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The use of extraction methods to assess the immobilization of metals in hardening slurries

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Abstract: In Poland, in recent years, there has been a rapid accumulation of sewage sludge – a by-product in the treatment of urban wastewater. This has come about as a result of infrastructure renewal, specifically, the construction of modern sewage treatment plants. The more stringent regulations and strategic goals adopted for modern sewage management have necessitated the application of modern engineering methodology for the disposal of sewage sludge. One approach is incineration. As a consequence, the amount of fly ash resulting from the thermal treatment of municipal sewage sludge has grown significantly. Hence, intensive work is in progress for environmentally safe management of this type of waste. The aim of the experiment was to evaluate the possibility of using the fly ash that results from municipal sewage sludge thermal treatment (SSTT) as an additive to hardening slurries. The article presents the technological and functional parameters of hardening slurries with an addition of fly ash obtained by SSTT. Moreover, the usefulness of these slurries is analyzed on the basis of their basic properties, i.e., density, contractual viscosity, water separation, structural strength, volumetric density, hydraulic conductivity, compressive and tensile strength. The research on technological and functional properties was carried out, the aim of which was to determine the practical usefulness of the hardening slurries used in the experiment. Subsequently, leaching tests were performed for heavy metals in the components, the structure of the hardening slurries. An experiment showed leaching of hazardous compounds at a level allowing their practical application. The article presents the potential uses of fly ash from SSTT in hardening slurry technology.

Introduction

Each year, millions of tons of municipal, mining, electroplating, dyeing and industrial sewage sludge is generated as waste. Sewage sludge is also produced as a specific type of waste in the wastewater treatment process. So far, the dominant trend in managing municipal sewage sludge was storage and accumulation within treatment plants (on landfills, lagoons and sedimentation ponds). There is an ongoing search for alternative sludge neutralization methods. One of such methods, with its share and significance in managing sewage sludge increasing over the recent years, is the sewage sludge thermal treatment (SSTT). The thermal sludge treatment methods include incineration, co-incineration, and the so-called alternative methods, such as gasification, pyrolysis, or wet oxidation. An important argument in favor of using incineration and co-incineration methods is the familiarity with the processes and the ability to utilize the resultant products. The indirect use of sludge in the manufacture of building materials, ceramics and bricks has been recognized as an ecological alternative to landfills (Chiang et al. 2009, Rodríguez et al. 2010, Teixeira et al. 2011). This enables eliminating sludge, and at the same time recovering energy and materials. This concept was developed and applied for co-treatment of problematic waste, such as municipal solid waste (MSW), sewage sludge, persistent organic pollutant (POP) waste, contaminated soil, and municipal solid waste incinerator fly ash (MSWI-FA) (Yan et al. 2009, Li et al. 2012a, 2012b, 2012c, Yan et al. 2014, Chen et al. 2016, Liu et al. 2015, Zhao et al. 2017a, 2017b). The methods for utilizing the hence-created fly ash are being sought. Hoi King Lam et al. (2010) studied the possibility of using sewage sludge fly ash for manufacturing cement clinker. They demonstrated that clinker containing 6% of heavy ash from municipal waste exhibits a chemical composition similar to ordinary Portland cement. However, materials created with the addition of municipal waste fly ash originating from solid waste may demonstrate CaO deficiency, which is necessary to produce alite (Hoi King Lam at el. 2010). Another application for SSTT fly ash is to use it in manufacturing hardening slurries. Falaciński and Szarek (2016) demonstrated a possible application of it for hardening slurries as a material in cut-off walls of flood embankments. A hardening slurry used in hydraulic engineering should exhibit appropriate splitting strength (Kledyński and Rafalski 2009).

Because of their ecological and toxicological importance, more and more attention is paid to micro-pollutants present in ash obtained from sewage sludge, thus, in products with ash as additive. Sewage sludge constitutes a waste heavily loaded with hazardous substances. Due to the sewage sludge being heavily loaded with chemical substances, including the high content of heavy metals originating from the chemical composition of sewage, there are restrictions associated with the environmental application of produced ash. Heavy metals (HM) found in high concentrations and in a wide range are especially dangerous. Zn^{2+}, Cu^{2+}, Cd^{2+}, Cr^{2+}, Pb^{2+}, Ni^{2+}, Ag^{+} and Hg^{2+} ions, the removal of which is very difficult, and accumulation in eco-systems dangerous, are found most commonly and in highest concentrations in generated ashes (Sánchez-Chardi, 2016). This is why the studies on the immobilization of these metals are required in terms of testing of new materials, including hardening slurries.

Ash, as an incineration product, has a completely different biological and chemical composition, and crystal structure in comparison to the substrates used within the incineration process. The metal ions contained in the ash can be bound by incorporating into the structures of the geopolymer formed at high temperatures or can be adsorbed by aluminium ions on a geopolymer backbone. This way, according to the methodology in (GUO, 2017), heavy metal immobilization is controlled by the adsorption mechanism and physical encapsulation. However, it is uncertain whether the used ashes will not be a source for the release of pollutants to the environment. At the same time, the substances contained in MSWI-FA can be beneficial and detrimental for the manufacturing of building materials. The high content of CaO, SiO_2, Al_2O_3 and Fe_2O_3 in ashes provides an opportunity to use them as a raw material and usually amounts for less than 50% of its composition. The high share of mineral substances, including Na, K and Cl salts, as well as toxic traces of heavy metals (HM) such as Hg, Cd, Pb, As, Cr and Tl will have a negative impact on the manufacturing of building materials. High amounts of sodium chloride (NaCl) and potassium chloride (KCl) cause concrete porosity and decrease its strength. Chloride compound deposition in induction fans and ducts may lead to corrosion and clogging of the system (Quina et al., 2008; Wang et al., 2010; Kikuchi, 2001; Pan et al., 2008). When co-processing MSWI-FA, it is believed that all non-volatile and semi-volatile HM can be transferred to created products when forming them, which would greatly increase the HM level therein.

The objective of the study was to evaluate sewage sludge thermal treatment (SSTT) fly ash in hardening slurries in terms of heavy metals immobilization. These studies were aimed at composing hardening slurries using sewage sludge thermal treatment (SSTT) ash and studying their behavior of deactivating metals (Cd, Cu, Zn, Pb, Ni), as an environmentally friendly approach to managing waste and reducing the amount of waste accumulated on sewage sludge and ash landfills. The conducted experiment involved assessing the suitability and potential applications of fly ash in manufacturing hardening slurries. The degree of immobilization of heavy metals was examined in the prepared hardening suspensions with the addition of ashes from SSTT.

Materials and methods

Hardening slurry preparation

Hardening slurries with the addition of SSTT ash were prepared according to three pre-specified recipes (Falaciński and Szarek, 2016). The following components made up the slurries: tap water at a temperature of 18°C, sodium bentonite, sewage sludge thermal treatment (SSTT) fly ash, and CEM I 32.5 R cement. Slurry samples were prepared in steel cylindrical molds with a height and diameter of 80 mm. The compositions of the prepared recipes are shown in Table 1.

Table 1. Composition of three hardening slurry recipes with added SSTT ash

No.	Recipe	R1	R3	R5
	1	2	3	4
1	Hardening slurry composition [g]			
2	water (w) [dm^3]	1500	1500	1500
3	Bentonite (b) [kg]	60	60	60
4	Ash (a) [kg]	450	675	885
5	Cement (c) [kg]	240	270	300
6	Dry ingredients C = b + a + c	750	1005	1245
7	Indicators			
8	w/b	2	1.49	1.2
9	w/a	3.33	2.22	1.69
10	w/c	6.25	5.55	5
11	c/a	0.53	0.4	0.34
12	Dry ingredient content relative to d.m. [%]			
13	Bentonite	8	5.97	4.82
14	Ash	60	67.16	71.08
15	Cement	32	26.87	24.10

Hardening slurries were prepared in laboratory conditions, according to the following procedure: bentonite was added to water and mixed for 3 minutes, followed by adding ash, and mixing for 1 minute. Finally, cement was added, and the entire blend mixed also for a minute. Next, the obtained mixture was transferred to pre-prepared steel molds (d=h=80 mm). The filled molds were left covered until the slurry solidified. After 4 days the samples were removed from the mold and put into containers with tap water, where they were cured until testing. The heavy metal content in the hardening slurry was tested after 7, 14 and 28 days of curing.

The process properties of the hardening slurry test were also examined. The bulk density (ρ) was determined using a Baroid mud scale, and the result was given in g/cm^3. One bulk density measurement was taken for each recipe. The relative viscosity (L) was determined using a discharge viscometer – a Marsh funnel. The structural strength of the slurry in liquid state was measured using a shirometer, whereas the daily water loss (after 2 and 24 hours) was determined in marked measuring cylinders. The additionally determined performance parameters included compressive and tensile strength in kPa, as well as the filtration ratio k_{10} in m/s.

SSTT ash cannot be used as fly ash (additive) for concrete based on its definition (origin) (EN–451-1, 2012). This material is characterized by high water demand and fineness, and a relatively low content of compounds desired from the perspective of binder binding. SSTT ash exhibits activity after 28 days of curing, at a level of 60% relative to the reference sample, which is problematic in the context of its application as a full-fledged building material ingredient. Selected physical and chemical properties of SSTT ash are shown in Table 2.

Figure 1 shows SEM images. They contain SSTT ash grains of various sizes. Larger grains constitute conglomerates of numerous mineral ingredients – Figure 1a. Figure 1b shows a spherical sinter characteristic for fly ash.

Figure 2 shows a SSTT ash diffraction pattern with applied reflections of identified phases. The most intensive reflections were recorded for quartz, which is the dominating compound in the ash. This confirms the test results for the ash chemical composition (Table 2), where silicon dioxide is the dominating compound. Intensive reflections were also obtained for calcium minerals – aluminium-calcium phosphates and anhydrite. Furthermore, a group of magnesium-ferrous phosphates was also distinguished. The diffraction pattern also contains reflections corresponding to hematite and anorthoclase. The sample background most likely indicates low material amorphism. The presence of phases containing phosphorous is confirmed by literature data (Łukawska 2014, Wzorek 2008).

Table 2. SSTT ash chemical and physical property test results (Szarek, Wojtkowska 2018)

No.	Chemical ingredient/Physical properties	Value [%] mass
1	Chlorides	0.027±0.003
2	Sulphates	2.54±0.17
3	Calcium oxide	16.3±2.8
4	Free calcium oxide	0.65±0.11
5	Reactive calcium oxide	13.5±3.6
6	Reactive silicon oxide	20.0±2.1
7	Total silicon dioxide content	39.0±1.8
8	Aluminium oxide content	18.4±0.3
9	Iron oxide content	5.8±0.3
10	Total oxide content (SiO_2 + Al_2O_3 + Fe_2O_3)	63.2±2.2
11	Total alkali content	5.40±0.20
12	Magnesium oxide	3.13±0.15
13	Phosphates	6.18±1.29 mg/kg
14	Loss during roasting (Category)	2.49±0.07 (A)
15	Fineness	47.0±0.5
16	Volume constancy	1.1±0.1 mm
17	Activation ratio after 28 days*	61.1±3.6%
18	Start of setting** (w/b***)	2.00 (0.40)
19	Water demand	132±1%
20	Density	2357.8±124.1 Mg/m^3
21	Specific area acc. to Blaine	3670±500 cm^2/g

* – compressive strength of cement mortar after 28 days of curing was 55.7 MPa.
** – reference sample setting time multiple (start of setting for only cement was 200 minutes).
*** – water/binder index

The high content of phosphorous in cement decomposes alite (C_3S), hence deteriorating clinker quality. The presence of phosphorous is also detrimental in terms of delaying the cement hydration process, which can lower the quality of concrete based on SSTT ash.

Heavy metal testing

Heavy metals were determined (after mineralization and leaching) in all components used for developing the hardening slurry and in dried slurry samples after 7, 14 and 28 days of curing. 2 g of each sample was collected for mineralization. In order to determine the total heavy metal content, each sample was hot mineralized with a 3:1 mixture of strong HNO_3 and $HClO_4$ acids. 10 g of each sample was weighed and placed in 50 cm^3 of an extracting liquid in order to evaluate the process of leaching metals from hardening slurry samples. Distilled water, 0.1 M of EDTA, 0.1 M of hydrochloric acid and 1 M of magnesium chloride were used for the extraction. The pre-set extraction solutions were left for 7, 14 and 28 days.

After mineralization and extraction, all samples were filtered into 100 cm^3 flasks. Zinc, copper, lead, cadmium and nickel were determined in 45 such solutions after mineralization and extraction. The metals were determined following an environmental sample methodology, which involves flame and graphite furnace atomic absorption spectroscopy, using Analyzer 300 (Perkin Elmer) spectrometers.

Process and performance parameters of the analyzed hardening slurry

The conducted analyses of the process and performance parameters within the analyzed hardening slurries with added sewage sludge incineration ash fall within the limits of

a) irregular ash grains (magnification 200×) b) ash grains (magnification 2500×)

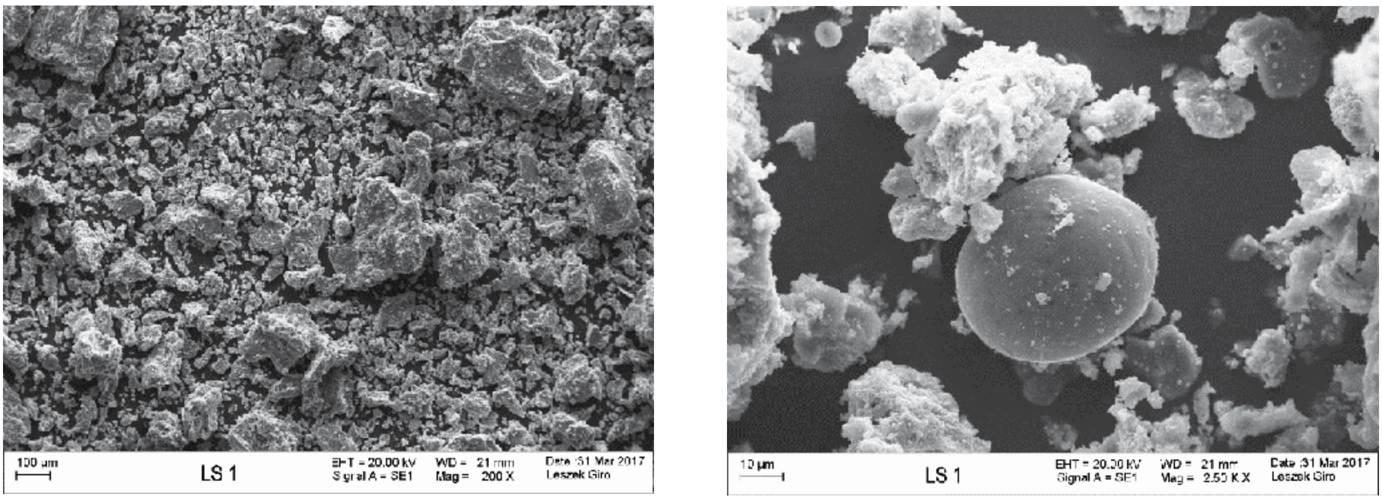

Fig. 1. SSTT ash grains (SEM)

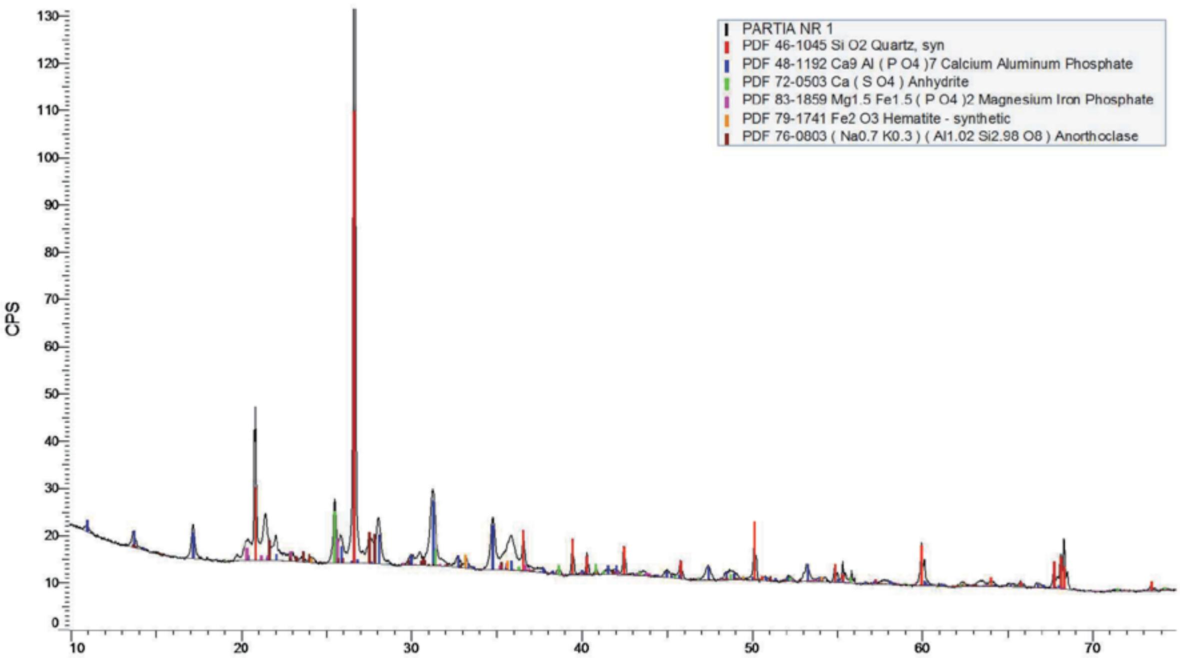

Fig. 2. SSTT ash diffraction pattern (SEM)

parameter values applied in engineering practice. The results of original tests are shown in Table 3.

Heavy metal content in a hardening slurry and components

Cement, bentonite and sewage sludge thermal treatment (SSTT) ash were used for preparing the hardening slurry. Dry ingredients were combined by adding distilled water. The heavy metal content (Zn, Cu, Pb, Cd and Ni) was determined in all hardening slurry components. The results indicated that used water and bentonite did not contain heavy metals. Cement, and above all, ash contained significant amounts of the analyzed metals. The amount of metals in three hardening slurry samples depended on the quantity of a given component (Tables 1 and 4).

The obtained results indicate a significant load of ashes with all tested metals. Table 4 summarizes the toxicity characteristics of the raw ash used (mean value for the samples tested) and cement. It should be noted that in the case of ash, apart from Pb and Ni, zinc concentration was relatively high. Cd concentration was at a similarly high level in both components. The analysis of source literature data on metal content in ash indicated various concentrations of individual metals in it (Poluszyńska and Ślęzak, 2015, Nowak et al. 2012).

In the case of the three samples of the hardening slurry composed using alternative materials, the concentration of five metals was diverse (Table 4). The results show that the differences in the concentrations of the three metals (Zn, Ni and Cu) between the three different slurry compositions were significant. Out of the 5 measured metals, notable differences in the concentration were recorded for Cd and Pb. In the suspensions after maturing in water, a slight decrease in the content of the analyzed metals was found. As shown in Figure 3, lead and nickel were washed to the extraction water to the greatest extent, and to a lesser extent – zinc and copper. Cadmium was the strongest bound in the hardening slurries.

The metal content tests involving extraction water, conducted after 7, 14 and 28 days of curing indicated a high degree of metal release from the solid phase to the solution (Fig. 4 and 5). Cadmium exhibited the highest mobility. Its leaching percentage amounted to 90% on average of the initial value whreas for zinc it was 77.5%. Among the ingredients used to prepare the hardening slurry, copper, lead and nickel were leached in 57%, 68% and 69%, respectively. The study showed that metals present mainly in ash, as well as in cement, tended to be released and move to an aqueous environment (Renbo et al. 2012). The degree of releasing metals to water from freshly prepared slurries is shown in Figures 4 and 5.

Figures 6 and 7 were drawn up for the purposes of a detailed analysis of the general heavy metal content in hardening slurries in tap water after 7, 14 and 28 days of curing. As indicated by the shown graphs, the greatest variability over time was exhibited by copper in the R3 slurry. The remaining metals exhibited a similar leaching level over three measurement periods for three slurry compositions. This indicates a high mobility of the metals remaining in the slurries,

Table 3. Process and performance parameters of the tested hardening slurries

No.	Parameter	Recipe			
		R1	R2	R3	remarks
Process parameters					
1	Density [g/cm3]	1.28	1.36	1.43	
2	Relative viscosity[s]	8	41	53	
	Structural strength	0	2.02	1.63	1 min
		0	1.97	1.87	10 min
	Water loss	5	5	3	2 h
		14	11	6	24 h
Performance parameters					
3	Compressive strength [kPa]	122.7	218.9	205.7	
4	Tensile strength [kPa]	29.86	39.91	93.55	
5	Filtration ratio [m/s]	3.71×10^{-6}	1.08×10^{-6}	8.84×10^{-7}	

Table 4. Average metal content in cement and ashes and in three recipes of hardening slurries [mg/kg d.m.].

No.		Zn	Cu	Pb	Ni	Cd
1	Cement	151.2	39.7	47.9	12.9	10.9
2	Ash	2302	599	31.6	39.1	11.5
3	R1	1429.68	372.10	34.29	27.59	10.40
4	R2	1556.79	412.98	34.09	29.73	10.67
5	R3	1672.87	435.36	34.00	30.90	10.81

regardless of the initial composition. Copper was characterized by high stability for the R1 and R2 slurries. The only high diversification was recorded for copper in the R3 slurry, which indicated Cu immobilization after 14 days of slurry curing and strong extraction after 28 days.

Extraction of metals from a hardening slurry

One of the criteria for using fly ash in manufacturing building materials is the stabilized chemical composition of obtained products. The single extraction process was utilized to assess heavy metal immobilization within the obtained hardening

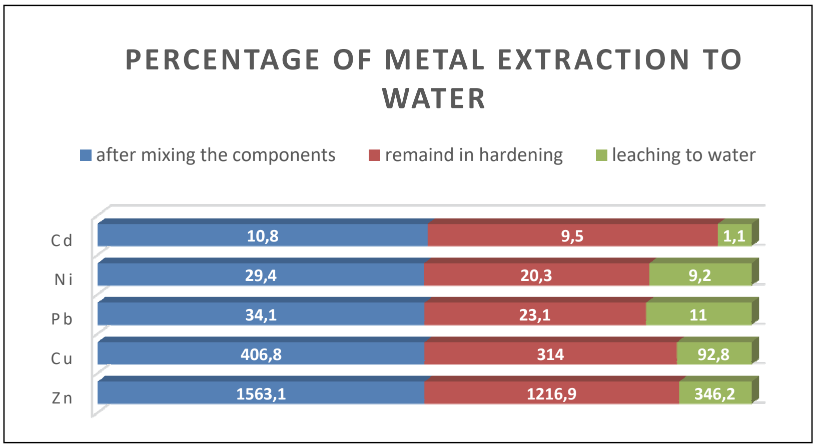

Fig. 3. The average content of metals in the initial composition of the hardening slurry, remaining in the slurry after water extraction and in the extraction water [mg/kg d.m.]

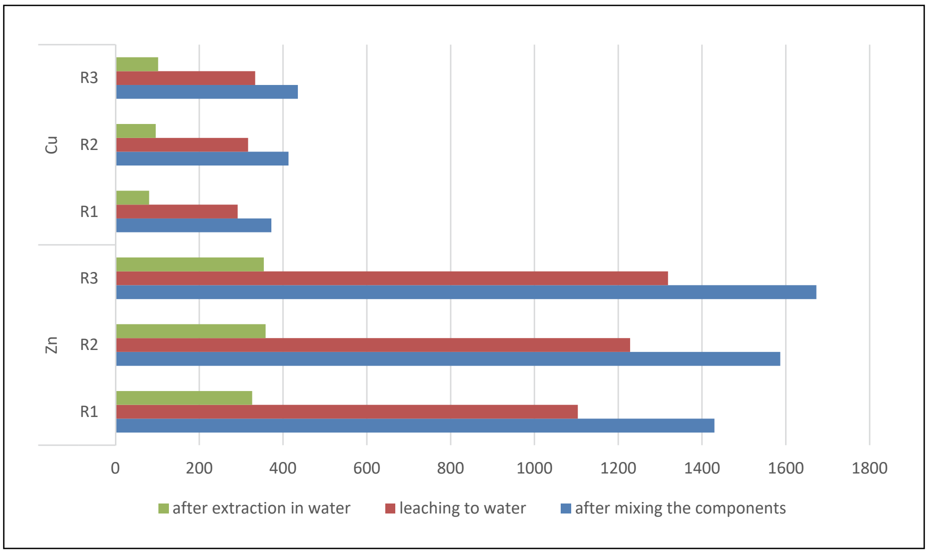

Fig. 4. Zinc and copper total content and content in water extract and hardening slurries [mg/kg d.m.]

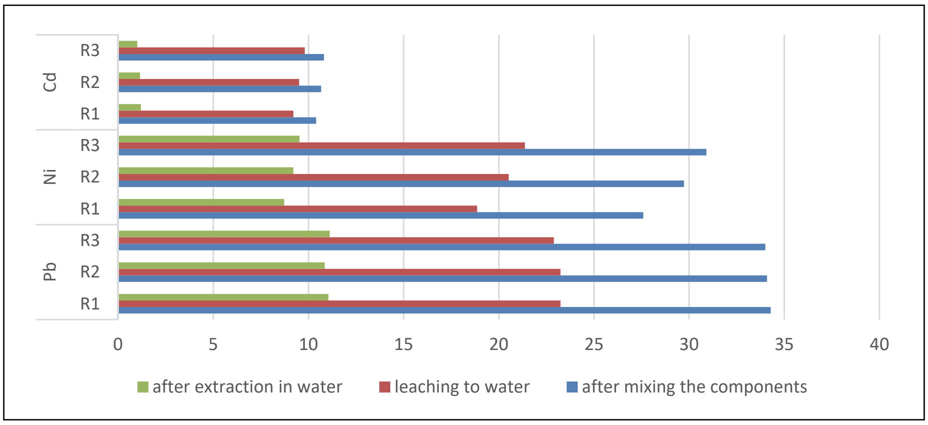

Fig. 5. Lead, nickel and cadmium total content and content in water extract and hardening slurries [mg/kg d.m.].

slurry samples. Metals were extracted from hardening slurry samples, of various composition, using four solutions, namely, distilled water, EDTA, hydrochloric acid and magnesium chloride. Table 5 shows the results of test extractions of metals from hardening slurry samples using four solutions, after three curing periods.

The obtained metal mobility test results for hardening slurry samples indicated the possibility of metals transferring to the liquid phase. The metal degree of immobilization depended on the properties of the metals and extractant solutions, as well as the proportions of the used ingredients. Hardening slurry samples of different composition (R1, R2, R3) exhibited strong immobilization of only zinc and copper in three extractant solutions – distilled water, acid and magnesium chloride solution, regardless of the curing time. The leaching percentage for these metals did not exceed 0.1% of the total metal content. Tests aimed at evaluating the immobilization of tracked pollutants indicated that cement and fly-ash based slurries turned out to be poorly effective in terms of lead immobilization. This metal was released in 10.5% in the course of water extraction, and 12.5% in the case of acid. The degree of leaching cadmium (5.1% and 7.4%) and nickel (2.8% and 4.8%) with water and 0.1 M HCl also indicated their high mobility. The degree of Ni and Pb leaching using obtained magnesium chloride extracts was at a similar level (20% and 26%, respectively). All studied solid phase metals most strongly transferred to the EDTA solution. Copper and zinc, also exhibiting the highest chemical stability, indicated also high immobilization in the presence of 0.1 M EDTA, reaching a leachability of 3.5% and 9%, respectively. Hardening slurries subject to EDTA extraction exhibited poor lead, nickel and cadmium bonds. Lead and nickel were released from the solid phase to the EDTA solution in 62% and 33% on average, regardless of the composition or curing times. Cadmium's behavior was different from that of other metals. Cadmium was least leached by a 0.1 M EDTA solution and 1 M $MgCl_2$ solution from the R1 slurry (lowest cement and ash content). It was least bound in the R2 slurry, from which it was gradually released over time, after 28 days reaching a 49% extraction in magnesium chloride, and even 70% in EDTA. In the case of the R3 sample, an average of 39% of cadmium contained in the slurry was extracted both in the $MgCl_2$, as well as the EDTA solutions. The study shows a dependence of metal leaching on the curing time. The concentrations of both metals in the eluates slightly increased over time. On the other hand, no metal stabilization depending on the mixture composition was found.

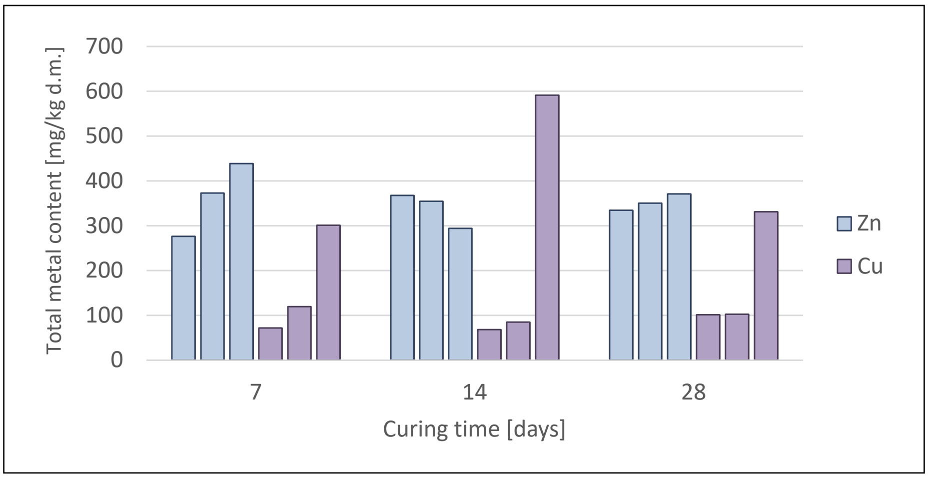

Fig. 6. Zinc and copper content in hardening slurries as a function of curing time

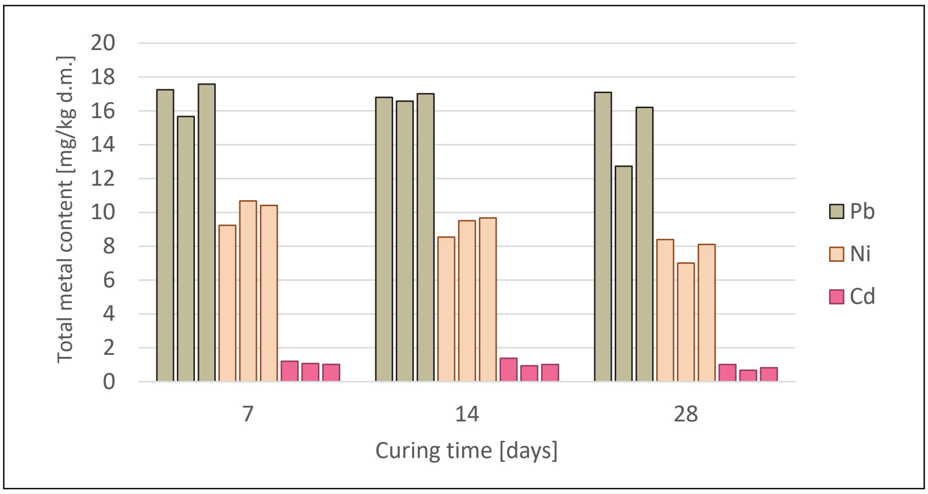

Fig. 7. Lead, nickel and cadmium content in hardening slurries as a function of curing time

Table 5. Summarized concentration of metals leaching from a hardening slurry [%]

Metal			Zn	Cu	Pb	Ni	Cd
Extraction solution	Recipe	Day					
H_2O	R1	7	0.05	0.07	4.00	0.54	4.17
		14	0.04	0.07	7.98	5.38	3.62
		28	0.07	0.05	8.66	7.03	4.95
	R2	7	0.05	0.11	8.74	4.96	4.67
		14	0.03	0.17	9.23	4.10	5.32
		28	0.03	0.12	8.17	1.28	7.46
	R3	7	0.04	0.09	6.37	0.67	4.90
		14	0.06	0.03	6.06	0.52	4.95
		28	0.07	0.09	3.64	0.62	6.10
HCl	R1	7	0.10	0.07	7.19	5.14	4.17
		14	0.13	0.07	7.74	4.92	3.62
		28	0.06	0.05	7.02	7.39	4.95
	R2	7	0.06	0.04	7.28	3.46	8.41
		14	0.06	0.06	6.51	2.52	7.98
		28	0.15	0.05	7.70	5.00	13.43
	R3	7	0.01	0.41	10.41	4.90	4.90
		14	0.02	0.31	9.35	4.75	8.91
		28	0.02	0.45	11.04	5.18	9.76
$MgCl_2$	R1	7	0.03	1.24	15.48	19.16	4.17
		14	0.04	0.92	16.61	22.47	3.62
		28	0.11	0.70	15.92	22.28	4.95
	R2	7	0.06	0.41	15.02	17.58	18.63
		14	0.09	1.98	16.83	20.03	19.15
		28	0.10	1.85	21.13	20.99	49.25
	R3	7	0.02	0.44	15.76	18.06	35.29
		14	0.03	0.24	16.11	15.50	32.67
		28	0.78	0.45	21.84	24.18	41.46
EDTA	R1	7	8.29	2.23	63.54	29.87	4.17
		14	12.88	2.71	66.79	31.25	3.62
		28	10.01	1.89	70.04	32.04	4.95
	R2	7	8.31	1.34	64.14	27.25	42.06
		14	7.70	2.13	59.05	31.34	46.81
		28	10.59	1.99	85.00	44.40	70.15
	R3	7	8.68	8.29	48.86	31.12	35.29
		14	8.91	3.82	48.56	30.08	35.64
		28	6.71	7.26	57.50	40.47	46.34

Discussion

The processes of solidifying ash in building materials are a quite commonly used technology for neutralizing hazardous waste. This method has been recognized by the US Environmental Protection Agency (EPA) as the best available technology for neutralizing such waste. In the course of the processes involving the binding of ash in building materials, the pollutants contained in the waste are transformed into sparingly soluble form, which are characterized by reduced toxicity (Szarek et al. 2018). The original studies used sewage sludge thermal treatment fly ash. This ash does not satisfy the requirements of standard EN 450-1 (2012) due to its physical/chemical and technological properties (exceeded chemical composition thresholds, low activity, high grain fineness and water (Szarek 2020; Szarek and Wojtkowska 2018), therefore it cannot be used for the manufacturing of concrete and cement.

Combining this fly ash with cement provided a hardening slurry, which is a product exhibiting process parameters that enable safe use. The parameters characterizing good properties and safe environmental impact of the obtained hardening slurries are density, viscosity and compressive strength. Original test results involving process and performance parameters are very similar to the same parameters for slurries prepared in the course of other research (Batchelor 2006; Woodard and Curran 2006; Asavapisit et al. 2006). They indicate the usefulness of the suggested methods for developing building materials with added SSTT fly ash in the implementation of civil projects, as well as in hydro engineering (Falaciński 2012; Falaciński and Szarek 2016; Kledyński and Rafalski, 2009). Similar experiments were conducted by Chang et al. (2010) who studied the possibility of using fly ash with heavy metals (Pb, Cd, Cu), as a replacement for traditional building materials. The hardening slurry with added ash that they obtained was characterized by higher water adsorption capacity.

The ash used within the study, as a product of sewage sludge thermal treatment, contained high concentrations of heavy metals. The hardening slurry obtained after mixing all components was characterized by heavy metal concentrations corresponding to the number of used components. According to the study by Bobrowski et al. (1997), the metal immobilization degree should not undergo significant changes after 28 days of curing. Different metal immobilization in the course of slurry curing was observed during the original tests. It was also demonstrated that the degree of metal immobilization depends on their chemical properties, chemical composition of ash and the ambient environment of the slurry. The heavy metals chosen for the tests (Cu, Cd, Zn, Ni and Pb) exhibit the ease of precipitating from sewage to the soil and groundwaters, as well as high toxicity (Wojtkowska and Bogacki, 2012). Therefore, these metals can be divided into two groups, namely, semi-volatile (Pb, Cd) and non-volatile (Zn, Cu, Ni) metals. The processing of municipal waste fly ash causes both evaporation (Jakob et al. 1995), as well as stabilization (Chou et al. 2009) of heavy metals, depending on the ash treatment temperature. Cd and Pb are usually highly volatile (Jakob et al. 1995), whereas Cu and Zn volatilization strongly depends on air quantity (Jakob et al. 1995, Serum et al. 2003), and Ni is not released during thermal treatment (Forestier and Libourel 2008). Their solubility is poor, therefore only a very limited quantity of heavy metals should be released into the aqueous solution through water leaching. A high degree of metal leaching from hardening slurry components was found in the course of the experiments. This was associated with the presence of readily soluble chlorides (sylvite, halite), sulphates (syngenite, ettringite, gypsum), oxides (CaO), hydroxides (portlandite), nitrates, carbonates and bicarbonates in ash used to manufacture hardening slurries (Vassilev et al. 2013a, b). The presence of NaCl, KCl and $CaCl_2$ can contribute to higher metal solubility to a certain degree, by increasing ion activity (Chang et al. 2010).

The pH value is quite important in terms of the efficient stabilization of a waste chemical system, which is why the presence of pH-impacting ingredients in a solidifying mixture is not negligible (Batchelor 2006; Marcinkowski 2004). This particularly applies to the alkaline reaction resulting from the presence of cement and lime. The pH value, at which effective leaching takes place, depends on the studied material, chemical nature of the metal and the environment. Single extraction under various environmental reactions (pH) was applied within the conducted original study to evaluate the immobilization of metals in a hardening slurry. For the purposes of single extraction, the researchers used solutions of various chemical properties, namely, distilled water characterized by high pollutant capacity and a neutral pH, HCl acid with pH=1, metal-complexing ethylenediaminetetraacetic acid (EDTA), and an $MgCl_2$ solution with high ionic strength and stable pH, causing the release of adsorbed components (Wojtkowska and Bogacki 2012, Ure 1995).

The degree of leaching of the heavy metals from the tested hardening slurries varies highly depending on the used eluates. The presence of H+ ions (low pH) in the solution, remaining in contact with the slurry, under varied solubility of heavy metal compounds, significantly accelerates the transition of tested metal cations into the solution. The conducted tests indicate high zinc and copper stability, regardless of the slurry composition and its surrounding environment. The high chloride concentration in a slurry environment did not contribute to the mobilization of these metals. Zn is found in pure MSW fly ash in the form of $Zn_5(OH)_6$ $(CO_3)_2$, willemite Zn_2SiO_4 and gahnite $ZnAl_2O4$ (Struis et al. 2004). Cu is found in MSW fly ash as CuO and $CuSO_4x5H_2O$. These are minerals that are hard-to-activate in low temperatures and with under neutral pH.

The conducted research showed that semi-volatile metals were more easily activated from a hardening slurry to a magnesium chloride solution. The highest percentage of leaching to all applied extractants was recorded for lead, which is found in ashes mainly in the form of oxides (Pb_2O_3 or PbO_2) and is not stable. Lead oxides are of amphoteric nature and, depending on the characteristics of the environment, Pb will transform into poorly soluble salts (chlorides) or highly soluble complex compounds. Poor solubility of lead salts can strengthen in an acidic, as well as alkaline (cement and ash) environment, where lead forms poorly soluble complex ions $[Pb(OH)_4]^{2-}$. The sparingly soluble $PbCl_2$ dissolves in excess reagent providing hydrochloric acid $H[PbCl_3]$. The study showed very high mobility of cadmium, which does not form persistent, sparingly soluble minerals in the natural environment. Similarly, high concentrations and high mobility of cadmium were identified in the course of studying the ash from Sitkówka – Nowiny (Gawdzik and Latosińska, 2014). Cadmium can be found in ashes in the form of a sulphide or oxide (CdS and CdO), as well as easily activated salts.

Fly ash, which is essentially aluminosilicates, is a good medium adsorbing heavy metals (Szarek 2020, Polowczyk et al. 2010). Ash behavior can be twofold. Coal combustion fly ash contains calcium and can act as an alkalizer within the chemical precipitation process. Ash particles, owing to their aluminosilicate structure, are also able to adsorb heavy metals from aqueous solutions, through ion exchange. Another factor impacting the stability of metals in a slurry is the gel form of hydrated calcium silicates (C-S-H) and hydrated calcium aluminosilicates (C-S-A-H) of a very large specific surface, which are formed as a result of calcium hydroxide reacting with silica and alumina. Heavy metal cations are chemisorbed on geopolymers, which limits their migration into the solution. The zinc and copper degree of immobilization in all analyzed samples was very high and exceeded 90%. Other metals behaved differently. The degree of cadmium, lead and nickel immobilization in the studied systems was very low. Lead immobilization in a hardening slurry mainly involves sorption of ions in the aforementioned geopolymers. Cadmium and nickel exhibit high affinity with chloride ions and undergo surface adsorption. Under the conditions of elevated chloride, sodium, and potassium ion concentrations, they will be displaced from their salts, and under low pH, they will undergo desorption. In his work, Ibragimow (2010) demonstrated that extraction using a $MgCl_2$ solution can be a measure for metal availability. The identified strong extraction of metals using the $MgCl_2$ solutions may also result from the competitiveness of heavy metal ions (e.g., Ni^{2+}, Cd^{2+}) relative to the large Mg^{2+} ion. A significant efficiency of leaching with water and used solutions can be associated with the presence of metals in mobile forms, which is a distinguishing feature of fly ash. Under the conditions corresponding to minor environmental changes (magnesium chloride leaching, slight pH changes) more toxic metals (Cd and Pb) were released, indicating the high availability of their forms.

The EDTA chelating solution was used to evaluate metal stability. It forms persistent, mostly water-soluble complexes with heavy metals, activating them from the solid phase. EDTA impacts metal distributions, releasing them from less active forms to soluble fractions (Li and Shuman 1996). The presence of chelates in an aqueous environment may, therefore, influence heavy metal redistribution and mobility, and may potentially increase their availability. Li and Shuman (1996) demonstrated that EDTA primarily released complexed or adsorbed metals, which could have been the reason for the high percentage share of metals in EDTA solutions.

CONCLUSIONS

This study demonstrated that:

1. The fly ash obtained from the thermal treatment of sewage sludge exhibited various concentration and different heavy metal bonding force.
2. High concentrations of soluble chlorides and salts in the ashes contributed to metal leaching in the course of simple extraction processes, confirming their poor bonding and high mobility, and consequently, indicating the high toxicity of metals in the ashes.
3. The leaching of mobile forms of metals during the maturation of the hardening slurries (Fig. 3) contributes to a reduction in the concentration of heavy metals in the obtained samples of the hardening slurries, and consequently increased the stability of other heavy metals (especially for zinc and copper) in the obtained materials.
4. The immobilization of the remaining metals depended on the metal properties, external environment specification, but also the hardening mixture composition and curing time.
5. Zinc and copper, the concentrations of which in the components were the highest, are bound stably within the hardening slurries.
6. The highest mobility was exhibited by lead and nickel, particularly in an environment of EDTA chelating solution, characterized by high leachability of metals that were complexed or adsorbed on the surfaces of produced materials.
7. Up to 90% of the particularly toxic cadmium was leached in the slurry curing period. Cadmium remaining in the hardening slurry (<0.4mg/kg d.m.) was most effectively extracted with EDTA and $MgCl_2$ solution, e.g., after 28 days, from slurries with a high ash content (R2 and R3).
8. The research showed that the total content of heavy metals in hardening slurries, containing ash from thermal processing of sewage sludge, is an objective criterion for assessing their mobility and environmental risk.
9. As shown by the conducted tests, the obtained hardening suspensions based on fly ash from incineration of municipal waste and sewage sludge do not meet the requirements of the standards for building materials (Tab. 1) and are not safe due to the content and high mobility of metals, especially exotoxic Cd and Pb.

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Ocena immobilizacji metali ciężkich w zawiesinach twardniejących

Streszczenie: W ostatnich latach, w Polsce, odnotowano dość szybki wzrost wytwarzania ubocznych produktów w procesie oczyszczania ścieków komunalnych – osadów ściekowych. W roku 2014 wytworzono 556,0 tys. ton suchej masy komunalnych osadów ściekowych. Jest to pochodna rozwoju cywilizacyjnego Polski i budowy nowoczesnych oczyszczalni ścieków. Zaostrzające się przepisy oraz założone, strategiczne cele gospodarki ściekowej determinują rozwój nowoczesnych metod utylizacji osadów ściekowych. Należą do nich techniki termiczne. W wyniku stosowania tych metod ilość powstałych lotnych popiołów po spaleniu komunalnych osadów ściekowych znacząco rośnie. Trwają intensywne prace nad możliwością bezpiecznego dla środowiska zagospodarowania tego typu odpadu. W artykule przedstawiono badania nad możliwością dodawania lotnych popiołów z TPOŚ jako składnika zawiesin twardniejących. Przeprowadzono badania właściwości technologicznych i użytkowych, których celem było określenie praktycznej przydatności zastosowanych w eksperymencie zawiesin twardniejących. Wykonano badania wymywalności metali ciężkich ze struktury zawiesin. Przeprowadzony eksperyment ekstrakcji metali wykazał wymywanie niebezpiecznych związków na poziomie umożliwiającym praktyczne ich zastosowanie. Przeprowadzone analizy wskazują na potencjalne możliwości wykorzystania ubocznego produktu spalania jakim jest popiół.