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POTENTIAL APPLICATIONS OF MUNICIPAL SOLID WASTE INCINERATION BOTTOM ASH IN CEMENT-BASED MORTARS AFTER TESTING DURABILITY PROPERTIES

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Today, municipal solid waste incineration (MSWI) is considered the most sustainable and advanced technology worldwide for municipal waste utilization, with the lowest environmental impact. Bottom ash (BA) and fly ash (FA) are the secondary raw materials generated in MSWI processes. The research focused on the effective utilisation of bottom ash (BA) from municipal waste incineration plants. Mechanical and durability properties of mortars, in which up to 40 % of fine aggregate was replaced with BA at 5 % increments, were tested in detail. BA structures were analysed using X-ray diffraction and SEM methods. Test results showed that the replacement of fine aggregate with BA increased water absorption of mortars and decreased compressive strength and frost resistance. The research leads to the conclusion that cement-based structures can be modified with MSWI bottom ash at the rate of 10–15 %.

INTRODUCTION

The European Commission has adopted a circular economy package to encourage countries to recycle more waste and reuse raw materials. Some countries have been incinerating municipal solid waste for many years. The incineration technique makes it possible to reduce the municipal solid waste mass by 70 % and the volume by 90 % [1]. MSWI process generates secondary raw materials, namely bottom ash (up to 85 %) and fly ash (up to 15 %). The development of the circular economy concept worldwide and the drive to minimise the amount of disposed waste have recently promoted the upgrading of recovered waste and the reuse of upgraded waste as raw materials in a wide range of industries while preserving natural resources.

BA is the major by-product generated in the MSWI process. BA is the remaining ash accumulated on the incinerator grate which is then collected into tanks with water underneath the boiler [3]. BA may contain glass, minerals, ceramics, ferrous and non-ferrous metals, small amounts of unburnt waste particles and organic carbon [4-5]. BA is a very porous lightweight aggregate having a large and peculiar particle surface area. Gas bubbles on the surface are a common feature of all types of BA. As the bubbles take 10-25 % of the total particle volume, bottom ash has higher porosity [3]. BA chemical compositions differ by country and also depend on the city, season, and people's lifestyle. The prevailing chemical compounds in bottom ash are oxides, hydroxides, and carbonates. The chemical and physical properties of bottom ash depend on the composition of combusted solid waste and incineration conditions [6-7]. The most common chemical elements are silicon (Si), aluminium (Al), iron (Fe), magnesium (Mg), calcium (Ca), potassium (K), sodium (N), and chlorine (Cl). SiO_2, CaO, Fe_2O_3, and AlO_3 form the biggest ash fraction (> 10 %), whereas Na_2O, K_2O, MgO and TiO_2 form only a small fraction (0-5 %) [1; 8-12]. Heavy metals, such as chromium (Cr), copper (Cu), mercury (Hg), and nickel (Ni), are also common in BA. Despite the presence of heavy metals in BA, it is often considered to be a safe material due to the low leaching potential of heavy metals. Further treatment can reduce the amount of harmful substances.

BA contains chemical elements which react with the agents present in the binder to form compounds that adversely affect the durability of concrete. Therefore, BA must be upgraded before recovery using chemical, biological and thermal treatment techniques [13].

The reaction of cement paste elements with aluminium is a major factor determining the durability of concrete mixtures with BA aggregates [14-16]. Chemical reactions in concrete produce aluminium hydroxide, aluminates and hydrogen. Chemical processes can last for a long time in the presence of water. Intense chemical processes close to the surface of concrete elements (e.g. that are constantly exposed to moisture) are detrimental. The processes can cause delamination of the upper layers.

There is a large potential for the recovery of BA in the construction industry. The Netherlands has made the biggest progress in BA treatment and recovery. BA is widely used in Germany, France, Switzerland, Sweden and Denmark. In these countries, BA is mainly used in road building and subbases for car parks [17]. BA is also often used in the construction of embankments, noise and wind barriers [18].

Bottom ash from municipal solid waste incineration is very similar to the widely used virgin aggregates; therefore, it can be used as a mineral aggregate/material to supplement various construction materials [11; 15; 19-24].

The analysis of concrete modified with untreated BA is provided in reference [25]. The authors noted that the properties of concrete mixes were suitable for practical applications irrespective of the non-compliance of the ash chemical composition with the requirements for concrete aggregates.

Other authors reported detailed test results and noted that the maximum ash content in concrete mixes shall not exceed 50 % of the aggregate content. The best results were obtained when traditional supplementary materials were replaced with secondary raw materials [26]. Ash can be used to modify specific concretes, namely permeable and high-performance concrete [11].

Given the long-term prospects for beneficial reuse of BA, a clear trend can be observed – most of the ash is used in road construction and mound erection (including landfills). However, to expand the potential uses of BA in the construction sector, considerable attention should be given to the secondary utilisation of ash as fine and/or coarse aggregates in cementitious systems.

EXPERIMENTAL

Materials and methods

Portland cement CEM I 42.5 R was used for the tests. The mineral composition of clinker (%) determined by X-ray diffraction method was as follows: C_3S – 57.9, C_2S – 15.6, C_3A – 7.5, and C_4AF – 11.9. Chemical composition (%): Al_2O_3 – 5.23, Fe_2O_3 – 3.44, SiO_2 – 20.63, CaO – 63.56, MgO – 3.13, SO_3 – 0.78, K_2O – 1.15, Na_2O – 0.1, Cl^- – 0.007, CaO_{free} – 1.4, LOI – 0.60. The eluate test results of bottom ash used in the tests are presented in the table below.

It should be noted that BA particle size distribution before the tests was different from that of 0/4 fraction sand. The particle size distribution of BA and sand 0/4 mm was intentionally normalised in order to know the exact effect of BA on the cement mortar.

A highly effective modified acrylic polymer-based superplasticiser with resin concentration in solution of 27 %, pH value of 6.5, viscosity of < 30 mPas and solution density of 1.06 $g \cdot cm^{-3}$ was used for the tests.

Sand of 0/4 mm fraction was used to prepare cement mortars. Particle size distribution of sand is given in Table 2.

Up to 40 % of sand 0/4 mm was replaced with BA at 5 % increments to determine the effect of BA on cement mortars. Nine mix compositions were prepared (Table 3).

The table illustrates that the mortar compositions differ by the ratio of fine aggregate (sand) and BA. Water content in all compositions is kept constant at 750 g, as well as plasticiser concentration at 0.5 % by weight of cement. The binder content is also constant.

Table 1. BA eluate test results.

Parameters	Test results and units of measurement	Test methods
Dry residue	82.6-85.6 %; 85.6 %*	DIN 38 414-S2
Humidity	14.4-17.4 %; 14.4 %*	DIN 38 414-S2
pH	12.24-12.73; 12.73*	DIN 38 404-C5
Dissolved organic carbon	31.6-81.8 $mg \cdot kg^{-1}$; 81.8 $mg \cdot kg^{-1}$*	DIN EN 1484-H3
Chlorides	2210-3066 $mg \cdot kg^{-1}$; 2210 $mg \cdot kg^{-1}$*	DIN EN ISO 10304
Sulfate	4575-8822 $mg \cdot kg^{-1}$; 5751 $mg \cdot kg^{-1}$*	DIN EN ISO 10304
Fluoride	< 3-3.69 $mg \cdot kg^{-1}$; < 3 $mg \cdot kg^{-1}$*	DIN EN ISO 10304
Arsenis	< 0.01-0.022 $mg \cdot kg^{-1}$; < 0.01$mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Lead	8.7-24.63 $mg \cdot kg^{-1}$; < 24.63$mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Cadmium	< 0.005-0.022 $mg \cdot kg^{-1}$; < 0.005$mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Chrome	0.13-0.31 $mg \cdot kg^{-1}$; 0.158 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Copper	0.91-3.65 $mg \cdot kg^{-1}$; 3.65 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Nickel	< 0.1$mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Mercury	< 0.002 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Zinc	7.9-25.67 $mg \cdot kg^{-1}$; 11.89 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Barry	1.5-2.39 $mg \cdot kg^{-1}$; 1.88 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Molybdenum	0.269-0.38 $mg \cdot kg^{-1}$; 0.269 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Antimony	0.0405-0.25 $mg \cdot kg^{-1}$; 0.0405$mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22
Selenium	< 0.03 $mg \cdot kg^{-1}$*	DIN EN ISO 11885-E22

** Results of slag eluate analysis used in this work*

Table 2. Particle size distribution of sand.

Sieve size (mm)	0	0.063	0.125	0.25	0.5	1	2.8	4
Dissolves (%)	0.67	2.06	16.25	42.47	69.3	91.81	97.5	100

Table 3. Compositions of mortars.

Composition	CEM I 42.5R (g/%)	Sand 0/4 (g/%)	BA (g/%)	Water (g)	Plasticizer (%)
BA0	3000/100	1500/100	0/100	750	0.5
BA5	3000/100	1425/95	75/5	750	0.5
BA10	3000/100	1350/90	150/10	750	0.5
BA15	3000/100	1275/85	225/15	750	0.5
BA20	3000/100	1200/80	300/20	750	0.5
BA25	3000/100	1125/75	375/25	750	0.5
BA30	3000/100	1050/70	450/30	750	0.5
BA35	3000/100	975/65	525/35	750	0.5
BA40	3000/100	900/60	600/40	750	0.5

X-ray tests were done with diffractometer DRON–7 with Cu anticatode, Ni filter, anode voltage 30 kV, anode current 12 mA, detector step 0.02º. Profiles of diffraction peaks were analysed and peak deciphering was done by means of EVA (Bruker AXS) software and ICDD licensed PDF–2 (2003) diffraction databases.

The microstructure of modified cementitious materials was analysed with the scanning electron microscopy (SEM) device SEM JEOL JSM-7600F. The following slectron microscopy parameters were used: Power 10 kV and 20 kV, and distance to specimen surface from 7 to 10 mm. Microstructure characteristics were identified by testing the specimen splitting surface. Before testing, the splitting surface was coated with an electrically conductive thin layer of gold by evaporating the gold electrode in the vacuum using the instrument QUORUMQ 150R ES.

The particle size distribution of sand 0/4 was measured using a set of sieves Haver EML 200.

BA eluate was prepared according to EN 12457-2: 2003 requirements. Extracts were made from 90 g of dry specimen and 900 ml distilled water, L/S = 10 l/kg.

The compressive strength of tested specimens was determined according to standard EN 12390-3: Testing hardened concrete – Part 3: Compressive strength of test specimens. The loading rate of used machine was 0.5 MPa/s.

The freeze-thaw resistance was determined according to LST 1428-17:2024 by freezing water-saturated concrete samples in air and deicing them in water.

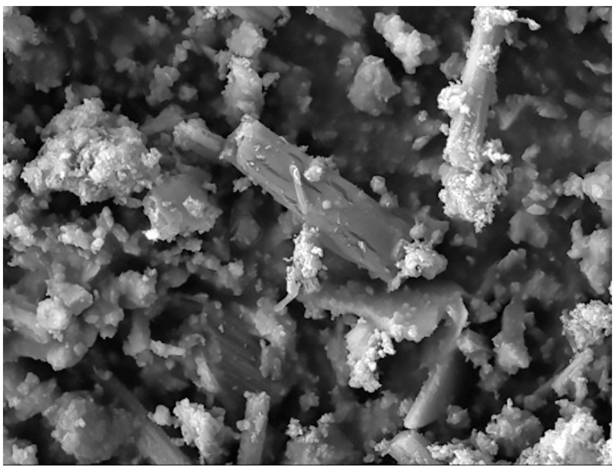
RESULTS AND DISCUSSION

The particle size distribution (PSD) of BA and fine aggregate was normalised in order to see the direct effect of BA on cementitious mortars disregarding the PSD.

The form, size, and porosity of mineral aggregate and BA particles differ significantly [12, 27]. The properties of the aggregates can impact the physical and mechanical properties of a cement mix and a hardened cement system.

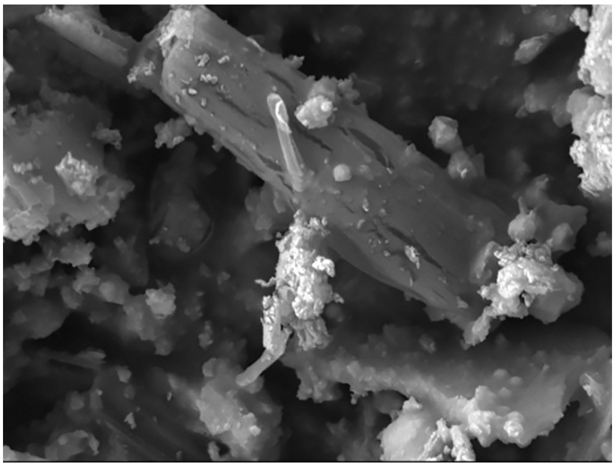
BA microstructure tests revealed the presence of coarse and porous particles of different shapes and rough surfaces consisting of smaller particles (Figure 1) These particles mainly consist of Ca (19.03 %), Al (6.65 %), O (57.60 %), Si (9.50 %), Mg (2.20 %), K (1.40 %), Zn (2.71 %), Cl (0.91 %).

Oblong particles with even surfaces, dense structures and lengths between 5 µm and 10 µm were also identified (Figure 1b). Small round particles are visible on their surface in some places. According to spectroscopy results, these particles mainly consist of Ca (24.20 %), Al (5.73 %), O (65.41 %), Si (2.63 %), Mg (0.40 %), K (0.28 %), Zn (0.90 %), Cl (0.46 %).



a) ×5000 magnification

Figure 1. Microstructure (SEM) of the BA. *(Continue on next page)*



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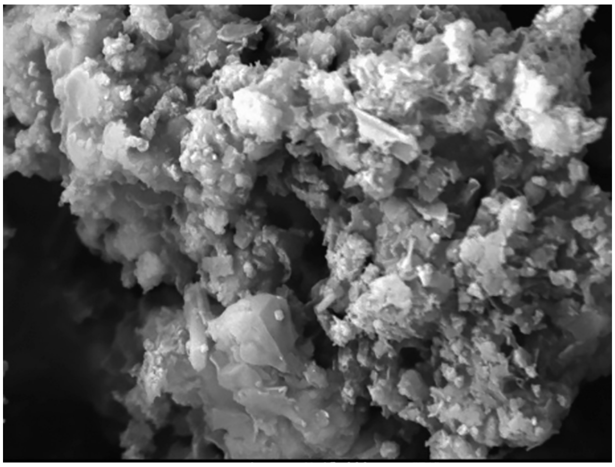

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Figure 1. Microstructure (SEM) of the BA.

The X-ray test of BA showed that quartz and calcite are the prevailing minerals in BA (Figure 2).

The main characteristics of BA were determined: electric conductivity of 899.5 μS·cm^{-1}, pH = 10.23, specific surface area of 3752 cm^2·g^{-1}, resistance to crushing of 14.32 MPa, water absorption of 8.7 %. The binder CEM I 42.5R had a specific surface area of 3746 cm^2·g^{-1}. The specific surface area of the binder was very similar or almost the same as that of BA.

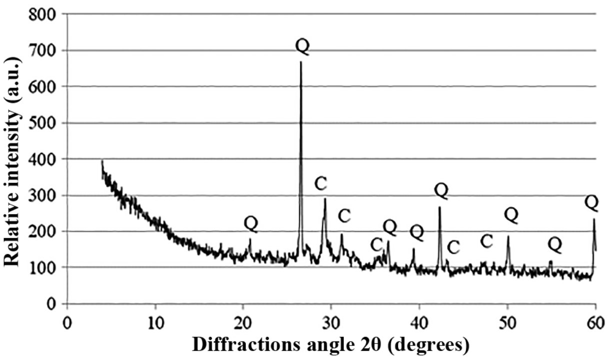


Figure 2. The X-ray diffraction pattern of bottom ash (nm): Q – quartz, C – calcite.

The compressive strength of the mortars modified with different amounts of BA was measured after 7 and 28 days of curing (Figure 3). The figure shows that both after 7 and 28 days of curing, the compressive strength decreased steadily with a higher content of BA adde to replace the fine aggregate. At 7 days, the control mortar had a compressive strength of 65.3 8 MPa, which decreased by 3 % in the samples with 5 % BA and by 6.46 % in the samples with 10 % BA. The compressive strength decreased even more at a higher BA content in the mortar: at 15 % BA the mortar strength dropped 9.9 %, at 25 % BA the strength decrease was 20.1 %, at 40 % BA the decrease was 30.2 %.

The results of compressive strength decline after 28 days of curing are very similar. At 28 days, the control mortar had a compressive strength of 83.25 MPa. When 5 % of sand was replaced with BA, there was an insignificant strength decrease of 0.83 %. At 10 % BA, the strength decreased 3 % and at 15 % BA it decreased 6.46 %.

There are several reasons for compressive strength decrease with the increase of BA content. First, it should be noted that BA is used to replace fine aggregate; second, the chemical composition of BA should be considered.

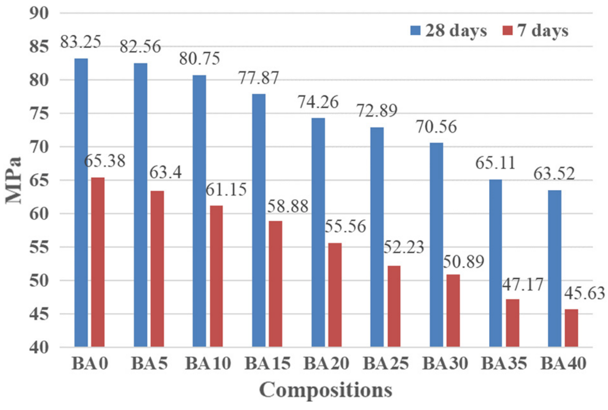


Figure 3. Compressive strength of concrete.

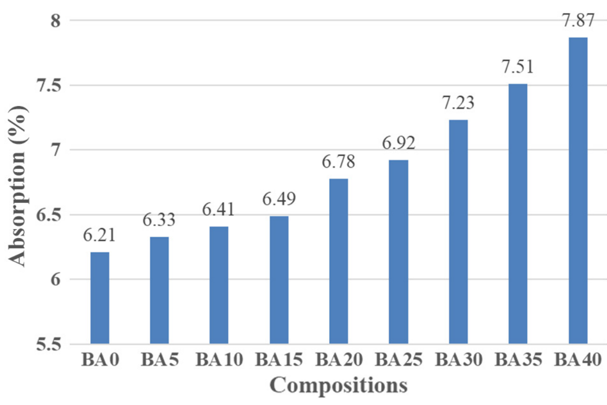


Figure 4. Absorption of mortars.

BA contains significant amounts of chlorides and sulphates, which impact cement hydration, and consequently, the compressive strength decreases. According to Cheung et al., additional amounts of chlorides and sulphates can affect (accelerate or retard) cement hydration processes [28]. In our tests, the hydration reactions were retarded. Other authors claim that MSWI bottom ash has a porous structure with a relatively large number of voids that reduce the strength of this aggregate [14, 16, 20]. The factors negatively impact the physical and mechanical properties as well as the durability of concrete mortars.

A negative trend similar to that of compressive strength was observed in water absorption tests (Figure 4). The addition of BA to cementitious mortars increases water absorption of the mortar. At lower BA content up to 15-20 %, water absorption is relatively low, i.e. 6.78 % compared to 6.21 % of the control sample. At higher BA content up to 40 %, the water absorption reaches 7.87 %. The increasing absorption rate of mortars modified with BA can be explained by the porous BA structure. In some cases, the aggregate porosity can have a positive effect on cementitious mortars, in other cases it can have a negative effect. Durability is negatively affected. If the filler absorbs much water, it means it has a lot of capillaries for the water to penetrate. In freezing and thawing conditions, the frozen water breaks the capillaries and causes the sample to collapse. In the case of mortars with a low water-to-cement ratio, it would be more beneficial for the aggregates to absorb sufficiently large amounts of water so that cement particles can then take up the water they need over time to facilitate further hydration of cement. In our case, the compressive strength decreased with a higher BA content indicating that up to 10-15 % of BA would be the optimum amount for the replacement of sand. Such an amount of BA would cause the minimum decrease in compressive strength and the minimum increase in water absorption.

In northern Europe or North America, the freeze-thaw resistance of concrete products is one of the key properties to assess the durability of the product. Although freeze-thaw resistance testing is an effort-intensive activity, these tests are very informative. We tested the durability of cementitious mortar samples using the volume (all-sided) freezing method. This method resembles the natural conditions the most when water-saturated samples are frozen in air and de-iced in water. 50 freeze-thaw cycles were used (Figure 5). Figure 5 illustrates that freeze-thaw resistance results of BA-modified samples correlate with water absorption and compressive strength results. Compressive strength decreases with a higher BA content in the mix. This can be explained by a sufficiently great number of open pores (capillaries) in BA. Water can easily enter the capillaries and stay there. In freezing and thawing conditions water turns into ice and destroys the structure of cementitious mortars and subsequently, the compressive strength of the samples decreases. It should be noted that the difference between the control samples and BA-modified samples was greater with the higher BA content in the mortar mix.

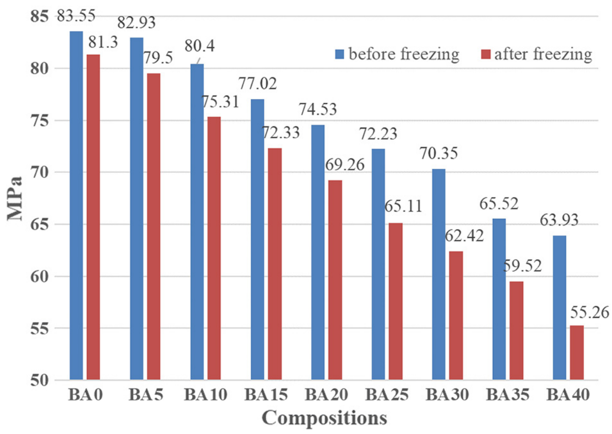
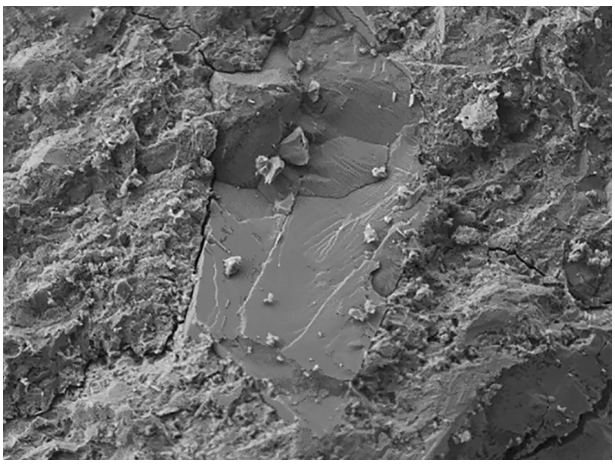
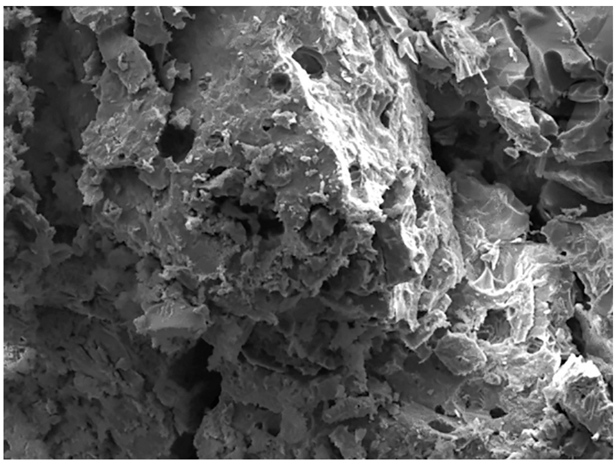


Figure 5. Frost resistance of cement mortars.

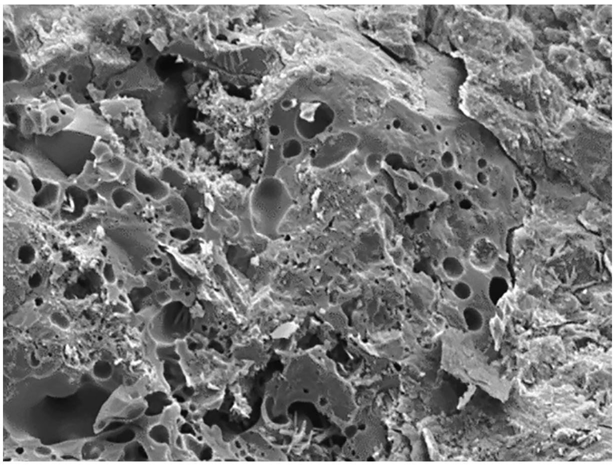


a) ×500 magnification



b) ×1000 magnification

Figure 6. SEM images of the modified cement systems with BA. *(Continue on next page)*



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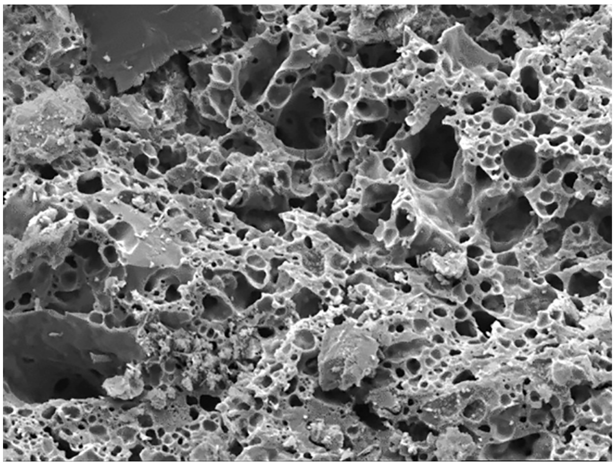

d) ×1000 magnification

Figure 6. SEM images of the modified cement systems with BA.

Keulen et al. tested the durability of BA-modified concretes using the one-sided freezing method according to EN 1338:2003. The researchers obtained similar results: higher mass losses were observed in the samples with a higher BA content in the cement structure. The increased mass loss indicates the collapse of the sample [29]. However, the mass loss measured in the one-sided method is not as big as in the all-sided (volume freezing) method. In the one-sided freeze-thaw test only one surface of the sample is subjected to freezing while all other surfaces are insulated; therefore the sample is less exposed to freeze-thaw conditions. The freeze-thaw test results showed that with a higher content of BA used to replace the fine aggregate the durability of mortar samples decreased.

SEM analysis (Figure 6) confirmed the results described above. A greater number of open capillaries or voids increased with a higher BA content in the mortar mix. These voids are detrimental to the properties of cementitious mortars.

Figure 6a shows that the control sample without BA has a dense structure without any open pores visible. Open pores or capillaries start to appear when 10 % BA is added to the mix. The results of the previous tests confirm the same: higher BA content reduces density, increases water absorption, reduces compressive strength and reduces freeze-thaw resistance. The porosity tends to increase when BA content is increased to 20 % and 40 %. Both small and large pores up to 10 µm in size develop. The pores are connected by capillaries.

CONCLUSIONS

Municipal solid waste incineration bottom ash was used to replace fine aggregate (sand 0/4 mm) in cement mortars tested. The particle size distribution of BA and fine aggregate was normalised. The test results showed that:

- BA can be used to replace fine aggregate and concrete mixes (mortars) but the chemical composition of the ash must be considered as it impacts the behaviour and durability of cementitious systems. It should be noted that BA is a toxic material as it contains various harmful inorganic and organic chemical components (heavy metals and dioxins) and various salts (chlorides, sulphates). All these elements affect the durability of concrete.
- Water absorption of cementitious mortars increases and compressive strength and durability decrease with a higher BA content in the mix. The assessment of the physical-mechanical and durability properties of cementitious mortars showed that the optimum amount of BA that can be added to the mix is 10-15 %. Such an amount of BA would cause the minimum decrease in compressive strength and the minimum increase in water absorption.
- SEM analysis confirmed the test findings. It showed that cement mortars with a higher BA content had a more porous structure with more open pores and capillaries, resulting in lower strength and durability properties.

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