

Article

Effect of Biomass Fly Ash on Fresh and Hardened Properties of High Volume Fly Ash Mortars

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Abstract: The objective of this work was to assess the use of biomass fly ash (BFA) as cement replacement material or as an alkalinity source in high volume fly ash mortar and concrete. Mortar formulations were prepared with different types of cement replacement: fly ash from thermal power plants, BFA, a blend of two pozzolans, and small amounts of BFA or/and hydrated lime (HL). Mortar formulations were tested both in the fresh and hardened state. The replacement of cement by the two fly ashes led to a decrease in the mechanical strength. The best strength values were obtained when higher HL content was introduced in mortars, however, mortars with the lower BFA content presented the best results for the majority of the tests. In general, BFA has a similar effect on cementitious mortars to coal fly ash, having good performance as cement replacement.

Keywords: biomass fly ash; cement replacement; concrete; mortar



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1. Introduction

Nowadays, the Green and Circular Economy is gaining standing among academics and policy markets worldwide [1,2]. This green economy results in “improved human well-being and social equity, while significantly reducing environmental risks and ecological scarcities” [2]. This means that a Green and Circular Economy is low-carbon, resource-efficient, and socially inclusive, leading to a development state that reduces carbon emissions and pollution, increases resource efficiency, and prevents the loss of biodiversity and ecosystems [2]. The use of clean and affordable renewable sources is one of the main achievements of this Green and Circular Economy.

The increase in energy supply by renewable sources is a key issue to achieve and adopt sustainable development in several countries, and among these sources is biomass [1,3]. Its utilization leads to a direct reduction in greenhouse gases emission when substituting fossil fuels [3,4]. Biomass combustion is taken as a sustainable and renewable resource of energy when the rate of consumption is lower than the rate of natural raw materials production and very important in this context is the use of residual biomass from several forestry and industrial operations [5]. A great number of biomass resources are used in several industrial sectors to produce heat and power process applications and the national electric grid, as it happens, in the pulp and paper production and wood and furniture industry. In those sectors, the raw biomass feedstock preparation generates significant amounts of residual biomass that is then valorized in energetic applications as fuel in thermochemical conversion processes, mostly combustion [3,6–10].

During thermochemical valorization of biomass for energy different types of ashes are produced, and these are dependent on the characteristics of the boiler and the treatment system of the fuel gases [3,10]. Usually, two types of ashes are produced (bottom and

fly ash) and according to the European List of Waste [11], they are considered as non-hazardous wastes. Several strategies have been adopted for ash management, such as the addition to forest soils and its incorporation in cement production [3,12]. Its utilization on the soil is limited by regulations, usually, biomass fly ash is enriched in heavy metals (e.g., Cr, Cd, Zn, and Pb) [10], when compared to the bottom ashes, those elements are leachable to the soil, and this could lead to the soil and groundwater contamination [13–15]. Thus, it is important to study alternative applications for specific types of ashes from biomass combustion.

Several types of biomass originate fly ash with similar pozzolanic activity as coal fly ash (CFA), such as rice husk, wheat straw, sugar cane straw, and wood [5,16–19]. The physical-chemical characteristics of ashes from biomass combustion are strongly influenced by the biomass type used as fuel [5,19,20]. Moreover, the same type of biomass may lead to different types of ashes, as the fly ash properties depend on growth and production parameters such as weather, season, storage, and geographic factors [19,21–23]. In Portugal, the BFA resulting from heat and power production in industrial combustion facilities has been increasing in recent years [24]. Portugal has no guidelines for biomass fly ash management; thus, the ashes are classified as industrial waste [10]. The chemical and physical characteristics of BFA are significantly different than coal fly ash. Usually, they are more alkali (higher Na and K content), have less alumina content, have a higher loss-on-ignition, and their mineralogical composition is very different than CFA [19,25,26].

Several studies [3,27–32] dealt with the use of BFA alone or blended with CFA and concluded that BFA may lead to similar or even better performances in cement-based mortars and ultimate strength and durability of concrete. Wang et al. [19] studied the properties of concrete with BFA ash and compared them with concrete containing coal fly ash. The results showed that 25% of cement replacement by BFA led to mechanical properties that could be considered statistically similar to those achieved with CFA concrete [19,33].

Several authors [12,25,34–38] studied the workability of cement materials. Results showed that the slump values decreased with the increase in cement replacement by BFA, which led to a decrease in the workability of fresh mixtures. Coelho [39], Rajamma et al. [29], and Barbosa et al. [3] studied the effect of the incorporation of wood fly ashes in the mechanical strength of concrete. The studies reported a decrease in the mechanical resistance with the increase in ash incorporation in concrete. Barbosa et al. [3] also studied the compressive strength for different curing periods and observed that BFA delayed the hydration. The authors verified that during the cure period, the concrete with a lower replacement level of cement had higher values for compressive strength [3]. It was possible to observe that, for 28 days of curing, concrete with 30–40%wt of cement replacement by BFA presented values for compressive strength between 20 to 30 MPa [29,39,40].

Udoeyo et al. [41] measured the water absorption capacity of concrete produced with 5, 10, 15, 20, 25, and 30%wt by weight replacement of binder. An increase in the water absorption with the increase of ash content was reported.

Despite several reported results on the use of BFA as cement replacement material, few studies that focus on its use in concrete with high volume of cement replacement by BFA, alone or blended with CFA. The main goal of this study was to understand the effect of using BFA in high volume fly ash (HVFA) mortar alone or blended with CFA. On the other hand, one of the issues related to HVFA concrete is the possibility of reinforcement corrosion that may be associated with its lower carbonation resistance. As BFA is more alkaline, with higher calcium content than CFA, an experimental study was carried out concerning the utilization of BFA on mortars to evaluate its effect on the carbonation of mortars. A comparison with the utilization of hydrated lime (HL) for the same purpose was also carried out.

2. Materials and Methods

2.1. Raw Materials

A CEM I 42.5R (from Outão, Secil, Portugal) cement and a commercial Portuguese river rolled sand 0/4 mm were used as main binder and aggregate, respectively. BFA was collected in a Portuguese pulp and paper industry, which uses forest residues, such as eucalyptus and pine bark, as fuel to produce heat and power in a bubbling fluidized bed combustor. The bubbling fluidized bed reactor used sand as the bottom bed. The fly ash was collected in an electrostatic precipitator used for air pollution control concerning the particulate matter. CFA was sampled from a Portuguese thermoelectric power plant (from Pegop, Pego, Portugal) using coal as fuel. The ashes were used in the mixtures as received, without any pre-treatment. In the preparation of some mortar and concrete formulations, hydrated lime (from the Lusical industry) was used as an addition, with the main goal of providing the alkalinity lost due to the cement replacement by high amounts of coal fly ash.

The physical and chemical characterization of CFA and BFA is shown in Table 1. The loss-on-ignition and the chemical composition were obtained by X-Ray Fluorescence using a Panalytical Axios spectrometer. The density was determined according to the ASTM C188-1995 standard [42].

Table 1. Chemical and physical characteristics of used materials.

Parameters	CFA	BFA	CEM 42.5I	Hydrated Lime	Sand
Chemical elements (by FRX) (%wt)					
SiO ₂	54.08	36.06	15.94	-	95.30
CaO	3.27	28.00	52.94	93.0 (CaOH) ₂ *	0.13
Na ₂ O	0.50	0.87	0.81	-	0.09
Al ₂ O ₃	26.38	8.42	3.27	-	2.22
MgO	1.55	3.53	4.43	≤3.0	0.11
K ₂ O	1.64	5.42	7.43	-	1.03
Loss on ignition	2.73	6.27	2.34	-	0.11
Physical Characteristics					
Diameter for 10% of retained material (µm)	1.53	5.91	1.33	-	550
Diameter for 50% of retained material (µm)	8.55	46.70	9.30	-	1400
Diameter for 90% of retained material (µm)	20.19	230.74	24.16	-	4000
Specific weight (kg/m ³)	2420	2619	3100	2230	2600

* given by the industry datasheet.

BFA showed the highest value for LOI, followed by CFA, cement, and sand. The silica compounds were present in higher content in sand, CFA, and BFA. But the calcium compounds were present in higher concentrations in cement and also in BFA. This higher content of calcium is also observed in several other studies [12,32,43,44], but not all biomass fly ash presents such a high content [14,19,29]. The differences in calcium concentration in fly ashes are related to the technology used for biomass combustion, biomass composition [45–48], and the operation conditions [33,49,50]. FA and BFA also presented considerable content of aluminum, magnesium, and potassium compounds.

2.2. Mortar Formulations and Characterization

A set of mortars were prepared, and their formulations are shown in Table 2. All mixtures were made with 1 wt. part of binder (considered as the sum of cement plus fly ash and hydrated lime): 2.5 wt. parts of aggregate and water–binder mass ratio (w/b) of 0.5. These proportions were chosen as the main aim of this study is to find a solution for the conventional concretes, and usually the cement dosage on a conventional plain cement concrete is around 300 kg/m³ and the content of sand is equal to 750 kg/m³ with a water/binder ratio of 0.5. These proportions for mortar production were chosen considering published studies that show that the results obtained for the properties of conventional

concrete are coincident with the results obtained in the corresponding mortars [51–55]. On the other hand, one of the issues related to HVFA concrete is the possibility of reinforcement corrosion that may be associated with its worst carbonation behavior. As BFA is more alkaline than CFA, an experimental study was carried out concerning the use of BFA on mortars to evaluate its effect on the carbonation of mortars. A comparison with the utilization of hydrated lime for the same purpose was also carried out as it was shown in other studies [56] that the introduction of lime minimizes the issues related to pH decreased by preventing the loss of alkalinity. Small amounts of HL (0.5, 1.3, and 5%wt) were studied, as these amounts of hydrated lime led to an increase in carbonation resistance [57]. For each mixture, three specimens were prepared, to guarantee the statistical representativeness of the results. Mortar mixtures were prepared according to the following procedure: (i) solid and liquid weighing, (ii) addition of water to the solids, (iii) mixing for 1 min at a low rotation speed, (iv) stopping for 1 min, (v) mixing again for 1 min at a high rotation speed, and (vi) testing the fresh properties of the mixture, according to EN 1015-2:1998 [58].

Table 2. Mortar formulations.

Nomenclature	Binder
100C	100% Cement
50C-50FA	50% Cement + 50% Fly ash
50C-50BFA	50% Cement + 50% Biomass fly ash
50C-49.5FA-0.5HL	50% Cement + 49.5% Fly ash 0.5% Hydrated lime
50C-48.75FA-1.25HL	50% Cement + 48.75% Fly ash + 1.25% Hydrated lime
50C-45FA-5HL	50% Cement + 45% Fly ash + 5% Hydrated lime
50C-49.5BFA-0.5HL	50% Cement + 49.5% Biomass fly ash + 0.5% Hydrated Lime
50C-48.75BFA-1.25HL	50% Cement + 48.75% Biomass fly ash + 1.25% Hydrated Lime
50C-45BFA-5HL	50% Cement + 45% Biomass fly ash + 5% Hydrated Lime
50C-49.5FA-0.5BFA	50% Cement + 49.5% Fly ash + 0.5% Biomass fly ash
50C-48.75FA-1.25BFA	50% Cement + 48.75% Fly ash + 1.25% Biomass fly ash
50C-45FA-5BFA	50% Cement + 45% Fly ash + 5% Biomass fly ash
50C-49.5FA-0.25BFA-0.25HL	50% Cement + 49.5% Fly ash + 0.25% Biomass fly ash + 0.25% Hydrated lime
50C-48.75FA-0.625BFA-0.625HL	50% Cement + 48.75% Fly ash + 0.625% Biomass fly ash + 0.625% Hydrated lime
50C-45FA-2.5BFA-2.5HL	50% Cement + 45% Fly ash + 2.5% Biomass fly ash + 2.5% Hydrated lime
50C-25BFA-25CFA	50% Cement + 25% Biomass Fly Ash + 25% Coal Fly Ash

The tests carried out for mortar characterization are presented in Table 3. The workability of fresh samples was determined via the flow spread test, by the measurement of diameters (in mm) in two perpendicular directions after 15 strokes on the flow table, according to EN 1015-3:1998 [59]. The density was determined according to EN 1015-2:1998 [58] and the air volume content of fresh mortar was measured according to EN 1015-7:1998 [60]. The bulk density was determined by the measurement of the mass of fresh mortar and the volume which it occupies when it was introduced and compacted into a vessel of a given capacity. For the air volume determination, a volume of mortar was placed in a vessel of 1L, water was introduced on top of the mortar surface, and pressurized air was forced into the mortar displacing air from within any pores. The water level falls and reflects the volume of air displaced from the mortar.

For the tests in the hardened mortar, the mixtures were placed in 40 × 40 × 160 mm³ molds. First, the molds were half-filled and then compacted for 60 s. After that, the molds were filled and compacted again. To avoid the loss of water, the molds were covered with plastic film and stored in a humidity control chamber (21 °C – 87% RH) for 24 h. Then, the samples were demolded, and mortars were cured in water immersion, at an environment temperature (±20 °C), the periods of curing are expressed in Table 3.

Table 3. Tests carried out in mortars in the fresh and hardened state.

Test	State	Period of Curing (Days)	Unit	Standard
Flow test	Fresh	After mixing	mm	EN 1015-3:1998
Density		After mixing	kg/mm ³	EN 1015-2:1998
Air volume content		After mixing	%	EN 1015-7:1998
Electric resistivity	Hardened	2,7,28,56,90,180	kΩ/cm	-
Ultrasound		2,7,28,56,90,180	μS	EN 12504-4:2007
Mechanical strength		2,7,28,56,90,180	N/mm ²	EN 1015-11:1999
Water absorption by Immersion		2,7,28,56,90,180	%	EN 1015-10:1999/LNEC E 394:1993
Water absorption by Capillarity		2,7,28,56,90,180	kg/(m ² ·min ^{0.5})	EN 1015-18:2002
Accelerated Carbonation		2,7,28,56,90,180	mm	EN 1015-3:1998

Several non-destructive tests were carried on the mortar specimens, such as electric resistivity and ultrasonic pulse velocity (UPV). These tests estimate the mechanical properties and the quality and the homogeneity of mortar materials and make the correlation with the destructive tests, such as compressive strength [61,62]. The electric resistivity was measured using Resipod Proceq equipment, which is composed of four equidistant (38 mm) electrodes. During this test, an alternating current between the external electrodes was provided and the electric potential difference between the internal electrodes was measured. The electric resistivity is measured through the Ohm law and computed by the equipment used.

The UPV was measured in the specimens prepared for the flexural test, according to EN 12504-4:2007 [63], in two directions, direct and semi-direct, with cells with 54 kHz. Before each analysis, a calibration (25.4 μS) of the UPV equipment was carried out. The samples were 160 mm long and 40 mm wide. The results are an average of the results obtained for the three specimens. The measure of UPV in direct position was obtained with the transmitter and receiver transducers positioned on top and bottom of each specimen, corresponding to a distance of 160 mm between transducers. The semi-direct measures were carried out placing the transmitter on one side and the receiver on a side perpendicular to the first one, leading to 80 mm distance between the two transducers. To mitigate the influence of voids between the transducers and specimens, an appropriate coupling gel was applied to the transducers. Three independent readings for each sample were registered.

The ultrasonic pulse velocity was calculated by dividing the time of the first wave arrival by the length of the specimen. Each result value corresponds to an average of five measurements done for three specimens for each mortar formulation (which correspond to fifteen measurements).

The dynamic modulus of elasticity was determined by ultrasonic pulse velocity and calculated through Equation (1), according to the works in [64,65].

$$E_{dn} = \rho c^2(((1 + \nu)(1 - 2\nu))/(1 - \nu)), \quad (1)$$

where

E_{dn} is the dynamic modulus of elasticity of mortars (GPa),

ρ is the hardened mortar density (kg/m³),

c is the UPV (km/s), and

ν is the Poisson's ratio was assumed as 0.2 for all mortar mixtures.

The samples for mechanical strength, water absorption, and carbonation tests were prepared based on EN 1015-11:1999 [66]. The flexural strength was carried out in a LLOYDS Instruments universal testing machine, with a maximum capacity of 50 kN. The compressive strength was performed in an ELE Auto Test press, with a capacity between 5 to 110 kN. The mechanical strength was measured at the curing ages listed in Table 3.

To measure the water absorption, the $40 \times 40 \times 160 \text{ mm}^3$ samples were previously subjected to be resulting from the 3-point flexural test. Then, one part of the specimen was used for the capillarity test and the other was used for the immersion test. All the mortar parts were dried at $60 \pm 5 \text{ }^\circ\text{C}$ until a constant mass was reached before the water absorption tests [67]. The determination of open porosity was carried out at atmospheric pressure and the samples were immersed in water for 24 h. After that period, the specimen's surface was wiped with a cloth to remove any adsorbed water from the surface, and then the samples were weighed. The specimens were immersed for 24 h periods until no further increase in apparent mass was observed. This was considered reached when two consecutive weight measurements do not differ by more than 0.1% wt. The open porosity was determined according to the works in [67–69] following Equation (2).

$$A_i = (m_1 - m_3)/(m_1 - m_2) \times 100, \quad (2)$$

where

A_i —open porosity (%),

m_1 —weight of water saturated specimen (g),

m_2 —weight of saturated specimen immersed in water (g), and

m_3 —weight of specimen (g).

The water absorption coefficient by capillarity was measured by placing the specimens in a box with the broken face of the prism downwards and immersed in water with a depth of 5 mm during the test; the other faces were covered with silicone to ensure that the water just enters in the sample by the capillaries of the face in contact with water. The water level was maintained through the test. Several weight measures were done: 0, 0.08, 0.17, 0.25, 0.33, 0.5, 0.75, 1, 1.5, 2, 2.5, 3–7, 24, 48, 72, 96, 120, 144, and 168 h. After 168 h of testing, the specimens were weighed every 7 days until a constant weight was reached. The water absorption by capillarity is determined by the calculation of the slope of the linear regression line that linked the points related to the measures carried out between 10 and 90 min [67,70].

For the carbonation test, the cured samples were preconditioned in an isolated container subjected to a constant temperature and relative humidity (RH) ($88.0 \pm 4.0\%$ and $17.5 \pm 1.6 \text{ }^\circ\text{C}$) for 14 days, to ensure the stabilization of humidity within the samples. After this period, the samples were sealed with paraffin, except for two opposed faces, and placed in a chamber to test the accelerated carbonation ($4.2 \pm 0.1\%$ wt of CO_2 , $52.6 \pm 8.3\%$ RH, and $20.0 \pm 0.8 \text{ }^\circ\text{C}$). To measure the carbonation depth, several cross sections were taken by diametric compression, and after they were sprayed with a phenolphthalein indicator.

3. Results and Discussion

3.1. Fresh Properties

The flow spread values obtained for each mortar formulation are shown in Table 4. One may observe that mortars with 50%wt of cement replaced by BFA and with cement replaced by BFA (48.5%wt) and HL (1.25%wt) presented flow spread values similar to those observed for the reference formulation, and in some cases lower than reference. These results are according to those achieved in other research studies [12,71]. They are related to the physical characteristics of biomass fly ash from wood. Wood fly ash presents a heterogeneous distribution of particles, with irregular shape and fineness, that determine the high specific surface area and control the compactness of mixtures [71,72]. Besides that, the high organic matter (Table 1) leads to the adsorption of water molecules, which leads to a decrease in the free water available for workability purposes [12,29,71]. The incorporation of CFA on the mixtures, alone or blended with BFA or /and HL, increased the value of spread flow when compared with the reference mixture and with the mixtures containing only biomass fly ash.

Table 4. Flow spread, density, and air content of fresh mixtures.

Mortar Formulation	Flow Spread (mm)	Density (kg/m ³)	Air Content (%)
100C	203.20	2231.80	2.80
50C-50FA	242.10	2190.30	0.70
50C-50BFA	209.23	2215.57	1.75
50C-49.5FA-0.5HL	236.68	2208.17	0.70
50C-48.75FA-1.25HL	234.64	2190.77	0.75
50C-45FA-5HL	230.36	2213.40	0.80
50C-49.5BFA-0.5HL	212.73	2213.40	2.10
50C-48.75BFA-1.25HL	200.45	2182.43	2.30
50C-45BFA-5HL	198.10	2172.57	2.10
50C-49.5FA-0.5BFA	242.82	2216.73	0.80
50C-48.75FA-1.25BFA	234.00	2201.83	0.75
50C-45FA-5BFA	231.95	2145.83	0.80
50C-49.5FA-0.25BFA-0.25HL	234.27	2191.40	0.50
50C-48.75FA-0.625BFA-0.625HL	231.41	2152.33	1.25
50C-45FA-2.5BFA-2.5HL	230.36	2200.57	0.85
50C-25BFA-25CFA	223.64	2173.23	0.80

In terms of the density of the fresh mixture, no significant differences were observed between the different mixtures (Table 4). On the other side, significant differences were observed in the amount of air content. The reference mixture presented more voids (almost 3% of air content) than the other mixtures. Once again, the mixtures with a high content of BFA present a similar behavior when compared with the reference. Mixtures with a high content of CFA presented lower values (below than 1%). Similar results were found in other studies [73–77]. In some of those studies, the results were explained by the smooth surface characteristics and the spherical shape of CFA which improved the fresh properties of concrete [75].

3.2. Hardened Properties

3.2.1. Electric Resistivity and Ultrasonic Velocity Pulse

The electric resistivity was measured for each mortar formulation, and its results are presented in Figure 1. The electric resistivity is affected by several parameters such as the free water content, the origin and the concentration of ionic species in the pore solution, the amount of hydration products, the particle size, and the specific surface area of raw materials [71].

The electric resistivity evolution is similar for all mortar formulations, increasing with the curing period. At early ages, reference mortar presents higher resistivity values in comparison with the mortars containing ashes (Figure 1). Similar results were found in other researches, and this behavior is explained by the fact that a higher content of cement (like in reference mortar) leads to a faster setting [71]. The time needed for the pozzolanic reaction between CFA or BFA and calcium hydroxide resulting from cement hydration leads to longer setting periods in these mortars. Besides, there is a delay in the gain of resistivity on mortars with ashes at the early ages, the values observed after 28 days of curing are higher than those registered in the reference mortar (Figure 1). The mortars with CFA alone or blended with BFA presented a higher electric resistivity and similar results were found in [78].

The electric resistivity is an important parameter to control the initiation and propagation of the corrosion of steel reinforcement in concrete [79–82]. The use of CFA and BFA and ternary binder on concrete may contribute to decrease this risk of corrosion and improve the durability of concrete, as the objective of using pozzolan in concrete is mainly for concrete durability improvement [79], namely, to increase the resistance to chloride diffusivity [81].

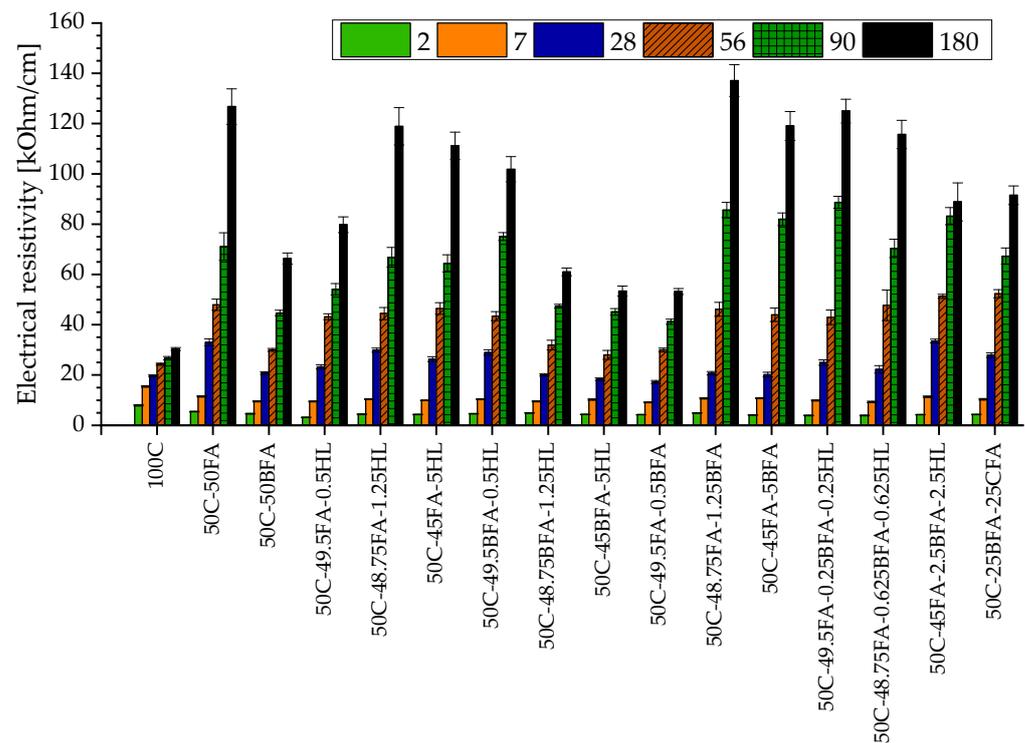


Figure 1. Electric resistivity evolution of mortars for 2, 7, 28, 56, 90, and 180 of curing.

Mortars with 50% cement replaced by BFA presented lower electric resistivity values when compared with CFA mortar, however they presented higher values than those observed in cement mortars.

The introduction of HL in a mortar with high volume fly ash content (CFA and BFA) has a different effect in electric resistivity. In mortars with CFA or with BFA, the increase of HL led to a decrease in the electric resistivity of mortars. The electric resistivity values of the three compositions are lower than the value for the mortar produced only with ashes (Figure 1). However, the values of electric resistivity of BFA/HL mortars were lower than those of CFA/HL mortars. The replacement of HL by BFA, in mortars with 50% of cement replaced by CFA, leads to an increase in the resistivity. The higher values were observed in the formulation with lower BFA content (50C-49.5CFA-0.5BFA, Figure 1). These results showed that the lack of cement is compensated by the synergistic effect between CFA with BFA [78].

The mixture of the three materials (CFA, BFA, and HL) with cement as a binder does not lead to a significant gain of electric resistivity, which shows that the synergetic effect of these four materials is not very effective.

The UPV increased with curing time in all samples until 90 days of curing. The maximum velocity was obtained in the reference sample for all curing periods. The decrease in velocity for mortars with the fly ashes reveals that the compressive strength of samples with ashes had lesser compressive strength than the plain cement mortars. The UPV depends on the density and elastic properties of the building materials [62,83,84]. As the UPV is influenced by the heterogeneity of samples, such as the presence of voids, the reduction of this parameter in mortars with BFA (Figures 2 and 3) showed that these samples were more heterogeneous. The UPV is related to the strength of the material, so a decrease in this parameter indicates a decrease in its mechanical strength [85].

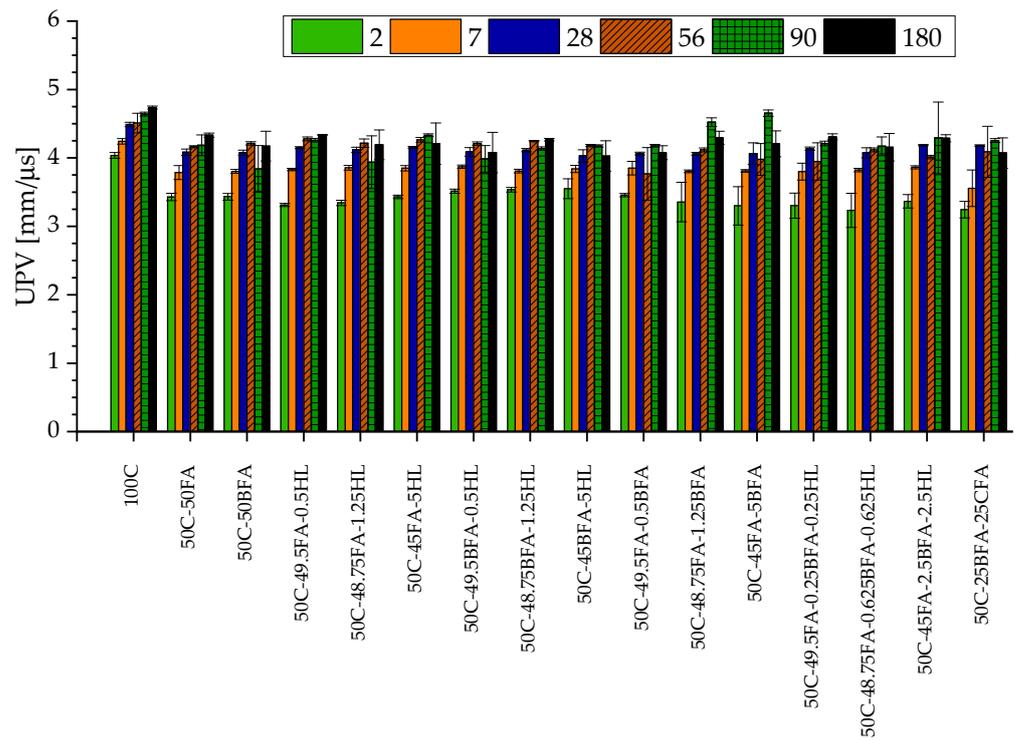


Figure 2. UPV values from the direct method for the different mortar formulations for 2, 7, 28, 56, 90, and 180 of curing.

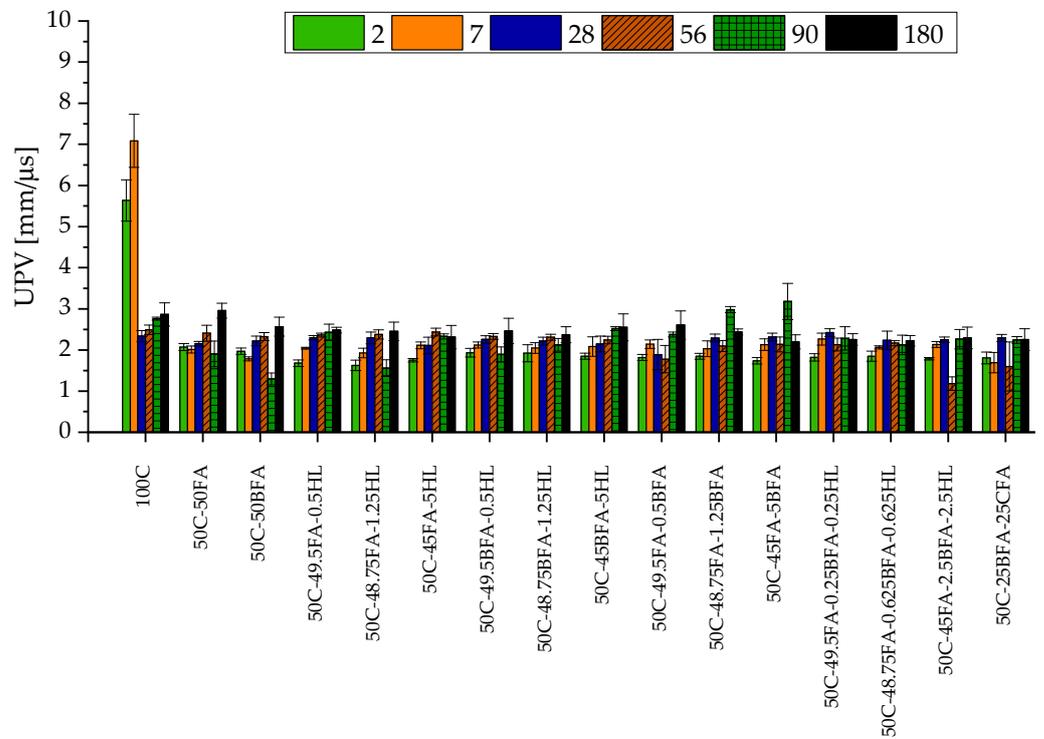


Figure 3. UPV values from the semi-direct method for the different mortar formulations for 2, 7, 28, 56, 90, and 180 of curing.

In terms of UPV measured in a semi-direct direction, significant differences may be observed when comparing the plain cement reference mortar and those containing ashes at early curing ages. A significant decrease in the UPV in mortars containing ashes may be noticed (Figure 3). However, with the increase in the curing age, UPV measured is similar for all mortars.

The dynamic modulus of elasticity determined by Equation (1) vs. curing time is presented in Figure 4.

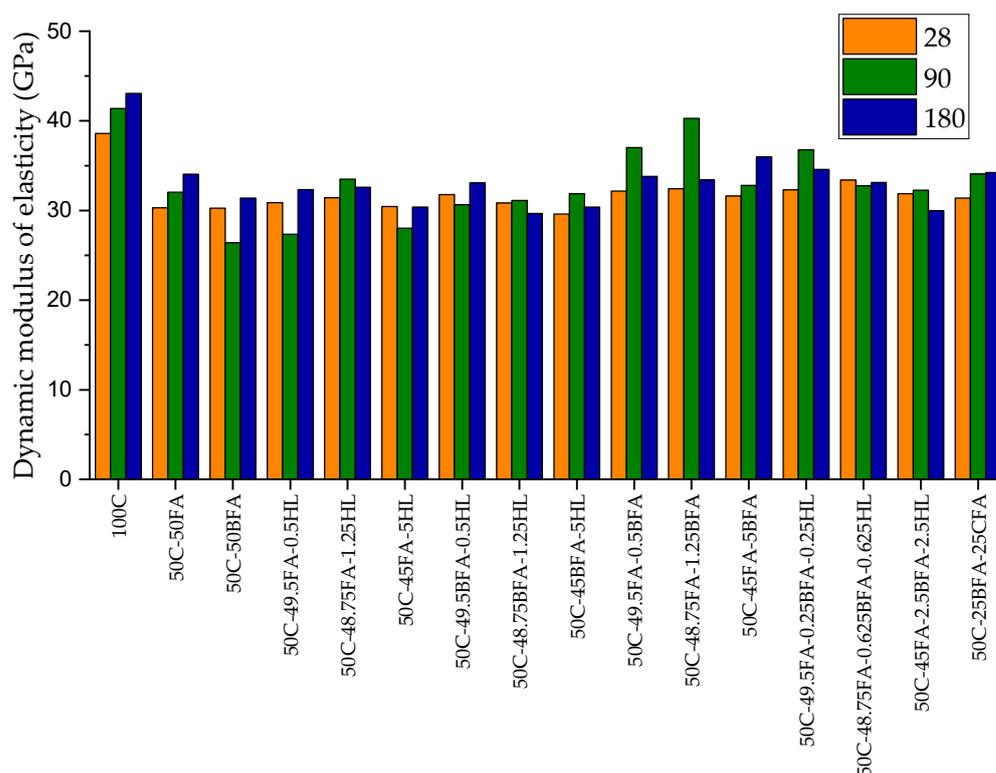


Figure 4. Dynamic modulus of elasticity for the different mortar formulations for 2, 7, 28, 56, 90, and 180 of curing.

The values observed, for each curing age, represent the average of three measurements on each sample. Mortars with CFA or/and BFA present lower values for the dynamic modulus of elasticity than that of reference mortar, for all curing ages. These results showed that the introduction of ashes as cement substitution has a significant effect on some mortar properties, such as the reduction of the hardened concrete density and the increase of heterogeneity of the resulting mortar [64].

An important observation is that the utilization of BFA as a reservoir of alkalinity in mortars with CFA presented higher values of dynamic modulus of elasticity when compared with the other mortars containing ashes. This phenomenon is particularly noticed at 90 days of curing (Figure 4). This can be related to a good synergic behavior between the two types of ash.

3.2.2. Flexural and Compressive Strength Results

In Figure 5, the values obtained for the flexural mechanical strength of the different mortars may be observed. The results showed an increase in flexural strength with the curing age. The replacement of cement by CFA, BFA, or/and a blend of the two ashes led to a decrease in the flexural strength when compared with the reference mortar. This was expected, because of the higher percentage of cement substitution, and it is known that higher contents of pozzolans in mortars or concrete contribute to decreasing the strength of

materials, despite the pozzolanic reaction, not sufficient to fulfill the lack of cement. Similar results were observed in other studies [29,31,85–88].

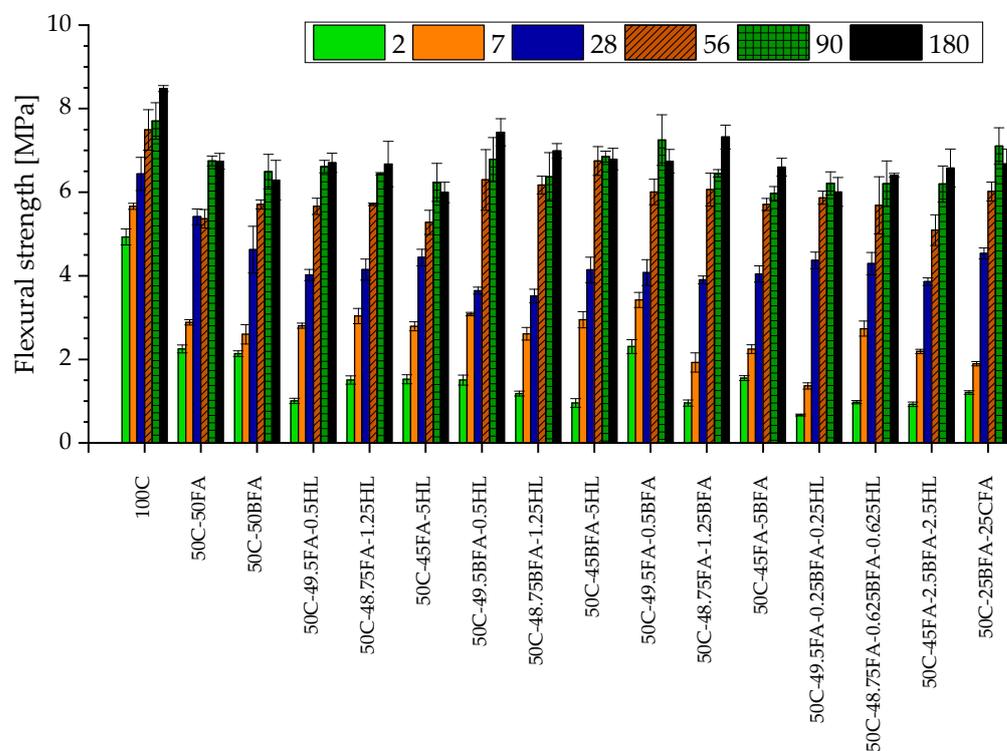


Figure 5. Evaluation of flexural strength values of mortars with the curing period for 2, 7, 28, 56, 90, and 180 of curing.

In terms of the utilization of HL, in the mortar with CFA and BFA, the best results were observed for the composition with the higher lime content. On the other side, when it is used BFA in mortars with CFA, the mortars with the lower biomass content present the best results. The utilization of the two ashes and HL has different effects on the flexural strength in the different periods of curing.

Similar results to those observed for flexural were also noticed for the compressive strength (Figure 6). A significant decrease was observed with the incorporation of ashes and HL as cement replacement in the compressive strength, when compared with the reference mixture (100C), was observed in some cases a 50% reduction on the values (e.g., for 28 days in 50C-50CFA) (Figure 6). An increase in the compressive strength with the curing age was also observed and similar results were found in [38,44,86,89–92]. The use of BFA as cement replacement led to a mortar with lower strength than the mortar with CFA after 56 days of curing (Figure 6), with values between 18.4 and 21.1 MPa for 50C-50BFA samples and 23.4 and 26.0 MPa for 50C-50CFA. Several studies showed that the use of BFA from wood as partial cement replacement in concrete leads to a decrease in the compressive strength [12,29,31,35,93].

The introduction of HL in mortars with CFA does not have a significant improvement in the strength of mortar when compared to the plain cement one. An increase in the compressive strength at early ages was observed for mortars with HL and CFA. This can be due to the breaking down of CFA particles at the high calcium hydroxide content and the inner silicate phase becoming suitable for the hydration reaction with the production of more calcium silicate hydrates [94]. However, its introduction in mortars with BFA leads to an increase in the mortar strength, being the cement substitution of 1.25% by HL, the content that provides the best results for the different curing ages.

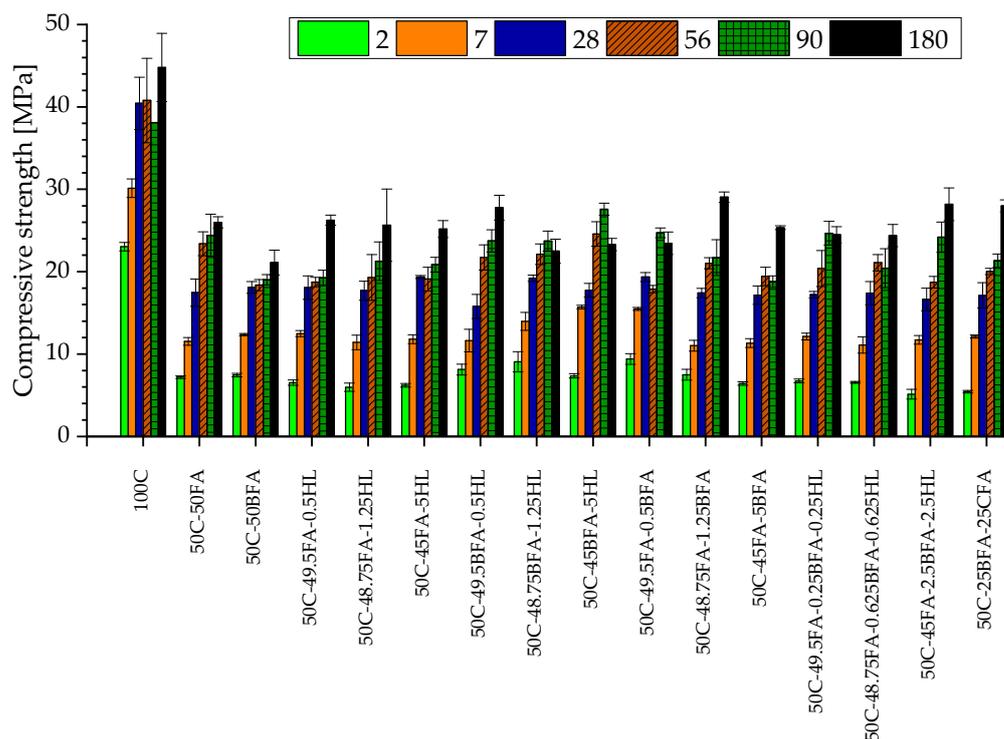


Figure 6. Evaluation of compressive strength values of mortars with the curing period for 2, 7, 28, 56, 90, and 180 of curing.

The introduction of BFA as a reservoir of alkalinity on the CFA mortar did not show a significant effect on the compressive strength at early ages. However, for 90 and 180 days curing, mortars with CFA and BFA presented the best results (50C-45CFA-5BFA-90 days and 50C-49.5CFA-1.25BFA) and similar results were observed when the two fly ashes were used together with HL.

3.2.3. Water Absorption by Immersion and by Capillarity

The water absorption by immersion is relevant for the concrete durability because it allows assessing the open porosity of concrete, by indirect measurement of the mass of the samples immersed in water for 24 h periods. This test is affected by several factors that control the porosity of concrete/mortar, and one of them is the water/binder relation and the content of cement replacement by pozzolanic materials. The water immersion was determined at 28, 90, and 180 days (Figure 7). All mortars containing ashes have a higher water immersion coefficient than cement mortar. BFA mortars have similar behavior in terms of water absorption to CFA mortars. In general, the porosity decreases with the curing age. This is due to the increase of hydrated compounds content and latent hydration during the pozzolanic reaction of ashes in the presence of calcium hydroxide [82].

The introduction of HL in mortars with CFA does not have a different effect on the water absorption coefficient, for the early ages, when compared with the mortar containing only CFA. However, for 180 days curing, the coefficient for mortar with 0.5% of cement replacement by lime has a lower value than that observed in the mortar with CFA, but still higher than the reference one. On the other side, the introduction of lime in mortars with BFA does not have a different effect on the open porosity when compared with the mortars made only with BFA.

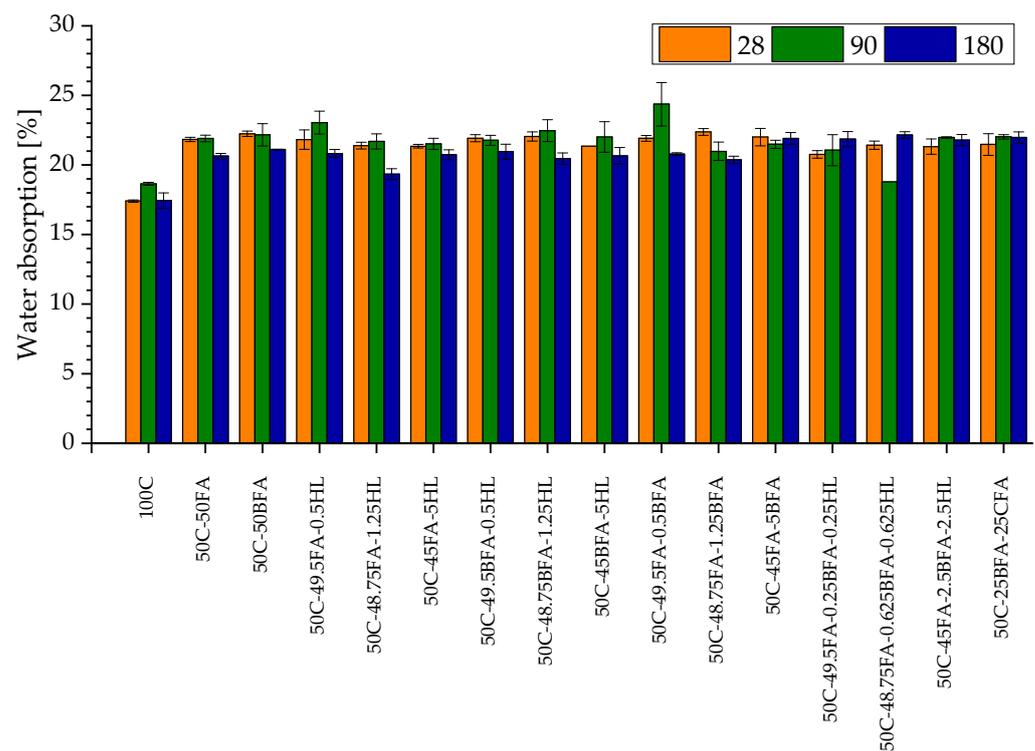


Figure 7. Open porosity of mortar samples determined by water absorption for 28, 90, and 180 days of curing.

The use of 0.5% of BFA on mortars with CFA leads to a decrease in the open porosity for mortar with 90 and 180 days curing, when compared with mortars made only with cement and CFA. The other replacements did not lead to an improvement in the open porosity when compared with the mortar containing CFA. The use of the two pozzolans and lime together did not allow an improvement on the open porosity of mortars when compared with the reference ones or with mortars containing only one pozzolan or with the two pozzolans.

The capillarity absorption curves are shown in Figure 8 and capillarity absorption coefficient is shown in Table 5.

In general, the coefficient of water absorption decreased with the curing age, and this was expected as during the curing, the reaction of hydration occurs, leading to a decrease in the voids and the physical structures of mortars. Similar results were found in Silva and Brito (2015) [95]. Mortar with CFA had a lower capillarity coefficient than the reference mortar. On the other side, mortars with BFA had a higher coefficient than the reference and CFA mortars, for all curing ages. It was observed that CFA mortars with lime had higher values for the coefficients (Table 5) than the mortars made only with cement and CFA. The higher results were achieved in the mortar with the higher lime content (50C-45CFA-5HL).

As can be seen from Figure 8, the replacement of cement by CFA did not have a significant impact on the mortar in terms of water absorption by capillarity. However, at 90 and 180 days curing, the values for the water absorption for mortars with CFA were lower than those observed in the reference. The presence of BFA led to mortars with higher absorption than the reference, for all curing ages. One interesting observation is the fact that for 180 days curing, mortars with the two pozzolans presented lower values than the reference mortar.

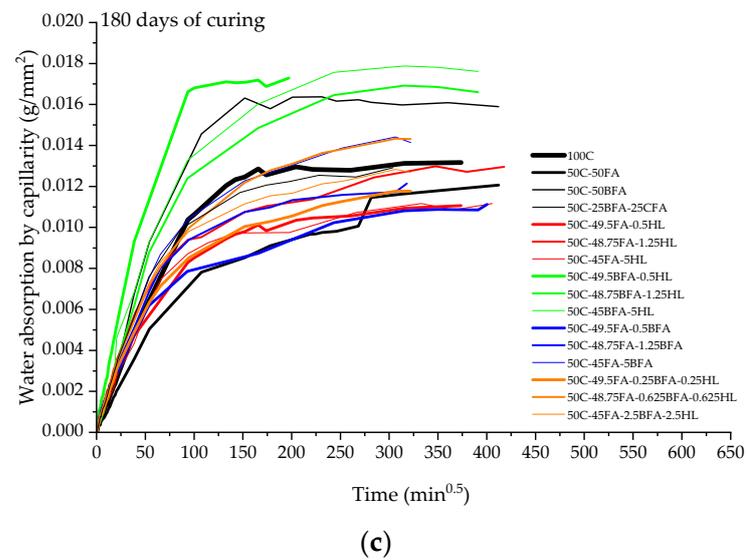
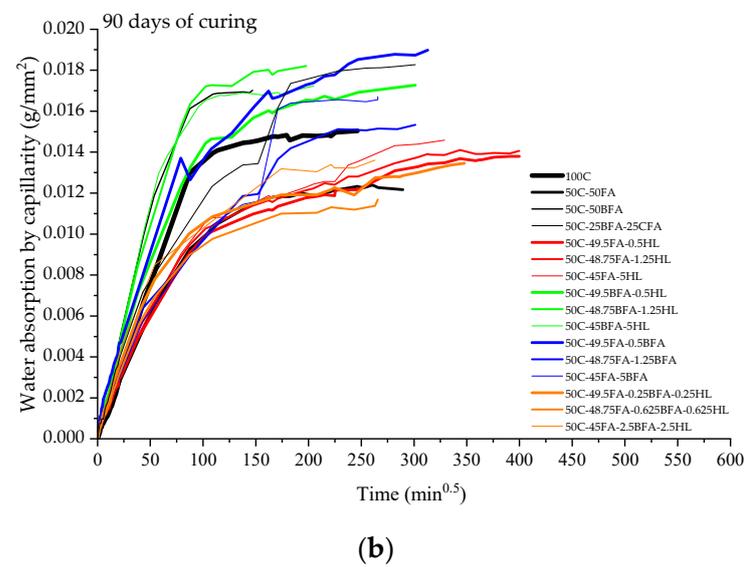
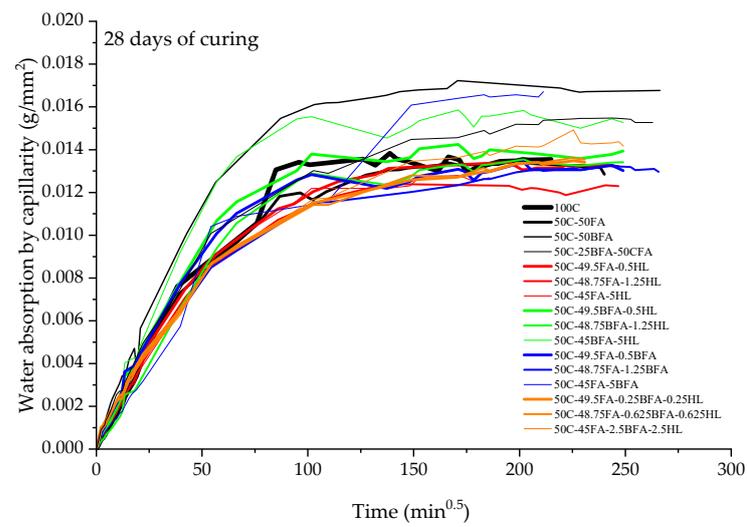


Figure 8. Curves for the capillarity absorption of mortars cured for (a) 28, (b) 90, and (c) 180 days of curing.

Table 5. Coefficient of water absorption by capillarity of mortars.

Mortar Formulation	Coefficient 28 Days	R ²	Coefficient 90 Days	R ²	Coefficient 180 Days	R ²
100C	1.67×10^{-4}	0.98	8.94×10^{-5}	0.96	1.04×10^{-4}	0.98
50C-50FA	1.08×10^{-4}	0.81	8.44×10^{-5}	0.86	7.71×10^{-5}	0.94
50C-50BFA	2.79×10^{-4}	0.96	1.20×10^{-4}	0.93	1.19×10^{-4}	0.96
50C-49.5FA-0.5HL	1.64×10^{-4}	0.99	1.26×10^{-4}	0.97	1.20×10^{-4}	0.96
50C-48.75FA-1.25HL	1.74×10^{-4}	0.99	1.28×10^{-4}	0.94	1.23×10^{-4}	0.98
50C-45FA-5HL	1.62×10^{-4}	0.99	1.21×10^{-4}	0.91	1.18×10^{-4}	0.95
50C-49.5BFA-0.5HL	1.74×10^{-4}	1.00	1.65×10^{-4}	0.98	2.17×10^{-4}	0.99
50C-48.75BFA-1.25HL	1.37×10^{-4}	0.94	1.71×10^{-4}	0.96	1.34×10^{-4}	1.00
50C-45BFA-5HL	2.29×10^{-4}	0.97	2.07×10^{-4}	0.98	1.52×10^{-4}	0.99
50C-49.5FA-0.5BFA	2.00×10^{-4}	0.98	1.91×10^{-4}	0.97	1.40×10^{-4}	1.00
50C-48.75FA-1.25BFA	1.61×10^{-4}	0.99	1.41×10^{-4}	0.99	1.33×10^{-4}	1.00
50C-45FA-5BFA	1.68×10^{-4}	0.99	1.26×10^{-4}	0.94	1.44×10^{-4}	0.99
50C-49.5FA-0.25BFA-0.25HL	1.78×10^{-4}	0.98	1.61×10^{-4}	0.98	1.33×10^{-4}	0.99
50C-48.75FA-0.625BFA-0.625HL	1.82×10^{-4}	0.97	1.29×10^{-4}	0.99	1.34×10^{-4}	0.99
50C-45FA-2.5BFA-2.5HL	1.76×10^{-4}	0.95	1.58×10^{-4}	0.98	1.52×10^{-4}	1.00
50C-25BFA-25CFA	2.19×10^{-4}	0.96	1.65×10^{-4}	0.94	1.47×10^{-4}	0.99

Mortars with CFA and HL present lower water absorption than the reference. The lower values were achieved for the mortar with 1.25% of HL for 28 days curing, with 0.5% for 90 days, and with 5% of HL for 180 days of curing. In the case of mortars with BFA and HL, the mixtures with 0.5% and 5% presented higher values than the reference, but the composition with 1.25% presented lower values, for 28 days curing. However, all the formulations presented lower values than the mortars made only with BFA. In mortars with 90 days of curing, the best results were achieved for mortars with 0.5% of HL. At 180 days of curing, all the mortars with BFA and HL presented higher values than the reference and mortars made only with BFA. This phenomenon is contrary to the results observed for 28 days of curing.

Similar results to the mortars with CFA and HL were achieved when HL was replaced by BFA. In this case, the best results were achieved for 1.25 and 5% of BFA mortars, at 28 days of curing. However, at 90 and 180 days of curing, mortars with CFA and BFA presented higher values than mortars containing only CFA. The use of the two pozzolans together with HL did not lead to better results than mortars made only with CFA, but they perform better than mortars made only with BFA, for all curing ages, except for the mortar with 0.625% of BFA and HL for 90 days curing (Figure 8).

3.2.4. Carbonation

The carbonation depth for the different mortars is expressed in Figure 9. As it can be seen, for 28 days of curing the reference mortar did not present carbonation zones. For 90 and 180 days of curing, plain cement reference mortar presented the lowest carbonation depth values of all studied mortars. All mortars presented increased values of carbonation depth along the test period. As it can be seen, mortars with BFA presented lower values of carbonation depth at the beginning of the test. However, at 30 days of the test, mortar with BFA presented higher values.

The use of HL to minimize the carbonation phenomena in mortars with CFA did not present good results for mortars with 28 days of curing. However, in mortars with 90 days of curing, all formulations with the HL exhibited better results in the beginning of the test when compared with CFA mortar, and similar results at 30 days of testing. Mortars with 180 days of curing showed that the formulation that has similar and good results in terms of carbonation is the 50C-49.5CFA-0.5HL when compared with CFA mortar that presents the best results. On the other side, HL use in mortars with BFA led to better results when compared with mortars made only with BFA. In this case, the best results were achieved for the 50C-45BFA-5HL at 28 days of curing; 50C-49.5BFA-0.5HL and 50C-45BFA-5HL at 90 days of curing; and 50C-49.5BFA-0.5HL for mortars with 180 days of curing.

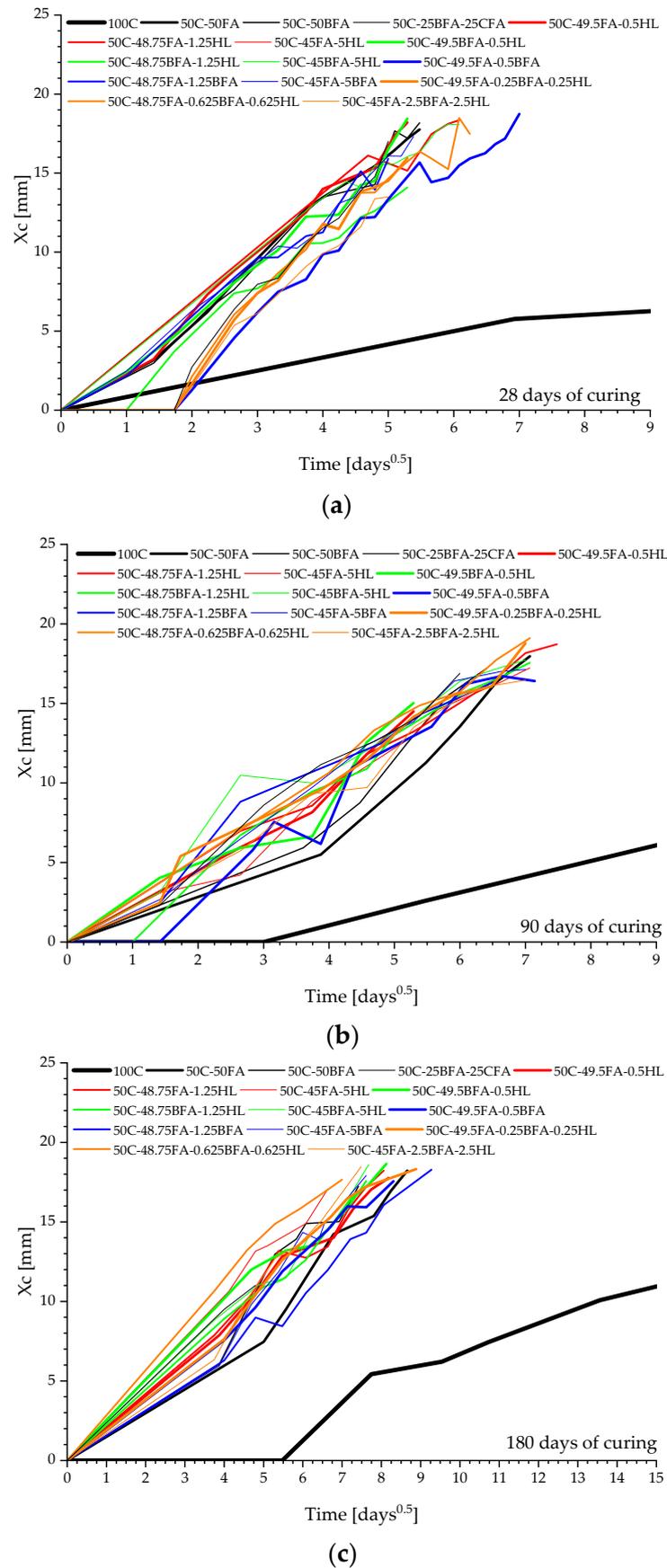


Figure 9. Carbonation depth measured in mortars with (a) 28, (b) 90, and (c) 180 days of curing.

The use of BFA and CFA in mortars showed good results at the beginning of the accelerated test but, with its development, CFA mortar had better behavior in terms of carbonation depth, for 28 days of curing. Mortars with 90 and 180 days of curing and with the two selected pozzolans presented good results along with the entire accelerated carbonation test, similar or better than mortars made only with CFA. Mortars with 180 days showed that the small quantity of BFA improved the performance. Similar results were observed when the two pozzolans and HL were used.

4. Conclusions

This study focused on mortars, due to the fact of mortars used less raw materials and allows to study a greater number of different mixes; however, the design of these mortar mixes was done considering the properties of the corresponding concrete mixes. It was notorious that biomass fly ash cannot be used as a supplementary cementitious material like coal fly ash as its incorporation decreases the mechanical and carbonation resistance and increased the porosity and the absorption of water. However, the use of small amount of biomass fly ash blended with coal fly ash in high volume fly ash mortar has better mechanical performance and similar water absorption and carbonation behavior than a high-volume coal fly ash mortar, which in terms of the concrete is a type of concrete very used at an industrial level. However, with an important significant difference, biomass fly ash is a more sustainable material than coal fly ash, and therefore the high volume of coal/biomass fly ash concrete will be also more sustainable than the high-volume coal fly ash concrete. Therefore, one of the solutions to minimize the problems of the high volume of fly ash concrete seems to be the utilization of a small amount of biomass fly ash blended with coal fly ash. The results obtained show that the synergic effect obtained by the simultaneous use of these two materials allows achieving better performance than the use of each one alone.

Despite this, these results show a good contribution of biomass fly ash as a reservoir of alkalinity for high-volume fly ash concrete. This needs to be verified in concrete compositions, and it will be done in a near future. Thus, the work developed in this study can be complemented to test the concrete in a more complete way, carrying out tests such as shrinkage, flexural strength, resistance to acids attack, alkali–silica reaction test, freeze–thaw resistance, porosity, and leaching tests. Those tests can be important to complement the study on concrete with a high volume of coal/biomass fly ash and to have a better understanding of biomass fly ash's benefits, risks, and applicability.

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