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Synergetic effect of biomass fly ash on improvement of high-volume coal fly ash concrete properties

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ABSTRACT

Sustainable construction is high on the agenda, especially regarding building materials. Using of by-products or waste materials from other economic sectors as cement replacement material in concrete production seems to be a more sustainable option than applying ordinary Portland cement concrete.

The main aim of this work was to evaluate the performance of biomass fly ash (BFA) when used as cement replacement material and as an alkalinity reserve material in high-volume fly ash concrete (HVFAC). Therefore, several compositions of concrete including BFA were tested for compressive strength, water absorption, accelerated carbonation, and chloride penetration resistance. It was noted that when small amounts of BFA were used, HVFAC properties were improved, compared with a high-volume coal fly ash concrete. These new concrete mixtures showed a positive contribution to the quality, durability and sustainability of HVFAC.

1. Introduction

Concrete is widely used worldwide and has many applications in the construction sector. Despite its advantages, concrete has a high environmental impact due to its production process, requiring high content of raw materials and energy consumption [1–4].

Portland cement is one of the most important components for concrete production [5,6]. Some cement production processes, such as limestone and clay extraction, blending, grinding and processing are very energy and resource intensive [1–4]. Moreover, during the decomposition of calcium carbonate into calcium oxide through the clinker sintering process and combustion of fossil fuels during heating processes, high quantities of CO₂ are released [5,7]. Cement production leads to high consumed embodied energy, and therefore the CO₂ emission of each ton of cement ranges between 0.82 and 1.0 metric tons [8,9]. Some other compounds, such as sulphur dioxide, nitrous oxides and methane are emitted during cement production and released into the atmosphere. These gases have a greenhouse effect, thus contributing to the problem of global warming [7]. In recent years, several decisions have been made to decrease the carbon footprint of the concrete sector by reducing raw material consumption, improving the energy efficiency in kilns, replacing fossil fuels with renewable energy sources (animal

residue, sewage sludge and waste oil), and using supplementary cementitious materials, such as coal fly ash (CFA) [5,10,11]. These pozzolanic materials can react with calcium hydroxide from cement hydration and form additional amounts of calcium silicate hydrates (C-S-H), thus having comparable properties to Portland cement. Their use can be a promising way to address concrete sustainability [6].

CFA is the supplementary cementitious material generally used in concrete production worldwide, mainly because of the numerous advantages it offers [12,13]. Nowadays, CFA is commonly used to replace cement in concrete in proportions from 0 to 40%wt [4,14,15]. Concrete containing 50 %wt or more cement replacement with CFA has some advantages, such as good resistance to chloride penetration and sulphate attack, no alkali-silica expansion occurrence and low heat [16,17]. High-volume fly ash concrete (HVFAC) has some disadvantages, such as the low early strength and the decrease in concrete pH, which could lead to carbonation issues [7,12,18–21]. Moreover, the energy sector is moving towards more just and sustainable systems and resources, which leads to low carbon energy production [22]. Thus, some coal-fired power stations are being withdrawn from service and this will lead to a significant decrease in CFA production. To minimize these issues, it is important to study the interaction between mineral additions [23] and cement hydration, trying to find new solutions for issues related to this

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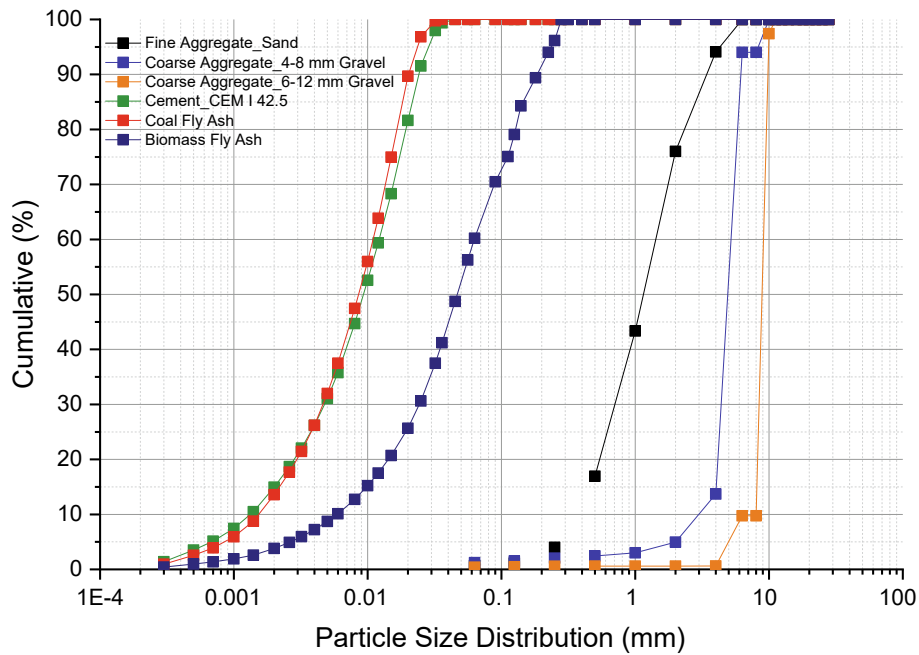


Fig. 1. Cumulative particle size distribution for Fine and Coarse Aggregates, Cement, CFA and BFA.

type of concrete.

Nowadays, some countries are showing a noticeable interest in producing energy using renewable sources such as biomass [23]. Combustion is the most widely used process to produce energy, with biomass as fuel [24]. The increase in biomass combustion has created a rise in biomass fly ash (BFA) content. In Portugal, BFA is classified as solid waste and usually managed by disposal in landfills [23]. However, landfill disposal raises social, economic and environmental issues [25,26].

Using BFA in concrete production has been studied and it has been found that BFA can have benefits for concrete [24,27–31]. However, using it in HVFAC has not been widely studied. Besides its pozzolanic

effect, BFA alkalinity may be another option to help solve the carbonation issue of HVFAC. This study is motivated by the fact that in Portugal most of the concrete used in the infrastructure market is made with high volume coal fly ash concrete. However, Portuguese coal-fired power plants are being closed as the energy sector and the local government are committed to producing energy using low carbon sources. So, this will lead to a significant decrease in the coal fly ashes supply in the concrete sector, and it is important to find some alternatives to substitute the coal fly ash in the HVFAC. Moreover, this work has been driven by the need to improve the functional and sustainable performance of HVFAC. An economically competitive and more sustainable material, which has far fewer of the issues related to this type of concrete using small amounts of

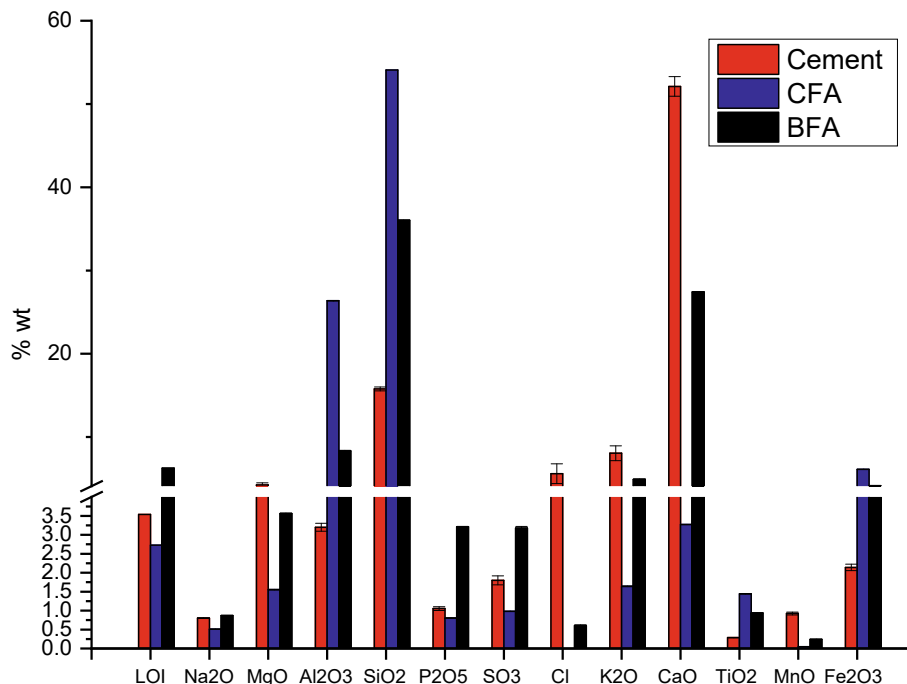


Fig. 2. Loss on ignition and major chemical element concentration in Cement, CFA and BFA.

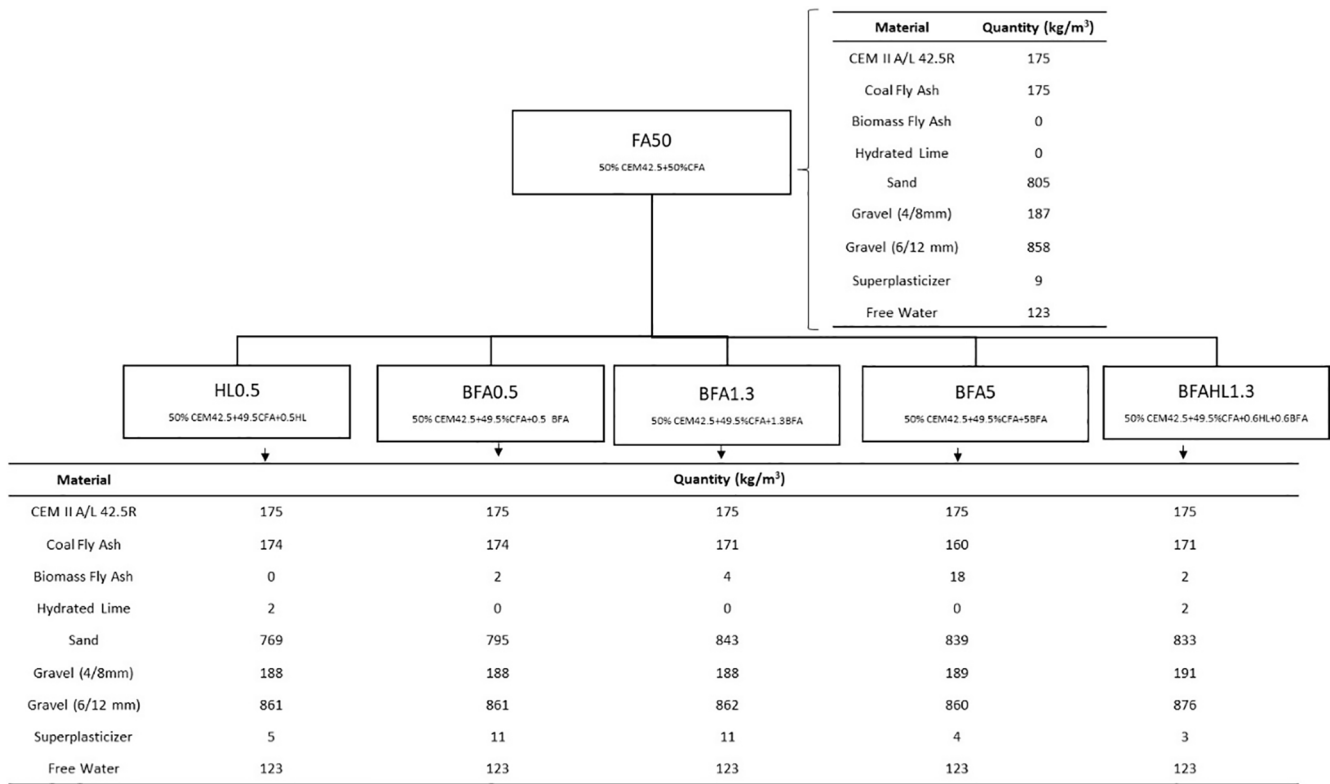


Fig. 3. Concrete Compositions.

BFA as an alkaline material, was studied. Laboratory tests were carried out on different concrete mixtures containing CFA and BFA. The potential influence of BFA as an alkaline material to offset the HVFAC characteristic loss of alkalinity was quantified. The present paper describes this study, as well as the main conclusions obtained.

2. Materials and methods

2.1. Raw materials

A CEM I 42.5R cement (from Outão, Secil, Portugal), commercial river rolled sand (0–4 mm), and granitic gravels (4–8 mm and 6–12 mm) were used as aggregates. CFA was sampled from a Portuguese thermo-electric coal-fired power plant. BFA was collected from a Portuguese pulp and paper manufacturer, which produced electric power and heat using forest residues such as eucalyptus and pine bark as fuel in a bubbling fluidized bed combustor. The ash was used in the mixtures as received, without any pre-treatment. Hydrated lime (from Lusical - Companhia Lusitana de Cal, SA) was used as an addition. The main purpose of adding this was to provide the alkalinity lost due to replacing a proportion of the cement with high amounts of coal fly ash and to act as a reference material to compare it with BFA. The physical and chemical characteristics of the different materials are presented in Figs. 1 and 2. The particle size distribution of CFA is similar to the particle size of cement with an average diameter of 9 μm. On the other hand, BFA presented coarser particles and its size distribution presented particles with a size between fine aggregates and CFA and cement, with an average diameter of 47 μm. As can be seen, BFA showed a LOI value of 6.27 % and CFA presented a value of 2.73 %, SiO₂ was the major chemical component presented in the CFA, followed by Al₂O₃, Fe₂O₃, CaO and K₂O. SiO₂ was also the major chemical component present in BFA, followed by CaO, Al₂O₃, K₂O, Fe₂O₃, MgO. As the main aim of this work was to evaluate the potential of BFA as an alkaline material that offsets the loss of the alkalinity characteristic of the HVFAC, a more detailed characterization of the BFA was carried out in terms of chemical

composition by SEM analysis, reactivity by determining the calcium hydroxide content using the Chapelle method and a reactivity dissolution test, and the pozzolanic reactivity index determined according to [32].

2.1.1. Reactivity analysis

The vitreous and crystalline phases of the supplementary cementitious materials can be identified and quantified by determining the reactivity by selective dissolution [33,34], using 1% of hydrofluoric acid (HF), at the end at the end, performing an SEM, EDS and XRD test. This method is explained in more detail in [23,35].

2.1.2. Modified Chapelle's method

The fixed calcium hydroxide content of the two fly ashes was determined using the Modified Chapelle's Method, according to ABNT NBR 15,895 [36]. The index of pozzolanic activity is determined in one representative sample for each fly ash by quantifying the calcium hydroxide content. The pozzolanic activity index is determined according to Eq. (1) and is expressed in mg of Ca(OH)₂ fixed per gram of material [23].

$$I_{Ca(OH)_2} = \frac{28 \cdot (V_1 - V_2) \cdot F_c}{W \cdot 1.32} \tag{1}$$

where

$I_{Ca(OH)_2}$ is the pozzolanic activity index, (mg of Ca(OH)₂ per g of material)

W is the mass of pozzolanic material, (g)

V_1 is the volume of 0.1 M HCl consumed in the sample test, (ml)

V_2 is the volume of 0.1 M HCl consumed in the blank test, (ml)

F_c is the correction factor of HCl for a concentration of 0.1 M

1.32 is the molecular relation of Ca(OH)₂/CaO

2.1.3. Activity index

The activity index was determined according to [32], where mortars with 75 %wt of cement and 25 %wt of CFA or BFA were prepared and tested for compressive strength after 28 and 90 days of curing.

2.2. Concrete mix design

A batch group of concrete was cast to study the use of BFA as cement supplementary cementitious material and as alkaline reserve material in HVFAC (Fig. 3). Previously, a large group of mortar formulations was studied with the same main goal and the results are shown in [23,37]. It was studied firstly in mortars as mortars allow to study multiple formulations and properties without consuming many resources, such as raw materials and time. Based on the mortar results, concrete formulations were chosen. In Portugal, concrete mostly used in the construction site is made with a high content of coal fly ash as a supplementary cementitious material. However, as coal power plants are closing down to comply with the goals established for the net-zero CO₂ emission agreement, the ash content is decreasing. In addition, the national government is focused on ensuring compliance with the sustainability goals established by the European Union, essentially those relating to a reduction in waste and minimizing the consumption of drinking water. Therefore, this study tries to find mixes that produce concrete with similar or higher mechanical strength, more durable and more sustainable than the HVFAC, commonly used in Portugal, with low content of water and cement. The total binder content of all concrete mixes was fixed to 350 kg/m³. The quantity of cement was adjusted, maintaining the cement content at 50 %, and the combined coal fly ash, biomass fly ash and hydrated lime at 50 %. The water/binder (w/b) ratio was kept at 0.35 for all mixes with more than one binder, and a superplasticizer (SP) Glenium Sky 617, produced by BASF was used to ensure similar workability between mixtures. Aggregates were used as received (not dry) and therefore the humidity of aggregates was considered to the amount of water added to the mix. The amount of each aggregate was determined by Faury's design method. This method has an empirical nature and can obtain the granulometric curve of the concrete aggregates, considering the nature of aggregate and the desired workability, which leads to high compaction of the hardened concrete.

2.3. Testing procedure

Initially, concrete solid materials were mixed as follows: gravel of the 6/12 mm fraction, gravel of the 4/8 mm fraction and sand were placed by this order in a laboratory concrete mixer and mixed for 3 min. The next step was the addition of cement, coal fly ash, biomass fly ash and hydrated lime to the aggregate mix. All the materials were mixed for another 3 min. After this, without stopping mixing, water and superplasticizer were added to the mix and mixed for 3 min more. The workability of concrete mixes was checked by the slump cone method. Samples were placed in standard moulds, as specified in [38]. Then, the samples needed for hardened state tests were moulded and after 24 h, the samples were demoulded and cured. HVFAC is very sensitive to curing. It is known that in water curing, some alkaline compounds of concrete are leached to water, which decreases the pH of concrete and leads to a lower carbonation resistance. Thus, taking this issue into account, all concrete formulations were subjected to two types of curing: i) wet curing immersed in water; and ii) water saturated with hydrated lime, alkaline solution (pH ≈ 14), both types of curing were done at approximately 20 °C. A comparison between the results obtained with each curing type was carried out to assess the influence of alkalinity loss minimization or inhibition in concrete properties. Concrete formulations were tested for compressive strength, water absorption, carbonation, and chloride penetration after 7, 28, 90 and 180 days (3 samples for each age of testing). The concrete analysis understands the effect of each formulation on the concrete properties to observe whether concrete that incorporates BFA blended with CFA has a better performance. The



Fig. 4. Slump test of BFA5 mixture.

focus was on aspects related to sustainable development, increasing the durability of concrete and producing a material with a lower initial cost, making it an economically competitive material.

2.4. Slump test

Slump tests were carried out by compaction of fresh concrete in Abram's cone to assess the workability of the HVFAC. The test was carried out according to EN 12350-2:2019 [39]. An example of a slump test made to one of the mixtures can be seen in Fig. 4.

2.5. Compressive strength test

The compressive strength test was carried out according to EN 12390-3:2003 [40]. Three cube samples measuring 100 × 100 × 100 mm³ were prepared and tested for each concrete. The tests were run at the age of 28, 90 and 180 days, in an ELE compressive strength testing machine (with a range between 50 and 3000 kN) until rupture.

2.6. Water absorption by immersion test

The open porosity was evaluated by water absorption by the immersion test performed according to LNEC E 394:1993 [41] at the curing ages of 28, 90 and 180 days. Cubes samples of 100x100x100 mm³ were dried in an oven at 105 °C until constant mass and then were immersed in water for 24 h. After this period, the excess water present on the surface of the specimen was wiped with a cloth and then the sample was weighed. This process was repeated until no further increase in apparent mass was observed. This was considered to have been reached when two consecutive weight measurements did not differ by more than 0.1 %wt. After this, the samples were immersed in water and the weight of the sample immersed in water was registered. The water absorption was determined as follows:

$$\text{Waterabsorption}(\%) = \frac{\text{Mass}_{\text{sat}} - \text{Mass}_{\text{dry}}}{\text{Mass}_{\text{dry}} - \text{Mass}_{\text{imm}}} \times 100 \quad (2)$$

where

Mass_{sat} is the mass of the saturated sample in air, (g)

Mass_{imm} is the hydrostatic mass of the saturated sample, (g)

Mass_{dry} is the mass of the dried sample, (g)

2.7. Water absorption by capillarity test

The water absorption by capillarity test was carried out according to LNEC E 393:1993 [42]. This test was carried out as it can indirectly obtain the volume and size of the pores of the samples, complementing the information on the open porosity obtained in the immersion water absorption test. Three cubic samples (100 × 100 × 100 mm³) were tested for each concrete mix, at curing ages of 28, 90 and 180 days.

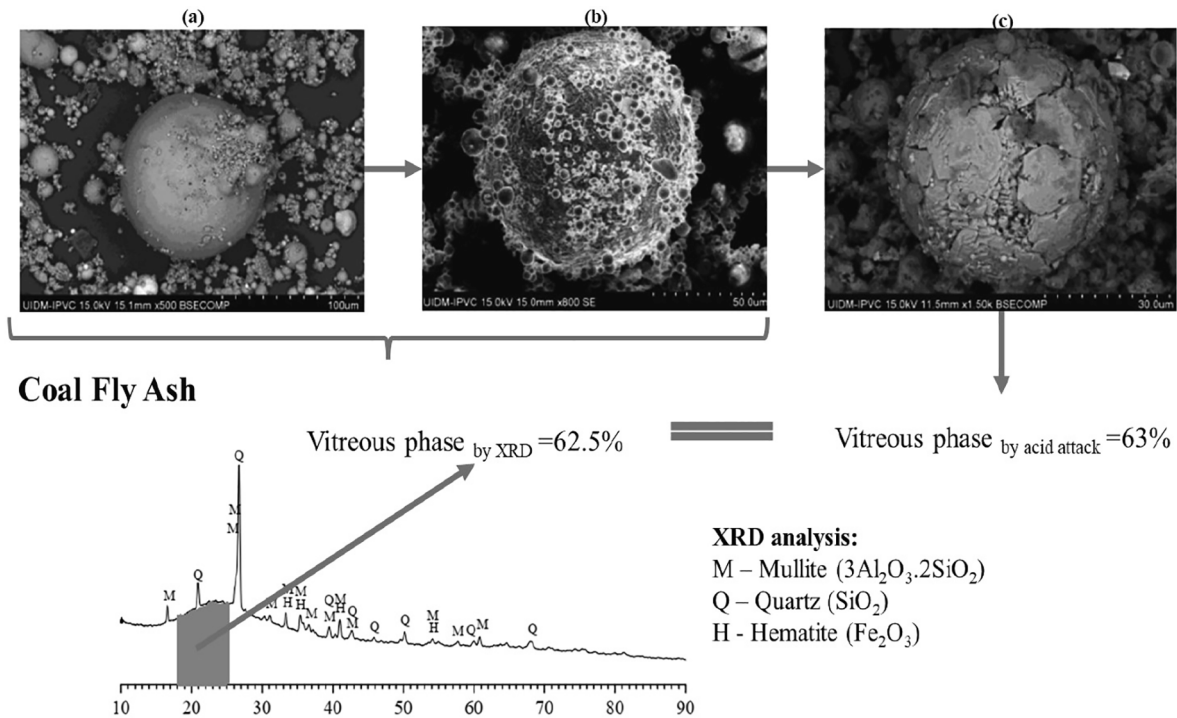


Fig. 5. Coal fly ash reactivity analysis by XRD and Acid Exposure: (a) SEM microstructure of CFA particles with $\times 500$ magnification; (b) SEM microstructure of CFA particles with $\times 800$ magnification; (c) SEM microstructure of CFA particles with $\times 1500$ magnification after acid attack.

Before the test, all specimens were dried at 60 ± 5 °C, until constant weight. After drying, lateral surfaces were coated with silicone to ensure that the water entered the sample by capillarity forces only through one side of the specimen. The test face of each cube sample was exposed to water with an immersed depth of 5 mm of water. The increased mass was measured and registered until no change was recorded in two consecutive mass measurements. The sample mass was weighed at various time intervals until a constant weight was reached. Water absorption by the capillarity coefficient is represented by a straight line linking the points of the measurements recorded until 3 h of testing.

2.8. Accelerated carbonation test

The accelerated carbonation test was performed on 100 mm cubes (for samples tested at 28 days of curing) and prisms measuring $100 \times 100 \times 855$ mm³ (for samples tested at 90 and 180 days), cured as previously referred, in tap water and cured in lime-saturated water (alkaline solution). After the curing period, samples were preconditioned in an isolated container subjected to a constant temperature and relative humidity (88.0 ± 4.0 % and 17.5 ± 1.6 °C) for 14 days to ensure the stabilization of humidity within the samples [23]. To measure the depth of carbonation, the samples were sealed with paraffin, except for two opposite faces. After sealing, the samples were placed in an accelerated carbonation chamber (4.1 ± 0.1 % of CO_2 , 55.0 ± 5.0 % RH and 20.0 ± 0.0 °C) [23]. The choice was made taking into account the results achieved in mortar formulations for 5 % of CO_2 made of the same blended mixes [23,37]. This may be questionable when adding fly ashes as these materials bring aluminium to the mixes [43]. However, several studies about on blended cements [43–45] used this test to investigate in detail the carbonation in a controlled environment, and for this reason, it was used in this study. Carbonation depth measurements were made on cross-sections sprayed with a phenolphthalein indicator, based on the procedure described in [46,47]. The carbonation depth (X_c) was evaluated over time and the carbonation coefficient (K_c) was determined considering a linear regression between the penetration depth and the square root of the time of exposure in the carbonation chamber.

2.9. Chloride migration coefficient from Non-Steady-State migration experiments

The chloride migration coefficient from the non-steady-state migration experiment was determined according to the specification NT BUILD 492:1999 [48]. This coefficient is a measure of the resistance of the concrete to chloride penetration. Three samples of cylindrical specimens of each concrete mix, with a diameter of 100 mm and 50 mm length were tested. In this method, an external electrical potential is applied axially across the sample, forcing the chloride ions outside to migrate into the sample [48]. After the test period, the sample was split axially, and a silver nitrate solution was sprayed on the freshly split sections. The chloride penetration depth was measured from the visible white silver chloride precipitation, after which the chloride migration coefficient was calculated [48]. The chloride migration coefficient was calculated according to Eq. (3) [48]:

$$D = \frac{RT}{zFE} \cdot \frac{x_d - \alpha \sqrt{x_d}}{t} \quad (3)$$

where

$$E = \frac{U - 2}{L} \quad (4)$$

$$\alpha = 2 \sqrt{\frac{RT}{zFE}} \cdot \text{erf}^{-1} \left(1 - \frac{2c_d}{C_0} \right) \quad (5)$$

D is the non-steady-state migration coefficient, (m²/s)

z is the absolute value of ion valence, for chloride, $z = 1$

F is the Faraday constant, $F = 9.648 \times 10^4$ J/(V.mol)

U is the absolute value of the applied voltage, (V)

R is the gas constant, $R = 8,314$ J/(K.mol)

T is the average value of the initial and final temperature in the anolyte solution, (K)

L is the thickness of the sample, (m)

x_d is the average value of the penetration depths, (m)

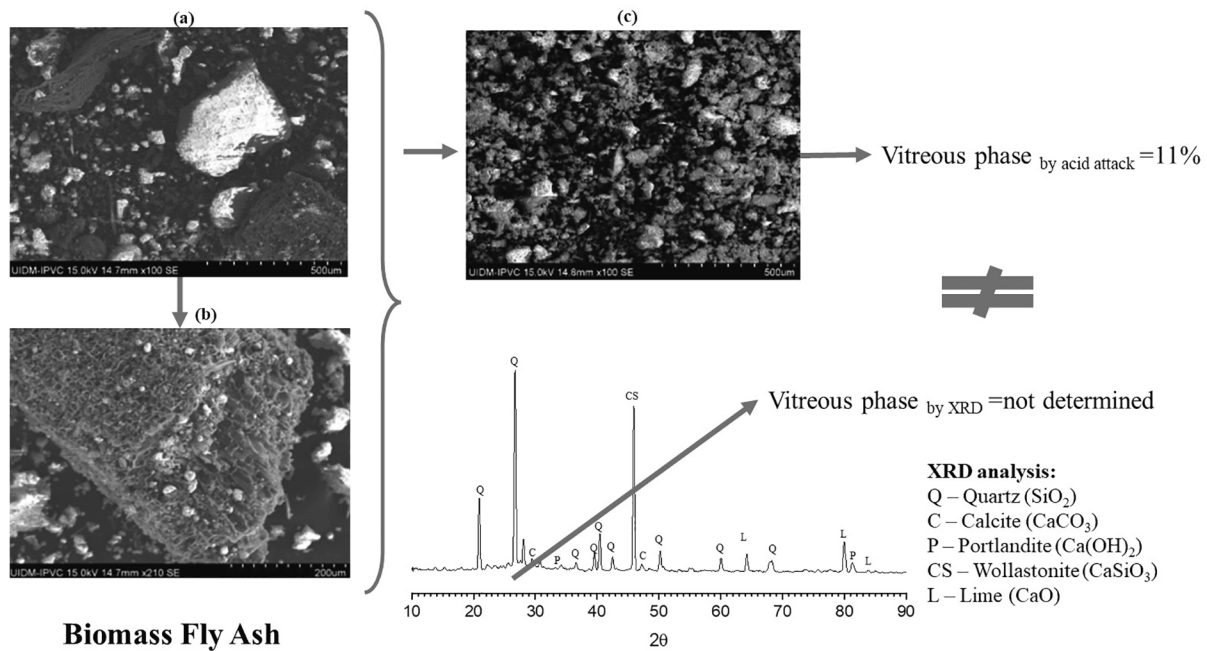


Fig. 6. Biomass fly ash reactivity analysis by XRD and Acid Exposure: (a) SEM microstructure of BFA particles with $\times 100$ magnification; (b) SEM microstructure of BFA particles with $\times 100$ magnification; (c) SEM microstructure of BFA particles with $\times 210$ magnification after acid attack.

t is the test duration, (s)

erf^{-1} is the inverse of error function

c_d is the chloride concentration at which the colour changes, $c_d \approx 0.07N$ for OPC concrete

C_0 is the chloride concentration in the catholyte solution, $c_0 \approx 2N$

Since $erf^{-1}\left(1 - \frac{2 \times 0.07}{2}\right) = 1.28$, the following simplified Equation

can be used:

$$D = \frac{0.0239(273 + T)L}{(U - 2)t} \left(x_d - 0.0238 \sqrt{\frac{(273 + T)Lx_d}{U - 2}} \right) \quad (6)$$

where

D is the non-steady-state migration coefficient, $\times 10^{-12}$ (m^2/s)

U is the absolute value of the applied voltage, (V)

T is the average value of the initial and final temperature in the anolyte solution, ($^{\circ}C$)

L is the thickness of the sample, (mm)

x_d is the average value of the penetration depths, (mm)

t is the test duration, (h)

It is important to note that this approach mimics real exposure under full immersion conditions and unidirectional chlorides penetration resistance [49]. However, Hemstad et al. [50] showed that the major influence of the pH on the chloride binding capacity and on the chloride penetration profiles in materials. Therefore, the availability of the paste to bind chlorides is a complex function and separating chloride diffusion and binding from a bulk diffusion test is a complex task, and even more when it used blended cementitious materials. Thus, it is important to take this into account in the results analysis.

3. Results and discussion

3.1. Reactivity and pozzolanic index of coal fly ash and biomass fly ash

BFA and CFA were characterized in terms of physical and chemical

Table 1

Pozzolanic performance of CFA and BFA.

Sample	Modified Chapellés Method (mg of $Ca(OH)_2/g$)	EN 450-1:2012 (%)	
		28 days	90 days
CFA	525	76.0	87.9
BFA	-71	76.1	75.0

properties which are described in [23,37,51]. To complete this characterization, the reactivity of each ash sample was determined through the selective dissolution method and the results are presented in Figs. 5 and 6. After the chemical acid exposure, CFA presented a weight loss of 63 % and the BFA of 11 %, showing that BFA was less reactive than CFA. After the acid exposure, the samples were subjected to XRD analysis to validate the results. The XRD analysis identified a positive salience (hump) on the baseline that corresponds to the presence of a vitreous phase in the CFA. The hump was located between 16° to 35° 2θ combined with the Rietveld refinement allowed the estimation of the amount of coal fly ash pozzolanicly reactive [35], approximately 62.5 %. For BFA samples, the results indicate the total absence of vitreous phases, which is analysed by the absence of the hump in the XRD baseline. One interesting observation is the way that the acid influences the morphology of ash samples. CFA particles presented some damage after acid exposure, but no significant changes were observed in the particle size. However, after the acid exposure, BFA particles presented a smaller size, indicating that the acid led to the cracking of BFA particles into smaller ones.

In Table 1, the pozzolanic performance of the BFA through the Modified Chapelle's Method and mechanical index according to EN 450-1:2012 [32] is compared with the CFA used to produce HVFAC. As expected, the CFA meet the normative conditions, presenting 525 mg/g of $Ca(OH)_2$ determined by the Modified Chapelle's Method, and the requirements related to the determination of free calcium oxide in fly ash (EN 450-1:2012): higher than 75 % at 28 days and higher than 80% at 90 days, showing a high reactivity index, similar to those observed in the literature [52]. BFA presented for 28 days a similar pozzolanic index to that of CFA for 28 days but did not meet the requirements for 90 days. The value obtained in the Modified Chapelle's Method shows an increase in the $Ca(OH)_2$ content. These results show that BFA is not a

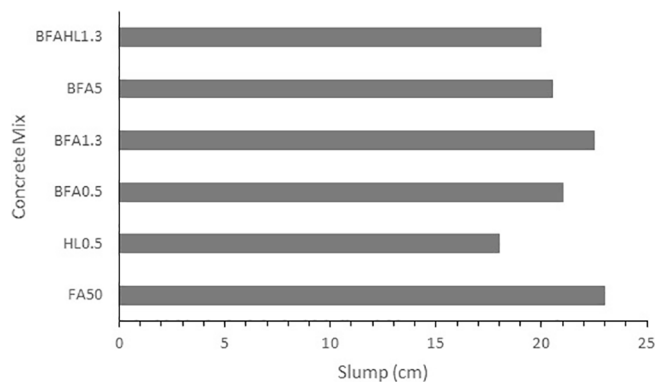


Fig. 7. Slump values for each concrete composition.

pozzolanic material, but an alkalinity material. This result was very important as the main focus of this study is to use this residue as a material to provide alkalinity to the mixes. These results confirmed and validated those achieved in the selective dissolution methods, where it was also observed that BFA did not behave as a pozzolanic material as it presented just 11 % of reactive material and did not verify an XRD baseline typical to pozzolanic materials (as was observed in the CFA samples).

3.2. Fresh properties

The fresh concrete workability was evaluated using the slump test. Fig. 7 gives the slump test values for the seven concrete mixes produced. One important observation is that the use of BFA did not have a significant effect on the slump values when compared with the results achieved when CFA is used. However, the increase in BFA content led to a decrease in the slump values. These results were expected as authors who have studied the incorporation of BFA in concrete found that the slump values are affected by high cement replacements [53,54], as these ashes are very hygroscopic, therefore it needs a higher content of water to maintain the same slump values. It is noted that BFA0.5 presented similar behaviour in terms of workability than the reference.

3.3. Compressive strength

Fig. 8 illustrates the relationship between compressive strength after 7, 28, 90 and 180 days of curing (in water and hydrated lime solution) and fly ashes/hydrated lime in the concrete mix. The values are an average of 3 samples for each concrete formulation and each curing period. After 7 days of curing, the compressive strength of the BFA0.5

mixture had the highest values for the two curing solutions, followed by FA50, BFA1.3, HL0.5, BFAHL1.3 and BFA5. The compressive strength decreases as BFA content increases. As found in BFA characterization tests, this ash was not a pozzolanic material (presenting non-reactive phases), and despite the two ashes exhibiting good synergy, the increase in the BFA content leads to a smaller amount of material that can react and gain strength [23]. The mixes with 0.5 and 1.3 %wt of BFA exhibited higher values than concrete containing only cement as a binder. This could be explained by the filler effect that BFA can induce in the concrete (Fig. 1), which improves its compactness. The presence of HL at early ages led to a decrease in the compressive strength, showing that its use does not result in an improvement in concrete performance at early ages. This can be attributed to the low amount of alite in the binder [55].

At 28 days, the highest values were observed for the FA50 and BFA0.5 with values of 56.6 MPa and 55.8 MPa, and 55.1 MPa and 57.0 MPa, respectively for water curing and hydrate lime solution curing. It is important to mention that BFA1.3 and HL0.5 presented higher values than plain cement concrete for both curing procedures. A high content of BFA and the introduction of HL led to a decrease in compressive strength values. The decrease observed for concrete containing HL is consistent with the hydration of belite, which is slower, and with the ongoing pozzolanic reaction, which continued after 28 days of curing [55]. At later ages, BFA0.5 had the highest compressive strength values for both curing solutions. At the same time, stagnation in the compressive strength development was observed on the mixture containing plain cement. This occurs because cement has a faster hydration reaction, which results in a strength gain at early ages. At 90 and 180 days, the incorporation of HL did not significantly affect the compressive strength. However, HL0.5 presented higher values than the mixture made just with CFA (FA50). Moreover, all mixes containing fly ash presented higher values than the reference concrete. It is known that concrete containing HVFA develops compressive strength more slowly than plain cement concrete and has lower early strength. This is due to the fact that the pozzolanic reaction of fly ash is slower, and thus retards the strength gain [14].

The results showed that BFA0.5 achieved the most satisfactory compressive strength values for the two curing solutions, in all curing periods. It is known that BFA presents a pH value in the range of 11–13 [56] and contains silicon and calcium carbonate as major phases, having a higher content of portlandite and lime than CFA [57].

The effect of the two different curing solution procedures on the compressive strength for each concrete formulation is analysed in Fig. 9. It is known that plain cement has an early gain of compressive strength. However, it is noted that the cure of concrete in a hydrated lime solution leads to higher compressive strength values for higher ages. Mixes with

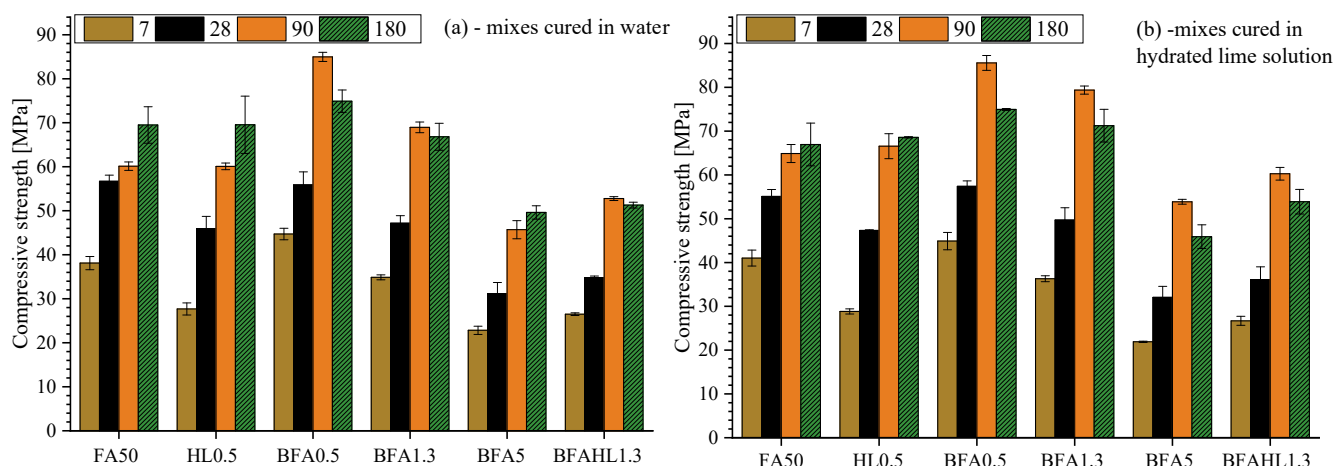


Fig. 8. Relationship between the compressive strength and biomass/coal fly ash and/or hydrated lime content after 7, 28, 90 and 180 days of curing.

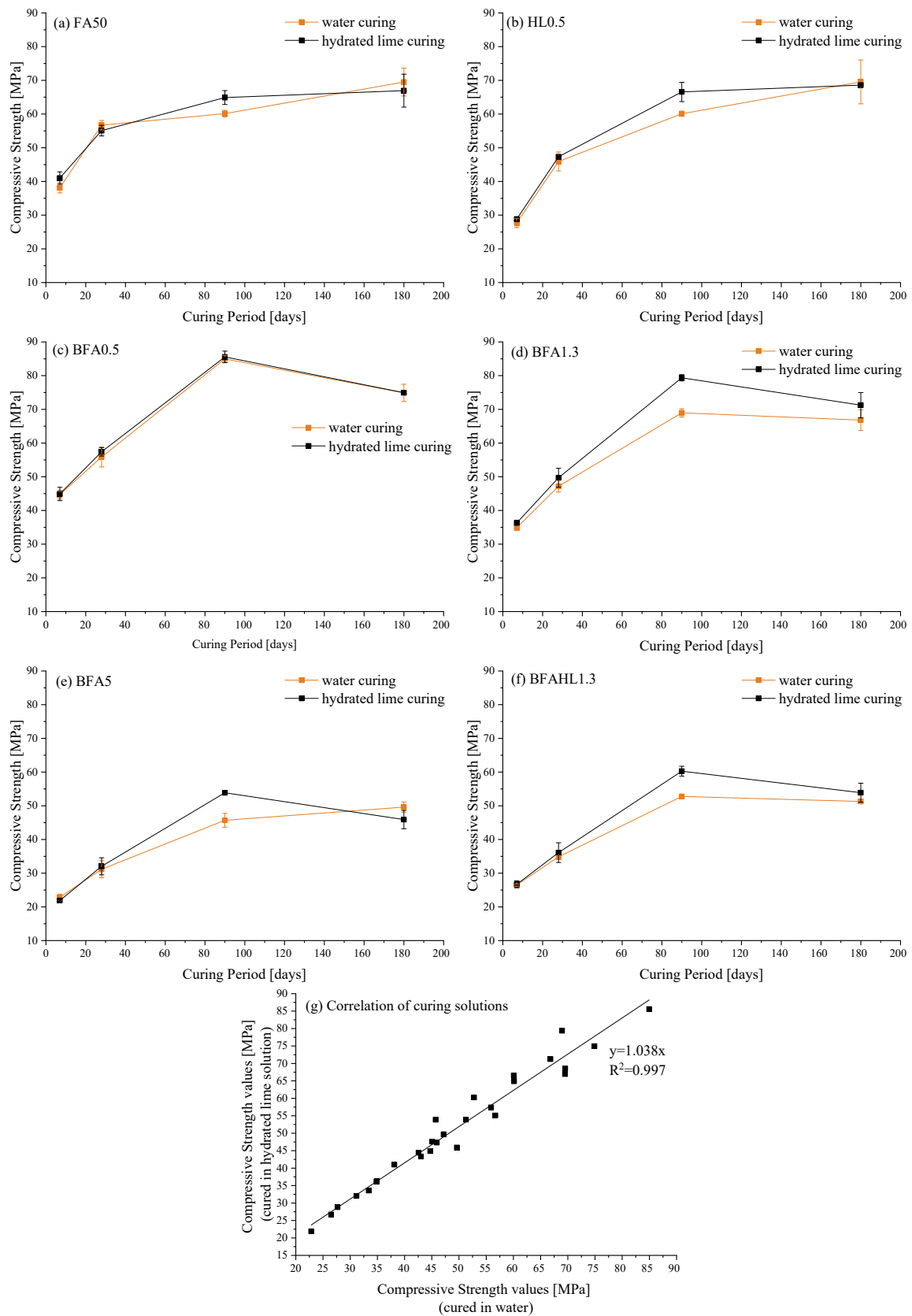


Fig. 9. Effect of curing solution on the compressive strength values for each concrete formulation.

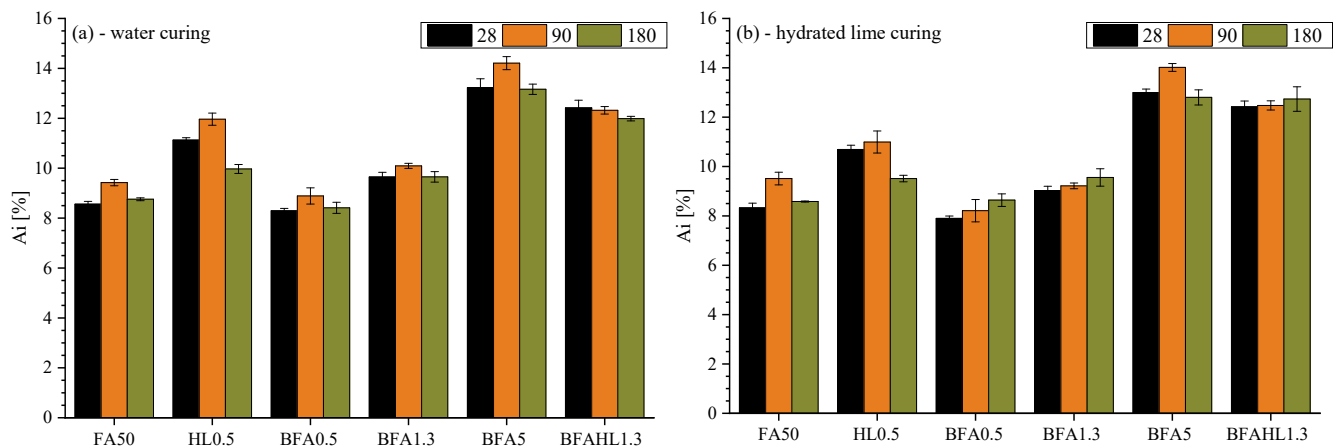


Fig. 10. Water absorption by immersion results for the concrete samples cured in water and cured in a hydrated lime solution.

hydrated lime or just coal fly ash achieve higher compressive strength for early ages when cured in a hydrated lime solution, but at 180 days the values were similar for both curing solutions. Concerning concrete with BFA, a different behavior was observed for each composition. The BFA0.5 mixture, for all curing periods, showed similar results for samples cured in water and cured in hydrated lime solution. However, the lime curing of specimens yielded slightly higher results. On the other hand, BFA1.3, the samples cured in the hydrated lime solution had values 4.1 % higher on average, for 7 and 28 days, and 15.1 and 6.6 %, for 90 and 180 days, respectively, when compared with water-cured test samples. Regarding the BFA5 mix, the samples cured in a hydrated lime solution presented higher values up to 90 days, increasing by the average of about 17.9 %, for this age, than water-cured test results. However, at 180 days, the compressive strength value of the specimens cured in water was higher than that of the specimens cured in the hydrated lime solution. A linear correlation between the compressive strength values of samples cured in water and a hydrated lime solution is noted (Fig. 9-h), showing that the two curing results in similar values for compressive strength.

3.4. Water absorption by immersion

Water absorption by immersion is an important test for concrete durability since it provides an indirect measurement of the open porosity [58]. In Fig. 10, the results for water absorption by immersion at atmospheric pressure for the samples cured in water and cured in a hydrated lime solution are shown. Concerning water curing, for the three curing ages, the BFA0.5 mixture had the lowest values, followed by FA50 and BFA1.3. The lowest values observed for BFA0.5 and BFA1.3 were also observed by other researchers, who observed that a more alkaline environment allows producing a higher hydrated compounds content, which increases the strength of concrete by reducing the porosity of the matrix [58,59]. However, the increase in BFA content and increase in the water absorption values can be observed, maybe because BFA presented hygroscopic properties, meaning they absorbed humidity, and consequently, this leads to higher absorption of water of concretes containing high amounts of this material [58].

The incorporation of hydrated lime, with the two fly ashes, did not correspond to the production of a less porous concrete than a coal fly ash concrete. Some studies [60] have shown that more C-S-H gel is formed in mixes containing CFA and HL than in plain cement concrete. This formation of more C-S-H gel and the filling of boundaries in the aggregate and their elongated micro gaps leads to a decrease in porosity and increases the homogeneity in the concrete.

The effect of the two different curing solution procedures on the porosity for each concrete formulation is analysed in Fig. 11.

In general, the samples cured in hydrated lime showed a slight

decrease in water absorption, meaning a decrease in the porosity of those samples. These results could be related to the absorption of the alkaline compounds presented in the solution, allowing a better hydration reaction of the cementitious compounds present in the mix. A linear correlation between the water absorption values of samples cured in water and in a hydrated lime solution is noted (Fig. 11-h).

3.5. Water absorption by capillarity

The water absorption by the capillary test is performed to quantify the capillary absorption coefficient. The water absorption by capillarity is presented in Fig. 12, for both curing solutions. It is possible to qualitatively classify the concrete based on the coefficient of water absorption by capillarity, using the classification proposed by Browne, 1991 [61] (Table 2).

In terms of samples cured in water, FA50 and HL0.5 presented a coefficient evaluated as concrete with normal quality for the three curing ages. After 28 days of curing, BFA0.5 samples had a high quality, while BFA1.3 had normal quality after 90 days of curing and high quality after 180 days of curing and BFA presented normal quality after 28 days. Samples cured in a hydrated lime solution, except for the reference, were generally regarded as concrete of normal quality.

In Fig. 13, the representative kinetic curves for capillarity water absorption are shown as a function of the test time for samples with 28, 90 and 180 days of age cured in water and a hydrated lime solution. In terms of samples cured in water, it was noted that at 28 days, mixture BFA0.5 had the lowest coefficient of water absorption by capillarity, since the mixture had the highest resistance to absorption of water by capillarity. This was followed by FA50 and BFA1.3 (Fig. 13). These mixtures had the lowest capillary absorption of water throughout the whole testing period. This is due to the synergetic effect of the two fly ashes, which led to a denser material with better pozzolanic activity [31,58]. The incorporation of HL did not lead to an improvement in the decreased water absorption compared with the mixes containing HVCFA. HL0.5 mix had the second-lowest value of the coefficient of absorption by capillarity. Moreover, at 90 and 180 days, it is also BFA0.5, FA50 and BFA1.3 the samples that presented the lowest values for the water absorption coefficient. However, the increase in BFA content led to higher coefficient values (Fig. 13). This could be explained once BFA is a hygroscopic material, which leads to a higher water absorption [62].

Similar results were observed in samples cured in the hydrated lime solution for 28 and 90 days, with BFA0.5, BFA1.3 and FA50 showing the lowest values. A slight difference was observed at 180 days, in which the BFA5 sample had the lowest values together with the FA50 sample.

Water absorption by capillarity of samples cured in hydrated lime was lower than for samples cured in water. This could be related to two

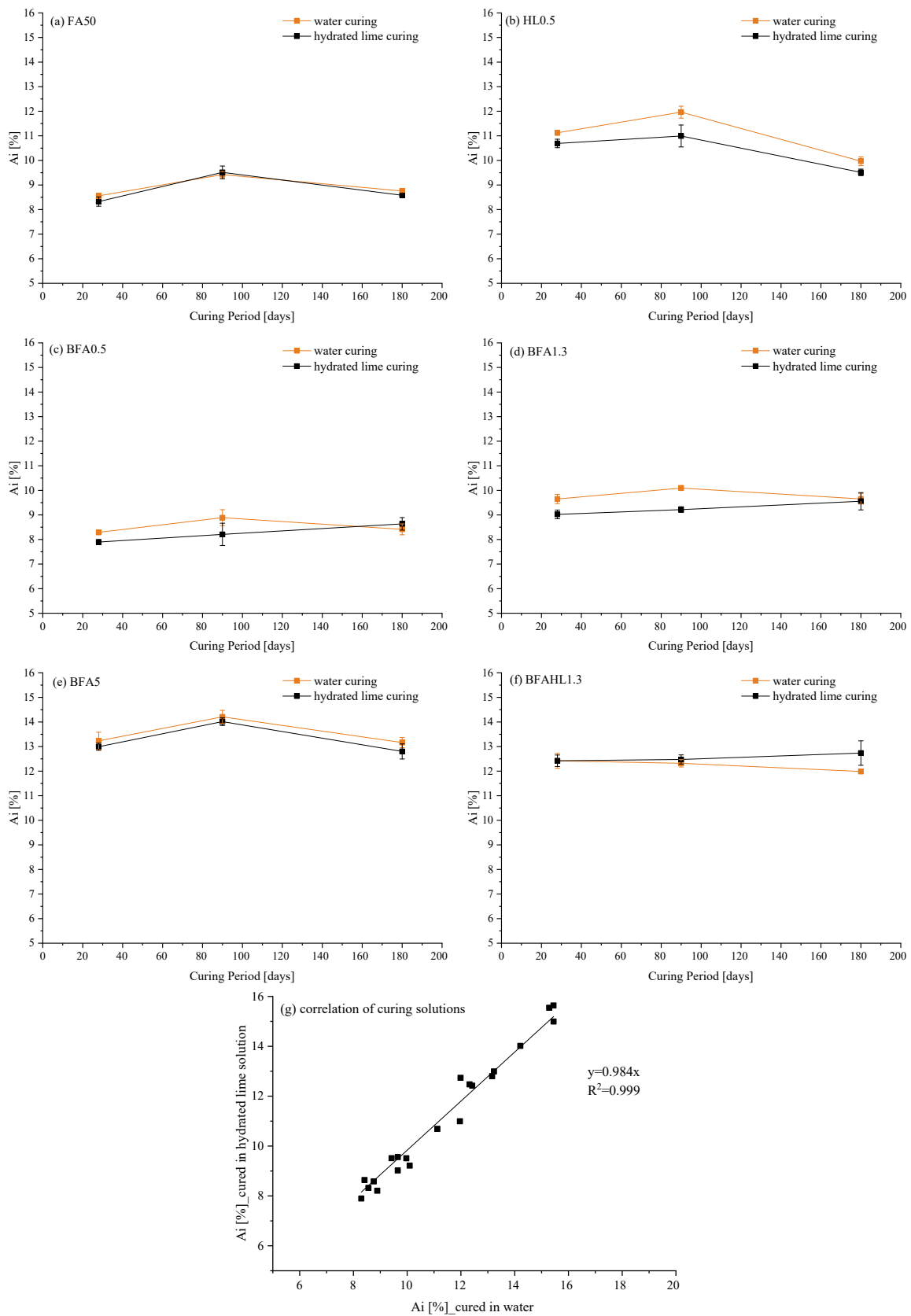


Fig. 11. Effect of curing in water or in a hydrated lime solution on water absorption by immersion for each concrete formulation.

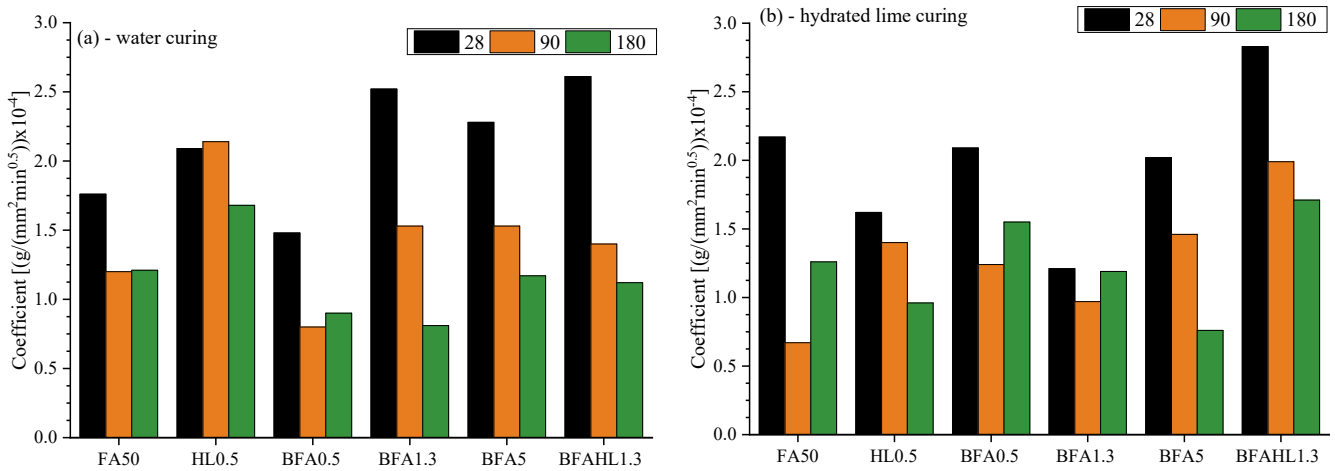


Fig. 12. Coefficient of water absorption by capillarity.

Table 2

Quality class of concrete as a function of its coefficient of water absorption by capillarity [61].

Coefficient of water absorption by capillarity	Quality class
$\geq 0.2 \text{ mg}/(\text{mm}^2 \times \text{min}^{0.5})$	Reduced
$0.1\text{--}0.2 \text{ mg}/(\text{mm}^2 \times \text{min}^{0.5})$	Normal
$\leq 0.1 \text{ mg}/(\text{mm}^2 \times \text{min}^{0.5})$	High

factors. The first concerns the leaching of some alkaline compounds (essentially Ca) from concrete to water. The lower concentrations of Ca^{2+} occurring in the water curing, by leaching effect, especially in an early hydration phase, produce low pozzolanic reactivity [23]. The dissolving and leaching of CH increase the porosity within the cement system, lowering the pH level and consequently compromising the strength and durability of the concrete [63]. The second factor concerns the fact of the hydrated lime solution gives rise to a more alkaline environment due to the hydrated lime saturation; the pH and the

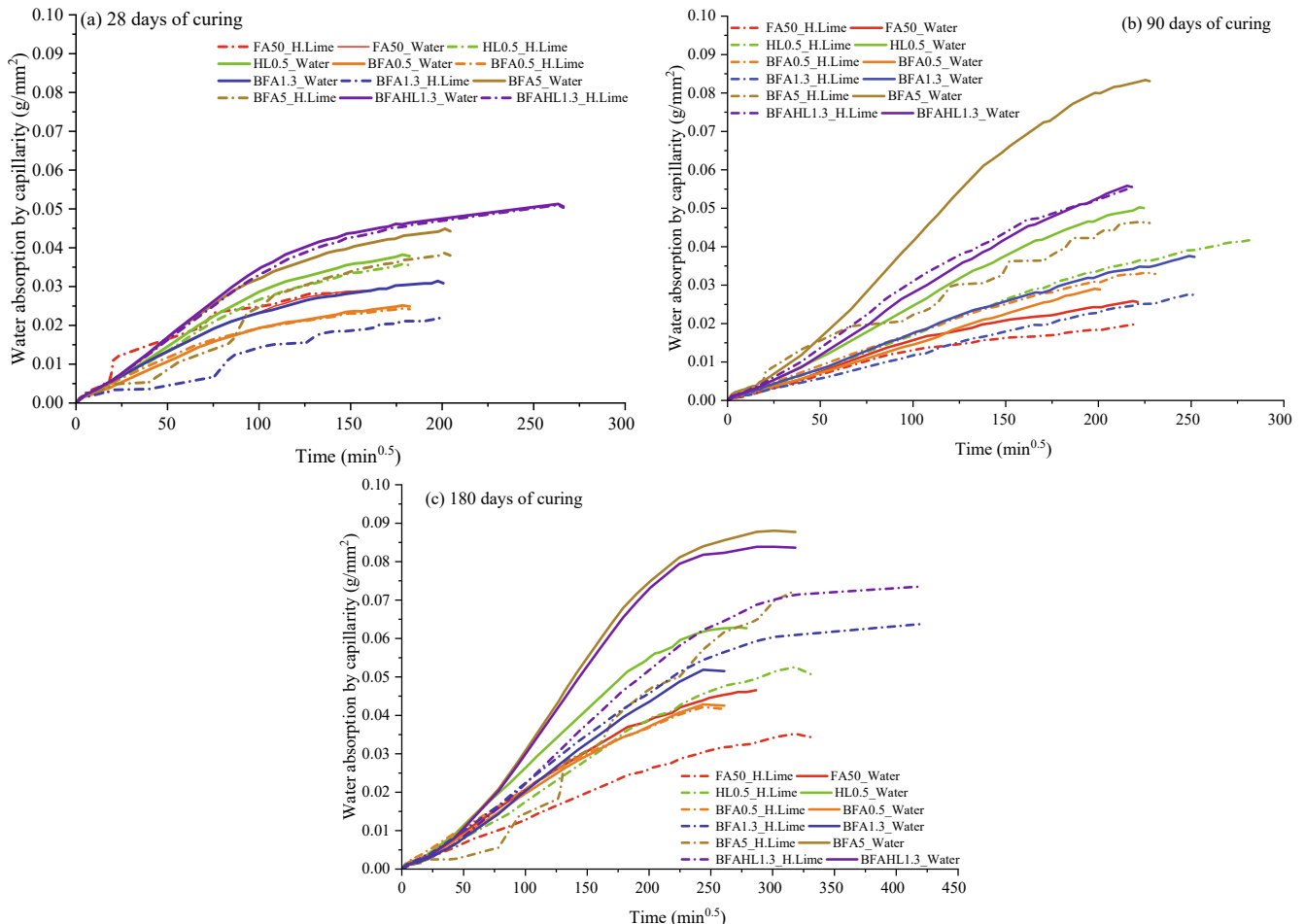


Fig. 13. Water absorption by capillarity coefficients for samples cured in water and in the hydrated lime solution, at 28, 90 and 180 days.

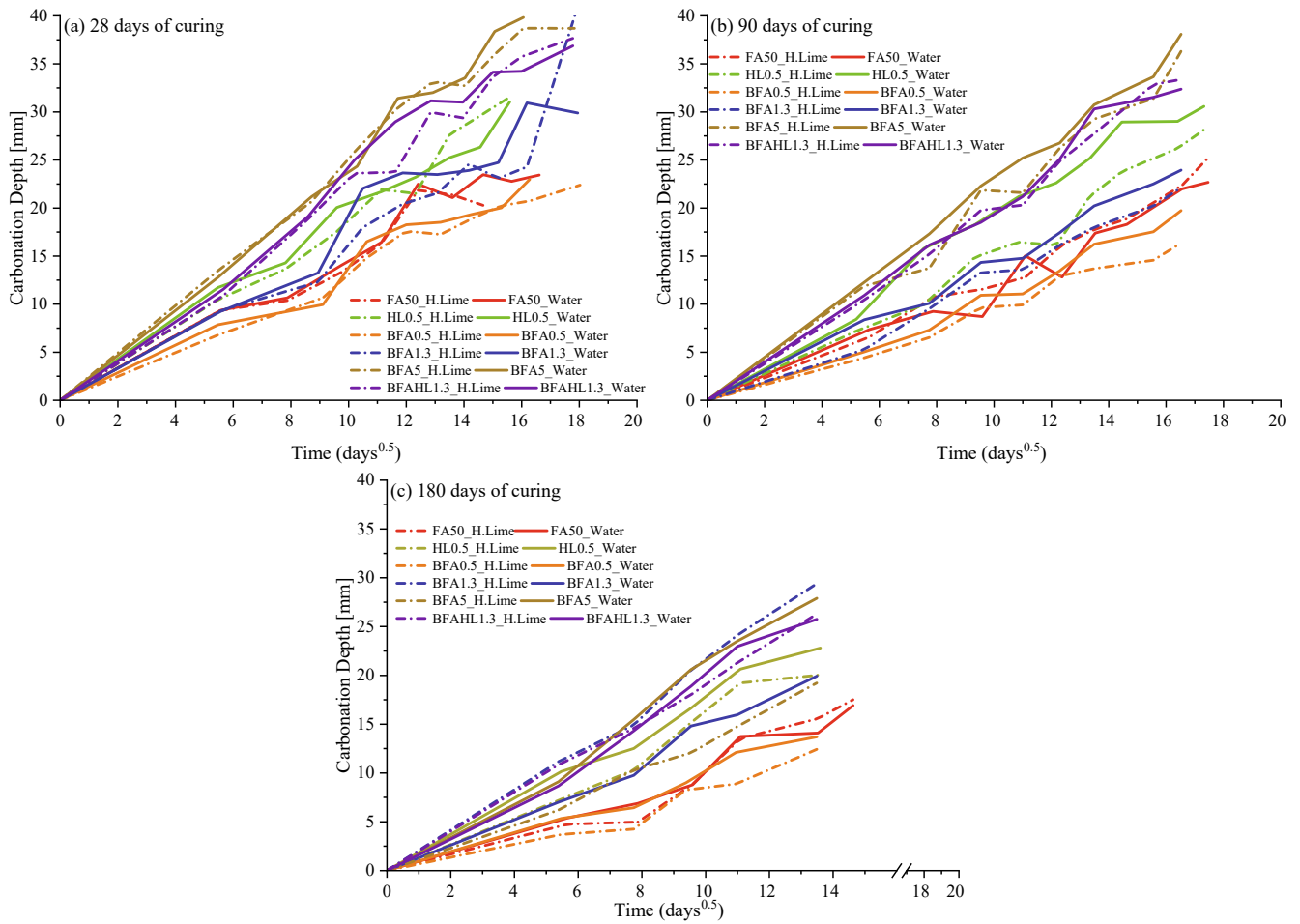


Fig. 14. Carbonation depth of samples cured in water and hydrated lime solution for 28, 90, and 180 days.

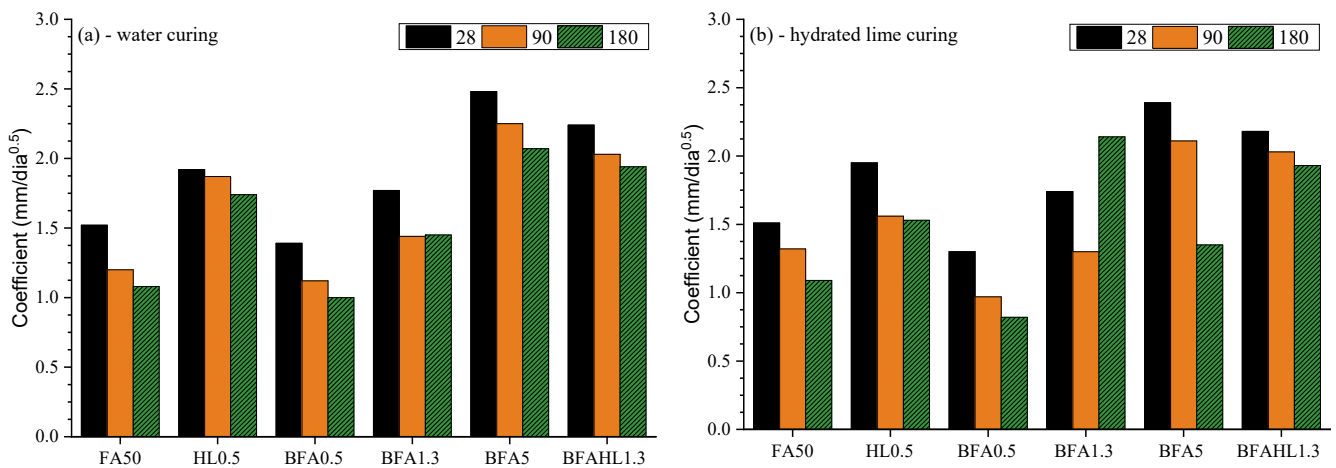


Fig. 15. Coefficient of accelerated carbonation test for the two curing solutions at 28, 90 and 180 days (K_c in $\text{mm}/\text{dia}^{0.5}$).

alkaline compounds are higher in the environment than in the concrete pores, and instead of leaching, there is a migration of the calcium compounds to the inside of the concrete to maintain the chemical equilibrium [23]. This leads to a filler effect, creating a protective surface layer, decreasing the water absorption of samples cured in the hydrated lime solution [23].

3.6. Accelerated carbonation test

Fig. 14 shows the results of the accelerated carbonation test of concrete samples cured in water and the hydrated lime solution for 28, 90 and 180 days during the test period. The carbonation depth can be expressed as a function of the square root of exposure time and it is possible to determine the carbonation coefficient as shown in Fig. 15. As can be seen, the BFA0.5 mixture had the lowest penetration coefficient

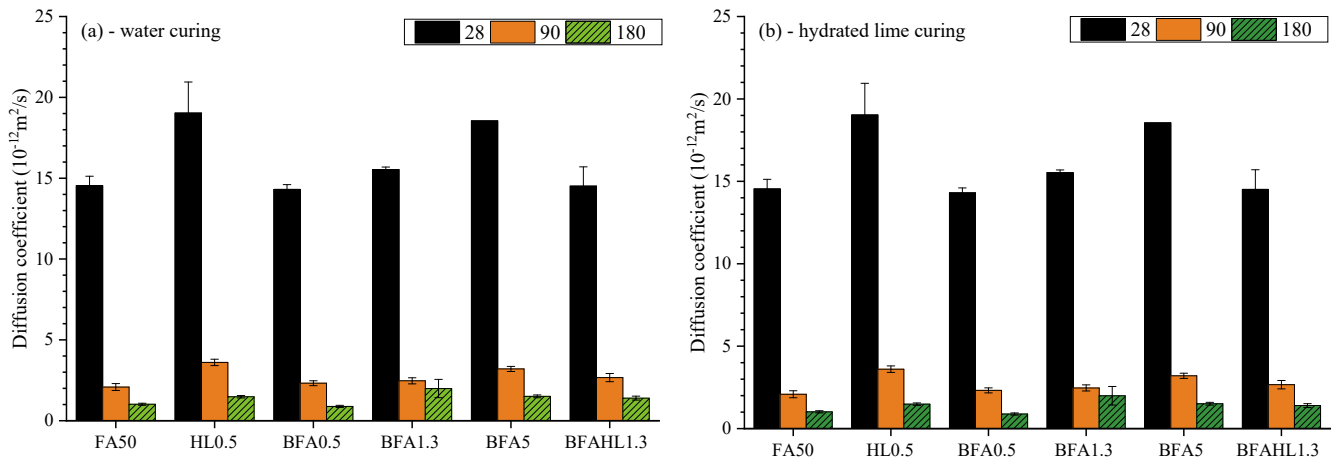


Fig. 16. Chloride migration diffusion coefficient for samples cured in water and in the hydrated lime solution.

values for the two types of cure, in all curing periods studied, with the same behavior that was observed throughout the whole test time. The results observed for the FA50 sample were expected, as the presence of pozzolanic additions decreases the alkalinity of the mixtures, due to the consumption of CH during the pozzolanic reactions, which were observed in mixtures with CFA. However, the introduction of BFA seems to give some alkalinity to the mix (which was lost by the introduction of CFA), leading to the production of concrete with higher carbonation resistance. Moreover, as BFA are not pozzolanic materials, the substitution of cement needs to be very careful, as the increase of BFA in the mixture decreases the content of amorphous silica minerals that react with calcium hydroxide, enabling the formation of hydrated compounds and decreasing the carbonation resistance [64,65].

Contrary to the BFA, incorporation of HL yielded poor results in terms of carbonation resistance. This result shows that possibly the CFA

glass silica does not react with all the available lime, therefore the extra amount of lime, despite contributing to the maintenance of the pH of the mixture, does not contribute to the production of C-S-H and consequently to the matrix densification [65]. It is also important to mention that in the test period used in this study, the hydration of the cementitious matrices may not have reached complete equilibrium.

The comparison between the values of the carbonation depth for the two types of curing showed that, in general, curing with hydrated lime solution improves the resistance to carbonation, and is justified by reducing the alkaline gradient between the samples and the curing solution, thereby avoiding the leaching of compounds [65].

3.7. Chloride penetration resistance

Fig. 16 shows the average results for the chloride diffusion

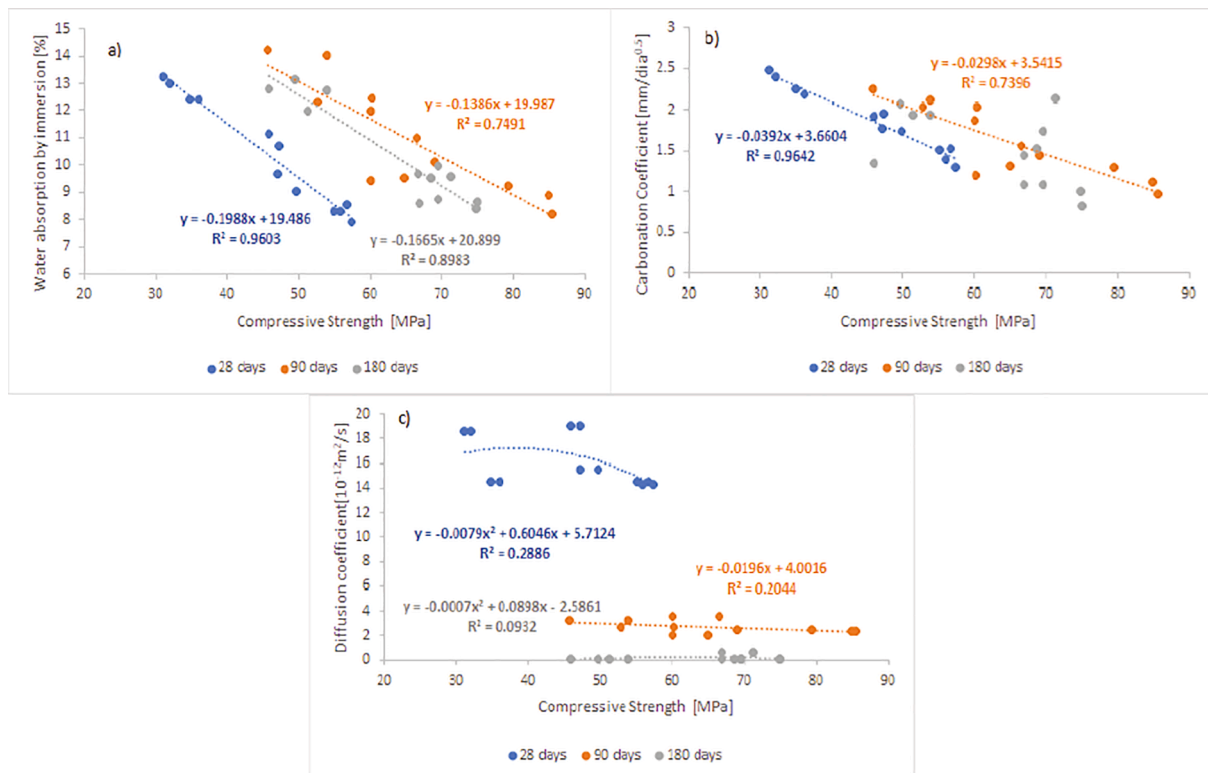


Fig. 17. Relation between compressive strength and: a) water absorption by immersion; b) coefficient of carbonation; and c) chloride diffusion coefficient.

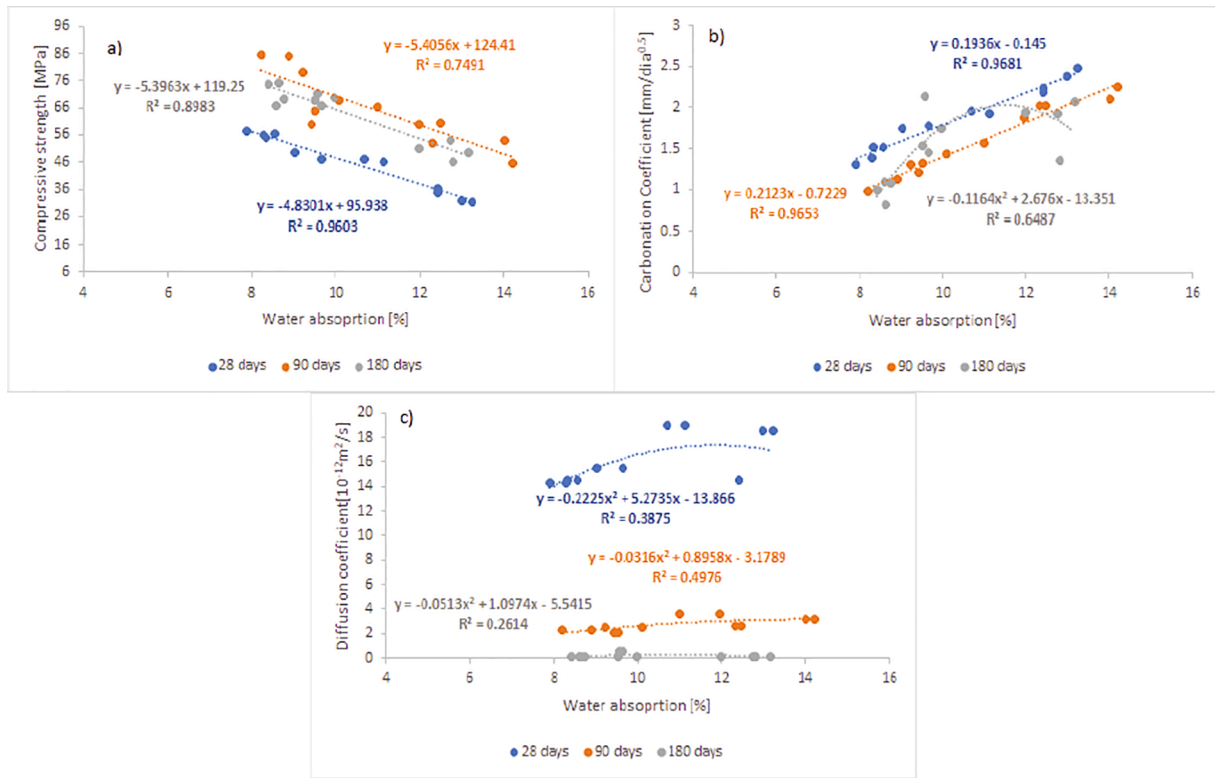


Fig. 18. Relation between water absorption by immersion and: a) compressive strength; b) coefficient of carbonation; and c) chloride diffusion coefficient.

coefficients. The addition of CFA mixed with BFA or hydrated lime led to concrete with higher resistance to chloride penetration. This better performance is more significant for samples cured for 90 and 180 days,

as a decrease of more than 80 % in the coefficient was recorded for all samples. It is known that chloride migration is influenced by the porosity of matrices and an increase in the water/binder ratio leads to a

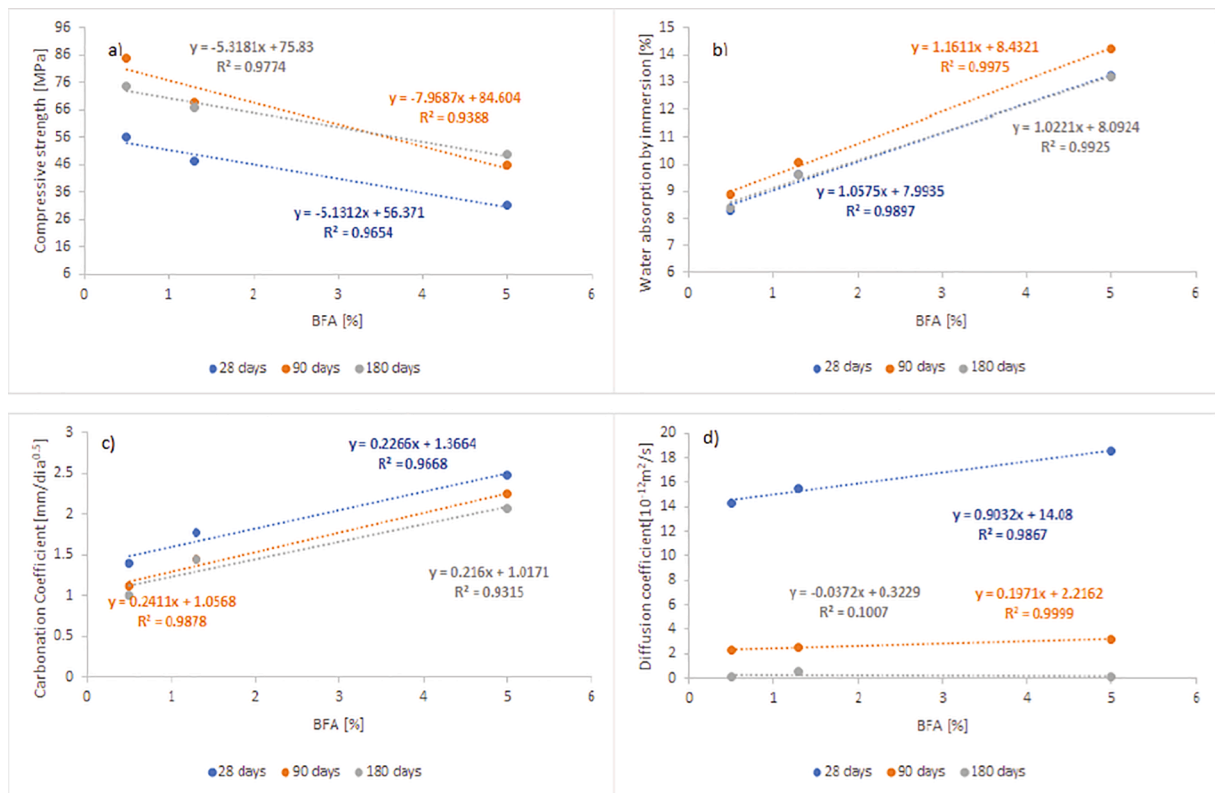


Fig. 19. Relation between content of BFA and: a) compressive strength, b) water absorption by immersion, c) coefficient of carbonation and d) chloride diffusion coefficient.

more porous concrete [23], and therefore a higher diffusion coefficient was observed [66].

The results showed that the mixtures BFA0.5 and FA50 had the lowest values for samples cured in water at 28 and 90 days. At 180 days, samples with BFA presented lower values than FA50 and C100. This result showed a good synergy between the two fly ashes for this level of cement replacement, and also, it could happen because of the higher quantity of aluminates, which in turn supports binding and a reduction of the content of free chloride ions capable of migrating into concrete, leading to a decrease of the diffusion coefficient [66]. Despite the good synergy, an increase in the diffusion coefficient with the increase in the BFA content was observed. Similar result was observed when HL was incorporated in the mix.

For samples cured in the hydrated lime solution, the results for the chloride diffusion coefficient showed slightly different behaviour. In general, for the three curing periods, the samples with BFA had the lowest diffusion coefficient values, with an exception for 180 days, for which FA50 had the second-lowest value. The addition of BFA, an alkaline material, together with an alkaline environment (hydrated lime solution) led to an improvement in the performance of the concrete. Furthermore, the synergy between CFA and BFA and/or HL was good, with better resistance to chloride penetration of these concretes than those with only CFA.

It is important to note that the chloride diffusion coefficient values were lower for samples cured in the hydrated lime solution (Fig. 16), which is once again explained by the decrease in the alkaline compounds leaching, needed for the hydration of concrete mixtures.

3.8. Discussion of the results

The study focuses on the evaluation of BFA incorporation on the properties of HVFAC. It can be observed that BFA has a significant effect on the concrete properties, namely in the porosity and in the carbonation resistance. However, it is important to take into account that the concrete properties are correlated and the influence of BFA in one property could lead to an influence on other properties, and therefore this analysis was made and it is presented in Figs. 17–19.

The relation between compressive strength and water absorption by immersion is presented in Figs. 17a) and 18a), for the three curing periods. It can be observed that a linear relation exists between compressive strength and water absorption, meaning a relation between strength and porosity, with a correlation coefficient of 0.96, 0.89 and 0.75, respectively for 28, 90 and 180 days. Therefore, the increase of BFA content increases the porosity and decreases the compressive strength (Fig. 19a) and b)).

An interesting observation was a correlation between compressive strength and porosity with the carbonation resistance, showing that a high porosity concrete, has low compressive strength, and therefore a less resistant concrete (Figs. 17b) and 18b)). For the case of compressive strength and carbonation resistance, a linear correlation was observed for 28 and 90 days of curing (R^2 equal to 0.96 and 0.74, respectively), however, for 180 days it was not possible to find a good correlation. Similar results were achieved for the relation of water absorption and carbonation resistance, but in this case, it was possible to establish a polynomial was established for the samples with 180 days of curing (R^2 equal to 0.65). The relation between carbonation depth and the percentage of BFA is presented in Fig. 19. There is a linear relation between the BFA content and the carbonation depth, in which the correlation coefficients are 0.97, 0.99 and 0.93, respectively for 28, 90 and 180 days. The increase in the BFA content results in less carbonation resistant concrete.

It was not possible to establish a relation between the porosity and compressive strength with the chloride diffusion coefficient (Figs. 17c) and 18c)). However, a linear correlation was established between the content of BFA and the chloride penetration for 28 and 90 days of curing, in which the correlation coefficient was 0.99 and 1, respectively,

showing a more chloride diffusion on concrete with high BFA content. However, this effect is more noticed at early ages of curing and this may be attributed to curing, since longer curing leads to higher hydration of cement, a better synergy between the two ashes, a higher pozzolanic reaction of coal fly ash, a reduction in permeability and therefore to a more compact microstructure, leading to a lower velocity of carbonation penetration for later ages [37,67]. Moreover, at 180 days of curing, it is clear that the increase in BFA does not influence the chloride penetration.

4. Conclusions

This study highlights the possibility of producing concrete with low cement content, but with similar or even better quality than conventional concrete. The developed low-cement content concrete was found to be more durable and more sustainable than the plain cement one. The main effects of incorporating small amounts of BFA into HVFAC were studied and the performance of these mixtures were also compared to HVFAC incorporating small amounts of LH, as the literature indicates that its use is beneficial to the properties of concrete. A high BFA content causes a decrease in compressive strength, increases the porosity, decreases resistance to carbonation and chloride ion penetration. However, 0.5 %wt and 1.3 %wt of BFA achieved compressive strength values similar to or higher than a HVFAC just with CFA. Moreover, good synergy between the two selected fly ashes was observed. In light of these results, it can be concluded that HVFAC with BFA can be produced, fulfilling the common requirements related to the mechanical strength of conventional concretes. It was also noted that small amounts of BFA led to lower water absorption by immersion and capillarity, indicating a lower porosity of this concrete. With pozzolanic additions, the consumption of CH during its reactions causes a decrease in the alkalinity of the concrete and the incorporation of BFA in its compositions. In small amounts, it appears to provide greater resistance to corrosion by carbonation and by chloride penetration.

Taking all results into account, the BFA0.5 mix seems to be the optimum studied solution, which can also be a solution for replacing conventional plain cement concrete. In fact, BFA blended with CFA seems to make a positive contribution to the quality, durability and sustainability of concrete compared with concrete in which CFA alone is used as supplementary cementitious material or compared with plain cement concrete. Thus, one option to mitigate the main issues of HVFAC can be the addition of a small amount of BFA mixed with CFA

CRediT authorship contribution statement

E.R. Teixeira: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Formal analysis. **A. Camões:** Supervision, Validation, Visualization. **F.G. Branco:** Supervision, Validation, Visualization.

Declaration of Competing Interest

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

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