MSWI bottom ash as binder replacement in wood cement composites

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HIGHLIGHTS

- The deterioration of paste mechanical properties is proportional to the BA replacement.
- In blended pastes containing BA, the thermal conductivity improved up to 47%.
- In WWCB the reduction of the board macro porosity improves the flexural strength.
- 10% BA substitution is the optimal replacement level for WWCB.

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ABSTRACT

Nowadays, the incineration of municipal solid waste (MSW) is widely applied, as it reduces the waste 90% by volume and 80% by mass. The main by-product coming from the MSW incineration is bottom ash (BA). Despite numerous studies concerning the uses of this by-product in the construction field, BA is not widely applied because of two main concerns: (1) the disadvantageous morphology of the particle, leading to a high porosity and water absorption and (2) the presence of harmful contaminants, leaching out from the by-product. Because of its porous structure, BA can be suitable as binder replacement for improving insulation properties of wood composites, usually requiring low flexural strength. Therefore, this study will evaluate the influence of a porous binder containing BA and cement on wood wool cement boards (WWCB). The BA and cement are chemically and physically characterized. Thereafter, cement pastes with different replacement levels of BA (0–50%) are produced to measure mechanical and thermal properties. The same mixes are then used to make WWCB. While the thermal conductivity remains unchanged, the mechanical properties benefit from the use of BA up to 30% wt. due to the reduced macro porosity of the final composite.

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1. Introduction

During the last 20 years, the debate concerning the disposal of municipal solid waste (MSW) has been growing in Europe. Among the strategies adopted for the management of MSW, landfilling, recycling, composting and incineration are the most applied. Landfilling is the most common approach in Europe [1] but has some disadvantages such as the pollution of soils and groundwater and the reduction of the available land for a country’s development [2]. As a result, alternative processes, such as incineration in Waste-to-Energy (WtE) plants (64 MT/y) were developed [1].

During incineration, MSW incineration bottom ash (MSWI BA) is produced, which consists of amorphous slag, glass, ceramics, ferrous and non-ferrous compounds. Depending on the quality of the incineration process, the final compositions might include some un-combusted organic constituents [3]. Finally, BA shows a high content of chlorides, heavy metals and sulfates, which mostly concentrate in the fine fraction (below 0.25 mm) [4]. Due to this, the separation of this fraction from the coarser ones is necessary. A common application for MSWI BA fines is often as cement replacement [3,5–7], due to the immobilization of contaminants during the cement hydration process. Previous studies [8,7] show that the replacement of Portland Cement (PC) by MSWI BA often results in lower mechanical performances, due to its porous structure. The high porosity is a result of the quenching treatment used after the incineration process [7]. This suggests that the use of BA in non-structural elements, such as partition walls or ceiling tiles might be a suitable option. Wood cement composites can represent a good option for the application of BA, since a low final flexural strength is required (1.7 MPa) [9]. Wood wool cement boards (WWCB) are mainly produced using Norway spruce and white Portland cement. In Europe, they are mostly applied as a sound absorbing and thermal insulation material, because of the porous...
structure given by the weave of wood wool strands [10,11]. The process contributing the most to the CO2 emission of the WWCB manufacture is the cement production [12]. The partial replacement of PC with MSWI BA would lower the environmental footprint of the board, providing an alternative use for this by-product. Moreover, the presence of the BA will not affect the life cycle of this material, as WWCB are often disposed by incineration for energy recovery [12] and in some countries as Denmark, the ashes are used as raw material for cement kiln production. Therefore, being the BA already an incineration by-product and having chemical composition similar to cement, its presence will not require modifications of the board life cycle. Despite the fact that the high porosity of MSWI BA might have a positive impact on the insulation properties of the composite, not many studies investigate the influence of MSWI BA replacement on the properties of wood wool cement boards.

This study will address the influence of different replacement of CEM I 52.5 RW by porous BA (5, 10, 20, 30, 40, 50% wt.) on the performances of plain pastes and wood cement composites. After washing the BA to remove most of the chlorides and sulfates, the mixtures of cement and BA are characterized physically and chemically. Then, bulk density specific density and water demand of the unreacted mixtures are tested. Afterwards, the mechanical performances and the thermal conductivity of the blended pastes are measured in the form of both standard cubes (40 mm × 40 mm) in absence of wood and as WWCB. The influence of BA on the early stages of hydration is analyzed by isothermal calorimetry together with the calculation of the water necessary for the wood composite manufacture, based on the spruce absorption behavior model [13]. Finally, the environmental impact of the materials is evaluated by the one batch leaching test (EN 12457-2) using the standard prisms and compared with the reference values of the Dutch Soil Quality Decree (SQD) [14].

2. Methodology

2.1. Material

Norwegian Spruce (Picea Abies) wood wool strands for the manufacture of WWCB are provided by Knauf (NL), with dimensions 2 mm wide, 0.4 mm thick and 250 mm long. CEM I 52.5 R White (PC) from ENCI (NL) is applied as reference binder. MSWI bottom ash fines (BA-S) (0.04–0.250 mm) produced by Heros Sluiskil (NL) are applied as cement replacement. Fig. 1 provides an overview of the treatments applied on the MSWI BA after incineration.

During the BA processing at the plant dry sieving is applied on the full fraction, separating coarse BA (CBA, 4–32 mm) from fine BA (FBA, below 4 mm). By using a wet separation technique, the CBA is cleaned from the more contaminated fines attached to the surface, generating the so called filter cake (FC, below 0.250 mm). The FBA is further sieved into 3 fractions in the laboratory. In this study, the fine fraction (BA-S, below 0.25 mm) is applied as cement replacement.

2.2. Methods

2.2.1. Characterization of materials

Specific density of the mineral binder (PC) and its replacement (BA-S) are measured by using a Helium pycnometer (AccuPyc II 1340), while their bulk densities are evaluated by a conventional pycnometer. The water demand is addressed by Punpte test using three measurements [15]. The morphology of the particles is characterized by Scanning Electron Microscopy (SEM, Quanta 650 FEG, FEI in low pressure (0.6 mbar). The particle size distribution (PSD) is measured by laser diffraction (Mastersizer 2000, Malvern) and the chemical composition in form of oxides is investigated by X-ray Fluorescence spectrometer (XRF, PANalytical Epsilon 3 range, standardless OMNIAN method), on pressed powders. The chemical composition of the mixtures are calculated combining the plain PC and BA-S oxide compositions, proportionally to the BA substitution. The same calculations are applied for the estimation of the C_{3}A content, initially obtained from the Bogue estimation [16] of the reactive phases of PC (79.9% wt. C_{3}S, 0.2% wt. C_{2}S, 9.2% wt C_{3}A, 1.2% wt. C_{4}AF). The calcite content of BA-S was measured by thermogravimetric analysis (Jupiter STA 449 F1, Netzsch), using the CO₂ mass loss between 640 and 740 °C, purged with synthetic air.

The loss of ignition (LOI) was evaluated after heating the samples to 1100 °C for 4 h. In order to reduce its contaminant leaching, a double washing treatment is applied on the BA-S, based on a liquid to solid ratio (L/S) of 3, at 250 rpm on a shaker for 60 min [17], minimizing the water usage and the time consumption. Henceforward, all the experiments are based on washed BA-S.
2.2.2. Kinetic study

The influence of the washed BA-S on CEM I 52.5 RW hydration is investigated by isothermal calorimetry (TAM AIR calorimetry) in presence and absence of wood wool. In absence of wood the samples are prepared including different replacement levels of BA-S (5, 10, 15, 20, 30, 40, 50% wt., named BA5, BA10, BA15, BA20, BA30, BA40, BA50, respectively), and mixed with a water to binder ratio \((w/b) 0.5\). In combination with wood, the same replacement levels and \(w/b\) ratio are used. The final \(w/b\) ratio is calculated based on the Spruce absorption model described elsewhere [13], by determining the optimal pre-soaking moisture content \(\left(M_{\text{opt}}\right)\). By applying this model, the competition between the water demand of a mineral binder and the wood wool water sorption is taken into account, ensuring a constant \(w/b\), independently of the water absorption of the components. In order to evaluate the contribution to the PC reaction, all calorimetry measurements are normalized based on the mass of PC. Moreover, the cumulative heat given in Table 4 is calculated for \(t_{\text{start}} = 0.3\) h and \(t_{\text{end}} = 50\) h, to avoid the influence of mixing the sample externally.

2.2.3. Mechanical performances

The compressive strength of the blended pastes including different replacement levels (0–50% wt., using 10% wt. steps) is tested at 28 days but also at 10 days. This curing time is chosen, as it corresponds to the curing time used in the manufacture of the WWCB. The pastes are based on a \(w/b\) ratio of 0.5 and tested without sand, according to EN 196-1. The samples are placed in a cubic mould \((40 \times 40 \times 40 \text{ mm})\), and stored in a humid environment \(\text{RH} 97\%\). The thermal conductivity of dried samples is measured by a heat transfer analyzer \((\text{ISOMET} 2104, \text{Applied Precision})\), after 28 days of curing.

The WWCB manufacture is based on the dry method applied in the production plant [18], where the wood strands are pre-soaked with water and then sprinkled with dry binder. Therefore during this manufacture the modification of viscosity of the paste caused by the presence of BA (Fig. 3b)) is not relevant. The boards will be produced with this material. If it has a maximum thickness of 15 mm and minimum flexural strength of 1.7 MPa [18], it will satisfy the requirements for obtaining comparable results during the board manufacture, \(\left(M_{\text{opt}}\right)\). Applying the model described in Caprai et al. [13], ensures that the effective \(w/b\) ratio in each board is the one chosen.

The DCB test is performed to study the mechanical properties of the pastes at 28 days. Flexural strengths are evaluated by a three point flexural test \((\text{Zwick} 2020)\) on samples sized \(15 \times 20 \times 1.5\) cm and a support span of 15 cm (Method A) [9]. The board satisfies the requirements if it has a maximum thickness of 15 mm and minimum flexural strength of 1.7 MPa [18].

2.2.4. Leaching assessment

After mechanical testing, the crushed pastes are sieved to below 4 mm. The environmental impact of the pastes, as unshaped material is evaluated according to the EN 12457-2 (One stage batch leaching test) [19,20], by using a dynamic shaker (ES SM-30, Edmund Buhler GmbH), in ambient conditions \((L/S 10, 250 \text{ rpm, 24 h})\). Previous studies [21,7] confirmed the comparability between one stage batch leaching tests \((\text{EN 12457-2})\) and the column tests \((\text{Percolation test – NEN 7383:2004})\), generally applied in the Soil Quality Decree (SQD) \((L/S 10, \text{PSD} < 4 \text{ mm, 21 days})\). The comparability of those leaching tests using the same \(L/S\) ratio has been shown by different studies [22,23], due to the overestimated concentrations of contaminants detected with the one batch leaching test. After filtration with 0.017–0.030 mm membrane filters, chlorides and sulfates are quantified by ion chromatography (IC) (Thermo Scientific Dionex ICS-1100). The remaining solutions have been tested for heavy metals in the leachates, by inductively coupled plasma atomic emission spectrometry (ICP-OES), according to NEN 6966 [24], after acidifying the samples with 0.2% HNO3. As a reference, the unshaped (granular) material values from the dutch SQD (Soil Quality Decree, 2015) are used.

3. Results and discussions

3.1. Raw materials characterization

The XRF analysis in Table 1 shows the oxide composition of cement (PC) and BA-S before any washing treatment. The CaO in BA-S is mainly in the form of CaCO3 (13.41% wt., Table 2), while the source of Na2O and K2O are commonly found salts, such as NaCl or KCl [4]. Contrary to PC, the silica content is relatively low \(\left(10.16\% \text{ wt.}\right)\), as it is commonly reported for BA fractions below 4 mm [25,26]. The environmental impact of the granular BA-S is assessed by comparison with the current Dutch regulation (Soil Quality Decree, SQD) in Table 3 [14]. The chloride and sulfate content is 17 and 13 times higher than the limit, respectively. Excessive leaching is also detected for Sb, Cr, Cu and Mo (Table 3). In order to reduce the environmental impact of the BA-S, a double washing treatment is used, before application. The total reduction in chloride and sulfate content is \(\approx 14,500 \text{ mg/kg and } \approx 15,100 \text{ mg/kg} \), respectively. For clarification purposes, henceforward the name BA-S will indicate the washed BA-S and all the samples discussed here will be produced with this material. Fig. 2 shows the powders particle size distribution. Compared to PC, BA-S has a coarser PSD, ranging between 0.250 and 0.04 mm. Furthermore, the powder shows a lower bulk density \((0.56 \text{ g/cm}^3)\) and specific density \((2.44 \text{ g/cm}^3)\), compared to PC. The BA-S particle morphology is characterized by a high surface area \((\text{SSA})\) and pore volume \((17.44 \text{ m}^2/\text{g and 0.064 cm}^3/\text{g})\), respectively indicating the presence of irregularly shaped grains.

3.2. Influence of the BA on the binder physical properties

Fig. 3a) displays bulk density and specific density of the blended cements as a function of the BA-S replacement. Both parameters show a decrease when BA-S content increases. The irregular morphology of BA-S reduces the packing of the particles lowering the bulk density of the mixtures, while the reduction of the specific density of the cement is mainly in the form of CaCO3 (13.41% wt., Table 2), while the source of Na2O and K2O are commonly found salts, such as NaCl or KCl [4]. Contrary to PC, the silica content is relatively low \(\left(10.16\% \text{ wt.}\right)\), as it is commonly reported for BA fractions below 4 mm [25,26]. The environmental impact of the granular BA-S is assessed by comparison with the current Dutch regulation (Soil Quality Decree, SQD) in Table 3 [14]. The chloride and sulfate content is 17 and 13 times higher than the limit, respectively. Excessive leaching is also detected for Sb, Cr, Cu and Mo (Table 3). In order to reduce the environmental impact of the BA-S, a double washing treatment is used, before application. The total reduction in chloride and sulfate content is \(\approx 14,500 \text{ mg/kg and } \approx 15,100 \text{ mg/kg} \), respectively. For clarification purposes, henceforward the name BA-S will indicate the washed BA-S and all the samples discussed here will be produced with this material. Fig. 2 shows the powders particle size distribution. Compared to PC, BA-S has a coarser PSD, ranging between 0.250 and 0.04 mm. Furthermore, the powder shows a lower bulk density \((0.56 \text{ g/cm}^3)\) and specific density \((2.44 \text{ g/cm}^3)\), compared to PC. The BA-S particle morphology is characterized by a high surface area \((\text{SSA})\) and pore volume \((17.44 \text{ m}^2/\text{g and 0.064 cm}^3/\text{g})\), respectively indicating the presence of irregularly shaped grains.

Table 1

<table>
<thead>
<tr>
<th>Table 1</th>
<th>XRF analysis of the materials used in this study. The BA-S chemical composition refers to the material before washing treatment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds</td>
<td>BA-S % wt.</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.93</td>
</tr>
<tr>
<td>MgO</td>
<td>1.67</td>
</tr>
<tr>
<td>Al2O3</td>
<td>7.19</td>
</tr>
<tr>
<td>SiO2</td>
<td>10.16</td>
</tr>
<tr>
<td>P2O5</td>
<td>1.11</td>
</tr>
<tr>
<td>SO3</td>
<td>5.99</td>
</tr>
<tr>
<td>K2O</td>
<td>1.08</td>
</tr>
<tr>
<td>CaO</td>
<td>29.63</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>6.53</td>
</tr>
<tr>
<td>CuO</td>
<td>0.52</td>
</tr>
<tr>
<td>Cl</td>
<td>1.78</td>
</tr>
<tr>
<td>Other oxides</td>
<td>3.41</td>
</tr>
<tr>
<td>LOI</td>
<td>30.00</td>
</tr>
</tbody>
</table>

* Based on the dry mass of the binder.
density is due to the introduction of more porous particles. Despite the coarser PSD of BA-S compared to PC, the water demand of the mixtures (Fig. 3b)) increases with the replacement level, due to the BA-S high surface area and pore volume which favors the water absorption. The presence of ultrafine incineration residues of the BA surface [27,28] introduces additional porosity in the system, favoring the hygroscopic behavior and leading to a higher water demand.

3.3. Analysis of the hydration of the mixtures including bottom ash

Fig. 5 a) and b) show the heat development of the mixtures including BA-S and PC. The influence of BA-S on the PC hydration is mainly detected in the extended dormant period (Fig. 4a)) and in the modification of the sulfate depletion peak (Fig. 4b)). The dormant period is influenced by the amount of sulfate available in the system. Generally sulfates are added to PC clinker in order to avoid the rapid reaction of C3A with water that causes flash setting. Sulphates decelerate hydration, because the ettringite (AFt phase) is formed in their presence[29]. Generally, once that the SO4 source is depleted, the AFt phase reacts with C3A to form monosulfate (AFm).

\[ 2C_3A + C_6A_S_3H_32 + 4H \rightarrow 3C_4A_SH_{12} \] (1)

A prolonged dormant period is often related to a greater production of AFt phases due to a higher availability of sulfates [30]. In this study, a prolonged dormant period is observed with increasing the BA-S substitution, as it contains 4.5% wt. sulfates, after washing treatment. BA5, BA10 and BA15 show a delay of 30 min, 1 h and 1.20 h, respectively. This delay is maximized for BA20, where the dormant period is extended by \( \frac{1}{4} \) h. The influence of the sulfate content is also visible in the behavior of the AFm peak. Compared to the reference curve with 0% BA-S, the increase of the replacement level results in an earlier AFm depletion peak (Fig. 4b)). The depletion peaks of BA5 BA10 and BA15 appear 1.5 h, 2 h, and 2.5 h earlier, respectively. For higher replacement levels the peak disappears (BA20) or results highly modified reactions (BA30, BA40, BA50) (Fig. 5b)).

Table 2

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Bulk density (g/cm³)</th>
<th>Specific density (g/cm³)</th>
<th>BET surface area (m²/g)</th>
<th>Water demand (% dw*)</th>
<th>Total pore volume (cm³/g)</th>
<th>CaCO₃ content (% wt.)</th>
<th>MC (% dw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-S</td>
<td>0.56</td>
<td>2.44</td>
<td>17.44</td>
<td>62.40</td>
<td>0.064</td>
<td>13.41</td>
<td>21</td>
</tr>
<tr>
<td>CEM I 52.5 RW</td>
<td>1.08</td>
<td>3.1</td>
<td>2.21</td>
<td>20.70</td>
<td>0.004</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Based on the dry mass of the binder.

Table 3

Leaching of unwashed BA-S and white cement in comparison to the Soil Quality Decree (SQD) limits [14].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SQD Reference Unshaped material mg/kg d.s.</th>
<th>CEM I 52.5 R White mg/kg d.s.</th>
<th>BA-S mg/kg d.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony (Sb)</td>
<td>0.32</td>
<td>&lt;0.1</td>
<td>1.20</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.90</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>22.00</td>
<td>12.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.04</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.63</td>
<td>0.20</td>
<td>1.00</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>0.54</td>
<td>0.10</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.90</td>
<td>0.20</td>
<td>11.90</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>2.30</td>
<td>&lt;0.1</td>
<td>0.10</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>1.00</td>
<td>&lt;0.05</td>
<td>2.60</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>0.44</td>
<td>&lt;0.05</td>
<td>0.30</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.15</td>
<td>&lt;0.02</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>0.40</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>1.80</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>4.50</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>616.00</td>
<td>81.00</td>
<td>10.440</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>1730.00</td>
<td>46.60</td>
<td>22.378</td>
</tr>
</tbody>
</table>

Fig. 2. Particle size distribution of the materials applied in this study.

Fig. 3. a) Specific density, bulk density and b) water demand trends depending on the washed BA-S replacement level. Parameters concerning the plain PC are also represented here as 0% replacement, for comparison reasons.
For a sulfate content higher than standard PC, literature studies [30] show the reduction or absence of AFm formation, in favor of a longer and greater production of AFt. Fig. 4c) represents the $SO_4/C_3A$ ratio of the blended system depending on the BA-S content. An increasing ratio is measured with increasing BA-S content, indicating that more $SO_4$ is available in the system for ettringite formation, compared to the plain PC. In this study the reference PC shows a $SO_4/C_3A$ ratio of 51%, leading to a full conversion of AFt to AFm (Fig. 4c)) [30]. However for BA-S replacement higher than 15%, the $SO_4/C_3A$ ratio of the mixture is around 67%, overcoming the threshold for which all AFt is converted to Afm [30]. This is also confirmed by the calorimeter curve of BA20 which does not show any depletion peak, confirming the absence of the AFm formation.

For the quantification of the $MC_{o,p}$, Table 4 shows the cumulative heat of the binders with the different BA replacement levels ($Q_B$) in comparison with the ones developed by the binder and wood mixtures ($Q_{BW}$), calculated as from literature [13]. The total water content in each mixture was adjusted according to the water demand of each component (PC, BA and wood). The measurement of the same cumulative heat within 48 h indicates the same reaction degree of the pastes in presence and absence of wood, signifying that the effective w/b ratio is the same for all mixtures. They are therefore comparable in regards to reaction degree and strength development.

3.4. Mechanical and thermal properties

3.4.1. Blended cement pastes

Fig. 6 shows an overview of the mechanical and thermal performances of the pastes with different BA-S replacement levels (0 to 50% wt.). Mechanically, the lowest performance is registered for 50% wt. replacement, where a 52% loss in compressive strength is measured. The increase of BA-S content leads to a reduction in compressive strength, at both 10 and 28 days, because BA-S replaces reactive clinker phases such as alite or belite. Due to the lower density of BA-S, it also provides additional porosity in the cement matrix, causing a reduction in mechanical strength proportional to its replacement level. Moreover, increasing the BA-S and thus, the sulfate content, the absence of the AFm in favor of the only AFt formation is observed (Fig. 4a) and c)). Due to the low stability of AFt phases, sulfates might further dissolve and recombine with calcium hydroxide (CH) creating additional porosity or favor the dissolution of C-S-H gel, resulting in micro-cracks formation [31]. Due to these factors, the high content of sulfate is proven to be detrimental for the mechanical performances of the PC [31,32], and it can contribute to the strength loss measured in the sample. On the other hand, increasing the porosity of the matrix the thermal performances are positively affected, decreasing by 47% the thermal conductivity for a replacement of 50% wt.

3.4.2. Wood wool composite boards

Fig. 7 displays the flexural strength and thermal conductivity of the WWCB produced with the blended cement pastes containing cement and BA-S at different replacement levels. Up to 30% wt. replacement, the presence of BA-S is beneficial, leading to 27% higher flexural strength and stable thermal conductivity. The further increase of the replacement causes a drop in strength, worsening the performance by 57% for BA50. Flexural strength performances of WWCB are related to the combined action of mineral binder and wood wool strands: the cement mainly participates in the absorption of the compressive stresses, whereas the wood is primarily responsible for the absorption of the tensile stresses [33]. Those stresses are distributed in the composite by interconnection points between two or more fibers. The higher the contact area, the lower is the porosity generated among the strands in the composite. Contrary to the thermal conductivity trend in absence of wood, the thermal conductivity of the boards has similar values independently on the replacement level (Fig. 7 b)). The properties of a WWCB are mainly related to the composite density, and thus porosity but also the moisture content [33]. Considering that the composites have the same MC, due to the oven dry conditions applied before testing, the porosity of the board is the main parameter affecting its properties. The overall porosity of the composite is the sum of air gaps in the matrix (macro porosity among the...
strands), but also the smaller pores of the wood and binder. The volume occupied by WWCB can be defined by Eq. (2):

$$V_{WWCB} = V_B + V_W + V_A$$

$$V_{WWCB}$$ is the volume of the board (15 × 20 × 1.5 cm) [cm³], $$V_B$$ is the volume of the binder [cm³], $$V_W$$ is the volume of wood wool [cm³] and $$V_A$$ is the air volume in a WWCB [cm³]. As shown in Fig. 3, the application of a cement replacement with lower density (BA-S) causes the decrease of the final bulk density of the mixtures.

Consequently, those mixtures have higher pore volume and surface area compared to plain PC, leading to a more porous structure of the binder, as confirmed by the mechanical and thermal performances measured on cubic specimens (Fig. 6). Therefore, being plain PC (B1) and blended binder (B2), it will be:

$$S_{GB1} > S_{GB2}$$

$$m_{B1} = m_{B2}$$

$$V_{B1} < V_{B2}$$

where,

$$S_{GB}$$ is the specific density of the binder [g/cm³], $$m_{B}$$ is the binder mass [g] and $$V_{B}$$ is the binder volume [cm³].

As for those blocks also in the WWCB, for the same mass a greater volume of mineral binder will be distributed on each strand compared to plain PC. From the schematization in Fig. 8 and the SEM cross sections, it is visible the different binder coating on the wood wool strands. The reference board (Cross section 8a)) shows presence of binder particles covering the fibers, but a uniform and thick binder coating is not visible. On the other hand,
the replacement of 50%wt. BA results in a more homogeneous layer, creating a visible binder coating around each strand. Therefore, a part of the air volume of the board will be filled with the higher volume binder, limiting its macro-porosity.

Since:

\[ V_{\text{WWCB1}} = V_{\text{WWCB2}} \]  

\[ V_{W1} = V_{W2} \]  

Therefore:

\[ V_{A1} > V_{A2} \]  

\[ \Phi_{\text{WWCB1}} > \Phi_{\text{WWCB2}} \]  

where, \( \Phi_{\text{WWCB}} \) is the macro porosity [%] created among fibers in a WWCB.

The reduction of macro porosity inside the board (Fig. 7c)) is shown as a function of the specific density of the binder, confirming their correlation in the performance of the composite. Incorporating a binder with a lower density causes the reduction of the macro-pores among strands, which are partially filled by the binder. The higher porosity of the binder does not seem to contribute to the improvement of the thermal performances, mainly due to its limited amount and the densification of the matrix obtained because of the greater contact area among the fibers. The presence of more of those interconnection points increases the compactness of the composite but does not increase the overall density of the board, as the low density of BA-S compensates for it (Table 2).

Considering the overall results, the 30% replacement of BA provides the optimal improvement of the final performances, both mechanically and thermally, increasing the flexural strength and favoring the insulation properties of the composite, comparable to the one of the reference.

3.5. Environmental impact

Fig. 9 shows the concentrations of the contaminants leaching out from the pastes after 28 days curing. The 0% replacement represents the plain PC. Apart from chromium and sulfates (Fig. 9 a) and b), respectively), the leaching increases according to the replacement level. The presence of PC seems beneficial for the immobilization of Cl, SO4, Cr and Cu, because of their partial incorporation into the reaction products [34,35]. The plateau shown by SO4 and Cr seems to indicate a high incorporation of those contaminants, as their solubility is constant independently from the BA-S content. As a consequence, the increase of their total amount (by increasing BA-S content) does not affect their concentration in solution, as they will leach according to the solubility of the reaction products they are incorporated in. This phenomenon further confirms the modification of the hydration behavior observed in the calorimetry, where most of the sulfates are used for the production of AFt (Fig. 4a and c)). On the other hand, the presence of an alkaline environment stimulates the leaching of Mo, Zn and Ba. Studies underline that the leaching behavior of those contaminants is sensitive to pH changes, increasing for alkaline conditions higher than pH 10 [36,37]. Therefore, the application in cementitious systems (pH 12.5) might have favored the release of those ions from the BA-S [38]. For replacement till 10% wt., the leaching is below the legal limit for all the contaminants. However, for replacements between 5% and 30% wt., Ba\(^{2+}\) is the only contaminant overcoming the reference value. The source of Ba\(^{2+}\) is not only the BA-S, but the clinker itself (Table 3), as this element is often incorporated into C\(_2\)S or C\(_3\)S [39,40].
4. Conclusions

This study investigates the possible application of MSWI bottom ash (BA) as replacement of cement in wood composites. From the study the following conclusion can be drawn:

- The replacement of cement with a porous by-product like bottom ash leads to a direct decrease of the physical binder properties such as bulk density, specific density and an increase in the water demand.

- The wood-binder absorption model for spruce wood wool cement board is applied. Although all the mixture have different water demands, calorimetry results show that the calculated w/b ratio in the composites is 0.5 in all WWCB. For a BA rate higher than 15% wt., the increasing SO4 content of the mixtures leads to a modification of the PC reaction kinetic.

- In pastes, bottom ash negatively affects mechanical performances, leading to a reduction in mechanical strength proportional to the BA-S replacement level (BA50, 52% reduction in compressive strength). On the other hand, thermal properties

Fig. 8. Graphical representation of the reduction of macro pore volume, caused by the presence of a binder with lower density (B2), including SEM cross section of a) reference WWCB with CEM I 52.5 R and b) WWCB manufactured using BA50 as binder.

Fig. 9. Leaching of the contaminants from 28 days pastes (PC+ washed BA-S), as a function of the replacement rate. Leaching trend for a) Zn, Mo Cu and Cr b) Cl and SO4 and Ba ions concentrations. Parameters concerning the plain PC are also represented here as 0% replacement, for comparison reasons.
benefit from the presence of a porous matrix, improving the final insulation performances (+50%).

• In wood composite boards, the presence of BA has a positive influence on the flexural strength performances of the WWCB (BA30, +27%), due to the less porous structure formed by the increasing the binder volume. In addition, this is not influencing the thermal insulation of the composites, which remains steady independently by the presence of BA.

• Due to the high leaching of Ba2+, the replacement level in pastes higher than 10% wt. does not satisfy the SQD legislation. Therefore, because of the influence of SO4 on the reaction kinetic, the most effective replacement is limited to this replacement level.

Conflicts of interest statement

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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