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Municipal solid waste incineration bottom ash fines: Transformation into a minor additional constituent for cements

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ABSTRACT

Increasing amounts of waste are incinerated every year; therefore, the amount of Municipal Solid Waste Incineration Bottom Ash (MSWI BA) also increases. At the same time, limited landfill space and the goal of achieving a circular economy dictate the search for MSWI BA applications. Large fractions are successfully used to replace aggregates in concrete, but the MSWI BA fraction < 3 mm has several disadvantages, such as high porosity and high contamination that make its application as aggregate or cement replacement difficult. However, finding a tailored treatment can turn these fines into a potential filler material (Minor Additional Constituent, MAC, 5% w/w). This paper investigates milled fines that were produced out of MSWI BA fines (0.125–3 mm) to match the size distribution of CEM I 52.5 R and CEM I 42.5 N. They are also compared to the untreated fines (< 0.125 mm) from the same MSWI BA. The influence of milling on the fines was investigated by SEM (morphological analysis) and the leaching test to assess the potential environmental impact. Studied by isothermal calorimetry, the effect of the designed fines on cement hydration appears to be very small and the results for the mechanical performance of mortars show that all fines examined in the study might be considered as potential MACs.

1. Introduction

The amount of Municipal Solid Waste (MSW) produced worldwide is increasing annually. To date, the Netherlands generate about 500 kg per capita of MSW per year (Eurostat, 2017). Most countries incinerate their MSW in order to reduce the volume up to 90% (Wiles, 1995). The MSW incineration process results in several types of by-products, such as bottom ash (MSWI BA), fly ash (MSWIFA), and air pollution control (APC) residues (Wiles, 1995). The quantity of produced by-products is still around 1.7 million tons per year. Some of them are used in applications such as road base and pavement, but most residues are currently landfilled. However, due to the reduction of landfill space, in 2012, the Dutch Green Deal was passed. According to the Deal, by 2020, 100% of by-products such as MSWI BA should be recycled instead of landfilled. The use in protective applications will also be eliminated (Verbinnen et al., 2016).

These by-products might be of value as potential secondary building materials due to their chemical and mineralogical composition, as well as physical properties (Sormunen et al., 2017). Many researchers focus on MSWI BA (80% w/w of all residues). As MSWIFA (15% w/w) and APC (5% w/w) are severely contaminated with salts and potentially toxic elements (PTEs) (van der Bruggen et al., 1998) and thus require expensive purifying treatment before they can pass the environmental standards. MSWI BA is a much cleaner material consisting of rocks, slag, ceramics, glass, unburned wood, etc. (Aubert et al., 2006).

Different particle-size fractions of MSWI BA are potentially attractive for various applications in the field of building materials (Zhu et al., 2018). Nowadays, the coarse fraction of MSWI BA (> 3–4 mm) is widely investigated as a substitute for natural aggregates in concrete (Jurčič et al., 2006; Keulen et al., 2016). For the fine fraction of MSWI BA (< 3 mm), which accounts for 50–60% of its total mass, there are several obstacles that still impede its use as secondary building materials (Keulen et al., 2015; Tang et al., 2016).

There are three major problems related to the direct use of the MSWI BA fine fraction as aggregates. The first one is the high porosity, which increases the water demand and reduces the final product strength (concrete or mortar) (Kim et al., 2012; Lynn et al., 2016). The second challenge is metallic Al pieces in MSWI BA that can cause cracks (micro and macro) in concrete due to the formation of hydrogen gas as a result of the reaction between aluminum and the cement paste’s alkaline
environment (Aubert et al., 2004; Saikia et al., 2008). The last obstacle is PTE leaching that sometimes exceeds the legislation limits (Aubert et al., 2007; Yang et al., 2018).

To date, there are many papers devoted to solving these problems and milling of MSWI BA seems particularly promising. It can reduce porosity and remove metallic Al, while at the same time making the material small enough to function as a cement replacement. Kim et al. studied 10–30% cement replacement levels by ground MSWI BA (from an unmentioned fraction) and received unsatisfactory compressive strength of pastes (loss of the strength from 30 to 10%) mainly due to the presence of metallic Al (An et al., 2017). Chen et al. studied the effect of different MSWI BA particle size fractions (untreated) on early hydration and milling of cement and concluded that fine fractions, due to a higher sulfate content, inhibit the hydration more than coarse ones, although the difference turned out to be small (Chen and Yang, 2017). In several papers, only one replacement level (30%) was tested and the compressive strength was unsatisfactory (either the compressive strength was significantly lower (>16%), or the leaching of PTEs was too high) (Tang et al., 2016; Yang et al., 2018). For this reason, researchers have investigated additional treatments. In one study, thermally treated, ground MSWI BA in the form of a slurry with an activator (up to 4% CaCl$_2$) was investigated as a cement replacement (20–40%) and showed satisfactory results for 20% replacement levels. The same MSWI BA without an activator showed a significant decrease in compressive strength of about 40% (21 days curing) observed for a 20% replacement (Polettini et al., 2009). However, the use of chlorides in concrete is generally avoided to prevent the corrosion of rebar. There are also studies conducted on the addition of acid-treated, ground, and sieved (0.074 mm) MSWI BA at the clinker production stage (with a replacement level of up to 3.5%) (Aubert et al., 2007; Pan et al., 2008). But acid treatments generate highly contaminated waste solutions, which is not desirable.

It can be concluded that untreated milled MSWI BA without additives is unlikely to demonstrate good performance for higher replacement levels (10–20%) and that additional treatments can have other drawbacks. However, according to regulations it is possible to use a Minor Additional Constituent (MAC) in cement, which cannot exceed 5% and have to be below 125 µm in size (EN 197-1, 2000). The usage of MACs reduces the costs related to the cement production (accompanied with the reduction of the carbon footprint) while utilizing the waste material. Low replacement levels are unlikely to have a noticeable detrimental effect. The Netherlands alone produce more than 1.4 million ton of cement per year. Using MSWI BA fines as a 5% MAC replacement would make it possible to use around 70 thousand ton (more than 10% w/w) of cement per year. Using MSWI BA fines as a 5% MAC replacement would make it possible to use around 70 thousand ton (more than 10% w/w) of cement per year.

The aim of this study is to demonstrate a novel approach for treating MSWI BA fines (0.125–3 mm) via milling close to cement size and using them as a MAC replacement material. The MSWI BA fraction of 0.125–3 mm is ground in three different ways to achieve the particle size below 125 µm and match the particle size distribution to two different cement types (CEM I 52.5 R and CEM I 42.5 N). The properties of these milled fines are compared to the “natural” fine MSWI BA fraction (< 125 µm) from the same MSWI BA. A comparative analysis of chemical, physical, and morphological properties of all types of fines was carried out using ICP–AES, IC, XRF, XRD, SEM and other methods. Their effect on the cement hydration and mechanical properties of the final products (mortars) containing a 5% w/w cement replacement by MSWI BA were studied using isothermal calorimetry and a standard compressive-strength test.

2. Materials and methods

2.1. Samples and reagents

Deionized water (a Milli-Q Academic system, Millipore) was used for the preparation of all the solutions and washing. Nitric acid (69%, for analysis, ISO-grade, AppliChem Panreac) was used for all the operations with ICP–AES. All standard solutions were from High Purity Standards. ICP-AM-6 (100 mg/L of Al, Sb, B, Ba, Be, Cd, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, K, Na, Si, Pb, Ti, Sr, V, Zn) and ICP-MS-68B (100 mg/L of Sb, Ge, Hf, Mo, Nb, Si, Ag, Ta, Te, Sn, Ti, W, Zr) standard solutions were used for the calibration in the range 0.01–10 mg/L. A mixture of an ICP-AM-15 standard solution (10,000 mg/L of Na, K, Ca, and Mg), P (10,000 mg/L), and S (10,000 mg/L) was used for the calibration in the range 1–100 mg/L. A solution of Sc (20 mg/L) was prepared from a standard solution (Inorganic Ventures, 1000 mg/L) and used as an internal standard.

2.2. Methods and equipment

2.2.1. Inductively coupled plasma atomic emission spectrometry

Inductively coupled plasma atomic emission spectrometry (ICP–AES) provides rapid and highly sensitive multielement quantification of MSWI BA with high accuracy and precision (Alba et al., 1997; Saqib and Backström, 2016). An ICP–OES 5100 SVDV spectrometer (Agilent Technologies) was operated in the axial mode (auxiliary gas flow, 1.2 L/min; coolant gas flow, 14 L/min; nebulizer gas flow, 0.8 L/min). All emission lines were measured simultaneously.

2.2.2. X-ray diffraction analysis

The mineralogical composition of MSWI BA fines and cement was determined by X-ray Diffraction (XRD) using a Bruker D2 PHASER (Co tube, 1,790266 [Å]) with a LYNXEYE D detector and fixed divergence slits. The XRD measurements were performed on pre-dried (105 °C) powdered samples. Phase identification was performed using X’Pert HighScore Plus 2.2 and the PDF-2 database.

2.2.3. X-ray fluorescence

A PANalytical Epsilon 3 (The Netherlands) energy-dispersive X-ray fluorometer (EDXRF) with a 9 W/50 kV rhodium X-ray tube, and a silicon drift detector and standardless Omnian software 1.0. E was used to analyze the composition of MSWI BA fines and cement.

2.2.4. Scanning electron microscopy

Scanning Electron Microscopy (Phenom ProX, PhenomWorld) with a backscattering electron (BSE) detector with a spot size of 4.0 and a voltage of 15.0 kV was used. The samples prior to analysis were covered with a 14-nm gold layer by means of a SOP K575X Dual Turbo sputter coater.

2.2.5. Ion chromatography

Ion chromatography (IC) was selected as a standard method for measuring chloride and sulfate in leachates (Ito et al., 2008). A Thermo Scientific Dionex ion chromatograph 1100, 2 × 250 mm AS9-HS ion-exchange columns with an isocratic flow (0.25 mL/min) was used. Ion detection was accomplished by measuring a suppressed conductivity making use of an electrolytically regenerated suppressor (Thermo Scientific Dionex AERS 500 2 mm). As eluent, a 9 mM solution of sodium carbonate was used.

2.2.6. Auxiliary equipment

An XP 504 analytical balance (Mettler Toledo), 15-D0438 riffle boxes (sample splitters, CONTROLS Group), an SM-30 shaking table (Edmund Bühler GmbH), a UF 260 drying oven (Memmert), and a Multiwave 3000 (Anton Paar) microwave oven for digestion with a 60-bar rotor were used throughout. Automatic Eppendorf Research pipettes (Eppendorf International) were used for the preparation of calibration
solutions. A-class polypropylene volumetric flasks (Vitlab) with volume (50.00 ± 0.12) mL and (100.00 ± 0.20) mL and polypropylene test tubes (Axygen) were used for the preparation of calibration and test solutions.

2.3. Materials

MSWI BA fines (< 3 mm) were supplied by the municipal solid waste-to-energy incinerator plant of Mineralz (The Netherlands), where they underwent the standard washing and ferrous and non-ferrous metal removal process. The material was processed in the laboratory as depicted in Fig. 1. Prior to each sieving step fines were oven-dried (105°C).

CEM I 52.5 R and CEM I 42.5 N supplied by ENCI (The Netherlands) were used as binders for references and mixtures with ground and non-treated MSWI BA FINES (MCF, SOF-52, SOF-42, and BF, respectively). They have the same chemical composition but different PSDs.

Fig. 1 depicts the route for obtaining all the fines examined in the study. The starting material is MSWI BA fines (a fraction of MSWI bottom ash < 3 mm, washed at the factory). Further, to obtain “natural” (unmilled) fines < 0.125 mm (BF, short for “basic fines”), the initial material was sieved with a 0.125 mm sieve. The remaining material of 0.125–3 mm (BACF, Bottom Ash coarse fines) was further milled to obtain “milled coarse fines” (MCF). The material was then sieved again, and the residuals (> 0.125 mm) were sieved out because the filler should not contain particles > 0.125 mm. The last two steps consisted of the additional grinding of MCF in two ways to match the particle size of the material with the particle size of the two cements. As a result, two additional grinding of MCF in two ways to match the particle size of the cement or aggregates is their porosity and the subsequent high water demand. Milling not only reduces the particle size to the desired value, but also diminishes the rugosity of the particle surface (which contributes to the materials total SSA). In addition, during the milling process, metallic Al particles are flattened and can be removed via sieving (the residual fraction in Fig. 1).

We aimed to reach the desired particle size with as little milling as possible to minimize the cost of milling. Thus, the first milling procedure was carried out in 4 cycles (10–10–20–20 min), and after each cycle, the material was sieved through a 0.5-mm sieve to remove flattened Al particles and a 0.125-mm sieve to obtain the MCF fraction. This was done to remove softer particles that had already reached a desired size while harder ones were ground for longer to guarantee a uniform particle size. The MCF was then milled again for 85 and 210 additional minutes (300 rpm) for SOF-42 and SOF-52, respectively, to obtain particles in the range of CEM I 42.5 N or CEM I 52.5 R. SOF-52 was then mixed with CEM I 52.5 R, and SOF-42 with CEM I 42.5 N.

2.4. Procedures and treatments

2.4.1. Milling conditions

One of the main challenges of using MSWI BA fines as a substitute for cement or aggregates is their porosity and the subsequent high water demand. Milling not only reduces the particle size to the desired value, but also diminishes the rugosity of the particle surface (which contributes to the materials total SSA). In addition, during the milling process, metallic Al particles are flattened and can be removed via sieving (the residual fraction in Fig. 1).

The standard leaching test (EN 12457–4, 2002) (24 h shaking, L/S 10, 200 rpm) was performed on sample groups denoted as 1–6 in Fig. 1 (3 replicates of 30 g each) as well as hydrated cement pastes containing 5% (w/w) of fines 3–6 to evaluate the level of PTEs, chloride, and sulfate. Samples 1–6 were submitted to the test as is (coarse or fine powders), and cement pastes were crushed and sieved (after 28 days curing) below 4 mm prior to testing. After the test, the leachates were filtered through 0.2-µm filters to prepare solutions for ion chromatography and ICP–AES (later filtrates were acidified with nitric acid (69%), for analysis, ISO grade, AppliChem Panreac).

2.4.3. Fused bead preparation

Fused beads (FB) were prepared by mixing 0.95 g of the sample (BF, MCF, and cement) with a lithium tetraborate/metaborate 2:1 flux (flux-to-sample ratio, 10:1) and lithium bromide as a non-wetting agent. Mixtures were put individually in the borate fusion oven (Claisse leNEO, Canada) for 24 min (full time of the program) at 1065°C.

2.4.4. Characterization of physical properties

Bulk densities of samples 3–6 (Fig. 1) were measured by a common pycnometer. Specific densities of samples 2–6 were measured by a He-lum pycnometer (AccuPyc II 1340). The Punke test was used to examine the water demand of powders: two types of cement, BF, MCF, SOF-52, and SOF-42 (Hunger and Brouwers, 2009). Particle size distributions (PSD) of all powders were measured by laser diffraction (Mastersizer 2000, Malvern). The absorption coefficient of 0.1 was used for

Fig. 1. MSWI BA fines used in the study.
all the materials, a particle refractive index of 1.68 was used for cement, and 1.54 for MSWI BA. The general-purpose analysis model was selected for all the materials. The specific surface area (SSA) of 4 types of fines and cement was assessed by a Micromeritics Tristar II 3020 analyzer (software, TriStar V1.03) using a single-point BET technique by volumetric nitrogen adsorption at 77.35 K. The Loss On Ignition (LOI) was estimated by heating all powders to 1000 °C to a constant mass.

2.4.5. Early day (72 h) hydration

The effect of MCF, BF, and SOF-52 as a partial replacement of cement in cement mixtures (0 and 5% w/w replacement) on the hydration process was studied by isothermal calorimetry (TAM AIR calorimetry). Mixtures were prepared with a water/powder ratio of 0.5. The additional reference used in the study was a sample containing 5% w/w quartz powder to control for the filler effect. The experiment was only performed on CEM I 52.5 R because the effect is easier to observe in a more reactive cement.

2.4.6. Mortar preparation

Mortars with cement-fines mixtures were prepared according to EN-196-1. A reference batch was made from 450 g of cement, 225 g of water, and 1350 g of sand. The batches containing 5% w/w of the cement replacement had 22.5 g of fines (MCF, BF, SOF-52, or SOF-42) and 427.5 g of cement: the rest of the recipe was the same. The mortars were prepared in Styrofoam molds and cured in water. All mixtures were premixed and homogenized with a vortex mixer prior to adding them to water.

2.4.7. Compressive strength

All prepared mortars (4 × 4 × 16 cm) were submitted to compressive-strength testing (Zwick Z020). All samples were tested after 2, 7, 14, 28, and 91 days of curing.

3. Results and discussion

Four types of fines were analyzed for their properties and performance in cement mortars. Along with the assessment methods, a comprehensive portrait of physical, chemical, mineralogical, and morphological properties of all studied fines is presented. (The scheme of all the experiments can be found in Supplementary Materials, Fig. S1).

3.1. Chemical properties of MSWI BA fines

3.1.1. Leaching

The leaching test on the initial materials (all types of fines and cement) was performed to estimate a potential environmental impact of the studied fines on their cement mixtures. All types of fines (Fig. 1, units 1–6) were analyzed for the leaching of PTEs, sulfates, and chlorides (Table 1). The values for BF are above the legislation limit for both anions. The BACF fraction, which was a precursor for MCF, is well below the limit for chlorides and above the limit for sulfates. Milling MCF to obtain two types of SOF resulted in a very slight increase in the leaching of both chlorides and sulfates with a decrease in the particle size.

The data for cement is presented here only for the sake of comparison. It can be seen that CEM I 52.5 R leaches a significant amount of Ba, while this is not the case for CEM I 42.5 N. CEM I 42.5 N also shows a much higher sulfate leaching than CEM I 52.5 R. The leaching of Ba$^{2+}$ and sulfate may be connected as Ba$^{2+}$ reacts with available SO$^{4-}$ to form insoluble BaSO$_4$, which removes Ba$^{2+}$ from the solution.

Regarding the leaching of PTEs of the initial fines: only BF shows leaching of Cu which is slightly above the limit (1.30 vs. 0.9 mg/kg). It is noteworthy that with an increase in the milling time, the leaching of Sb increased: for BACF it is below the detection limit; for MCF it is 0.7 mg/kg; for SOF-42, 0.80 mg/kg; and for SOF-52, 0.90 mg/kg, while the legislation limit is 0.32 mg/kg. No other excess of the legislation limit in the studied MSWI BA was observed.

As can be seen from Table 1, the leaching of sulfate and chloride shows the same trend. Increased milling time leads to an increase in leaching. This is unexpected, since the solubility of chloride especially is very high and should be independent of milling time. An explanation is the fact that more contaminated small particles from the surface quenching layer are liberated during milling (Section 3.3). This quenching layer is very porous, and these pores get filled with the water used for MSWI BA quenching after incineration. The water tends to accumulate large quantities of chloride and other elements, because it is constantly reused. During drying and weathering, the porosity is...
partially closed, which creates small pockets inside the quenching layer that are rich in Cl. Normal washing is only partially effective in removing this physically trapped Cl, but it is made accessible by breaking up this layer during milling. This finding is consistent with literature (Alam et al., 2020; Marchese and Genon, 2011).

### 3.1.2. Main oxide composition of fine MSWI BA

The main oxides of the investigated fines (BF and MCF) are depicted in Table 2. The compositions of SOF-42 and SOF-52 are the same as that of MCF because they are produced from the same material. CEM I 52.5 R and CEM I 42.5 N are also almost identical.

The most obvious differences are in SiO₂ and CaO contents. Both types of fines (BF and MCF) contain significantly lower amounts of CaO; 3 and 4 times, respectively, than cements. A large amount of it is present in the form of calcite. The SiO₂ in MSWI BA fines is mainly present in the form of quartz (whose contribution to the hydration process is limited to providing nucleation sites only (Lawrence et al., 2003)).

The LOI should not exceed 5% in cement (CEM I 52.5 R). Thus, all tested types of MSWI BA fines can be safely used. For MCF, SOF-42, and SOF-52, the LOIs in the case of 5% additions is approx. 1.8%, which is well below the standard requirement limit (max. 5%).

#### 3.1.3. Mineralogical composition of MSWI BA fines

As can be seen from Figure 2, these two MSWI BA fractions (MCF and BF) differ slightly. The predominant mineral of both fractions is quartz, which agrees with previously published works, as well as the results of XRF analysis (Loginova et al., 2019; Minane et al., 2017). In both fractions, various iron-containing minerals, such as magnetite, hematite, and wustite, are present in noticeable amounts (Wei et al., 2011). Of the calcium-containing minerals, calcite, gypsum, anhydrite, and bassanite are found in both fractions, and in the BF fraction they appear to be present in larger quantities, which correlates with XRF data (Section 3.1.2) and the literature (Johnson and Furrer, 2002). Silicates of different types, such as feldspar, pyroxene, and mellite are also present in small quantities in both fractions (Dabo et al., 2008).

#### 3.2. Physical properties of MSWI BA fines

Bulk and specific densities, water demand, PSD, and SSA were determined for all four types of fines (BF, MCF, SOF-42, and SOF-52) and cement (both types) for comparison (Table 3).

Water demand is an important parameter to consider for cement replacement materials such as MSWI BA. A high water demand will either lower workability or increase the water/binder ratio resulting in strength loss of the final product. Table 3 shows that the water demand of BF is two times larger than that of cement, and all milled fines (MCF, SOF-42, and SOF-52). Noteworthy, with a decrease in the particle size during milling, from MCF to SOF-42 and SOF-52, the water demand increases slightly, while the SSAs seem to decrease with the milling time. However, the SSA of SOF-52 is slightly higher than of SOF-42. This can be explained by the complex nature of particle interaction, which would ensure random agglomeration and breaking of those agglomerates. As mentioned in the previous sections, the unmilled MSWI BA particle normally has a solid core with a very fine particle layer attached to it. Presumably, the particles from this layer are being liberated during the milling, and then agglomerate (Caprai et al., 2018a). The agglomeration might be due to the changes in the ratio of sulfate and OH-groups that are generated appearing during milling (Patil and Anandhan, 2015; Wilińska and Pacewska, 2018). There is no literature found on these phenomena occurring with MSWI BA. However, similar observations have been mentioned in the literature with such materials as pulverized coal fly ash or clay. The emergence of such new mechanochiral groups may also result in binding very fine particles together (agglomeration, Section 3.3) (Sadique et al., 2013; Vdovic et al., 2010).

In turn, all this might affect the availability of groups responsible for «wetting» the particles and nitrogen adsorption (in the BET measurements of the SSA) due to a presumed difference in the availability of the functional groups prone to react covalently (e.g. those that participate in the nitrogen exchange in BET), and groups responsible for adhesion of the water molecules. Therefore, we see a decrease in SSA, while the water demand changes little (Wei et al., 2011). This effect of milling on selective physicochemical activation is worth further studies.

Comparing SSA values of unmilled BA shows that the value for MCF is about 6 times higher than for cement, while the original fines (BF) have an SSA that is ca. 13 times higher. Such a high SSA in the latter case can be caused by either a high surface area due to small particle size or high porosity of the particles or both. In the case of BF, the high porosity appears to be the main contributing factor, because natural MSWI BA fines (< 0.125 mm) contain only the porous outer layer of MSWI BA that was removed from larger particles during the treatment at the plant (Alam et al., 2020). The high porosity is expected to have no negative effects on the water demand/workability at MAC replacement levels. It may even be beneficial in terms of internal curing to reduced shrinkage (Al Saffar et al., 2019), but more research is needed to determine this effect.

Fig. 3 (left part) shows that the PSDs of all fines are quite different.
from cement. MCF contains significantly larger particles ($d(0.5) = 39$ μm, $d(0.9) = 140$ μm) than cement ($d(0.5) = 11$ μm, $d(0.9) = 26$ μm) but the condition that all particles should be in the range of < 125 μm was met (Bentz et al., 1999). It can also be seen that the PSD of MCF is closer to the cement PSD than the non-treated BF.

Fig. 3 (right part) shows that the PSD of SOF-42 is close to the PSD of CEM I 42.5 N ($d(0.5) = 20$ μm, $d(0.9) = 72$ μm vs. $d(0.5) = 20$ μm, $d(0.9) = 72$ μm for CEM I 42.5 N). However, with increasing milling time from MCF to SOF-42, the amount of relatively large particles barely changes, while the number of small particles (1–10 μm) increases.

Even though the $d$-numbers appear to be close to those for cement (for SOF-52 $d(0.5) = 13$ μm, $d(0.9) = 46$ μm vs. for CEM I 52.5 R $d(0.5) = 11$ μm, $d(0.9) = 26$ μm), PSDs differ significantly.

### 3.2.1. Morphological properties of all fines

Changes in MSWI BA particles during the milling are shown in Fig. 4. The upper left image is a representative particle from the original MSWI BA fraction of 0.125–3 mm. It has an irregular shape and is covered with a rough layer with high porosity previously reported as a “quenching layer” (Inkaew et al., 2016). The upper right image is MCF, i.e. the material after the first stage of the initial milling of BACF. A smaller particle is visible that is still covered in a quenching layer. In SOF-42 (Fig. 4, lower right), the size of particles has decreased significantly. In any case, both SOF-42 and SOF-52 show a cleaner particle surface free from the porous quench layer. This effect explains the reduction in SSA with increased milling time (Table 3). Similar behavior has been reported previously with MSWI sludge (Caprai et al., 2018). Thus, it is likely that milling not only decreases the particle size due to fracturing, but also peels off small porous particles from presumably harder particles that then agglomerate themselves. This is consistent with the more pronounced bimodal size distribution of the fines on an increase in milling time (Section 3.2).
3.3. Effect of MSWI BA fines on cement hydration

Fig. 5 depicts the effect of different types of MSWI BA fines (MCF, SOF-52, and BF) on the hydration of cement pastes. Cement with 5% quartz is used as a reference with the same water/cement ratio. The difference between all fines is small and no significant negative effect on the hydration rate is observed at these replacement levels. Some delay could have been expected due to the presence of sulfates in the fines, but peak shapes and the absence of additional peaks indicate that there are no side reactions associated with a higher sulfate content in MCF compared to cement (2.83% for cement vs. 5.3% for MCF, 9.9% for BF, and 6.1% for SOF-52) (Pelletier-Chaignat et al., 2011).

Fig. 5 also shows that the cumulative heat (normalized per cement) is the lowest for BF, suggesting that even though it does not lower the rate of cement hydration, it has a negative effect on the reaction degree. MCF shows the highest cumulative heat for reasons that are unclear. A higher cumulative heat could have been expected for SOF-52 as it has the smallest particle size and could therefore be more reactive. But it is possible that the milling and the associated removing of the quenching layer releases not only more sulfate but also other components such as organic matter that have a negative influence.

3.4. Leaching properties of hardened pastes containing MSWI BA fines

Even though the initial MSWI BA fines contain some contaminants above the legislative limit, all pastes containing 5% (w/w) fines did not exceed the legislative limit after 2 and 28 days of curing. The concentrations of PTEs and anions are much lower than the limits or below the detection level and are therefore not shown.

3.5. Mechanical properties of mortars containing MSWI BA fines as a filler

The suitability of fines to be used as a MAC was assessed by testing mechanical properties of mortars containing MCF, BF, SOF-42, and SOF-52 (Fig. 6). After two days of hydration, SOF-52 shows the best results and reaches a compressive strength similar to the reference (100% cement), while MCF and BF are slightly lower and comparable to one another. All the samples are above the standard value for this type of cement (30 MPa). After 7 days, SOF-52 becomes comparable with the reference, and BF is noticeably lower. At 14 days, the difference between the reference and MCF becomes more obvious (as well as for BF). After 28 days, all the samples with additives are noticeably below the...
4. Conclusions

Four types of MSWI BA fines were analyzed to assess their suitability and limitations as MAC in cement: “BF”, unprocessed fines < 0.125 mm (washed at the plant), and 3 derivatives from a fraction of “coarse” fines (0.125–3 mm); MCF (Milled Coarse Fines), SOF-42, and SOF-52 (Size Optimized Fines for CEM I 42.5 N, and CEM I 52.5 R, respectively). These fines were milled in three different ways to achieve a size distribution close to that of two types of cement.

Among the analyzed fines, MCF and SOF-52 gave the best results regarding compressive strength. However, MCF generates a slightly higher heat flow as measured with calorimetry. SOF-52 shows worse results (strength) but taking into consideration that the material preparation is more intense, perhaps its use will not be justified (at least for such a percent of the additive). However, SOF-42 showed better results for the respective type of cement reducing the compressive strength of the sample at 28 days only for 2%. That might be due to the fact that CEM I 52.5 R is finer, and, therefore, more reactive than CEM I 42.5 N, any additional reactions/interactions would result in more noticeable (harmful for the strength properties) effects. Ergo, it is necessary to study this phenomenon further. Regarding the application of BF, it is necessary to take into account relatively high concentrations of certain metals (total composition) (Loginova et al., 2019) which might exceed the limitations for cement even being added in small amounts.

The main results of this study can be summarized in the following:

- Mechanical treatment for the MSWI BA fraction of 0.125–3 mm was applied in several steps to generate fines that have a similar size distribution as CEM I 42.5 and CEM I 52.5 and can be used as a MAC, while also reducing the porosity of the fines and removing metallic AI particles.

- The mechanical treatment results in polishing MSWI BA particles by removing the attached quenching layer from larger particles along with an overall size reduction. The breakup of the quenching layer results in increased leaching of chlorides and sulfates, while the surface area of the material decreases probably due to the agglomeration of small particles removed from the quenching layer.

- The hydration study has proven milled coarse MSWI BA fines (MCF) to be contributing the most to the cement hydration (+5% cumulative heat), while the “natural” unmilled fines (BF < 0.125 mm), slightly hindered the hydration (~2.5% cumulative heat) during the first 72 h.

- The compressive strength decrease for 28 days is 7% for milled coarse fines, 9% for non-treated fines, 11% for size optimized fines (for CEM I 52.5 R), and 7% for size-optimized fines (for CEM I 42.5 N). All the mortars showed the compressive strength above the standard with a minimum value of 58.5 MPa for a mixture with CEM I 52.5 R, and 49.1 MPa for a mixture with CEM I 42.5 N.

- The use of MCF fraction “as is” appears to be most suitable for a MAC application. Further milling to produce SOF-42 and SOF-52 does not appear to be beneficial based on the compressive-strength results. This is positive, as less energy and effort are required to produce this fraction. However, to fully support the validity of this statement, a lifecycle analysis must be performed.

- Physical, chemical, and mechanical properties suggest that all types of fines might be considered as potential MACs; however, milled coarse fines appear to be most desirable from two viewpoints: (i) its effect on the cement hydration, and, therefore, mechanical properties and (ii) its low environmental impact.

To ensure the suitability of milled MSWI BA fines, the inevitable next step would be a full-scale analysis. This would include testing at least two ways of the cement-BA mixtures preparation; the first one would be as described in the study, and the second one is a combined milling of the clinker with the MSWI BA fraction. However, it should be considered that the clinker–BA milled mixture would require the sieving procedure, unless the combined milling is not performed on already milled and sieved MSWI BA because this is a vital step to remove Al particles. Furthermore, the cement-BA mixture should be tested in concrete rather than in mortars. The finalization of this research would be a life cycle assessment of the costs including additional sieving and milling.

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Fig. A1. Compressive strength of mortars (CEM I 42.5 N) containing 0 and 5% w/w of SOF-42.

CRediT Author Statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial
interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials


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