



Recycling of biomass and coal fly ash as cement replacement material and its effect on hydration and carbonation of concrete

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ABSTRACT

The construction sector has been using supplementary materials in concrete production worldwide, such as coal fly ash. Nowadays, several sub/products or wastes have been studied to be incorporated in construction materials, and one of those wastes is biomass fly ash. However, using high volumes of these materials has some drawbacks, one of them being carbonation. In order to understand phenomena such as this, it is important to study the interaction between the additions and hydration of cement. This paper focuses on the study of hydration and carbonation of cementitious pastes containing biomass fly ash and/or coal fly ash by using thermogravimetric analysis and X-ray diffraction analysis and by accelerated carbonation tests. BFA present different chemical and mineralogical composition than CFA. The results show that incorporating biomass fly ash into construction materials has a similar carbonation behaviour to coal fly ash. Biomass fly ash seems to give some extra alkalinity to the mixtures, and this may present benefits to the construction materials and for the ash management.

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1. Introduction

Pozzolanic materials containing silica and alumina compounds with a low degree of crystallization present in their composition (Jain, 2012). These materials are rich in siliceous or aluminosiliceous compounds that in the presence of moisture, chemically react with calcium hydroxide to form products that have cementitious properties (Bediako, 2018). The pozzolanic reactivity is connected to the internal structure of the material (Cordeiro et al., 2011; Van et al., 2013).

Calcium hydroxide is one of the most important reaction products in Portland cement hydration. $\text{Ca}(\text{OH})_2$ does not contribute greatly to the mechanical strength of hydrated cement paste. However, its presence makes a very important contribution regarding the protection of the concrete reinforcement against corrosion, since they contribute to an alkaline pH (Bertolini et al., 2004; Papadakis, 2000a; Shi et al., 2011). Pozzolanic materials react with calcium hydroxide and produce silicate hydrates, which are the principle binding compounds in cement (Wang et al., 2008a). Pozzolans minimize the limitations of cement and add additional cementitious material, which leads to an increase in the concrete strength (Dembovska et al., 2017; Schneider et al., 2011;

Shannag, 2000). The pozzolanic material leads to a slower strength gain and a longer setting time, but after long term curing ages, concrete is often stronger and more durable than a plain cement concrete (Chen et al., 2013; Dembovska et al., 2017; Isaia et al., 2003).

The use of renewable sources, such as biomass, to produce heat and power has been increasing in recent years and it is part of the energetic strategies all over the world (Tarelho et al., 2015; Teixeira et al., 2016b). An important issue related to thermochemical conversion of biomass to energy is related to the ashes produced, their characteristics and management (Tarelho et al., 2015). In Portugal, there are no guidelines for biomass fly ash management. The ashes are classified as an industrial solid waste, with code 100103 according to the (European List of Wastes, 2000) and is usually managed by disposal in landfill. However, this disposal has economic, environmental and sustainable implications (Ban and Ramli, 2011; Miller et al., 2006; Tarelho et al., 2012). In some countries, fly ash is sometimes recycled in agricultural fields or forests, but in most cases without controlling it (Rajamma et al., 2015). Therefore, it is important to find alternative applications for fly ash from biomass combustion, in order to make the valorisation of this material and save natural resources (Miller et al., 2006; Tarelho et al., 2015, 2012).

Several types of biomass, during their combustion, produce ash with pozzolanic activity similar to the most common pozzolana (coal fly ash - CFA) in concrete such as: rice husk, wheat straw,

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sugar cane straw and wood (Wang and Baxter, 2007). The characteristics of ash and its management are very important in terms of operating and environmental aspects (Tarelho et al., 2012; Teixeira et al., 2016b).

Using biomass fly ash (BFA) as a partial substitute for cement in building materials will minimise the use of natural resources used in cement production (Tarelho et al., 2012), mitigation of greenhouse gas emissions and a better solution for ash management, avoiding the landfilling of the biomass combustion residues (Tosti et al., 2018). Nowadays, the use of fly ash in concrete is regulated by European standard (EN 450-1, 2012). Some studies showed good performances when blends of coal and biomass fly ash or only biomass ash were used in concrete (Ban and Ramli, 2011; Barbosa et al., 2013; Cordeiro et al., 2009; Rajamma et al., 2009; Wang et al., 2008b).

However, the European standard does not take into account any material not derived from coal combustion, which limits the use of biomass fly ash in cement because coal-fired power plants can use only up to 20% of biomass to replace coal. (Tosti et al., 2018). However, some studies have demonstrated that biomass fly ash can be used as cement replacement material to produce concrete with good mechanical and durability performance (Ban and Ramli, 2011).

The effect of BFA on the concrete properties is dependent on the physical-chemical characteristics of the biomass fly ash (type of biomass feedstock combusted, the thermal conversion system and the flue gas cleaning system (Oberberger et al., 1997; Sarabèr, 2014; Tarelho et al., 2015). Siddique and Wang et al. observed that the mechanical strength of concrete decreased with increasing wood ash content but, when pozzolanic activity is present, the strength increases with the age (Siddique, 2012; Wang et al., 2008b). Furthermore, biomass fly ash with high calcium content can contain reactive crystalline phases that can contribute to strength development, and some researches focus their work in higher replacements (20–40%wt) (Lothenbach et al., 2011; Tosti et al., 2018).

Usually, pozzolanas, such as BFA, are used by replacing some portion of cement. This leads to a decrease in the cement requirement, which then results in a decrease in the total cost of concrete and reduces its carbon footprint as the production of each ton of cement results in CO₂ emission of approximately one ton (Hasanbeigi et al., 2012; Kuder et al., 2012; Paris et al., 2016; Shi et al., 2011). So, using biomass fly ash as cement replacement material, helps concrete to change ash from environmental concern to a useful resource with the production of a highly effective alternative cementitious material (Chowdhury et al., 2014; Nagrockienė and Daugėla, 2018; Teixeira et al., 2019, 2016b).

Besides that, one important disadvantage related to the incorporation of pozzolans in concrete is the carbonation phenomenon that can lead to reinforcement corrosion. This phenomenon is even worse in high cement substitutions by pozzolanic materials. Therefore, it is important to understand the carbonation of calcium hydroxide (CH or Ca(OH)₂) and the calcium silicate hydrate (CSH) formation process. The carbonate reacts with Ca²⁺ from CH, CSH and the hydrated calcium aluminates and this leads to the formation of different forms of calcium carbonates (Borges et al., 2010). In the initial phase of carbonation, porosity decreases mainly due to the fact that CH is the first phase attacked and the volume of calcite produced is greater than the volume of CH (Borges et al., 2010; Morandeu et al., 2014; Reis et al., 2014). Usually, the carbonate samples present an increase in their weight, a lower porosity and a higher compressive strength at early ages (Borges et al., 2010). This usually occurs in low porosity pastes, where calcite formation decreases porosity, preventing CO₂ diffusion, reducing carbonation attacks. Pastes with a high porosity could allow the diffusion of a constant CO₂ content, in which case the CH is depleted and the

interlayer calcium from CSH also reacts with the CO₂ (Borges et al., 2010; Morandeu et al., 2014).

Concrete with blended cement pastes has a lower CH content due to the pozzolanic reaction, and for that reason the carbonation of C-S-H is more dependent on the permeability of pastes. High permeable pastes have a rapid decalcification of C-S-H by carbonation shrinkage (Borges et al., 2010; Lilkov et al., 2014).

It is important to study the content of Ca(OH)₂ and the carbonation products when pozzolans are used in a high level of cement replacement. Various studies have been done for Ca(OH)₂ in cement pastes containing pozzolanas by thermogravimetric analysis (Antoni, 2013; Kroehong et al., 2011; Morandeu et al., 2014; Pacheco Torgal et al., 2012).

Thermogravimetric analysis (TGA) is a method adopted when the objective is to characterize the reactivity of the pozzolanic mixture, mainly in terms of the hydration and kinetic reaction rate and the study of the hydration reaction products. The main aim of this method is to determine the loss masses that are attributed to different compounds, which occur in different temperature classes. For example, the C-S-H has a loss mass essentially in the class of 100–200 °C. On the other hand, portlandite is in the range of 350–450 °C (Anjos et al., 2017). Several other methods can be used, such as mineralogy analysis by diffraction of X-ray (XRD) or scanning electron microscopy, as can be seen in (Haha et al., 2010; Lee and Lee, 2015; Shi et al., 2016).

The main goal of this work was to evaluate the effect of using BFA, as cement replacement, on the hydration compounds and on the extent of carbonation in cement pastes, using TGA and XRD analysis and by accelerated carbonation tests. During the study, a comparison between plain cement pastes and pastes with BFA or/and pastes with CFA was made.

2. Materials and methods

2.1. Materials

Portland cement CEM I 42.5R, coal fly ash and biomass fly ash were used to produce cementitious pastes. Portland cement was obtained from the Secil Industry and is produced according to (NP EN 197-1, 2001).

CFA was sampled from a Portuguese thermoelectric power plant that burned coal as fuel. BFA was sampled in a Portuguese pulp and paper industry, which used forest residues, such as bark from eucalyptus and pine, as fuel to produce heat and power. Both ashes were characterised in terms of loss on ignition, chemical composition and thermal analysis. The two ashes were grinded in order to obtain samples with a particle size lower than 90 μm for its characterisation in terms of loss on ignition (LOI), chemical and thermogravimetric analysis. The chemical composition was determined by X-Ray Fluorescence (XRF) using a Panalytical Axios spectrometer. The thermal analysis (TG and DTA) was done using a STA, Netzsch 402 EP with a heating rate of 10 °C/min.

2.2. Methods

Four different cement pastes were set, using coal and biomass fly ash as supplementary cementitious materials (Table 3). The content of fly ash in blended cement pastes was 50 wt% by mass of cement. A constant water-binder ratio of 0.5 was used. The selection of these quantities was due to the fact that this study focused on the effect that BFA can have on the part corresponding to the binder of high volume fly ash concrete (with 50 wt% of cement replacement), as a solution for the conventional concretes. Usually, a conventional plain cement concrete presents a binder with 350 kg/m³ and a water-binder ratio of 0.5.

The pastes were mixed in a standard mechanical mixer as described in (NP EN 196-1, 2006), for three minutes, and six cubic specimens with 20 mm edge for each formulation were cast. After demoulding, which was made after 24 h, all samples were cured in a humidity chamber (with approximately 87% of relative humidity and 21 °C of temperature) up to the date of the tests (28 and 90 days).

The samples were milled until all particles had a diameter below 63 µm and stored in a bag closed using a vacuum system, before the TGA and XRD analysis. The TGA and XRD were done according to what was described before. It was important to seal the samples before the TGA and DRX analysis, to prevent the process of sample carbonation that occurs when the samples contact with CO₂ present in the atmosphere. The thermal analysis was carried out using a STA, Netzsch 402 EP with a heating rate of 10 °C/min and XRD was done in a Bruker D8 Discover diffractometer (Teixeira et al., 2016a).

The level of free calcium hydroxide presented in the pastes after hydration was calculated by Eq. (1). The overall hydration was determined according to Eq. (2), which represents the chemically combined water content (Anjos et al., 2017; Baert et al., 2008). The calculation of calcium carbonate was made according to Eq. (3).

$$CH_F = Ca(OH)_2 [\%] = ML_{Ca(OH)_2} [\%] \cdot MM_{Ca(OH)_2} / MM_{H_2O} \quad (1)$$

$$H_2O_{Q,comb} = mass(loss\%)_{1000^\circ C} - mass(loss\%)_{105^\circ C} \quad (2)$$

$$CaCO_3 [\%] = ML_{CaCO_3} [\%] \cdot MM_{CaO} / MM_{CO_2} \quad (3)$$

where

CH_F is the content of free calcium hydroxide produced during the hydrate of the paste; ML_{Ca(OH)₂} is the mass loss in % observed in the TG curve for Ca(OH)₂; MM_{Ca(OH)₂} is the molecular weight of Ca(OH)₂; MM_{H₂O} is the molecular weight of H₂O; H₂O_{Q,comb} is chemically combined water; mass(loss%)_{1000°C} is the total mass loss from 0 to 1000 °C; mass (loss%)_{105°C} is mass loss referring to free water, from 35 to 105 °C; ML_{CaCO₃} [%] is the mass loss in % observed in TG curve for CaCO₃; MM_{CaO} is the molecular weight for CaO; and MM_{CO₂} is the molecular weight of CO₂.

The hydration degree (α) was calculated, which is the weight fraction of original cement that has become completely hydrated (0 ≤ α ≤ 1) (Aiad et al., 2017), as observed in Eq. (4).

$$\alpha = \frac{W_n}{W_\infty} \quad (4)$$

where: α is the hydration degree; W_n is the combined water content (%) at a presented curing age; and W_∞ is the whole combined water content after full hydration (approximately 0.23). The factor of 0.23 represents the non-evaporable water content per gram of cement in a mix for complete hydration (Aiad et al., 2017; Lam et al., 2000).

The carbonation reaction of those pastes was investigated by thermal analysis but was also measured in paste samples, using the accelerated carbonation test. For the carbonation test, three samples for each paste formulation with the dimensions of 40 × 40 × 160 mm³ were prepared. The samples were cured in a humidity chamber with relative humidity and temperature control (with approximately 87% of relative humidity and 21 °C of temperature). After curing, the cured samples were preconditioned in an isolated container subjected to constant temperature and relative humidity (RH) (88.0 ± 4.0% and 17.5 ± 1.6 °C) for 14 days, to ensure the stabilization of humidity within the samples. To measure the depth of carbonation, the samples were sealed with paraffin, with the exception of two opposite faces. After sealing, the samples were placed in an accelerated carbonation chamber (4.1 ± 0.1% of

CO₂, 43.7 ± 16.2% RH and 20.0 ± 0.0 °C). To measure the carbonation depth, cross-sections were sprayed with a phenolphthalein indicator, based on the procedure described in (CEN/TS 12390-12, 2010; LNEC E 391, 1993). The pastes were compared at 28 and 90 days of curing.

Carbonation mainly occurs because CO₂ adsorption in alkaline media to form CaCO₃, decreasing the pH value of mixes. For this reason, the pH was measured in the samples before and after curing, and after the accelerated carbonation test finished. Solid samples of milled pastes were placed in a glass with distilled water at a solid to liquid ratio of 1:20. The glass was covered with plastic film to prevent the evaporation of water and the reaction of water with the atmospheric CO₂ and was stored for 24 h. The procedure used in this study was based on (McPolin et al., 2007). After 24 h, the pH of each sample was measured using Crisonmicro pH 2000 equipment.

3. Results and discussion

3.1. Physical and chemical characterization of cement, CFA and BFA

The data on the physical and chemical analysis of cement was obtained via the datasheet provided by the manufacturer, and are showed in Table 1. The Portland cement presented a specific weight of 3.12 g/cm³ and a Blaine specific surface of 4072 cm²/g. In terms of chemical composition, a higher percentage of calcium oxide, more than 63 wt%, followed by silicon oxide (around 20 wt%) and aluminium oxide (3.4 wt%) is observed. These values are expected and usual for a Portland cement (Gesoglu et al., 2013; Tangchirapat et al., 2009).

The obtained LOI and the chemical composition of the selected materials are showed in Table 2. As can be seen, BFA showed a LOI value of 6.27% and CFA presented a value of 2.73%. Silica is the major chemical element (54.08%wt) present in the CFA, followed by Al₂O₃, Fe₂O₃, CaO and K₂O. SiO₂ was also the major chemical present in BFA (36.03%), followed by CaO, Al₂O₃, K₂O, Fe₂O₃, MgO. CFA represents a typical composition of Class F fly ash, according to (ASTM C618-15, 2015). However, BFA is not included in the ASTM C618 classes, since the sum of SiO₂ + Al₂O₃ + Fe₂O₃ is lower than 50%.

Table 1

Physical and chemical characteristics of cement (Secil - Companhia Geral de Cal e Cimentos, 2013).

Analysis	Average of values measure in one year
<i>Chemical composition</i>	
Loss on ignition (%)	2.33
Insoluble Residue (%)	1.35
SiO ₂ (%)	19.07
Al ₂ O ₃ (%)	4.43
Fe ₂ O ₃ (%)	3.50
CaO (%)	63.80
MgO (%)	1.87
SO ₃ (%)	3.28
K ₂ O (%)	0.90
Na ₂ O (%)	0.21
Cl ⁻ (%)	0.05
<i>Physical Composition</i>	
Specific weight (g/cm ³)	3.12
Blaine specific surface (cm ² /g)	4072
Sieve Residue (%)	45 µm 3.20 32 µm 9.26
Water demand (%)	28.8
Setting Time (min)	Initial 189 Final 260
Soundness (mm)	0.84

Table 2
Physical and chemical composition and loss-on-ignition of BFA and CFA samples.

Parameters	Materials	
	CFA	BFA
Chemical characteristics (by FRX)		
	%wt	
SiO ₂	54.08	36.03
CaO	3.27	27.41
Na ₂ O	0.51	0.87
Al ₂ O ₃	26.38	8.33
MgO	1.55	3.56
K ₂ O	1.64	4.92
P ₂ O ₅	0.80	3.21
SO ₃	0.98	3.18
Cl	–	0.60
TiO ₂	1.44	0.94
MnO	0.05	0.24
Fe ₂ O ₃	6.12	4.12
Loss on ignition	2.73	6.27
Physical characteristics		
Diameter for 10% of retained material (μm)	1.53	5.91
Diameter for 50% of retained material (μm)	8.55	46.70
Diameter for 90% of retained material (μm)	20.19	230.74
Bulk density (kg/m ³)	2420	2619

The thermogravimetric (TG) and DTA signals registered for cement, CFA and BFA are shown in Fig. 1. A slight decrease was observed around 100 °C for both ashes. This loss of weight is related to the release of water adsorbed in the ash. With increasing temperature, a significant decrease in weight of the two fly ashes was observed in the range of 600–835 °C, associated with an endothermic process. This weight loss must be related to the ther-

Table 3
Paste Formulations.

Nomenclature	% of Cement	% of CFA	% of BFA	w/b ratio
100C	100	0	0	0.5
50C-50CFA	50	50	0	0.5
50C-50BFA	50	0	50	0.5
50C-25CFA-25BFA	50	25	25	0.5

mal decomposition of carbonates such as CaCO₃ (Teixeira et al., 2016a). The total weight loss was approximately 2–3% for the CFA and 6–7% for BFA and these results are similar to the values observed in LOI analysis (Table 2). The thermal behaviour of the biomass fly ash and coal fly ash presented in this study is similar to that described in other researches (Girón et al., 2013; Li et al., 2017; Tarelho et al., 2015; Vassilev et al., 2013a).

3.2. Thermal analysis

3.2.1. Chemically combined water and degree of hydration of pastes

Fig. 2 presents the TG/DTA curves of the tested hydrated pastes at 28 and 90 days of curing. The TG/DTA profiles showed typical reactions occurring in cement hydrated pastes, when submitted to a continuous increase in temperature. The differences were related to the values of mass loss verified for each hydrated product and for the carbonated products, as shown in Table 4, where the values obtained in pastes at 28 and 90 days are shown.

The first peak observed in the graphs of TG/DTA was related to the loss of free water that occurs between 0 and 105 °C. The water in the large pores evaporated for temperatures up to 35 °C. Above

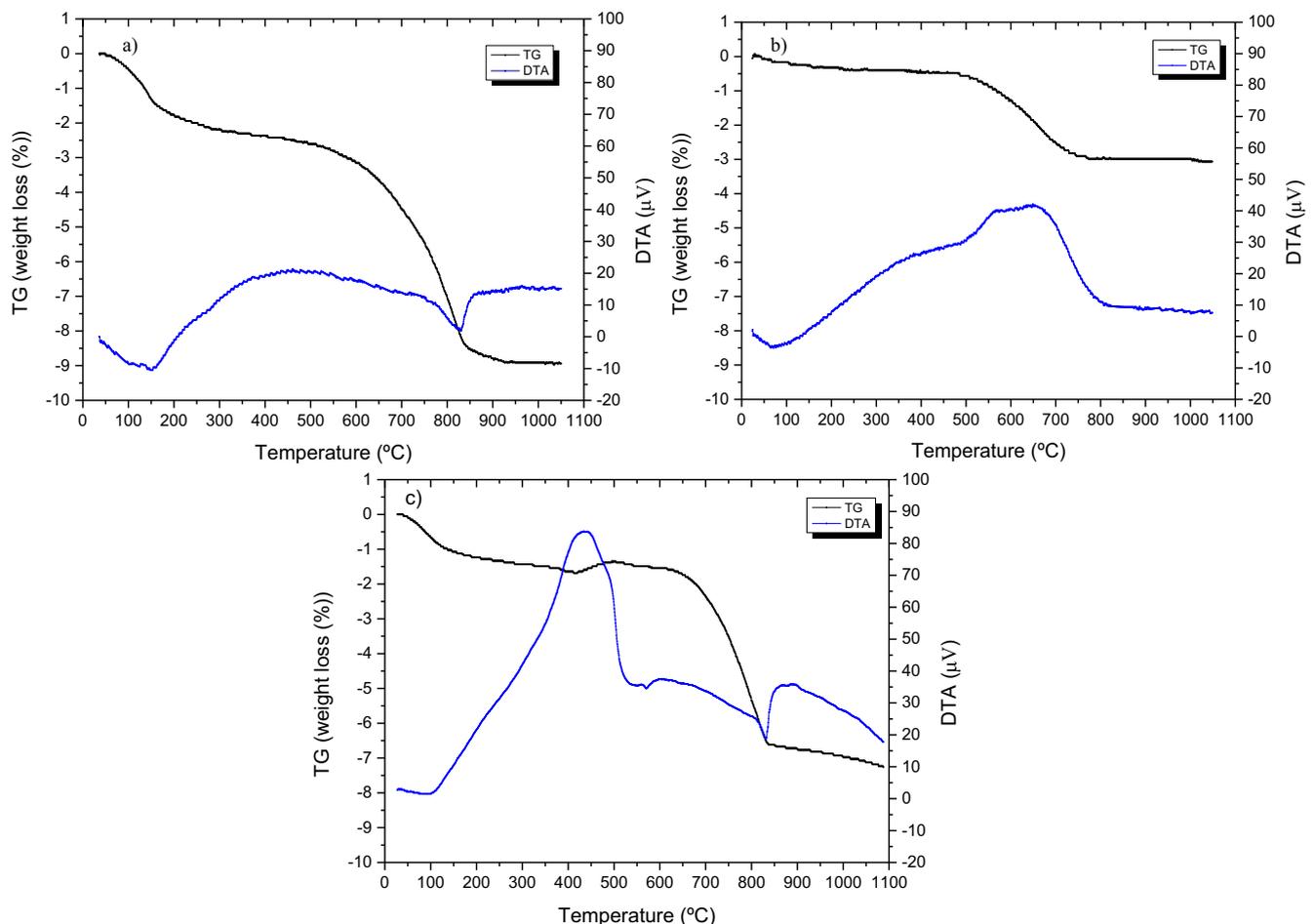


Fig. 1. Thermogravimetric analysis of: Cement (a), CFA (b) and BFA (c).

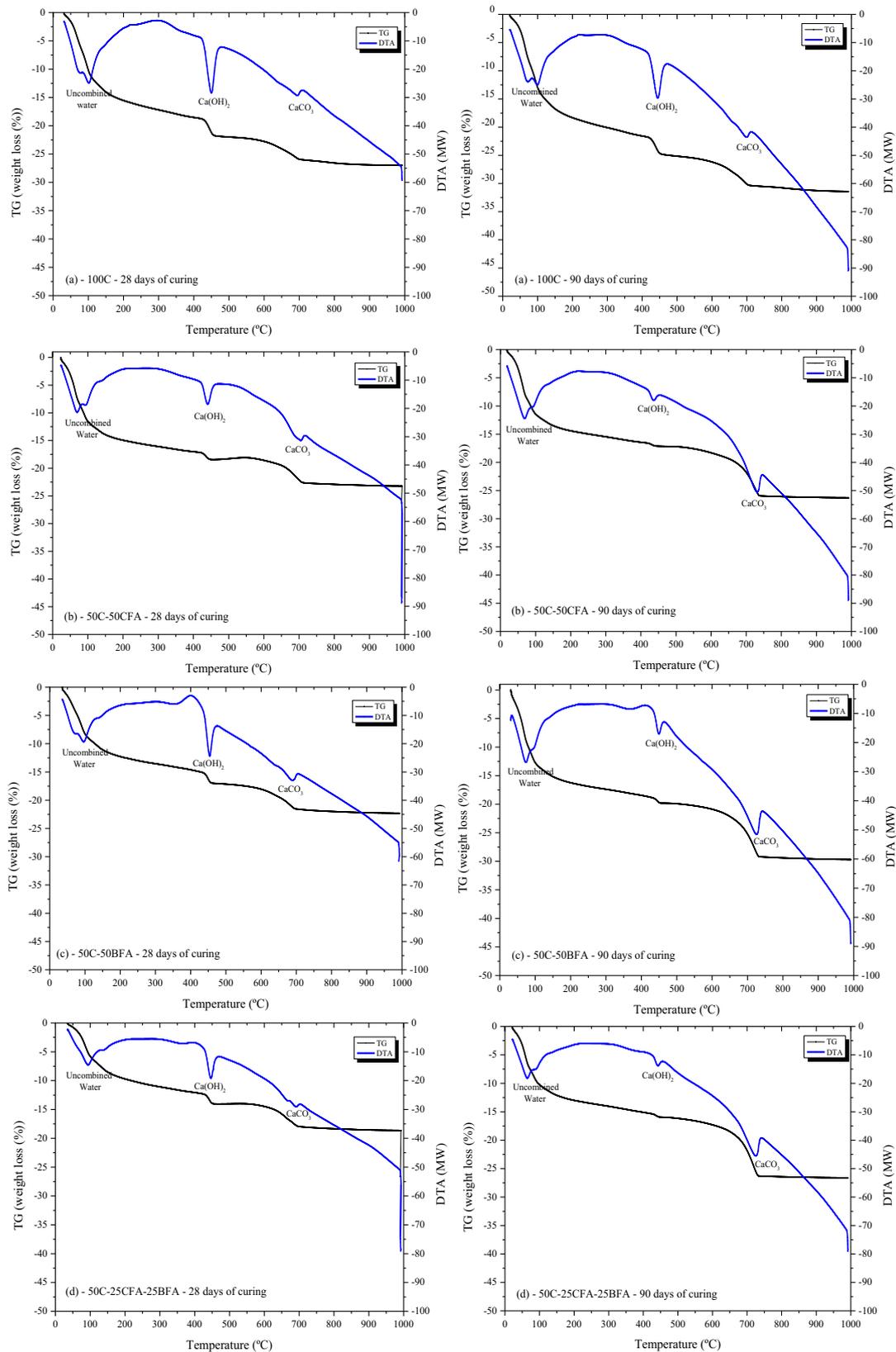


Fig. 2. Thermogravimetric analysis of 100C (a), 50C-50CFA (b), 50C-50BFA (c) and 50C-25CFA-25BFA (d) specimens.

this temperature, the retained water is released by capillarity tension in the capillarity pores (Anjos et al., 2017). The water that is not chemically combined is not used for the calculation of the level

of hydration (Alarcon-Ruiz et al., 2005; Anjos et al., 2017; Baert et al., 2008). A weight reduction of samples was observed for temperatures between 150 and 400 °C (Fig. 2). This is due to the evap-

Table 4
Mass losses at 28 and 90 days.

Sample	Uncombined water		Ca(OH) ₂ (wt%)		CaCO ₃ (wt%)		Total mass loss	
	at 28 days	at 90 days	at 28 days	at 90 days	at 28 days	at 90 days	at 28 days	at 90 days
100C	9.66	11.78	3.46	3.32	2.79	3.15	27.00	31.44
50C-50FA	10.21	9.97	1.30	0.67	3.15	6.05	23.23	26.30
50C-50BFA	8.27	11.62	2.32	1.27	2.97	6.83	22.33	29.70
50C-25FA-25BFA	5.80	8.83	1.88	0.84	2.98	7.62	18.65	26.63

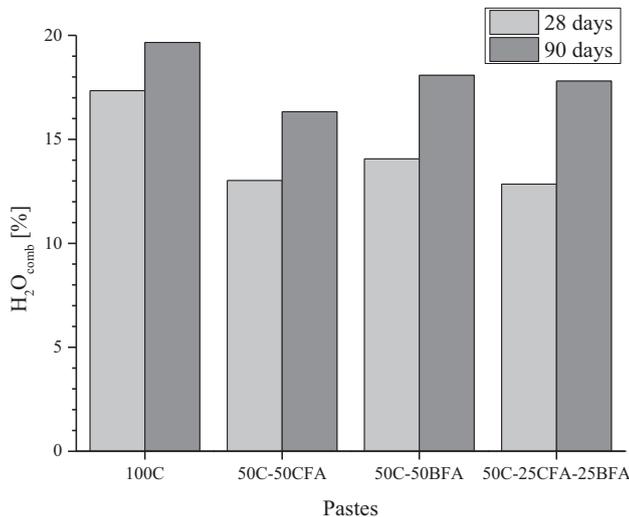


Fig. 3. Chemically combined water content after 28 and 90 days.

oration of the physically combined water from the reaction products (for example C-S-H gel and aluminosilicate gel) (Bernal et al., 2011; Kong and Sanjayan, 2010; Lee and Lee, 2015).

Fig. 3 shows the chemically combined water found in hydrated pastes after 28 and 90 days, determined by Eq. (2) (as described in Section 2.2). The rate of increase of the chemically water content from 28 and 90 days was 13.4, 25.4, 28.6 and 38.5% for 100C, 50C-50CFA, 50C-50BFA and 50C-25CFA-25BFA, respectively. (Eq. (4))

The degree of hydration obtained for the hardened cement pastes can be found in Table 6. It can be observed that the degree of hydration was similar for all samples, and the hydration degree values of pastes with fly ash were lower than of the reference sample.

3.2.2. Ca(OH)₂ content

The Ca(OH)₂ content for the different pastes is presented in Table 5. This compound is formed during the hydration of dicalcium silicate (C₂S) and tricalcium silicate (C₃S) contained in the cement. Some authors showed that for cement CEM I 42.5, this is formed at 3 days of curing (Sisomphon and Franke, 2011). One of

Table 5
The degree of hydration (α) of the hardened cement pastes.

Sample	Days	
	28	90
100C	0.75	0.86
50C-50CFA	0.57	0.71
50C-50BFA	0.61	0.79
50C-25CFA-25BFA	0.56	0.77

the most noted peaks on the TG/DTA curve (Fig. 3) corresponds to the mass related with the dehydroxylation of calcium hydroxide, which occurs between the temperatures of 410 and 480 °C (Scrivener et al., 2015). The content of free calcium hydroxide is an important parameter to assess the hydration and is shown in Fig. 5.

Pastes with CFA and BFA showed a significant reduction in the level of free calcium hydroxide with an increase in the age of hydration, when compared to the cement paste. This can be explained by the pozzolanic reactions and with the calcium hydroxide (CH) produced by the hydration of cement (Anjos et al., 2017). A 50 wt% cement replacement was studied for each paste sample. If the ash contributed nothing to the pozzolanic reaction, the Ca(OH)₂ presented in the samples with ash should be 50 wt% of that determined for the plain cement paste. On the contrary, if the two ashes were highly pozzolanic, the Ca(OH)₂ would be very low. At 28 days, the Ca(OH)₂ of 50 wt% of CFA, 50 wt% of cement replaced with BFA and the blend of the two ashes is 38, 67 and 55% of the value obtained for cement paste, respectively (Fig. 2). The results showed that BFA did not have a contribution for the pozzolanic reaction and seems to add some calcium hydroxide to the paste.

Pastes with CFA and BFA presented a decrease in Ca(OH)₂ content at 90 days, but in these pastes the total consumption was not observed. Similar results were observed in (Sakai et al., 2005; Tkaczewska and Małolepszy, 2009). This is related with the pozzolanic reaction but also justified by the carbonation, because during the chemical reaction Ca(OH)₂ is consumed to produce calcium carbonate (Chatterji et al., 2002; Jiang et al., 2000; Visser, 2014).

3.2.3. CaCO₃ content

The last peak observed in the thermogravimetric analysis was related with calcium carbonate (650–800 °C) (Fig. 2). Similar results were observed in various studies (Bernal et al., 2011; Chindaprasirt et al., 2014; Kong and Sanjayan, 2010; Lee and Lee, 2015). The CaCO₃ analysis is very important, because it is related with the carbonation phenomena and can consequently affect the corrosion of concrete reinforcement. However, the TG/DTA analysis showed an exothermic signal around 500–650 °C for CFA and 300–600 °C for BFA, this weight loss can most probably be a result of elemental carbon oxidation, according to (Rocca et al., 2013; Zomerer and Comans, 2009).

The CaCO₃ content for different pastes is presented in Table 4 and was determined by the results expressed in Fig. 4. As can be seen, the content of calcium carbonate was higher for pastes with two types of fly ash than for paste containing cement only. The content of CaCO₃ duplicated from 28 to 90 days of curing, with the exception of cement paste (100C). This is explained by the fact that the carbonation mechanism is a lengthy process due to the low CO₂ concentration in atmosphere and the physical characteristics of materials, which allow some resistance to the CO₂ penetration (Monteiro, 2010).

In terms of total loss mass (Table 5), an increase of mass loss was observed with the increase of the curing age. This is related to the increase in the CaCO₃ content at 90 days.

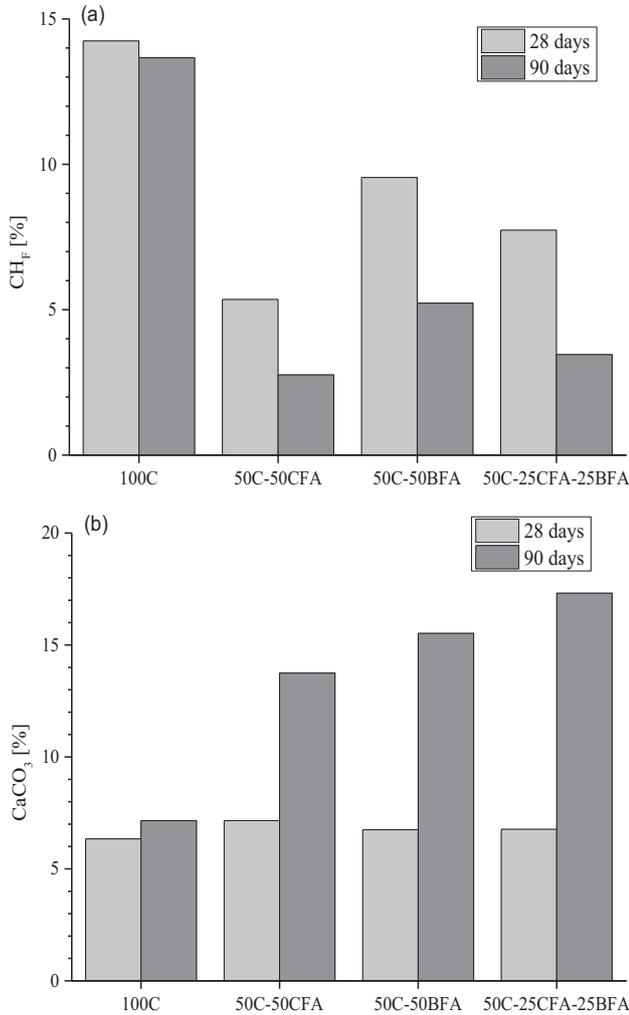


Fig. 4. Content of CH_F (a) and CaCO₃ (b) in pastes after 28 and 90 days.

3.3. Mineralogical analysis of pastes

Fig. 5 presents the XRD patterns of pastes after 28 and 90 days of curing. Calcium silicates are responsible for the gain in mechanical strength of construction materials (Tkaczewska and Małolepszy, 2009) and are part of the chemical composition of Portland cement (Aitcin, 2008). The presence of C₂S peaks for pastes with fly ash can be observed for both ages that show the presence of unhydrated cement grains. C₃S peaks were not observed and this is expected, since this compound has a higher reaction rate with respect to C₂S (Anjos et al., 2017).

It was verified that the intensity of the portlandite (Ca(OH)₂) peak was significantly higher for the plain cement mix (Fig. 5) and similar results were observed in (Kocak and Nas, 2014). This indicates higher hydration and corroborates the values obtained from chemically combined water and CH_F obtained by TG/DTA (Figs. 3 and 4).

A significant increase in the calcite peak was observed between 28 and 90 days for all pastes, but this was related to the cement hydration. BFA pastes presented a significant increase in the CaCO₃ peak. As observed in the TGA analysis, the content of calcite differed with the increase in the curing age and this can be seen by the increase in the peak intensity in the XRD analysis.

The presence of quartz in the samples with BFA and CFA (alone or blended) is due to the presence of this compound in the chemical composition of each ash, as seen in Table 2. CFA is usually a little finer than Portland cement, and its major chemical constituents, silica, alumina and iron and calcium oxides (Joshi and Lohita, 2001; Lothenbach et al., 2011; Reis et al., 2016a). Usually, BFA presents a high content of silicium compounds, which is also related with the chemical composition of biomass (mostly with the inorganic part – ash), but also related with the inert material, e.g. soil particles, which are fed mixed with biomass during combustion (Vassilev et al., 2010). The high silica content is explained by the fine particles from the inert material fed with biomass and in the case of the bubbling fluidized bed reactor, by the fine particles that belong to the bed sand, which are reduced by the combustion of flue gas and

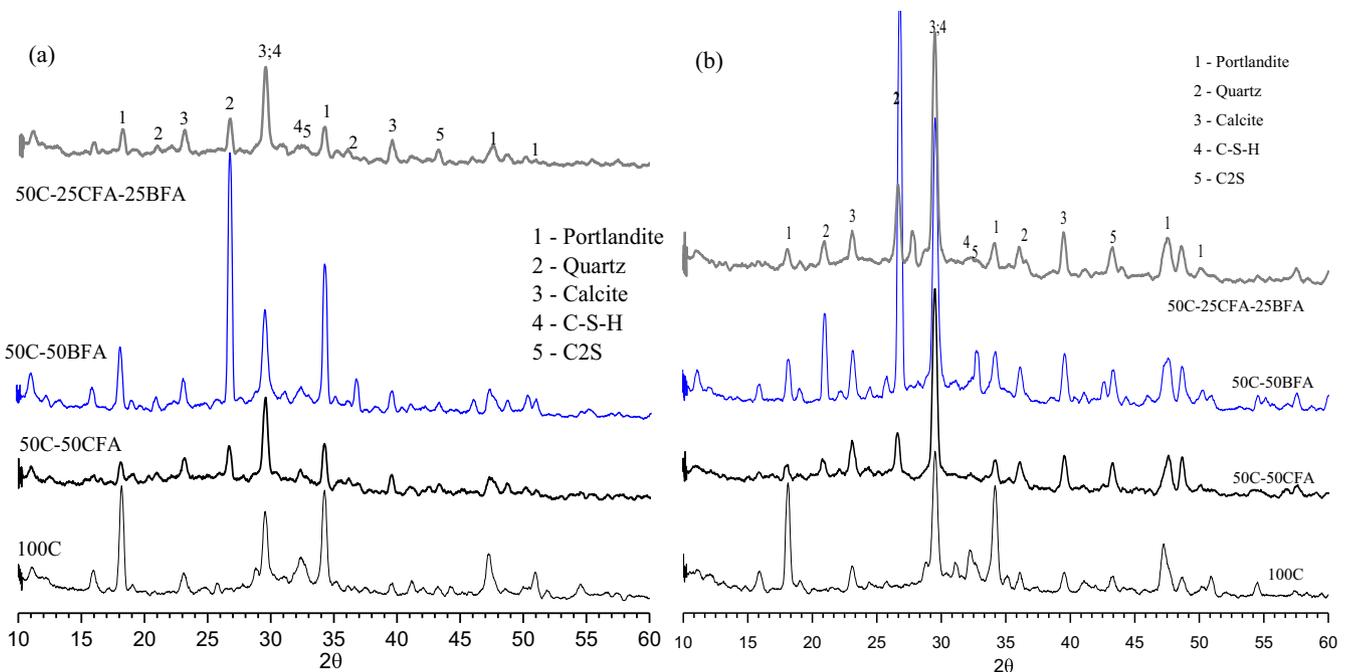


Fig. 5. XRD patterns for pastes with: (a) 28 days and (b) 90 days.

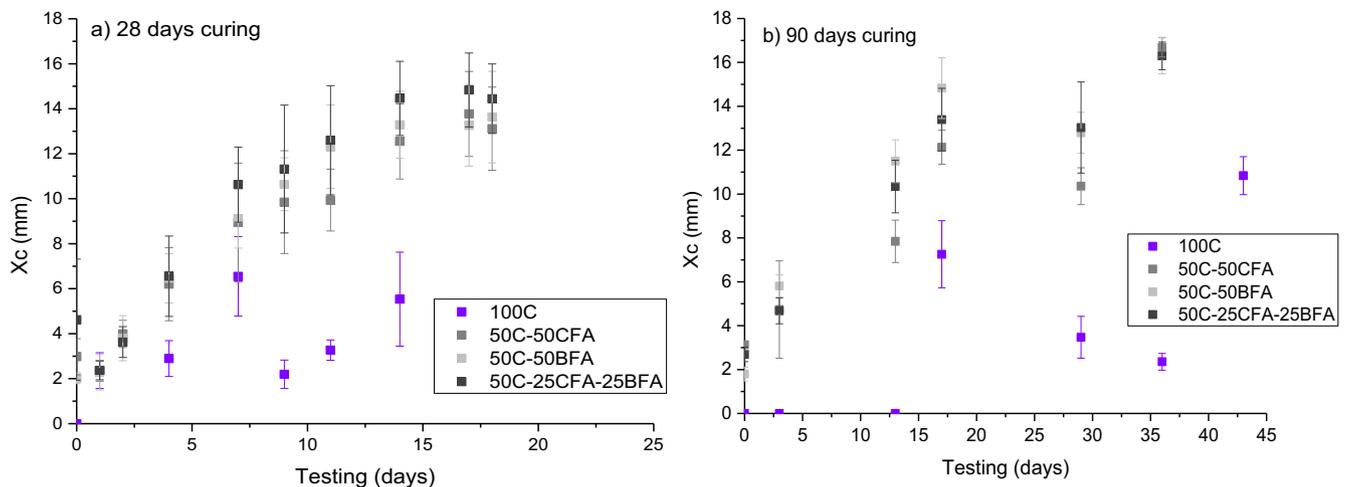


Fig. 6. Variation of carbonation depth for the different pastes.

Table 6
Values of pH measured in pastes.

Samples	After demoulded	28 days		90 days	
		After curing	After total carbonation (20 days)	After curing	After total carbonation (36 days)
100C	12.24 ± 0.008	12.69 ± 0.009	11.65 ± 0.008 ^a	12.44 ± 0.012	12.50 ± 0.012 ^a
50C-50CFA	12.35 ± 0.008	12.70 ± 0.008	9.94 ± 0.012	12.07 ± 0.008	10.27 ± 0.008
50C-50BFA	12.34 ± 0.005	12.72 ± 0.000	9.90 ± 0.012	12.23 ± 0.009	10.00 ± 0.005
50C-25CFA-25BFA	12.38 ± 0.005	12.71 ± 0.008	9.89 ± 0.012	12.16 ± 0.000	9.97 ± 0.008

^a The pH value is the value that cement paste had at the time when the samples of pastes with ash are totally carbonated.

captured by the control devices (Tarelho et al., 2015, 2012; Teixeira et al., 2013; Vassilev et al., 2013b, 2010).

3.4. Accelerated carbonation test using phenolphthalein indicator and pH for cement based pastes

The results for the carbonation depth for the two curing ages during the test period are presented in Fig. 6. No initial carbonation was observed for any pastes before being exposed to CO₂ at the two curing ages. The reference paste showed very slow progress in the carbonation depth. As can be seen, at the two curing ages, pastes that contain ash had a very high carbonation depth when compared to the reference one. Similar results were observed in various studies (Atis, 2003; Khan and Lynsdale, 2002; Khunthongkeaw et al., 2006; Papadakis, 2000b; Reis et al., 2014; Shi et al., 2016) and this is due to the consumption of calcium hydroxide and the consequent decrease in pH (Ramos et al., 2013; Reis et al., 2014; Reis et al., 2016b).

The test was carried out until the sample did not show a colour change, when sprayed with phenolphthalein, which means that the sample is completely carbonated. After 20 days of testing, all fly ash pastes were completed carbonated. On the other hand, during this period the cement paste presented low values of carbonation depth. Similar results were observed for pastes with 90 days of curing. Once again, pastes with fly ash reached the total carbonation of samples after 36 days of testing and the cement paste presented low values of carbonation depth. No significant differences between the values for the carbonation depth were observed in the pastes with fly ash and this confirmed the results shown in the TGA analysis (Table 4). As observed in Table 4, 50C-25FA-25BFA presented the highest values for the calcium carbonate at 28 days of curing. At 90 days, the sample 50C-50BFA presented higher values for the carbonation depth, but at the end of the test the results were similar for all paste samples (Fig. 6).

In Table 6, the values of pH measured for the different pastes are shown. Pastes with fly ash presented slightly higher values than the reference (100C) for fresh samples. Some authors observed that with the increase in the two fly ash in paste samples, the pH increases (Zhang et al., 2000). There was an increase in the pH during hydration for 28 and 90 days curing, when compared with the fresh sample.

The pH decreased when the carbonation was increased from an initial value of around 12.7 to a value in the range of 9–10 after the samples are totally carbonated (Table 6). This decrease is diagnosed to result from carbonation of the high-Ca C-S-H to a decalcified phase C-S-H and calcium carbonate (Shi et al., 2016). The pH analysis of solid samples after the carbonation test was in agreement with the phenolphthalein indicator, which shows colour changes around 9.

4. Conclusions

In this paper, the effect of the use of biomass fly ash on the hydration process and carbonation of construction materials was studied. Pastes with 50 wt% of cement replacement by coal/biomass fly ash exhibited lower amounts of chemically combined water, compared with the cement paste, from which it can be inferred that the level of cement hydration is lower. The XRD analysis corroborates this achievement and suggests that fly ash increased the kinetics of the cement hydration and that the pozzolanic reaction is still occurring.

The results show that pastes with biomass fly ash promote mixes with higher alkalinity reserves and probably the biomass fly ash increases the hydrated calcium silicates formed in their pozzolanic reaction. A decrease in the calcium hydroxide can be observed in these pastes, when compared to cement paste. However, the content of this compound is much higher than in pastes with coal fly ash, even at 90 days of age.

In terms of calcium carbonate formation, no significant differences were observed between using coal fly ash or biomass fly ash, which indicated similar resistance to carbonation. However, a higher consumption of calcium hydroxide during the carbonation mechanism of coal fly ash paste was observed. The use of biomass fly ash seems to have a similar behavior to that of the use of coal fly ash in terms of carbonation.

The results show that it is important to carry out future studies using biomass fly ash in concrete, due to the fact that its use has a significant impact on the hydration and carbonation of the pastes and their development over time.

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