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Evaluation of the Immobilization of Fly Ash from the Incineration of Municipal Waste in Cement Mortar Incorporating Nanomaterials—A Case Study

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Abstract: Fly ash generated in the process of combustion of municipal waste is classified as hazardous waste. Its management today has become a significant problem. One of the methods of safe management of such ash may be using it for the production of concrete as a partial replacement for cement. Using immobilization, the number of hazardous compounds could be limited so that the obtained new material would be safe for the natural environment. Recovery of byproducts—in this case, fly ash—complies with the business models applied in the production cycle in the circular economy model. Such a solution may result in saving energy, limiting CO_2 emissions, reducing the use of natural resources, and management of dangerous waste. It should be added that concretes with the addition of hazardous waste would be used for industrial purposes according to the binding legal regulations. This article presents the influence of the addition of fly ash on the selected mechanical properties of concrete. Fly ash from the incineration of municipal waste was used as a partial replacement of CEM I concrete at amounts of 4%, 8%, and 18% of its mass. The compressive strength and flexural strength of such concretes were tested after 28 days of concrete curing. This article also presents the tests of the leachability of contaminants from fly ash and concretes produced with Portland cement CEM I. The test results confirm that immobilization is an effective process that limits the amount of contamination in the water extract. Zinc, lead, and chrome were almost completely immobilized by the C-S-H (calcium silicate hydrate) concrete phase, with their immobilization degree exceeding 99%. Chloride content also underwent immobilization at a similar level of 99%. The sulfates were immobilized at the level of 96%. The subject matter discussed in this article is essential because, to protect the natural environment and, thus, reduce the use of natural resources, it is increasingly necessary to reuse raw materials—not natural, but recycled from the industry. Waste often contains hazardous compounds. A proposal for their safe disposal is their immobilization in a cement matrix. An important aspect is reducing leachability from concrete as much as possible, e.g., using nanomaterials. The effectiveness of reducing the leachability of hazardous compounds with the proposed method was checked in this study.

Keywords: combustion; fly ash; recovery; immobilization; leaching

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1. Introduction

The constant development of the economy and the worldwide increase in consumption are reflected in the production of an enormous amount of municipal waste. According to the provisions of Directive 2008/98/EC [1] and the national waste law [2], each action related to waste must comply with the binding hierarchy of dealing with waste. According to the listed legal acts, first of all, it is recommended to prepare the wastes for their reuse, after which they should undergo recycling or other recovery processes, including energy recovery. The last element of the waste management hierarchy is their neutralization, e.g., by storage [1,2].

According to Statistics Poland's data, in 2021 in Poland, 13.6 M tons of municipal waste was collected. This represents an increase of about 4.2% compared to 2020 [3]. In 2021, 60% of the stream of collected municipal waste was directed for recovery (82,070 thousand tons), and 40% was neutralized. It needs to be underlined that in 2021 a stream of mixed fractions constituted 60% of all of the collected municipal waste, accounting for 8234 thousand tons [3]. This represents a decrease of 2% compared to 2020. Depositing mixed municipal wastes in landfills is no longer reasonable. An alternative is thermal processing with energy recovery. The idea of constructing an incineration plant is very popular, as it at least partially solves the problems that many local governments face. In order to decrease the environmental issues and follow the idea of a circular economy (i.e., the concept of rationally reusing resources and limiting the negative impacts of manufactured products on the environment), it is worth identifying other methods of management of combustion byproducts such as fly ash [4–10]. Fly ash generated as a result of incineration may be used in the construction industry, saving natural resources. It needs to be emphasized that the construction materials produced using fly ash from incineration plants are most frequently characterized by low strength and, therefore, they are used mainly for the construction of local roads. Irrespective of where they are applied, the final product cannot be harmful to the environment [11]. In the scientific literature [12–19], there is little information on how fly ash from municipal waste incineration plants affects the properties of cement mortars, making the subject discussed in this paper a novelty. However, the use of fly ash in construction has been recognized for a long time now [20–27]—for example, considering fly ash generated as a side product during the combustion of hard coal or biomass. Because of its properties, fly ash is used as a mineral additive to cement; as a matrix for sand formation, concrete admixtures, bituminous masses, and ceramic tiles; in geotechnics; in the foundations of road pavement; and for soil stabilization [22,25].

According to the data found in the literature, the immobilization process is usually applied to hazardous wastes such as industrial dust and sludge, galvanic waste, gravels and ashes from thermal processes (e.g., in the iron and steel industry), nonferrous metals from municipal waste incineration plants, waste sediments, or dusts and sludges from gas purification processes [6,11,28–33]. In many cases, the basic management method of such hazardous wastes should be the immobilization of the waste, due to its low costs and the possibility of managing a wide range of wastes. Solidified waste is not harmful to the environment and may be applied in industry [11,28]. Solidification/stabilization methods may be divided into six groups depending on the main components and processes applied: cement-based, lime-based, based on thermoplastic processes, based on organic polymers, based on encapsulation, or vitrification processes. The abovementioned process groups vary in their application, costs, and requirements for the initial processing of the waste. However, all of them aim at modifying the physicochemical properties of the wastes in such a way as to limit the migration of the contaminants to the environment, produce homogenous concrete matrixes suitable for their reuse, and facilitate the transport and disposal of wastes to landfills [34–36]. This article analyzes fly ash obtained from the seasonal removal of ash from boilers and water heaters. The purpose of this work was to test the elemental composition of the ash in light of its impact on the environment and to determine the possibilities of using it for the production of modern construction materials. This idea fits into the concept of the circular economy (CE).

The tests adhered to the CE business model, which is based on the recovery of the side products. This model consists of actions where residues or secondary products of one process become inputs for another process. The actual management method of fly ash from the incineration of municipal waste is storage in landfills, where the potential raw material is irreversibly lost. The undertaken actions aim at extending the life cycle of the fly ash. It is estimated that the extension of the fly ash life cycle will result in a decrease in the use of natural resources, which translates into economic and financial savings. Today, the possibility of using fly ash from the incineration of municipal waste in the construction industry is under investigation. Fly ash could be a valuable material for the production of cement, concrete, and precast elements for industrial use.

2. The Analyzed Installation of Thermal Processing of Municipal Waste—Case Study

The discussed municipal waste incineration plant (MSWI) is located in Poland in the Lesser Poland Voivodeship—specifically in the southeast part of the city of Cracow in District XVIII (Nowa Huta). The analyzed MSWI mainly transforms mixed municipal waste. Additionally, residues from the mechanical processing of municipal fractions and large construction waste products are combusted [4]. The waste comes from the area of Cracow City Commune. The yearly capacity of the plant is 220,000 Mg, and the calorific value of the waste is 8.8 MJ/kg. The thermal power of the plant is 35 MWt, and the electrical power is 10.7 MWe [4]. On two parallel lines, 700 tons of waste is combusted within 24 h. The waste from incineration processes includes boiler dust, fly ash, and solid residues from the purification of the exhaust fumes. It is estimated that the residues from the incineration of municipal waste constitute approx. 25% of the input stream. Hazardous waste products—i.e., boiler dust, fly ash, and solid residues from the purification of the exhaust fumes—are transferred with a pneumatic transporter to silos adapted to cistern loading. This makes it possible to transport them for further processing and management in other specialist plants or for deep storage in former salt mine pits (e.g., in Germany).

Figure 1 presents a simplified scheme of the analyzed municipal solid waste incineration plant.

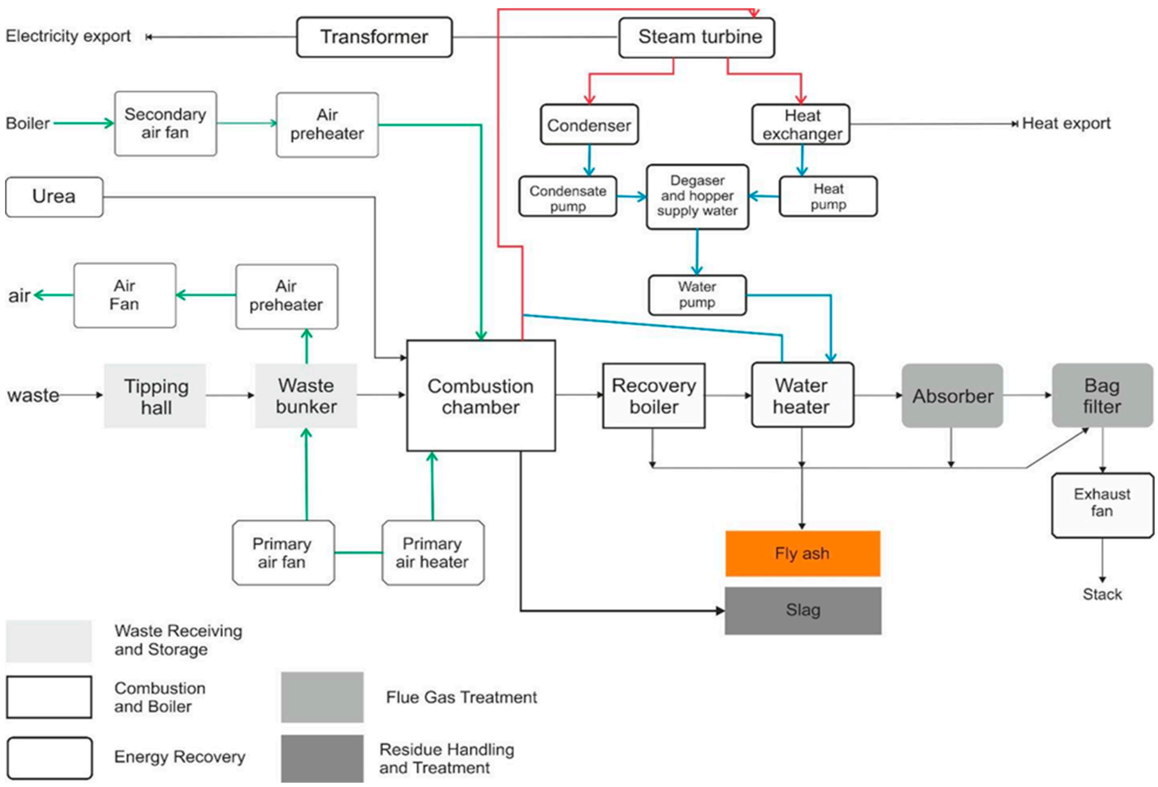

Figure 1. Simplified scheme of the analyzed municipal solid waste (MSW) incinerator.

3. Materials

The material that was the basis for the tests was fly ash (FA; Figure 2) generated in the process of incineration of municipal waste in grid furnaces. It consisted mainly of non-flammable substances (e.g., silicates, aluminum, and iron oxides that are insoluble in water). According to European Waste Codes [37,38], it has a code of 19 01 13*—fly ash containing hazardous substances. This is hazardous waste and may have the following characteristics: irritant, dangerous, toxic, allergenic, and ecotoxic. However, to a small degree, it has some features of a flammable fraction—unburned coal particles (Figure 2a).

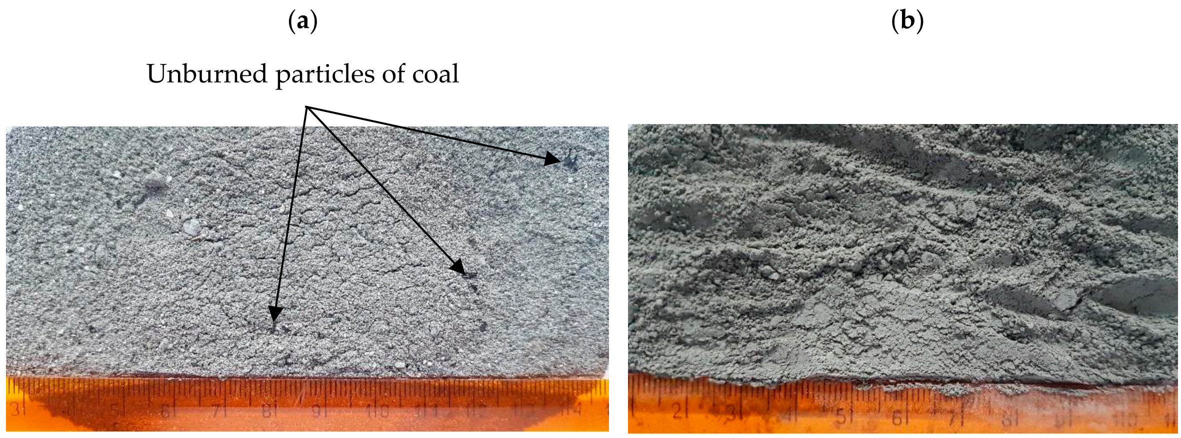

Figure 2. The tested fly ash (FA): (**a**) draw; (**b**) mechanically crushed.

Figure 3c presents the loss on ignition (LOI) determined according to the standard PN-EN 15935:2013-02 [39]. The tested fly ash was incinerated until constant mass at temperatures of 600 °C and 950 °C in a laboratory muffle furnace. Fly ash can be divided into three categories based on the loss on ignition determined at a temperature of 950 °C, according to the standard PN-EN 450-1:2012 [40]: category A (LOI ≤ 5%), category B (LOI ≤ 7%), and category C (LOI ≤ 9%) (Figure 3a). Based on the performed analyses, the tested fly ash could be classified as category B. Furthermore, with the loss on ignition determined at a temperature of 600 °C, it was noted that the tested fly ash met the requirements for waste other than hazardous (LOI ≤ 8%) or neutral waste (LOI ≤ 10%) that are accepted at the landfill [41] (Order of the Minister of Economy 2015) (Figure 3b).

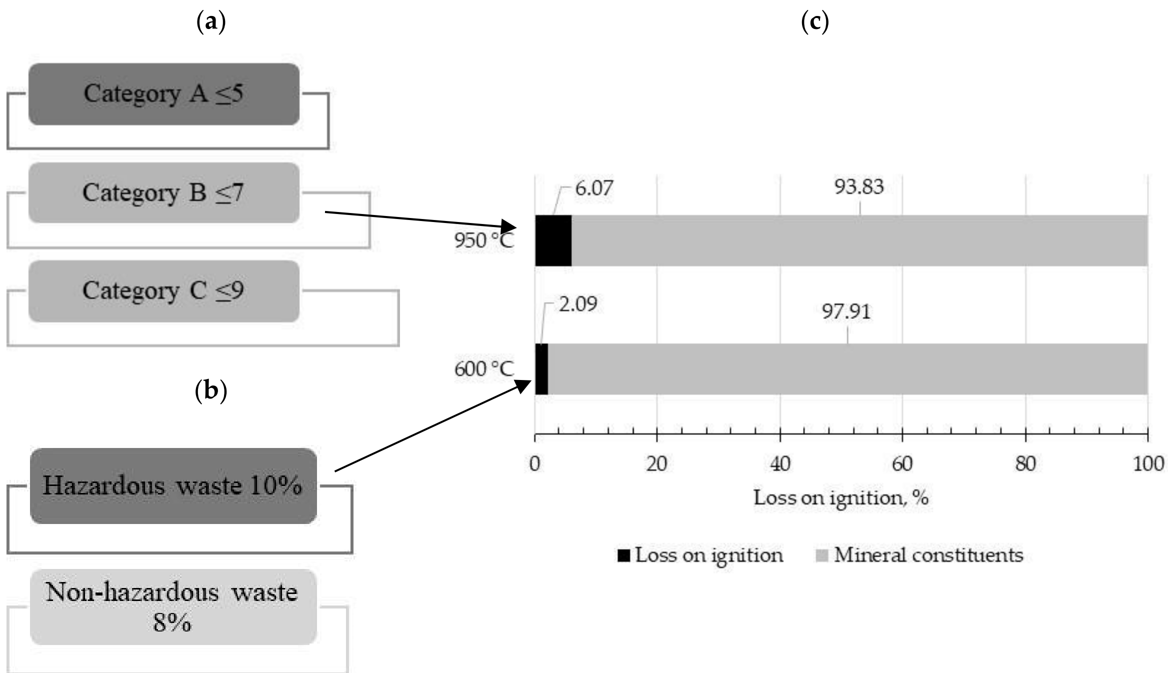

Figure 3. Loss on ignition (LOI): (**a**) requirements; (**b**) other criteria for waste acceptable at landfills; (**c**) tested fly ash.

At the beginning of the research, an analysis of oxide and heavy metal contents was carried out. The obtained results (Tables 1 and 2, respectively) were compared with the requirements concerning, among others, the chemical properties of fly ash used as a type II additive for the production of concrete [40] (PN-EN 450-1:2012). The main phase components of fly ash from the municipal solid waste incineration plant were CaO and SiO_2.

Table 1. Contents of oxides (%) in the tested fly ash.

Parameter	Symbol	Fly Ash		Requirements for Fly Ash for the Production of Concretes (PN-EN 450-1:2012) [40]
Silicon dioxide	SiO_2	29.50	41.60	ΣSiO_2, Al_2O_3 i $Fe_2O_3 \geq 70$
Iron (III) oxide	Fe_2O_3	2.81		
Aluminum oxide	Al_2O_3	9.29		
Manganese (II, III) oxide	Mn_3O_4	0.12		nr **
Titanium dioxide	TiO_2	2.23		nr **
Calcium oxide	CaO	30.10		nr **
Magnesium oxide	MgO	2.60		≤4.0
Sulfur trioxide	SO_3	8.71		≤3.0
Phosphorus pentoxide	P_2O_5	1.77		≤5.0
Sodium oxide	Na_2O	2.67		nr **
Potassium oxide	K_2O	1.95		nr **
Barium oxide	BaO	0.22		nr **
Strontium oxide	SrO	0.06		nr **

** nr—no requirements.

Table 2. Heavy metal concentrations, expressed in mg/kg.

Parameter	Symbol	Fly Ash
Zinc	Zn	7242.0
Copper	Cu	325.0
Lead	Pb	586.0
Nickel	Ni	113.0
Chrome	Cr	334.0
Cadmium	Cd	23.3
Arsenic	As	7.3
Vanadium	V	39.1
Thallium	Tl	<1.0
Mercury	Hg	0.02

The concentrations of heavy metals in the dry mass of tested FA were high, and the sequence was as follows: Zn > Pb > Cr > Cu > Ni > V > Cd > As > Tl > Hg. The highest value was reported for zinc, which reached 7242.0 mg/kg, while the lowest was recorded for thallium (<1.0 mg/kg).

4. Methods

The testing procedure was planned and carried out in such a way as to determine the characteristics of the fly ash from the MSWI plant with respect to the physical and chemical properties that are important in the context of the use of fly ash as a partial replacement for cement. The impact on the environment was also taken into account. The testing procedure included eight stages:

- Testing the physicochemical properties of the fly ash;
- Preparation of the aqueous extract with fly ash considering the impact on the environment;
- Designing and preparing mortars with the 4% and 18% addition of fly ash;
- Testing the flexural and compressive strengths of the mortars (beams 40 × 40 × 160 mm) produced with 4% and 18% addition of FA as compared to the reference sample;
- Preparation of aqueous extracts with crushed mortars after 28 days of curing, and executing chemical tests, with an evaluation of the impact on the environment;
- Designing and preparing mortars with 4% and 8% addition of fly ash modified with nanomaterials;
- Testing the flexural and compressive strengths of the designed cement mortars (beams 40 × 40 × 160 mm) with 4% and 8% addition of FA modified with nanomaterials as compared to the reference sample;

- Preparation of aqueous extracts with crushed mortars after 28 days of curing, and executing chemical tests, with an evaluation of the impact on the environment.

4.1. The Procedure for the Preparation of the Aqueous Extract with Fly Ash

The aqueous extract was produced according to the standard PN-EN 12457-2:2006 [42]. From the 2 kg of sample ash, a representative laboratory sample was prepared. For the purpose of the analysis, the tested ash was sieved through the screen of a 2 mm mesh. From this sample, an aqueous extract was prepared with a liquid/solid ratio (L/S) of 10 L/kg. The elution water was distilled water with pH 7.4 and electrical conductivity of 61.18 µS/cm. The prepared samples were shaken in a laboratory shaker for 24 h, and the obtained extracts were left for 15 min for decantation of solid particles, followed by filtering. The pH was determined using an Elmetron CPC-501 device (PN-EN ISO 10523:2012, PN-EN 27888:1999) [43,44]. The analysis of the aqueous extracts of fly ash included a number of specifications. The content of chlorides was determined via the Mohr method with the use of silver nitrate as a titration agent and potassium chromate as an indicator (PN-ISO 9297:1994) [45]. Sulfates (VI) (SO_4^{2-}) were determined via a gravimetric method with barium chloride (PN-ISO 9280:2002) [46]. The contents of sodium, calcium, potassium, lithium, and barium in the aqueous extracts from fly ash were determined via flame emission spectrometry (PN-ISO 9964-3:1994) [47]. The phosphorus content was determined as described in [48]. In order to evaluate the heavy metal composition (Zn, Cu, Pb, Cd, Cr, Co, Fe, Ni) in the aqueous extract, inductively coupled atomic absorption spectroscopy (AAS) was performed using GBC's AVANTA PM apparatus.

4.2. Composition and Methodology of Preparation of Cement Mortars with the Addition of Fly Ash

The subject of the test was cement mortars with the addition of fly ash from the municipal waste incineration plant, with and without modifications with nanomaterials. The mortars were produced with Portland cement CEM I 52.5R (ÓRAŻDŻE CEMENT S.A., Poland) meeting the requirements of PN-EN 197-1 [49], and a standardized sand of fraction 0 ÷ 2 mm, compliant with PN-EN 196-1 [50]. Four cement mortars were prepared: CEM-I reference mortar; CEM I+4% FA—mortar with 4% fly ash from the incineration plant; CEM I + 4% FA + N—mortar with the addition of nanomaterial; and CEM I + 8% FA + N—mortar with 8% fly ash from the incineration plant and nanomaterial. The compositions of the mortars are specified in Table 3.

Table 3. Composition of the concrete mortars, expressed in grams.

Type of Waste	Symbol of Mortar	CEM I	Nano Al	Water	Sand Acc. (PN-EN 196-1) [50]
Reference sample from Portland cement 52.5R	CEM I	450	-	225	1350
CEM I 52.5R + 4% fly ash	CEM I + 4% FA	402.5	-	171	1350
CEM I 52.5R + 18% fly ash	CEM I + 18% FA	354.21	-	171	1350
CEM I 52.5R + 4% fly ash + nano-Al	CEM I + 4% FA + N	402.50	10.5	171	1350
CEM I 52.5R + 8% fly ash + nano-Al	CEM I + 8% FA + N	386.36	10.5	171	1350

Tests of the water demand of the cement grout and fly ash were carried out using a Vicata automatic device according to the standard PN-EN 196-3c:2016-12 [51]. Determination consisted of measuring the time required from mixing the grout components to the commencement and completion of the binding process. Subsequently, three beams of dimensions 4 × 4 × 16 cm and compliant with the standard PN-EN 196-1 [50] were made from each mortar. The samples were removed from their forms after 24 h and stored in water at a temperature of 20 °C ± 2 °C for 28 days. After 28 days of concrete curing, the flexural and compressive strengths of the samples were tested according to the standard PN-EN 196-1 [50].

4.3. The Procedure of Preparing Aqueous Extracts from the Crushed Cement Mortars with the Addition of Fly Ash

The aqueous extracts from the crushed mortar cement after 28 days of concrete curing were prepared according to the standard PN-EN 12457-4:2006 [52]. The mortars were crushed to a grain size of <10 mm and then shaken for 24 h, maintaining a liquid–solid ratio (L/S) of 10. The elution water was distilled water with pH 7.4 and conductivity of 61.18 µS/cm. After the completion of shaking, the obtained extracts were filtered. The analysis of the aqueous extracts from the crushed cement mortars was performed as described in Section 4.1.

5. Results and Discussion

5.1. The Evaluation of the Leachability of Hazardous Substances and Heavy Metals from the Fly Ash

Table 4 presents the leachability from fly ash of hazardous substances and heavy metals that may be a nuisance to the environment and negatively affect the properties of the concrete mix, potentially affecting the concrete's strength. The obtained results were compared to the binding national [41] and European [53] legal regulations. The tested fly ash was characterized by a strong alkaline reaction—above pH 12. The leachability of chlorides (Cl^-) and sulfates (SO_4^{2-}) from tested fly ash did not exceed the acceptable levels for depositing wastes other than hazardous and neutral wastes in landfills. Only the barium content (Ba) exceeded the permissible values for wastes other than hazardous and dangerous stored in landfills (by about 36%). The leachability of heavy metals in the tested fly ash could be considered to be low. The contents of Zn, Cr, and Pb did not exceed the permissible values, and in some cases (i.e., Cu, Cd, Ni) the contents were below the limit of quantitation.

Table 4. Leachability of hazardous substances and heavy metals from fly ash, expressed in mg/kg.

Parameter	Symbol	Fly Ash	Criteria for Landfills [41,53]	
			For Non-Hazardous Waste	For Hazardous Waste
pH	pH	12.9	min. 6	-
Chloride	Cl^-	352.51	15,000	25,000
Sulfate	SO_4^{2-}	12,350.23	20,000	50,000
Phosphate	PO_4^{3-}	<0.005	-	-
Potassium	K	49.82	-	-
Calcium	Ca	459.90	-	-
Lithium	Li	1.90	-	-
Sodium	Na	55.81	-	-
The sum of chloride and sulfate	$(Cl^- + SO_4^{2-})$	12,702.74	60,000	100,000
Barium	Ba	156.90	100	300
Zinc	Zn	9.55	50	200
Copper	Cu	<0.20	50	100
Lead	Pb	4.93	10	50
Cadmium	Cd	<0.05	1	5
Chrome	Cr	2.26	10	70
Cobalt	Co	0.50	-	-
Iron	Fe	0.40	-	-
Nickel	Ni	<0.40	10	40

5.2. Evaluation of the Degree of Immobilization of Contaminants from Cement Mortars with the Addition of Fly Ash

The cement batch with the addition of 4% fly ash showed higher water demand. The use of FA in the MSWI plant as a partial replacement for cement required the addition of more water when producing the concrete mix or concrete batch. Replacing 4% of the cement mass with FA resulted in minor shortening of the early binding time. The early binding time was 11 min shorter than in the reference batch, for which the manufacturer of cement 52.R guarantees an early binding time of 186 min. Figures 4 and 5 present the designed cement mortars with 4% and 18% fly ash from the incineration plant, respectively.

(**a**) (**b**)

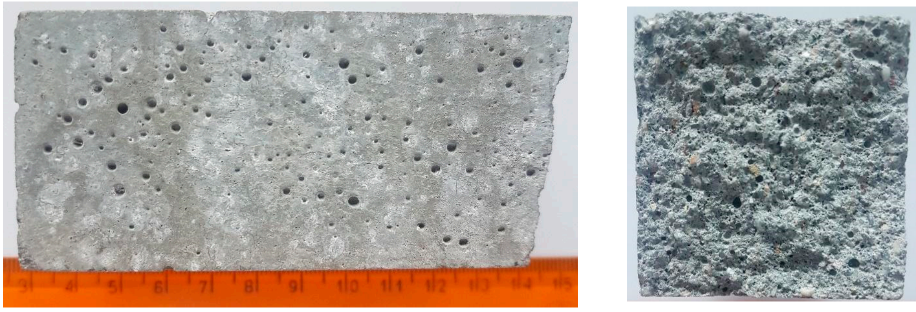

Figure 4. Cement mortar with the addition of 4% fly ash from the incineration plant (CEM I + 4% FA): (**a**) outer surface; (**b**) internal structural view.

(**a**) (**b**)

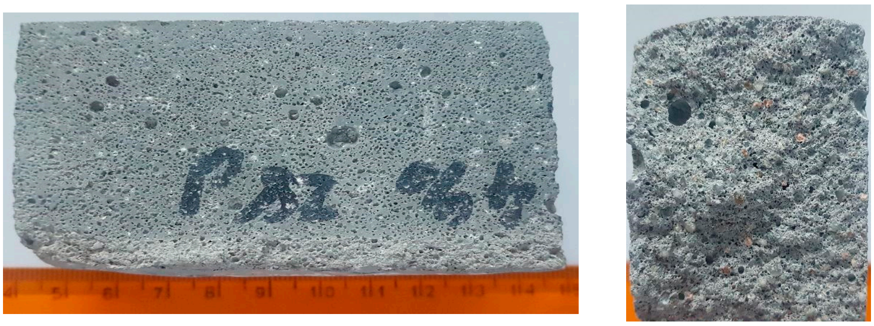

Figure 5. Cement mortar with the addition of 18% fly ash from the MSWI plant (CEM I + 18% FA): (**a**) outer surface; (**b**) internal structural view.

The results of the flexural and compressive strength tests of the cement mortars with 4% and 18% addition of fly ash from the incineration plant after 28 days of concrete curing are presented in Figure 6. The compressive strength of a beam with 4% addition of FA was 71.37 MPa, which was about 16 MPa less than the reference value. The flexural strength of the beam with 4% FA was about 8.85 MPa, which was about 0.75 MPa less than the reference value.

(**a**)

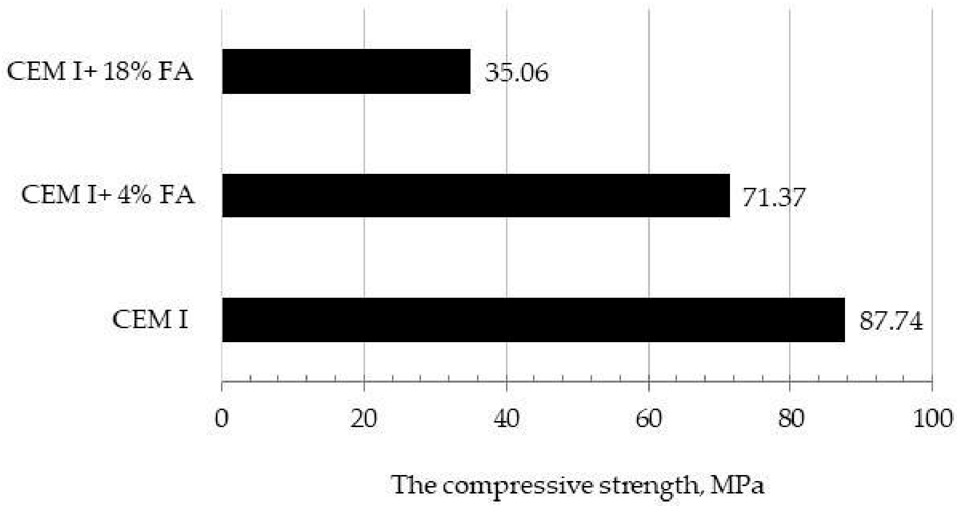

Figure 6. *Cont.*

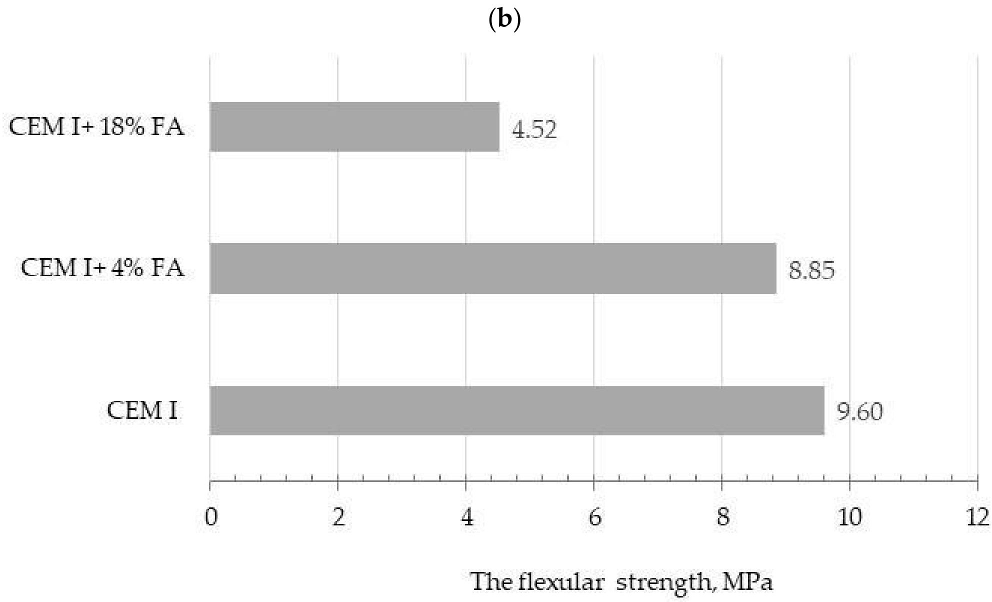

Figure 6. Strength of cement mortars with 4% and 18% addition of FA after 28 days of concrete curing: (**a**) compressive strength; (**b**) flexural strength.

In the case of concrete mortars with 18% fly ash, it was noted that the compressive strength and flexural strength were lower than in the reference sample, by about 52.68 MPa and 5.08%, respectively. Moreover, a swelling effect was observed (Figure 7). This is an undesirable effect because it causes volume changes in the concrete, resulting in cracking. Therefore, such material is useless for the construction industry. It was noted that 4% content of fly ash in the concrete mass is a limit value that does not negatively affect the mechanical properties of cement mortars. The use of more than 4% fly ash is impossible due to the swelling effect that occurs during binding.

Figure 7. Swelling of the cement mortar with the addition of 18% fly ash.

Table 5 presents the results of the leachability of the hazardous substances and heavy metals from the crushed cement mortars with the addition of 4% and 18% FA. The obtained results were compared with the highest permissible values for contaminants introduced to the water environment (Order of the Minister of Marine Economy and Inland Navigation 2019) [54]. The analyzed cement mortars had a highly alkaline reaction—above pH 11—which may result in high immobilization of heavy metals. The mobility of heavy metals is controlled by pH. In a highly alkaline environment (pH $\geq$ 11), FA could solidify/stabilize the majority of tested metals [55–57]. Out of all of the tested parameters (i.e., Cl^- SO_4^{2-}, NH^{4+}, P, K, Ca, Li, Na), excessive values—about 70.47 mg/L—were noted only for sulfates (SO_4^{2-}) in samples with 18% fly ash. The leachability of heavy metals in the tested cement mortars was very low—below the limit of quantification. Only for barium did the values exceed the highest acceptable value (Order of the Minister of Marine Economy and Inland Navigation 2019) [54].

Table 5. The leachability of hazardous substances and heavy metals from cement mortars with the addition of fly ash, expressed in mg/L.

Parameter	Symbol	CEM I + 4% FA	CEM I + 18% FA	Highest Permissible Value [54,58]
pH	pH	11.6	11.1	6.0–9.0
Chloride	Cl^-	0.14	0.28	1000
Sulfate	SO_4^{2-}	455.28	570.47	500
Ammonium nitrogen	NH_4^+	blq **	blq **	10
Phosphorus	P	<0.005	<0.005	2
Potassium	K	5.83	8.75	80
Calcium	Ca	144.00	230.80	nr *
Lithium	Li	1.10	1.30	nr *
Sodium	Na	9.77	13.40	800
The sum of chloride and sulfate	$(Cl^- + SO_4^{2-})$	455.42	570.75	1500
Barium	Ba	15.20	35.50	2
Zinc	Zn	<0.10	<0.10	2
Copper	Cu	<0.20	<0.20	0.5
Lead	Pb	<0.50	<0.50	0.5
Cadmium	Cd	<0.50	<0.50	nr *
Chrome	Cr	<0.50	<0.50	0.1
Cobalt	Co	<0.05	<0.05	1
Iron	Fe	<0.04	<0.04	10
Manganese	Mn	<0.20	<0.20	nr *
Nickel	Ni	<0.40	<0.40	0.5

* No requirements, ** blq—values below the limit of quantification.

5.3. Evaluation of the Degree of Immobilization of Contaminants from Cement Mortars Modified with Nanomaterials with the Addition of Fly Ash

In many kinds of research, it is indicated [59,60] that the mechanical properties of cement mortars may be improved with the addition of nanosilica. At the next stage of this research, cement mortars with the addition of 4% and 8% FA were modified with nanosilica. Figures 8 and 9 present cement mortars with 4% and 8% fly ash from the incineration plant, respectively, modified with nanosilica.

(**a**) (**b**)

Figure 8. Cement mortar modified with the addition of 4% fly ash modified with nanosilica: (**a**) outer surface; (**b**) internal structural view.

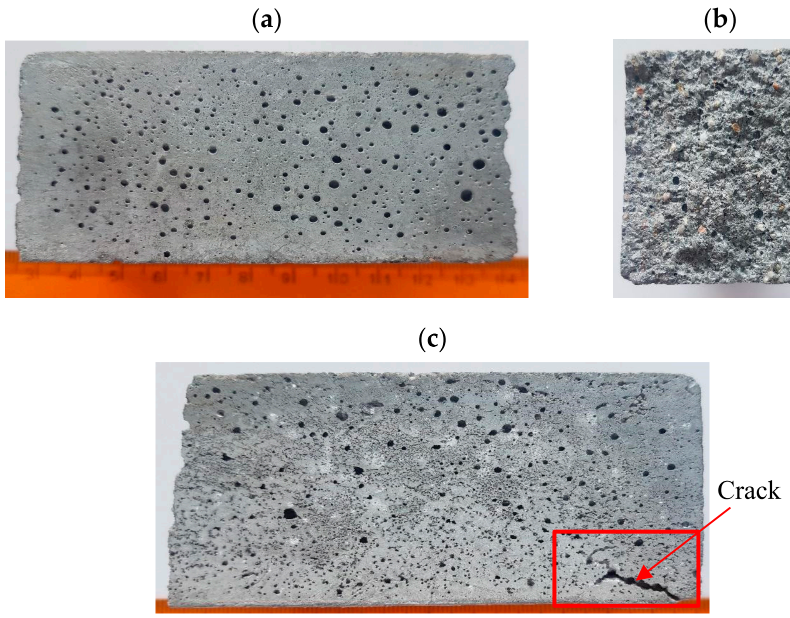

Figure 9. Cement mortar with the addition of 8% fly ash modified with nanosilica: (**a**) outer surface; (**b**) internal structural view; (**c**) crack in the cement mortar.

The results of the compressive strength and flexural strength tests of the concrete mortars with the addition of fly ash and modified with nanosilica after 28 days of curing are presented in Figure 10. In the case of mortars with the nanomaterial additive (CEM I + 4% FA + N), the strength of the samples was similar to or lower than the strength of samples without the nanomaterial added. The compressive strength of CEM I + 4% FA + N was 69.78 MPa, which is about 1.5 MPa less than that of the mortar without the nanomaterial additive. Its flexural strength was at the level of 9.00 MPa. In the case of mortars with 8% FA modified with nanosilica, the compressive strength and flexural strength were 35.06 MPa and 5.57 MPa, respectively. After modifying the mortar with nanosilica, its flexural strength increased by about 1 MPa. During visual analysis, cracks were noted in the CEM I + 8% FA + N mortar (Figure 9c), limiting its application in the construction industry.

(**a**)

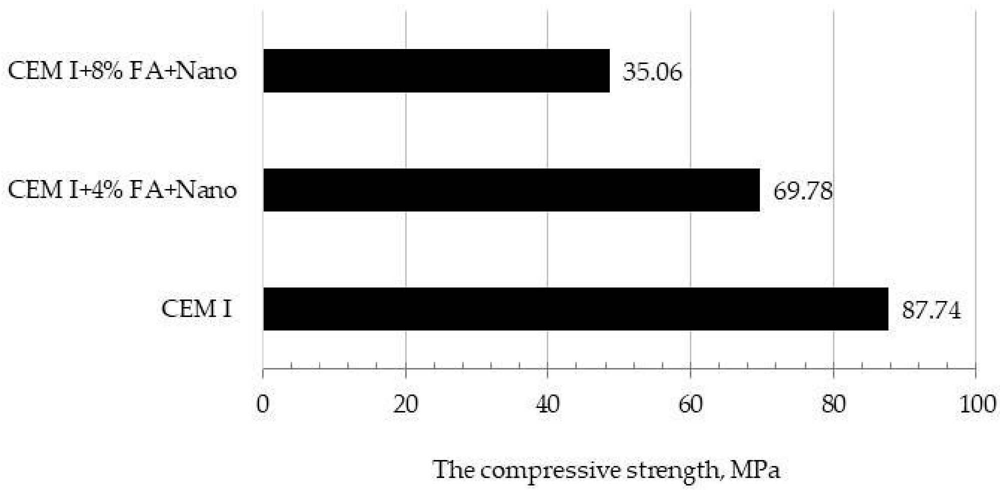

Figure 10. *Cont.*

(**b**)

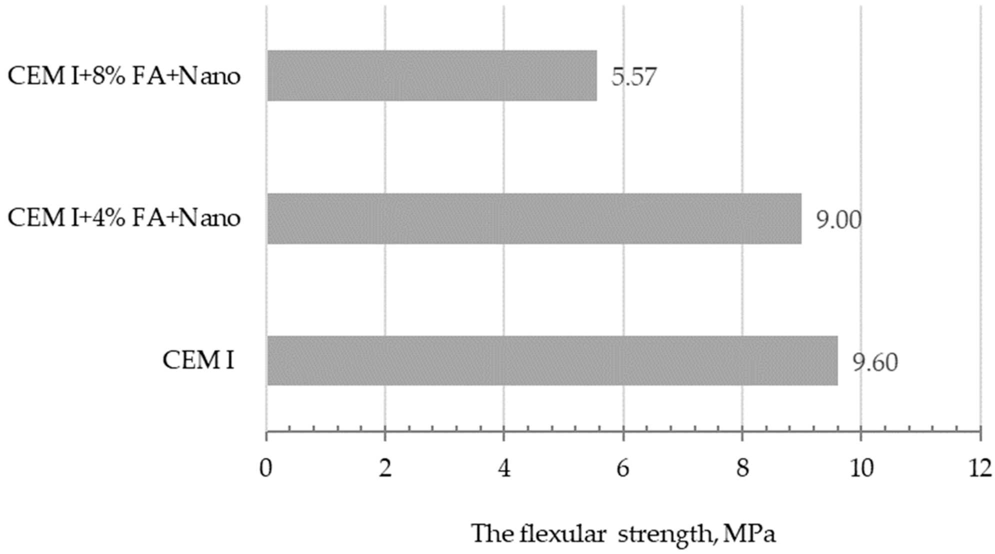

Figure 10. Strength of cement mortars with the addition of FA modified with nanosilica after 28 days of curing: (**a**) compressive strength; (**b**) flexural strength.

Table 6 presents the leachability of hazardous and heavy metals from cement mortars with the addition of FA modified with nanosilica. The discussed cement mortars had a strong alkaline reaction—above pH 11. It was noted that none of the tested parameters (i.e., Cl^-, SO_4^{2-}, NH_4^+, P, K, Ca, Li, Na) exceeded the permissible values determined in the Order of the Minister of Marine Economy and Inland Navigation 2019.

Table 6. Leachability of hazardous substances and heavy metals from cement mortars with the addition of fly ash modified with nanosilica, expressed in mg/L.

Parameter	Symbol	CEM I + 4% FA + Nano	CEM I + 8% FA + Nano	Highest Permissible Value [54,58]
pH	pH	11.8	11.1	6.0–9.0
Chloride	Cl^-	0.28	0.28	1000
Sulfate	SO_4^{2-}	285.24	331.86	500
Ammonium nitrogen	NH_4^+	blq **	blq **	10
Phosphorus	P	<0.005	<0.005	2
Potassium	K	4.01	6.70	80
Calcium	Ca	154.30	145.60	nr *
Lithium	Li	1.10	1.10	nr *
Sodium	Na	9.06	11.5	800
The sum of chloride and sulfate	$(Cl^- + SO_4^{2-})$	285.52	332.14	1500
Barium	Ba	8.70	17.80	2
Zinc	Zn	<0.10	<0.10	2
Copper	Cu	<0.20	<0.20	0.5
Lead	Pb	<0.50	<0.50	0.5
Cadmium	Cd	<0.05	<0.05	nr *
Chrome	Cr	<0.50	<0.50	0.1
Cobalt	Co	<0.50	<0.50	1
Iron	Fe	<0.04	<0.04	10
Manganese	Mn	<0.20	<0.20	nr *
Nickel	Ni	<0.40	<0.40	0.5

* No requirements, ** blq—values below the limit of quantification.

The contents of heavy metals were below the limit of quantification, except for the barium content, which was excessive. The barium content in the cement mortar with 4%

FA modified with the nanosilica was two times lower than that of the mortar without the addition of nanosilica.

6. Conclusions

Growing difficulties in the coal market, the uncertainty of supplies, and the dynamics of price changes in energy carriers give rise to legitimate concerns in the heating sector. Waste management regulations, including those for municipal waste, meet the needs of the market, providing space for the energetic use of the combustible fraction of municipal waste as fuel in combined heat and power plants and heating plants. However, such solutions translate into the formation of post-process waste, which is often classified as hazardous. One such byproduct is fly ash, whose chemical properties, toxicity, and dust emissions make it impossible to deposit in landfills for hazardous wastes. It should be noted that the actual method of neutralization of these wastes—i.e., depositing in the salt mine pits in Germany—slowly depletes. Looking to the future, it is necessary to search for alternative methods for the management of this waste that are neutral for the environment, economically justifiable, and compliant with the principles of the circular economy. The research conducted in this study is a natural response to the needs of the industry, which currently has limited possibilities for managing environmentally harmful waste products.

Based on this research, the following conclusions can be drawn:

- Tested fly ash from the MSWI plant was characterized by high leachability of sulfur ions, chlorides, calcium, sodium, zinc, lead, and chrome.
- The addition of fly ash in cement mortars increased the water demand. The use of fly ash as a partial replacement for cement will require the addition of more water or appropriate chemicals when designing the concrete mix.
- Replacing 4% of the cement mass with fly ash results in a slight reduction in the setting time of the cement grout (the beginning of the setting time guaranteed by the manufacturer is 186 min).
- Using nanosilica as an additive to cement mortar with fly ash does not improve its compressive and tensile strength.
- Test results proved the high immobilization of hazardous compounds by the C-S-H phase of the concrete. The leachability test confirmed the almost complete immobilization of chlorides and heavy metals by the C-S-H phase. The degree of immobilization exceeded 99%. Additionally, the leachability of the sulfate was limited to the level of 96–97%. The presented results are preliminary tests in a program designed to limit the impact of contaminants from the waste generated in the process of incineration of the mixed municipal waste fraction.
- The addition of nanosilica reduced the leaching of harmful substances (e.g., Cl^-, SO_4^{2-}, Ba) from cement mortar with 4% and 8% municipal waste fly ash. On the other hand, heavy metal immobilization was very high (99.9%). The level of immobilization did not depend on the addition of nanosilica to the mortar; in both analyzed variants, it was at a high level.
- Taking into account the current requirements for types of cement, fly ash from the incineration of municipal waste could be used only in small amounts (4%) for special cement that is chemically resistant and not commercially available.
- In the next steps of this research, the designed mortar with the addition of fly ash should be tested in various environmental exposure classes according to the standard PN-B-06265:2018-10 [61] to determine whether the leachability parameters change with the alteration of the structural behavior of concrete in various exposure classes.
- In future research, chemical ash degassing should be carried out to eliminate its influence on the swelling and cracking of cement mortars. Furthermore, the research should be continued by introducing it to a geopolymer.

The research conducted in this study is a natural response to the needs of the industry, which currently has limited possibilities for managing environmentally harmful waste products.

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