Scientific Journals
of the Maritime University of Szczecin

Zeszyty Naukowe
Akademii Morskiej w Szczecinie

2023, 75 (147), 35–41
ISSN 2392-0378 (Online)
DOI: 10.17402/571

Received: *11.07.2023*
Accepted: *14.07.2023*
Published: *30.09.2023*

Influence of waste ashes from biomass combustion on frost resistance of cement mortars

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Keywords: cement mortar, fly ash, bottom ash, biomass, durability, road infrastructure

JEL Classification: Q2, Q3, Q4, Q5

Abstract

This article presents the influence of ashes generated in the combustion processes of various types of biomasses on the durability (resistance to freezing and thawing after 25 cycles) of cement mortars. Three types of ashes were used for the tests: two fly ashes and one bottom ash. These differ in chemical composition and microstructure in the amounts of 10%, 20%, and 30% of the cement mass and are used as a substitute for standard sand. The ashes are characterized in terms of microstructure and chemical composition. The research shows that, regardless of the type of ash used, all the cement mortars containing ash are characterized by higher durability than the control mortars. Among the modified mortars, the smallest decrease in resistance (by 0.54%) to the process of freezing and thawing is shown by cement mortars containing 10% fly ash from the combustion process of biomass with the addition of sunflower, and the largest (by 7.56%) show mortars containing 30% bottom ash from the combustion of biomass with the addition of sunflower. These findings suggest that the incorporation of biomass ashes, particularly fly ash, into the cement matrix mixes has the potential to improve their durability for road infrastructure applications.

Introduction

Currently, for the production of building materials, various types of waste materials from both the construction sector and other sectors of the economy are used increasingly more often in addition to and instead of natural resources. Many of them are used as reused material, in accordance with its intended purpose, as well as after slight processing or fragmentation as an additive to cement matrix composites. In this way, there can be managed inter alia ceramic waste (Nayana & Rakesh, 2018; Mohit & Sharifi, 2019), concrete waste (Bogas, Carriço & Real, 2022; Yang et al., 2022), glass waste (Jeleniewicz et al., 2023), polymeric waste (Pietrzak, 2018; Ulewicz & Pietrzak, 2021; Pietrzak & Ulewicz, 2023), metallurgical waste (Lis & Nowacki, 2022), or ashes (Pietrzak, 2019; Jura, 2020; Jura & Ulewicz, 2021; Rutkowska & Żółtowski, 2022; Kalak et al., 2023). Zeolite (Hunyak et al., 2019) and waste nanosilica (Skoczylas & Rucińska, 2018; Khan et al., 2020) were also used to produce cement-based composites.

The hard coal combustion products obtained from them, due to the improvement of boiler efficiency, increased the awareness of energy producers and the production of ashes with repeatable and defined properties, which makes it possible to use them more easily and effectively. These repeatable chemical, rheological, and pozzolanic properties of fly ashes enable proper management of this type of waste. 47% of ashes from coal combustion are used in construction, while an additional 45% is employed for mine reclamation (Popczyk, 2022), 6% is sold, and the remaining 2% is landfilled (Blissett & Rowson, 2012). Most often, ashes from fossil fuels are used as a component of cement, an additive to concrete, or as a material for geotechnical works (Figure 1). The possibility of using ashes from coal combustion as an additive in the production of cement is conditioned by the standards PN-EN-197 1:2012, PN-B-19707:2013-10, and PN EN-14216:2015-09. The use of ash for concrete depends on the quality of the fly ash, i.e., mainly its chemical composition. In the case of fly ash, the content of unburned coal (loss-on-ignition, LOI) is important, which increases the water demand of the ash and reduces the frost resistance of the resulting materials with a cement matrix. The European standard PN-EN 450-1 specifies the requirements and compliance criteria for fly ash for use in concrete; it distinguishes three categories of fly ash in terms of their chemical composition and loss-on-ignition. Category A ashes may have a loss-on-ignition of 5%, category B is 7%, and category C is 9%.

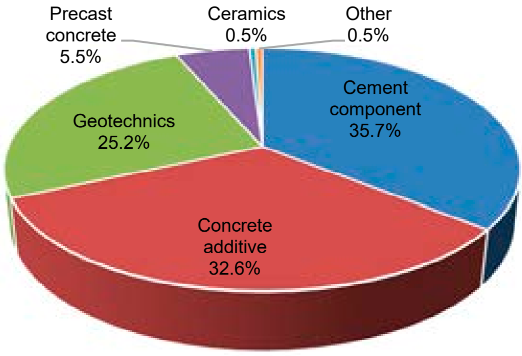

Figure 1. Use of waste ashes from the fuel combustion process conventional in Europe (Blissett & Rowson, 2012)

In Poland, it is also possible to use concrete ashes from the co-incineration process, which is also defined by the PN-EN 450-1 standard. Materials for co-incineration may include plant materials, wood and biomass from crops, animal waste, municipal sewage sludge, paper sludge and wastepaper, refining coke and ash-less liquid, and gaseous fuels. According to the standard, the maximum amount of combusted biomass can amount to 50% of the dry mass if the co-incinerated material is mainly wood waste; otherwise, it is 40%. In contrast, the maximum content of fly ash from co-incinerated materials cannot be higher than 30% if they are to be used for concrete mixes, mortars, and grouts.

The composition of ashes resulting from the combustion of biomass mainly depends only on the type and quality of the biomass burned and the type of boiler. Since there are many types of combusted biomass, the ashes acquire different physical and chemical properties, which is important from the point of view of searching for methods of their management. Currently, there are no regulations in Poland that allow for this type of ash to be used as a component of cement or as an additive to concrete mixes. The main directions of use of such ashes at the present time are agriculture (for soil fertilization) and road construction for the construction of road foundations. Each country in which biomass ash is to be used should be required to define guidelines, limit values, and test standards protocols. In addition, the employment of biomass ashes may be an alternative to the decreasing amount of coal ashes in the future, which results from the closure of coal mines and power plants.

As shown by the author's previous research (Ulewicz & Jura, 2017; 2019; Jura, 2020; Jura & Ulewicz, 2021) and literature reports (Omran et al., 2018; Gabrijel, Skazlić & Štirmer, 2022; Teixeira, Camões & Branco, 2022), the use of biomass ashes has a positive effect on the strength properties of materials with a cement matrix, i.e., cement mortars and concretes.

In the literature, a few studies on cement composites in terms of their frost resistance show that, depending on the type of ash used, the composites have a similar resistance or are more resistant to freezing and thawing compared to the control samples without such an addition. Ashes from hard coal have been tested many times in this respect; it can be concluded from a significant part of the research that samples with ash obtain similar properties as samples without the addition (Li et al., 2006). Ashes from co-incineration obtained similar relationships to composites with ashes from coal alone. In the previous tests, even samples that obtained 40% less compressive strength than control samples had a similar loss in terms of strength loss after freezing compared to the control samples (Johnson, Catalan & Kinrade, 2010). In an extensive number of publications, the authors inform on the optimal amount of ash addition in the concrete mix to obtain a frost resistance greater than the control samples, which is up to 25–30% of ash (Kosior-Kazberuk, 2013).

Much less research on the frost resistance of concrete composites with the addition of ash from biomass combustion can be found in the literature. Mainly important is what type of biomass was burned (the different chemical composition of the ash) and whether fly ash or bottom ash was added. The impact of such a component, depending on the type of combusted biomass and whether it was used as an additive to the concrete mix or as a replacement for part of the cement, caused various effects. Composites with a cement matrix, in which ash was only an additive, increased frost resistance in most studies. Although, if it was used as a replacement for part of the cement, it often resulted in a lower frost resistance (Nagrockienė & Daugėla, 2018). Researchers also noted that in some cases, in order for concrete to obtain adequate frost resistance, it is necessary to use more air-entraining admixture (Wang et al., 2008).

Ensuring the frost resistance of cement matrix mixes used in elements of the so-called green road infrastructure, such as those designed to retain and collect rainwater and snowmelt, as well as in hydrotechnical elements, is of utmost importance (Gavardashvili & Vartanov, 2023; Hlushchenko et al., 2022). These infrastructure components are vital for sustainable urban development since they contribute to effective stormwater management, groundwater recharge, and the preservation of natural water resources.

However, the exposure of such elements to freeze-thaw cycles poses significant challenges. The expansion and contraction of water during freezing and thawing can lead to the deterioration of the cement matrix materials, resulting in cracking, loss of structural integrity, and reduced service life. Therefore, it is crucial to enhance frost resistance through the incorporation of suitable materials, such as ashes from biomass combustion, as demonstrated in the aforementioned study. By ensuring the durability and frost resistance of these cementitious materials, the green road infrastructure can continue to fulfill its crucial role in sustainable water management and the overall resilience of urban environments (Deja et al., 2021; Nedeliaková, Hranický & Valla, 2022).

Research materials and methodology

This study examines the effect of the addition of various waste ashes from biomass combustion in a fluidized bed boiler on the resistance of mortars to cyclic freezing and thawing.

Materials

CEMEX Portland cement with high early strength, CEM I 42.5 R, was used for the tests. Certified standard sand, in accordance with PN EN 196-1, was used as the aggregate.

Fly ash (FA1) and bottom ash (BA) from the combustion of 80% wood biomass and 20% sunflower, as well as fly ash (FA2) from the combustion of 80% wood biomass and 20% coconut shell, was used in the tests as an additive modifying the composition of the mortar. Table 1 shows the chemical composition of the ashes employed, obtained using an XRF X-ray spectrometer (Thermo Fisher Scientific, USA). For both fly ashes, it can be observed that over half is SiO_2, over 10% is CaO, while Al_2O_3 in the case of FA1 is over 12%; for FA2, the latter is over 6%. In the composition of both fly ashes, K_2O is about 8%. Other elements were present in small amounts. Compared to the tested fly ashes, the bottom ash contains more than 86% SiO_2. BA ash had also about 3% K_2O, CaO, and Al_2O_3. The remaining elements in the composition of this ash are below 1%. As part of the tests, in accordance with the PN EN 450 1:2012 standard, the loss-on-ignition of individual ashes was examined. Loss-on-ignition for FA1 is 2.9%, for FA2 is 3.5%, and for BA is 0.28%. According to the PN-EN 450-1 standard, in this respect, all of the tested ashes could be classified as category A.

Table 1. Chemical composition of ashes [%]

Oxide / Element	FA1	FA2	BA	Oxide / Element	FA1	FA2	BA
SiO_2	50.20	60.05	86.94	BaO	0.06	0.041	0.03
CaO	11.82	10.02	3.42	Cr_2O_3	0.012	0.011	0.05
K_2O	7.99	8.47	3.80	SrO	0.046	0.024	0.02
Al_2O_3	12.29	6.32	2.21	ZrO_2	0.025	0.021	0.04
MgO	3.34	1.53	0.83	CuO	0.019	0.018	0.01
Fe_2O_3	1.46	0.88	0.74	Rb_2O	0.014	0.013	0.01
P_2O_5	2.04	2.00	0.38	NiO	0.006	0.005	0.01
Na_2O	0.44	0.35	0.21	PbO	0.016	0.011	0.01
MnO	0.28	0.18	0.11	SO_3	4.91	7.78	0.58
TiO_2	0.30	0.17	0.13	Cl^-	1.63	2.31	0.06
ZnO	0.05	0.03	0.03	Other	3.05	2.08	0.38

The microstructure of the fly ash was studied using the SEM/EDS X-ray energy dispersion spectrometer (LEO Electron Microscopy Ltd., UK) (Figure 2). Due to the very fine structure of the fly ash (almost 99% of fly ash passes through a sieve with a mesh size of 0.045 mm), it is necessary to magnify the image of the sample by at least 400 times in order to visualize the individual grains. The analysis shows that the fly ash grains have a heterogeneous structure and sharp edges, which can be compared to the appearance of crushed aggregate. In the case of bottom ash, due to the much larger

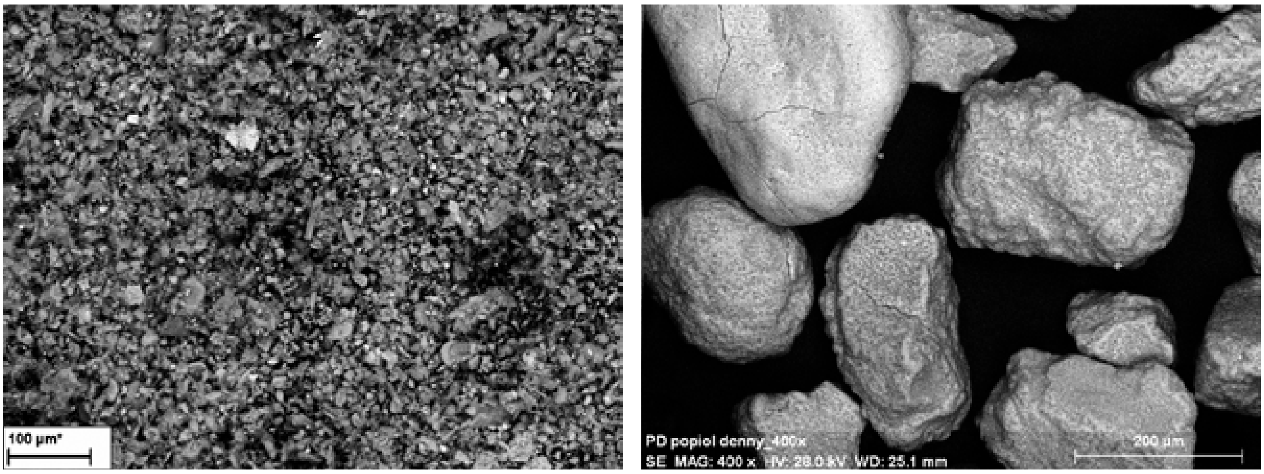

Figure 2. Microscopic photo of ashes (left-hand and right-hand side images are FA1 and BA, respectively)

Table 2. Composition of tested cement mortars

Component	Unit	Series									
		CM	FA1-10	FA1-20	FA1-30	FA2-10	FA2-20	FA2-30	BA-10	BA-20	BA-30
Sand	g	1350	1299,3	1248,5	1197,8	1303,0	1256,1	1209,2	1304,3	1258,62	1212,9
Cement	g	450	450	450	450	450	450	450	450	450	450
Water	g	225	225	225	225	225	225	225	225	225	225
Ash PL1	g	–	45	90	135	–	–	–	–	–	–
Ash PL2	g	–	–	–	–	45	90	135	–	–	–
Ash PD	g	–	–	–	–	–	–	–	45	90	135

grains, a magnification of 400 times enables an accurate showing of the surface of a single grain. The structure of the bottom ash is more homogeneous than that of the fly ash, while the grains have a more spherical shape, a smoother surface, and resemble grains of sand.

Each of the ashes (FA1, FA2, and BA) was used as an addition to the mortar in the amounts of 10%, 20%, and 30% of the cement weight, replacing the aggregate in a volume ratio. The results were compared with those obtained by the standard mortar (marked as CM). Table 2 presents the composition of the standard mortar and modified cement mortars.

Methodology

All the tests were carried out on laboratory-prepared samples of the cement mortars, in accordance with the PN EN 196-1 standard, in the form of bars with dimensions of 40×40×160 mm.

The determination of the water absorption of cement mortars was carried out in accordance with the requirements of the PN B 04500 standard. The determination of this property finds the mass of water absorbed by a mortar sample immersed in water under atmospheric pressure. After the mortar maturing period, the bars were dried to a constant weight at 105 ± 5 °C until two consecutive weight measurements (made every 24 hours) did not differ by more than 1 g. The weights of the samples were recorded, and then the bars were placed in a tub on a grate, immersing them in water at a temperature of 20 ± 2 °C until the weight was determined, i.e., the moment when subsequent weigh measurements did not differ from each other by more than 2 g. Water absorption was calculated as the ratio of water-saturated samples to the weight of dry samples and expressed as a percentage. The arithmetic mean of the test results of three samples is presented as the final result.

The frost resistance of the cement mortars was tested in accordance with the PN-B-04500 standard. After maturation for 28 days, the samples were weighed and subjected to 25 cycles of freezing at −18 ± 2 °C for 4 hours and thawed in water at +18 ± 2 °C for 4 hours. Next, the samples were weighed again and subjected to compressive strength tests. The obtained results were presented as a percentage decrease in the compressive strength and a percentage loss in mass after the frost resistance tests in relation to the control samples that were not subjected to freezing and thawing during this timeframe.

Research results and discussion

In the first stage of the research, the absorbability of the tested cement mortars (modified with waste ash from biomass combustion) is determined. The standard mortar of the CM series achieved water absorption equal to 9.6%. In the case of the FA1 series of mortars containing fly ash from the combustion of sunflower biomass, it can be seen that all the samples of this series show slightly higher water absorption than the standard mortar (Figure 3). On the other hand, the samples of the FA2 and BA series obtained slightly lower water absorption than the standard mortar. Of the three types of ashes used, the lowest absorbability is achieved by samples with BA ash in the amount of 10% of the cement mass. Moreover, it is also observable that, in each type of additive, the increase in the absorbability of the samples occurred with an increase in the amount of added ash in the range of 10–30%. It should also be noted that the mortars of each series meet the requirements for cement mortars in terms of water absorption and do not exceed the permissible limit of 10%.

The cement mortars were also subjected to frost resistance tests in accordance with the PN B 04500 standard. After these frost resistance tests, the standard mortar lost over 15% of its compressive strength compared to the control samples of the same batch, which had not been freeze-thawed at that time (Figure 4).

The use of FA1 resulted in a significant decrease in the loss of compressive strength in the tests of the cement mortars in comparison with the standard mortar. The use of 10% FA1 resulted in a decrease in compressive strength of only 0.54%. A similar trend can be observed for the second fly ash, i.e., FA2, in which the use of 10% fly ash resulted in a decrease in strength of only 0.85%. The use of bottom ash (BA) also led to limiting the strength loss, with the lowest decrease of 3.28% in the series containing 10% ash. None of the tested samples after frost resistance tests had any visible cracks, damage, or defects. The bars were of uniform structure, with slightly visible and very fine surface cracks. In terms of weight loss after frost resistance tests, all the samples achieved similar results since this loss was up to 1% of the weight, which proves a minimal mass loss (Figure 5). There is also a relationship between the lowest water absorption, the smallest decrease in compressive strength, and the smallest weight loss of the sample.

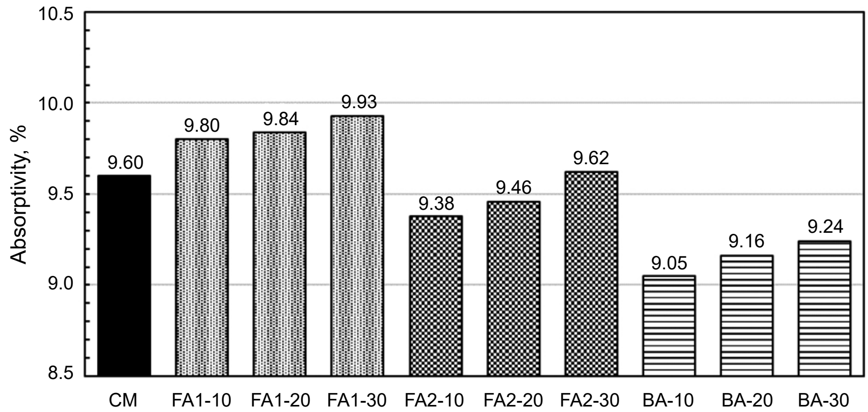

Figure 3. Water absorption of the cement mortars

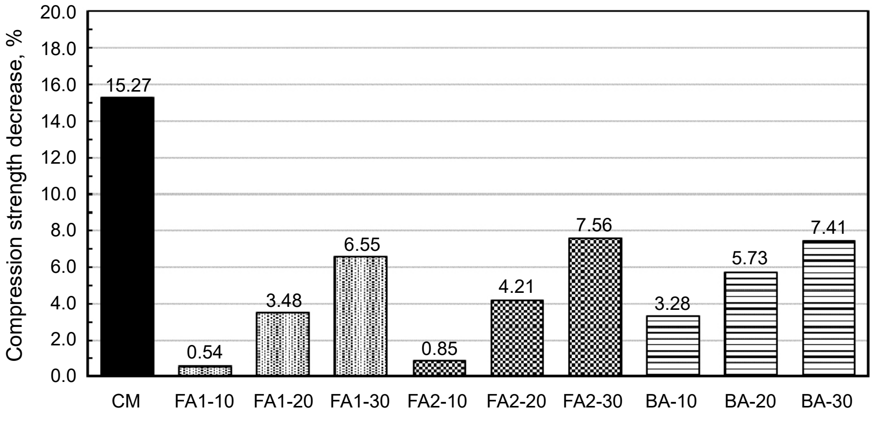

Figure 4. Drop in compressive strength after the frost resistance tests

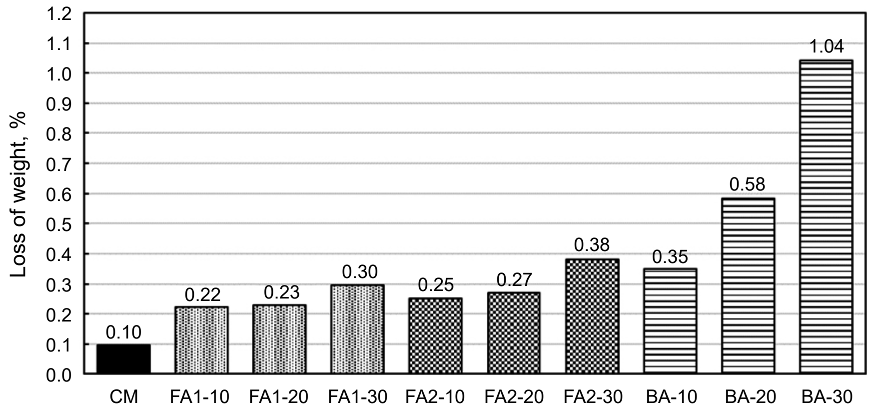

Figure 5. Weight loss after the frost resistance tests

Conclusions

In the near future, due to the reduction of fossil fuel combustion because of their negative impact on the natural environment and the shrinking natural resources of raw materials, the share of energy and heat obtained from the biomass combustion process will increase. It is, therefore, important to find methods of management of the waste ashes generated in this process, which are currently deposited in landfills. One method may be to use them in composites with a cement matrix, such as cement mortars and concretes. As the research shows, after a proper recognition of the properties of the ashes, we can use them for the production of concrete composites without losing their mechanical properties, including, for example, the most important compressive strength for concrete. The conducted tests showed that the absorbability of the composites modified with ash from biomass does not differ significantly from the standard mortar. In terms of frost resistance, the tested samples with three types of ashes achieved improved frost resistance, i.e., the loss of compressive strength after 25 cycles of freezing and thawing was lower compared to the control mortar in relation to the unfrozen control samples. The control mortar lost more than 15% of its compressive strength after the test, while the samples with FA1, depending on the amount of additive, were 0.54–6.55%. Samples with FA2 had a 0.85–7.56% loss, while it was 3.28–7.41% for BA. Samples with the addition of ashes lost slightly more weight after the frost resistance tests, but this was not visible when assessing surface damage. In addition, the lessening of water absorption also reduced the loss of compressive strength after the frost resistance tests. Due to the favorable results of the compressive strength (up to 25%, as previously tested), and the frost resistance of the cement mortars containing ashes from biomass combustion, an attempt to use them as an additive to composites with a cement matrix can be considered.

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Cite as: Jura, J. (2023) Influence of waste ashes from biomass combustion on frost resistance of cement mortars. *Scientific Journals of the Maritime University of Szczecin, Zeszyty Naukowe Akademii Morskiej w Szczecinie* 75 (147), 35–41.