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Research article

Evaluation of the influence of mechanical activation on physical and chemical properties of municipal solid waste incineration sludge

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ABSTRACT

Despite numerous studies concerning the application of by-products in the construction field, municipal solid waste incineration (MSWI) residues are not widely used as secondary building materials. In some European countries, washing treatment to the full bottom ash (BA) fraction (0–32 mm) is applied, isolating more contaminated particles, smaller than 0.063 mm. Therefore, a MSWI sludge is produced, having a high moisture content, and thus a limited presence of soluble species. In order to enhance its performance as building material, here, dry mechanical activation is applied on MSWI sludge. Thereafter, a reactivity comparison between reference BA and untreated and treated MSWI sludge is provided, evaluating their behaviour in the presence of cement and their pozzolanic activity. Moreover, the mechanical performances, as 25% substitution of Portland cement (PC) are assessed, based on the EN 450. Mechanical activation enhances MSWI sludge physically due to the improved particle morphology and packing. Chemically, the hydration degree of PC is enhanced by the MSWI sludge by about 25%. The milling treatment proved to be beneficial to the residues performances in the presence of PC, providing 32% higher strength than untreated sample. Environmentally, the compliance with the unshaped material legislation is successfully verified, according to the Soil Quality Decree.

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1. Introduction

In recent times, the management of municipal solid waste (MSW) has become important to guarantee an economically and environmentally sustainable way of living. After collection, MSW is initially processed in waste-to-energy plants, by incineration. The created municipal solid waste incineration (MSWI) residues consist of various products such as bottom ash (BA) (80% wt.), grate siftings, heat recovery ash, fly ash and air pollution control residues. Despite the risk of releasing harmful substances into the soil (Sabbas et al., 2003; Florea, 2016), in the EU, BA is usually applied for road construction or landfilled (Allegrini et al., 2015; Forteza and Far, 2004; Hjelmar, 1996; Lam et al., 2010; Lin et al., 2012). Due to the increasing environmental concern, since 2011, the Netherlands defined stricter limitations for leaching of contaminants from landfilled materials (Soil Quality Decree, 2015), aiming to reduce the number of landfilling sites and to address the design of secondary raw materials from incineration by-products (Zhen et al., 2013). Nowadays, various applications of bottom ash (BA) in the construction field have been studied (Bertolini et al., 2004; Boesten et al., 2012; Polettini et al., 2009; Revathi et al., 2014). Among them, the application of BA as inert replacement of Ordinary Portland Cement (PC) has found successful, up to 30% of the binder mass (Kula et al., 2002; Tang et al., 2014a; Targan et al., 2003). Before being reused, BA undergoes additional treatments, such as removal of ferrous and nonferrous compounds, in order to achieve a more homogeneous and less contaminated material (Keulen et al., 2012). Among these procedures, a washing separation treatment is applied to the full fraction of BA (below 32 mm), isolating most of the incineration residues smaller than 0.063 mm, generally more contaminated (Biganzoli, 2012; Alam et al., 2016). Therefore, a MSWI sludge is produced characterized by a high moisture content (MC), and consequently limited ions available for dissolution. Due to the restrained application of this washing separation treatment, the use of MSWI sludge as secondary building material is generally not taken into account outside the Netherlands. Consequently, to the authors’ knowledge, the investigation of MSWI sludge is not extensively performed, due to the low availability of the by-product in Europe. Furthermore, the storage conditions of MSWI sludge lead to particles agglomeration, increasing the particle size of the supplied material. As mentioned,
due to the source of this by-product, the monitoring of contamina-
tion levels and leaching is also a concern. In addition to this, the
initial MC of MSWI sludge favors the dissolution of soluble phases,
reducing the final reactivity of the by-product.

The suitability of a by-product as cement replacement is linked
to its chemical and physical contribution to the PC hydration. In
general, the reactivity of ashes is affected by many aspects, from
the source of the waste to its collection and disposal. In the case of low
reactivity ashes, many studies propose activation treatments to
increase the final dissolution of particles (Cherif et al., 1999; Onori
et al., 2011; Polettini et al., 2009; Qiao et al., 2009, 2008; Tang et al.,
2014b). There are three main methodologies applied for this pur-
purpose: thermal, chemical and mechanical activation (MA). Thermal
activation is not suitable from an environmental point of view, due
to the high incineration temperature (between 800 °C and 1500 °C)
(Hernandez-Montoya et al., 2012; Zen et al., 2013). Chemical
activation of MSWI residues is not always possible, due to the po-
tential high organic content of the by-products (Fernandez-Jimenez
and Palomo, 2003; Sathonsaowaphak et al., 2009). Therefore,
economically and environmentally, the most sustainable method
for increasing the reactivity of ashes is MA. Generally, MA improves
the bulk and surface area of the solid through physicochemical changes
(Kumar and Kumar, 2011), which might lead to the
acquisition of additional pozzolanic activity. However, the minera-
alogical changes are not always remarkable in case of MA of ashes
(Temuujin et al., 2009). Its application is beneficial also due to the
formation of smaller less reactive particles (external core of coarser
particles), which act as a filler among cement grains (Hela and
Orsáková, 2013). Increasing the fineness, the prolonged grinding
raises the amount of active centres with higher energy state respect
to the rest of the structure. The more of those sites, the faster the
rate of reactivity in the presence of PC (Onori and Polettini, 2011;
Sajedi and Razak, 2011; Temuujin et al., 2009). Until now, the
application of MA on MSWI sludge has not been deeply investig-
gated. However, the improvement achieved can lead to perfor-
mances comparable to BA fines, favouring the application of MSWI
sludge in the construction field. Since the behaviour of BA fines as
cement replacement has been more extensively studied, a com-
parison with this residue provides a useful reference for the eval-
uation of MSWI sludge performances.

This study provides an evaluation of the influence of MA on
MSWI sludge, compared with reference fines of two streams of BA.
The enhancement of MSWI sludge properties aims to achieve
comparable results with BA in mechanical and environmental
performances, in order to provide an alternative application for this
municipal residue. Firstly, the by-products provided by Heros
Sluiskild (NL) are characterized physically and chemically. Addi-
tionally, the MA treated sludge is compared to the untreated
material and reference BA, regarding the impact of the MA on
physical properties. Thereafter, this paper will address the reac-
tivity of the two reference streams of BA and MSWI sludge (before
and after MA), based on the pozzolanic activity index and by
isothermal calorimetry analysis. Finally, the application of the by-
products as secondary building materials is evaluated by the
strength activity index and by the one stage batch leaching test, for
the compliance to the Dutch SQD legislation for the unshaped
(“Soil Quality Decree,” 2015).

2. Experimental

2.1. Materials

Three different streams of MSWI residues are considered in this
study: two types of bottom ash fines (BA1 and BA2) and MSWI
sludge (Ss), all coming from Heros Sluiskild (NL). All the MSWI
residues are characterized by a particle size below 0.250 mm. After
dividing the BA full fraction in a coarse and a fine particle size
streams (Bac and Baf, respectively), a wet separation treatment is
initially applied to produce sludge, by removal of fine residues from
the Bac. The MSWI sludge is further processed by using a centrifuge
to limit the water content of the final product. In parallel, the fine
size stream (Baf) is fractioned and particles below 0.250 were
isolated (BA1). Part of the BA1 is further clean, by air separation
removal, limiting the presence of the ultrafine ash particles,
forming BA2. Due to the agglomeration of particles caused by the
storage conditions, the application of Ss as untreated material is not
possible. Hence, in this study, an implementation by MA was
attempted for this residue, and compared with the two BA streams,
for evaluation. The pozzolanic activity of BA1, BA2 and MSWI sludge
was evaluated in the presence of calcium hydroxide (CH) (CH ≥ 96%
pure, Fluka Analytical), CEM I 42.5 N (PC) and inert standard sand
(98% SiO2, Norm sand, ISO 679, EN 196-1). The analysis of reactivity
was performed without any additional laboratory treatment, since
the washing processing might affect the final dissolution rate of the
by-products in water.

2.2. Methods

2.2.1. Characterization of the raw materials

Firstly, all materials were dried at 50 °C for 72 h, to constant
mass. The PSD was measured by laser diffraction (Mastersizer 2000,
Malvern). The specific gravity of the dry powders was tested by
Helium pycnometer (AccuPyc II 1340), while the bulk density by a
conventional pycnometer. The chemical composition of the by-
products was determined by X-ray Fluorescence spectrometer
(PAnalytical Epsilon 3 range, standardless OMNINAN method), on
pressed powder. The specific surface area and total pore volume
were measured using nitrogen adsorption measurements (Micro-
ermetics, Tristar II 3020 V1.03). The water demand of the powders
was measured by the Punkté test (Hunger and Brouwers, 2009).
Information about the morphology of the particles was provided by
Scanning Electron Microscopy (SEM, Quanta 650 FEG, FE). The
analysis was performed in high vacuum, at chamber pressure of
0.6 mbar, spot size 3.0, voltage 20.0 KV and in low vacuum by
coupling large field detector, GSED detection (LFD) and BSE-
detector, at chamber pressure 0.6 mbar, spot size 4.0, voltage10 KV.
The quantification of CaCO3 was computed from the CO2 mass loss
between 640 and 740 °C (Gabrovsek et al., 2006), with thermog-
ragimetric analysis (TGA), using Jupiter STA 449 F1, Netzsch, heating
rate 5 °C/min, purged with N2 and synthetic air. The evaluation
of the metallic Al content was performed by treatment in alkaline
environment (3 M NaOH solution) for 24 h (Porciúncula et al.,
2012). The loss of ignition was evaluated by heating the samples
to 1100 °C for 4 h and measuring the mass loss at constant RH. The
evaluation of the Ca2+ ions dissolution in the presence of water was
measured by ion chromatography (IC) (Thermoscientific Dionex
ICS-1100), after 1 h, at 20 °C.

2.2.2. Mechanical activation treatment of MSWI sludge

The MA of Ss was carried out using a Fritsch Pulverisette 5
planetary ball mill, at a constant speed of 200 rpm. Bottom ash
particles are characterized by a rigid inner core, mainly composed
of stony or glassy material, and a surrounding loose coating layer
in the order of few hundred microns, composed by ultrafine ash
particles. Due to its structure, composed by light materials as
organic matters, fine melt glass and remnants of metallic matter,
this layer is defined as “fragile zone” and it contributes to the in-
crease of the final porosity in BA particles (Saffarzadeh et al., 2011).
Due to the presence of these dust-like residues on the Ss particles
surface and its fine PSD, zirconia grinding balls size 10 mm were
chosen. This setup aimed to limit the further increase of specific surface area (SSA), by avoiding high speed collisions caused by the use of high rotational speed and balls size. The excessively high SSA would further increase the water demand of the blended mixtures, preventing its application in cementitious systems. A material to media ratio 1:1 by weight was maintained during the MA (according to the instruction of the planetary mill ball) and three treatment periods were selected (30, 60, 90 min). The samples were consequently named as Ss30, Ss60 and Ss90, respectively. The procedure paused at intervals of 15 min, for 5 min, to avoid overheating the sample.

2.2.3. Evaluation of the pozzolanic activity of MSWI residues

The pozzolanic activity of the considered BA streams and the treated and untreated MSWI sludge was evaluated chemically, according to the ISO recommendation R 863-1968 (Cheriaf et al., 1999), which defines the pozzolanic activity by the reduction in Ca\(^{2+}\) ions, when a pozzolan reacts in a saturated lime environment. Consequently, pastes containing 50% wt. by-product and 50% wt. CH were mixed, with a liquid to solid ratio (L/S) of 0.8 (due to the high surface area of the ashes) and named SSCH, BA1CH, BA2CH. The treated SS samples were named SS30CH, SS60CH and SS90CH, depending on the stirring time. Specimens cured at constant RH (97%) were tested by TG analysis at 7, 14, 28 days. Before each test, the pastes were placed in alcohol (2-Propanol) for 24 h to stop hydration and dried at 60 °C for 24 h. The reference (named q1CH) contained 50% wt. CH and 50% wt. quartz (q1), acting as inert material. Here, the mass loss due to water evaporation allowed the quantification of the total CH available for pozzolanic reaction in the samples. The difference between those two mass losses (sample and reference) led to the reacted CH content in time: the higher the reacted CH, the greater the pozzolanic activity of the ash. The temperature range selected for CH decomposition was 390°–460 °C (Gabrovšek et al., 2006). The use of this methodology was initially applied for fly ash and metakaolin, but it is considered suitable also for by-products (Cheriaf et al., 1999).

2.2.4. Kinetic study of bottom ash reactivity in the presence of cement

The determination of the influence of the by-products on PC hydration was investigated by Isothermal Calorimetry (TAM AIR calorimeter), at 5 days of reaction. There are two main effects involved in the replacement of PC by supplementary cementitious materials: the first is the heterogeneous nucleation effect, a physical process able to influence the chemical activity of the PC, by catalysing the nucleation process on the surface of particles, extraneous to the cementitious system (Cyr et al., 2005; Lothenbach et al., 2010). The second one is the effective influence coming from the chemical dissolution of reactive phases in the presence of water. Initially, the availability of soluble phases in water was tested, by measuring the cumulative heat on 100% by-product pastes with an L/S 0.8. Thereafter, the quantification of the heterogeneous nucleation effect (Q\(_\text{nucl}\)) was estimated by cumulative heat analysis on samples prepared by 75% PC and 25% quartz, named q1PC, q2PC and q3PC, depending on the fineness of the quartz. q1 resembled the PSD of BA1 and BA2, q2 the one of SS, while q3 mimicked the PSD of the treated samples. To define the contribution due to chemical dissolution (Q\(_\text{diss}\)), reference sample based on plain PC was tested and compared with samples prepared with 75% wt. PC and 25% wt. incineration residues (named SS3PC, BA1PC and BA2PC). Treated MSWI sludge was also tested in the same conditions, and termed SS30PC, SS60PC and SS90PC, according to the grading times. Contrary to the TGA, all the pastes were characterized by an L/S 0.5, as the reduced replacement level of the sludge in the presence of cement (25% wt.) did not affect the rheological behaviour as much as in the TG analysis, where samples are characterized by higher replacement (50% wt.). The measurement of the heterogeneous nucleation effect allows the quantification of the contribution of the chemical dissolution of the residues, using the formulas:

\[
Q_{\text{nucl}} = Q_{\text{q1PC}} - Q_{\text{PC}}
\]

(1)

\[
Q_{\text{diss}} = Q_{\text{BA}1\text{PC}} - Q_{\text{PC}}
\]

(2)

where, \(Q_{\text{nucl}}\) is the cumulative heat contribution due to the heterogeneous nucleation effect [J/g], \(Q_{\text{q1PC}}\) is the cumulative heat of plain PC [J/g], \(Q_{\text{diss}}\) is the contribution caused by the dissolution of reactive phases in BA [J/g] and \(Q_{\text{BA}1\text{PC}}\) is the cumulative heat of the mixture MSWI residues + PC [J/g]. Each contribution calculated by Formula (1) and (2) was expressed in the graph as rate of the plain PC cumulative heat. In order to evaluate the contributions of the by-products on the PC hydration, the normalization of the cumulative heat trends were based on the mass of PC. Moreover, the cumulative heat measurements were collected after 20 min from the beginning of the reaction, to avoid the influence of stirring time and ensure the stabilization of the calorimetry conditions.

2.2.5. Evaluation of the strength activity index

The slump flow of the pastes evaluated the rheological behaviour achieved before and after the grinding procedure, at different milling times. The flowability of the fresh mortars was determined using the flow table test according to EN 1015-3 (EN 1015-3, 2007). The final L/S ratio of the mortars was fixed at 0.5. In the mortars, the sand to binder ratio was 3, while the replacement level of by-products was set at 25%, by mass of the binder. The bending strength results were based on the average of three specimens, while for the compressive strength an average of six samples is provided. The mechanical performances of the same mixtures used for the slump flow were tested according to EN 196-1 (EN 196-1, 2005) and cured at constant RH (97%) and room temperature.

The curing procedure was not performed in water, to avoid the leaching of contaminants during the curing period. The compressive strength was measured for determining the strength activity index (SAI), according to EN 450. Although originally drafted for combustion coal fly ash, the standard EN 450 has also been used to assess the suitability of BA replacement in concrete in other studies (Cheriaf et al., 1999). The SAI calculation was based on the ratio of compressive strength at a specific curing time of specimens based on 75% wt. PC and 25% wt. ash by mass and the reference 100% PC. The replacement rate was fixed by the standard. Exceeding the value 0.75 defined the suitability of the BA as concrete replacement, as specified in EN 450. The calculation applied, for a time interval \(t_n\) read:

\[
\text{SAI}_{BA(t)} = \frac{\text{F}_{BA(t)}}{\text{F}_{PC(t)}}
\]

(3)

where, SAI BA is the strength activity index, \(F_{BA(t)}\) is the compressive strength of the (residues + PC) mix [MPa] and \(F_{PC(t)}\) is the compressive strength of plain mortars [MPa]. During the evaluation, three time intervals were used: \(t_1 = 7\) days, \(t_2 = 14\) days and \(t_3 = 28\) days.

2.2.6. Environmental impact evaluation

The environmental impact of all the different MSWI residues streams and 28 days mortars was addressed by the application of a leaching test procedure according to EN 12457-2 (one stage batch
leaching test) (Florea et al., 2015; Holm and Hansen, 2003) under continuous shaking (constant speed 250 rpm, 20 °C, 24 h) (ES SM-30, Edmund Buehler GmbH). The suspensions were filtered with 0.017–0.030 mm membrane filters. The analysis of heavy metals in the leachates, was performed by inductively coupled plasma atomic emission spectrometry (ICP-OES) according to NEN 6966 (NEN-EN, 2005), acidifying the samples with 0.2% HNO3 before filtration with 0.030 mm membrane filters. The analysis of chloride and sulphates concentrations, ion chromatography (IC) (Thermoscientific Dionex ICS-1100) was used. The limit for the leaching of contaminants from unshaped (granular) materials were set by the Dutch Soil Quality Decree (SQD) (Soil Quality Decree, 2015). From preliminary tests, it was used. The limit for the leaching of contaminants from unshaped (granular) materials were set by the Dutch Soil Quality Decree (SQD) (Soil Quality Decree, 2015). From preliminary tests, it was determined that the results from the one stage batch leaching test (EN 12457-2) provided higher concentrations of contaminants compared to the column test, due to the more severe testing conditions (Florea et al., 2015). Therefore, the compliance to the SQD requirements in these conditions indicated the adequacy of the leachates also for the column test, applied in the SQD. As performed in other studies (Abdel-Kader et al., 2013), the retention rate, indicating the rate of retained ions in the system after leaching test in the presence of PC, was calculated using the formula:

\[
I = \frac{(r^*L_{BA}) - (L_{BAr})}{(r^*L_{BA})} \times 100
\]

where, I is the retention rate [%], r is the replacement level (25% in this case), \(L_{BA}\) is the incineration residue leaching for the chosen contaminant [mg/Kg], \(L_{BAr}\) is the incineration residue leaching in the presence of PC [mg/Kg].

3. Results and discussion

3.1. Characterization of the material

Table 1 presents the chemical composition of the reference by-products (BA1 and BA2), PC and Ss, evaluated by XRF. All the ashes have a similar chemical composition, with an estimated equivalent content of calcium oxide between 27 and 29%, silica between 10 and 12% and alumina between 7 and 9%. This similar chemical composition allows an easier comparison among the performances of the residues. Part of the Ca\(^{2+}\) is not available for reaction because it is mostly bonded in CaCO\(_3\), formed during weathering. Excluding the calcium present in this form, the amount of the corresponding remaining calcium species (in form of oxides) is also provided in Table 1, under “remaining oxides”. The particle morphology of untreated by-products is presented in Fig. 1a). Conversely, BA1 and Ss show a similar morphology, with non-spherical particles and a disorganized structure, due to the low incineration temperatures (850–900 °C), applied by the incineration plant in comparison with other combustion systems (Lam et al., 2010). Contrary to BA2, which displays a smoother particle surface, BA1 and Ss exhibit ultrafine ash residues on the surface of the particles. The differences in the particles morphology are owed to the removal of the fragile zone, by air separation, which BA2 undergoes in the plant. Table 2 defines the physical properties of MSWI residues, in agreement with the SEM pictures. Compared to PC, all MSWI residues present a high total pore volume, maximized in the case of Ss. These data are correlated with the high water demand measured, indicating a physical capillary absorption of part of the water. The high total surface area, and thus water demand of BA1 an Ss is explained by the presence of ultrafine ashes characterizing the fragile zone layer on the particles surface, as it seems to supply effective porosity to the bottom ash particles (Inkaew et al., 2014; Saffarzadeh et al., 2011). On the other hand, the lower surface area and pore volume detected for BA2 reflects the uniform surface displayed in Fig. 1a). In general, the undefined morphology supports the low bulk density of the by-product, compared to PC (Table 2).

Fig. 2 provides the PSD of the reference by-products and materials used in the study. For MSWI sludge the agglomeration of
Table 3 illustrates the characteristic diameter sizes of the application of the treatment, in comparison with references BA1 and properties aims to determine improvement achieved after the treatment: the longer the time, the finer the distribution. However, the effectiveness in the particle size reduction is limited, as a reduction in dmin is not achieved and the shift in PSD usually observed is much greater.

Despite the different materials, Chauruka et al. (2015) also observed this “equilibrium state of milling” during the milling procedure, by using a planetary ball mill. This limited reduction in PSD is attributed to the conversion of the fines produced during grinding in coarser agglomerated particles, joined by van der Waals forces (Chauruka et al., 2015; Filio et al., 1994). During the MA, the particle zone layer, loosely attached to the BA particles, is compacted and agglomerated with other fines, creating a spherical shape. Fig. 4 shows the particle morphology of MSWI sludge samples after the grinding treatments. For comparison, the untreated MSWI sludge Ss can be visualized in Fig. 1c (Section 3.1). SEM proves the presence of spherical particles, shaped by the grinding action and result of agglomeration. Fig. 5a) provides an overview of the total pore volume and BET surface area as a function of the grinding time. Among the treated samples, the longer the milling, the lower the total pore volume and surface area. Although decreased, the BET surface area of the treated Ss is higher than the ones of BA1 and BA2.

During the MA, by agglomerating, the dust-like particles reduce the porosity of the BA, resulting in a drop in SSA due to the formation of a more polished and smooth surface (Chauruka et al., 2015). The MA mainly acts on the mesopores (between 2 nm and 50 nm), reducing the pores between 2 and 40 nm (Fig. 5b). Compared to the BA1 and BA2, the reduction in porosity of treated Ss leads to a total pore volume similar to the reference by-products (between 0.06 and 0.051 cm³/g for treated Ss and 0.06–0.048 cm³/g for BA1 and BA2, respectively). Table 4 shows the physical features of the treated MSWI sludge, for each milling time. The water demand of Ss30, Ss60 and Ss90 is reduced by around 60%, from 88.8% (Table 2) to about 25–29% (Table 4). It can be concluded that, after treatment, less water is absorbed and entrapped physically inside the porosity of the particles. An additional evidence of the

Table 2
Summary of the physical parameters of these MSWI by-products.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Bulk density g/cm³</th>
<th>Specific gravity g/cm³</th>
<th>BET surface area m²/g</th>
<th>Ca²⁺ concentration mg/L</th>
<th>Water demand % dw</th>
<th>Total pore volume cm³/g</th>
<th>MC % dw</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA1</td>
<td>0.56</td>
<td>2.44</td>
<td>17.44</td>
<td>949</td>
<td>62.40</td>
<td>0.064</td>
<td>21</td>
</tr>
<tr>
<td>BA2</td>
<td>0.56</td>
<td>3.70</td>
<td>10.23</td>
<td>593</td>
<td>53.70</td>
<td>0.048</td>
<td>21</td>
</tr>
<tr>
<td>Ss</td>
<td>0.84</td>
<td>2.55</td>
<td>34.63</td>
<td>465</td>
<td>88.80</td>
<td>0.098</td>
<td>28</td>
</tr>
<tr>
<td>Ss90</td>
<td>2.07</td>
<td>3.43</td>
<td>0.29</td>
<td>-</td>
<td>20.70</td>
<td>0.003</td>
<td>-</td>
</tr>
</tbody>
</table>

* % dw identifies the rate based on the dry mass of the powder investigated.

3.2. The influence of the mechanical activation on physical properties of MSWI sludge

The investigation of the influence of MA on the Ss physical properties aims to determine improvement achieved after the application of the treatment, in comparison with references BA1 and BA2. Table 3 illustrates the characteristic diameter sizes of the residues, before and after milling treatment. Starting from the original material, the 30 min grinding affects the fineness of smaller particles, as a reduction is mainly observed for particle diameters smaller than 20 μm. Longer treatments (60 and 90 min) alter the distribution of coarser particles, resulting in 90% of the material finer than 70 μm and 50 μm, respectively. On the other hand, the minimum diameter dmin is not affected by longer milling times. The different particle size distributions achieved after MA are displayed in Fig. 3. The reduction of PSD is directly linked with the time of treatment: the longer the time, the finer the distribution. However, the effectiveness in the particle size reduction is limited, as a reduction in dmin is not achieved and the shift in PSD usually observed is much greater.

Table 3
Characteristic sizes (dmin, d₅₀, d₉₀, d₉₀ and d₃₉₅) of the untreated samples and samples milled for different time intervals (30, 60, 90 min).

<table>
<thead>
<tr>
<th></th>
<th>dmin μm</th>
<th>d₅₀ μm</th>
<th>d₉₀ μm</th>
<th>d₉₀ μm</th>
<th>d₃₉₅ μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ss</td>
<td>0.4</td>
<td>3.1</td>
<td>23.4</td>
<td>78.5</td>
<td>261.5</td>
</tr>
<tr>
<td>Ss30</td>
<td>2.8</td>
<td>21.8</td>
<td>78.2</td>
<td>174.1</td>
<td></td>
</tr>
<tr>
<td>Ss60</td>
<td>1.7</td>
<td>17.2</td>
<td>70.3</td>
<td>174.1</td>
<td></td>
</tr>
<tr>
<td>Ss90</td>
<td>1.7</td>
<td>16.8</td>
<td>49.5</td>
<td>115.9</td>
<td></td>
</tr>
</tbody>
</table>
agglomeration phenomena is provided by the increase of bulk density of the powders, testifying an improved packing due to the spherical particle shape obtained after treatment.

3.3. Evaluation of the pozzolanic activity

The influence of MA on pozzolanic activity is investigated to evaluate the modification in chemical reactivity after the treatment, for late strength development. Fig. 6a)–c) provides an insight into the pozzolanic activity of the incineration residues, by CH consumption in time. In general, calcium ions are responsible for the aggregation and gelation processes, as they could either (a) react with silicates and aluminates, (b) replace cations within the geo-polymers, or (c) precipitate as CH (Guo et al., 2010). The carbonation of the free Ca\(^{2+}\) ions is frequently observed after exposition to the ambient conditions. Therefore, for every sample, the total mass is divided by the mass of the residues and the CH content, as reacted, unreacted and carbonated during the curing time.

After 7 days reaction (Fig. 6a), SsCH shows the greatest pozzolanic activity (17.6%) among to the by-products, due to its high surface area available for dissolution (Table 2, Madani et al., 2012). The similar physical properties support the high CH consumption observed also for the Ss30CH, Ss60CH and Ss90CH (14.3%, 14.7% and 16.4% respectively), within this time frame. Although the pozzolanic activity of SsCH is fluctuating due to heterogeneity of the sample, increasing rate of the "CH reacted" is observed at 14 days for every by-product. The milling treatment does not provide additional dissolution of pozzolanic phases within 14 days, as a similar rate of CH reacted is observed for treated and untreated samples (12.4% against 14.0%, 15.2% and 17.1% respectively). This

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk density g/cm(^3)</th>
<th>Specific gravity g/cm(^3)</th>
<th>Water demand %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ss30</td>
<td>0.97</td>
<td>2.44</td>
<td>25.4</td>
</tr>
<tr>
<td>Ss60</td>
<td>1.02</td>
<td>2.47</td>
<td>29.8</td>
</tr>
<tr>
<td>Ss90</td>
<td>1.07</td>
<td>2.46</td>
<td>28.4</td>
</tr>
</tbody>
</table>

* Water demand is expressed by dry mass of the powder.
difference is considered within the experimental error. Within 28 days, the "CH reacted" content in the treated samples is rising, achieving between 16.4 and 20% of the sample mass. On the other hand, the "CH reacted" content results decreased in the untreated and reference mixture (SsCH and BA2CH), leading to an increase of the unreacted CH content by 8.3% and 15.8% respectively, compared to 14 days results. It appears that the decreasing concentration of pozzolan leads to the saturation of the solution with respect to CH and its consequent precipitation. Although it requires specific conditions, the precipitation of CH is a phenomenon taking place also during PC hydration. It takes place at a pH of 12.5–12.8 (Mohammadi et al., 2012) and it occurs in the matrix porosity,
when the saturation with respect of Ca$^{2+}$ is reached in the pore solution. The ions concentration to generate a saturated Ca$^{2+}$ solution is indicated to be around 22 mmol/L (Bullard, 2008). In the analysed system, the presence of those conditions can also occur. Although CH is usually considered as a weak base, MSWI by-products are able to rise p$H$ of water, due to the dissolution of alkalis like Na$^+$ or K$^+$ (Ahn et al., 2007). Therefore, both CH and MSWI residues contribute to the creation of the alkaline environment, suitable for the CH precipitation. Moreover, the presence of soluble Ca$^{2+}$ species dissolved from BA1, BA2 and Ss favours the achievement of the optimum concentration for the CH precipitation (Table 2), while their high porosity of the by-products favours the formation of pores within the matrix. The precipitation of CH has the negative effect of lowering the $pH$ of the alkaline solution, due to the removal of OH$^{-}$ ions, which will compromise the further dissolution and precipitation process (Millogo et al., 2012; van Deventer et al., 2007). On the other hand, Ss30CH, Ss60CH and Ss90CH limit the CH precipitation within 28 days, underlining the continuation of a slow pozzolanic activity. Compared to the untreated system SsCH, the CH reacted increases by 3.7%, 4.2% and 7.3% depending on the milling time. To conclude, the MA leads to a small improved pozzolanic activity after 28 days, due to the continuation of the CH consumption, and thus pozzolanic activity, in time.

3.4. Influence of by-products in cementitious systems

In addition to the pozzolanic activity, the evaluation of the contribution of the residues in early stage reaction is performed in the presence of PC. Fig. 7a) describes the cumulative heat released by the pure MSWI residues in the presence of water. Although without the presence of any alkali activator or a hydraulic binder, all the by-products register a minimal heat development, due to the dissolution of ions in contact with water; BA1 and BA2 results in a greater cumulative heat released within 5 days, compared to Ss. Due to the wet separation treatment of Ss, the presence of soluble species is reduced, leading to the lower cumulative heat registered within 5 days. This phenomenon underlines a possible contribution to the hydration of PC, due to dissolution of reactive phases, previously described in Section 2.2.4. Fig. 7b) shows the cumulative heat for the blended pastes and the reference samples containing pure PC or PC and inert quartz to emulate the nucleation sites contributions (PC, q1PC, q2PC and q3PC). The mixtures including quartz prove the presence of the heterogeneous nucleation effect, increasing the intensity of the heat released at 5 days (Q$_{\text{nucl}}$ in Formula (1)). Due to the catalysis of the reaction products around the new nuclei, the presence of additional active sites acts also on the chemistry of the PC hydration (Cyr et al., 2005). Moreover, the presence of MSWI residues has an influence on the main reaction of PC, due to the dissolution of additional species unrelated to the standard PC reaction (Q$_{\text{diss}}$ in Formula (2)).

Fig. 8 displays the contributions of nucleation sites (Q$_{\text{nucl}}$) and of the dissolution of phases (Q$_{\text{diss}}$) from BA, calculated by formulas (1) and (2). These contributions are expressed as rate of the reference reaction degree. Although all the powders are ranging between 0.04 and 0.250 mm, the contribution provided by the heterogeneous nucleation increases with the content of fines. Despite the finer PSD, Ss results in a total lower contribution in the hydration degree compared to BA1 and BA2 (22.6% compared to 24.8% and 26%, respectively). These data underline the greater amount of phases available for dissolution at early stages in BA1 and BA2. The presence of a reduced amount of soluble phases in Ss is mainly due to the wet treatment that it undergoes during the upgrade of BAc (4–32 mm). The MA seems minimally beneficial for the improvement of the reaction degree of the PC, due to the small increase of heterogeneous nucleation sites.

The contribution due to this factor increases the hydration degree from 12% to 15%, while the contribution caused by the dissolution of ions is constant independently form the MA, leading to a final enhancement of hydration degree of SsPC by 2–3%, depending on the treatment. This increment, within the experimental error, cannot be taken into account as a clear evidence of the improvement of early reaction degree after the MA. Summing the two

![Fig. 7. Isothermal calorimetry analysis of the influence of by-products in the hydration of PC: a) Cumulative heat of pure by-product (100% BA or Ss) b) Cumulative heat of blended cement (25% by-products 75% PC), 25% quartz 75% PC and 100% PC, within 5 days.](Image 65x75 to 520x222)

![Fig. 8. Contribution to the reaction degree of MSWI by-products, depending on the PSD and chemical dissolution, at 5 days (Formula (1) and (2)).](Image 305x574 to 550x727)
contribution, the treated samples increases the hydration degree of PC by 23.8%, 25.1% and 24.4% depending on the milling time. As shown from calorimetry results, by increasing the heterogeneous nucleation effect, the early hydration degree is mainly affected. However, the enhancement of early hydration of PC does not necessarily correspond to the increase of the final early strength of mortars, as the latter depends on both chemical and physical properties of the MSWI residues.

3.5. Evaluation of mechanical performances of the blended cements

Based on the results of the characterization and reactivity analysis, the performances of MSWI residues as cement replacement are tested. Fig. 9a) illustrates the average slump diameter of the treated and untreated residues, replacing 25% of the PC, by mass. In the case of both BA1 and BA2, the replacement of 25% of untreated by-products does not seem to affect the rheological behaviour of the paste. Their reduced total pore volume, and thus water demand, and the coarser PSD compared to Ss (Table 2), explain the less viscous behaviour, detected in Fig. 9. On the other hand, the replacement of untreated Ss reduces the slump flow diameter by 8%, compared to the reference PC. Differently to BA1 and BA2, the total pore volume and surface area of Ss result in a high water absorption, entrapping part of the water necessary for reaction by capillary suction. The grinding treatment is beneficial, since, increasing the slump flow diameter by 20–40%, it allows for a better distribution and compaction of the paste. Fig. 9b) describes the mechanical performances of the mortars, based on the same mixtures. The lower porosity of BA2 (Table 2) allows a proper distribution of the paste and an enhanced mechanical performance within 14 days, compared to BA1PC and SsPC.

By replacing cement with Ss, its finer PSD is expected to provide higher density mortars due to a better packing of the particles. However, the excessive water demand leads to a high viscosity of the paste, which limits its distribution and causes an inadequate compaction of the mortars and low strength. As also discussed in Section 2.2.6. This analysis is performed on reference, untreated and treated residues, replacing 25% of the PC, by-products. BA1PC and BA2PC are able to fulfill the requirement for strength after 7 and 14 days, but not after 28. For both mixtures, the increase in SAI is not linear, but shows fluctuations, with a maximum after 14 days. A similarly variable trend is seen with the untreated MSWI sludge, while the SAI is satisfied for Ss60PC and Ss90PC at any time. Among the treated samples, Ss60PC leads to the most steady and high results. The achieved improvement is not only linked to the influence of chemical reactivity (Section 3.3 and 3.4) but mainly to an optimisation of packing and reduction of total porosity (Section 3.2).

3.6. Leaching behaviour

In order to evaluate the immobilization properties of the PC mixtures, leaching tests are performed on the mortars as described in Section 2.2.6. This analysis is performed on reference, untreated material and on the treated one, after 28 days curing and displayed in Table 6. In the presence of cement the leaching of contaminants is reduced, fulfilling the requirements for Cl− and SO42−, out of range in the pure material leaching (Section 3.1). Independently from the treatment, the MA is inconsequential to the leaching properties of the blended pastes, since it does not differ from the untreated

Table 5

<table>
<thead>
<tr>
<th>Time</th>
<th>7 days</th>
<th>14 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>SsPC</td>
<td>±0.29</td>
<td>±0.81</td>
<td>±0.63</td>
</tr>
<tr>
<td>BA1PC</td>
<td>±0.93</td>
<td>±0.86</td>
<td>±0.69</td>
</tr>
<tr>
<td>BA2PC</td>
<td>±0.83</td>
<td>±1.08</td>
<td>±0.71</td>
</tr>
<tr>
<td>Ss30PC</td>
<td>±0.56</td>
<td>±0.74</td>
<td>±0.93</td>
</tr>
<tr>
<td>Ss60PC</td>
<td>±0.86</td>
<td>±0.85</td>
<td>±0.91</td>
</tr>
<tr>
<td>Ss90PC</td>
<td>±0.75</td>
<td>±0.77</td>
<td>±0.89</td>
</tr>
</tbody>
</table>

Fig. 9. a) Mini slump flow test on the reference PC and pastes including residues, before and after MA of the by-products, according to EN 1015-3: b) Compressive strength evaluation of blended pastes, characterized by 25% MSWI residues and 75% PC and reference PC.
material. In the presence of PC, the retention rate for chlorides ranges between 88% wt. (BA1) and 77% wt. (Ss30 and Ss60). For SO4\textsuperscript{2-} the value is around 99%, independently from the type of residue applied. The retention rate of Cu varies around 80% wt. for the references and 76% wt. for Ss, while for Mo it is around 60% wt. for references and 20% wt. for Ss. Furthermore, Ss levels are within the reference values, with retention rate of 66% wt. for BA1 and 83% wt. for Ss. The low concentration of Cr is owed to the dilution effect, created by replacing 25% wt. of the binder. In conclusion, all the contaminants are below the reference values, respecting the SQD legislation for unshaped materials ("Soil Quality Decree," 2015), and ensuring environmentally the application of MSWI sludge as secondary building material.

4. Summary and conclusions

This study evaluates the behaviour of MSWI sludge (Ss), a waste stream created by the washing treatment of coarse MSWI bottom ash (BAc). Because of its reduced availability of soluble phases (due to wet treatments) and the porous and irregular morphology of its particles, Ss is not widely studied as building material. However, the PSD and chemical composition of the MSWI sludge are similar to BA fines (0.04 mm–0.250 mm), often applied in construction field. Therefore, to address in environmental impact of Ss, two BA streams (BA1 and BA2) are used as reference in combination with Portland cement (PC). An enhancement of the properties of Ss is provided by dry mechanical activation (MA) at different durations (30, 60, 90 min). The following conclusions are drawn:

1. The MA treatment has a beneficial effect on the physical properties of the MSWI sludge. The applied milling treatment reduces the total pore volume of the powder, and thus its water demand. After the treatment, a reduction of the surface area is registered due to fines agglomerating in spherical particles.
2. Chemically, the pozzolanic activity within 14 days is slightly affected by the MA of Ss. However, while the precipitation of CH over time in the untreated samples is observed, treated MSWI sludge continues to react, increasing the pozzolanic activity in time, up to a maximum of 73%.
3. The replacement of the tested by-products results in a contribution of the final PC hydration degree, independently on the treatment. After the MA treatment of Ss, the small increase (≈ 3%) due to the heterogeneous nucleation contribution does not ensure the efficacy of the treatment, for the further enhancement of the hydration degree of the paste.
4. By the reduction of total pore volume and due to the enhanced packing, the mechanical treatment affects the rheological behaviour of the pastes. Due to a better distribution and compaction of mortars pastes, the MA of Ss allows the improvement in mechanical strength by ≈ 32% compared to the untreated material and by ≈ 25% compared to the other references BA1PC and BA2PC. The SAI is satisfied in time for both Ss60 and Ss90.
5. Environmentally, for all the samples (including reference) the leaching of all contaminants is below the legal limit, including Cl\textsuperscript{−} and SO4\textsuperscript{2-}. For the MA treated samples, the retention rate is ≈ 77% for the chlorides, ≈ 99% for the sulphates and ≈ 83% for antimony.

The results of MA treatment underline the possible use of MSWI sludge as secondary building material, both mechanically and environmentally. In order to optimize the treatment and application, further research will include the analysis of higher replacements of PC with MSWI sludge, to find the maximum substitution level, which satisfy the requirements of strength and leaching behaviour. The same treatment will be applied to BA1 and BA2 to improve the final mechanical behaviour and fulfill the SAI threshold.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.05.024.

References


Hin, J., Hansen, B., 2013. CEN EN 12457 Leaching Test: Comparison of Test Results Obtained by Part 1 and 2 with Test Results Obtained by Part 3 Dorthe Larke Nielsen, Jeppe Holm Nielsen, Bjørn Hansen Margarethe Buhl Nielsen.


