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ENVIRONMENTAL ASPECT OF USING ASH FROM THERMAL TREATMENT OF MUNICIPAL SEWAGE SLUDGE IN HARDENING SLURRIES

Owing to the increasing popularity of the thermal treatment of municipal sewage sludge (TTMSS) in Poland, constant growth in the quantity of ash generated within this process has been recorded. Due to their properties, it is difficult to utilize this type of ash within the concrete production technology. One of the methods of waste utilization is to add it to hardening slurries, used in, among others, cut-off walls. The slurry operating conditions (contact with groundwater) and elevated heavy metal content in ash raise justified concerns in terms of environmental safety of the aforementioned methods. In the study, the release of heavy metals from a matrix, namely, the hardened slurry has been examined. The so-called "batch test" dynamic leachability testing method was applied for this purpose. A high level of heavy metal immobilization in the slurry was achieved. The obtained results indicate an environmentally safe possibility of using TTMSS ash in hardening slurries in cut-off walls.

1. INTRODUCTION

In line with the circular economy idea, the industry should more eagerly look at utilizing waste, hence limiting emissions and the consumption of natural materials. However, modern manufacturing processes often lead to waste products acquiring properties, which are undesirable from the perspective of the environment and human surroundings (e.g., the concentration of hazardous substances, among others, heavy metals) and the possibilities of their economic utilization (negative impact of waste on the features of a product manufactured using it). Such waste includes, among others, fly ash derived from the thermal treatment of municipal sewage sludge (TTMSS).

The thermal treatment of sewage sludge is a widely applied waste management method in highly-developed countries. According to the archives, in the first decade of

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the 20th century, it involved 76% of the annually generated sludge in Switzerland, more than 50% in the Netherlands and Belgium, and almost 20% in the United Kingdom [1]. The most popular method for the thermal treatment of sewage sludge is incineration, which is most often conducted in fluidized-bed furnaces [2] (e.g., incineration plant Dębogóra in Gdynia, Czajka in Warsaw), which is recognized as the best available technology (BAT).

Fluidized-bed thermal treatment of sludge involves the combustion of a raw material batch in a suspension of fine solid particles in a gas stream. The process temperature is 600–900 °C, which enables limiting the content of nitrogen compounds in flue gases. The quantity of combustion by-products generated in Poland, the highest share of which is constituted by fly ash, code 19 01 14 [3], is growing year after year [4].

TTMSS fly ash is characterized by high water demand and fineness, and relatively low content of compounds desirable from the perspective of chemical binding, which impacts its low hydraulic and pozzolanic activity [5]. Furthermore, the high content of phosphorus [6, 7] and certain heavy metals [8] causes additional difficulties in terms of utilizing ash, in its raw form in concrete technology or the construction industry in the broader sense, without increasing the cost of the material.

One of the methods for utilizing TTMSS ash, which seems to be resistant to difficulties resulting from certain properties of the waste (e.g., high water demand) is using the ash in a hardening slurry [9] – a thixotropic mixture of water (a predominant ingredient in terms of volume), binder and a clayey material (bentonite), as well as, depending on the purpose, other ingredients used for building structures in a subsoil [10], e.g., coal combustion by-products [10, 11]. Hardening slurries are used as a material for constructing cut-off walls in water engineering structures, i.e. dams or flood embankments. They are also used for counteracting the spread of groundwater pollution caused by landfill leachates, which helps limit the negative impact of such facilities on the environment.

Hardening slurries, as structures operating in the soil, are exposed to contact with groundwater. As a result, it has to be determined whether, due to waste materials contained, they do not pose a threat to the environment. One of the possible criteria for assessing the environmental impact is the release of heavy metals.

The research focused on studying the leachability of selected heavy metals (Zn, Cu, Pb, Cd, Cr) in a hardening slurry based on TTMSS fly ash. A short-term, dynamic leachability testing method, the so-called batch test was applied for this purpose [12].

2. EXPERIMENTAL

Test subject. The test subject included 3 samples of a hardening slurry composed for use in cut-off walls, based on TTMSS ash, with a recipe given in Table 1.

Table 1

Hardening slurry composition

Ingredient	Content [kg/1000 dm^3 of batched water]
Tap water	1000
Sodium bentonite	25
TTMSS fly ash	100
CEM I 32.5 R cement	450

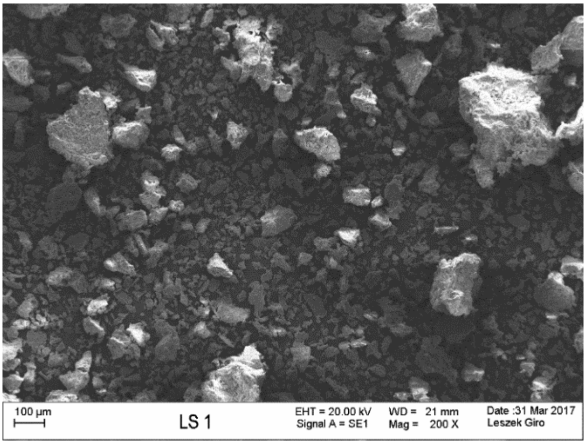

Fig. 1. Irregular grains of TTMSS ash,
magnification 200×, SE technique

Table 2

Components of TTMSS ash

Species	Contents [wt. %]
Chlorides	0.038±0.003
Sulfates	2.78±0.18
Calcium oxide	13.2±1.8
Free calcium oxide	0.12±0.01
Reactive calcium oxide	10.5±2.0
Reactive silicon oxide	9.1±0.9
Total silicon dioxide	36.4±1.2
Aluminum oxide	18.1±0.3
Iron oxide	5.7±0.3
Total oxide content ($SiO_2 + Al_2O_3 + Fe_2O_3$)	60.2±1.3
Total alkali content	4.20±0.12
Magnesium oxide	4.15±0.26
Phosphates (soluble)	5.50±1.02 mg/kg

The hardening slurry was composed using tap water, CEM I 32.5 R Portland cement by Cement Ożarów, and Volclay® sodium bentonite by CETCO. The TTMSS fly ash originated from the Czajka municipal wastewater treatment plant, which is equipped with the largest MSS mono-incineration system in Poland, where the TTMSS process takes place in a Pyrofluid™ technology fluidized bed furnace. In Figure 1, a photo of irregular ash grains taken in the SEM technique is shown, using a ZEISS LEO 1430 scanning electron microscope. Selected chemical and physical properties of the fly ash are given in Table 2.

Selected technological (in liquid state) and functional (after hardening) properties of a hardening slurry with a reference to the test procedure are shown in Table 3. The following properties were determined for the liquid state (number of samples $N = 9$):

- bulk density using a Baroid scale,
- relative viscosity using a flow viscometer (Marsh funnel),
- daily water loss,
- structural strength after 10 min using a shearometer.

After twenty-eight days of the hardening slurry curing in tap water, the following was tested (number of samples $N = 4$):

- compressive strength,
- hydraulic conductivity k_{10} (filtration coefficient) of hardening slurries (at water temperature 10 °C), with a variable hydraulic gradient, using distilled water.

Table 3

Properties of hardening slurry

Parameter	Value	Reference
Technological properties (liquid state)		
Bulk density, kg/m^3	1332±3	[13]
Relative viscosity, s	50±2	
Structural strength after 10 min, Pa	5.8±1.5	
Daily loss, %	3.6±0.8	[14]
Functional properties (solid state, after 28 days of curing in tap water)		
Compressive strength, MPa	1.74±0.10	[15]
Bulk density, kg/m^3	1341±19	[16]
Hydraulic conductivity k_{10}, m/s	$(9.2±2.9)\cdot10^{-9}$	[9]

Table 4 shows the content of selected heavy metals in hardening slurry ingredients, determined by the flame atomic absorption spectroscopy (FAAS) method after wet mineralization and extraction. Assuming that batched water and bentonite do not carry heavy metals, the heavy metal content in a hardening slurry was determined by the calculation method (taking into account the daily water loss, weight absorbability, and the bulk density of saturated slurry samples).

Table 4

Content of selected heavy metals in a hardening slurry
and its components [mg/kg d.m.]

Heavy metal	Hardening slurry	TTMSS fly ash	CEM I 32.5R
Zinc	1057±66	3290±83	804±24
Copper	206±14	808±24	120±4
Lead	84.5±8.8	83.0±6.5	104±7
Cadmium	9.6±0.9	14.0±0.7	10.8±0.6
Chromium	71.8±6.8	179±9	64.4±4.2

Leachability test method. Eluates for determining the heavy metal content were acquired using the batch test method [12]. The essence of this approach is to subject a crushed material sample to the action of a leaching liquid for 24 hours of dynamic mixing. The main assumption of this method is that a state of equilibrium (or a state close to a state of equilibrium) between the liquid and solid phases is achieved in the course of this test. The liquid/solid phase ratio of $L/S = 10$ dm^3/kg d.m. of material was used for the tests, because the research by, among others, Mizerna and Król [17] identified significantly higher heavy metal concentrations in water extracts (from metallurgical slag) obtained for $L/S = 10$ dm^3/kg d.m. than for $L/S = 2$ dm^3/kg d.m. (depending on the analyzed metal, from 41 to 78%). Distilled water was used as the leaching liquid.

Three hardening slurry samples, prepared similarly, were tested after 28 days of curing in tap water. Cured samples were broken down to a particle size below 10 mm and then immersed in an appropriate quantity of distilled water. Hence prepared samples were subject to continuous mixing for 24 h, using a roller mixer. After decantation, eluates were vacuum-filtered using a hydrophobic membrane filter (pre-wetted with ethanol) made of polyetrafluoroethylene (PTFE), with a pore diameter of $\varphi = 0.45$ µm. The specific conductivity and pH of the eluates were measured immediately after filtration. The filtrates were fixed with a small addition of concentrated nitric acid(V). Next, the content of selected heavy metals was determined.

Table 5

Limits of determination for heavy metals tested [mg/dm^3]

Heavy metal	Determination limit
Zinc	0.01
Copper	0.02
Lead	0.03
Cadmium	0.01
Chromium	0.03

The heavy metal content (Zn, Cu, Pb, Cd, Cr) was determined using flame atomic absorption spectroscopy (FAAS), based on reference curves determined for a series of pre-prepared reference solutions by MERC [18]. Table 5 contains the method's determination limits for analyzed elements.

The concentrations of heavy metals in the eluate expressed in mg/dm^3 were converted to the ingredient quantity relative to the total sample mass

$$A_i = C_i \left(\frac{L}{M_D} + \frac{MC}{100} \right) \tag{1}$$

where: A_i – released component quantity with $L/S = 10$ dm^3/kg d.m., mg/kg d.m., C_i – ingredient concentration in the eluate, mg/dm^3, L – leaching liquid volume, dm^3, M_D – dried analytical sample mass, kg, MC – humidity ratio, %.

The uncertainties regarding the released ingredient quantity for each of the samples were determined using the total differential method.

To determine the level of heavy metal immobilization within a matrix (hardening slurry), the following relationship was used [19]:

$$W_i = \frac{m_{i,e}}{m_{i,m}} \times 100\% \tag{2}$$

$$I_i = 100 - W_i \tag{3}$$

W_i – leachability of the ith heavy metal, %, $m_{i,e}$, $m_{i,m}$ mass of the ith heavy metal in the eluate (e), and material subjected to leaching (m), mg, I_i – immobilization level of the ith heavy metal.

3. RESULTS AND DISCUSSION

The obtained eluates of hardening slurry samples were characterized by pH 12.6 and similar specific conductivities (average value for 3 tested samples $\kappa_{av} = 8.91$ mS/cm; standard deviation $\sigma = 0.14$ mS/cm). A strongly alkaline reaction of the water extracts resulted from the presence of overhydrated (at least partially) cement in the hardening slurry and was similar to the porous liquid reaction in cement matrices (Tables 6, 7).

The most strongly released elements were zinc ($A_{i,av}$ for 3 tested samples of 4.52 mg/kg d.m., standard deviation $\sigma = 0.64$ mg/kg d.m.) and lead ($A_{i,av} = 4.60$ mg/kg d.m., $\sigma = 0.57$ mg/kg d.m.). The leachability of chromium, as well as cadmium (Tables 6 and 7), with the concentration in eluates varying around the determination limit of the method (chromium, in particular), was lower by a single order of magnitude. Copper concentration in each of the obtained eluates was below the determination limit. Similar relationships were obtained elsewhere [20].

Table 6

Results of the eluate test

Eluate	pH	Specific conductivity [mS/cm]	Metal concentration [mg/dm³]				
			Zn	Cu	Pb	Cd	Cr
1	12.6	9.01	0.505±0.021	<0.02	0.317±0.016	<0.01	0.045±0.015
2	12.6	8.97	0.381±0.023	<0.02	0.425±0.06	0.010±0.004	0.038±0.005
3	12.6	8.76	0.471±0.025	<0.02	0.339±0.034	0.011±0.004	<0.03

The hardening slurry was characterized by higher leachability of lead and zinc, within a similar pH range, compared to, e.g., concrete (0.2–0.4 and 0.25–0.40 mg/kg d.m., respectively) [21] and concrete debris (0.45 and 0.1 mg/kg d.m., respectively), as well as concrete in recycled aggregate (0.24–0.35 and 0.01 mg/kg d.m., respectively) [19], whereas copper was leached with a similar, low intensity. Relative to concrete debris and concrete in the recycled aggregate, cadmium was leached from the slurry more intensively (0.03 and 0.025–0.028 mg/kg d.m., respectively), just like chromium (0.27 and 0.13–0.19 mg/kg d.m., respectively) [19].

Table 7

Quantities A_i of heavy metals released
from hardening slurry samples [mg/kg d.m.]

Eluate	Zinc	Copper	Lead	Cadmium	Chromium
1	5.05±0.22	<0.20	3.17±0.16	<0.10	0.45±0.15
2	3.81±0.24	<0.20	4.25±0.61	0.10±0.05	0.38±0.06
3	4.71±0.26	<0.20	3.39±0.35	0.11±0.05	<0.30

Owing to the content of cement binder and bentonite in the hardening slurry, which are ingredients characterized by sorptive properties [22, 23], the heavy metal immobilization level in the hardening slurry shall be considered as high (Table 8). Similar relationships for hardening slurries were achieved in [24], however, compared to [19], the tested material immobilized lead to a greater extent than cement mortar.

According to other authors [25], directly comparing the heavy metal content in eluates sampled from building materials operating in the ground with the requirements for potable water is inappropriate in most cases. This is due to numerous factors influencing the element content in a liquid flowing in the ground (percolation), especially when the path to an intake is long. For example, during percolation through a ground medium, pH can change, resulting in the dissolution or precipitation of the ingredients therein.

A material placed in the ground very rarely comes in contact with the entire stream of flowing liquid, and its impact is more or less local.

Table 8

Heavy metal immobilization in hardening slurry samples [%]

Eluate	Zinc	Copper	Lead	Cadmium	Chromium
1	99.59	>99.92	96.75	>99.1	99.46
2	99.69	>99.92	95.64	99.10	99.54
3	99.61	>99.92	96.53	99.01	>99.64

Furthermore, it is worthwhile for the analysis to take the application scenario into account. Although potable water reservoirs can be made of concrete (in this case, comparing the concentrations in eluates with the limit values for potable water is fully justified), hardening slurry structures have a completely different application.

In light of the above, heavy metal concentrations in eluates were compared with the requirements for landfill leachates [26] (Table 9). All obtained eluates were characterized by concentration below the limit value, which is why the studied hardening slurry should not pose a threat to the natural environment. Besides, its properties (Tables 2, 7) enable its utilization as a cut-off wall material, which limits groundwater being polluted with landfill leachates.

Table 9

Highest permissible concentrations [mg/dm^3]
for selected heavy metals present in landfill leachates [26]

Metal	Concentration
Zinc	2.0
Lead	0.5
Copper	0.5
Cadmium	0.4
Chromium(VI)	0.1
Total chromium	0.5

4. CONCLUSIONS

- A hardening slurry based on TTMSS fly ash exhibited high heavy metal immobilization properties.
- The most leached elements were zinc and lead, however, their release intensity was relatively low (minimum immobilization level for selected metals was 99.59 and 95.64%, respectively).

• All of the obtained eluates were characterized by heavy metal concentration below the limit value for landfill leachates [26], which indicates a possibility of an environmentally-safe utilization of hardening slurries with a TTMSS ash addition, including, e.g., as cut-off walls in landfills.

• The obtained heavy metal release levels are consistent with the hardening slurry heavy metal leachability test results available in source literature, however, in the case of concrete, concrete debris, recycled aggregate concrete, or cement mortar, differences were observed, which prove the complexity of this process.

• It is suggested to conduct further research over the leachability of heavy metals in hardening slurries, which take into account their operational nature (filtration through material) and conditions (contact with aggressive media) and the speciation of released elements.

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