DESIGN AND PROPERTIES OF ECO-FRIENDLY BINARY MORTARS CONTAINING ASH FROM BIOMASS-FUELLED POWER PLANTS

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Abstract

The use of biomass to produce electric power and heat will intensify in the years to come, in pursuit of sustainable growth. Stockpiling the vast amounts of fly and bottom ash generated in that process wastes resources and has an adverse impact on the environment.

The viability of bottom ash as a supplementary cementitious material in new eco-efficient cements is studied, including its effect on binder chemical, rheological, mechanical and microstructural properties. The findings show that these additions induce improvements in later age mechanical performance relative to conventional mortars. An ANOVA conducted to determine the impact of waste type, replacement ratio and curing time on compressive and flexural strength reveals that the latter two have a significant effect on mechanical properties. The new cements meet the requirements laid down in EN 197-1 for CEM II/A and CEM IV/A cements, making them apt for use in construction.

Keywords: *biomass ash, blended cement, strength development, supplementary cementitious materials, porosity*

1. Introduction

Portland cement is the binder most widely used in construction. Cement is manufactured with raw materials such as ground and blended limestone (CaCO_3 , 80%) and clays (SiO_2 , Al_2O_3 and Fe_2O_3 , 20%) [1]. The mix is subsequently burnt at a temperature of $\sim 1450^\circ\text{C}$ to form the clinker phases alite, belite, tricalcium aluminate and ferrite. In CEM I portland cement, the cooled clinker is then ground and mixed with $\sim 5\%$ gypsum, which acts as a setting regulator. The vast volumes of GHGs belched by cement plants due to limestone and fossil fuel decarbonation account for 5% to 7% of worldwide CO_2 , the primary cause of global warming [2]. The industry is also raw material- and

energy-intensive: 1 t of clinker is estimated to require 1.7 t of raw materials and 3.2 GJ to 6.3 GJ of energy [3].

With a view to reducing both noxious effects of cement manufacture, clinker is often partially replaced by amorphous silica-rich waste with fine particle sizes such as fly ash and blast furnace slag, the use of which is regulated in EN 197-1 [4].

In conjunction with those measures, a number of legislative provisions are in place to further environmentally sustainable policies. More specifically, European Directive 2009/27/EC [5] and Spain's renewable energy plan PER 2011-2020 [6] prescribe measures to foster renewable energy use, energy savings and energy efficiency. The target is for renewables to constitute a 20 % share of the total energy consumed in 2020 [5]. Compliance with such policies should reasonably lead to an increase in biomass-fuelled electric power and heat generation in the years to come. The combustion of forestry, woody and non-woody plant (corn, oil, seed, sugar cane, wheat) biomass generates vast amounts of ash that are presently stockpiled in spoil heaps.

The two types of such ash are: biomass fly ash, BFA, generated during combustion and escaping into chimneys [7] where it is retained by cyclones, precipitators or baghouse filters to prevent release into the atmosphere [8, 9]; and biomass bottom ash, BBA, also known as slag, which is the non-combustible waste remaining in furnaces or incinerators [7] that is removed from the combustion chamber [8, 10]. As a rule BFA has a smaller particle size than BBA [11].

Recent research has addressed the use of ash from laboratory-combusted agro-industrial waste (such as sugar cane [12, 13], bamboo leaves [14-16], rice husk [17, 18] and elephant grass [19]) as supplementary cementitious materials (SCMs). Very few studies have been conducted, however, on the use in construction of biomass waste from large-scale combustion of a variety of agro-industrial by-products at power and heat plants, and the results have been inconclusive. Most of those studies focus on biomass fly ash (BFA), and very few on biomass bottom ash (BBA).

The first group studies have dealt, for instance, with applying olive grove or pine forest pruning [11] or olive milling [20] combustion ash to manufacture brick. Woody biomass has been used as a natural filler in self-consolidating concretes (for a priori this waste exhibits pozzolanicity too low for direct inclusion as a cement addition, with a low $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and a high CaO content [7, 21]) or as an addition in concrete design, in research showing that at replacement ratios of under 25% mechanical performance remained unaltered and at over 25% declined after 28 d [22]. It has also

been used as a cement replacement, i.e., a supplementary cementitious material (SCM) in mortar and cement manufacture.

Rajamma et al. [23, 24] analysed mortar containing 10 %, 20 % or 30% forest waste combustion BFA at a power plant in Portugal, observing that at over 20 % mechanical performance declined substantially, whereas at 10% it was comparable to that of OPC. A similar line of research (Horsakulthai et al. [25]) studied the viability of BFA from the combustion of 82.5% bagasse, 15% rice husk and 2.5% chopped wood at a small steam power plant supplying electricity for sugar mills. When they replaced 10% and 20% of the cement to manufacture concrete they found that the new concretes exhibited compressive strength slightly higher than the control and high resistance to chloride penetration and corrosion, i.e., good durability. Jidrada et al. [26] analysed the viability of valorising rice husk and eucalyptus combustion ash ground to different particle sizes as SCMs at replacement ratios of 15% to 45%. They observed that the inclusion of the ash raised water demand and lowered mechanical strength, more intensely at higher ratios. Ramos et al. [27], researching the use of 10% and 20% fly ash from wood combustion at a power plant as an SCM, observed that at later ages mechanical strength in the experimental and reference cements was similar. Another study in this group conducted by Gan and Ramli [28] using woody biomass ash as an SCM at 10%, 20% or 30% found mechanical performance to rise at 10% and to decline at the higher percentages. At this writing, the short number of papers published on BBA valorisation can be divided into three classes, depending on the use: as SCMs or fillers in mortars; as sand in mortar design [29] or granular material in structural layers for roads [30, 31]; and as a raw material in brick manufacture [32].

The first group includes research conducted by Rosales et al. [33] in which olive waste combustion BBA (40% olive cake and 60% woody biomass from poplar, olive and pine trees) was used to replace cement at 20wt% and 38.5vol% with a decline in mechanical performance. In contrast, García et al. [34] observed higher 28 d compressive strength in standardised mortars containing 5% or 10% woody or forestry biomass and lower strength in earlier age materials. Sklivaniti et al. [35], using olive pruning combustion bottom ash as a filler, observed 20% to 30% declines in compressive strength at 2% to 10% replacement ratios.

BBA valorisation is, then, an innovative line of research for a number of reasons. Very little has been published on the use of BBA in new cement design. No references are found in the literature on the

valorisation of simultaneous woody and non-woody plant combustion ash. The reuse of this material has not been addressed in the legislation, while its volume is increasing yearly due to the rise in the number of biomass-fuelled power plants. Scientific understanding of the mechanical behaviour and microstructure of these new materials is consequently needed.

This study attempts to fill the existing scientific-technical lacunae on the viability of using BBA in civil and building construction. It assesses the effect of replacing cement with 10% or 20% BBA from three Spanish power plants on the chemical, rheological, mechanical and microstructural properties of the new sustainable binders, comparable to II/A and IV/A cements. A univariate analysis of variance (ANOVA) is run to assess the impact of age, replacement ratio and BBA type (factors) on compressive and flexural strength (dependent variables).

2. Materials and procedures

2.1. Materials

Three types of BBA were sourced from three non-woody (straw, rye, oats, corn...) and woody (pine, eucalyptus, fruit tree) biomass-fuelled power plants in Spain [36], labelled S1, S2 and S3. A ternary diagram (Vassilev et al. [21, 37, 38]) drawn from the XRF chemical composition, determined previously [36], showed the biomass waste to be type S, sub-type MA (see Figure 1). The silica content in all three was over the 25% minimum required in EN 197-1 [4] to qualify as a pozzolanic material. The silica content in the three types of waste was, in decreasing order: $S1 > S2 > S3$ [36].

Figure 1. Position of three types of biomass waste on the ternary diagram proposed by Vassiliev et al. [21, 37, 38] for the chemical classification of the inorganic matter in biomass ash

The chemical composition of the ordinary CEM I 42.5R cement used, supplied by Lafarge, a cement manufacturer sited in the Spanish province of Toledo, included: CaO (62.05%), SiO₂ (18.71%), Fe₂O₃ (2.53%), Al₂O₃ (4.29%), and small amounts of MgO (1.95%), alkalis (Na₂O_{equivalente} = 0.63%) and SO₃ (3.23%).

The mortars were prepared with CEN-standardised EN 196-1 [39] -compliant sand with a particle size ranging from 2.0 mm to 0.078 mm.

2.2. Methods

2.2.1. Frattini test

Pozzolanicity was determined with the Frattini test described in EN 196-5 [40]. That test determines the 8 d and 15 d calcium ion concentration in the aqueous solution present in the cements studied (10% biomass waste/90% OPC and 20% biomass waste/80% OPC).

2.2.2. Setting and slump test

The initial and final setting times for the new blended cements were determined using a Vicat needle as described in EN 196-3 [41]. Cement soundness in normal consistency cement paste was studied with a Le Chatelier instrument as specified in the aforementioned standard.

2.2.3. Mechanical properties

Blended cements S1, S2 and S3 bearing 10 wt% and 20 wt% BBA were tested for compressive and flexural strength as per EN 196-1 [39]. Prismatic (4x4x16 cm) mortar specimens were prepared with a sand/cement ratio of 3/1 and a water/cement ratio of 1/2, de-moulded after 24 h and cured at 20±1 °C and 100% relative humidity until the test time (2 d, 7 d, 28 d, 90 d, 180 d or 365 d). Nine specimens per mix and age were tested for flexural strength and 18 for compressive strength.

2.2.4. Strength activity index (SAI)

The procedure followed was similar to the one proposed in EN 450-1 [42] for fly ash used as an admixture in concrete manufacture: a control mortar was prepared by mixing 1350 g of standard sand, 450 g of cement and 225 mL of distilled water in a planetary mixer for 5 min. The 4x4x16 cm specimens prepared were de-moulded after 24 h and soaked in water at 20±1 °C for 27 d. In the eco-friendly cements 90 g (20%) of the cement was replaced with one of the three types of biomass studied (S1, S2 or S3). The resulting mortars had the same consistency as the reference, with a tolerance of ±5 mm.

The compressive strength findings shown are the mean of six measurements, represented as a percentage relative to the control mortar (SAI), as per Equation 1:

$$SAI = (\sigma_{\text{blended mortar}} / \sigma_{\text{control mortar}}) \times 100 \quad (1)$$

where: $\sigma_{\text{blended mortar}}$ is the compressive strength of the additioned mortars and $\sigma_{\text{control mortar}}$ is the compressive strength of the reference mortar, both expressed in MPa.

2.2.5. Eco-efficient material

Inasmuch as a full life cycle analysis lies outside the aim of this study, the eco-efficiency of the new cements was found with a simplified calculation of the energy required relative to the energy required for OPC manufacture.

The method, proposed by Hamidi et al [43], is based on the energy consumed in cement manufacture (heating raw materials, burning additions and clinkerisation) and grinding (clinker and BBA). The energy needed was consequently calculated as shown in Equation 2:

$$E(kW \cdot h/t) = C \cdot (E_{cement}^{process} + E_{cement}^{grinding}) + BBA \cdot (E_{BBA}^{process} + E_{BBA}^{grinding}) \quad (2)$$

where: E is the energy consumed to produce 1 t of binder; C the proportion of cement (1, 0.90 or 0.80); and BBA the proportion of biomass bottom ash (0, 0.10 and 0.20); $E_{cement}^{process}$ and $E_{BBA}^{process}$ are the energy consumed (kW·t/h) in cement and BBA manufacture, respectively; and $E_{cement}^{grinding}$ and $E_{BBA}^{grinding}$ the energy consumed (kW·t/h) in cement and BBA grinding, respectively.

The values obtained from Equation 2 were then used to calculate mortar energy performance with Equation 3:

$$E_{performance}(kW \cdot h/t \cdot MPa) = \frac{E}{f_{cm}} \quad (3)$$

where: E is the energy consumed to produce 1 t of binder and f_{cm} is the compressive strength of the mortars studied.

2.3. Instrumental techniques

The pore size distribution of the mortars was analysed with a Micromeritics Autopore IV 9500 mercury porosimeter operating at pressures of up to 33 000 psi (227.5 MPa) to measure pore diameters of 0.006 µm to 175 µm. This trial was conducted to ASTM standard D 4404 [44].

The microstructure and morphology of the blended cements were analysed on a Hitachi S4800 (Tokyo, Japan) scattering electron microscope (SEM) coupled to a Bruker Nano XFlash 5030 silicon drift detector for energy-dispersive spectroscopic (EDX) determination of the chemical composition of the samples. The C/S ratio of the gels was based on at least 30 microanalyses per mix at 40 000x on samples secured to a metallic holder with a two-sided graphic adhesive after carbon coating the surface to ensure conductivity and detection of all the signals sought.

3. Results and discussion

3.1. Eco-friendly cement compliance with chemical and physical requirements

Table 1 lists the chemical specifications laid down in EN 197-1 [4] for ordinary cements. The data show that binary cements OPC+20S1, OPC+20S2 and OPC+20S3 met the requirements to be deemed either cements II/A additioned at 6wt% to 20wt% or cements IV/A with 11wt% to 35wt% additions.

Table 1. Compliance of eco-friendly cements with chemical specifications

The physical properties of the new cements designed are listed in Table 2, together with European cement legislation specifications [4]. The initial and end setting times were longer than in OPC, irrespective of the percentage and type of waste, whilst the values for S1 and S2 were similar and for S3 slightly higher than both at all replacement ratios. The latter observation was attributed to the mineralogy of the three types of waste, for S3 is the least reactive given its higher crystallinity [36] and lower reactive silica content. That translated into a delay in initial and end setting times for the cements bearing 10% and especially 20% S3. Nonetheless, the new binders met the standard requirements for ordinary strength 42.5 MPa cements.

Table 2. Cement compliance with physical requirements

The longer initial and end setting times observed in the binary cements relative to OPC were probably due to a number of factors. Replacing the cement with this waste lowered the C_3A content, which plays an important role in the early hours of cement hydration [45]. The very small (specific surfaces of 3.25 m²/g in S1, 0.77 m²/g in S2 and 6.63 m²/g in S3 [36]) waste particles competed for water, minimising the proportion available for cement hydration and thus retarding initial setting. Lastly, setting could also have been retarded by the presence of a heavy metal (such as Zn or Cu) [46]. Delayed setting times were also observed for other cements containing ash sourced from woody waste combustion [46], a steam power plant burning logging industry waste and a paper pulp co-generation plant burning eucalyptus bark [24].

Expansion was not induced by any of the eco-friendly cements, all of which met the EN 197-1 requirement (slump ≤ 10 mm).

3.2. Pozzolanicity test

Further to the 8 d and 15 d Frattini test results for the new cements shown in Figure 2, after 8 d (Figure 2(a)) the additioned cements were positioned slightly above the CaO solubility curve and rightward of the OPC reference cement. The rightward shift was wider with rising replacement ratios, irrespective of the type of addition (S1, S2 or S3), and attendant upon a decline in the concentration of the Ca^{2+} released during cement hydration.

Figure 2. Frattini diagrams for determining pozzolanicity at: (a) 8 days; and (b) 15 days

In the 15 d trial, the cements with a 10% addition were also positioned above the solubility curve, whilst the materials bearing 20% waste lay below it due to the pozzolanic reaction-mediated

reduction of the Ca^{2+} released in hydration. Therefore, further to the provisions of EN 197-1, cements OPC+20S1, OPC+20S2 and PC+20S3 would qualify as pozzolanic cements (IV/A).

The percentage reduction of the maximum $[\text{CaO}]$ for the 8 d and 15 d mixes containing 20% additions given in Table 3 shows that the 8 d cements all had negative values, indicating a position above the solubility curve and therefore no pozzolanic activity. Duly normalised, those negative values denote 0% CaO removal. The positive values for the additioned 15 d cements confirmed pozzolanic activity in this BBA. In descending order pozzolanicity was $\text{S1} > \text{S2} > \text{S3}$ and the pozzolanicity indices were, for S1 25.6%, for S2 6.8% and for S3 0.4%.

Table 3. Frattini test results for cements containing 20% BBA

The index for S1 was close to the laboratory value reported by Wang et al. [47] for switchgrass combustion ash (~30%) and lower than found for silica fume (~75%) and the 68% to 83% found for corncob ash laboratory-combusted at 400 °C, 500 °C or 600 °C [48]. The values for $[\text{CaO}]$ reduction in S2 and S3 were comparable to the 3.3% observed by Memon and Khan [48] for corncob ash burnt at 700 °C.

3.3. Mechanical properties of eco-friendly cements

3.3.1. Compressive and flexural strength

As Figure 3 shows, the compressive strength of the 2 d mortars designed was consistently higher than 10 MPa (42.5 N) or 20 MPa (42.5 R) and greater than or equal to 42.5 MPa (42.5N/ 42.5R) in the 28 d materials, denoting compliance with the mechanical specifications set out in EN 197-1 [4] for 42.5 MPa strength class cements.

Figure 3. Mortar compressive strength versus time

At early ages (≤ 28 d) compressive strength was lower in all the new cements than in the reference because the effect of clinker dilution prevailed over the pozzolanicity of the new additions; the gap widened with rising replacement ratios. At ≥ 90 d, particularly after 180 d, the new cements performed similarly to or better than the control cement. That finding was directly related to the changes induced by these additions in mortar microstructure, specifically pore structure refinement as discussed later in section 3.4.

Relative compressive strength is plotted versus time in Figure 4. The lesser strength loss in the 2 d and 7 d 10% S3 than in S1 or S2 cements was determined by its higher specific surface, the physical property predominating in SCMs lacking significant pozzolanicity at early ages. At later ages (28 d

to 180 d) all the cements with 10% addition exhibited relative strength of >1 , whereas the cements with 20% addition had relative strengths of ~ 1 . All the 365 d cements, irrespective of type and percentage of waste, had relative strengths of over 1. The failure of the cements with 20% addition to exhibit relative strength greater than 1 until 365 d attests to the long life of the pozzolanic reaction that offsets the strength loss induced by clinker replacement.

Figure 4. Relative compressive strength vs time

The relative strength findings were consistent with results for 5% and 10% BBA from woody plant and forest waste combustion ash: García and Sousa-Coutinho [34] found relative strength in those 90 d mortars with those additions to be >1 . Other authors, however [33, 35, 49], using 10% to 40% BBA from olive tree and other plant material combustion ash observed declines in strength relative to the reference of up to 30% and 45% for 20% and 40% replacement due to the effect of these ashes on the pore structure of the new mortars.

A similar pattern was observed for flexural strength (Figure 5): after 365 d the new mortars exhibited flexural strength from 0.5% to 3% greater than in OPC, depending on the percentage and type of addition. The highest rise was recorded for S1, followed by S2 and S3 in that order, in keeping with their relative pozzolanicities.

Figure 5. Mortar flexural strength versus time

The data in Table 4 show that the inclusion of biomass waste as additions did not alter the logarithmic regression between compressive or flexural strength curing age, with correlation coefficients (R^2) consistently >0.94 . A similar pattern was observed by Medina et al. [50] for ornamental granite industry sludge.

Table 4. Correlation between mechanical properties and curing age

3.3.2. Significance of factors in mechanical strength

The MANOVA results for the effect of the factors curing age ('age') and waste percentage ('PW') and type ('waste') and of their interactions on compressive and flexural strength are given in Table 5. Further to the data, all the factors except waste (values=S0 (without waste), S1, S2, S3) and their interactions had a significant effect on compressive strength ($p\text{-value} < 0.05$). The findings for flexural strength were similar, except that the interaction among all the factors (age*PW*waste) had no significant effect on the dependent variable ($p\text{-value} > 0.05$).

Table 5. MANOVA values for mechanical strength

The statistical model explained 99% of the variation in compressive and 97% in flexural strength. Table 5 shows that the factors age and PW affected the two variables similarly, with the former contributing over 90%, and the latter around 2%, to both. The interaction of the factors age*PW explained 1% of the variation in flexural strength, and age*waste 2%. The rest of the factors had only a marginal effect on either variable.

The statistical models by mortar family (OPC+XY, where X is the replacement ratio and Y the type of waste) also showed that curing time and replacement ratio and their interaction had a significant effect ($p\text{-value} < 0.05\%$) on compressive and flexural strength. Those models explained 96% of the variation observed, with no differences (see Figure 6) in the contribution of the factors [age (>93%) > PW (>2.5%) > age*PW (>2.4%)] to the performance of mortars with different types of waste (S1, S2, S3). Those findings further support the lack of significance of the type of waste.

Figure 6. Participation of factors in the compressive and flexural strength of mortars bearing different types of waste: (a) curing age; (b) percentage of waste; (c) interaction age*percentage of waste

The groups resulting from Tukey's HSD multiple range tests for compressive and flexural strength in the mortar families (OPC+X and OPC+Y, where X is 10% or 20% and Y is S0 (no waste), S1, S2 or S3) are listed in Tables 6 and 7, by order of the highest mean value for the factor studied. Several inferences can be drawn from this table. Three groups were defined for early age (≤ 28 d) compressive and flexural strength, whereas for later ages one group was defined for flexural and two for compressive strength. In the 365 d mortars, the mean compressive strength was greater in the 10% additioned materials than in the 20% materials, and the latter value greater than in the unadditioned mortars ($10\% > 20\% > 0\%$). The former two were positioned in group 1 and the OPC in group 2. Likewise in the 365 d mortars, the type of waste (S0, S1, S2, S3) had no significant effect on mean mechanical performance. The mean compressive strength values for mortars with biomass waste differed significantly from the mean for the mortars with no waste (S0), with a $p\text{-value} < 0.05$. Those findings were consistent with the pozzolanicity exhibited by the waste.

Table 6. HSD multiple range groups by age, and percentage and type of waste: compressive strength

Table 7. HSD multiple range groups by age, and percentage and type of waste: flexural strength

3.3.3. Strength activity index

The 28 d strength activity indices for the cements containing a 20% addition, found with Equation 1, are shown in Figure 7(a). Although replacing cement with the three types of biomass waste induced a decline in strength relative to the reference, all the cements studied had SAI values of over the 75% required by ASTM C618 [51] for 28 d cements bearing 20% fly ash or natural pozzolans.

Figure 7. (a) Strength activity index for new 28 d cements; (b) correlation between 28 d strength activity index and CaO removed after 15 d

Those findings were consistent with the results reported by Sarabér [52] and Jidrada [26], who observed 28 d strength activity indices greater than or equal to 77% for cements containing agricultural biomass, meat and bone meal and combined coal and biomass combustion ash.

Figure 7(b) attests to the good linear correlation ($R^2=0.96$) between the 15 d Frattini test results and the 28 d strength activity index, in keeping with earlier observations by Mohammed et al. [53]. That correlation is attributable primarily to the higher strength (SAI) associated with the formation of additional C-S-H gels induced by intense portlandite reduction (Frattini test).

3.4. Total porosity and pore diameter distribution in cements

The total porosity and mean pore diameter ($4V/A$) values for the 7 d, 90 d and 365 d mortars given in Table 8 show that both declined over time, irrespective of the mortar. The mortars containing 10% waste had total porosity similar to that of the control, whereas the materials with 20% exhibited slightly greater porosity than the reference, although at <13% the rise was smaller than the replacement ratio.

Table 8. Total porosity and mean pore diameter in 7 d, 90 d and 365 d mortars

The mean pore diameter values clearly attested to pore system refinement with rising age and replacement ratio, with a decline relative to OPC in 365 d mean pore size of 9% to 32% in mortars with 10% waste and 22% to 44% in the materials with 20% addition. Those values were greater than observed earlier by Moretti et al. [54], who recorded a 9% decline in cements containing 20% bagasse ash.

Further to the plots in Figures 8 and 9, both macropore volume and mean pore diameter were linearly correlated to compressive strength. The same pattern was observed for flexural strength.

Figure 8 shows that for a given mortar, as the macropore ($>0.05 \mu\text{m}$) volume declined, compressive strength rose linearly ($R^2 \geq 0.94$), confirming this fraction's significant role in mechanical strength

reported by other authors [55, 56]. The graph further reveals that the mortars containing additions had a similar or smaller volume of macropores than conventional OPC.

Figure 8. Macropores volume vs compressive strength

As may be deduced from Figure 9, pore system refinement translated into a linear rise ($R^2 \geq 0.93$) in compressive strength (see section 3.3), corroborating earlier findings reported by Neville [57], who contended that in cement-based materials pore diameter distribution must be analysed in addition to total porosity, for pore system refinement enhances mechanical performance (see Figures 3 and 5).

Figure 9. Mean pore diameter vs compressive strength

Figure 10 plots the pore diameter distribution curves for 365 d mortars. The mortars containing 10% BBA had a 1.10 to 1.83-fold ($S_2 > S_3 > S_1$) greater volume of mesopores ($0.05 \mu\text{m} < \Phi < 0.007 \mu\text{m}$) than the OPC mortar, and those with 20% BBA, 1.55 to 1.93-fold greater ($S_2 > S_3 > S_1$). The figure also clearly shows that the inclusion of the additions induced a rise in the capillary pore ($0.01 \mu\text{m} < \Phi < 0.007 \mu\text{m}$) fraction. Here also, the behaviour observed was intrinsically related to waste pozzolanicity and the formation of extra C-S-H gel that filled the pores at later ages [58].

Figure 10. Pore diameter distribution in 365 d mortar

3.5. Microstructure

Figure 11 depicts the microstructure of 2 d and 365 d OPC and OPC+20S2 mortars. Irrespective of age, the partial replacement of cement with waste had no adverse effect on matrix uniformity nor did it alter cement hydration products (C-S-H gel, portlandite plates and ettringite needles or rods) or the presence of sand. The traces of unreacted addition in the 2 d new mortars disappeared with hydration time due to SCM pozzolanicity. The reaction mechanism involved is known to consist in OH^- ion-mediated breakage of Si-O and Al-O bonds and the reaction of silicon and aluminium anions with Ca^{2+} cations in the bottom ash, giving rise to C-S-H gels that form on the surface of the waste (SCM – see Figure 11) [58].

Figure 11. SEM micrographs of 2 d and 365 d mortars: (a) 2 d OPC (1000x); (b) 2 d OPC+20S2 (1000x); (c) 365 d OPC (4000x); and (d) 365 d OPC+20S2 (4000x) [Note: **CH**, portlandite; **C-S-H gel**, calcium silicate hydrate gel; **Ett**, ettringite; **SCMs**, supplementary cementitious materials]

The calcium silicate hydrate gels (C-S-H gels) in the 2 d and 365 d mortars depicted in Figure 12 densified the matrix, which at the later age was compact, continuous and strong. These C-S-H

materials would be type I gels on the Diamond [59] scale, given their common fibrous structure. The same morphology was reported by Zhang et al. [60], who noted that this typology was typical of cement paste or C_3S hydration, particularly when the materials are cured at high humidity.

Figure 12. SEM micrographs of C-S-H gel in: a) 2 d OPC; b) 2 d OPC+20S2; c) 365 d OPC; and d) 365 d OPC+20S2

The calcium-silicon (C/S) ratio in the C-S-H gels in the reference OPC mortar was 2.04 ± 0.10 and 1.61 ± 0.10 in S1, S2 and S3. The C/S ratios in the new BBA mortars lay within the usual range (1.2 to 2.3) for C-S-H gels in commercial cements [58, 61]. The lower C/S ratios in the BBA than in the OPC mortars were consistent with the range of values ($C/S = 0.98$ to 1.88) observed by Wang et al. [62] for pastes containing fly ash.

The C-S-H gels in the new cements also took up potassium in their structure, presumably in the interlayer or on the gel surface to offset the negative charges [63]. The K/Ca ratio found was 0.04 and the K/Si ratio 0.03, both of which were higher than the 0.01 [64] for unadditioned cements and near the value ($K/Si \approx 0.02$) [65] observed for synthetic gels with a C/S ratio of 1.6 in which the uptake of these alkalis was studied [66]. As observed in earlier research [58, 65, 67], that uptake was favoured when the C/S ratio declined and the $Ca(OH)_2$ content was lower, both of which conditions are found in the presence of additions.

The portlandite store visible in Figure 13 consisted in elongated hexagonal crystals with well-defined edges resulting from the hydration of the calcium silicates alite and belite. The crystal size observed, under $10 \mu m$ wide, concurred with findings reported by both Neville [57] and Metha and Monteiro [56].

Figure 13. Portlandite store: a) 365 d OPC (6000x); b) 365 d OPC+20S2 (5000x)

The micrographs in Figure 14 show the ettringite (Et) deposits [68], with longer and thinner needle-like crystals in the mortars containing additions (Figure 13b)) than in the reference mortars (Figure 13a)), as Hewlett [58] observed for pozzolan-bearing cements.

Figure 14. Ettringite needles a) 365 d OPC (10 000x); b) 365 d OPC+20S2 (13 000x)

This hydration product was found locally and in small quantities in all the mortars, primarily inside pores (where it normally forms, in addition to cracks), given the presence of the specific conditions required for its formation, including pressure and ionic species, particularly $Al(OH)_4^-$ [69].

3.6. Eco-efficient material

Table 9 lists the values used to estimate the energy consumed to manufacture one tonne of binder. The values attributable to cement manufacture are known [43, 70, 71]. No references are available for BBA, however, for which consumption was estimated from the energy required to grind other materials. Grinding the fired clay-based fraction of construction waste (CW) consumes 36 kW-h/t (Asensio, [72]), for instance, whilst Hamidi et al. [43] estimated the value for andesite to be 75 kW-h/t. Given that BBA is softer than those materials, consumption close to the CW value was taken to be the least favourable.

Table 9. Values used to calculate the energy consumed

The energy consumption per MPa of strength versus BBA content plot in Figure 15 shows that the BBA-bearing cements had higher energy performance than OPC, consuming less energy to manufacture a cement with the same mechanical strength. Consumption continued to decline with rising replacement ratio and curing age, with the 28 d materials consuming minimally 4% less and the 365 d mortars at least 15% less than OPC.

Figure 15. Energy performance in 28 d and 365 d mortars

The use of BBA as a supplementary cementitious material would also entail CO₂ emissions abatement at rates near the replacement percentage, as observed by a number of authors for other SCMs: fly ash, 20% [73, 74] ($\Delta=-19.8\%/ -17.8\%$ CO₂ emissions); blast furnace slag, 35% [73] ($\Delta=-33.7\%$ CO₂ emissions); coal spoils burnt at 600 °C, 20% [70] ($\Delta=-12.0\%$ CO₂ emissions); steel slag, 10% [75] ($\Delta=-9.5\%$ CO₂ emissions).

4. Conclusions

The following conclusions can be drawn from this study.

- New cements containing 10wt% or 20 wt% S1-, S2- or S3-type BBA are EN 197-1-compliant in terms of chloride and sulfate content.
- The pozzolanicity test findings show that the new cements with 20 % BBA (irrespective of type) qualify as CEM IV/A (11% to 35 %) pozzolanic cements.
- Adding 10% or 20% biomass waste (S1, S2, S3) to cement pastes retards initial setting times 1.5 to 1.9-fold relative to OPC pastes. The new cements have no adverse effect on workability, meeting the EN-197-1 minimum initial setting time requirement (≥ 60 min). These eco-efficient cements also comply with EN 197-1 soundness specifications.

- BBA-bearing mortar mechanical strength declines as the replacement ratio rises, particularly at early ages, although the difference narrows with curing time due to the pozzolanic activity of the additions. After 365 d mortars S1, S2 and S3 exhibit higher mechanical performance than OPC mortar, with strength rising relative to OPC by 6.5% in 10% additions and 3.5% in mortars with 20% waste.
- Irrespective of the waste type and replacement ratio, the mortars designed are EN 197-1-compliant for strength class 42.5 MPa.
- The type of waste (S1, S2, S3) has no statistically significant effect ($p\text{-value} > 0.05$) on long-term mechanical performance in the new cements. The variation observed in performance is explained primarily by curing time (>90%) and to a lesser extent by the replacement ratio (>2%) and the interaction between the two (>2%).
- SCM pozzolanicity induces a slight rise in total porosity in the 365 d mortars, at a rate lower than the replacement ratio. The additions also refine the pore structure, with a macropore ($>0.05\text{ }\mu\text{m}$) volume similar to that observed in OPC and a 5 % increase in the mesopore ($0.05 < \Phi < 0.007\text{ }\mu\text{m}$) fraction with 10 % replacement and a 30% rise in the materials with 20 % waste.
- S1, S2 and S3 induce no significant morphological change in the hydration products (C-S-H gel, portlandite and ettringite), although their inclusion lowers the C/S ratio and favours K uptake in the C-S-H gels as well as the formation of longer ettringite needles.
- The new cements exhibit higher energy performance than OPC, requiring less energy to produce a cement with the same compressive strength.

The BBA generated in biomass-fuelled electric power plants could be used to manufacture eco-efficient, lower clinker content II/A and IV/A cements, with all the associated economic, social and environmental benefits ensuing.

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(a)

(b)

Table 1. Compliance of eco-friendly cements with chemical specifications

Blended cement	Chemical constituent (wt%)		Pozzolanicity	Compliance with EN 197-1 [4] requirements	
	SO ₃	Cl		CEM II/A ^a	CEM IV/A ^b
OPC+10S1	3.04	0.003	-	Yes	No
OPC+10S2	3.03	0.006	-	Yes	No
OPC+10S3	3.06	0.020	-	Yes	No
OPC+20S1	2.77	0.006	Frattini positive	Yes	Yes
OPC+20S2	2.74	0.01	Frattini positive	Yes	Yes
OPC+20S3	2.80	0.04	Frattini positive	Yes	Yes
^a SO ₃ ≤ 4.00% and Cl ≤ 0.10%					
^b SO ₃ ≤ 4.00%; Cl ≤ 0.10% and Frattini positive					

Table 2. Cement compliance with physical requirements

Cement	Property		
	Setting time (± 10 min)		Soundness (mm)
	Initial time	End time	
OPC	135.0	207.6	0
OPC+10S1	186.0	252.6	1
OPC+10S2	192.0	258.0	1
OPC+10S3	204.0	268.2	1
OPC+20S1	192.0	274.8	1
OPC+20S2	196.0	265.2	1
OPC+20S3	264.0	367.8	1
EN 197-1 [4] limit	≥ 60	-	≤ 10

Table 3. Frattini test results for cements containing 20% BBA

Blended cement	[OH] (mmol/l)	[CaO] (mmol/l)		[CaO] reduction (%)
		[CaO] _{test}	Max [CaO]	
OPC+20S1-8d	79.75	5.55	5.41	-2.68
OPC+20S1-15d	83.50	3.80	5.11	25.63
OPC+20S2-8d	70.75	7.20	6.28	-14.69
OPC+20S2-15d	73.75	5.55	5.96	6.84
OPC+20S3-8d	77.25	6.35	5.62	-12.94
OPC+20S3-15d	84.75	5.00	5.02	0.36

Table 4. Correlation between mechanical properties and curing age

Mortar	Mechanical property					
	Compressive strength			Flexural strength		
	A	B	R ²	A	B	R ²
OPC	19.63	42.71	0.964	2.20	6.88	0.955
OPC+10S1	24.23	37.68	0.997	2.26	6.65	0.944
OPC+20S1	25.77	31.04	0.986	2.57	6.02	0.946
OPC+10S2	25.01	35.82	0.997	2.63	6.24	0.974
OPC+20S2	26.25	30.12	0.986	2.67	5.68	0.949
OPC+10S3	23.58	38.60	0.981	2.55	6.59	0.982
OPC+20S3	25.90	30.14	0.990	3.12	5.34	
Note. - $y = A \cdot \ln x + B$; where: y is the mechanical property (compressive or flexural strength) value (MPa); A and B are constants; and x is mortar age						

Table 5. MANOVA values for mechanical strength

Source of variation	Compressive strength			Flexural strength		
	Type III sum of squares	p-value	CF (%)	Type III sum of squares	p-value	CF (%)
Corrected model	41845.16 ^{a)}	0.00	-	551,59 ^{b)}	0.00	-
Intercept	741415.71	0.00	-	15741.65	0.00	-
Age	39756.73	0.00	95.42	453.14	0.00	90.25
Percentage of the waste (PW)	1157.18	0.00	2.78	10.02	0.00	2.00
Waste	15.01	0.06	0.04	1.33	0.05	0.27
Age * PW	159.46	0.00	0.38	5.45	0.00	1.09
Age * Waste	52.27	0.03	0.13	10.68	0.00	2.13
PW * Waste	19.09	0.03	0.05	0.92	0.02	0.18
Age * PW * Waste	69.61	0.00	0.17	2.02	0.06	0.40
Error	434.22	-	-	18.52	-	-
Corrected total	41663.57	-	-	502.09	-	-
Note. – CF: contribution of factor; ^{a)} $R^2 = 0.991$ (adjusted $R^2 = 0.989$); ^{b)} $R^2 = 0.968$ (adjusted $R^2 = 0.960$)						

Table 6. HSD multiple range groups by age, and percentage and type of waste: compressive strength

Compressive strength								
Mean ↑ +	Factor	Group	Curing age (d)					
			2	7	28	90	180	365
↑ +	Percentage	1	0	0	0	0 > 10	10	10 > 20
		2	10	10	10	20	0 > 20	0
		3	20	20	20	-	-	-
↑ +	Type of waste	1	S0	S0	S0	S0	S1> S2 >S3> S0	S1> S2 > S3
		2	S1> S3 >S2	S1> S3 >S2	S3> S2 >S1	S2> S1 >S3	-	S0

Table 7. HSD multiple range groups by age, and percentage and type of waste: flexural strength

Flexural strength								
Mean ↑ +	Factor	Group	Curing age (d)					
			2	7	28	90	180	365
↑ +	Percentage	1	0	0	0	0 > 10 > 20	0	10 > 20 > 0
		2	10	10	10	-	10 > 20	-
		3	20	20	20	-	-	-
↑ +	Type of waste	1	S0	S0	S0 > S2	S2 > S1 > S0	S1 > S0	S1 > S2 > S3 > S0
		2	S1	S1	S1> S3	S1> S0 > S3	S2 > S3	-
		3	S3> S2	S3> S2	-	-	-	-

Table 8. Total porosity and mean pore diameter in 7 d, 90 d and 365 d mortars

Mortar	Total porosity (vol.%)			Mean pore diameter (μm)		
	7 d	90 d	365 d	7 d	90 d	365 d
OPC	12.60	10.36	10.20	0.087	0.072	0.065
OPC+10S1	12.67 (+0.57)	10.69 (+3.15)	10.22 (+0.16)	0.084 (-3.79)	0.070 (-1.96)	0.059 (-9.40)
OPC+20S1	14.40 (+14.27)	11.77 (+13.62)	11.47 (+12.39)	0.078 (-10.10)	0.064 (-10.75)	0.050 (-22.34)
OPC+10S2	13.07 (+3.74)	11.49 (+10.90)	10.44 (+2.30)	0.095 (+9.30)	0.066 (-7.54)	0.044 (-32.20)
OPC+20S2	13.58 (+7.80)	12.49 (+20.58)	11.57 (+13.35)	0.080 (-8.61)	0.064 (-11.31)	0.036 (-44.22)
OPC+10S3	13.88 (+10.18)	11.27 (+8.75)	10.32 (+1.16)	0.086 (-0.92)	0.071 (-1.12)	0.053 (-18.95)
OPC+20S3	13.25 (+5.12)	11.79 (+13.74)	11.33 (+11.04)	0.087 (-0.57)	0.062 (-13.55)	0.037 (-43.76)
Note. -- in brackets, percentage variation relative to OPC						

Table 9. Values used to calculate the energy consumed

Process	Energy consumed [ref.]	
	Cement	BBA (S1, S2 y S3)
Manufacture	$E_{\text{cement}}^{\text{process}} = 1039 \text{ kW} \cdot \text{h/t}$ [70]	$E_{\text{BBA}}^{\text{process}} = 0 \text{ kW} \cdot \text{h/t}$ *
Grinding	$E_{\text{cement}}^{\text{grinding}} = 50 \text{ kW} \cdot \text{h/t}$ [43]	$E_{\text{BBA}}^{\text{grinding}} = 30 \text{ kW} \cdot \text{h/t}$
Note. - * BBA is not thermally treated		