Assessment of a Municipal Solid Waste Incinerator Bottom Ash as a Candidate Pozzolanic Material: Comparison of Test Methods

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Abstract: New generations of green concretes are often consuming large amounts of industrial waste, as recycled or manufactured aggregates and alternative binders substituting ordinary Portland cement. Among the recycled materials that may be used in civil engineering works, construction and demolition waste (C&DW), fly ashes, slags and municipal solid waste incinerator bottom ashes (MSWI BA) are those most diffused, but at the same, they suffer due to a large variability of their properties. However, the market increasingly asks for new materials capable of adding some specific features to construction materials, and one of the most interesting is the pozzolanic activity. Hence, this work deals with an experimental study aimed at assessing the technical feasibility of using an industrial waste comprised largely of MSWI BA, with small quantities of C&DW and electric arc furnace slag (EAFS), in green cement-based mixtures (cement paste and mortars). The aim of the work is to achieve the goal of upcycling such waste and avoiding its disposal and landfilling. Particularly, the test methods for assessing the pozzolanic activity of this waste are discussed, analyzing the efficacy of indirect methods such as the strength activity index (SAI), the conductivity test and the efficiency factor (k), together with a direct method based on lime consumption.

Keywords: mortars; MSWI bottom ash; pozzolanic activity; supplementary cementing materials; sustainability

1. Introduction

Pozzolanic materials have been largely adopted in construction materials, since the Roman ages, when pozzolanic systems were developed to realize the opus caementicium using the volcanic ashes from the area close to Pozzuoli, Naples, from which they take their name. Probably, the adoption of these kinds of materials has even an older origin, as it is believed that pozzolanic concrete was used in Mesoamerica too, in the period between 1100 and 850 B.C. More recently, pozzolanic materials have found large application in concrete aiming to realize blended cement mixes, with the twofold objective of reducing cement environmental footprint and costs. The definition of a pozzolan material can be found in reference [1], as “a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties”. According to such definition, it is well recognized that pozzolans may have varying sources, being both natural and man-made, and the mechanisms behind their interaction with cement might differ significantly [2–4]. As a result, the intensity of the pozzolanic reaction may differ depending on the materials. Furthermore, pozzolans can also be considered as supplementary cementing materials (SCMs), a category of materials
that include those compounds contributing to the properties of hardened concrete through both hydraulic and pozzolanic activity.

SCMs are often used in the construction industry to minimize ordinary Portland cement consumption in cement-based materials, such as concrete and mortar mixes. Some advantages are the ability to make concrete mixtures more economical, reduce permeability, increase strength, or influence other properties, both in the hardened and fresh state [5]. Further, their use significantly lowers the environmental footprint of concrete. It is indeed worth recalling that ordinary Portland cement is responsible for 866 kg CO$_2$/t of clinker [6]. This amount is due to the process of CO$_2$ release via the calcination of carbonate minerals in the kiln feed, which accounts for about 60% of the CO$_2$ release, whereas the remaining 40% is associated to the combustion of the fuels used to heat the kiln feed [6]. This high carbon footprint may be lowered only by adopting strict environmental policies within the same cement industry (e.g., by means of energy efficiency, alternative fuels, biomasses, clinker substitution), developing alternative cements, favoring carbon capture and sequestration, and lastly, adopting SCMs.

The most common SCMs are pulverized fly ashes (PFA), ground granulated blast furnace slags (GGBFS) and silica fume (SF), whose consumption has greatly increased in recent years [7–11] and whose availability in the near future is questionable. Indeed, according to the Paris agreement, EU countries will no longer invest in coal power plants after 2020, thus posing a serious risk in the future supply of all their by-products, including PFA and SF [12]. Accordingly, many researchers have turned their attention to finding alternative materials to be used as SCMs, focusing on industrial or agriculture waste. Within the first group, it is worth mentioning rock-wool waste [13], electric arc furnace dust (EAFD) [14] and other steel slags, i.e., ladle furnace slag (LFS) [15–19], glass waste [20], co-combustion fly ashes [21] and municipal solid waste incineration (MSWI) bottom ash [22]; in the second, we can mention sugarcane bagasse ash [23] and rice husk ash [24,25]. When dealing with these materials, there are two main challenging objectives that need to be reached: ensuring that the waste is stable, both from a chemical and volumetric point of view, and that it is able to develop a pozzolanic behavior.

On one side, indeed, the leachability of heavy metals is a key concern when managing these materials, and thus weathering processes are often recommended before their reuse as secondary building material. For instance, weathering of MSWI BA for a period of 1–3 months is typically adopted, aiming at allowing oxidation, carbonation, neutralization of pH, dissolution and precipitation reactions to occur and chemically stabilize the ash, and this will reduce the solubility of the main toxic elements which might be released into the environment [26]. Such a topic is also worth being analyzed as it is directly linked to the classification of such materials (i.e., to define if it should be considered as a waste or a by-product). Particularly, if the “end-of-waste” status of inert waste [27] is achieved, such a classification allows simpler authorization processes than full and ordinary ones asked of waste treatment plants.

On the other side, technical feasibility of the waste use is of fundamental importance. For such scope, it is worth recalling that a material can be classified as a SCM if it contributes to the properties of hardened concrete through the development of hydraulic of pozzolanic reactions, in such a way to ensure some target properties, according to both EN 450-1 [28] and ASTM C618 [29]. According to international regulations and literature, there is a consensus that the activity of most SCMs is linked to some main parameters: the content of active silica, fineness, specific surface area, water to powder ratio, curing temperature and alkalinity of the pore solution [30].

To assess the reactivity of SCMs and thus if a material displays pozzolanic activity, several tests have been proposed in literature, which may be divided mainly into two classes: direct and indirect. In the first group, the pozzolanic activity of a material can be analyzed through a Frattini test and simplified saturated lime (SL) [31,32], which are the most well-known. These methods consist of a direct evaluation of the consumption of Ca(OH)$_2$ through X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) or chemical
titration. They differ on the kind of solution that the candidate pozzolanic materials are added to, being in the former case a solution containing Portland cement and in the latter saturated lime water.

In the second group of test methods, i.e., the indirect ones, a property of the concrete where the SCM is added is analyzed and compared to that of ordinary concrete. Particularly, it is possible to analyze the strength activity index (SAI), which measures the relative compressive strength ratio between the SCM-concrete and the ordinary one [28]. Further test methods and indexes have been derived in literature to evaluate the reactivity of SCMs, and it is worth citing the conductivity test (an indirect method), proposed by Luxan et al. [33], and the definition of the efficiency factor $k$ of a SCM [34], which is defined as the part of the SCM in a pozzolanic concrete, which can be considered as equivalent to Portland cement, having the same properties as concrete without SCM.

However, according to several works carried out on different waste materials and SCMs, such tests do not always correlate with each other [35]. Furthermore, the roadmap for identifying if a material can be suitably used as a pozzolanic material is very complex, and often, at least some indicators typically used for this characterization fail [36]. Reasons for the observed discrepancies in the results obtained with different methods were associated to various causes, including: the amount of entrapped air in the mortars used to evaluate the SAI due to the use of admixtures; the adoption of blended cements, having different particles fineness; and uncertainties in the absolute amount of Ca(OH)$_2$ when adopting lime saturated test methods [37]. Donatello et al. [35], who analyzed comparatively the pozzolanic activity of incinerator sewage sludge ash (ISSA), coal fly ash (FA), metakaolin (MK), silica fume (SF) and silica sand (SS) through both direct and indirect test methods, recommended using a combination of these tests to provide a robust evaluation of the reactivity of a potential pozzolanic material. Particularly, they found that the SAI index and Frattini test methods correlated better and were tightly controlled methods.

The above context shows that prior to proceeding into a complex and long process for qualifying a recycled material as a SCM or as an industrial pozzolan, it is fundamental to verify if it is able to display pozzolanic activity. This work is developed with the following aims: to compare different test methods to assess the pozzolanic potential of a waste material; to evaluate if the raw material displays pozzolanic potential for being activated through a further process; to identify the optimum cement substitution ratio. Thus, the reactivity of an industrial waste, used in its raw state, is analyzed through different indirect methods, namely the SAI index, $k$-value and conductivity test. Further, the Frattini test is also carried out as a direct test method. The material selected as a candidate pozzolanic material is an industrial waste, obtained from the treatment of a municipal solid waste incinerator bottom ash (MSWI BA), blended with a minor content of electric arc furnace slag (EAFS) and construction and demolition waste (C&DW). Particularly, MSWI BA production in Italy is very high: in 2016, more than $10^6$ kg of MSWI BA were produced, and among them, 80% comes from plants located in North Italy [38]. The results allow us to discuss the correlation between the different test methods adopted, and in the specific case for this industrial waste, to suggest the best technological process for improving the reactivity of the analyzed material.

2. Materials and Methods

2.1. Raw Waste Material: Characterization

The industrial waste is a blended mix of MSWI BA, EAF slag and C&DW. This blend is produced in a waste treatment plant in Italy with varying grading fractions, being an all-in (0–31 mm), a fine (0–4 mm) and a coarse (4–16 mm) fraction, the application of which is intended for civil engineering purposes with non-structural properties. Particularly, the (0–4 mm) fraction contains more than 95% of MSWI bottom ash, and it is shown in Figure 1.

In this study the waste is used in a 0–4 mm and 0–1 mm grading, the latter being sorted from the raw material fine fraction, without any further treatment except the mechanical
sorting and a weathering of three-to-six months at atmospheric conditions carried out at the treatment facility.

Figure 1. MSWI BA (0–4 mm).

MSWI BA density (s.s.d.) is 2285 kg/m³, whereas the chemical composition obtained through XFR is listed in Table 1, together with the composition of cement type CEM II/A-LL 42.5R, used as a reference. The XRF test method has been often adopted in literature when characterizing the composition of MSWI BA [39–41]. The main constituents are Ca, Si, Al, Fe and Mg oxides; particularly, SiO₂ + Al₂O₃ + Fe₂O₃ content is about 42.4%, which is below the limit proposed by EN450-1 for fly ashes [28], and that proposed by ASTM C618-19 [29] for natural pozzolans, but it is close to the latest limits proposed for fly ashes.

Table 1. Chemical composition of MSWI BA and cement.

|          | MgO (%) | Al₂O₃ (%) | SiO₂ (%) | P₂O₅ (%) | SO₃ (%) | K₂O (%) | CaO (%) | TiO₂ (%) | Cr₂O₃ (%) | MnO (%) | Fe₂O₃ (%) | CuO (%) | ZnO (%) | PbO (%) |
|----------|---------|-----------|----------|----------|---------|---------|---------|----------|-----------|---------|-----------|---------|---------|---------|
| MSWI BA  | 8.13    | 12.55     | 21.76    | 2.56     | 0.91    | 36.90   | 1.31    | 0.39     | 8.09      | 0.59    | 1.24      | 0.16    |         |         |
| Cement   | 2.38    | 4.79      | 19.71    | 0.10     | 2.95    | 1.03    | 65.46   | 0.21     | -         | 0.04    | 3.28      | -       | 0.16    | <0.3    |

Additionally, to complete the characterization of this material for its application as a SCM, the authors are focusing also on environmental safety issues, through leaching and ecotoxicological tests, that may be adopted to verify the potential presence of harmful substances. Some preliminary results on this aspect can be found in [42], showing that a low risk exists when the material is tested in monolithic mortar and concrete specimens.

XRD tests were carried out using a Siemens/Bruker D5000 Diffractometer, with CuKα radiation and operation conditions of 40 kV and 30 mA, on a pulverized sample of the material. The XRD pattern is shown in Figure 2, identifying as the most relevant crystalline phases quartz, calcite, gehlenite, magnetite, wuestite, mayenite, larnite and then calcium sulfate tetrahydrate. Quartz, calcite and magnetite are often found in MSWI BA in large quantities [43,44], whereas the other constituents generally appear less abundantly. It is worth mentioning the presence of mayenite and gehlenite, which in literature were found in activated MSWI, obtained after thermal treatment [45,46]. Particularly, mayenite (C12A7) is widely used in calcium aluminate cements as a minor phase, and even in geopolymers to improve setting and early-age strength. It is well recognized that this mineral could lead to an improvement in the hydraulic reactivity of cements, especially at young ages [47,48]. However, recent studies demonstrated that rapid hydration of C12A7 may cause flocculation in the system, leading to the formation of regions with local defects within their mineralogic structure and, thus, to possible weakening of the paste matrix in cement-based materials [49]. Lastly, between 25° and 35° 2θ it is possible to identify the main hump in the spectrum, representing an amorphous phase.
2.2. Methods

In this work, the reactivity of the raw waste material is analyzed through different methods. Among the indirect tests to evaluate the pozzolanic activity, the evaluation of the strength activity index (SAI) and the efficiency k-factor is performed, together with the rapid conductivity test. Further, the Frattini test is carried out to evaluate CaO consumption, thus being considered a direct test method. For this scope, varying mortar mixtures were created and tested under compressive and flexural strength tests; in addition, cement pastes were realized to evaluate the setting time evolution and their mechanical properties.

2.2.1. Mortar Specimens—Mechanical Tests

Overall, twelve mortar mixes were realized and tested, four being the reference (labelled as “Mix Ref”) and eight being the experimental ones where MSWI BA replaces cement at a 20%w ratio. It is worth noting that the proportioning followed the direct weight replacement (DWR) instead of the direct volume replacement (DVR) method, i.e., a certain amount of MSWI BA replaces the same amount of Portland cement in weight. Among the MSWI BA mixes, four were realized with the raw (0–4 mm) grading, named with the letter “F”, and four with the (0–1 mm) particle fractions, named with the letters “EF”. For casting all the mortars, the same cement type was used, classified as a CEM II-A/LL 42.5-R, with rapid strength gain. Tap water without any deleterious materials was used for mortar realization, together with a natural sand (0–4 mm) and a water reducing agent, added in all the mortar mixtures except for those realized with the highest water/cement (w/c) ratio.

The addition of the plasticizer allowed the mortars to have a fluid workability, even if the mixes containing the MSWI BA had a slightly reduced flow compared to the references. Indeed, it is worth recalling that BA typically has a high water demand, but the addition of the plasticizer can control it well. Table 2 shows the features of the analyzed mortar mixes.

Other than compressive strength at 28 days, flexural strength was also evaluated at the same age. For the reference and “Mix EF” samples, the same tests were carried out also at a longer age, i.e., after 56 days. For the tests, 40 × 40 × 160 mm prismatic mortar samples were casted, demolded after two days, maintained under controlled humidity and temperature conditions (20 ± 2 °C, >95% relative humidity) and tested under a three-point bending test in a 25 kN capacity universal loading machine; with the two parts of the samples remaining after the test, the compressive strength test was carried out in a 600 kN capacity universal loading machine.
Table 2. Mix design of mortars (in kg/m$^3$).

|        | Water | Cement | Water/Binder | Natural Sand (0–4 mm) | MSWI BA (0–1 mm) | Plasticizer |
|--------|-------|--------|--------------|-----------------------|------------------|-------------|
| Mix Ref 1 | 315   | 525    | 0.6          | 1575                  | -                | -           |
| Mix E1  | 315   | 420    | 0.6          | 1575                  | 105              | -           |
| Mix EF1 | 315   | 420    | 0.6          | 1575                  | -                | 105         |
| Mix Ref 2 | 266.7 | 533    | 0.5          | 1600                  | -                | 5.33        |
| Mix E2  | 266.7 | 426.7  | 0.5          | 1600                  | 106.67           | 5.33        |
| Mix EF2 | 266.7 | 426.7  | 0.5          | 1600                  | -                | 106.67      |
| Mix Ref 3 | 240   | 533    | 0.45         | 1600                  | -                | 5.33        |
| Mix E3  | 240   | 426.7  | 0.45         | 1600                  | 106.67           | 5.33        |
| Mix EF3 | 240   | 426.7  | 0.45         | 1600                  | -                | 106.67      |
| Mix Ref 4 | 220   | 550    | 0.4          | 1650                  | -                | 5.50        |
| Mix E4  | 220   | 440    | 0.4          | 1650                  | 110              | 5.50        |
| Mix EF4 | 220   | 440    | 0.4          | 1650                  | -                | 110         |

2.2.2. SAI index

Strength activity index (SAI) values of the studied MSWI BA were calculated according to ASTM C618 [29], which defines SAI as the ratio of the compressive strength of the 20% SCM mortar to that of a control mortar. SAI should not be less than 70% after 28 days to classify a material as pozzolanic. In this work, other than the SAI for compressive strength, the same index was also evaluated for the flexural strength, both at 28 and 56 days of curing (the latter only for “Mix EF” samples).

2.2.3. Efficiency k-Factor

The $k$-value of the MSWI BA mortars is estimated here using the $\Delta w$ concept, which is described in detail in the work conducted by Babu and Rao [50] and Schiessl and Hardtl [51]. For such scope, the results in terms of compressive strength evaluated at 28 days of the mortar mixes are used. The $k$-value is hence defined in such a way that the $w/c$ ratio of the reference mix and the ratio $[w/(c + k \cdot MSWI)]$ of the mix with pozzolan material are the same, given a fixed strength level. Recall that the second ratio has the meaning of water to “effective” cementitious materials. For such scope, it is first necessary to obtain the compressive strength evolution vs. $w/c$ (water/cement) or vs. $w/b$ (water/overall binder as cement + MSWI BA) ratio, based on the experimental results. The strength model used is based on Abrams relation, where $\sigma_c$ is the compressive strength, $w$ is the water content, $b$ is the overall binder content and $\mu_1$ and $\mu_2$ are the regression coefficients:

$$\sigma_c = \mu_1 \cdot (w/b)^{\mu_2}$$

Comparing the curves of the pozzolanic mortars and that of the reference mix, $\Delta w$ can be expressed as:

$$\Delta w = (w/c) - (w/b)$$

In the above relation, the water to effective cementitious materials ratio $w/(c + k \cdot MSWI)$ should substitute the $w/c$ term, and the water to overall binder content $w/(c + MSWI)$ substitutes $w/b$. Then, the $k$-value can be calculated via Equation (3):

$$k = w/(MSWI \cdot (\Delta w + w/(c + MSWI))) - c/MSWI$$

2.2.4. Conductivity Test

The test is based on the procedure developed by Luxán et al. [33], which aims to experimentally assess the compensated conductivity of a calcium hydroxide (CH) saturated solution, to which the potential pozzolanic material is added, over time which is applicable to natural products (about 120s). This method is recognized as an indirect test method
characterized by a high rapidity, which however might suffer from some weaknesses, most in terms of the presence of soluble salt in non-natural pozzolans which typically deposit on the bottom of the solution.

The test is carried out as follows: first, 200 mL of a CH saturated solution prepared with distilled water is soaked under controlled temperature conditions (40 ± 1 °C) and the electrical conductivity is measured using a WTW MultiLine P4 Universal Meter. Then, the electrical conductivity measure is repeated after 120s from the addition of 5 g of the MSWI BA to the solution, here used in the (0–1 mm) fraction. The variation of the pH and of the conductivity indicates the reaction of dissolved [Ca]$^{2+}$ and [OH]$^{-}$ ions.

2.2.5. Frattini Test

The Frattini test method is considered as a direct evaluation of the pozzolanic activity according to the European standards. The procedure follows the work of Baki et al. [52], which consists of the preparation of a 20 g sample made of cement (80%) + MSWI BA (20%). The initial sample of MSWI BA is extracted from the (0–1 mm) fraction. This sample is then added to 100 mL distilled water at 40 °C and vigorously soaked for 20 s, after which it is placed in an electric oven at 40 °C for four days. After, it is filtered under vacuum conditions and then analyzed via titration to quantify both [OH]$^{-}$ and [Ca]$^{2+}$ ions, the former using 0.1 mol/L HCl solution and five drops of methyl-orange indicator, the latter with 0.03 mol/L EDTA solution and Pattond and Reeders indicator. The last titration is performed after a pH correction to achieve a pH value of 12.5 ± 0.2. The same test was carried out for a sample made using cement only and another where 20% of the cement was replaced by natural sand.

2.2.6. Cement Paste Specimens—Setting Times and Mechanical Properties

Seven cement pastes (one reference and six with MSWI BA) were realized to evaluate both initial and final setting times and also compressive strength at 28 days. Cement pastes were realized with a fixed $w/b$ ratio equal to 0.3 and a varying cement replacement ratio (adopting the DWR method), up to 50%w. MSWI BA was used in the (0–1 mm) fraction.

Setting time was evaluated using Vicat apparatus, which measures paste resistance to the penetration of a needle under a load of 300 g. The time elapsed between zero and the instant at which the distance between the needle and the baseplate is 6 ± 3 mm is taken as the initial set time. Instead, the final setting time was considered as the time elapsed between zero and the instant at which the needle penetrates the paste to a maximum depth of 3 mm. Instant zero is considered from the moment when mixing water is added to the mixture. Set tests were carried out in a room with relative humidity and temperature of 54 ± 2.0% and 19 ± 1.0 °C, respectively.

Compressive strength tests on hardened cement pastes were carried out on 50 mm side cubic specimens, at 28 days of curing in a room with relative humidity and temperature of 95 ± 5.0% and 20 ± 2.0 °C, respectively. Tests were carried out in a 600 kN capacity universal loading machine.

3. Results and Discussion
3.1. SCM-Mortars and SAI Values

Table 3 lists the mechanical properties of the analyzed mortars in terms of hardened density ($\rho$) and compressive ($f_c$) and flexural strength ($f_{cf}$), after 28 days for all the samples and also after 56 days for the reference and “Mix EF” samples. Values refer to the average results of at least three samples.
Table 3. Mechanical properties of the mortars (ave. = average results; st. dev. = standard deviation).

|                | 28 Days | 56 Days |
|----------------|---------|---------|
|                | ρ (kg/m³) |  f_c (MPa) | f_cf (MPa) | ρ (kg/m³) |  f_c (MPa) | f_cf (MPa) |
| Mix Ref 1 (ave.) | 2174     | 26.87    | 5.55     | 2250     | 42.62    | 7.50      |
| (st. dev.)     | 9        | 0.91     | 0.23     | 8        | 1.34     | 0.19      |
| Mix E1 (ave.)  | 2052     | 10.33    | 3.37     | -        | -        | -         |
| (st. dev.)     | 39       | 0.38     | 0.38     | -        | -        | -         |
| Mix EF1 (ave.) | 2046     | 17.12    | 5.55     | 2066     | 20.28    | 5.09      |
| (st. dev.)     | 21       | 0.16     | 0.46     | 22       | 0.83     | 0.76      |
| Mix Ref 2 (ave.) | 2195    | 32.29    | 6.78     | 2214     | 44.89    | 8.34      |
| (st. dev.)     | 20       | 1.45     | 0.05     | 4        | 0.70     | 0.23      |
| Mix E2 (ave.)  | 2049     | 22.74    | 4.71     | -        | -        | -         |
| (st. dev.)     | 9        | 0.94     | 0.13     | -        | -        | -         |
| Mix EF2 (ave.) | 2082     | 23.70    | 6.05     | 2137     | 28.48    | 5.71      |
| (st. dev.)     | 6        | 0.62     | 0.13     | 5        | 2.56     | 0.27      |
| Mix Ref 3 (ave.) | 2193    | 42.86    | 7.94     | 2285     | 47.78    | 8.65      |
| (st. dev.)     | 31       | 0.71     | 0.19     | 26       | 0.64     | 0.35      |
| Mix E3 (ave.)  | 1990     | 22.66    | 5.27     | -        | -        | -         |
| (st. dev.)     | 24       | 1.14     | 0.21     | -        | -        | -         |
| Mix EF3 (ave.) | 2175     | 29.00    | 6.91     | 2160     | 29.12    | 6.16      |
| (st. dev.)     | 28       | 1.72     | 0.24     | 27       | 2.95     | 0.12      |
| Mix Ref 4 (ave.) | 2240    | 43.50    | 7.38     | 2208     | 50.38    | 8.85      |
| (st. dev.)     | 30       | 2.45     | 0.70     | 31       | 1.82     | 4.86      |
| Mix E4 (ave.)  | 2164     | 33.86    | 6.73     | -        | -        | -         |
| (st. dev.)     | 28       | 0.71     | 0.08     | -        | -        | -         |
| Mix EF4 (ave.) | 2133     | 29.58    | 6.81     | 2105     | 28.22    | 5.14      |
| (st. dev.)     | 11       | 0.42     | 0.33     | 27       | 0.33     | 0.21      |

Results highlight that the hardened density is lower when the MSWI BA partially substitutes cement, despite the grading used, than in the reference mortars. Due to long-term hydration, hardened density increases with time for all the analyzed mixes. Further, substituting 20% of cement with the MSWI BA has a severe impact on both compressive and flexural strength, even if this last parameter is affected in a slighter way, despite the grading of the ash added. The reasons for strength losses can be argued to be the replacement of a stronger material (cement matrix) with a weaker one (MSWI BA) and the increase in the pore fraction of the concrete, due to the ash particles reduced fineness compared to that of cement particles. Additionally, the DWR method adopted here might have an impact too, as it influences the water demand of the mix. Further, the impact of the substitution is less influential for those mortars realized with the (0–1 mm) MSWI BA, rather than for the mixes made with the coarser fraction of this material; the only exception applies for the mixes with a low w/b ratio, which have comparable strength both when MSWI is used in the (0–4 mm) and (0–1 mm). Instead, mixtures realized with (0–4 mm) MSWI BA show a higher strength loss when a low w/b ratio is used.

Table 4 lists the values of the SAI, both for the compressive and flexural strength ratios, evaluated for all the mixtures containing the MSWI BA. Analyzing the SAI for compressive strength, the target value of 0.7 at 28 days is exceeded only for Mix E2 and E4 when using the coarse ash and for Mix EF2 when using the fine fraction of the ash. However, when using the fine MSWI BA, the SAI index is generally higher (average value a. v. = 0.68; standard deviation st. dev. = 0.04) than when using the coarse ash (a. v. = 0.60; st. dev. = 0.177). Particularly, on average, the (0–1 mm) fraction allows limited strength losses, showing a maximum decrease of 37% compared to the reference mix, and the variability of results is limited. Instead, when the ash is used in the coarse fraction, the variability of the results is larger, as demonstrated by the high st. dev. value of the results.
ever, when using the fine MSWI BA, the SAIc index is generally higher (average value)
pressive strength, the target value of 0.7 at 28 days is exceeded only for Mix E2 and E4
the highest maturation age, SAIf values of “Mixes EF” decrease, similarly to SAIc, with an
a. v.

Concerning instead SAIf at 28 days, the best result is obtained in Mix E4 for the
mortars realized with the coarse ash, whereas for the fine ash mortars Mix EF1 behaves
best, displaying the same flexural strength as the reference mortar. As discussed for the
compressive strength parameter, when the ash is used in the (0–1 mm) grading, the average
SAIf values is higher (a. v. = 0.92), with a small variability of the results (st. dev. = 0.05),
than when it is used in the (0–4 mm) grading (a. v. = 0.72; st. dev. = 0.13). Furthermore, at
the highest maturation age, SAIf values of “Mixes EF” decrease, similarly to SAIc, with an
a. v. = 0.66 and st. dev. = 0.06.

According to the above results, it is possible to derive compressive strength evolution
as a function of the \( w/b \) ratio according to Equation (1), as shown in Figure 4a–c, respectively
for reference, MSWI BA (0–4 mm) and MSWI BA (0–1 mm) mortars. Regression equations
have a high \( R^2 \) value, demonstrating the goodness of the fitting relations. According to
these regressions, it is possible to observe that at the lowest \( w/b \) value, mortars realized
with the coarser fraction of the MSWI BA provide higher strength; conversely, at the
highest \( w/b \) ratio, the mortars realized with the finest MSWI BA fraction suffer less strength
losses than the counterparts with the coarse ash. Indeed, the slope of “Mix E” is steeper
than that of “Mix EF”. According to reference [53], where the influence of the \( w/b \) ratio
on strength development of pozzolanic mortars was studied, the overall water content
available in a mix for binder hydration impacts also pozzolan reactivity. Particularly, the
compressive strength of mortars due to pozzolanic reaction increases with the \( w/b \) ratio:
this suggests that probably the (0–1 mm) fraction, which performs sufficiently well also at
high \( w/b \) ratios, has also a positive filling effect due to its reduced size compared to the
coarser fraction.

### Table 4. SAI values (for compressive and flexural strength).

|          | 28 Days | 56 Days |
|----------|---------|---------|
| Mix E1   | 0.38    | 0.38    |
| Mix EF1  | 0.63    | 0.63    |
| Mix E2   | 0.70    | 0.70    |
| Mix EF2  | 0.73    | 0.73    |
| Mix E3   | 0.53    | 0.53    |
| Mix EF3  | 0.68    | 0.68    |
| Mix E4   | 0.78    | 0.78    |
| Mix EF4  | 0.68    | 0.68    |

Values of SAIc at 56 days were evaluated for the “Mixes EF”, and they are lower than
those for 28 days; particularly, the a. v. decreases to 0.57, with a st. dev. = 0.07. This result
is due to a more pronounced strength gain of the reference mixes over time than in those
containing the MSWI BA, as shown in Figure 3, which displays the compressive strength
for reference and “Mixes EF” mortars. Indeed, “Mixes EF” display less strength increase
than reference mixes, despite the \( w/b \) ratio adopted.

![Figure 3. Compressive strength of reference and MSWI BA (0–1 mm) mortars at 28 d and 56 d.](image-url)
3.2. $k$-Value of MSWI BA Mortars

The efficiency of the mortars is evaluated using the Δ$w$ method, obtained starting from the equations shown in Figure 4. Here, the $k$-value is determined for each $w/b$ ratio of the (0–4 mm) MSWI BA, and it is plotted in Figure 5. Results highlight how the best efficiency is obtained for mortars having the lowest $w/b$ ratio, and those values are similar to those typical of PFA and GGBFS, but lower than SF. Indeed, according to reference [34], $k$-values of supplementary cementing materials used at 25%w (with cement at 75%w) range from 0.1 up to 1.4 at 28 days, for a reference mortar realized with $w/b = 0.5$ and aggregate/cement ratio = 3. The highest values refer to high-calcium fly ash of high sulfur content and low-calcium fly ash, whereas the lowest values are typical of nickel slag, Milos earth and diatomaceous earth. However, it is worth observing that the efficiency of MSWI BA is almost null when the $w/b$ ratio is high.
3.3. Conductivity Test

The first measure of the solution without any ash addition revealed a conductivity value of 14 mS/cm, whereas the second measure, at 120 s from the addition of the MSWI BA, was about 7.30 mS/cm. The measure was repeated in triplicate, showing similar results. According to the classification provided by Luxán et al. [33], when the variation of the conductivity in this time window exceeds 1.2 mS/cm, the material can be classified as pozzolanic. However, it should be recalled that several studies indicated this test might provide approximated results [54], as it does not consider the presence of soluble salts in non-natural pozzolans, and thus should not be used as a conclusive test method.

3.4. Frattini Test

The test provides the values of the \([Ca]^{2+}\) and \([OH]^-\) oxides, which decrease in the solution as a consequence of the calcium hydroxide depletion after the pozzolanic reaction. Such values are then plotted in a graph together with the lime saturation curve: the experimental values measured here lay below this curve, indicating that the material can be considered active, and thus, it displays pozzolanic activity. The result is illustrated in Figure 6, together with the values typically displayed by other pozzolanic materials, i.e., metakaolin, PFA and silica fume [35]. Further, Figure 6 displays the results of the tested cement, used to realize the mortars, which is a cement CEM II/A-LL 42.5 R type, including metakaolin, PFA and silica fume [35].

Seven cement pastes were tested to evaluate the initial and final setting time. Results are listed in Table 5, where the time values are expressed in minutes. It is worth highlighting how cement replacement with a large amount of MSWI BA reduces significantly the initial and final setting time, with a decrease of about \(-70%\) and \(-62%\) respectively, at 50%w replacement ratio. Conversely, at a low substitution rate, i.e., at 10%w, the initial setting time increases by about 40%, with few reductions as regards the final setting (\(-10\%\)). The results obtained here can be justified according to the mineralogic composition of the raw MSWI BA, which displays some relevant XRD peaks corresponding to mayenite, a mineral that hydrates very quickly and is responsible for rapid-strength gain in some calcium-aluminate cements [47,55,56]. Mayenite is a crystalline phase that has been detected in other materials such as iron slags [58,59]. Particularly in the second case, its presence has been associated to a reduc-tively impermeable shell around the slag particles [62].
bottom ashes too, e.g., in references [38,57], and in ladle furnace slags [58,59]. Particularly in the second case, its presence has been associated to a reduction in the setting times of pastes [60,61] and flash set phenomena [48], which typically hinder strength development at a higher age because of the formation of a hard and relatively impermeable shell around the slag particles [62].

Table 5. Setting time of cement pastes with MSWI BA.

| Initial Setting (min) | Final Setting (min) |
|-----------------------|---------------------|
| Reference             | 205                 |
| MSWI BA 5%w           | 245                 |
| MSWI BA 10%w          | 285                 |
| MSWI BA 15%w          | 255                 |
| MSWI BA 20%w          | 205                 |
| MSWI BA 25%w          | 135                 |
| MSWI BA 50%w          | 65                  |

Table 6 lists instead the results of compressive strength tests carried out on the same cement paste mixes at 28 days: it is possible to clearly see how the mechanical strength is severely affected when high replacement ratios are used. Indeed, for a 50%w replacement ratio, about 50% strength loss is displayed. However, when small amounts of MSWI BA are added as a substitute for cement, the strength does not change significantly, and for up to a 10% replacement ratio, even a slight strength enhance is instead observed. Such results almost agree with those of setting times: indeed, it is argued that replacing huge amounts of cement with the MSWI BA induces flash set phenomena, due to the rapid hydration of mayenite. This process leads the other particles with little available water for longer hydration and strength gain, thus inducing the severe strength loss observed. Instead, when the amount of the substitution is low (i.e., about 10%), the overall content of mayenite is not sufficient to induce any flash set, and thus, the water is available for hydration of the cement particles, and possible further pozzolanic activities can take place. Other reasons why the pastes exhibit such strength loss at replacement ratios equal to or higher than 15% might be linked to both the physical and chemical properties of MSWI BA, e.g., the weaker nature of the ash than cement, the different water demand of the particles and its less fineness.

Table 6. Compressive strength of cement pastes with MSWI BA (average values ± standard deviation).

| Compressive Strength $f_c$ (MPa) |
|----------------------------------|
| Reference                        | 48.71 ± 0.60 |
| MSWI BA 5%w                      | 49.21 ± 1.33 |
| MSWI BA 10%w                     | 49.00 ± 1.61 |
| MSWI BA 15%w                     | 38.14 ± 0.36 |
| MSWI BA 20%w                     | 36.08 ± 1.03 |
| MSWI BA 25%w                     | 34.89 ± 1.05 |
| MSWI BA 50%w                     | 23.62 ± 1.23 |

4. Conclusions

This work shows the results of an experimental campaign aimed at addressing the pozzolanic activity of a grossly grounded MSWI BA. Different test methods were used, both direct and indirect, to evaluate if their adoption allows the same judgement to be obtained. Even though the material is classified as a non-pozzolanic material, due to the insufficient
fineness and the lower SiO₂ + Al₂O₃ + Fe₂O₃ content than that typically required by the main codes, it has been demonstrated that it owns some pozzolanic potentials. Indeed, some amorphous structures and the positive outcomes of almost all the tests carried out here demonstrate that the material may be further treated to ensure an increase of its pozzolanic ability. However, the presence of mayenite in the mineralogic composition of the material may compromise the ability to realize cement-based materials with a high replacement ratio of this MSWI BA, due to the occurrence of a possible flash set. Such phenomena could avoid the longer hydration of cement particles, and thus, it may hinder achievement of the required compressive strength. At this stage, a cement replacement ratio up to 10% seems feasible to not compromise the strength gain. A further study aimed at assessing the microstructure and morphology of mortars realized with this MSWI BA may help to understand better the reactions governing the hardening phase of this material.

Author Contributions: Conceptualization, F.F. and K.B.; methodology, F.F. and K.B.; formal analysis, F.F. and F.A.; investigation, F.F., K.T., K.B., M.A.Z., F.A. and A.G.S.; resources, F.F. and C.P.; data curation, K.T. and F.A.; writing—original draft preparation, F.F. and M.A.Z.; writing—review and editing, F.F., K.T. and M.A.Z.; supervision, F.F.; project administration, C.P.; funding acquisition, F.F. and C.P. All authors have read and agreed to the published version of the manuscript.

Funding: The APC was funded by the University of Padova, Department of Civil, Environmental and Architectural Engineering—BIRD.

Data Availability Statement: Data are available at corresponding author request.

Acknowledgments: The authors would like to acknowledge Eng. Sabrina Pastore for her help during the experimental campaign.

Conflicts of Interest: The authors declare no conflict of interest.

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