashes obtained from the incineration of large-sized, plastic, and textile wastes (except for Co) under conditions similar to those in domestic furnaces (Poluszyńska 2020).

Table 4 presents literature data on the contents of selected heavy metals in Portland cement and CCFA.

The cement used in the experiment contained heavy metals at levels comparable to those reported for Portland cements from various countries (Table 4). The heavy metal content in cement is largely influenced by the use

Table 3. Content of heavy metals in SHS components

Heavy metal	Bentonite	CEM I	CCFA	MSW FA
	[mg/kg d.m.]			
Cd	0.33±0.06	2.91±0.49	136.45±2.33	0.27±0.24
Co	8.78±0.69	22.39±0.67	23.62±0.3	27.47±1.36
Cr	<0.10	73.26±0.91	33.38±0.53	34.62±1.03
Cu	24.41±0.08	124.79±0.36	205.94±1.8	58.66±0.33
Ni	5.13±0.53	39.51±0.63	30.53±1.17	49.72±13.27
Pb	73.64±11.24	179.27±14.04	2878.69±31.81	164.79±1.79
Zn	255.75±0.43	603.82±4.52	853±6.08	377.37±2.21

Table 4. Content of heavy metals in Portland cement and CCFA – literature data

Heavy metal	CEM I 32.5R* from Poland [1)]	CEM I 52.5R*[2)]	Portland Cement from Japan[3)]	Portland Cement from Germany	CCFA from Greece[4)]	CCFA from Polan[5)]	CCFA from India[6)]	CCFA from China[7)]	CCFA from Netherlands[8)]	CCFA from Finnland[8)]
	[mg/kg]									
Cd	2-10.8		0.60	0.03-6	11.6-14.4			0.34-0.84	0.05	0.15
Co	4÷7		-	3-21	-			-	-	-
Cr	26÷113	68	80	25-712	110-160		64.8	77.87-87.64	-	-
Cu	7÷138	32	51	14-98	31.8-63.3	55		67.68-118.24	-	-
Ni	14÷35	-	-	14-97	-	78	51.6	34.54	6.8	58.2
Pb	<5*÷89.7	110	240	5-254	123-143	67	34.8	51.84-77.18	6.7	19
Zn	42÷824	460	60	21-679	59.6-86.9			14.28-107.10	14	-

* - Acc. (PN-EN 197-1:2012 2012)

1) (Kalarus and Garbacik 2008, Kalarus et al. 2016, Kledyński et al. 2017b)

2) (Dell'Orso et al. 2012)

3) (Yu et al. 2005)

4) (Fytianos et al. 1998)

5) (Smołka-Danielowska 2006)

6) (Verma et al. 2016)

7) (Fu et al. 2019, Xiang et al. 2012)

8) (Sandelin and Backman 2001)

of alternative fuels in cement plants. Commonly used materials include tires, which are sources of Cd, Co, Cr, Cu, Pb, and Zn, as well as fractions of municipal, commercial, and industrial waste, which contribute mainly Cd, Cu, and Zn (Achternbosch et al. 2003). The analyzed heavy metal concentrations may indicate substantial use of alternative fuels in Polish cement plants. Table 4 also presents ranges of selected heavy metal contents reported for ashes from conventional hard-coal-fired power plants. The ashes used in this study exhibited higher cadmium and lead contents and a lower chromium content than those reported in the literature (Table 4), while the concentrations of the remaining metals were comparable. Based on the available literature data (Table 4), the metal content in ash depends on the composition of the burned coal, combustion conditions, and the applied flue-gas-cleaning systems.

The levels of heavy metals in the tested MSWFA were lower than those reported in the literature for ashes from China and Europe in the early 1990s (Table 5). This trend may indicate an increasingly effective process of selective waste collection. Morf et al., in a full-scale MSW incinerator study, reported that the following percentages (by mass) of heavy

Table 5. Content of selected heavy metals in MSFA – literature data

Content of heavy metal [mg/kg]						Place of origin
Cd	Cr	Cu	Ni	Pb	Zn	
36.71	157.0	563.2	-**	1515	3269	Shanghai (Shi and Kan 2009)
116	510	981	-	1960	6470	China* (Wang et al. 2019)
77.83	566.15	3080.77	1583.92	13583.92	37383.47	Shenzen (Wang et al. 2015)
50-450	140-1100	600-3200	60-260	5300-26000	9000-70000	Europe (early 1990s) (Sawell et al. 1995, Wiles 1996)
29.5	-	1047	103.5	538.3	11324.2	Liaoning province (Su et al. 2016)

* - arithmetic mean for about 200 samples

** - not tested

Table 6. Content of heavy metals in Polish soils and limit values for different soil groups.

Heavy metal	Clay soils	Soils in Poland in general [1)]	Soils in industrial areas[1)]	IV group according to JL 2016 0-0,25 m b.g.l*. [2)]	III group according to JL 2016 0-0,25 m b.g.l. [2)]	II-3 group according to JL 2016 0-0,25 m b.g.l. [2)]	I group according to JL 2016 0-0,25 m b.g.l. [2)]
	[mg/kg]						
Cd	1.0	0.8	1.4	15	10	5	2
Co	4	3	3	200	100	50	50
Cr	9	6	9	1000	500	500	200
Cu	14	10	95	600	300	300	200
Ni	10	6	8	500	300	300	150
Pb	42	35	98	600	500	500	200
Zn	131	88	226	2000	1000	1000	500
* - below ground level							
1) (PIG-PIB 2012)							
2) (Journal of Laws 2016, item 1395 - implementation of EU Directive 32008R1272)							

metals originally present in the waste remained in the fly ash (FA) after incineration: Cd-89.8%, Pb-55.5%, Zn-53.1%, and Cu-6.9% (Morf et al. 2000).

Because the SHS materials are intended for use in soil, the heavy metal contents in their components were compared with the metal contents in Polish soils. Table 6 presents the limit concentrations of hazardous substances for land-use groups IV (communication areas), III (forests and the green areas covered by nature protection), II-3 (agricultural areas) and I (residential areas), as specified in the Journal of Laws (2016, item 1395), implementing EU Regulation No 32008R1272). In addition, Table 6 shows the average concentrations of selected heavy metals in Polish soils (PIG-PIB, 2012). All tested materials exhibited higher concentrations of selected heavy metals than the average values for Poland soils, as well as for clay soils and soils from industrial areas. Only bentonite was characterized by lower or comparable concentrations of cadmium, chromium and nickel relative to the average concentrations of these metals in clay soils in Poland. Zinc and lead concentrations were comparable to those found in industrial soils, whereas cobalt concentrations exceeded those values. The results indicate that exceedances of heavy metal limits were observed only for CCFA in the case of lead and cadmium. Cement and MSWFA exceeded the limits for residential areas only with respect to zinc.

Scanning Electron Microscopy test results

Figure 2 presents the microstructure morphology of the SHS for recipes 1 and 2 (Figure 2). SEM observations confirm the presence of a well-crystallized C-S-H phase with layered double hydroxide (LDH) formations in the form of hydrocalumite (HC). In both recipes, the internal microstructure is similar. Figure 3 presents the EDS analysis of the marked points 1 and 2 (Figure 2), which confirms the presence of HC formations. Due to the dense C-S-H matrix and the presence of HC formations, heavy metals are effectively immobilized within the SHS structure. Similar immobilization effects associated with hydrocalumite formations have also been reported in the literature (Yang et al. 2022, Ponce-Antón et al. 2018).

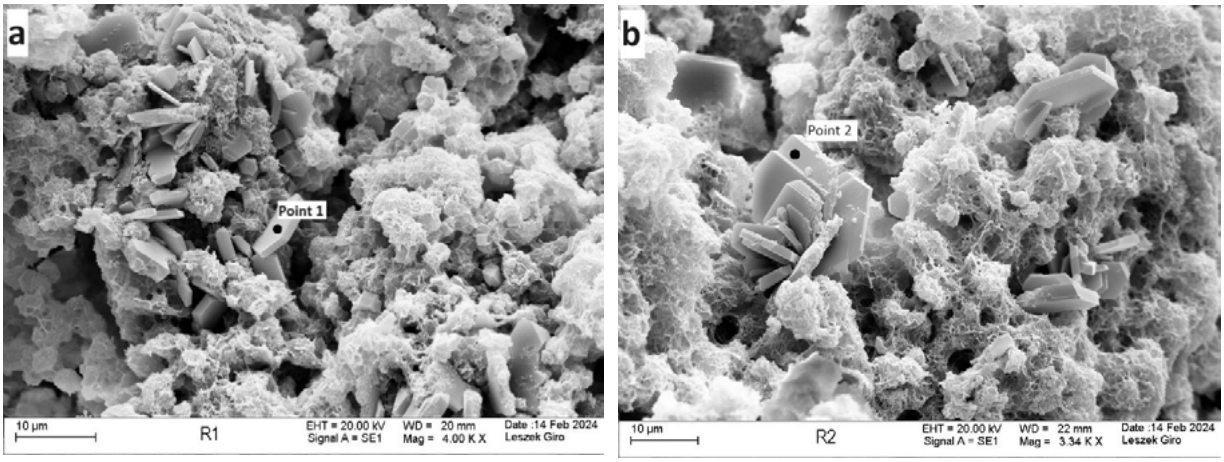

Fig. 2. Scanning Electron Microscopy images of SHS of recipe 1 (a) and recipe 2 (b) after 180 days of curing. Point 1 and point 2 indicate the particles analyzed by EDS.

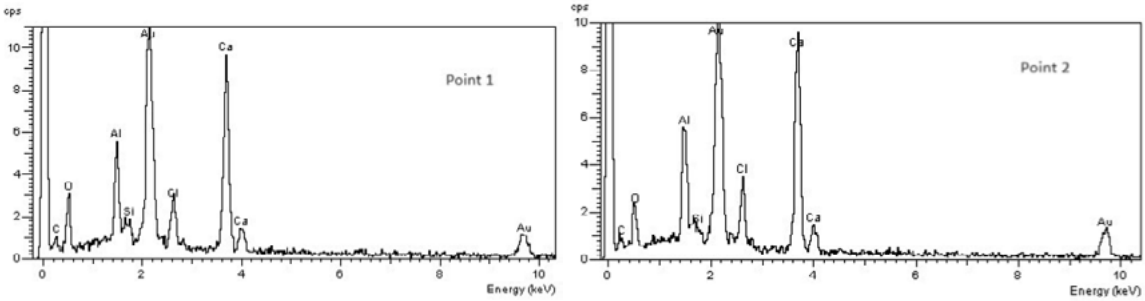

Fig. 3. Energy dispersive X-ray analyses (EDS) results of double hydroxides (LDH) of recipe 1 shown in Figure 2. Point 1 and 2 is Ca-enriched anion clay: hyrocalumite (HC).

X-ray Diffraction test results

The X-ray diffraction (Figure 3) confirm the presence of hydrocalumite (HC) and other major phases, such as ettringite (E), quartz (Q), and calcite (Cal), in the tested SHS. The higher intensities of the characteristic reflections of the HC and E phases may indicate a denser microstructure of the SHS. This effect is observed for recipes 1 and 2. Similar microstructural sealing effects in self-hardening slurries have also been reported in the authors' earlier studies (Falaciński 2011, Falaciński 2012), (Kotwica et al. 2016).

Immobilization of heavy metals

Table 7 shows the analytically determined content of heavy metals in the analyzed SHS recipes.

The relatively high heavy metal concentrations in the analyzed SHS samples (Table 7) results from the high proportion of CCFA in their composition. The concentrations of cadmium and lead significantly exceed the legal limits for substances posing a risk in soils (Table 6). In contrast, the concentrations of the remaining elements are within the limits permitted for soils in residential areas (Journal of Laws 2016, item 1395). Compared to the average metal contents in Polish soils, the metal concentrations in SHS are considerably higher (Table 6). Table 8 presents the properties of the aqueous extracts obtained from the SHS samples.

The pH of the aqueous extracts of all samples was alkaline and close to that of the pore solution in non-carbonated concrete. Similar results have been reported in previous studies (Szarek and Krysiak 2020, Kledyński et al. 2021, Kledyński et al. 2017, Szarek et al. 2018). No significant variations in pH of aqueous extracts were observed between recipes or with curing time (average at 28 days: 12.52, standard deviation: 0.11, average at 90 days: 12.54, standard deviation: 0.13). Due to their amphoteric nature, many heavy metals of environmental concern (e.g., Pb, Cu, Ni) show parabolic concentration curves in leachates as a function of pH. Higher pH values of aqueous extracts (8÷11) are favorable for heavy metal immobilization. For copper, the minimum concentration is observed at pH 10, with increasing concentrations at both lower and higher pH values. Concentrations are considerably higher at pH values around 6 than at pH values between 11 and 13 (Kabe et al. 2008). Most cations (e.g., Ni, Zn, Cd, Pb, $Cr^{(III)}$) form more soluble compounds under acidic conditions (van der Sloot and Dijkstra 2004, van der Sloot and Mulder 2002, Mizerna and Król 2015).

Measuring the conductivity of aqueous extract provides information about their mineral content and can indicate whether the tested material dissolves during the test. Conductivity increases under strongly acidic and strongly alkaline conditions (Rauba 2016). The specific conductivity of the SHS aqueous extracts was similar across curing times (average at 28 days: 9.00 mS/cm, standard deviation: 0.70, average at 90 days: 8.49 mS/cm, standard deviation; 0.63). Although the average conductivity decreased slightly after 90 days of curing, the difference between the means was not statistically significant. Similar conductivity values for SHS aqueous extracts after 28 days of curing have been reported in previous studies (Szarek and Krysiak 2020, Kledyński et al. 2021, Kledyński et al. 2017), while significantly lower values were observed in Szarek et al. (2018). It should be noted that in the cited works, the SHS contained a smaller proportion of combustion by-products. The conductivity of the obtained aqueous extracts is comparable to that of surface waters in Poland (<0.1-37.57 mS/cm) (Panek and Ciećko 2019) and

Table 7. Content of heavy metals in SHS

Heavy metal	R1	R2	R3	R4	R5
	[mg/kg d.m.]				
Cd	50.5	47.2	40.4	45.2	39.2
Co	24.9	24.7	24.8	24.5	25.1
Cr	40.7	42.9	41.9	42.8	41.9
Cu	124	124	115.1	121.8	113.6
Ni	40.2	40.2	41.0	39.9	41.5
Pb	1156.6	1090.1	953.7	1048.7	931.0
Zn	590.5	591.4	562.1	584.3	557.5

Table 8. Properties of water extracts from SHS samples

Recipe	R1		R2		R3		R4		R5	
Curing time [days]	28	90	28	90	28	90	28	90	28	90
pH [-]	12.4	12.3	12.6	12.6	12.6	12.6	12.4	12.6	12.6	12.6
Conductivity [mS/cm]	9.58	7.66	9.2	8.43	9.3	8.25	7.77	8.76	9.13	9.37
Substance	[mg/dm^3]									
Cd	0.015	0.018	0.013	0.020	0.015	0.020	0.012	0.019	0.015	0.020
Co	0.134	0.123	0.133	0.130	0.131	0.116	0.126	0.130	0.135	0.128
Cr	0.031	0.029	0.031	0.025	0.027	0.033	0.025	0.027	0.027	0.032
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0.458	0.501	0.408	0.386	0.381	0.291	0.396	0.236	0.425	0.376
Zn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

higher than the conductivity of groundwater in the vicinity of municipal waste landfills (Przydatek 2013, Wiater 2011, Motyka et al. 2005, Talataj 2001), indicating a relatively high salinity of the extracts.

The concentrations of metals in the aqueous extracts were generally low, with the highest values recorded for lead. Zinc, nickel, and copper concentrations did not reach the limits of quantification. Similar, though slightly lower, metal concentrations in aqueous extracts from MSWFA–cement solidification bodies have been reported by Shi and Kan (2009), although methodological differences must be considered. Higher metal concentrations aqueous extracts from MSWFA stabilized with other agents were reported by Wang et al. (2015); however, differences in the pH of the leaching solutions make direct comparison with the present study difficult.

To assess the effect of curing time on metal release, the average concentration of each element from all samples at a given curing time was calculated. Statistical significance of differences between means was evaluated using the nonparametric Mann-Whitney U test, while Spearman's rank correlation coefficients were calculated to assess the relationship between metal concentrations in the eluates and curing time. Statistical analyses were performed at a significance level of α=0.05. The Mann-Whitney U test and Spearman's rank correlation were chosen due to the limited number of samples and the non-normal distribution of the results. Only metals with concentrations above the limit of quantification were included in the analysis. Results are presented in Table 9.

At the assumed significance level, curing time had a statistically significant effect on the concentration of cadmium, with both the Mann-Whitney U test and the Spearman's rank correlation coefficient indicating a directly proportional relationship. For cobalt, a significant Spearman's rank correlation coefficient was observed, showing an inverse relationship with curing time. For the Mann–Whitney U test, the difference between means for cobalt would have been significant at α=0.0556, slightly above the selected threshold. No statistically significant relationships were observed for the remaining metals between aqueous extract concentrations and curing time.

Table 10 presents the amounts of heavy metals released from SHS samples. For analytical purposes, it also includes the limit values for the leaching of substances at a liquid-to-solid ratio of 10 dm^3/kg d.m. from non-hazardous waste intended for disposal in a non-hazardous waste landfill, in accordance with the European Landfill Directive (EU 2024). Table 11 presents the level of heavy metal immobilization in the tested samples.

The most released element was lead, regardless of formulation and curing time. In other studies of metal leaching from SHS (Kledyński et al. 2017, Kledyński and Szarek 2021), lead was also released in the highest amounts. The concentration of lead was approximately one order of magnitude higher than the limit value for non-hazardous waste

Table 9. Selected statistics for analysis of heavy metal concentration in aqueous extract

Heavy metal	Medium concentration [mg/dm^3]		p*	Spearman's rank correlation coefficient
Curing time	28 days	90 days		
Cd	0.014	0.019	0.0079**	0.8703
Co	0.132	0.125	0.0556	-0.6635
Cr	0.028	0.029	0.547619	0.2437
Pb	0.414	0.358	0.222222	-0.4526

* - exact p-value for small numbers
** - statistically significant results are marked in red

Table 10. Released amounts of heavy metals from SHS samples with legal limits

Recipe	R1		R2		R3		R4		R5		Non-hazardous waste European Landfill Directive (EU 2024)
Curing time [days]	28	90	28	90	28	90	28	90	28	90	
Heavy metal	[mg/kg d.m.]										
Cd	0.153	0.178	0.128	0.203	0.147	0.195	0.115	0.189	0.145	0.196	0.04
Co	1.371	1.231	1.333	1.301	1.285	1.161	1.234	1.301	1.340	1.281	-
Cr	0.313	0.286	0.311	0.248	0.267	0.328	0.246	0.272	0.264	0.320	0.5
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2
Ni	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4
Pb	4.69	5.012	4.092	3.862	3.736	2.916	3.881	2.366	4.215	3.762	0.5
Zn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4

(Journal of Laws 2015, item 1277) (EU 2024). Despite the relatively high amount released, lead was immobilized to a very high degree (≥99.995%) in all SHS samples (Table 12). The low variability of the immobilization results is particularly noteworthy.

Cadmium was also released from the slurry samples at levels exceeding the limit for non-hazardous waste (Journal of Laws 2015, item 1277) (EU 2024). However, the degree of immobilization was also very high (≥99.995%) and did not differ significantly between formulations and curing times.

In the case of remaining tested heavy metals, release levels were below the limits for non-hazardous waste (Journal of Laws 2015, item 1277; EU 2024), and immobilization levels were close to 100%. As with lead and cadmium, no significant differences between formulation or curing time were observed.

Available literature on heavy metal leaching from waste-based SHS reports similarly very high immobilization levels (Kledyński et al. 2021, Szarek and Krysiak 2020, Szarek et al. 2018, Szarek 2020). The results of this experiment are comparable to those reported for cement mortars (Król 2012).

In the study by Aubert et al. (2006), treated MSWFA samples were subjected to leaching tests in accordance with PN-EN 12457-4:2006 2006. Two different stabilization/solidification processes ("A" and "B") resulted in distinct heavy metal release behaviors. In the case of process "A", the release levels of all metals except lead were higher than those observed in this experiment. In the case of process "B", higher release levels were recorded for chromium, copper, and zinc. In a subsequent study (Aubert et al. 2007), crushed cement mortars based on the previously treated MSWFA were subjected to leaching. Compared to the present experiment, higher release levels were observed for zinc, nickel, and copper, while release levels for the remaining metals were lower by several orders of magnitude.

Overall, the results indicate that SHS may represent an environmentally safe and practically applicable method for the stabilization/solidification of raw fly ash.

Summary and conclusions

Based on the study, the following conclusions can be drawn:

1. Bentonite, as a natural resource-based material, contains a natural load of heavy metals.
2. CCFA exhibited the highest contents of cadmium, copper, lead, and zinc. The contents of cobalt and nickel in both ashes and cement were at comparable levels, with the highest values observed in MSWFA. The CCFA used in the study was characterized by higher cadmium and lead contents and lower chromium content than CCFA reported in the literature, while the contents of the remaining metals were similar.
3. MSWFA contained lower amounts of cadmium, copper, lead, and zinc than the cement used in the experiment. Among the anthropogenic materials analyzed, MSWFA exhibited the lowest total content of heavy metals. Furthermore, the heavy metal content of the studied MSWFA was lower than that reported in the literature.
4. The pH of eluates from SHS samples was alkaline and independent of curing time, corresponding to the pH of pore solution in non-carbonated concrete and consistent with literature data.
5. The specific electrical conductivity of eluates from SHS indicated high salinity, was independent of curing time, and was comparable to the conductivity of surface waters in Poland.
6. A statistically significant effect of curing time on metal concentration in the eluate was observed only for cadmium, showing a directly proportional relationship at α=0.05. In the case of cobalt, an inversely proportional relationship was observed at a slightly lower level of statistical significance (α=0.0556).
7. The release of chromium, copper, nickel and zinc from SHS was below the limit for non-hazardous waste in accordance with the European Landfill Directive (EU, 2024). In contrast, the release limits for lead and cadmium were exceeded.
8. The immobilization levels of all metals tested in SHS samples were very high and close to 100%, regardless of metal type, formulation, or curing time, indicating strong binding of these elements within the slurry matrix.
9. The dense SHS matrix plays a key role in the immobilization of hazardous compounds. In addition, the formation of mineral phases such as ettringite, calcite, and hydrocalumite further enhances the immobilization potential of the material.

Table 11. Heavy metal immobilization level in SHS samples

Recipe	R1		R2		R3		R4		R5	
Curing time [days]	28	90	28	90	28	90	28	90	28	90
Heavy metal	[%]									
Cd	99.997	99.996	99.997	99.996	99.996	99.995	99.997	99.996	99.996	99.995
Co	99.945	99.951	99.946	99.9473	99.9482	99.9532	99.9496	99.9469	99.9466	99.949
Cr	99.992	99.993	99.993	99.994	99.994	99.992	99.994	99.994	99.994	99.992
Cu	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999
Ni	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999
Pb	99.996	99.996	99.996	99.996	99.996	99.996	99.996	99.998	99.995	99.996
Zn	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999	>99.999

10. The results of the present experiment suggest that SHS may represent a potentially environmentally safe method for the stabilization and solidification of CCFA and MSWFA in their raw forms. However, further research is needed to reduce cadmium and lead release rates, investigate the leaching behavior of other elements and compounds, and elucidate the mechanisms governing heavy metal release from SHS. It is also essential to assess heavy metal immobilization under real-use conditions, where hardened SHS may be exposed to the infiltration of liquids with varying degrees of aggressiveness.

Further research on MSWFA management is essential to support circular economy objectives and minimize material leakage. Moreover, the anticipated increase in ash generation is expected to raise waste treatment costs, further emphasizing the need for effective stabilization and reuse strategies.

Acknowledgment

This study was financially supported by a grant from the Scientific Discipline of Environmental Engineering, Mining and Energy (6/2023) and by the Dean's Grant of the Faculty of

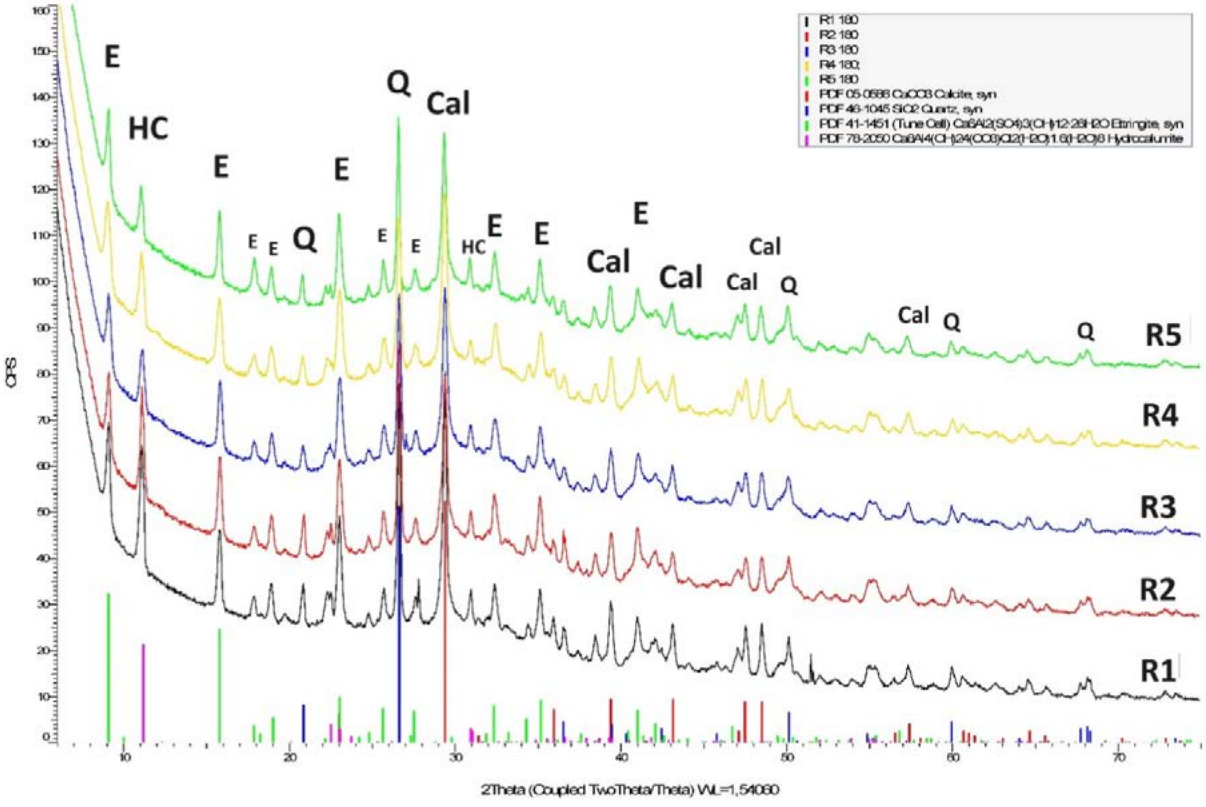

Fig. 4. X-ray diffraction patterns of self-hardening slurries of recipes from 1 to 5, after 180 days of maturation. HC: hyrocalumite, E: ettringite, Q: quartz, Cal: calcite.

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Ocena immobilizacji metali ciężkich w zawiesinach twardniejących z dodatkiem popiołów ze spalania odpadów komunalnych i węgla w kontekście zastosowań w inżynierii wodnej

Streszczenie. Celem niniejszego badania było określenie stopnia immobilizacji metali ciężkich (Cd, Co, Cr, Cu, Ni, Pb, Zn) w stwardniałych zawiesinach twardniejacych (SHS) opartych na popiele lotnym ze spalania stałych odpadów komunalnych (MSWFA) oraz popiele lotnym z konwencjonalnego spalania węgla (CCFA), przeznaczonych do budowy przesłon przeciwfiltracyjnych. Przygotowano pięć receptur SHS z wykorzystaniem wody wodociągowej, cementu portlandzkiego, bentonitu sodowego, CCFA oraz MSWFA. Mikrostrukturę i skład fazowy stwardniałych próbek SHS analizowano za pomocą technik SEM oraz XRD. Próbki SHS poddano wymywaniu metodą batch testu zgodnie z normą PN-EN 12457-4:2006, po 28 oraz 90 dniach dojrzewania. Stężenia metali oznaczono w eluatach z próbek SHS oraz w roztworach po mineralizacji ich komponentów, wykorzystując technikę płomieniowej absorpcyjnej spektrometrii atomowej (AAS). Wyniki porównano z wymaganiami prawnymi dotyczącymi zawartości metali ciężkich w odciekach składowiskowych oraz glebach. CCFA charakteryzował się najwyższą zawartością kadmu, miedzi, ołowiu i cynku, podczas gdy MSWFA wykazywał najniższą całkowitą zawartość metali ciężkich wśród analizowanych materiałów antropogenicznych. Eluaty cechowały się odczynem alkalicznym (≈12,5) oraz wysokim zasoleniem. Uwalnianie ołowiu i kadmu przekroczyło dopuszczalne wartości dla odpadów innych niż niebezpieczne, podczas gdy pozostałe metale pozostały poniżej wartości granicznych. Wszystkie badane metale wykazały wysoki stopień immoblizacji (≥99,99%), niezależnie od składu receptury czy czasu dojrzewania. Istotnym czynnikiem sprzyjającym immobilizacji metali była gęsta matryca C-S-H z obecnością hydrokalumitu. Przeprowadzone badania wskazują, że SHS mogą stanowić potencjalnie bezpieczną i przyjazną środowisku metodę stabilizacji i solidyfikacji popiołów lotnych w formie nieprzetworzonej. Metale ciężkie zostały mocno związane w strukturze zawiesiny. Konieczne jest jednak prowadzenie dalszych badań w tym zakresie.