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Elisabete Rodrigues Teixeira
High Volume Coal and Biomass Fly Ash
Eco-Efficient Concrete

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Universidade do Minho
Escola de Engenharia

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High Volume Coal and Biomass Fly Ash Eco-Efficient Concrete

Doctoral thesis
Civil Engineering

Work performed under the supervision of
Aires Camões
Fernando G. Branco

março de 2019

DECLARAÇÃO DE INTEGRIDADE

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High Volume Coal and Biomass Fly Ash Eco-Efficient Concrete

Abstract

The environmental impact related with the use of several materials in construction sector is in the order of the day. It is well known that the production of Portland cement, one of the materials most used in the construction sector, has a significant contribution to the environmental impacts, mainly related with carbon dioxide emission. Therefore, the study and utilization of by-products or wastes usable as cement replacement in concrete can supply more sustainable options, but maintaining or improving the quality and durability properties of plain cement concrete.

Worldwide, coal fly ash (CFA) is the most used supplementary cementitious material in concrete production, mainly because it presents several advantages such as: it is a by-product of coal combustion, is available in great quantities worldwide and is cheaper than Portland cement. Nowadays, coal fly ash is commonly used as cement replacement in concrete from 0 to 40%wt. Using high volumes of these materials has some drawbacks, one of them being the decrease of the pH of concrete thus leading to carbonation issues. In order to understand phenomena such as this, it is important to study the interaction between the mineral additions and hydration of cement and try to find new solutions for the issues related with this type of concrete.

The utilization of biomass fly ash (BFA) as partial replacement of cement in concrete production has been studied by several authors and it was verified that this alkaline material can have benefits for concrete. However, its application in high volume fly ash concrete has not been so much studied and because of its characteristics, mainly chemical characteristics, can be a solution to, for example, the carbonation issue of these concretes.

So, the main objective of this work was to assess the use of biomass fly ash as cement replacement material or at least as an alkalinity source in high volume fly ash concrete, with a focus on the effect of using biomass fly ash on the quality, durability and sustainable properties, such as: workability, mechanical resistance, resistance to carbonation, resistance to chlorides ions penetration, shrinkage, porosity, leaching of toxic compounds and environmental performance.

The results of this study showed that biomass fly ash can improve the properties of high volume fly ash concrete when it is used in small amounts, being the best results verified for 0.5%wt and 1.3%wt of BFA blended with the equivalent proportion of coal fly ash to maintain 50%wt of cement replacement. The two fly ashes seem to have a good synergy in those situations. BFA blended with CFA seems to have a positive contribution on the quality, durability and sustainability of concrete when compared with concrete containing only coal fly ash as supplementary cementitious material or when compared to a plain cement concrete. Thus, with the utilization of BFA, at an industrial level of concrete production, some issues can be minimized, such as the decrease on energy and raw materials consumption related to cement production, and also issues related with the concrete properties and a more sustainable option on the ash management can be applied, than its landfill deposition.

Keywords

Biomass Fly Ash, Coal Fly Ash, Durability, High Volume Fly Ash Concrete, Sustainability

Betão Eco-eficiente com Elevado Teor de Cinzas de Carvão e Biomassa

Resumo

O impacte ambiental relacionado com o uso de diversos materiais no sector da construção está na ordem do dia. É bem sabido, que a produção do cimento Portland, um dos materiais mais usados na construção, tem uma contribuição significativa para os impactes ambientais, essencialmente relacionados com a emissão de dióxido de carbono para a atmosfera. Assim, o estudo e a utilização de subprodutos ou resíduos, usáveis como substitutos do cimento na produção de betão, podem oferecer opções mais sustentáveis, mas mantendo ou melhorando a qualidade e a durabilidade do betão convencional.

Por todo o mundo, as cinzas volantes de carvão (CVC) são o material cimentício suplementar mais utilizado na produção de betão, principalmente por apresentarem diversas vantagens, tais como: ser um subproduto da combustão do carvão e estar disponíveis em grandes quantidades, e serem mais baratas do que o cimento *Portland*. Hoje em dia, as cinzas volantes de carvão são utilizadas em proporções de substituição do cimento de 0-40%m. A utilização de grandes volumes de cinzas tem alguns problemas e um deles é a diminuição do pH do betão que conduz a problemas de carbonatação. Para entender fenómenos como este, é importante estudar a interação entre as adições minerais e a hidratação do cimento e tentar encontrar novas soluções para os problemas relacionados com este tipo de betões.

A utilização de cinzas volantes de biomassa (CVB) como um substituo parcial do cimento na produção de betão tem sido estudada por diversos autores e foi verificado que este material alcalino pode trazer benefícios para o betão. Contudo, a sua aplicabilidade em betões com elevado teor de cinzas volantes não foi ainda muito estudada e, devido às sua características, principalmente químicas, pode ser uma solução para o problema da carbonatação destes betões.

Assim, o principal objetivo deste trabalho foi o de avaliar se é possível o uso de cinzas volantes de biomassa como substituto material do cimento ou como reservatório de alcalinidade nos betões com elevado teor de cinzas volantes, focando-se no efeito do uso das cinzas volantes de biomassa na qualidade, durabilidade e sustentabilidade, tais como: trabalhabilidade, resistências mecânicas, resistência à carbonatação e à penetração de iões cloretos, retração, porosidade, lixiviação de compostos tóxicos e o desempenho ambiental.

Os resultados, obtidos neste estudo, mostraram que as cinzas volantes de biomassa podem melhorar as propriedades dos betões com elevado volume de cinzas volantes, quando utilizadas em pequenas quantidades, sendo os melhores resultados observados para valores de 0.5%m e 1.3%m de CVB misturada com a proporção equivalente de cinzas volantes de carvão, que correspondem a uma substituição de cimento de 50%m. As duas cinzas parecem apresentar uma boa sinergia nestas situações. A mistura das duas cinzas aparenta apresentar uma contribuição positiva na qualidade, durabilidade e sustentabilidade dos betões, quando comparada com betões só com CVC como material cimentício suplementar ou quando comparada com o betão de cimento, sem incorporação de adições minerais. Assim, a utilização das CVB num nível industrial de produção de betão pode resolver alguns problemas, nomeadamente conduzindo à diminuição de energia e matérias-primas consumidas na produção do cimento e, também problemas relacionados com as propriedades do betão, apresentando-se como uma opção mais sustentável para a gestão das cinzas do que a sua deposição em aterro.

Palavras-chave

Betão com Elevado Volume de Cinzas Volantes, Cinza Volante de Biomassa, Cinza Volante de Carvão, Durabilidade, Sustentabilidade

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List of Symbols

List of Latin Upper Case Letters:

Ac - Cross-sectional Area of Sample where the Force is Applied [mm^2] (Eq.17);

ADP_FF - Abiotic depletion Potential of Fossil Resources [MJ eq];

Ai - Water Absorption [%] (Eq. 18)

AP - Acidification Potential [kg SO_2 eq];

C - Coefficient of Water Absorption [kg/(m^2.min$^{0.5}$)] (Eq.16) and calcite in Figure 3.7;

C_o - Chloride Concentration in the Catholyte Solution $C_0 \approx 2N$ (Eq.21);

CH_F – Content of Free Calcium Hydroxide [%] (Eq. 10;

D - Non-steady-state Migration Coefficient [m^2/s] (Eq.19) and x10^{-12}[m^2/s] (Eq.22);

DTA - Differential Thermogravimetric Analysis [µV] (Figure 3.9);

EP - Eutrophication Potential [kg PO_4 eq];

F - Maximum Load Applied to the Specimen [N] (Eq.15) and Maximum Applied Load [N] (Eq.17) and Faraday Constant F=9.648×10^{4}J/(V.mol) (Eq.19 and Eq.21);

Fc - Correction Factor of HCl for a Concentration of 0.1M (Eq.5);

GWP100 - Global Warming [kg CO_2 eq];

H- Hematite (Figure 3.7)

$H_2O_{Q,comb}$ - Chemically Combined Water [%] (Eq.10);

$I_{Ca(OH)_2}$ - Pozzolanic Activity Index [mg of $Ca(OH)_2$ per g of material] (Eq.5);

I_{Filter} - Filter Impurities [%] (Eq.4);

Kc - Carbonation Coefficient [mm/day$^{0.5}$];

K_t - Intrinsic Air Permeability [m^2];

L - Thickness of the Sample [m] (Eq.20) and [mm] (Eq.22) and Lime in (Figure 3.7);

M – Mullite (Figure 3.7)

M0 - Mass of the Specimen after Soaking for 10 min [g] (Eq.16);

M1 - Mass of sample before acid attack [mg] (Eq.3) and Mass of the Saturated Aggregate with Dry Surface [g] (Eq.8 and 9) and Mass of the Specimen After Soaking [g] (Eq.16);

M2 - Mass of filter plus sample after filtration [mg] (Eq.4) and Pyknometer Mass with the Saturated Aggregate Sample [g] (Eq.6-8);

M3 - Mass remaining after calcination [mg] (Eq.3 and Eq.4) and Pyknometer Mass only Full with Water [g] (Eq.6-8)

M4 - Mass of Aggregate Sample Dried in Woven [g] (Eq.6, 7 and 9);

$ML_{Ca(OH)_2}$ - Mass Loss observed in the TG curve for $Ca(OH)_2$ [%] (Eq.10);

$ML_{CaCO)_3}$ - Molecular Weight of $CaCO_3$ [g/mol] (Eq.12);

MM_{CaO} - Molecular Weight of CaO[g/mol] (Eq.12);

MM_{CO_2} - Molecular Weight of CO_2 [g/mol] (Eq.12);

$MM_{Ca(OH)_2}$ - Molecular Weight of $Ca(OH)_2$ [g/mol] (Eq.10);

MM_{H_2O} - Molecular Weight of H_2O [g/mol] (Eq.10);

ND_A - Overall Environmental Performance [-] (Eq.26);

ODP - Ozone Layer Depletion [kg CFC-11 eq];

P – Portlandite (Figure 3.7)

POCP - Formation Potential of Tropospheric Ozone [kg C_2H_4 eq];

$\bar{P}_i$ - Normalized Value of i^{th} Sustainability Parameter (Eq. 25 and Eq.26);

P_i - Value of i^{th} Sustainability Parameter [units dependent on the i^{th} value] (Eq.25);

P_{*i} - Worst Value of i^{th} Sustainability Parameter [units dependent on the i^{th} value] (Eq.25;

P_i^* - Best Value of i^{th} Sustainability Parameter [units dependent on the i^{th} value] (Eq.25);

Q- Quartz (Figure 3.7)

R - Gas Constant R=8,314J/(K.mol) (Eq.19 and 21);

RH - Relative Humidity [%];

T - Average Value of the Initial and Final Temperature in the Anolyte Solution [K] (Eq.19 and Eq.21) and [ºC] (Eq.22);

TG - Thermogravimetric [weight loss %] (Figure 3.9);

U - Absolute Value of the Applied Voltage [V] (Eq.20 and Eq.22);

V_2 - Volume of 0.1M HCl Consumed in the Sample Test [ml] (Eq.5);

V_3 - Volume of 0.1M HCl Consumed in the Blank Test [ml] (Eq.5);

V_{CO_2} - Carbonation Rate Constant [mm.min$^{0.5}$] (Eq.24);

V_F - Vitreous Phase Amount [%] (Eq. 3);

Vs - Volume of Specimen of Hardened Mortar [m^3] (Eq.14);

Vv - Volume of Measuring Vessel [m^3] (Eq.13) and Air Volume of Fresh Mixes [%] (Figure 4.19);

WA_{24} - Water Absorption for 24h of immersion [%] (Eq.9);

W_n - Combined Water Content [%] (Eq.23);

W_∞ - Whole Combined Water Content after Full Hydration [%] (Eq.23);

Xc - Depth Penetration of Carbonation [mm] (Eq.24) and Figure 4.6

List of Latin Lower Case Letters:

b - Binder and Width of Specimen [mm] in (Eq.15);

c_d - Chloride Concentration at which the Colour Changes $c_d \approx 0.07N$ (Eq.21);

d - Depth of the Specimen [mm] (Eq.15);

erf^{-1} - Inverse of Error Function [-] (Eq. 21);

f - Flexural Strength [MPa] (Eq.15);

fc - Compressive Strength [MPa] (Eq.17);

i^{th} - Indicator of Sustainability (Eq.26);

l - Distance between the Axes of the Support Rollers [mm] (Eq.15);

m_1 - Mass of the Empty Vessel [kg] (Eq.13) and Mass of Water Saturated Specimen [g] (Eq.18);

m_2 - Mass of Pozzolanic Material [g] (Eq.5) and Mass of the Vessel Filled with Sample [kg] (Eq.13) and Mass of Saturated Specimen Immersed in Water [g] (Eq.18);

m_3 - Mass of Specimen [g] (Eq.1);

$m_{s,I}$ - Apparent Mass of Saturated Specimen of Hardened Mortar Immersed in Water [kg] (Eq.14);

$m_{s,sat}$ - Mass of Saturated Specimen of Hardened Mortar [kg] (Eq.14);

t - Test Duration [s] (Eq.19) and [h] (Eq.22) and time [days] (Eq.24);

w – Water Content;

w_i - Contribution of the i^{th} indicator for the overall environmental performance (Eq.26);

wt – Weight;

z - Absolute Value of Ion Valence for Chloride z=1 (Eq.19 and Eq.21).

List of Greek Lower Case Letters:

α – Hydration Degree [-] (Eq.23);

ρ – Density [kg/m3] (Figure 4.18);

ρ_a - Volumic Mass of the Waterproof Material [Mg/m^3] (Eq.6);

ρ_m - Bulk Density of Fresh Mortar [kg/m^3] (Eq.13);

ρ_{rd} - Volumic Mass of the Dry Particles in Woven [Mg/m^3] (Eq.7);

ρ_{ssd} - Volumic Mass of the Saturated Particles with Dry Surface [Mg/m^3] (Eq.8);

ρ_w - Volumic Mass of the Water at the Registered Temperature in the Determination of M2 [Mg/m^3] (Eq.6-8) and Density of Water [kg/m^3] (Eq.14);

x_d – Average value of the Penetration Depths [m] (Eq.19) and [mm] (Eq.22).

List of Chemical Symbols and Chemical Compounds

$3Al_2O_32SiO_2$ – Mullite (M);
AFm - Alumina, Ferric oxide, Monosulphate;
Ag – Silver;
Al – Aluminium;
Al_2O_3 - Aluminium Oxide;
$Al_2O_3SiO_2$ - Aluminium Silicate;
As – Arsenic;
Ba – Barium;
Br - Bromine
C_2S - Dicalcium Silicate; Belite;
C_3A - Tricalcium Aluminate; Aluminate;
C_3S - Tricalcium Silicate; Alite;
C_4AF - Tricalcium Aluminoferrite; Ferrite;
CS – Calcium Silicate
C-S-H - Calcium Silicate Hydrate;
Ca – Calcium;
Ca^{2+} - Calcium ion
$Ca_2Fe_2O_5$ - Dicalcium Diiron Pentaoxide;
$CaAl_2SiO_7$ – Gehlenite;
$Ca_3(Si_8O_8(OH)_2)$ – Calcium Silicate Hydroxide
$CaCO_3$ - Calcium Carbonate or Calcite (C);
$CaMg(CO_3)_2$ - Calcium Magnesium Carbonate;
$CaMgSi_2O_6$ – Diopside;
CaO - Calcium Oxide or Lime (L);
$Ca(OH)_2$ - Calcium Hydroxide or Portlandite (P);
$CaSO_4$ - Calcium Sulphate;
$CaSO_4.2H_2O$ - Dehydrate Calcium Sulphate;
CS – Calcium Silicate
Cd – Cadmium
CH - Calcium Hydroxide;
Cl – Chloride;
Cl^- - Chloride ion;
Co – Cobalt;
CO_2 - Carbon Dioxide;
CO_3^{2-} - Carbonate Ion;
Cr – Chromium;
Cs – Caesium;
Cu – Copper;
Fe_2O_3 - Iron (III) Oxide or Hematite (H);
Ga – Gallium;
Ge – Germanium;
HCl - Hydrochloric Acid;
HCO_3^- - Hydrogen Carbonate;
H_2CO_3 - Carbonic Acid;
H_2O – Water Molecule;
H_3O^+ - Hydronium ion;
HF - Hydrofluoric Acid;
$HnSiO_4^{(4-n)}$ – coordinated precursors originated by conversion of silicate anions
K – Potassium;
K_2O - Potassium Oxide;
K_2SO_4 - Potassium Sulphate;
$KAlSi_3O_8$ – Orthoclase;
KCl - Potassium Chloride;
La – Lanthanum;
MgO - Magnesium Oxide;
Mn – Manganese;
Mn_2O_3 - Manganese (III) Oxide;
MnO - Manganese Oxide;
Mo – Molybdenum;
Na – Sodium;
$NaAlSi_3O_8$ – Albite;
$NaAl_3O_8$ - Aluminium Sodium Oxide;
Na_2O - Sodium Oxide;
Nb – Niobium;
Ni – Nickel;
O - Oxygen
O^{2-} - Oxygen ion;
OH^- - Hydroxide
PAH - Polycyclic Aromatic Hydrocarbon;
Pb – Lead;
P_2O_5 - Phosphorous Oxide;
P_3O_5 - Triphosphorus Pentoxide;
Rb – Rubidium;
Sb – Antimony;
Sc – Scandium;
Se – Selenium;
Si – Silicon;
SiO_2 - Silicon Dioxide or Quartz (Q);
SiO_4^{4-} - Orthosilicate;
Sn – Tin;
SO_3 - Sulphur Trioxide;
Sr – Strontium;
TiO_2 - Titanium Oxide;
V – Vanadium;
Y – Yttrium;

Zn – Zinc;

Zr – Zirconium.

List of Acronyms

AAR - Alkali Aggregate Reaction;
ASR - Alkali-Silica Reaction;
BBA - Biomass Bottom Ash;
BFA - Biomass Fly Ash;
BFB - Bubbling Fluidized Bed;
BRWA - Bagasse, rice husk and chip wood;
BSE - Backscattered electron;
C – Cement;
CCPs – Coal Combustion Products
CEM I 42.5R - Portland Cement Type I with a Class of 42.R;
CFA or FA - Coal Fly Ash;
CFB - Circulated Fluidized Bed;
DTA - Differential Thermal Analysis;
EDS - Energy Dispersive Spectroscopy;
EPD - Environmental Product Declaration;
FTIR - Fourier Transform Infrared Spectroscopy;
HF – Hydrofluoric Acid
HL - Hydrated Lime;
HVFA - High Volume Fly Ash;
HVFAC - High Volume Fly Ash Concrete;
LCA - Life Cycle Assessment;
LCI - Life Cycle Inventory;
LCIA - Life Cycle Impact Assessment;
LNEC - National Laboratory of Civil Engineering;
LOI - Loss-on-ignition;
MARS_SC - Methodology for the Relative Sustainability Assessment of Building Technologies;
MIP - Mercury Intrusion Porosimetry;
PC - Portland Cement;
REF – Reference;
S – Sand;
SAB - Science Advisory Board;
SCM - Supplementary Cementitious Material;
SEM - Scanning Electron Microscopic;
SP – Superplasticizer;
SW – Sawdust;
TG - Thermogravimetric
TGA - Thermogravimetric Analysis;
XRD - X-ray Diffraction;
W – Water;
WBFA - Wood Biomass Fly Ash;
WSW - Wastepaper De-inking Sludge and Wood;

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Chapter 1

Introduction

1.1 General Remarks

Concrete is one of the most used materials in the construction sector worldwide as it is locally available, it is a cheap material, it has good mechanical and durability properties and has relatively good resistance to fire [1,2]. Concrete has a wide range of applications and different types of this material are used in the construction sector. However, concrete also has a significant impact on the environment since it incorporates a high content of natural resources and energy flows to produce it, and some of these raw materials may can have a significant impact on the environment [1,3–5].

Portland cement is an essential compound for concrete [6,7]. In traditional cement production, some raw materials, namely limestone and clay, need to be mined, blended, grounded and heated at high temperatures. These processes are energy and resource intensive [1,3–5] and result in high CO_2 emissions as a result of the decomposition of calcium carbonate into calcium oxide during the clinker sintering process [8] and by the combustion of fossil fuels during the heating process [6]. In 2010, the estimation of global average gross CO_2 per ton of cement was around 900 kg, accounting for 5-8% of total human atmospheric CO_2 emission [6,9]. However, not only is CO_2 emitted in cement production, but also sulphur dioxide, nitrous oxides and methane. Furthermore, it is well known that these gases contribute to the greenhouse effect and acid rain and have a major impact on global warming [8]. In recent years, several solutions have been used to reduce the carbon footprint of the cement and concrete industry: improving energy efficiency in cement production; replacing fossil fuels with renewable energy sources; replacing Portland cement with alternative cementitious materials, such as coal fly ash (CFA), blast furnace slag and silica fume [6,10,11]. These alternative materials have similar properties to Portland cement and partial replacement of cement by them has been shown to be a promising solution to minimize the sustainable issues of cement and concrete [7]. These materials offer a potential reduction in global carbon dioxide emissions [12], reducing the cost of concrete production, enhancing the workability of fresh concrete, in some cases improving the durability of concrete and the resistance to thermal cracking, alkali-aggregate expansion, sulphate attack and penetration of chloride ions [2].

Coal fly ash (CFA) is the most used artificial supplementary cementitious material in concrete production all over the world [2,13]. CFA has been widely used because it is a by-product of coal combustion for energy production in electrical power plants, and is therefore cheaper than Portland cement [1]. Nowadays, CFA is commonly used as cement replacement in concrete from 0 to 40%wt. However, it is known that concrete with 50%wt or more cement replacement by fly ash may have some benefits in technical and environmental terms [1,12,14]. Malhotra and Metha [15] defined concrete with 50% or more of CFA by mass of total cementitious materials as High Volume Fly Ash Concrete (HVFAC). This type of concrete has high workability, ultimate strength and durability [9,15]. However, the increase of the cement replacement by CFA at such a high content leads to retardation in the early gain of mechanical strength, due to slow pozzolanic reaction. Furthermore, its carbonation resistance is lower than that of plain cement concrete [8,13,16]. Cement replacement by CFA at a high content leads to a higher consumption of the alkaline compounds, mainly calcium hydroxide, decreasing the value of the pH of the porous system, and consequently results in the decrease of the carbonation resistance [13,17–19]. Carbonation is one of the most important sources of reinforcement corrosion that affects the durability of concrete structures [13,17–19] and therefore its minimization or mitigation is very important for the concrete industry. Some studies [20,21] showed that adding other materials to HVFAC, such as hydraulic lime, could slow the carbonation process. Some studies showed that the introduction of lime, in these concretes, leads to an increase in the calcium concentration and a decrease in the concrete porosity that results in a significant reduction in carbonation [20]. However, lime is a chemical product also resulting from raw materials and needs energy consumption for its production. Therefore, using more sustainable materials for the mitigation of HVFAC issues is needed.

1.2 Motivation

Nowadays, some countries such as Portugal show a marked interested in increasing the energy production using renewable sources, such as biomass, instead of using non-renewable sources, for instance coal. Combustion is the mostly used operation to produce energy via biomass [22]. The increase in biomass consumption creates an increase in the ash volume, a by-product of the combustion activities. In Portugal, fly ashes from biomass combustion are classified as solid waste and usually are managed by disposal in landfill. However, this disposal has economic, environmental and sustainable issues [23,24].

Biomass fly ash (BFA) has similar characteristics to CFA, however with higher pH [23,25,26]. The replacement of cement by biomass fly ash is progressively being investigated and several studies have been carried out using BFA as a supplementary cementitious material [27–30] and its incorporation on concrete alone or blended with CFA showed good results in terms of quality and durability [22,30,31]. Thus, it may be a solution for the decrease of alkaline compounds in concrete due to high additions content, mainly by the fact that these ashes can be used to provide higher calcium content to the concrete mix. In other words, it can have a similar effect to that of hydraulic lime. Besides reducing greenhouse gas emissions due to lower energy and raw material consumption, the use of BFA in concrete could result in the beneficial effects of avoiding landfilling of the BFA [6]. However, some technical issues, commercial barriers and concerns about the availability and quantity of BFA are still an issue when those ashes are used at an industrial level [22]. Contrary to CFA, BFA still needs more in-depth research concerning about its use, mainly in HVFAC, and its commercial utilization is not yet widely reported [27].

Thus, the main motivation for this work was to evaluate the use of BFA as a cement replacement material on HVFAC alone or blended with CFA. The use of BFA as a reservoir of alkalinity (in small amounts) was also studied to assess the possibility of minimizing the issues related with this type of concrete since a more alkaline material is used in cement replacement.

The motivation of this work focuses on intending to improve the quality and sustainable performance of HVFAC and reducing the utilization of raw materials and energy consumption, making a material economically competitive and more sustainable by replacing cement with a waste material, biomass fly ash.

1.3 Objectives

In this context, an experimental program was developed that sought to contribute to the knowledge of the potential of high volume fly ash concrete with BFA incorporation, adopting technologies commonly used in conventional concretes and current materials but with cement replacement by BFA alone or blended with CFA.

The aim of this work was to evaluate the overall performance of the material and to study the most relevant characteristics that must be ensured: workability, mechanical behaviour, durability and sustainability. In order to meet these objectives an experimental program was designed to:

- Formulate more sustainable HVFAC incorporating different amounts of binder and cement replacement with biomass fly ash/coal fly ash or/and hydrated lime and using aggregates currently available on the national market;
- Evaluate the workability of these formulations;
- Characterize the mechanical performance of HVFAC with BFA;
- Assess the durability and sustainability of HVFAC with BFA.

The experimental program proposed in the literature focuses on: i) the characterisation of all materials (cement, ashes, aggregates, superplasticizer and hydrated lime) selected for this study; ii) a series of tests, which were run using pastes and mortars that led to the individual study of concrete components; and iii) after studying the individual components, some concrete formulations were analysed. This study was performed in a way to focus on the workability, mechanical strength, carbonation resistance and chloride ion penetration resistance of concrete with BFA incorporation, as well as to study the environmental performance of the produced materials.

1.4 Description of Thesis Content

In addition to this chapter, this thesis comprises seven more chapters that are organized as explained below.

Chapter 2 (*Literature Review*) is divided into two main points: Firstly, the most relevant aspects related to the high volume fly ash concrete components and their influence on the final product, both in terms of fresh and hardened properties are studied. The main problems related to HVFAC, such as the early age strength, carbonation performance and curing effect are also discussed. The second most important topic of this chapter is the literature review concerning the biomass fly ash characteristics and its use in concrete, focusing on its effect on the fresh and hardened properties of HVFAC and in its use to minimise the issues related with the HVFAC.

The literature review chapter defines the methodology and the materials that were used during the PhD study, which is presented in Chapter 3 (*Materials and Methods*). In this chapter the characterization of all materials used during the experimental campaign is presented. Furthermore, the pastes, mortars and concrete formulations studied are described and the methodologies used for achieving the goals of this study are presented.

The results obtained during the study of the effect of BFA on the hydration and carbonation pastes and on the fresh and hardened properties of mortars are presented in Chapter 4 (*Pastes and Mortars: Results and Discussion*). In this chapter a comparison between the use of BFA or/and CFA on paste hydration and carbonation with a plain cement paste is presented. This analysis was carried out using thermogravimetric and mineralogical analysis. This study aims at understand what happens in the main important component of concrete, binder, not taking into account the effect of aggregates, and this is the reason of studying pastes.

The study of the effect of using BFA alone or blended with CFA in mortars, is also presented in this chapter, as it was important to find some HVFAC with BFA incorporation that provide a similar behaviour to that of plain cement concrete, but minimising the issues related with that type of concrete and with higher durability and a better environmental performance. It was necessary to study a large group of formulations with different percentages of cement replacement by BFA, alone or mixed with CFA, and to carry out a large test group to understand its effect on the fresh and hardened properties of the HVFAC. Since it was such a large study, it was decided to use mortars, instead of concrete, because of the raw materials and time consumption that concrete preparation would require.

This chapter shows the results obtained for the fresh and hardened properties of mortars with BFA, but also focuses on sustainability parameters (such as leaching). As BFA are more alkaline than CFA, an experimental study was carried out concerning the utilization of BFA in mortars to evaluate its effect on the carbonation of mortars, using small amounts of biomass fly ash. A comparison with the use of hydrated lime for the same purpose was also carried out and the results obtained are described in this chapter.

The experimental evaluation of the basic assumptions of this work, related to the production of a high volume fly ash synergic pozzolan eco-efficient concrete using the selected formulations (obtained in Chapter 4) is described in Chapter 5 (*Concrete: Results and Discussion*). This experimental campaign was programmed in order to verify the influence of selected BFA content on different concrete aspects and with the objective of characterizing concrete produced in relation to the fundamental properties (workability, mechanical resistance, porosity, carbonation and chloride ion penetration resistance). The results assess the feasibility, advantages and disadvantages related to their practical application, mainly in terms of quality, durability and sustainability.

The most important aspects related to the sustainable behaviour of concrete with different percentages of BFA incorporation are presented in Chapter 6 (*Environmental Life-cycle Analysis of Biomass/Coal Fly Ash Concrete*). In this chapter, a life-cycle analysis of 1 m^3 of concrete made with 0.5, 1.3, 5, 20, 40, 50 and 60%wt of cement replacement by BFA was carried out to analyse the environmental performance of each concrete. Furthermore, in this chapter the comparison between the environmental behaviour of those concretes with a plain cement concrete was made.

Chapter 7 (*Conclusions and Further Developments*) draws the main conclusions and contributions of the work carried out, as well as some suggestions for future developments in the field of the subject: pozzolan eco-efficient concrete with the incorporation of biomass fly ash residues.

Chapter 8 presents the references used to support all decisions and the methodology used in this study.

Chapter 2

Literature Review

2.1 Introduction

Concrete is one of the most used materials in the world [32]. Initially, cement concrete consisted only of three components: cement, aggregate and water. However later, to improve its properties (in the fresh or hardened state) small quantities of chemical products were added to the mix. After that, other inorganic materials were introduced into the mix due to economic reasons, since they were cheaper than Portland cement. Some of them are available as natural deposits requiring little or no processing, mainly because they were a by-product or waste from other industries [33,34]. The success of concrete is mainly due to it being available locally. Its components are inexpensive, it can be easily prepared and it is a durable material [35].

Using large amounts of concrete results in the production of large amounts of Portland cement, which is the main binder of concrete [35]. Portland cement production results in significant emissions of CO_2 to the atmosphere. Some authors reported that every ton of Portland cement produced around 900 kg of CO_2 sent to the atmosphere, causing greenhouse effects [32,35–37]. Moreover, clinker production is the most energy intensive phase in cement production. Nowadays, environmental issues play an important role in the sustainable development of all industries, including the concrete industry [32]. These issues affect the economy and sustainability of these industries, and thus need to be mitigated.

Some other supplementary cementitious materials in concrete play an important role in terms of cost reduction, technical benefits and ecological concerns [33,38]. Pozzolanas are natural or artificial materials containing silica in a reactive form, meaning pozzolanas are siliceous or siliceous and aluminous materials that in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds that have cementitious properties [33]. Examples of pozzolanic materials are blast furnace slag, fly ash resulting from coal combustion and silica fume, and their functionality was demonstrated by several studies in terms of technical, environmental and economic benefits [39–43].

Annually, approximately one billion tons of coal fly ash (CFA) are produced worldwide in coal-fired power plants [8]. Hence, CFA is the most used artificial pozzolana in concrete production and is being used worldwide [2,13]. CFA has a lower hydration heat, it is a by-product of coal combustion and thus cheaper than cement [1]. CFA is commonly used as a cement replacement (from 0 to 40%wt) in concrete. However nowadays, it is known that concrete with 50% or more cement replacement by fly ash can have benefits in technical and environmental terms [1,12,14]. Malhotra and Metha [15] defined concrete with at least 50% of CFA by mass of total cementitious materials as High Volume Fly Ash Concrete (HVFAC). HVFAC shows high workability, ultimate strength and durability [9,15].

However, the increase in cement replacement by CFA in such a large content leads to some problems related to early strength and carbonation resistance [13,16]. High Volume Fly Ash (HVFA) has a slow pozzolanic reaction, and therefore the early strength of concrete is lower than that of plain cement concrete [8]. Moreover, it leads to a higher consumption of the alkaline compounds, mainly calcium hydroxide. This is due to the pozzolanic reaction, which leads to the pH reduction of the porous system, and consequently results in the decrease of the carbonation resistance [13,17–19]. Carbonation is one of the most important sources of steel reinforcement corrosion [13,17–19] and therefore its minimization or mitigation is very important for the concrete industry.

Nowadays, some countries, for instance Portugal are more interested in increasing the energy production using renewable sources, such as biomass, instead of using non-renewable sources such as coal. Combustion is the mostly used operation to produce energy using biomass [22]. The increase in biomass consumption creates an increase in the ash content, as a by-product of the combustion activities. In Portugal, fly ashes from biomass combustion is classified as solid waste and is usually are managed by disposal in landfill. However, this disposal has economic, environmental and sustainable issues [23,24].

Biomass fly ash (BFA) has similar characteristics to CFA, but it is more alkaline [23,25,26]. Several studies were made by using BFA as a supplementary cementitious material [27–30] and its incorporation in concrete alone or blended with CFA showed good results in terms of quality and durability [22,30,31]. Contrary to CFA, BFA still needs more significant research in terms of its use and commercial utilization is not yet widely reported [27].

Thus, in this section some important characteristics about HVFAC will be present, focusing on the main issues related with this type of concrete (early age strength, carbonation behaviour and curing). After that, a detailed revision of the utilization of BFA on HVFAC will be presented, with the main goal of understanding the consequences of its use on the quality and durability of concrete.

2.2 High Volume Fly Ash Concrete

Nowadays, the addition of HVFA in concrete has been used mainly by the fact that it presents some advantages such as: fly ash is an efficient resource, the resulting concretes are durable, the effective cost of concrete production is low and it is a sustainable option when compared to using Portland cement [14]. Those types of concrete are sustainable and have high performance [30]. A concrete is considered an HVFA if it contains a fly ash content of 50%wt or more by mass of the total cementitious materials [14,15,44].

The production of cement represents a high consumption of energy and raw materials, but also a large content of carbon dioxide is emitted to the atmosphere [1,3–5,8]. On the other hand, large amounts of CFA are available around the world at a low cost, and the use of HVFA as cement replacement in concrete production can be one of the solutions for cement demands. HVFA concrete mixes are defined by the following properties: i) minimum of 50% of CFA by mass of the binder, ii) low water content, iii) usually the cement content is no more than 200 kg/m^3, iv) mixes with a specified compressive strength of 30 MPa or higher for 28 days curing, slump value higher than 150 mm, water/binder ratio about 0.30, and the use of superplasticizers is mandatory and v) concrete with compressive strength less than 30 MPa (after 28 days of curing) and slump value higher than 150 mm, a water/binder ratio of 0.40 made with no addition of superplasticizers [15].

The use of HVFA in concrete has several benefits such as the improvement of fresh properties and durability of concrete [15,45–48]. Durability is improved by the fact that HVFA leads to a reduction in the calcium hydroxide (that is the most soluble compound from the hydrated products) and allows some changes in the pore structure [14,49].

HVFAC is more resistant to cracks than conventional plain cement concrete and this is due to a decrease in shrinkage [14]. The shrinkage decrease is a result of the reduction of the mixing water, of the water to cementitious materials ratio and of the total volume of cement paste that is needed for the HVFA [14,50]. Mehta [15] verified that the incorporation of fly ash as cement replacement reduces the water requirement up to 20%. Besides that, the decrease of the heat of hydration in early ages also reduced the potential for thermal shrinkage and cracking [14,44]. Furthermore, other important parameters of the durability of concrete are permeability and the rate of water absorption by capillarity. Some studies showed that HVFAC has lower water permeability than plain cement concrete [14].

Therefore, the chemical composition of this fly ash and its high content in fine particles can perform four simultaneous functions: i) decrease the pore size; ii) decrease the free calcium content; iii) decrease the permeability to water and the ionic mobility; and iv) decrease the hydration heat in the cement replacement. The utilization of a high content of fly ash in concrete can also minimise the expansive alkali-silica reaction and the acid attack resistance [15,51,52].

2.2.1 Portland Cement

Portland cement is produced by a mix of calcium carbonate, aluminium silicates, clays and other substances rich in silica, alumina or iron. The substances used in the production process are reduced to a fine powder and homogenized. After that, the substances are subjected to a temperature of approximately 1400 to 1650 ºC, inside a rotary oven. During this heating process, the raw materials react with each other [23, 51]. The liquid phase obtained in this process (approximately 20% of raw materials) helps promote of these reactions and originates new compounds. During refrigeration, they agglomerate into pieces with different sizes, forming clinker. Therefore, clinker is an artificial rock produced by a thermochemical treatment of the mixed and milled raw materials [53]. During the milling of clinker or after, gypsum is added to the clinker to delay the setting. A typically composition of Portland cement is presented in Table 2.1 [33,54,55]. It can be seen that CaO and SiO_2 contents are much higher than other oxide contents. CaO content is almost three times the SiO_2 content, and the two oxides represent more than 85 % of the chemical composition of the Portland cement [56,57]. These oxides are followed by Al_2O_3 and Fe_2O_3 which are normally lower than 8%. The four oxides represent what are normally called the cement main oxides [57]. The other oxides are usually smaller in cement. However, these minor oxides can have an important role in certain properties of fresh and hardened concrete [57,58].

Table 2.1 - Typical Portland cement composition [33,54,55]

Component	%
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
SO_3	2.0-3.5
Fe_2O_3	0.5-6
MgO	0.5-4
Alkalis	0.3-1.2

Portland cement is a complex multiphase material comprising mostly of tricalcium and dicalcium silicates and other mineral phases in much smaller fractions [35,57,59–62]. It is essentially a mix of tricalcium and dicalcium silicate, tricalcium aluminate, tetracalcium ferroaluminate and calcium sulphates (Figure 2.1) [57]. The chemical analysis shows that in Portland cement these compounds are in the impure form, thus tricalcium silicates are usually referred to as alite and dicalcium silicate is called belite [21,59,63–72].

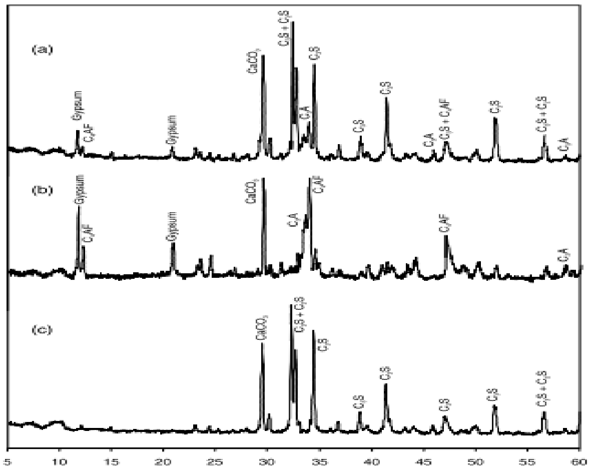


Figure 2.1 – X-ray diffractogram of a Portland cement [57]

Hydration of Portland cement is a complex process. The constituents do not appear isolated in one particle of cement, but associated in small particles with sizes in the range of microns.

Hydration only occurs in components that are in the exterior of particles. These reactions need time to occur, and in some cases a total reaction is not reached [73].

Hydration is a reaction between the several cement constituents and water. This reaction promotes chemical and physical-mechanical changes in the system that lead to the hardening of cement [33,55,74–78]. Thus, the water/cement ratio influences: i) the rheology of the suspensions produced by adding water to the cement; ii) the progress of cement hydration; and iii) the final properties of the hardened material [70,79]. The most common water/cement ratio used varies between 0.3 and 0.6. Ratios in this range allow the production of suspensions with an adequate consistence. Those suspensions are designated fresh cement pastes. With the progress of hydration, the paste loses plasticity when compared with the fresh paste, and turns into a solid material with some mechanical strength, which increases over time (hardening) [55].

The hydration process and its kinetics are influenced by several parameters: i) composition of phases and presence of strange particles in the crystalline net of each phase; ii) size particle cement distribution and superficial area of particles; iii) water/cement ratio; iv) curing temperature; v) presence of low quantities of chemical admixes; and vi) presence of significant quantities of inert material [49, 50].

In cement, the usual impure form of C_3S is alite. Its composition and reactivity vary among the different cement types [21,33,55,59,63–72]. The reaction of C_3S with water at environment temperature originates calcium silicate hydrate. When the CaO/SiO_2 ratio is lower than 3, this phase is designated C-S-H and its current formula is $\mathrm{xCaO.SiO_2.yH_2O}$. The hydration reaction of C_3S occurs according to Equation 1 [55]:

$$\mathrm{3CaO.SiO_2 + (3 + y - x)H_2O \rightarrow xCaO.SiO_2.yH_2O + (3 - x)Ca(OH)_2} \qquad (1)$$

The C_3S hydration process is staged and the first step is the pre-induction. This step occurs immediately after the contact of cement with water. The reaction begins with the output of Ca^{2+}, O^{2-} and SiO_4^{4-} of C_3S crystals, to the liquid phase where they stay as Ca^{2+}, OH^- and $HnSiO_4^{(4-n)}$, respectively. Therefore, the first calcium silicate hydrates are formed. Some theories state that they are deposited in the surface of the grains of C_3S. In this low process (about few minutes) the release of heat and the increase of the mix pH values near 12 occur. Thus, the C_3S hydrolysis decreases significantly and the induction period starts. The induction leads to a significant decrease in the hydration reaction velocity. After the induction process, the C_3S hydration reaction velocity increases and reaches the acceleration stage. In this stage, the reaction velocity reaches its maximum values and occurs mostly between 5 and 10 hours after the first contact of cement with water. After the accelerating phase, the reaction velocity starts to slowly decrease. Nevertheless, after some months of curing some activity may still be detected, and this stage is called slowdown [55,58,80,81].

In terms of dicalcium silicate (C_2S), the most important form present in cement is belite that is an impure form. The reaction of C_2S is similar to that of C_3S, but its velocity is slower with a long induction period, followed by a slow increase in the reaction velocity and a slow decrease [55].

The amount of tricalcium aluminate (C_3A) in the majority of cements is small. However, its structural relationship and behaviour with other phases in cement, is very important [33,82]. The reaction of pure C_3A with water in Portland cement is violent and leads to immediate stiffening of the paste. To minimize this problem, gypsum (dehydrate calcium sulphate - $CaSO_4.2H_2O$) is added to the clinker [33,55,82]. The presence of C_3A has some advantages. Despite this component not having a significant contribution to the mechanical strength of cement except at the early ages, it influences the sulphate attack resistance. Hardened cement can be attacked by sulphates and this causes the expansion due to the formation of calcium sulfoaluminate leading to a disruption of the hardened paste [33,55]. On the other hand, C_3A acts as a flux and this reduces the burning temperature of clinker and makes the combination of lime and silica easier. For these reasons, the presence of C_3A is useful during the production of cement [33].

In Portland cement, some minor components, such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O, are present in a low quantity and hence they are referred to as minor constituents. However, two of them are very important: the oxides of sodium and potassium, which are originated in the clays used as raw materials in the clinker production. These oxides, known as alkalis, react with some aggregates and can cause the disintegration of concrete and affect the strength of cement [33,55,59,83,84].

2.2.2 Aggregates

In HVFAC, at least ¾ of the volume is occupied by aggregates. The type of aggregates used is similar to that used in the conventional concrete [85]. Thus, their quality is very important since they will influence several concrete characteristics. In fact, the aggregates' mechanical strength is usually higher than that of cement, and aggregates will influence the stability and durability of concrete, as well as the shrinkage and final mechanical strength [33,54].

Aggregates are classified according to their particle size distribution. Aggregates with a size higher than 5 mm are designated “coarse aggregates” and may be divided into cobble (sedimentary nature), rolled (pebble or jackstone) or gravel (when artificially crushed). Aggregates with a size less than 5 mm are designated “sand”, which can be divided into rolled (natural sand with sedimentary nature) or crushed (artificially obtained) [33,78]. The quality of sand is affected by its particle size, mainly due to the shape of the particles and to the presence of impurities (clays) [33,54].

2.2.3 Mixing Water

The mixing water makes the connection between the cement and the aggregate particles, and is required for the hydration reactions. The mixing water is divided into three components: the hydration water needed for the chemical reaction of the cement particles, the wetting aggregates water, which allows the connection between the particles presented in the system and the water required to ensure the desired workability [54,61,78,86].

The quality of mixing water is important for the final properties of the products, because some impurities or minimal variations in the water content have implications on fresh mixes [54,87] and may affect the strength of the concrete [33]. Therefore, potable water that does not have a smell, taste or colour can be used. However, it is necessary to take into account other characteristics, such as the chloride content and pH [33,54].

2.2.4 Admixtures

Admixtures are chemical substances used in percentages of less than 5% of the cement mass and their use is related to the fact that these substances have considerable physical and economic benefits regarding concrete [33,54]. These substances are added during mixing with the main aim of modifying some properties of concrete in the fluid phase, or in the solid phase, or the crossing from one phase to the other [54]. Admixes can be used in the solid or liquid state. Its use in the liquid state is usual because a liquid can be more rapidly dispersed in an uniform manner during concrete mixing [33]. Admixes can be classified as water-reducing (e.g. superplasticizers), retarding, accelerating and air entrainers [33,54].

Nowadays, a new class of water-reducing admixes exists and it is classified as superplasticizers (SP) (or high range water-reducing admixes), which can be used to reduce the required amount of water without inhibiting the hydration reactions [33,54]. There are several categories of superplasticizers [33], and a new generation of carboxylic ether polymer is the most common ones [88]. Hence, admixes are water-soluble organic polymers that are synthesized by a complex polymerization process. Therefore, SP are relatively expensive [33,54]. However, mainly because they are manufactured for a specific purpose, their properties can be optimized in terms of length of molecules with minimum cross-linking. Superplasticizers have a low content of impurities, even when used at high dosages [33].

The action of superplasticizers is to wrap themselves around the cement particles or the cement plus fly ash particles (in HVFAC) and provide them with a negative electrical charge, so that the particles repel each other. These results in more efficient deflocculation and dispersion of cement particles. Thus, it is important to select a superplasticizer compatible with the cement used [89]. The use of superplasticizers improves concrete´s workability leading to more fluid concrete. Its action as a water reducing agent also leads to concrete with a very high strength and durability (high-performance concrete) [33,88,90]. Using superplasticizers leads to a decrease in the water/cement ratio achieving similar workability without influencing the hydration process [54,91,92]. Superplasticizers cannot directly influence the shrinkage, creep, modulus of elasticity or resistance to freezing and thawing and durability of concrete [33]. On the other hand, the use of SP allows the use of a higher content of mineral admixes in concrete, for instance High Volume Fly Ash, with low water/cement ratios since the presence of SP will ensure a proper workability of the concrete mixes without increasing the water content [61,88,93–98].

2.2.5 Coal Fly Ash

Worldwide, power and heat production is carried out by using coal as the most reliable, affordable and safe energy source [99]. However, using coal for power generation has an impact on the environment and these needs to be mitigated. During coal conversion, several coal combustion products are produced: boiler slags, bottom ash and fly ash, which are called CCPs. In 2003, 550 million tons of CCPs in the world and 95 million tons in EU25 were produced. Coal fly ash represents almost 68 %wt of the total CCPs produced. In recent years, the content of CFA produced decreased, but the content of CFA that is used for different applications represents less than 50%wt of the content produced (Figure 2.2). Most ash is used in concrete production and blended cements (almost 75%wt of the content that is used), but there are other possible applications such as mining applications, waste stabilisation, agriculture, as can be seen in [100]. The high amount of fly ash that is not used shows that its utilization in HVFAC is not an issue and can be a solution for the mitigation of environmental problems associated with cement production.

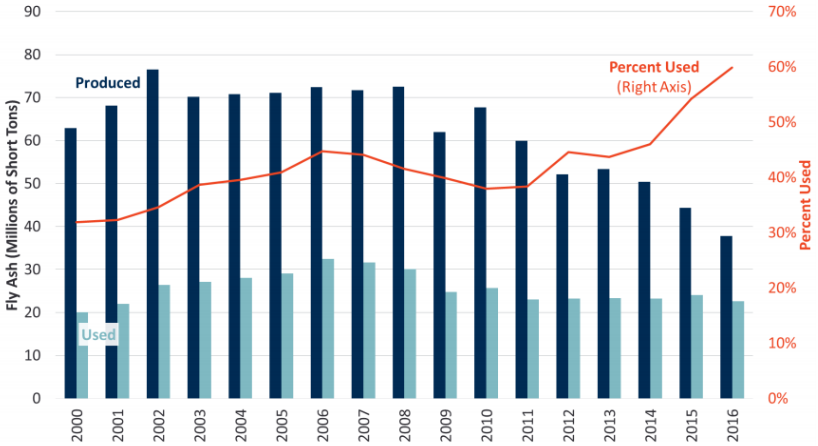


Figure 2.2 – Fly ash production and percentage of use [100]**.**

CFA consists of thinly divided ashes from conversion of coal in electric power plants, and it is the most common artificial pozzolan used to produce concrete [2,13,78,101]. It is collected in the dust collection systems from the exhaust gases of coal power plants for electric energy production. Due to its fineness and mineralogy, including its amorphous and pozzolanic nature, and in some cases, to its self-cementitious nature, CFAs are widely used in cement and concrete [102].

CFA is usually a little finer than Portland cement, and its major chemical constituents, silica, alumina and oxides are from iron and calcium [72,102]. The CFA composition varies with the origin of coal. Silica normally varies from 40% to 60% and alumina from 20% to 30%. The lime content is usually low (2% to 5%), alkalis are present in appreciable amounts but potassium overcomes sodium [78]. CFA particles are typically spherical and glassy (Figure 2.3), but they can also show other typologies [61,78,103–106].

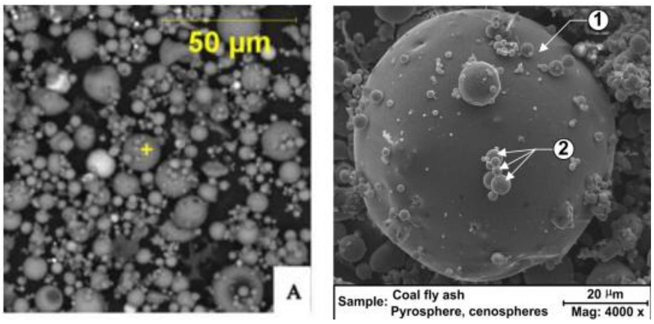


Figure 2.3 - Backscattered electron (BSE) images of (A) typical fly ash spheres [107] **and SEM images of microstructures of CFA – pyrosphere and cenospheres (Mag: 4000×): 1 - pyrosphere, 2 – cenospheres** [108]

CFA has been widely used by the concrete industry as a supplementary material [109]. According to EN 450-1-2012 [110] fly ash is a fine powder composed mainly of vitreous particles with a spherical form that result from the combustion of pulverized coal, with or without co-combustion materials. This powder has pozzolanic properties and it is composed essentially comprises SiO_2 and Al_2O_3. According to ASTM C618, coal fly ash is divided into two classes [111]: Class F, with low calcium oxide content (< 10%) and Class C, with high calcium oxide content (> 10%). Class F ashes are a result of the combustion of anthracite or coal and are considered an artificial pozzolan. Class C ashes are produced from the burning of lignite or sub-bituminous coal and it presents hydraulic characteristics [39,112].

In chemical terms, Class F ashes present low calcium content and in the form of hydroxides, sulphates and some amorphous components in combination with silica and alumina. In these ashes $Al_2O_3SiO_2$, $3Al_2O_32SiO_2$ and some calcium oxide predominate [9,33,39,97,113,114]. Its pozzolanic activity is well known, but for concrete and cement production a constant fineness and constant carbon content is required. In most of the cases, the two parameters are interdependent because the carbon particles tend to be coarser [33]. The utilization of Class F ashes can affect the colour of concrete, making it darker, due to its carbon content. This can be important when comparing the appearance of a concrete with and without fly ash [33].

On the other hand, Class C ashes are originated from lignite coal and for that reason are richer in lime [14,39,115]. High-lime ashes have some cementitious properties of their own, but since its lime combines with the silica and alumina present in the ash, a lower content is available to react with the lime liberated by the hydration of cement. In these ashes, the carbon content is low, the fineness is high and the colour is lighter [33]. However, they comprise high concentrations of alkaline elements (sodium and potassium), magnesium oxides and sulphates [33,112].

The degree of reactivity depends on the type of fly ash used. Usually a Class C fly ash has better hydraulic properties than a Class F one [109]. Both types of ashes lead to lower strength in HVFA concrete at early ages [116]. The reactivity of CFA has been studied and is more relevant nowadays, due to the current tendency of using larger amounts of CFA as a cement replacement material in concrete [117–119].

The reaction kinetics between CFA and cement are complex, mainly because of the interaction between the two materials and the difficulty in measuring the degree of reaction of each material independently [120]. Several studies have been carried out in order to understand the reactivity and the hydration process of materials with HVFA contents [11,120–122].

Supplementary cementitious materials (SCM), such as CFA, react with the calcium hydroxide formed during hydration of calcium silicates in the clinker, which modifies the hydration reactions [78]. The pozzolanic reaction only occurs after the cement hydration reaction. The CaO content has a significant relevance in the hydration reaction, but the amorphous or silica content and the aluminium oxides play an important role in the pozzolanic reaction [123].

SCM changes the phase assemblage and the composition of C-S-H composition that has propensity to have a lower Ca/Si ratio and a higher Al/Si ratio than in a plain cement paste [56,65,72]. Otherwise, depending on the reactivity and composition of the materials the amount of ettringite and AFm phases is also affected [72].

The presence of these materials affects the rate and extent of the reaction of the ground clinker component [66,72,101]. Nevertheless, the reactivity of SCMs is usually confused with this effect [72]. Their reactivity is highly dependent on the alkalinity of the pore solution that builds up over the first few days [19,29,41,57,72,76,80,124–129]. Therefore, the amount of reaction of SCM on the first day is negligible and the changes in the hydration kinetics are dominated by the filler effect [37,72]. The filler effect has two important components:

a) The dilution effect that results from substituting the clinker for an SCM in the same water to binder ratio. Because there are fewer clinker grains, there is more space for the formation of clinker hydrates and consequently the degree of reaction of the clinker component will be higher than in a plain clinker cement paste [65,66,72,101,130].

b) The other mechanism is the heterogeneous nucleation of C-S-H on the filler surface, in other words the surfaces of the SCM can act as nucleation sites for hydrates [66,72,101]. Increasing nucleation sites enhances the hydration rate since the C-S-H formation is the control process during this period. This effect is not significant for SCMs with a particle size distribution similar to that of Portland cement [66].

Assessing the reaction kinetics of SCM blends is challenging as it is difficult to measure independently the degree reaction of the SCM independently, as well as the clinker phases which is a result of the filler effects [72]. The reaction rate is influenced by several parameters: composition of the SCM, replacement level, solution pH, temperature, Portland cement (PC)-fly ash. In terms of composition, each SCM has a different range of chemical compositions and for the same conditions (pH, temperature) the solubility of the resulting glassy phases varies [72,131–134]. Fly ashes with a high calcium content contain reactive crystalline phases that lead to an acceleration and an increase of the complexity of the hydration reactions [72]. The solubility amorphous silica is sensitive to pH increases. The higher the pH, the faster the rate of reaction [72]. In high volume fly ash concrete, the pH drops, which reduces the solubility of the amorphous silicates and delays the rate of reaction [72].

The degree of reaction of SCM in blended cement pastes can be determined by various methods. Scrivener and Lothenbach [101] divided several techniques into direct methods and indirect methods. Direct methods try to measure directly the amount of supplementary cementitious materials directly remaining at a certain time, e.g. microscopy combined with image analysis and selective dissolution [101]. Indirect methods quantify the amount of SCM, which reacts, through the calculation of other measured quantities, for example calcium hydroxide consumption [101]:

a) Selective dissolution

Selective dissolution targets unreacted clinker phases and clinker hydrates, and the SCM reaction that can be dissolved, in which unreacted fly ash is residue [72,135]. However, several studies [72,135–138] reveal incomplete dissolution and significant amounts of clinker and hydrate phases that remain after dissolution. It is important to note that a large number of non-quantifiable errors remain, which may explain why different authors report different amounts of e.g. fly ash reaction to similar systems [72,135–138].

b) Backscattered electron image analysis

This analysis allows some features of the microstructure to be identified and quantified according to their brightness that is dependent on their average atomic number [101,139]. There are some studies that showed the amount of unreacted cement measured like this and that corresponded well to other measures of degree of hydration, for example X-ray diffraction with the Rietveld analysis [36,59,65,66,71,82,101,118,120,131,136,137,140–152].

c) X-ray Diffraction (XRD)

In the X-ray diffraction coupled with the Rietveld analysis, crystalline phases or the total amount of amorphous materials are measured and quantified if an internal or external standard is used [101]. The analysis of XRD diffractograms is essentially used to: quantify the degree of hydration of the crystalline clinker phases; and the formation from crystalline hydration products [101,150,151,153,154]. In the case of blended materials, it is difficult to measure the main hydrate compounds, because the C-S-H forming in cementitious pastes usually display no long-range ordering of its atoms [155] and because it is in the amorphous phases [101]. In spite of these problems, several studies showed the determination of the C-S-H phases via XRD [136,147,155–157].

d) Bound water

One of the most used tests to determine the degree of the reaction of Portland cement is the evaluation of the bound water content based on the weight loss of samples between 105 and 1000 ºC [101]. However, the analysis of blended cement materials is more complex, because the separation of the bound water is very difficult due to the reaction of the coal fly ash due to the reaction of the clinker phases [78]. Most studies assume that the evaporable water is driven at temperatures lower than 105 ºC [158,159]. Nevertheless, there are some authors who report that evaporable water can still be lost at temperatures between 105 and 130 ºC or even 150 ºC [160]. Therefore, most of the cement hydrates (C-S-H and ettringite) lose part of the chemically combined water at temperatures below 105 ºC. The mass loss related to chemically bound water should also be corrected for the mass related to decarbonation, at around 650 ºC [161]. For this reason, the estimation of the bound water is usually made by thermogravimetric experiments, which continuously measure the weight under a constant heating rate [75,101,148,157,162–165].

e) Portlandite consumption

Several methods have been used to assess the rate at which portlandite is consumed by CFA as a measure of the reactivity of coal fly ash [120]. One of these methods is to analyse Portlandite decomposition determined by thermogravimetric analysis. Portlandite decomposes at between 410 ºC and 480 ºC, to CaO and H_2O. A mass loss is registered due to the loss of water [101]. The pozzolanic reactions lead to a decrease in the amount of portlandite in the mix [161,166].

Several methods specify amounts of CFA and portlandite that are mixed with water and the consumption of portlandite is quantified at defined ages [120]. Initially, this type of analysis was made at environment temperatures, but this approach has some disadvantages, such as a very low reaction velocity, thus the tests often took up to 90 days. To minimise these issues, the new approaches raise the temperature. The La Chapelle test and its modifications are the most widely used. These methods are based on a classical alkalinity titration. These methods solved the problem of the test duration, but they have a weakness, which is related to the alkali released from the supplementary cementitious materials that can have a significant influence on the alkalinity titration measurement [120]. The standard methods that specified the pozzolanic reaction of SCMs, based on Frattini’s work, compare the Ca concentration in the solution of Portland cement blended with e.g. coal fly ash to the Ca concentration in a $Ca(OH)_2$ saturated solution of the same alkalinity. The two solutions are titrated and compared to the portlandite saturation curve [167].

2.2.6 Workability and Curing

Workability is defined as a physical property of concrete. This definition is based on what happens when concrete is poured into moulds [78]. Even if compaction is applied, done by ramming or vibration, the compaction process consists of eliminating entrapped air from concrete until it has achieved a given mix as close as possible [33]. This is used to overcome the friction between the individual particles of concrete and also between concrete and the surface of the mould or of the reinforcement. This can be called internal friction and surface friction, respectively. Due to the fact that only the internal friction is an intrinsic property of the mix, workability can be defined more correctly as the amount of useful internal work necessary to produce full compaction [33]. In conventional concrete, workability is mainly affected by the water content and is usually measured or evaluated by slump tests [33,168].

Workability is influenced by the composition of the mix. The addition of CFA as a cement replacement improves workability, increases stability and reduces segregation. This is due to the spherical shape of the fly ashes that operate as ball bearings [33,168,169] and improve the packing density of cementitious materials [168,170]. With the increase of the percentage of CFA in the concrete paste, a better lubrication of aggregates and a better flow of concrete occurs due to the ball bearing effect of the fly ash particles [171,172].

A CFA with a high fineness and low carbon content has a propensity to reduce the water demand of concrete and should allow concrete to be produced with a lower water content when compared to a conventional concrete with similar workability (Figure 2.4) [172]. It was shown that for low water/cement + fly ash mixes, an increase in the superplasticizer’s dosage is needed for a slump and air content similar to a conventional concrete [173].

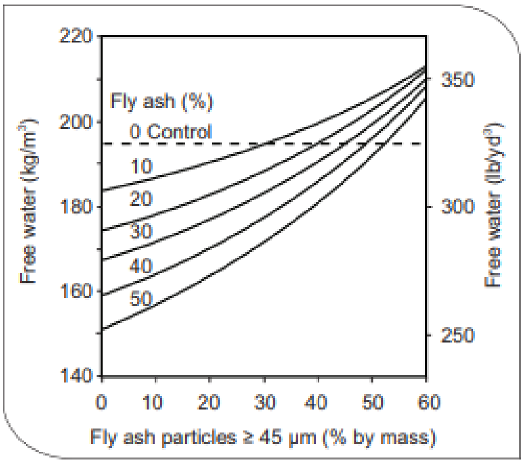


Figure 2.4 – Effect of fly ash fineness on water demand of concretes designed for equal slump [172]**.**

Using some supplementary cementitious materials, such as metakaolin or BFA, changes the workability of concrete, because some water is absorbed by those materials and this increases the water demand [31,174]. There are some models to predict the workability even when SCM are used [175]. In these situations, the incorporation of superplasticizers also improves the workability of concrete with SCM [91,176,177].

After mixing, to obtain a good performance concrete, it is necessary to attain a careful curing of the mix. During curing, the hydration of cement is promoted, at a controlled temperature and moisture movement from and into concrete [33,178–181]. Curing has the objective of keeping concrete saturated, until the original water-filled space of the cement paste has been filled by cement hydration products [33]. There are two curing methods, namely wet curing and membrane curing, which are most used in practice. The first one is the most used method and the second one is used in places where is a shortage of water [33,57,182]. In wet curing, the concrete surface is continuously in contact with water during a specific length of time and has been used in various studies [33,77,88,183–186]. Furthermore, some authors studied the effect of curing at room temperature and in a chamber with temperature and humidity control on the properties of concrete [88,185,186].

The content of water in concrete is important to decrease the adverse effects on the strength to increase the permeability and to reduce the resistance to abrasion [33]. Cement hydration takes place in the water-filled capillaries, thus the evaporation of this water must be prevented. On the other hand, some water is lost internally during the chemical reactions of cement hydration (self-desiccation) and it is necessary to replace this water with outside water [33,98]. Self-desiccation is important in mixes with water/cement ratios below 0.5 [33,61,187].

Curing is very important in concrete with supplementary cementing materials, such as CFA, mainly due to the fact that that concrete is more influenced by inadequate curing when compared to concrete made with Portland cement only [185]. The rate of the pozzolanic reaction is slower than the rate of Portland cement hydration, and for that reason concrete with fly ash needs to be properly cured [172]. When high levels of fly ash are used the cure is even more important since the content of cement is low and the pozzolanic reaction needs to occur, and therefore it is usually recommended that concrete needs to be moist cured and as fast as possible to prevent plastic shrinkage at the concrete surface. The strength of concrete is influenced by curing and this is more noticeable in smaller specimens or in specimens cured with low moisture content [33,77,88,185,186].

One of the most important parameters that affect HVFAC is the curing temperature, since it is related with the pozzolanic reaction and strength development of concrete [171]. At common temperatures (20-35 ºC), fly ashes retard the hydration at early ages but at later ages hydration is accelerated. However, for higher curing temperatures and high replacement ratios of cement by fly ash, the hydration at later stages is retarded due to the pozzolanic reaction of fly ash and it competes with cement hydration for water consumption, and as a result the hydration is impeded [188].

2.2.7 High Volume Fly Ash Concrete Issues

Despite the fact that HVFAC has many advantages, it also has some disadvantages. The strength development of this concrete is slower than that of concrete with low fly ash content and the early strength is normally lower than that of plain cement concrete [14,44,51,114,123,189,190]. This is because the pozzolanic reaction of fly ash is slower and leads to retardation of the strength gain. The increase of the long term strength is mainly because, as a result of these pozzolanic reactions, concrete has a denser microstructure and smaller size of capillary pores [14].

Siddique [114] studied the effect of HVFA content as cement replacement (40%, 45% and 50%wt) on the mechanical strength and the elasticity modulus. All the HVFAC presented a reduction in the compressive, flexural strength and modulus of elasticity at 28 days, when compared with a conventional concrete. However, a continuous and important improvement of strength with curing time was observed by the author. However, this increase was dependent on the level of cement replacement, on the type of CFA and on the age of concrete. It was observed that the rate of early strength gain of Class C fly ash was higher than that of Class F. However, in the long term, the compressive strength of Class F was higher than that of Class C [14].

The strength of HVFAC is also dependent on the consistency and on the presence of different chemical admixtures. Using a superplasticizer is necessary in HVFAC to guarantee workability, especially in concrete with a low water/cementitious materials ratio [44,88]. Usually, the setting time of HVFAC is longer than that of plain cement concrete [44,48,191]. This increase is mostly due to the reaction between cement and water [49,192]. A decrease in cement content influences this reaction and leads to an increase in the setting time of concrete. The increase in the setting time occurs for the two fly ash classes and at all levels of cement replacement [193].

Naik and Singh [194] studied the effects of the amount of Class C fly ash on the setting time characteristics of non-air-entrained concrete. They studied a cement replacement with CFA that varied between 0 and 100%wt. The results showed that the initial and final settings were retarded up to 60%wt of cement replacement and beyond that a reverse trend was observed. However, the mixes with HVFA content presented reasonable compressive strengths for most construction applications at all ages. The problem associated with the retardation of setting times can be solved by using some chemical admixtures [194].

Huang *et al.* [48] conducted an investigation to demonstrate the feasibility of the utilization of HVFA content (up to 80%wt of Class F fly ash) as cement replacement in concrete with moderate and high strength. They observed that concrete with fly ash of up to 80%wt can have adequate workability using suitable superplasticizer content. The air content and the setting time increased with the increase of cement replacement with fly ash. Higher mechanical strengths for the control concrete than for the fly ash concrete were also observed at early ages. However, a significant gain was verified for the HVFAC with the increase of curing time. The utilization of CFA in concrete promoted an increase of the drying shrinkage at various ages.

The use of a high volume content of pozzolanas in concrete requires certain care in the initial curing periods, due to the fact that even the mechanical resistance and the durability parameters are influenced by the initial curing time [14]. HVFA concrete is more vulnerable to dry curing conditions than plain cement concrete [88].

The most important issue related with this type of concrete is reinforcement corrosion. The Reinforcement corrosion is the most important process related to the deterioration and decrease of the life cycle of structures [195] and hence this issue will be more debated in the next section.

Reinforcement corrosion is one of the most important issues related to the durability of concrete. Corrosion leads to the degradation of reinforced concrete structures that, in turn, leads to an effect on the concrete lifetime [21]. This process could be classified based on its nature or by its morphology and is divided into: generalized, localized or cracking corrosion [195].

Generalized corrosion occurs mainly due to the loss of the passivation layer in a generalized way [76], resulting from the carbonation of concrete, by leaching of $Ca(OH)_2$. This type of corrosion can occur in a uniform way, with a regular surface, or in a non-uniform way, in this case presenting a rough and irregular surface. This corrosion could affect the mechanical characteristics of the reinforcement but the most significant consequence is the cracking of concrete [195].

Localized corrosion occurs by the localized dissolution of the passivation film typically induced by the penetration of chlorides that came from the exterior or that are part of some material belonging to concrete [18,195].

Finally, there is corrosion that is related with steel under high tension. In this case, microcracks are created on the surface that rapidly progress and provoke a sharp and rapid rupture of the metal, even in cases that do not show evidence of attacks. This phenomenon is normally related to the bad quality of concrete, leaching of concrete or the presence of certain ions. The mechanisms of this corrosion have been studied but its effects are extremely dangerous in concrete structures, because they are characterized by sharp cracks, without significant deforming of the structural elements and without visual symptoms of corrosion [15,18,195].

2.2.7.1 Carbonation

One of the most important sources of corrosion is carbonation that is a physical and chemical attack, where the aggressive agents are primarily carbon dioxide, sulphur dioxide and hydrogen sulphide [21,167,195]. These gases diffuse into the pore solution of the porous system that leads to the occurrence of cracking in the interfacial transition zone between the cement paste and the aggregates in concrete [21]. Carbonation decreases the alkaline compounds that results in a pH decrease, which can destroy the passive protection layer allowing corrosion to occur [21].

Therefore, it is important to examine the chemistry of carbonation: first carbon dioxide penetrates in gaseous form in concrete [190,196]. After its diffusion into concrete, part of the CO_2 dissolves in the pore solution. Equilibrium is established over the interface between the pore air and the pore solution [196]. Some of the CO_2 in the pore solution reacts and becomes carbonic acid (H_2CO_3) and this acid dissociates in HCO_3^- and CO_3^{2-} [195]. This dissociation promotes a decrease in the pH, since a result of this process is the formation of H_3O^+. In the pore solution, some calcium ions are dissolved and the CO_3^{2-} reacts with this calcium and forms calcium carbonate (Equation 2 [196]).

$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3\ (s) \tag{2}$$

The calcium carbonate precipitates into a solid compound [196]. All of the reactions are demonstrated in Figure 2.5. Calcium carbonate presents three mineralogical forms: calcite, aragonite and vaterite. The predominance of each form in concrete provides some additional information about the chemistry of carbonation reaction. However, the major mineralogical form of calcium carbonate in concrete is calcite [197]. The formation of calcium carbonate depends on the CO_3^{2-} concentration, and therefore the calcium concentration in pore water becomes a function of the pH [196].

One of the most important parameters of carbonation is the pH [197]. Calcium carbonate is almost insoluble for pH higher than 5, as seen in Figure 2.5 for the $CaCO_3$-dissol line. Thus, the reaction moves to the right and continues as long as there is carbonate and calcium. Carbonate only exists in pore water at a pH above 9 [195] since above this value the carbonation reaction stops (Figure 2.5 for the $CaCO_3$precip. line).

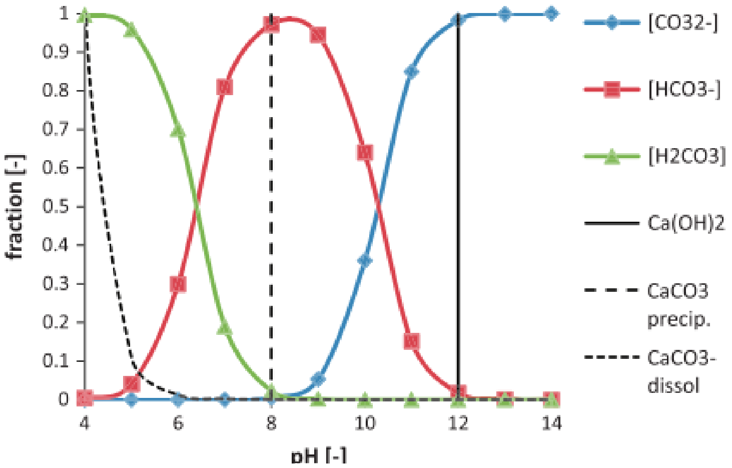


Figure 2.5 - Normalized distribution of the CO_2 phases and precipitation boundaries for $CaCO_3$ and $Ca(OH)_2$ [196]**.**

The open pores of concrete are in contact with the air and for that reason the pH in the pore water tries to be in equilibrium with the CO_2 of the air [196]. This is mainly because the amount of CO_2 dissolved in the pore water is proportional to the concentration of CO_2 present in the air [196]. Pure water in equilibrium with non-carbonated concrete has a pH in the range of 12.5 to 13.5. This is a result of dissolved calcium hydroxide and some soluble alkali compounds from the aggregates. The reaction of carbon dioxide leads to a decrease in the pH, and this is a result of the carbonation of some calcium compounds. A layer that is totally carbonated presents a pH lower than 9 [21,196]. The intermediate layers between the totally carbonated zone and the non-carbonated zone can have some additional calcium hydroxide that diffuses from the interior due to the concentration difference, a consequence of carbonation [197].

In general, the carbonation mechanism is a lengthy process due to the low CO_2 concentration in the atmosphere and due to the high content of calcium hydroxide on concrete and to its low permeability, which allows a high resistance to CO_2 penetration [195].

a) Carbonation of CH and C-S-H

The carbonate reacts with Ca^{2+} (as described before) from calcium hydroxide (CH), calcium silicate hydrate (C-S-H) and the hydrated calcium aluminates and this leads to the formation of different forms of calcium carbonates [198,199]. From a thermodynamically point of view carbonation of CH occurs first, then C-S-H carbonation follows [86]. 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 [21,86,198]. Usually the carbonated samples present an increase in its weight, a lower porosity and higher compressive strength at early ages [198]. This usually occurs in low porosity pastes, where calcite formation decreases the porosity preventing CO_2 diffusion, reducing the carbonation attack. Pastes with high porosity could allow the diffusion of a constant CO_2 content, in which case the CH is depleted and the interlayer calcium from C-S-H also reacts with the CO_2 [86,198]. The removal of interlayer Ca^{2+} ions provokes an excess of negative charge. This deficit is balanced with the formation of Si-OH groups [196,198]. The condensation of the Si-OH groups into Si-O-Si linkages then forms a silica gel [198]. This condensation leads to an increase in the silicate chain length with a formation of bridges between adjacent regions. Hence, CO_2 causes polymerization of these chains, leading to shrinkage and cracking [198,200].

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 [10,198]. C-S-H carbonation has been studied and all verified a complex decalcification-polymerization process of the C-S-H with the formation of amorphous silica gel was observed [86,198]. Carbonation of CH is initially more rapid than C-S-H carbonation, but this situation soon changes due to the formation of a layer of calcium carbonate micro crystals at the CH surface [201]. In mixes with high amounts of cement substitution with supplementary cementitious materials, the amount of CH is reduced due to the pozzolanic reaction and the carbonation of C-S-H is even more dependent on the permeability of pastes, accompanied by carbonation shrinkage which accelerates when the C/S molar ratio decreases to values below 1.2 [198].

b) Parameters that affects the carbonation process and its mitigation

Natural carbonation of concrete is dependent on environmental factors, such as: CO_2 concentration, aggressive agent concentration, relative humidity, temperature, air pressure, precipitation and the intensity and orientation of wind. Carbonation is also dependent on the quality of concrete, in terms of: amount of alkaline material capable of suffering carbonation, mix-design of concrete, type and quantity of mineral additions, w/b ratio, porosity, interface of paste and aggregates, diffusion, mechanical resistance and cracking. The production of concrete could also lead to carbonation and for that reason some parameters need to be taken into account, e.g. curing, compaction, placing and transportation [18,33,90,164,190,195,202–208].

CO_2 concentration affects the carbonation velocity. In natural environments, CO_2 varies in the range of 0.035% in volume to 1% for industrial areas, but this concentration is dependent on the temperature and pressure. The diffusion of carbonic gas by pores follows the first law of Fick, and this shows that the diffusion of the gas occurs in a direct ratio of the concentration gradient. The different CO_2 contents, found in the atmosphere, are related directly with the carbonation velocity but they do not change the physical and chemical mechanisms [195].

The relative humidity is also an important factor since water is an important parameter in the carbonation process. The relative humidity is responsible for blocking the pores, which decreases the diffusion process and allows an environment adequate for the reaction between

CO_2 and $Ca(OH)_2$. In the absence of humidity, CO_2 penetrates into the concrete pores, however the carbonation process does not occur because the dissolution of the gas is not possible. On the contrary, in a case of 100% of humidity, CO_2 is dissolved but, due to its low diffusion in water, the carbonation process is retarded. Therefore, the maximum velocity of carbonation occurs in an intermediate situation [195,204].

The influence of temperature follows the Arrhenius theory. The increase in temperature implies an increase in the chemical reactions. For that reason, zones with a higher solar exposition are carbonated faster [195].

The compaction and curing of concrete are factors that affect the carbonation depth, since they determine the dimension and continuity of pores that compose the zone where CO_2 penetrates [164,209]. A good compaction during concrete production is very important to ensure a good cover of the reinforcement and a good distribution of the different aggregates that compose concrete. A better compacted concrete has a lower diffusion coefficient when compared to poorly compacted concrete [195]. An insufficient curing influences some hydration reactions and produces a more porous concrete which is much more vulnerable to the carbonation process [209].

The water/cement ratio has a significant influence on the CO_2 penetration [81,210]. For a higher ratio, the permeability and porosity of concrete is higher, and this leads to a higher diffusion of CO_2 [195,203]. Concrete with a lower water/cement ratio is more compacted, and consequently more resistant to carbonation. The depth of carbonation decreases with the increase of cement content per m^3 of concrete. This is due to the fact of carbonation being inversely proportional to the alkaline content in the mix [195].

Several methods can be used to verify which concrete zone is carbonated and to determine the depth of carbonation. Usually, some indicators of pH are used, but the X-ray Diffraction, thermogravimetric analysis (TGA), microscopic analysis and Fourier transform infrared spectroscopy (FTIR) can also be used [17,21,94,195,203].

XRD is used because it allows the determination of the intensity of crystal distribution, namely of $Ca(OH)_2$ and $CaCO_3$ crystals [80]. TGA is a quantitative analysis that determines the concentration of those crystals. The Fourier Transform Infrared Spectroscopy (FTIR) method provides the infrared spectrum, where it is possible to determine the depth until which the carbon oxygen bond that belongs to the $CaCO_3$ crystals occurs [21]. Microscopic analysis can also detect the presence of $CaCO_3$ crystals [203]. These methods are very reliable and accurate, but the utilization of indicators, such as phenolphthalein, is more practical [195].

The application of indicators is done by alcoholic solution and allows a rapid, easy and economical form to determine the depth of carbonation. The advantage of using phenolphthalein is that the turning point of the indicator is similar to the pH values related to the carbonation process. The indicator reacts with the liquid phase presented in the concrete pores and exhibits the colour correspondent to the range of pH. Other indicators can be used, e.g. thymolphthalein, but those indicators are not as distinctive as phenolphthalein [164,195,203]. The process of using an indicator involves spraying the faces of concrete with 1% phenolphthalein in 70% ethyl alcohol. If the pH of the pore solution is less than 7.5 a carbonation degree of 100% is considered, if it is between 7.5 and 9.0 it is considered that the carbonation degree is between 50% and 100%. When it presents a pH of 9.0 to 11.5 the degree of carbonation is between 0% to 50% [164].

The incorporation of a high volume of fly ash leads to the formation of binders with low calcium hydroxide content and decreases the concrete alkalinity, which may help the carbonation process [13,195]. Carbonation is more significant in concretes with HVFA [90] and, for that reason, some authors defend the introduction of hydraulic lime to increase the alkalinity, and therefore to control the carbonation process [211]. Its introduction leads to an increase in the alkalinity but also increases the formation of OH^-, and can produce a higher content of calcium silicate hydrates [212].

2.2.7.2 Chloride Ions

Chloride-induced rebar corrosion is an important form of environmental attack of reinforced concrete. This leads to a decrease in the strength, serviceability and aesthetics [213]. The accumulation of oxides and hydroxides in the concrete’s pore space near the steel rebars can cause stress around them and result in cracking or even spalling of the concrete cover. This facilitates the ingress of moisture, oxygen and chlorides up to the embedded rebar and increases corrosion [214]. Corrosion by chlorides occurs more frequently in places where concrete is exposed to a marine environment, where the concentration of chlorides is higher. Chloride ions may occur in concrete through its components or through penetration from the exterior through the pores. In this case, it is more frequent in marine environments or when salts are used, such as deicing salts [195].

The definition of the chloride content that breaks the layer of passivation oxides and begins corrosion of the reinforcement is difficult, mainly due to the many variables it involves, such as: type and cement content, water/binder ratio, humidity content and the fly ash content [13,94,115,195]. The depassivation mechanism by chloride ions is related to the incorporation of those ions in the passive layer, changing its oxygen content and increasing its conductibility. Therefore, the layer loses its function of protection and allows the corrosion of steel involved by concrete. For this reason, the most important parameters that influence the penetration of chlorides are the ratio of water/binder and curing of concrete [15,18,195]. Chlorides have a slower penetration in blended cements due to a more refined pore network or to a higher content of AFm phases [215]. Chloride penetration can be characterized by the chloride diffusion coefficient and by the binding ability of matrix-forming solids [216]. Chlorides can react with unhydrated aluminate phases to form new compounds, as for example Friedel´s salt [217] or hold to the surface of hydrated products [218]. The diffusion of chlorides is dependent on pure diffusion for the water-saturated concrete and capillarity absorption of salty water for non-saturated concrete [219]. However, chloride penetration in concrete depends on several factors. The chemical and physical bond that exists between chloride ions and the hydrated products of cement have an influence on the microstructure and the chloride diffusion coefficient changes with exposure conditions [220,221]. Meanwhile, concrete structures are affected by several environmental factors that can accelerate the destruction process [216].

Mineral admixtures such as CFA enhance concrete durability, by increasing chloride binding [7,40,45,52,62,68,222–224], decreasing chloride permeability [225], increasing the threshold chloride [219] content and improving the distribution of pore size and shape of the concrete matrix [213]. Some authors reported that the chloride-binding capacity increased with the increase of CFA replacement level up to 50%wt and this can be due to the high alumina content presented in CFA and some authors found a positive effect even in concrete with chloride environment exposure [226,227]. However, it was reported that an increase in the CFA content leads to a decrease in the chloride threshold required to initiate corrosion [228]. This decrease is related with the reduction of OH^- content that leads to an increase of Cl^-/OH^- in the pore solution and with the decrease in the pH in the pore solution as a result of CFA addition [52,229]. Regardless of the lower chloride threshold values for CFA concrete, this type of concrete provides a better corrosion protection due to its higher resistance to chloride penetration [52].

2.3 Biomass Fly Ash

Nowadays, biomass combustion for electricity and heat production is a promising solution to reduce the problems related to non-renewable sources, such as CO_2 emissions [230]. Over the last years, the use of biomass has been increasing and, consequently, the production of sub-products and waste resulting from biomass conversion is also increasing, and one of those is biomass fly ash.

BFA is divided into different flows, and this division is made through the place where they are sampled such as: super-heaters, economizers, and control devices (cyclones, bag filters and electrostatic precipitator) [23]. Usually, the different flows are mixed and managed together but each one has distinct properties [23,231–237]. Biomass fly ash is influenced by the technology used for biomass combustion, such as: grate, fluidized bed and fixed bed [235,237–239], but also by the type of fuel (biomass) [238,240–244] and operation conditions [23,24,245].

The most common type of biomass fly ash produced in Portuguese industries is from wood, and it is this type that will be discussed and used throughout this study, called biomass fly ash.

2.3.1 Physical and Chemical Composition

The physical and chemical characterisation of BFA is important to understand the benefits of its use [246]. BFA has a low density, high specific surface and is very alkaline with a pH in the range of 9 to 13 [23,25,26,233,247,248]. Barbosa *et al.* [249] studied the physical characteristics of size fractionated wood fly ash. It was observed that these ashes were composed of finer particles and most of the mass was separated into three size ranges: 48% in the 20-50 µm range, 36.3% in the range of 50-200 µm and 10.5% in the range of 200-500 µm. However, the particle size of wood fly ash can be significantly different [249,250], because it depends on the combustion technology and the origin of the biomass.

Wang *et al.* [251] and Lessard *et al.* [252] studied the particle size distribution of five ashes. The results are shown in Figure 2.6 and Figure 2.7.

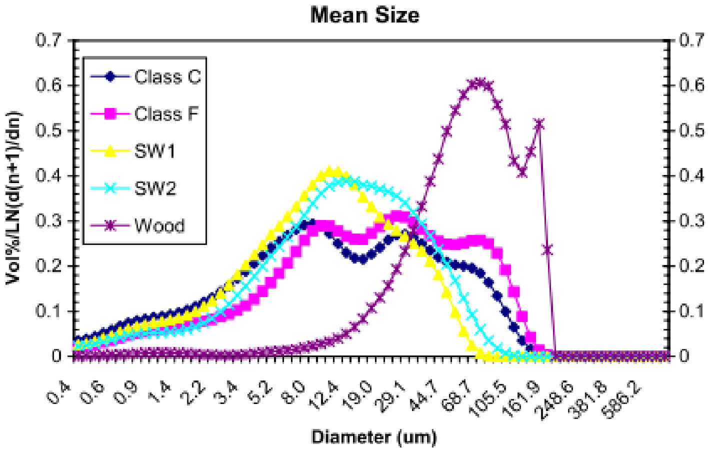


Figure 2.6 - Particle size distribution of fly ashes with different origins: coal (Class C and Class F), sawdust (SW1 and SW2) and wood [251]**.**

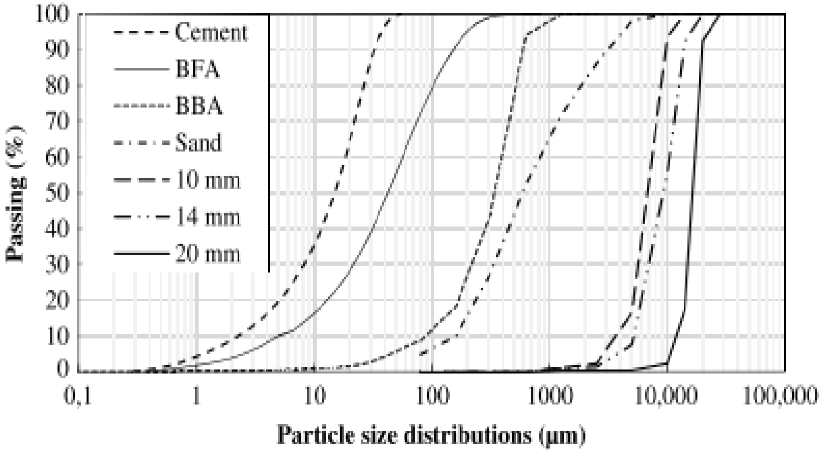


Figure 2.7 - Particle size distribution of biomass fly ash (BFA), biomass bottom ash (BBA), cement, sand and aggregates (10, 14 and 20mm) [252]**.**

They observed that Class C, Class F (according to ASTM C618) [253] and sawdust ash have a similar particle size distribution, and most particles are between 3 and 50 µm [251]. However, wood fly ash has particles with much larger sizes than the other fly ashes. Particles with a higher size when compared to cement are also present in the particle size distribution [252]. As seen in Figure 2.8, a wide range of particle shapes and sizes is observed. Some particles are angular, of rough textures, and some particles are spherical with some impurities attached to their surface and some have smooth surfaces [252,254].

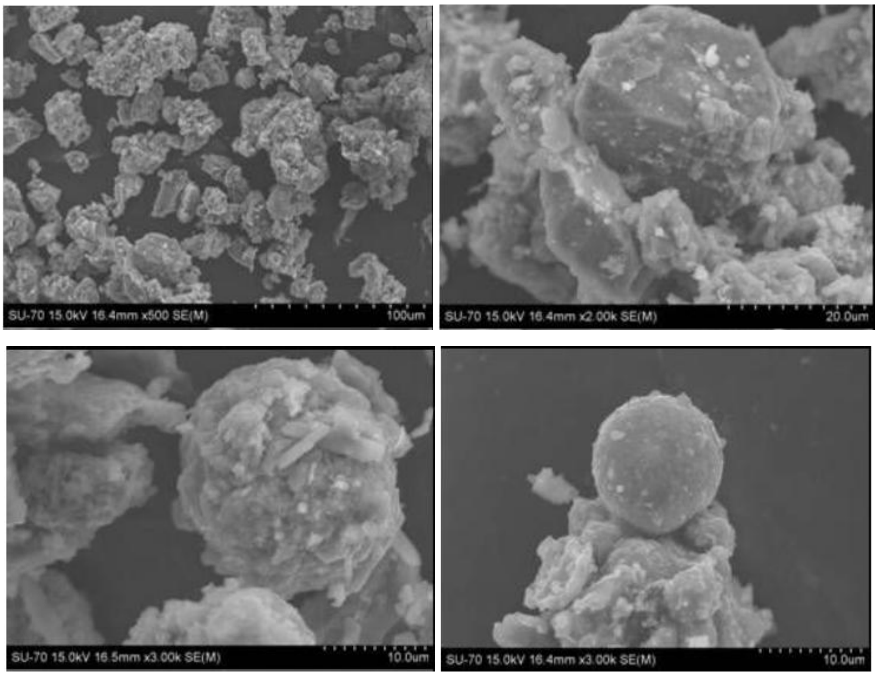


Figure 2.8 - Microscopic aspect (SEM images) of the wood fly ash from fluidized bed [254].

In terms of density, Berra *et al.* [255] studied three types of wood biomass fly ash (WBFA1 – combustion of chestnut, WBFA2 – combustion of poplar virgin wood chips, and WBFA3 – combustion of scraps of treated wood) and observed that, the values for the density varied between 2.35 and 2.76 g/cm^3. Rajamma *et al.* [27,30] observed that for two BFA collected in two Portuguese facilities (one collected in a biomass thermal power plant and the second one collected from a biomass co-generation plant) the specific surface area and bulk density were respectively 40 m^2/g and 2.59 g/cm^3 for one of the ashes and 8 m^2/g and 2.54 g/cm^3 for the other. Tarelho *et al.* [254] studied two BFA (one from wood combustion on a fluidized bed reactor and the other from wood combustion in a grate combustor) and observed specific surface areas of 13 and 14 m^2/g and a bulk density of 2.23 g/cm^3.

In Table 2.2, it can be observed that the LOI content of BFA is significantly higher than that of CFA. The LOI content is a very important parameter since it is known that fly ash with high LOI values may affect the concrete properties. Fly ash with high LOI has higher carbon content, thus it can absorb more water and chemical admixtures, for example superplasticizer, resulting in increasing the slump loss, decreasing the air-entraining effect and bleeding and decreasing the strength of concrete [48,256,257]. Lime and quartz are the oxides, which have a higher concentration in the chemical composition of ashes (Table 2.2), but several other oxides are present in significant concentration such as aluminium, potassium, iron, sodium, magnesium, chloride and sulphur [23,25,30,68,231,235,238,239,247,250,254,258–263]. The high content of lime is related with the presence of this oxide in the chemical composition of biomass [244] that is released during its combustion.

The high content of silicium compounds 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 [244]. 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 captured by the control devices [23,231,241,244,264].

BFA has a high content of heavy metals, e.g. Cr, Cd, Pb, Zn, Co, As, and some of them present organic compounds in their composition, e.g. PAH, and this has an environmental importance [23,26,233,234,236,247,249,265–268]. BFA is different from coal fly ash it has more content in Ca, Na and K, less Al and more variety in composition and in inorganic content material [26,251,266]. The presence of microelements in BFA is much more variable when compared to coal, e.g. elements as Mn, Zn and Cd have higher concentration; on the other hand, it has lower As, Se and Cr content [26,248,266]. These findings are sometimes not true, because of the variability on the composition of those elements in biomass [26]. The elemental chemical analysis and the high pH are an indication that some of the metals present in BFA may be in the form of basic metals salts, oxides or hydroxides [269]. To better understand the metal forms presented in ashes, some authors did an X-Ray Diffraction analysis of different types of BFA. The results achieved reported the presence of calcium compounds (CaO, $Ca_2Fe_2O_5$, $CaCO_3$, $CaSO_4$, $CaAl_2SiO_7$, $CaMgSi_2O_6$, $CaMg(CO_3)_2$), but also compounds with silica, sodium, magnesium, iron, potassium and aluminium (SiO_2, MgO, Fe_2O_3, Al_2O_3, $KAlSi_3O_8$, K_2SO_4, KCl, $NaAlSi_3O_8$, $NaAl_3O_8$), which confirms the chemical results [25,26,30,68,80,238,245,247,248,250,255,260,263,270–274].

Table 2.2 - Loss-on-ignition (LOI) and chemical composition of ash resulting from biomass and coal combustion

Type of fuel ash	Nomenclature of fly ash	Combustion Technology	LOI	SiO_2	CaO	K_2O	Al_2O_3	MgO	Fe_2O_3	SO_3	Cl	Na_2O	MnO	P_2O_5	TiO_2	Ref.
Class C	CFA	-	0.7	37.3	24.2	0.4	19.6	5.4	6.1	1.8	-	1.5	0.01	1.2	1.5	[251]
Class F	CFA	-	1.7	54.9	1.1	2.4	27.8	0.8	7.5	0.4	-	0.2	0.02	0.3	1.6	[251]
Wood	BFA	-	7.9	48.9	13.6	3.4	12.5	3.2	5.5	1.3	-	1.7	0.1	1.0	0.8	[251]
Forest wastes	BFA	Grate	25.0	41.0	11.4	3.9	9.3	2.3	2.6	-	-	0.9	0.3	0.9	0.4	[27,30]
Forest wastes	BFA	BFB	20.0	28.0	25.4	3.2	6.2	5.0	2.2	-	-	3.3	0.7	0.9	0.3	[27,30]
Forest wastes	BFA	BFB	<0.5	-	53.4	4.2	-	5.5	-	3.7	-	0.6	0.6	0.1	-	[25]
Wood	BFA	BFB	9.4	45.8	25.7	8.2	4.6	3.6	2.9	4.2	0.6	0.6	-	3.4	0.3	[250]
Virgin wood	BFA	BFB	4.5	29.9	33.1	3.6	9.6	3.5	5.8	2.9	1.1	1.3	0.8	2.3	-	[255]
Treated wood	BFA	BFB	10.3	40.4	20.8	2.1	9.5	3.0	6.1	9.3	1.7	3.0	0.2	0.7	-	[255]
Wood	BFA	-	13.5	31.0	24.0	2.7	8.5	4.8	3.0	2.3	-	6.6	-	-	-	[87]
Forest wastes	BFA	Grate	10.4	52.1	15.9	4.1	13.3	3.3	5.3	0.5	0.1	-	-	-	-	[263]
Forest wastes	BFA	BFB	3.5	25.1	40.1	2.1	11.3	6.6	5.2	1.1	0.3	-	-	-	-	[263]
Wood chips, peat	Blend	CFB	-	11.5	8.5	3.6	2.5	1.0	2.0	0.5	0.1	0.7	0.7	0.2	0.1	[260]
Wood chips	BFA	CFB	-	9.3	12.0	3.6	1.9	1.1	1.1	0.2	0.3	0.7	0.9	0.4	0.1	[260]
Wood chips, bark	BFA	BFB	-	7.5	11.7	3.9	1.3	1.0	0.9	0.6	0.6	0.7	1.2	0.6	0.1	[260]
Wood	BFA	CFB	6.2 (550ºC)	13.7	12.0	4.7	3.0	1.2	3.2	4.0	1.0	0.7	0.9	-	-	[274]

Legend: BFB – Bubbling Fluidized Bed; CFB – Circulated Fluidized Bed

Several ash materials have cementitious properties since they react with moderate amounts of water [274]. Normally, the major minerals present in BFA are those described before. However, when these ashes react with water, secondary hydrated minerals, such as ettringite, portlandite and calcite, are formed during the process, but can also form calcium-silicate-hydrates, aluminate-hydrates and gypsum [274]. Steenari *et al.* [274] showed that the main reaction that occurs is the hydration of calcium oxide and the formation of ettringite. During the hydration of CaO, portlandite is formed that subsequently reacts with CO_2 present in the air that leads to the formation of calcium carbonate. The carbonation of portlandite is the most important parameter in the self-hardening properties of BFA. Therefore, for the formation of ettringite, the presence of dissolved portlandite, aluminate and calcium sulphate in the mix is necessary and this reaction occurs in a solution.

The differences between ashes with the same origin can be related with the combustion system, the characteristics of the fluidizing agent and the treatment system of the gaseous effluents [249]. The physical and chemical characteristics of BFA are important parameters to be taken into account for the valorisation of this material, such as its application in construction materials, namely concrete.

2.3.2 Legal Framework of Biomass Fly Ash on Concrete

BFA has been incorporated into concrete as a substitute of cement [22,29,246,251,275–283] mainly due to their physical and chemical properties. Fly ashes from rice husk, wood, wheat straw and sugar cane straw have similar pozzolanic properties to those of coal fly ash. The use of BFA, as a partial cement replacement, showed many positive effects on cement mixtures, and some of these results are summarized in [31,246]. However, there are some BFA that do not have pozzolanic properties.

Some BFA are incorporated into construction materials, but, there are no adequate standards for their utilization, and for that reason the standards used for the specification for CFA utilization in concrete are used as a comparison [110,253].

ASTM C 618 [253] shows two classes for CFA: Class C and Class F. This classification is based on some chemical and physical requirements. One of the biggest differences between Class C and Class F is the content of calcium oxide, CFA with CaO less than 7% belong to Class F and with more than 20% belong to Class C. Most parameters are the same for the two classes, and the difference is in the sum of SiO_2 plus Al_2O_3 plus Fe_2O_3 (minimum of 70% for Class F and minimum 50% for Class C).

EN 450-1 [110] defines the chemical and physical properties and conformity criteria for the utilization of CFA in concrete mixtures. The standard divided ashes into three categories in terms of LOI (A - ≤ 5%wt, B - ≤ 7%wt and C – 9%wt). As seen in Table 2.2, most biomass ashes belong to category A, one belongs to category B and another one to category C. But there are some BFA that have LOI values higher than 9%, which is the last category. In terms of chlorides, the content must not exceed 0.1%w, but most BFA present higher values (Table 2.2). On the other hand, in terms of SO_3 (≤ 3%wt), MgO (≤ 4%wt) and P_3O_5 (≤ 5%wt), most BFA meet the requirement.

Figure 2.9 compares the calcium content with the sum of oxides (SiO_2+ Al_2O_3+ Fe_2O_3) for BFA and compares it with coal fly ashes. Most BFA and CFA blends are considered by ASTM C 618 [253] as Class C ashes. One important parameter is the sum of SiO_2 plus Al_2O_3 plus Fe_2O_3 for which the standard requirement is a minimum of 70%, and it can be seen in Figure 2.9 that most BFA do not meet the requirement.

It can be observed that the classification of BFA by the European and American standards is very complex. Some BFA are considered Class C, but the diversity of wood fly ashes in terms of oxides or calcium content does not allow their classification by the standards used for classification of ashes to produce concrete. The classification of BFA leads to important issues, because BFA showed a wider variation in composition than CFA, but generally wood leads to the production of Class C fly ash [251].

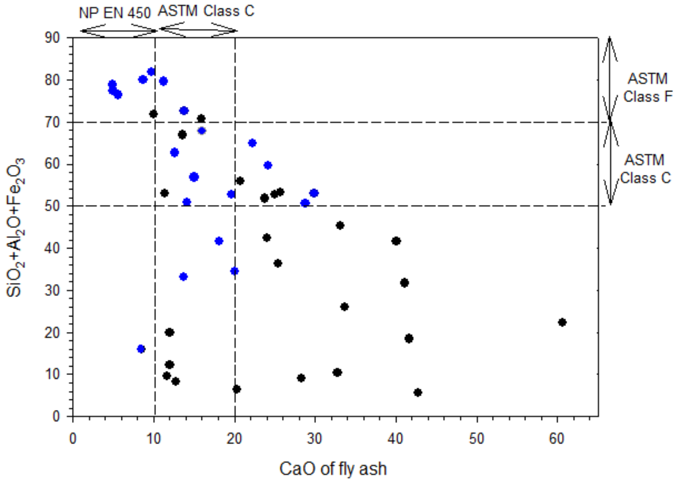


Figure 2.9 - Relationship between calcium oxide content and the sum of oxides for several biomass fly ashes (black colour) and a comparison with coal fly ashes (blue colour) based on [27,30,68,76,80,87,250,251,255,260,263,274,284–291]**.**

2.3.3 Effect of Using BFA on Concrete Properties

2.3.3.1 Microstructure of Cement Based Materials

The microstructure influences the mechanical behaviour of concrete. Rajamma *et al.* [30] studied the composition of pastes made with cement and two BFA after 28 days of curing by XRD and thermal analysis (TG/DTA). The main peaks that they observed were calcium hydroxide, calcium aluminium hydrate and calcium silicate, but they also found ettringite, calcite and silica. This result indicated that BFA has an influence on the phase formation in the mix. The results of XRD were corroborated by thermal analysis, which led to observing three peaks related to the decomposition of calcium silicate hydrated and ettringite (135-185 ºC), and calcium hydroxide decomposition (525-575 ºC). Pastes with BFA presented a decrease in the intensity of the calcium-hydrate peak. This was due to the fact that the CH produced is a function of the relative content of alite and belite contained in cement [30]. The variation in CH indicates the amount of calcium silicate gel formed. The pozzolanic reaction is also responsible for the decrease of CH, which can be a cause for one of the BFA, since it was determined that it presented high pozzolanicity. Firstly, the pozzolanic reaction occurs between amorphous siliceous materials and portlandite and forms calcium silicate hydrated [30]. The ratio of calcium/silicate and the water molecules agrees with the stoichiometry of the elements present in the reaction [30]. The third peak was related to the thermal decomposition of calcium carbonate (800 ºC).

Maschio *et al.* [68] observed in a semi-quantitative analysis of BFA from combustion of wood chips, in a small power plant, that those ashes mostly contained calcite, diopside, lime and periclase. The presence of diopside did not have a significant modification on the behaviour of the samples when compared to the reference mortars. This fact was related with the ratio of $(CaO+MgO)/SiO_2$ in those compounds that was similar to that in cement [68,292]. The high content of CaO and MgO present in ashes could improve the strength resistance of concrete or mortars with respect to the reference provided that the silica present in BFA is higher than the silica present in cement [68,293]. The presence of calcium carbonate could enhance the hydration heat because it allows a faster reaction of C_3S, which leads to the formation of carbosilicates and/or carboaluminates. However, it was not able to lead to better mechanical strength than pure C_3S. BFA has a high content of metals and during production of construction materials they can be dissolved in water in the original materials [68].

A comparison of the influence of coal-biomass blended fly ash and only coal fly ash on the hydration of cement was made in [80], in terms of unreacted C_3S content (by XRD analysis) and in terms of estimation of cement microstructure (by SEM-EDS analysis) (Table 2.3).

Table 2.3 - X-ray diffraction intensity of $Ca(OH)_2$ and C_3S during hydration of cement and a blend of cement plus coal-biomass fly ash mixtures. Adapted from [80]

Sample	**X-ray diffraction intensity of (%)**			
	$Ca(OH)_2$ (34.1º2θ Cu Kα)		C_3S (34.4º2θ Cu Kα)	
	At 28 day	At 180 day	At 28 day	At 180 day
0% of cement replacement	100.0	100.0	100.0	100.0
20% of cement replacement	82.8	66.8	85.2	82.7
40% of cement replacement	65.8	35.9	70.2	64.0

In terms of XRD analysis (Table 2.3), it was observed that the intensity of the $Ca(OH)_2$ peak in the presence of coal-biomass fly ash was higher than in the CFA mix. Mixtures with coal-biomass fly ash presented a lower degree of C_3S hydration compared to CFA mixtures [80]. The scanning microscope analysis showed that the incorporation of coal-biomass fly ash in cement changed the content and the morphology of calcium silicates hydrates (C-S-H). The pores content of C-S-H increased and this was due to the coarse grinding of these ashes and its low pozzolanic activity [80]. The analysis reported a higher CaO/SiO_2 molar ratio of C-S-H in the mix with coal-biomass ash than in the mix with CFA, which can be due to different degrees of polymerization of silicate anions in the mix with coal-biomass fly ash. Therefore, the C-S-H is less amorphous and the permeability of water and aggressive solution into the core of the specimen of coal-biomass fly ash was increased [80].

2.3.3.2 Fresh State Rheological Properties

Slump is a measure of consistency of concrete and shows the existence of variations in the uniformity of the mixtures [33]. This characteristic and workability are important due to the fact they are responsible for transporting of concrete [57]. The slump values of concrete decrease as cement is replaced by BFA [278]. Berra *et al.* [255] studied the effect of using three wood BFA on the workability of cement pastes. They observed that the partial cement replacement with those ashes decreased the mix’s workability, which was more distinct as the ash content increased. Several authors attributed this to the shape of particles and the higher specific surface area of porous of ashes in comparison with cement [156,255,277,285,294]. However, Sata *et al.* [280] observed that the amount of superplasticizer needs to maintain a given slump for a constant water to cement rate, increased when there was more cement replacement with BFA. This increase was due to the ash particles’ angular shape, irregular shape and high porosity and due to their high loss-on-ignition. This led to an increase in the water requirement and consequently to a high dosage of superplasticizers to maintain the same workability as the reference concrete [13,182,280].

The cementitious materials blended with cement are less reactive than plain cement during setting and early hardening. The water amount is very important in the fresh state of concrete mainly due to the fact that it controls: the rheology of the fresh concrete, the position of the binder particles in the mix, the initial solubility of the different ionic species of the binder, the electrical and thermal conductivity of the fresh concrete, and it creates the cohesion that makes concrete workable and at the same time it decreases segregation [33,61].

Some studies [31,255,276,277,280,295] showed that the use of BFA as a partial cement replacement material has interference on the workability of mortars and concrete. The incorporation of BFA leads to an increase in the amount of water required to produce pastes with a desired consistency [27,30]. Rajamma [98] and Coelho [295] observed interesting findings in their studies, with 10% replacement of cement with BFA, in the total binder's weight. The consistency and the water demand were similar to those of a plain cement mix, but for higher percentages of replacement the water demand increased. The water demand increased proportionately to the increase of cement replacement with biomass ashes (expressed as a percentage of the total binder's weight) [31].

Wang *et al.* [251] studied the water demand of different concrete mixtures using different supplementary materials (coal fly ash class C and F, sawdust and wood ash) (Figure 2.10). They observed that all samples had similar or lower water demand than pure cement mix, with the exception of the wood mix. The lower water demand of BFA mixtures is an advantage relative to plain cement mix and arises from the high-temperature treatment producing less pores and finer spherical particles, which has a role of filling mixtures. This leads to an increase of the fluidity of fresh concrete and reduces the water demand [193,251,257,296]. The effect of BFA on the consistency and water demand of concrete can be explained by the physical properties of the ashes. The high surface, the high organic content and the irregular shape allow the adsorption of water by the ash particles during mixing and, because they are hygroscopic by nature, this leads to higher water demands, as well as issues to maintain the same consistency [98,277].

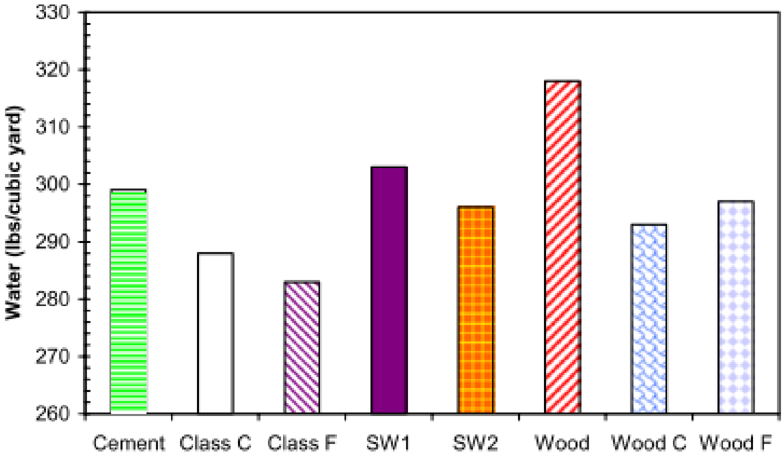


Figure 2.10 - Water demand for each design mix developed. Legend: coal fly ash (Class C and Class F), sawdust ash (SW1 and SW2), wood fly ash and blends with biomass and coal fly ash (Wood C and Wood F) [251]**.**

Fresh rheology explains the plastic state of fresh concrete and this parameter has been described in various studies [31,68,91,95,114,152,278,297–301]. Rajamma *et al.* [27] studied the rheological behaviour of mortars with 0, 10, 20 and 30%wt of cement replacement with two wood fly ashes. This parameter was evaluated in a Viskomat PC Rheometer [27]. The testing time was from 15 to 60 min, depending on the ash content. The authors estimated the yield stress and the plastic viscosity from the Bingham´s model (Figure 2.11).

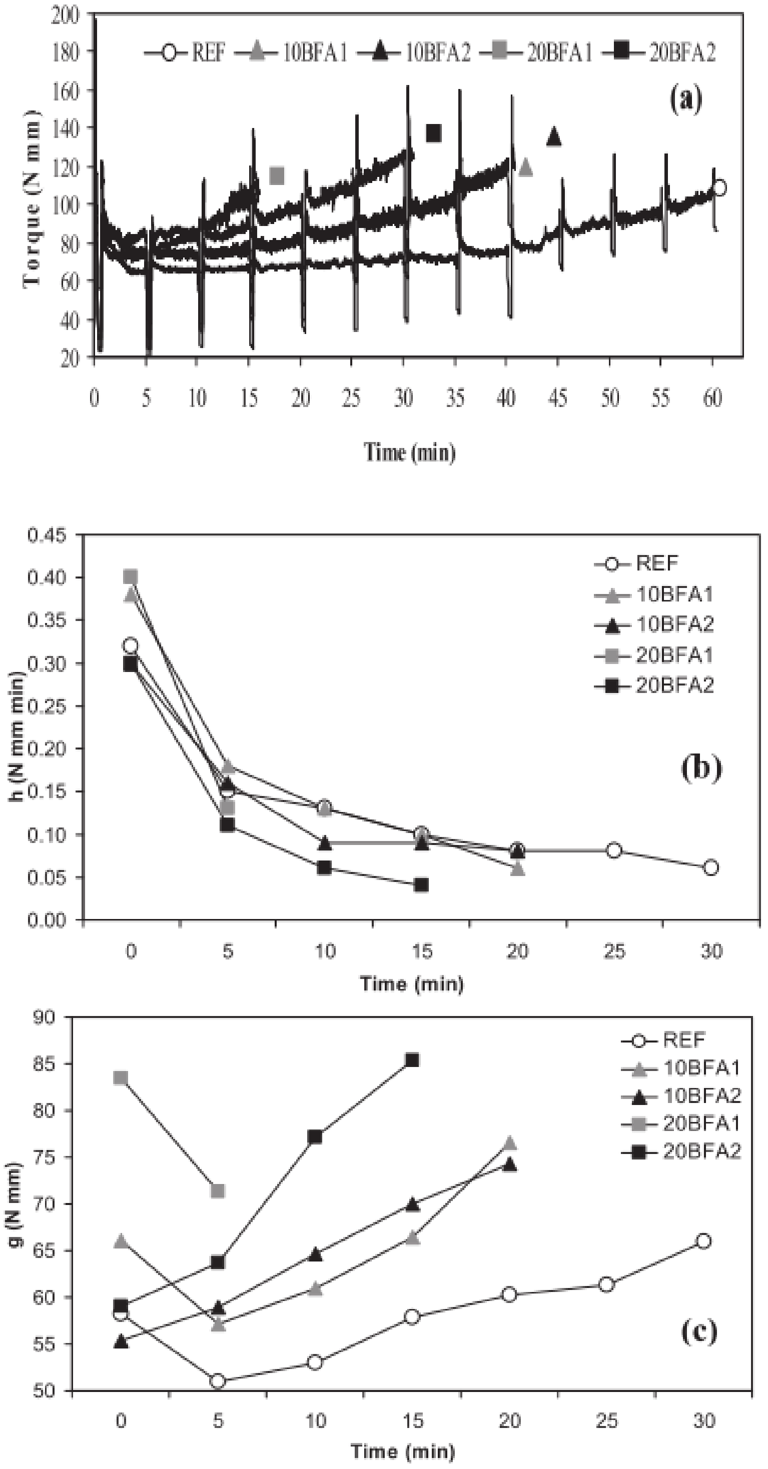


Figure 2.11 - Rheological behaviour for the different mortars with different percentages of cement replacement with biomass fly ashes (BFA). Legend: (a) torque, (b) plastic viscosity – h, (c) yield stress variation – g [27].

The authors reported that it was not possible to test this parameter in mortars with 30%wt of ashes, because the torque was insufficient to overcome the yield stress and plastically deform the material. Another interesting result was the fact that the torque increased at a constant rate directly dependent on the BFA fraction. The authors reported that the desirable fluidity was found when the amount of water added to the mix was enough to fill the pores, which avoids an intense interparticle friction of solid particles. This was contrary to what BFA particles do to the system since those particles tend to absorb water molecules, reducing the amount of free water and act as a lubricant for the movement of solid particles [27]. This leads to an increase in the particles friction and the plasticity of the mixtures reduces.

As seen in Figure 2.11, the viscosity of the different mortar mixtures tends to decrease and the differences between the mortars were attenuated. However, the yield stress increased after 5 minutes of tests and the mortars with ashes were stiffer than the cement mortar. Usually, the plastic viscosity depends on the volume of solid particles and their packing density; on the other hand, the yield stress is related to the flocculation and strength of the forces responsible for flocculation and represents the initial resistance to the flow [302–304].

Maschio *et al.* [68] studied the influence of replacing cement with BFA (in equivalent mass of 5%, 10%, 20% and 30%wt) on the rheological behaviour of mortars. The authors observed that the presence of those ashes caused modifications in the rheological behaviour when compared to the reference blend. They concluded that those changes were due to the presence of KCl and K_2SO_4 in the ashes, which led to the precipitation of gypsum and portlandite during the beginning of the hydration of the mixes.

The initial and final setting times are significant for practical applications of cement-based materials. Those times are an indicator of the workable state of the concrete fresh mix [134]. Some studies showed that using BFA blended with cement as a binder, delayed cement setting, and this effect increased with the increase when the level of cement substitution with ashes [27,30,31,251]. Berra *et al.* [255] observed a little retarding effect on the setting due to the substitution of cement with wood ashes. The dosage of BFA affects the setting times (Table 2.4), and the delay in setting time is greatest when a higher dosage is used. It is known that with the increase of alkali elements and organic matter present in ashes, there is a higher absorption of water by the ashes in the mixes and the setting times usually increase [30]. On the other hand, if in the mix some materials with low sulphur content but with high potassium content, such as the BFA, exist, the setting times tend to increase [78].

Several researches showed that various BFA (alone or blended with CFA) presented results within the range of results from CFA, indicating that even though BFA leads to a retardation of the setting times it does not have a disproportionate impact on concrete strength development [78,116,193,251].

Table 2.4 - Setting times of cement pastes. Adapted from [255]

Mix	Initial setting time (min)	Final setting time (min)
Paste Control	290	450
15% BFA1	360	460
30% BFA1	350	490
15% BFA2	290	520
30% BFA2	500	800
15% BFA3	270	650
30% BFA3	620	960

The heat evolution indicates the rate of the exothermic hydration reaction of concrete binder [33,61] and its determination is important to detect and record some modification induced by the presence of biomass fly ashes [78]. The evaluation of the effect of fly ashes from biomass conversion on the hydration behaviour was studied using calorimetric analysis by Rajamma *et al.* [30]. The authors showed that the highest temperature of hydration was observed in the sample containing cement only. The hydration process in all samples reached a steady temperature of approximately 24 ºC within 3 days. The authors observed that the hydration peak of samples with BFA was reached earlier than for samples consisting of cement only. They also observed that the heat of hydration decreased with the increase of the biomass ash content, indicating a reduction in the hydrating phases for the ash replaced cements. The authors reported that the differences observed in the hydration peak and in the hydration rate are probably influenced by the alkalis and chloride present in the BFA [78]. One important observation was the influence of the amount of ashes on the heat. As the content of ashes increased, the heat of hydration decreased, indicating a decrease in the hydration phases in the ash replaced cements. The decrease of the heat peaks showed that BFA influences the pastes and leads to a decrease in the hydration rate. This is related to the specific area [78] of BFA but also with the influence on pastes of the alkalis and chlorides present in the ashes [30]. The low heat in concrete contained BFA could be an advantage, because when the temperature gradients of concrete are large and if there are too many restraints to thermal contraction, the concrete may crack [61].

A comparison of the influence of a fly ash, resulting from co-combustion of coal and biomass, and a coal fly ash (Class F) on the hydration of cement (with 20%wt and 40%wt of replacement) was made by [80]. They observed that the effect of the type of fly ash on cement hydration is variable and that for coal-biomass fly ash mixes, the induction period was longer and the heat evolution main peak was smaller than for CFA mixes [80]. Furthermore, a delay of cement hydration in the presence of coal-biomass fly ash was reported. This led to the conclusion that some calcium ions were released to the solution. They observed that the presence of ash, from a co-combustion of coal and biomass, prolonged the induction period, due to the increase of the time when the supersaturated state could be reached and similar results were verified in [162]. The heat of hydration can be proportionally related with the number of nucleation sites by fly ashes for cement hydrates. This leads to the conclusion that the presence of coal-biomass fly ashes in cement provides a lower amount of nucleating sites for the precipitation of the hydration products [80].

2.3.3.3 Hardened State Properties

a) Mechanical Strength

Several authors [22,27,30,80,251,255,277,280,281,295] reported the influence of using biomass ashes as partial cement replacement on the mechanical strength of hardened concrete and mortars. In these studies it can be observed that the particle size of ashes, the level of replacement and the curing period influence the mechanical strength of concrete, and an example of those results is presented in Table 2.5.

Horsakulthai *et al.* [281] analysed the compressive strength of concrete mixes produced by incorporating of bagasse, rice husk and chip wood (BRWA) ashes blended. The level of cement replacement by ashes was 10%, 20% and 40% of the total binder weight; the tests were done after 7, 28, 91 and 180 days of curing (Table 2.5 and Figure 2.12-(a)). After 7 days of curing, only the concrete mixed with 20% of BRWA ash had higher compressive strength than the control plain cement concrete mix. After 28 days of curing, the concrete mixed with 10% and 20% of BRWA ash had higher compressive strength when compared with the control plain cement concrete mix. These results were due to the micro-filler effect and the fast pozzolanic reaction of the fine BRWA ash, which had a contribution to the denser filler of the cement paste matrix [31,281]. Concrete with 40% BRWA content, by total binder weight, showed lower compressive strength after 7 and 28 days of curing compared to the control concrete. After longer curing periods, the compressive strength had higher rates with 10 and 20% and similar with 40% of incorporation than the control mixes, and this was due to the pozzolanic reaction of high reactive ground BRWA ashes [281]. From these results, the authors [281] concluded that the optimum level of replacement was 20%, because it led to higher values of the compressive strength at 28 days of curing.

The incorporation of blends of BFA with CFA was done by [80]. The authors found that, at an early stage of curing, the compressive strength was lower than that of the reference mixes, and this was related with the delayed pozzolanic reaction [80]. The low compressive strength values for mixes with coal-biomass fly ash was due to its particles, which were coarser than those of coal fly ash and led to a decrease in the density of the binder matrix [80].

In Portugal, forest residues and wood biomass for the production of heat and power are widely used. Therefore, it is very important to understand the applicability of the ashes, produced during forest residues combustion, as cement replacement. Some studies were done using these type of ashes and are reported in Coelho [295], Rajamma *et al.* [30] and Barbosa *et al.* [22]. All studies showed a decrease in compressive and flexural strength with the increase of fly ash percentage. The authors concluded that a partial replacement of cement with BFA can be done at a level of up to 20%wt in order to maintain an acceptable mechanical strength. However, the substitution of cement with 10%wt of BFA provided the best results of mechanical strength.

Table 2.5 - Values of mechanical strength obtained for different construction materials produced with wood fly ash

Origin of ash	Curing time (days)	Construction Material	w/b	Level of cement replacement (%)	Compressive strength (MPa)	Ref.
Coal-Bio	2	Mortar	-	**0,20**,40	**24.6/15.7**/10.3	[80]
Forest Residues	3	Mortar	0.50	**0,5,10**	**32.2/34.8/36.7**	[305]
Forest Residues	7	Mortar	0.5	**0,5,**10	**42.9/39.1/**36.5	[305]
Wood	7	Concrete	0.40	**0,5,10,**15,18,20	**35.7/34.1**/33.9/32.7/33.1/30.4	[286]
Wood	7	Concrete	0.49	**0,20**,30,40	**46/39/**32/26	[306]
BRWA	7	Concrete	0.6	**0**/10/**20**/40	**19.0**/18.5/**21.0**/16.0	[281]
Forest Residues	28	Mortar	0.55/0.55/0.60/0.65	**0**,**10**,20,30	**41.5**/**43.3**/32.5/22.6	[30]
Forest Residues	28	Mortar	0.55/0.55/0.55/0.60	**0**,10,**20**,30	**41.5**/**35.8**/30.1/26.7	[30]
Forest Residues	28	Mortar	0.55	**0**,**10**,20,30	**30.1**/**33.8**/29.8/20.9	[295]
Forest Residues	28	Mortar	0.55	**0**,**10**,20,30	**30.1**/**31.0/**25.4/20.8	[295]
Forest Residues	28	Mortar	0.5	**0,5,**10	**49.5/47.5/**44.3	[305]
Wood	28	Concrete	0.45	**0,5,**10,15,**18,**20	**33.0/**31.1/30.7/**32.3/**30.1/27.7	[286]
Wood	28	Concrete	0.49	**0,20**,30,40	**57/47/**42/39	[306]
Coal-Bio	28	Mortar	-	**0**,**20**,40	**44.7**/**30.9**/20.8	[80]
BRWA	28	Concrete	0.6	**0**/**10**/**20**/40	**24.6**/**24.5**/**26.0**/20.5	[281]
Wood	56	Concrete	0.49	**0,20,30,**40	**66/53/53/**52	[306]
Wood	84	Concrete	0.49	**0**,20,30,**40**	**68**/56/57/**60**	[306]
Forest Residues	90	Mortar	0.5	**0,5,10**	**52.3/56.8/50.7**	[305]
Coal-Bio	90	Mortar	-	**0**,**20**,40	**54.4**/**45.1**/32.6	[80]
BRWA	91	Concrete	0.6	**0**/**10**/**20**/**40**	**29.0**/**33.4**/**38.5**/**29.0**	[281]
Wood	112	Concrete	0.49	**0**,20,**30**,**40**	**69**/58/**62**/**61**	[306]
Coal-Bio	180	Mortar	-	**0**,**20**,40	**60.2**/**56.0**/42.0	[80]
BRWA	180	Concrete	0.6	**0**/**10**/**20**/40	**31.5**/**36.5**/**40.5**/**34.5**	[281]
Forest Residues	365	Mortar	0.5	**0,5,10**	**53.4/62.4/57.4**	[305]

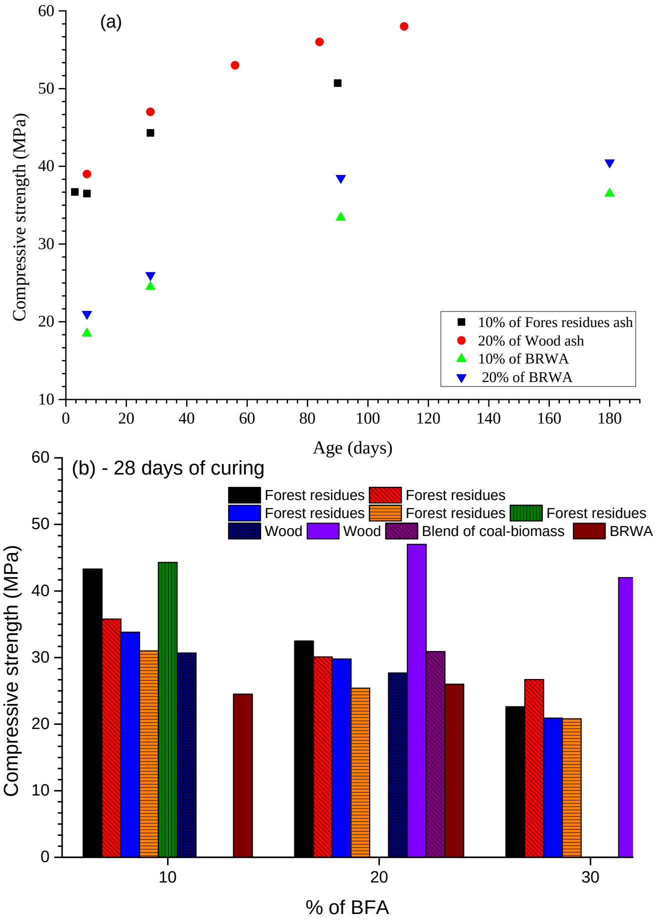


Figure 2.12 - Compressive strength development over time for two (10% and 20%) cement replacement fractions (a). Compressive strength development over the cement replacement by biomass fly ash, for samples with 28 days of curing (b) based on the values presented in Table 2.5.

Furthermore, Barbosa *et al.* [22] also studied the relationship between the curing period and the compressive strength and observed that BFA delayed the hydration process for the curing time studied (60 and 90 days) (Table 2.5 and Figure 2.12-(b)). The authors verified that during the curing period, concrete with lower replacement level of cement had a higher compressive strength.

The literature shows that, for different particle sizes of BFA and for different percentages of cement replacement, the values for compressive strength change (Table 2.5), even though all of the BFA discussed in this section had a wood origin. On the other hand, for a replacement of high content of cement by BFA, the values of compressive strength were lower than for the reference mixes.

b) Porosity

One of the ways to determine the open porosity of concrete is by the water absorption test. During the water absorption test, the water will occupy the outside empty spaces connected present in dry concrete. Thus, the water absorption by immersion analysis gives a measure of the open pore volume or open porosity of hardened concrete [283]. Udoeyo *et al.* [307] measured the water absorption capacity of concrete made with a BFA resulting for the combustion of wood waste ash. BFA of pre-treated timber at 5-30%wt by weight of cement was added as a supplement to the concrete mix. The authors observed an increase in the water absorbed with the increase in ash content and similar results were observed in [308]. At 5%wt of BFA the water absorption content was 0.4% that increased to 1.05% at 30%wt of BFA content [307]. It is important to note that the values observed by the authors are far lower than the maximum accepted for construction materials (10%) [309].

Rajamma [98] studied the porosity by water absorption with a water immersion (during 48 hours) test on mortars, as seen in Figure 2.13. The results showed an increase of the porosity level of all mortars with BFA as cement replacement material, for all ages. It can also be observed that there is a significant decrease in the porosity for BFA mortars between 28 and 180 days, compared to the cement mortar (in Figure 2.13 it is denominated REF1). The author stated that these variations in the results are mainly due to the decrease of hydrated compound content and to the latent hydration of BFA when reacting in the presence of $Ca(OH)_2$. Rajamma [98] also studied the porosity and the pore diameter of mortars by mercury intrusion porosimetry (MIP). The results showed an increase in the total porosity with the increase of cement replacement by BFA, although the median pore diameters decreased. The mean diameter decreased due to the finer particle inclusion (since the BFA was sieved at 75 μm before incorporation on mortars) which acted as a better packing filling effect. However, the porosity increased due to less net hydration in the BFA incorporated mortars [98]. The authors reported that by the end of 720 days the differences between the samples in terms of porosity were insignificant.

Tkaczewska and Malolepszy [80] studied the porosity of coal-biomass cement pastes by the mercury intrusion porosimetry method also. The authors studied two cement replacement fractions 20% and 40% by mass. Using coal-biomass ash in cement increases the total porosity of pastes at 180 days compared to the control one (only cement as binder). This result is caused by the coarser fineness of the coal-biomass fly ashes and its low pozzolanic activity [80]. The authors reported that this ash is less effective in reducing the average pore diameter and this is a result of worse packing of its coarse particles and with a little amount of amorphous C-S-H resulting from the pozzolanic reaction [80,310].

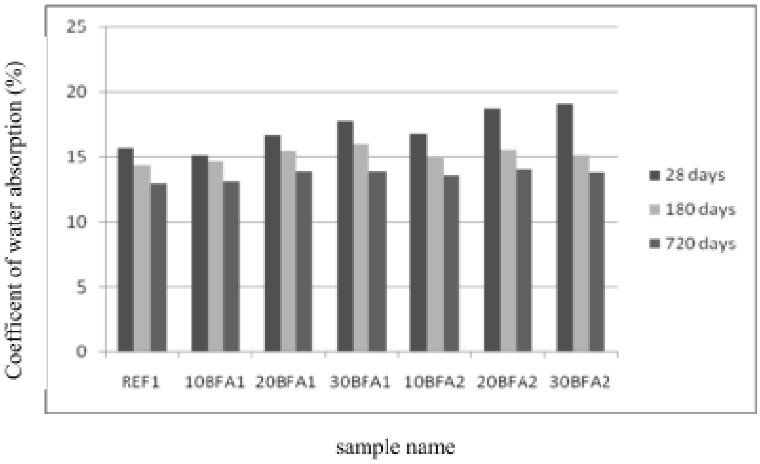


Figure 2.13 - Porosity of biomass fly ash cement mortars determined by water absorption [98]**. Legend: Ref1 is the reference cement mortar, BFA1 and BFA2 are two types of biomass fly ashes, the numbers 10, 20 and 30 before the BFA are the percentage of cement replacement.**

c) Coefficient of Air Permeability

Cheah and Ramli [311] studied the intrinsic air permeability values of hardened mortar using an air permeability cell in accordance with the method proposed by [312]. The tests were done in mortars with different percentages of high calcium wood ash for two curing ages (28 and 90 days) as can be seen in Table 2.6. The authors reported that, at 28 days, a decrease in the air permeability degree for mortars containing BFA with high calcium compared to the reference mortar, and the mortars with 5% of high calcium BFA presented the lowest. The values of air permeability increased gradually with the increase of cement replaced with high calcium BFA, which was probably due to the dominating effect of micro-filler action of wood ash particles. This has a contribution to the refinement of the pore structures of high calcium BFA mortars at an early age. Furthermore, an increase in high calcium BFA content and a corresponding reactive silica amount did not contribute to a reduction in intrinsic air permeability of the mix at 28 days of curing [311].

Table 2.6 - Intrinsic air permeability of mortars with various high calcium BFA contents. Adapted from [311]

%High calcium BFA	28 days K_t (x10E^{-16}m^2)	90 days K_t (x10E^{-16}m^2)
0	0.36	0.29
5	0.25	0.22
10	0.27	0.25
15	0.28	0.25
20	0.33	0.32
25	0.35	0.33

A decrease of the air permeability of the mortars with 5-15%wt of high calcium BFA was also observed, but an increase in mortars with 20 and 25%wt of cement replacement was observed. For mortar with 5-15%wt of BFA, there is a presence of fine factions of ashes in the aggregate-cement paste interfacial transition zone resulting in a significant enhancement of the quality of the zones. Therefore, the degree of continuing the pores of mortar was reduced in that order, which resulted in a lower level of mix permeability. For a higher cement replacement, the dilution of cement content in the mix results in a lower rate of hydration and microstructure development of cement paste [311].

d) Electrical Resistivity

The results in the electrical resistivity are associated with the effect of the overall reduction of the pore size [10, 55]. Its measure is an important instrument to study the hydration reaction [27]. Rajamma *et al.* [27] studied the electrical resistivity of pastes with different cement substitutions with two BFA. The authors observed a similar behaviour for all pastes in terms of electrical resistivity. Initially, this parameter increased due to the formation of ettringite. After that, they reported a constant rate until a second steep stage. This second step was coincident with the final setting. The important observation was that the reference paste (with cement only) showed higher resistivity values and a faster increase with curing when compared to the pastes with biomass ashes. This was due to a faster setting of the cement pastes. A retardation of electrical resistivity of the pastes containing higher ash content was noted [27].

The electrical resistivity also gives some indications about the permeability of concrete and the probability of corrosion in reinforced concrete [252]. Lessard *et al.* [252] studied the resistivity of paver-compacted concrete at 28 and 91 days of age through the application of an electrical current through two electrodes attached to the concrete specimen ends. The results showed that BFA concrete is classified as having very low permeability, according to the ACI Committee 222 [313], with values in the range of 58 and 146 kΩ·cm [252]. One important observation reported by the authors was that with the increase in the cement replacement with BFA, a decrease in the electrical resistivity was noted. One of the explanations for this fact is that these concretes (with BFA) are less dense and have a porous binder matrix [252].

e) Resistance to Chloride Penetration and Diffusion

One important issue related to the durability of concrete structures is the ingress of chloride ions, which can lead to the corrosion of the steel reinforcement [116,314]. This corrosion can occur when a certain threshold value of chloride concentration in the interface between the reinforcing bars and the cementitious matrix is exceeded causing the disruption of the steel's protective passive film. This value is dependent on the type of material and environmental factors, such as water/cement ratio, curing conditions and testing date [222,277,314,315].

The literature showed that the introduction of pozzolanic materials improves the protection against chloride-induced corrosion of steel reinforcement, mainly because it reduces the permeability and diffusivity of concrete [86, 89]. Wang *et al.* [277] studied the rapid chloride permeability of concrete with wood fly ash, coal fly ash type C and type F (Class C and Class F - Figure 2.14) and blends (80%wt of CFA type C or CFA type F and 20%wt of BFA (Wood C and Wood F - Figure 2.14)) according to ASTM C 1202-91. The authors observed that the wood mixes had similar passing charges than the pure cement mix, the class C fly ash mixes had lower permeability than the wood mixes and class F fly ash had the lowest permeability and the blend coal type C-biomass ash presented permeability between the mixes (wood and class C).

The differences observed can be related with different parameters: i) the fly ash particle size, the modification of pore size distribution and the changing of the chemistry pore mainly during the pozzolanic reaction. During the discussion of the results, the authors took into account several facts: i) wood fly ash has a much coarser particle size than Class C and Class F ashes as can be seen in [251]; ii) wood ashes, class C and class F have similar pozzolanic reactivity that was indicated by the hydrated lime consumption at, in case of this study, two months [277]; iii) in this case wood fly ash and Class C fly ash had better pore size modification than Class F fly ash mainly due to their higher reactivity; and iv) the equivalent alkali percentage as per ASTM C 33 is wood – 1.78, class C – 1.03 and class F -0.53 [277]. These results can also be due to the fact that the aluminates presented in the coal fly ash adsorb the chlorides on the surfaces of the fly ash particles forming chloroaluminates, which led to a decrease in the free chloride. In other words, coal fly ash has a greater chloride binding capacity [317].

The authors reported that because wood fly ash had a larger particle size and higher alkalis, the wood mixes had the highest permeability among all fly ash concrete (the blend ashes had a permeability values between the concretes with wood ashes only and the concrete with CFA only). Class C has higher equivalent alkali than Class F, and this was the reason for a higher permeability of Class C concrete than Class F. Similar results were found in [318].

The binding capacity of chlorides in hydrated cement paste affects the transport rate of chlorides into concrete and the amount of chlorides required to initiate active corrosion [319]. The aluminate and ferrite phases present in the binder are capable of binding chlorides by forming chloroaluminates hydrates and chloroferrite hydrates, but the last forms are considered less important because they have high solubility and a slow rate of formation [317]. CFA cement blends have a greater chloride binding capacity when compared with normal cement, mainly because of the adsorption of chlorides on the surface of the fly ash particles [320] and chlorides are incorporated in the aluminate-rich pozzolanic products of fly ash cement blends, removing large quantities of chlorides from the aqueous phases [317]. Some studies [321,322] showed that BFA has a similar behaviour to CFA. However, it is not very well described in the literature if BFA presents similar chloride binding capacity to CFA.

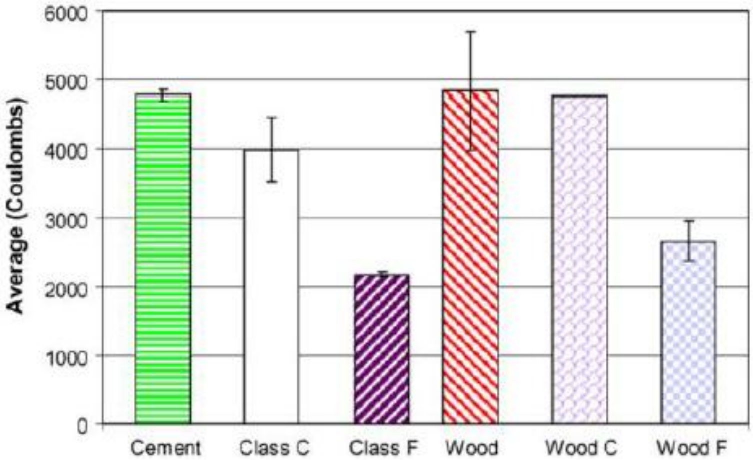


Figure 2.14 - Rapid chloride permeability test (average of two samples) at 56 days of concretes with: cement, coal ash (Class C and Class F), wood ash and blend of coal-biomass ash (Wood C and Wood F). Adapted from [277]

Pavoine *et al.* [224] studied the rapid chloride ion penetration of concrete with fly ash from the combustion of wastepaper de-inking sludge and wood (WSW) residues in a fluidized bed for two water/binder ratio (w/b=0.4 and w/b=0.55). After 28 days, the chloride ion penetration resistance was similar for the two water/binder ratios tested. For the w/b ratio of 0.55, the electrical charge of WSW and cement concretes was comparable and never achieved the moderate domain comprised between 2000 and 4000 Coulombs.

Horsakulthai *et al.* [281] studied the rapid chloride migration of bagasse-rice husk-wood ash concrete, with 10, 20 and 40%wt of cement replacement with biomass ashes. The use of BRWA led to a decrease in the depth of penetration of chloride ions with the increase in the replacement ratios. For concretes with a w/b of 0.6, the highest chloride penetration depth was registered for the control concrete (44.5 mm). The depth observed for the 10, 20 and 40%wt BRWA concrete was 31.6, 15.4 and 11.0 mm, respectively. One of the possible reasons for these results was the reduction in the average pore size of concretes [323], the porosity of the interfacial transition zone between the matrix aggregate [275] and the chloride binding effect [317]. Similar results were observed in concretes with a water/binder ratio of 0.45. The non-steady state chloride diffusion coefficients from modified Fick's second law were calculated. In general, a similar trend of the chloride diffusion coefficient of concrete was observed to that of the penetration depth results. The coefficients for the two control concrete were 21.1E-12 m^2/s (w/b=0.6) and 7.0E-12 m^2/s (w/b=0.45). The coefficients for concrete with w/b of 0.6 were 14.8E-12, 7.0E-12 and 5.0E-12 m^2/s for 10BRWA, 20BRWA and 40BRWA concrete, respectively. And for concrete with a w/b of 0.45, the chloride diffusion coefficients were 7.8E-12 and 3.6E-12 m^2/s for 10BRWA and 20BRWA, respectively. These results showed an improvement in the chloride penetration resistance, with a reduction of 30-40%, 65-70% and 75% of the chloride diffusion for 10%, 20% and 40 % of BRWA, respectively.

f) Carbonation

Carbonation is the chemical reaction between the CO_2 present in the air with the calcareous components of hardened cement paste [116]. Fly ashes react with $Ca(OH)_2$ to form similar C-S-H phases to the hydrates. The calcium hydroxide is consumed and the alkalinity of material decreases, but this consumption depends on the amount of reactive silica present in fly ash and on the duration of hydration [116]. Ramos *et al.* [324] studied the resistance to carbonation of mortars with 10 and 20%wt of BFA as a cement replacement. The authors reported that the carbonation depth for blended cement mortars was greater than for the plain cement mortar. The carbonation increased with the increase in the BFA content, which is similar to the trend of other pozzolanic materials. They suggested that this result is due to CH reduction and consequent pH reduction.

Cheah and Ramli [311] studied the carbonation depth of mortar containing high calcium wood ash as cement replacement (5-25%). The results showed that 5%wt of BFA contributed to the reduction of the average depth of the carbonation zone compared to mortar made only with cement. For the other cement substitutions, the carbonation depth was higher than for the control mortar and varied proportionately with the cement replacement level. This behaviour is consistent with the results achieved by [92,325].

At higher levels of cement replaced with BFA, there are more amorphous silica minerals for a reaction with $Ca(OH)_2$ produced from the hydration reaction of cement, forming calcium silicate hydrated gel leaving less quantity of free $Ca(OH)_2$ in the hardened mix [311]. Therefore, less quantity of CO_2 is needed for the reaction with $Ca(OH)_2$ to produce $CaCO_3$ [33]. The mortars with 5%wt of BFA had less carbonation depth most probably due to low pozzolanic activity and due to an inadequate quantity of amorphous silica and low permeability of the mix. The authors confirmed this conclusion by the chemical analysis of the 5%wt of BFA mortar [311].

It is known that the replacement of cement with a high volume of coal fly ash increases the carbonation of concrete [326]. This is usually, this is due to the consumption of $Ca(OH)_2$ in the pozzolanic reaction even before the initiation of carbonation [326]. In blended concretes, the reactions which involve un-hydrated constituents and calcium hydrate result in the calcium carbonate and hydrated silica, as the end products of reaction [327]. The hydrated calcium silicate is dissolved when the pH value and the calcium ions concentration drops, due to consumption of $Ca(OH)_2$. The monosulphate and ettringite decomposes at pH of 11.6 and 10.6, respectively. Then, the calcium ions bind to $CaCO_3$ of which there are only some ions in silica gel [328]. This leads to a lower CaO/SiO_2 content in concrete. To compensate these issues, some authors [21,211] use a commercial hydrated lime (calcium hydroxide) in the binder composition to provide more alkalinity to the concrete solution with good results. The utilization of BFA in a lower concentration leads to an improvement in terms of carbonation resistance, as shown in [311], and this could be due to the fact that BFA gives extra alkalinity (an extra calcium content) to the concrete mix.

g) Freezing and Thawing Resistance, Acid and Sulphate Resistance, Alkali Silica Reaction

There are other studies and tests that show the effect of BFA on the durability of concrete. However, not much information is available and in addition it was not the focus of this study, and for that reason, only a brief synopsis is presented.

There are not many studies on the behaviour of freezing and thawing resistance of concrete with the incorporation of biomass fly ash. Wang *et al.* [277] studied the durability of BFA concrete in terms of freezing and thawing resistance according to ASTM C666. They studied concrete containing CFA only (Class C or F), BFA only or blends with Class C and Class F fly ash. The results showed a less than or equal or weight loss of all concrete mixes relative to the control plain cement concrete, with the exception of the concrete made with CFA Class C. This suggests that the impact on freezing and thawing behaviour is reduced when BFA is used, and these results are in accordance with those of other studies [116,329].

The harmful action that involves sulphate ions is defined as the sulphate attack [330]. The utilization of pozzolans and cement as binder in mortars or concrete revealed an improvement in the resistance against sulphate attack [331–333]. However, there is no information about the effect of several types of BFA on the sulphate resistance of concrete, such as wood waste ash.

The acid resistance of BFA blended cement concrete mix was studied by [334]. Two sets of concrete specimen with mix proportions of 1:2:4 by weight and water to binder ratio of 0.65 were prepared. The first one contained cement only as binder and the other contained 15%wt of cement replaced with BFA. The hardened specimens were immersed in 20% of nitric acid. A loss of the mass of specimens was noted, but after 9 weeks, a slight increase of the mass was observed, due to absorption of water. After 10 weeks of testing, a decrease in the mass was registered for both types of concrete. However, the loss of mass was more significant in concretes made only with cement [309,334].

Inside concrete some internal expansive phenomenon’s can occur, namely an alkali aggregate reaction (AAR) [112]. One particular reaction, the alkali-silica reaction (ASR), is in the origin of several problems in concrete structures [112]. The hydroxyl ions react with potassium and sodium ions present in the interstitial solution of concrete. The reaction allows the formation of an alkaline hygroscopic gel [335,336], which absorbs water and expands. The expansion and water absorption originates some internal stresses in concrete and this promotes its cracking. This leads to a decrease in the mechanical resistance and durability of concrete [112]. Esteves *et* *al.* [263] studied the incorporation of 20 and 30%wt of BFA from Portuguese industrial plants, in mortars. The main goal was to test the BFA’s ability to resist damage due to alkali silica reaction. They observed that mortar containing 20 and 30%wt of BFA resisted to the alkali silica reaction. They found a significant reduction in the expansion of mortars, and this expansion decreased with the increase in cement replacement content. The substitution of cement by BFA has an improvement to the mitigation of ASR [29,263], even better than when CFA is used as cement replacement material. This is due to the fact that BFA has more alkalinity than CFA [29].

2.3.3.4 Effect of Using BFA on Concrete Sustainability

a) Leaching of Eluates of Construction Materials

Barbosa *et al.* [22] studied the influence of BFA on the leaching and ecotoxicological properties of concrete, using water or marine eluates. The pH of eluates with water was around 10. This indicates that there is some release of some oxides from concrete to water, but this finding was the same for concrete with cement and/or BFA. However, when marine eluates were used, the pH did not change. The results showed low concentrations of chemical elements on the eluates, using fresh water or a marine solution. Similar results were found in [246]. The emission of chemical elements was similar or lower than that verified for the reference concrete. In terms of ecotoxicological levels, it was observed that the levels of ecotoxicity were reduced and similar to those of the plain cement concrete.

b) Global Warming Potential

Using blended cements in concrete production led to several environmental advantages that include reduced CO_2 emissions, reduced fuel consumption and material valorisation of the supplementary cementing materials [32]. The understanding of the environmental impact of concrete with wood fly ash is related to the study of economic and ecological characteristics of materials [337]. Kara *et al.* [306] estimated the energy consumption of concrete with cement substitution with BFA. They reported that using BFA as a construction material is beneficial to the landfill and decrease CO_2 emissions to the atmosphere. Teixeira *et al.* [338] studied the environmental performance of concrete with BFA as a cement substitute. The authors observed that concrete made with BFA had a better environmental performance than concrete with CFA or/and with cement.

2.4 Conclusions

Biomass fly ash has been used as a partial cement substitute, as a pozzolanic material. However, there are still some doubts about whether all BFAs are pozzolanic materials or if some of them have very low pozzolanic activity. Using BFA affects the fresh properties of concrete (workability, setting times and consistency). As a consequence of the changes on the workability and consistency promoted by the incorporation of BFA in concrete, there is an influence on the rheological properties of concrete.

The heat of concrete hydration binders is influenced by BFA and it was observed that an increase in the amount of BFA leads to a decrease in heat. This showed that the hydration phase in materials with cement replaced with ashes also decreases too. In this case, the decrease in the heat could be an advantage, because it could prevent the occurrence of cracking phenomena.

BFA retards the reactions of hydration and causes some changes in the rheological behaviour and microstructure of concrete. BFA leads to an increase of the open porosity and a decrease in the air permeability of hardened concrete. However, some electric resistivity tests showed that mortars with BFA are classified as having very low permeability.

Concrete with BFA showed different behaviours in terms of mechanical strength, and this parameter is dependent on the percentage of cement replacement. In some cases the mechanical strength decreased with the increase in cement replacement with BFA and in general, BFA is less reactive than CFA.

In terms of durability, some authors observed an increase in the chlorides penetration but others observed a decrease in this parameter when BFA was used. The decrease in this parameter was observed when BFA was used mixed with another pozzolanic material as a cement replacement, in this case the synergetic behaviour of the two materials was better than when BFA is only used. Furthermore, in terms of carbonation, it can be concluded that only when it is used a small content of BFA is used, constructions materials have more resistance to carbonation than mixes made with cement only as a binder or than CFA concrete.

BFA leads to mortars and concretes with more resistance to alkali-silica reactions. On the other hand, the presence of BFA in concrete does not cause a different behaviour from that of the reference concrete in terms of freezing and thawing resistance, and neither one has a significant influence on its leaching. However, in terms of environmental performance, BFA concrete presents better results than plain cement concrete.

Furthermore, there is a lack of information concerning their effect in HVFAC and the synergic effect of these two materials in this type of concrete. This allows the production of concrete with low environmental impacts. It is important to understand if the incorporation of the two fly ashes or just BFA can minimize the issues related with HVFAC, namely retardation of gain of mechanical strength and resistance to carbonation, which will be the focus of the experimental study presented in this thesis. As was observed, BFA is more alkaline than CFA, but there are not studies incorporating small amounts of BFA as an alkaline material, which gives alkalinity that is lost by replacing high amounts of cement with fly ash from coal.

Chapter 3

Materials and Methods

3.1 Introduction

In this chapter, the description and characterization of the used materials, as well as the analysis, equipment and procedures used to develop the studied compositions is presented.

The used materials were selected according to their quality and conformity to minimize the interferences that may influence the results of the analysis. After selecting the materials and performing their extensive characterization, the study of the different paste and mortar formulations was carried out in order to assess the effect of biomass fly ash (BFA) as a cement replacement material and as alkaline material, with the main goals of finding some optimized formulations that can minimize the issues related with the cement replacement in high contents. These optimized formulations were used to produce high volume fly ash concretes (HVFAC). The objective of these formulations is to minimize issues related to: i) retardation of early gain of mechanical strength; ii) durability issues, mainly focused on the carbonation resistance; and iii) sensitivity to curing.

The laboratory experiments were focused on: i) the hydration of cement-based pastes with an incorporation of biomass/coal fly ashes, to study just the binder part of concrete; ii) the study of the fresh and hardened properties of mortars; iii) the study of the fresh and hardened properties of HVFAC. The hydration study was done by thermogravimetric analysis and X-ray diffraction analysis. Fresh state mortars and concrete physical parameters were quantified, namely: the consistency (workability), density and air voids of the mixtures. Tests carried out in hardened state mortars and concrete, focused on the mechanical characteristics and durability of the different compositions. Most analyses were performed in the Construction Materials Laboratory at the Department of Civil Engineering, at the University of Minho.

To study the influence of curing, two different curing procedures for the HVFAC were analysed and will also be presented and discussed in this chapter.

3.2 Materials

3.2.1 Cement

In the course of this study, Portland cement type I, class 42.5 R (CEM I 42.5R), was used. This cement is certified according to [339] and was kindly provided by the Secil Group. The cement was delivered in two batches: the first one was used to produce the pastes and mortars (batch1) and the second one was used in the concrete production (batch 2). The physical and chemical characteristics of the two cement batches are shown below. However, as batch 1 was used for the study of hydration reactions of cement/fly ashes pastes and also to produce mortars in order to find the optimized formulations, this batch of cement was also characterised in terms of particle size distribution and thermogravimetric analysis.

The particle size distribution of cement is presented in Figure 3.1 and it was determined, in a liquid environment, by laser diffraction using CILAS 920 equipment. As can be observed, the particles presented an average diameter of 9.3 µm.

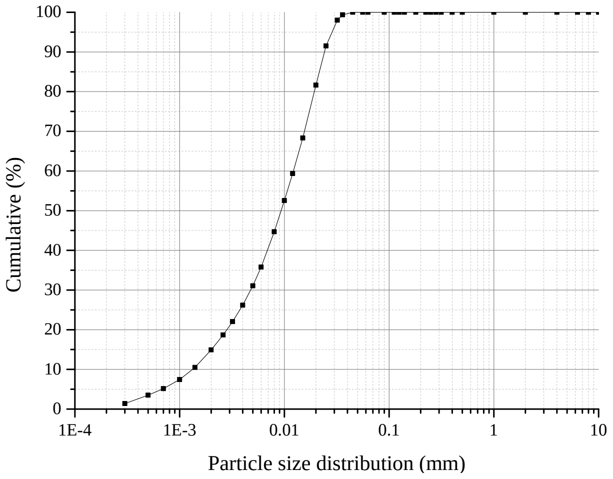


Figure 3.1 – Cumulative particle size distribution of cement

The thermal analysis of cement was done using a STA, Netzsch 402 EP with a heating rate of 10 ºC/min and it is presented in Figure 3.2. A slight decrease in weight around 100 ºC was observed. This loss of weight is related with the release of water adsorbed in the cement particles. With an increasing temperature, a significant decrease in weight was observed in the range of 600 to 835 ºC, associated with an endothermic process. This weight loss must be related to the thermal decomposition of carbonates such as $CaCO_3$. Similar results were observed in several studies [340,341].

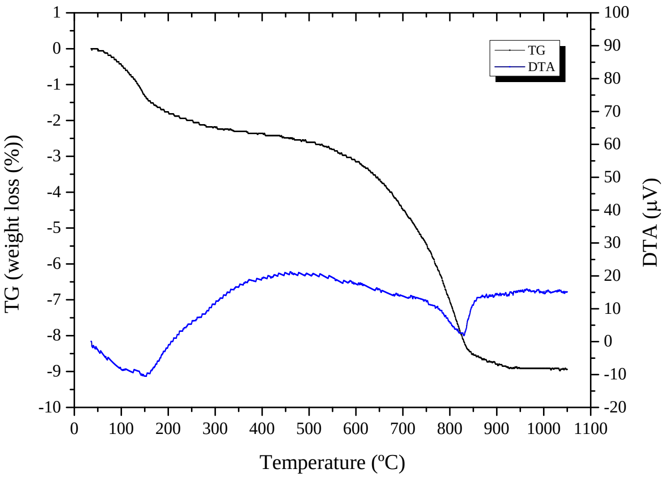


Figure 3.2 - Thermogravimetric analysis of Cement

Several other physical properties and the chemical composition were obtained by the datasheet provided by the manufacturer and are shown in Table 3.1, Table 3.2 and Table 3.3. The two batches of cement presented similar characteristics, with a specific weight of 3.12 and 3.13 g/cm^3 and with a Blaine specific surface of 4072 and 4099 cm^2/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 and 3.5%wt) is observed. These values are expected and usual for a Portland cement [85,342].

Table 3.1 – Mechanical test [343]

Age (days)	Flexural Strength (MPa)		Compressive Strength (MPa)	
	Lot 1	Lot 2	Lot 1	Lot 2
2	5.9	5.9	32.2	32.7
7	7.8	7.9	47.7	47.2
28	9.0	9.0	58.2	57.9

Table 3.2 – Physical tests

Tests		Year	
		Lot 1	Lot 2
Specific weight (g/cm^3)		3.12	3.13
Blaine specific surface (cm^2/g)		4072	4099
Sieve Residue (%)	45 µm	3.20	3.42
	32µm	9.26	9.50
Water demand (%)		28.8	28.9
Setting Time (min)	Initial	189	172
	Final	260	241
Soundness (mm)		0.84	1.10

Table 3.3 – Chemical composition and loss-on-ignition

Analysis	Year	
	Lot 1	Lot 2
Loss on ignition (%)	2.33	2.34
Insoluble Residue (%)	1.35	1.22
SiO_2 (%)	19.07	20.17
Al_2O_3 (%)	4.43	4.41
Fe_2O_3 (%)	3.50	3.40
CaO (%)	63.80	62.97
MgO (%)	1.87	1.80
SO_3 (%)	3.28	3.20
K_2O (%)	0.90	0.79
Na_2O (%)	0.21	0.20
Cl^- (%)	0.05	0.08

3.2.2 Coal Fly Ash and Biomass Fly Ash

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. Coal fly ash (CFA) was sampled from a Portuguese thermoelectric power plant (Figure 3.3). Both ashes were characterised in terms of particle size distribution, loss on ignition, chemical composition, X-ray diffraction, thermal analysis, reactivity and pozzolanic activity index.

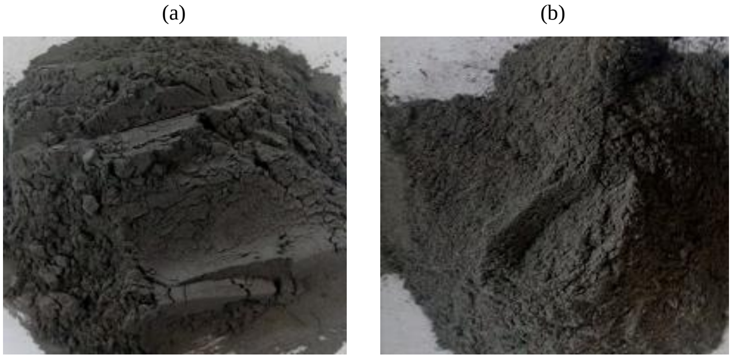


Figure 3.3 – Coal fly ash (a) and biomass fly ash (b)

3.2.2.1 Particle Size Distribution and Density

The particle size distribution of the ashes was determined, in a liquid environment, by laser diffraction using CILAS 920 equipment. The particle size of the fly ashes is presented in Figure 3.4. The particle size distribution of CFA is similar to that of cement with an average diameter of about 9 µm (Figure 3.1). However, BFA presented coarser particles and its size distribution is significantly different from that of CFA and cement. The average diameter of BFA is about 47 µm. The density of CFA and BFA is 2420 and 2619 kg/m^3, respectively. The density was determined according to [344].

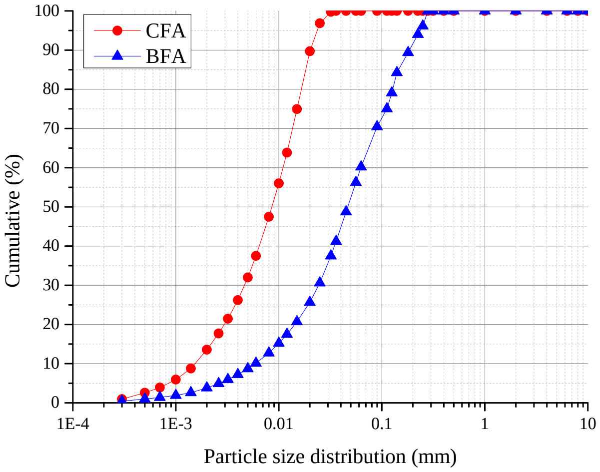


Figure 3.4 – Cumulative particle size distribution for CFA and BFA

3.2.2.2 Loss-on-ignition and Chemical Composition

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, chemical and thermogravimetric analysis. For the LOI and chemical composition, the milled samples were previously dried at 101±1 ºC. LOI was determined using a 1.5 g dried sample heated at 1100 ºC for 3 h, in a Carbolite furnace. The chemical composition was determined by X-Ray Fluorescence using a Panalytical Axios spectrometer. The obtained LOI and the chemical composition of the selected materials are shown in Figure 3.5.

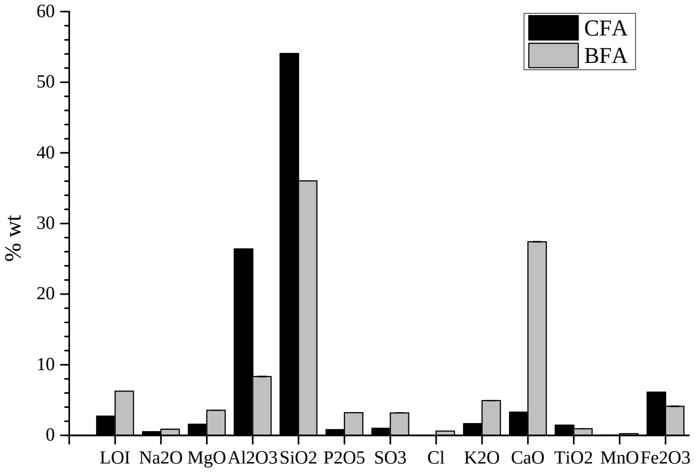


Figure 3.5 - Loss on ignition and major chemical element concentration in CFA and BFA

As can be seen, BFA showed a LOI value of 6.27% and CFA presented a value of 2.73%. According to the EN 450-1:2012 standard [110] that defines and reports the specifications and conformity criteria for fly ash incorporation on concrete, in terms of loss-on-ignition, BFA belongs to category B (LOI ≤ 7%) and CFA to category A (LOI ≤ 5%). It is important to reiterate that EN 450-1:2012 [110] and ASTM C 618 [253] are not applicable to BFA; however, they are the most approximate standards that there are to make the comparison between the two fly ashes.

SiO_2 was the major chemical element (>54 %, dry basis (bs)) presented in the CFA, followed by Al_2O_3, Fe_2O_3, CaO and K_2O. SiO_2 was also the major chemical present in BFA (>36 % dry bs), followed by CaO, Al_2O_3, K_2O, Fe_2O_3, MgO. One of the criteria of EN 450-1:2012 [110] is that the sum of SiO_2, Al_2O_3 and Fe_2O_3 needs to be higher than 70%. Only CFA meets this requirement.

On the other hand, ASTM C 618 [253] showed two classes for CFA: Class C and Class F. One of the biggest differences between Class C and Class F is the content of calcium oxide: coal fly ash with CaO less than 7% belongs to Class F and with more than 20% belongs to Class C. In this study, the CFA belongs to Class F (3.3% of CaO) and BFA can be considered as Class C, since it presents 27% of CaO. It is important to reiterate that in ASTM C 618, most parameters are similar for the two classes, the difference is in the sum of SiO_2, Al_2O_3 and Fe_2O_3 (minimum 70% for Class F and minimum 50% for Class C). For this requirement, once again CFA belongs to Class F (86.6%), but BFA does not meet the requirement for the two classes, but is close to that of Class C (48.5%).

An interesting observation was the fact that only BFA showed Cl and SO_3 in its composition, and this is due to the inorganic content of biomass [244], but also to the fact that these ashes have the capacity of allowing the adsorption of those chemical elements, in the form of HCl and SO_2, from the gases during biomass combustion [345]. In terms of BFA conformity with EN 450-1:2012 [110], the SO_3 content verifies the standard requirement (< 3.0%wt).

Among the minor chemical elements (Figure 3.6) in the BFA sample, Ba presented the highest value, followed by Zn, Sr, Zr, Rb and Cu. In the case of CFA, Sr was the minor chemical element with higher concentration, followed by Ba, Br, Zr, and Cr.

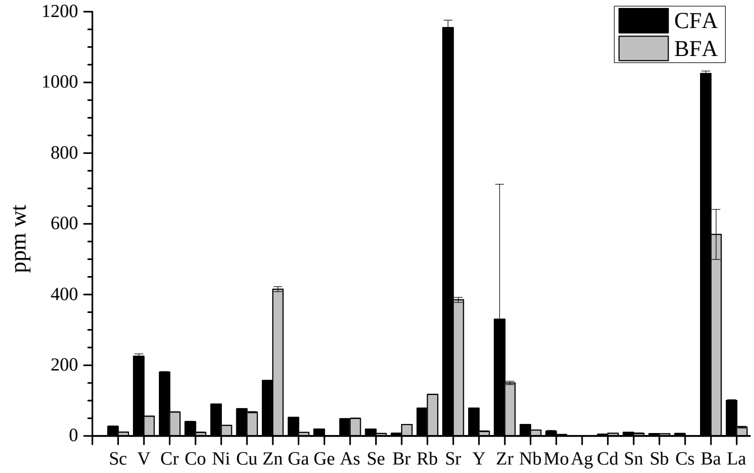


Figure 3.6 - Minor chemical elements concentration in CFA and BFA

3.2.2.3 Mineralogy and Microstructural Analysis

The mineralogical analysis of the two fly ashes was done by X-ray diffraction, using Bruker D8 Advance diffractometer. Mineralogical composition for crystalline phases of CFA is quartz, mullite and hematite, with collection codes PDF01-070-7344, PDF01-074-4144 and PDF01-077-9927 respectively (Figure 3.7). The dominant phase was mullite, one alumino-silicate that is not normally found in natural elements, and may assume variable stoichiometry [346]. The mineralogical composition of BFA showed quartz, calcite, portlandite, calcium silicate, lime and calcium silicate hydroxide, with collection codes 01-083-0539, 00-004-0637, 00-004-0733, 00-001-0720, 00-003-1123 and 00-029-0378, respectively (Figure 3.7).

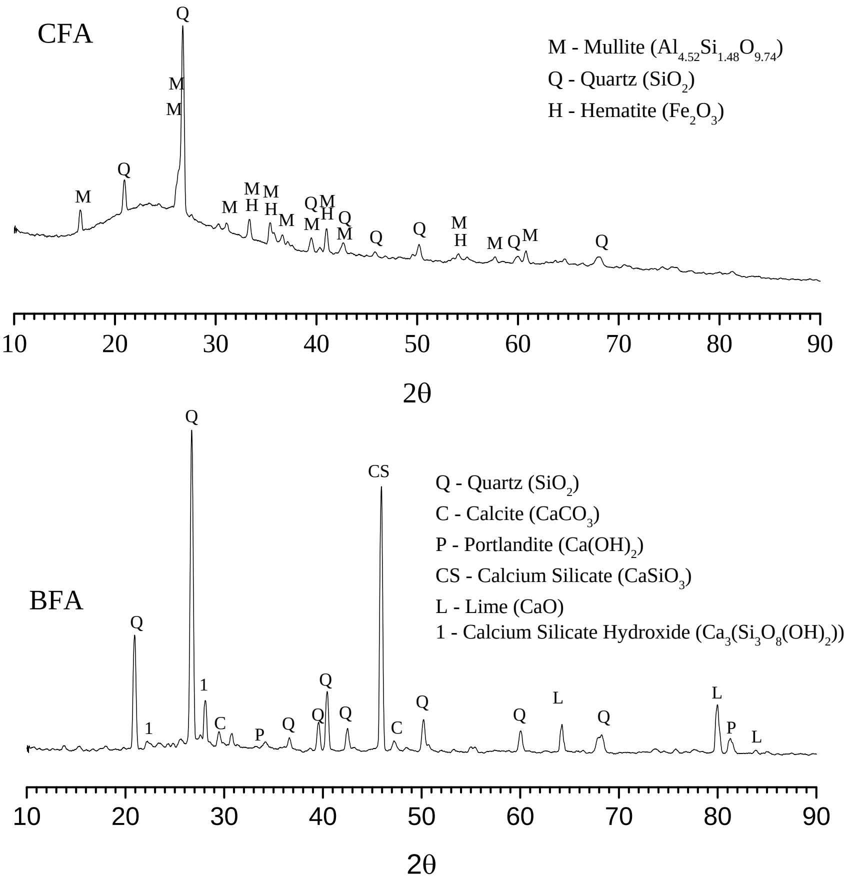


Figure 3.7 - XRD patterns for CFA and BFA

Scanning electron microscopy (SEM – Hitachi SU1510) was used to perform the microstructural characterization, equipped with energy dispersion spectroscopy (EDS with detector Bruker AXS, software: Quantax) used in chemical homogeneity studies. To improve the SEM analyses, a carbon thin-layer was deposited in the samples by sputtering, while other ones without carbon deposition were used to find organic remain particles by the EDS analyses. For a general chemical analysis, the average of three different readings was considered. The morphology of the fly ash particles is presented in Figure 3.8. As expected, CFA is mainly composed of cenosphere particles. The carbon remaining was too rare, which confirms the results observed for the LOI analysis. On the contrary, the BFA presented particles with different shapes and not as spherical as those of CFA. The presence of carbon particles and unburned organic matter is noted (Figure 3.8 – (c), probably a piece of unburned wood).

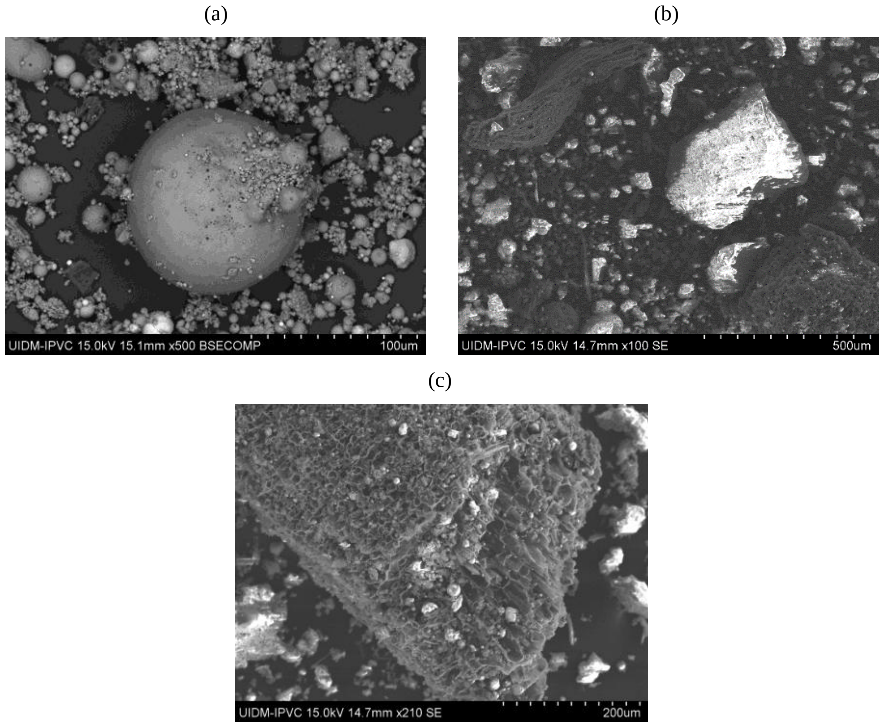


Figure 3.8 - SEM microstructures of fly ash particles: (a) – coal fly ash; (b) – biomass fly ash; (c) – Biomass fly ash – unburned organic material

3.2.2.4 Thermogravimetric Analysis

The thermal analysis was done using a STA, Netzsch 402 EP with a heating rate of 10 ºC/min. The thermogravimetric (TG) and DTA signals registered for CFA and BFA are shown in Figure 3.9. A slight decrease was observed around 100 ºC for both ashes. This loss of weight is related to the release of water adsorbed in the ash. In BFA, a slight increase of the weight near 430 ºC was observed, and this is related to the change of the iron phase. With increasing temperature, a significant decrease in weight of the two fly ashes was observed in the range of 600 to 835 ºC, associated with an endothermic process. This weight loss must be related to the thermal decomposition of carbonates such as $CaCO_3$. 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 the LOI analysis (Figure 3.5).

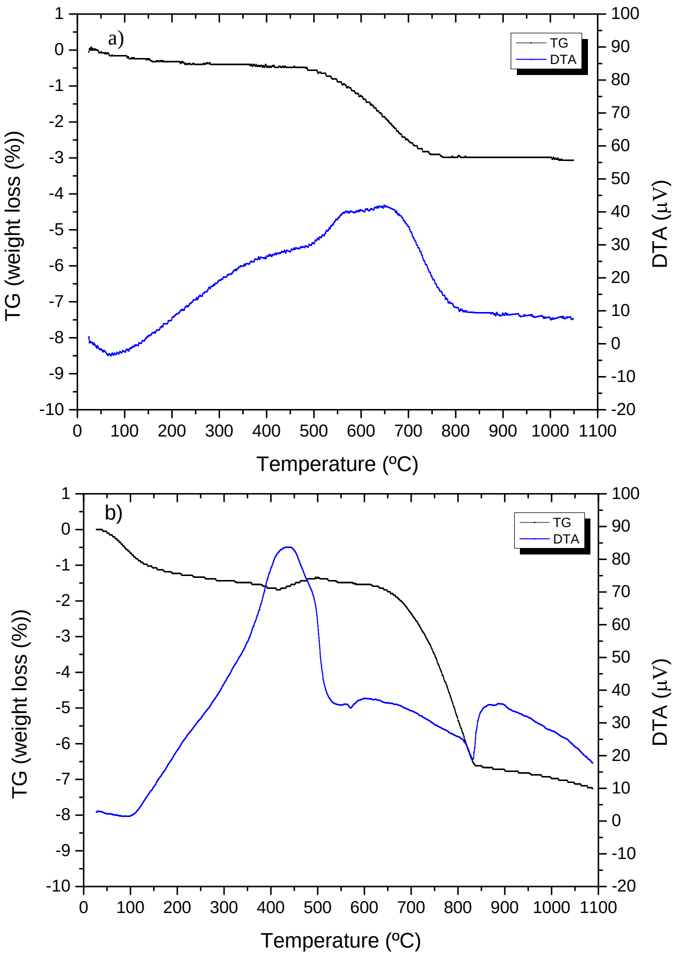


Figure 3.9 - Thermogravimetric analysis of CFA (a) and BFA (b)

3.2.2.5 Selective Dissolution – Reactivity

Several methods can be used to identify and quantify the vitreous phase and the crystalline phase of the supplementary cementitious materials. Among those, the one most used to measure the reactivity of these materials is selective dissolution [72,135]. This method consists of the dissolution of the vitreous phase by an acidic or basic chemical agent, considering that the crystalline phase will not be attacked [126]. For the characterisation of the two fly ashes under study, a selective dissolution method with hydrofluoric acid (1% of HF) used for the vitreous phase quantification was prepared. The dissolution test was carried out at room temperature, and it was done following several steps (Figure 3.10): i) a dilution of HF in distilled water was performed to obtain 150 ml of acid solution, in which 2000 mg of fly ash were added (M1), resulting in a mass ratio of 1% that was kept in a plastic-mixer during the acidic attack for 6 h; ii) after this step, the solution was filtered. Quantitative filters were used in the slow filtration, 80 g/m^2 and 0.160 mm thickness, with pore size between 2 to 4 µm and an ash content < 0.01%. To remove the ash stuck in the plastic-mixer and in the container, they were washed with distilled water, which was also filtered in a new filter; iii) step ii) was repeated, guaranteeing that all the fly ash remained in the filter and that the remaining solution did not present a dark coloration; iv) in a platinum crucible, the mass of the filters with fly ash was weighed (M2); v) the crucible was heated in an oven at 110 ºC for 2 h to dry the filters plus sample. After this period, the oven started a heating program with three temperature levels: 25 to 1000 ºC with a heating rate of 5 ºC/min, 10 min at 1000 º C and the third one was a natural cooling. To control an undesirable outflow of fly ash, the heating rate was relatively low; vi) after the heating program, the crucible was put in a desiccator to cool and weight (M3), to determine the calcined mass referred to the unattacked fly ash; viii) the last step was a slight grinding of fly ash to promote the particle disaggregation needed to perform the subsequent SEM, EDS and XRD analyses. This method is explained in more detail in [126].

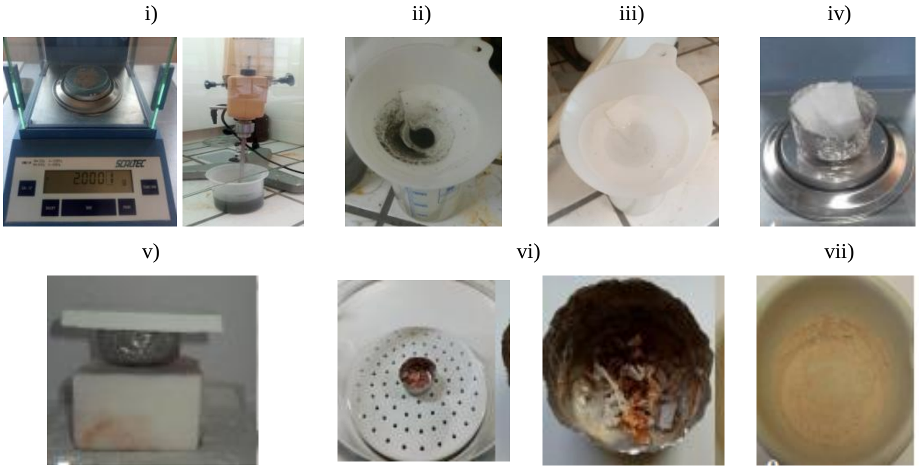


Figure 3.10 – Detailed approach of selective dissolution method

The vitreous phase amount in percentage was computed according to Equation 3 and the percentage of filter impurities was calculated by Equation 4.

$$V_F = \frac{M_1 - M_3}{M_1} \tag{3}$$

$$I_{Filter} = \frac{M_2 - M_3}{M_2} \tag{4}$$

Where:

V_F is the vitreous phase amount, (%);
I_{Filter} is the filter impurities, (%);
M_1 is the mass of sample before acid attack, (mg);
M_2 is the mass of filter plus sample after filtration, (mg);
M_3 is the mass remaining after calcination, (mg).

Since the amount of oxide, the molar mass of crystallized phases and their relative percentages are known, it was possible to estimate the mineralogical composition of the crystalline and vitreous phases [126,149]. As can be seen, the weight loss after the chemical attack was 63.0% (Table 3.4), similar to the results obtained in the XRD analysis (62.5%). To validate the obtained results, the sample after the chemical attack was subjected to an XRD analysis and the results denote a total absence of vitreous phase (absence of a hump in the XRD-baseline).

Table 3.4 – Fly ash attack results

Test samples	**Weight loss Vitreous phase (%)**
CFA	63.0
BFA	10.8
Filter	100

To confirm the results, the samples were analysed by SEM-EDS after the acid attack. The EDS analysis gives the chemical-mapping elements that identify all phases, as observed in Figure 3.11. As an example, it can be seen that a quartz grain of CFA is mostly formed by SiO_2, because Si and O are the major chemical elements detected (Figure 3.11 – green for Si and blue for O). A BFA particle was also analysed, as observed in Figure 3.12. In this case, the particle presented Si (green), O (purple), Al (orange), Ca (pink) and Mg (yellow) in its composition. Another particle was mapped (Figure 3.13) and it was observed that it is mostly composed of calcium, aluminium and silicon, showing once again the heterogeneity of the BFA.

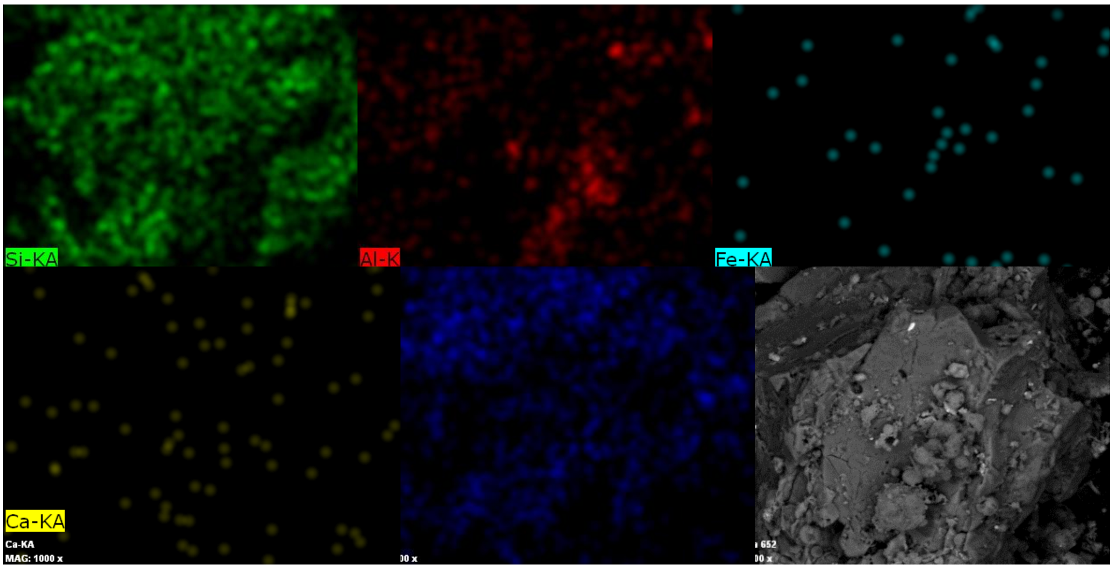


Figure 3.11 – Microstructure (right and below) and EDS analysis of a quartz grain of coal fly ash. Mapping of relevant elements is also given [126]**.**

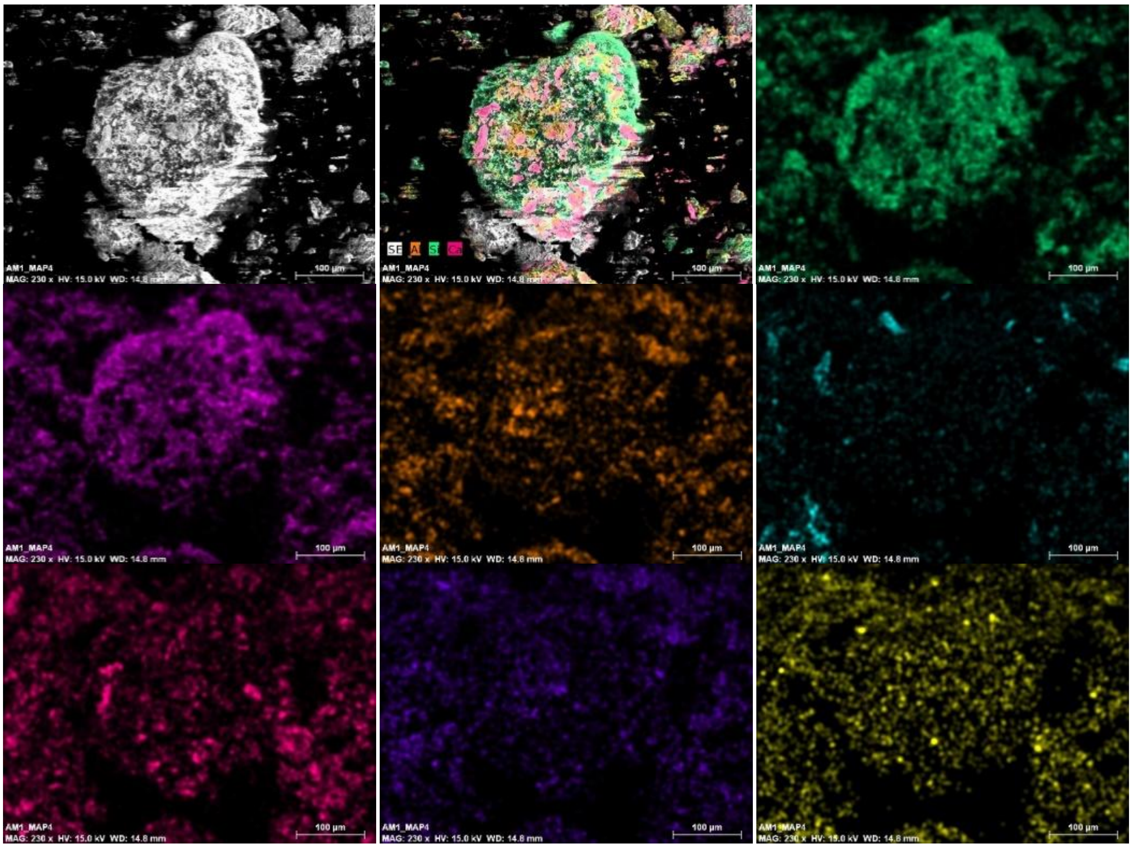


Figure 3.12 - Microstructure (left and upper) and EDS analysis of a biomass fly ash particle before acid attack

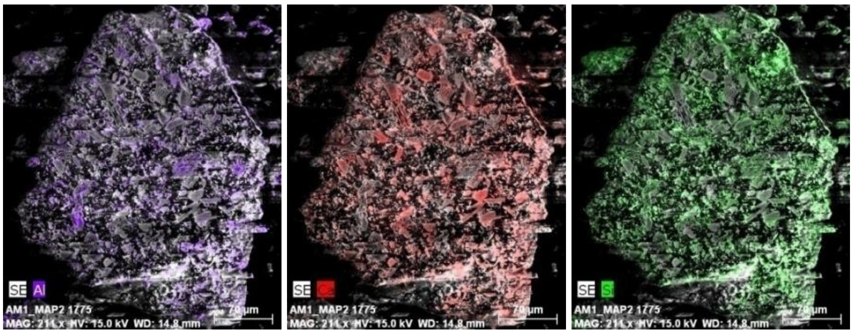


Figure 3.13 - EDS analysis of a biomass fly ash particle before acid attack

The morphology of fly ash particles before and after the HF attack is presented in Figure 3.14. The CFA particles after an acid attack presented various areas where there was damage, some of them predictable. BFA particles also presented some damage. Since no big particles were observed, the results seem to indicate that the acid attack leads to cracking the BFA particles in smaller particles. It can be also observed that the remaining BFA particles after an acid attack mainly composed of Si, Al, Ca, K and O (Figure 3.15).

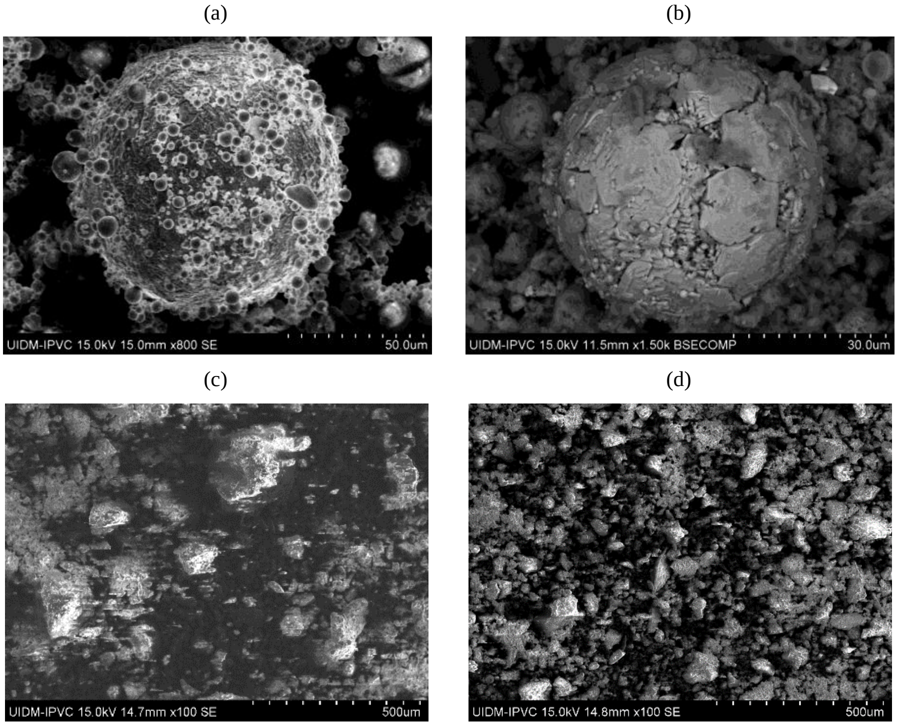


Figure 3.14 - SEM microstructures of fly ash particles: particle with and without chemical attack

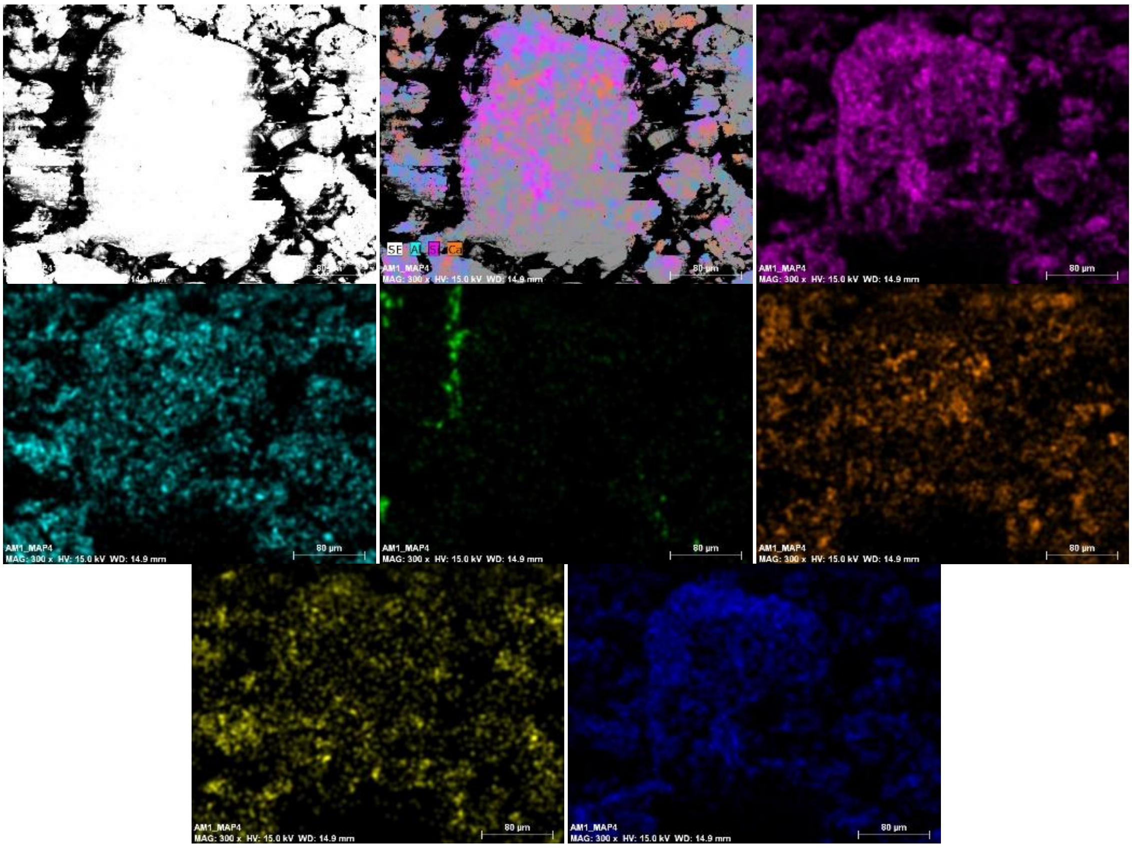


Figure 3.15 - Microstructure (left and upper) and EDS analysis of a biomass fly ash particle before acid attack

3.2.2.6 Chapelle’s Modified Method

The content of fixed calcium hydroxide of the two fly ashes was determined using the modified Chapelle’s method, according to ABNT NBR 15895 [347]. This method determines the index of pozzolanic activity by the quantification of calcium hydroxide content. One gram of sample (Figure 3.16 (a)) was mixed with two grams of calcium oxide (Figure 3.16 (b)) added to 250 ml of water without CO_2 (Figure 3.16 (c)) in a flask and sealed (Figure 3.16 (d)). Calcium oxide is obtained from the calcination of pure calcium carbonate that is heated at 1000±50 ºC for 1 h. After that, the material was mixed and calcined for an additional half hour. The mix of the sample with lime and the blank test are kept at 90±5 ºC, in a water bath (Figure 3.16 (e)). The mix is maintained in this bath with shaking for 16 h, with some Teflon rods. After cooling, 250 ml of a saccharose solution (240 g/l) was added to the mix (Figure 3.16 (f)). The flask was closed and the solution was shaken for 15 min. After this, the solution is filtered, and titled with 0.1 M of HCl, which is standardised before titration. These three phases of tests need to be carried out as fast as possible, to avoid carbon dioxide absorption (Figure 3.16 (g, h and i)). A blank test was also carried out, to verify the consumption of calcium hydroxide by the sample (Figure 3.16 (j)). The pozzolanic activity index is determined according to Equation 5 and is expressed in mg of $Ca(OH)_2$ fixed per gram of material.

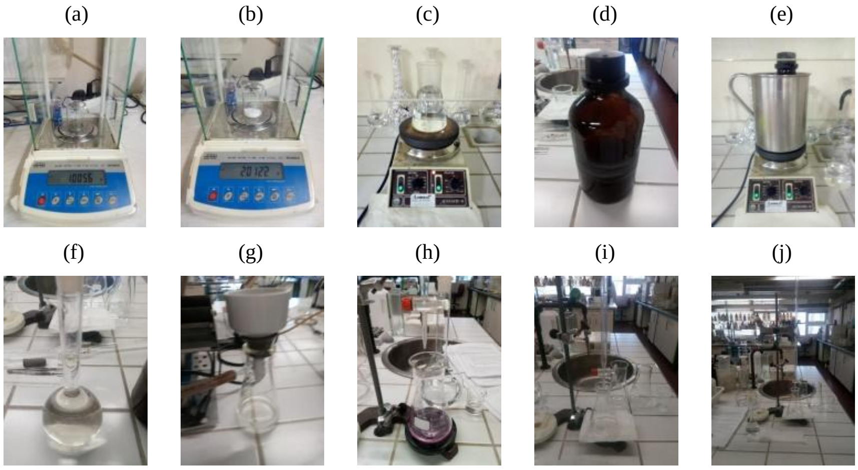


Figure 3.16 – Detailed approach of modified Chapelle’s method

$$I_{Ca(OH)_2} = \frac{28 \cdot (V_3 - V_2) \cdot F_c}{m_2} \cdot 1.32 \tag{5}$$

Where,

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

m_2 is the mass of pozzolanic material, (g);

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

V_3 is the volume of 0.1M 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 $Ca(OH)_2/CaO$.

In Figure 3.17, the pozzolanic performance of the two fly ashes is illustrated. The reactivity index of CFA is 525 mg of $Ca(OH)_2$/g and similar values were observed in other studies [348]. In the case of BFA, the results showed an increase in the content of $Ca(OH)_2$, leading to the conclusion that BFA is not a pozzolanic material but a material that provides alkalinity to the mixes.

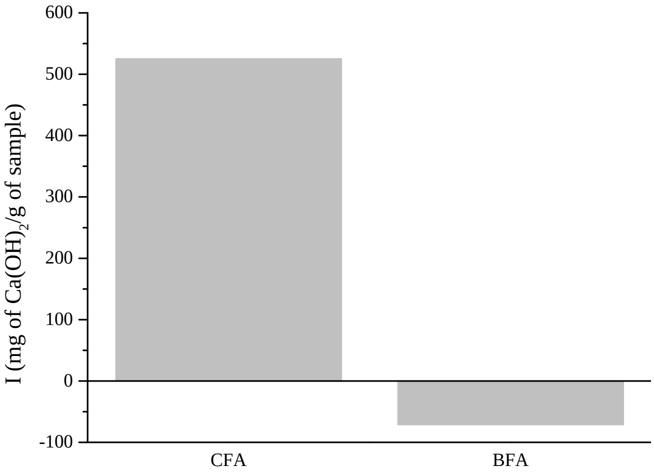


Figure 3.17 - Pozzolanic behaviour of the coal and biomass fly ash

3.2.2.7 Pozzolanic Mechanical Activity Index

The pozzolanic mechanical activity index was determined according to [110]. Mortars with 75%wt of cement and 25%wt of CFA/BFA were prepared and tested for compressive strength after 28 and 90 days of curing. According to the standard, the pozzolanic activity index at 28 and 90 days cannot be below 75% and 85%, respectively. As can be seen, CFA meets the requirements of the standard, but did not present high pozzolanicity. On the other hand, BFA has an index lower than the one required for 90 days (Table 3.5). This result confirms the one achieved in the Chapelle's modified method.

Table 3.5 – Pozzolanic activity index

Sample	**28 days**	**90 days**
CFA	76.0	87.9
BFA	76.1	75.0

3.2.3 Hydrated Lime

In the preparation of some mortar and concrete formulations, hydrated lime (HL) (from *Lusical* industry) was used as an addition, with the main goal of providing the alkalinity lost due to the cement replacement with high amounts of CFA. The physical and chemical composition of HL given by the industry datasheet is presented in Table 3.6.

Table 3.6 – Physical and chemical characteristic of hydrated lime

Granulometric: retained in 125µm	≤0.0%
Free water content	≤1.0%
Stability (expansion)	≤0.2%
$Ca(OH)_2$ content	≥93.0%
MgO content	≤3.0%

3.2.4 Aggregates

Three different aggregates were used in mortar or concrete production: a 0-4 mm river rolled sand, a 4-8 mm granitic gravel and a 6-12 mm granitic gravel (Figure 3.18). Aggregates were characterised in terms of particle size distribution water absorption and particle density.

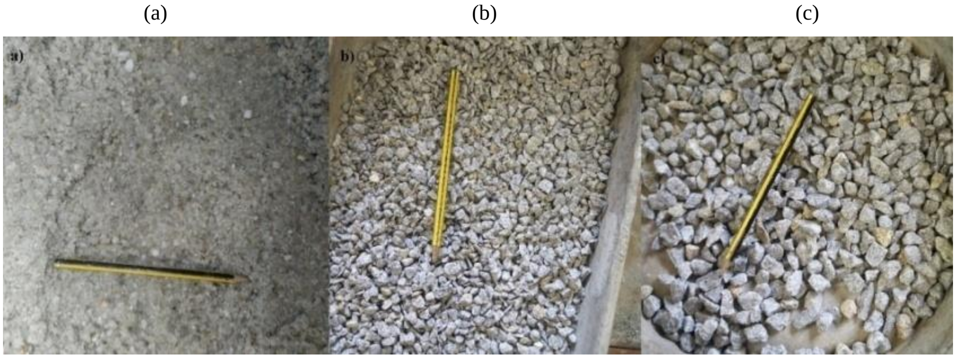


Figure 3.18 – Sand (a), gravel 4-8mm (b), gravel 6-12mm (c)

The determination of the volumetric mass was done according to EN 1097-6:2008 [349]. The mass is determined not only by the measuring of the sample with saturated particles but with the surface dried and the mass of the same sample dried in oven. The volume is determined by the mass of water displaced by the measures of the pynnometer method. The volumetric mass of the aggregates is calculated following Equation 6, 7 and 8:

$$\rho_a = \frac{M_4}{[M_4 - (M_2 - M_3)]/\rho_w} \tag{6}$$

$$\rho_{rd} = \frac{M_4}{[M_1 - (M_2 - M_3)]/\rho_w} \tag{7}$$

$$\rho_{ssd} = \frac{M_1}{[M_1 - (M_2 - M_3)]/\rho_w} \tag{8}$$

Where:

ρ_a is the volumetric mass of the waterproof material, (Mg/m^3);
ρ_{rd} is the volumetric mass of the dry particles, in woven (Mg/m^3);
ρ_{ssd} is the volumetric mass of the saturated particles with dry surface (Mg/m^3);

M_1 is the mass of the saturated aggregate with dry surface, (g);

M_2 is the pycnometer mass with the saturated aggregate sample, (g)

M_3 is the pycnometer mass only full with water, (g);

M_4 is the mass of the aggregate sample dried in woven, (g);

ρ_w is the volumetric mass of water at the registered temperature in the determination of M_2, (Mg/m^3).

The water absorption of the aggregate (in dry mass percentage) after 24 h of immersion in water was determined by Equation 9:

$$WA_{24} = \frac{100 \times (M_1 - M_4)}{M_4} \tag{9}$$

Where:

WA_{24} is the water absorption, (%);

M_1 is the mass of the saturated aggregate with dry surface, (g);

M_4 is the mass of the aggregate sample dried in woven, (g).

The results obtained for the volumetric mass and water absorption of the studied aggregates are shown in Table 3.7.

Table 3.7 – Volumetric mass and water absorption of aggregates

	Sand (0-4 mm)	Gravel (4-8 mm)	Gravel (6-12 mm)
Volumetric mass (kg/m^3)	2547	2617	2390
Water absorption (%)	0.70	5.24	2.41

The particle size distribution of the aggregates was determined according to [350], via the sieving method. Before sieving, the aggregates were washed and dried. The particle size distribution of the three aggregates is presented in Figure 3.19.

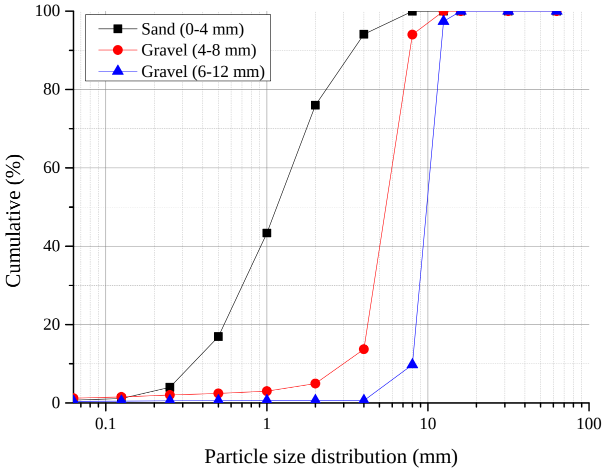


Figure 3.19 - Particle size distribution of aggregates

3.2.5 Water

The water used to make all the mixes (pastes, mortars or concrete) came from the public supply network of Guimarães. The water was not analysed, since the standard EN 1008:2003 [351] reports that it is enough that the water is drinkable to be considered acceptable for the production of mortars and concrete.

3.2.6 Superplasticizer

In the study, a superplasticizer (SP) Glenium Sky 617, manufactured by BASF was used. Superplasticizers are chemical admixtures used in concrete. This material is used in percentages lower than 5% of the cement mass. These substances are added to the mixes with the main goal of reducing the water content of mix without changing the workability of the mix.

Glenium Sky 617 is a superplasticizer of new generation, based on a modified ether polycarboxylic chain. The technical datasheet of the product recommends a dosage of 1.3 kg per 100 kg of binder. However, it is possible to use lower and higher dosages (1 to 1.7 kg per 100 kg of binder), provided some previous studies have been carried out, in function of the water/binder ratio, of cement type and particle size distribution. The plasticizer effect can be maximized if Glenium Sky 617 is added to concrete with 70% of the mixing water already introduced. This superplasticizer cannot be added to dry sand or aggregates. In Table 3.8 the technical characteristics of Glenium Sky 617 provided by the industry are shown.

Table 3.8 - Technical characteristics of superplasticizer (datasheet)

Technical characteristics	
Main function	Superplasticizer/High water reducer
CE marking	According EN 934-2 as T11.1, T11.2
Aspect	Brown liquid
Relative density (20ºC)	1.05±0.02g/cm^3
pH	7.3±1.5
Chloride ions content	< 0.1%

3.3 Pastes

The effect of using BFA on the hydration compounds and on the extent of carbonation in cement pastes was evaluated 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.

Four different cement pastes were set, using coal and biomass fly ash as supplementary cementitious materials (Table 3.9). 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 HVFAC, and for the determination of the quantities it was considered a conventional concrete (with 350 kg/m^3 of binder and with a w/b of 0.5), with 50 %wt of cement replacement.

Table 3.9 - Paste formulations

Nomenclature	%wt of Cement	%wt of CFA	%wt of BFA
100C	100	0	0
50C-50CFA	50	50	0
50C-50BFA	50	0	50
50C-25CFA-25BFA	50	25	25

The pastes were mixed in a standard mechanical mixer as described in [343], for three minutes, and six cubic specimens with 20 mm edge for each formulation were cast for the hydration studies and prisms with 40x40x160 mm^3 were prepared for carbonation tests. After demoulding, which was made after 24 h, all samples were cured in a humidity chamber (with approximately 87% of relative humidity and 21 ºC of temperature) up to the date of the tests (28 and 90 days).

3.3.1 Hydration and Mineralogical Analysis

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. It was important to seal the samples before the TGA and XRD analysis, to prevent the continuation of samples carbonation that occurs due to the contact of samples with CO_2 present in the atmosphere. The thermal analysis was carried out using a STA, Netzsch 402 EP with a heating rate of 10 ºC/min and XRD was done in a Bruker D8 Discover diffractometer [352].

The level of free calcium hydroxide presented in the pastes after hydration was calculated by Equation 10. The overall hydration was determined according to Equation 11, which represents the chemically combined water content [212,353]. The calculation of calcium carbonate was made according to Equation 12.

$$CH_F = Ca(OH)_2[\%] = ML_{Ca(OH)_2}[\%] \cdot MM_{Ca(OH)_2}/MM_{H_2O} \tag{10}$$

$$H_2O_{Q,comb} = mass(loss\%)_{1000\,°C} - mass(loss\%)_{105\,°C} \tag{11}$$

$$CaCO_3[\%] = ML_{CaCO_3}[\%] \cdot MM_{CaCO_3}/MM_{CO_2} \tag{12}$$

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 $Ca(OH)_2$, (g/mol);

MM_{H2O} is the molecular weight of H_2O, (g/mol);

$H_2O_{Q,comb}$ is chemically combined water (%);

$mass(loss\%)_{1000ºC}$ is the total mass loss from 0 to 1000 ºC;
$mass(loss\%)_{105ºC}$ is mass loss referring to free water, from 35 to 105 ºC;
ML_{CaCO3} [%] is the mass loss in % observed in TG curve for $CaCO_3$;
MM_{CO2} is the molecular weight of CO_2 (g/mol).

3.3.2 Carbonation Resistance

The carbonation test was performed using an accelerated test method, with the main goal of measuring the penetration resistance of CO_2 into the samples. For the carbonation test, three samples for each paste formulation with the dimensions of 40x40x160 mm^3 were prepared. The samples were cured in a humidity chamber with relative humidity and temperature control (with approximately 87% of relative humidity and 21 ºC of temperature) for 28 and 90 days. 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 ºC) 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 CO_2, 43.7±16.2% RH and 20.0±0.0 ºC). To measure the carbonation depth, cross-sections were sprayed with a phenolphthalein indicator, based on the procedure described in [354,355]. The procedure was done until the samples stay completely carbonated.

3.3.3 pH

It is well known that carbonation occurs mainly due to the fact that pozzolanic materials decrease 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 CO_2 and was stored for 24 h. The procedure used in this study was based on [356]. After 24 h, the pH of each sample was measured using Crisonmicro pH 2000 equipment.

3.4 Mortars

An evaluation of the potential of BFA as a replacement for ordinary Portland cement in mortar applications was carried out (Table 3.10). The effect of BFA incorporation on cement mortars was discussed in terms of impact on the fresh and on hardened properties. The tests performed on the different mortar mixes are listed in Table 3.11.

Table 3.10 – Mortar formulations

Nomenclature	%wt of binder				w/b	SP %	Curing	Tests Table 3.11
	C	CFA	BFA	HL				
REF1	100.0	0.0	0.0	0.0	0.5	-	Humidity chamber	A
REF2	100.0	0.0	0.0	0.0	0.5/0.35	-/3.0	Water	B
CFA20	80.0	20.0	0.0	0.0	0.5	-	Humidity chamber	A
CFA16BFA4	80.0	16.0	4.0	0.0	0.5	-	Humidity chamber	A
CFA12BFA8	80.0	12.0	8.0	0.0	0.5	-	Humidity chamber	A
CFA8BFA12	80.0	8.0	12.0	0.0	0.5	-	Humidity chamber	A
BFA20	80.0	0.0	20.0	0.0	0.5	-	Humidity chamber	A
CFA25BFA25	50.0	25.0	25.0	0.0	0.5/0.35	-/0.5	Water	B
CFA40	60.0	40.0	0.0	0.0	0.5	-	Humidity chamber	A
CFA32BFA8	60.0	32.0	8.0	0.0	0.5	-	Humidity chamber	A
CFA24BFA16	60.0	24.0	16.0	0.0	0.5	-	Humidity chamber	A
CFA16BFA24	60.0	16.0	24.0	0.0	0.5	-	Humidity chamber	A
BFA40	60.0	0.0	40.0	0.0	0.5	-	Humidity chamber	A
CFA50	50.0	50.0	0.0	0.0	0.5/0.35	-/0.3	Water	B
CFA49.5HL0.5	50.0	49.5	0.0	0.5	0.5/0.35	-/0.3	Water	B
CF48.8HL1.3	50.0	48.8	0.0	1.3	0.5/0.35	-/0.3	Water	B
CFA45HL5	50.0	45.0	0.0	5.0	0.5/0.35	-/0.3	Water	B
BFA49.5HL0.5	50.0	0.0	49.5	0.5	0.5/0.35	-/1.3	Water	B
BF48.8HL1.3	50.0	0.0	48.8	1.3	0.5/0.35	-/1.3	Water	B
BFA45HL5	50.0	0.0	45.0	5.0	0.5/0.35	-/1.3	Water	B
CFA49.5BFA0.5	50.0	49.5	0.5	0.0	0.5/0.35	-/0.3	Water	B
CFA48.8BFA1.3	50.0	48.8	1.3	0.0	0.5/0.35	-/0.3	Water	B
CFA45BFA5	50.0	45.0	5.0	0.0	0.5/0.35	-/0.3	Water	B
CFA49.5BFA0.3HL0.3	50.0	49.5	0.3	0.3	0.5/0.35	-/0.5	Water	B
CF48.8BFA0.6HL0.6	50.0	48.8	0.6	0.6	0.5/0.35	-/0.5	Water	B
CFA45BFA2.5HL2.5	50.0	45.0	2.5	2.5	0.5/0.35	-/0.5	Water	B
BFA50	50.0	0.0	50.0	0.0	0.5/0.35	-/1.3	Water	B
CFA60	40.0	60.0	0.0	0.0	0.5	-	Humidity chamber	A
CFA48BFA12	40.0	48.0	12.0	0.0	0.5	-	Humidity chamber	A
CFA36BFA24	40.0	36.0	24.0	0.0	0.5	-	Humidity chamber	A
CFA24BFA36	40.0	24.0	36.0	0.0	0.5	-	Humidity chamber	A
BFA60	40.0	0.0	60.0	0.0	0.5	-	Humidity chamber	A

The study was divided into two parts. Firstly, a set of cement mortars was prepared by replacing ordinary Portland cement with different amounts of BFA (20%, 40% and 60 % by mass basis of binder), alone or blended with CFA. In this case, the main goal was to understand if the increase of BFA amount on mortars influences the fresh and hardened properties of mortars. A comparison with mortars with the same percentage of CFA and with mortars just with Portland cement as binder was also made. The mixes 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 of 0.5. For each mix, three specimens were prepared, to guarantee the statistical representativeness of the results. Mortar mixes were prepared according to the following procedure: i) solid and liquid weighing, ii) addition of water to the solids, iii) mixing for 1 minute at a low rotation speed, iv) stopping for 1 minute, v) mixing again for 1 minute, vi) testing the fresh properties of the mix, v) the mix was placed in the moulds (dimensions according to the analysis test) and compacted twice; vi) the moulds were covered with plastic film to avoid loss of water; vii) the moulds were stored in a humidity chamber for 24 h; viii) after 24 h, the mortars were demoulded. After demoulding, the samples were cured in a humidity chamber with temperature and relative humidity control (at approximately 87% of relative humidity and 21 ºC of temperature), according to [357], and ix) the mortars were tested for hardened properties (Table 3.11 – Group A of tests).

Table 3.11 - Tests done in mortars and number of samples needed for each test

Group of tests	Type of test	Period of curing (days)	Number of test	Number of samples for each w/b	Total number of samples
A	Flow test	fresh	1	1	1
	Shrinkage	After demoulding	1	3	3
	Leaching	28	1	1	1
	Mechanical resistance	2,7,28,90,180	5	15	30
	Water absorption/dry bulk density	28	1	3	6
B	Flow test	fresh	1	1	2
	Density	Fresh	1	1	2
	Air content	fresh	1	1	2
	Electric resistivity	2,7,28,56,90,180	6	18	36
	Ultrasound	2,7,28,56,90,180	6	18	36
	Mechanical resistance	2,7,28,56,90,180	6	18	36
	Water absorption/dry Bulk density	28,90,180	3	9	18
	Accelerated Carbonation	28,90,180,270,360	5	15	25

As the focus of this thesis is the production of concrete with HVFA content, the second part of this study focused on the preparation of a set of mortars, which were prepared with the incorporation of BFA as cement replacement material, alone or blended with CFA. The cement substitution percentage in all mixes was 50%wt. The effect of using this residue in the fresh and hardened properties of mortars was verified, as well as the synergic effect of the two fly ashes when blended. As is known, one of the problems of HVFAC is the loss of alkalinity, by the pozzolanic reaction, and this is important for the hardening of concrete. This loss leads to a pH decrease and may accelerate the carbonation phenomenon. As BFA are more alkaline than CFA, a study was carried out with the incorporation of small amounts of BFA as an alkaline material to this mix, to compare with an alkaline material (e.g. hydrated lime) used in concrete. The mortars were prepared according to the procedure described above but, in this case, the mortars were cured immersed in water. The mortars were tested for fresh and hardened properties as described in Table 3.11 (Group B). For this work, two water/binder ratios (0.5 and 0.35) were tested. With the decrease of the water content, it was necessary to add superplasticizer to the mixes to keep a similar workability.

3.4.1 Workability

The consistence of fresh mortar was determined according to the procedure presented in EN 1015-3:1998 [357]. The flow values are determined by the measuring of the average diameter of a fresh sample. The fresh sample was introduced in a defined mould in two layers, each layer being compacted with 15 short rod strokes to ensure uniform filling of the mould. After this, the mould was lifted vertically and the mortar was spread out on the table disc by jolting the flow table 15 times at a constant frequency (1 per sec). Afterwards, the diameter was measured in two directions and the average result was expressed in mm (Figure 3.20).

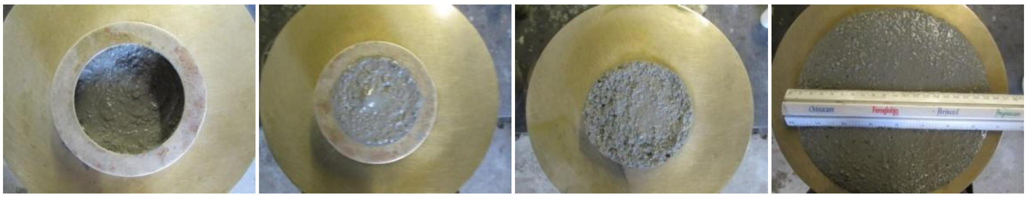


Figure 3.20 – Flow table test

3.4.2 Bulk Density in the Fresh State

The bulk density of fresh mortar was determined according to EN 1015-6:1998 [358]. This parameter was determined by measuring of the mass of fresh mortar and the volume that it occupies when it is introduced and compacted in a vessel of a given capacity. The bulk density was calculated from the following equation:

$$\rho_m = \frac{m_2 - m_1}{V_v} \tag{13}$$

Where,

ρ_m is the bulk density of fresh mortar, (kg/m^3);
m_1 is the mass of the empty vessel, (kg);
m_2 is the mass of the vessel filled with the sample, (kg);
V_v is the volume of the measuring vessel, (m^3).

3.4.3 Air Content in the Fresh State

The determination of the air content of fresh mortar was done according to EN 1015-7:1998 [359]. A volume of mortar was placed in a vessel of 1 l, water was introduced on top of the mortar surface and air-pressure was applied to the mortar displacing air from within any pores (Figure 3.21). The water level falls and reflects the volume of air displaced from the mortar.

Figure 3.21 – Test apparatus showing the metal vessel and cover assembly

3.4.4 Dry Bulk Density of the Hardened Mortar

Mortar specimens with dimensions 40x40x160 mm^3 were prepared for the dry bulk density tests. The samples were first tested for flexural strength and then one part of each mortar was used for the capillarity test and the other was used in this test. All the mortar parts were dried at 60±5 ºC until the constant mass was reached before the test, according to EN 1015-10 [360]. The samples were immersed in water until no further increase in apparent mass was observed. This was considered when two consecutive (with a period between each measurement of 24 h) measures did not differ by more than 0.1% by mass. After this, the samples were weighted in water. The volume of each sample was determined according to Equation 14:

$$V_s = \frac{m_{s,sat} - m_{s,i}}{\rho_w} \tag{14}$$

Where,

V_s is the volume of specimen of hardened mortar, (m^3);
$m_{s,sat}$ is the mass of saturated specimen of hardened mortar, (kg);
$m_{s,i}$ is the apparent mass of saturated specimen of hardened mortar immersed in water, (kg);
ρ_w is the density of water, (kg/m^3).

3.4.5 Electric Resistivity

The electric resistivity was measured using Resipod Proceq equipment, which comprises 4 equidistant (38 mm) electrodes, as shown in Figure 3.22. During this test, an alternated current between the external electrodes was provided and the electric potential difference between the internal electrodes was measured. The electric resistivity was measured through Ohm’s law, and computed by the equipment used. For each mortar formulation, three samples were tested at 2, 7, 28, 56, 90 and 180 days of curing.

Figure 3.22 - Electric resistivity measurement

3.4.6 Mechanical Strength

The mortar specimens for the mechanical strength were prepared in 40x40x160 mm^3 moulds. After the mortars' casting, the moulds were covered with plastic film to avoid the loss of water and stored in a wet chamber (at approximately 87% of relative humidity and 21 ºC of temperature) during 24 h. After that time, the mortars were demoulded and again stored in the humidity chamber, according to EN 1015-11:1999 [361]. The flexural strength was determined in a LLOYDS Instruments universal testing machine (with a maximum capacity of 50 kN), the compressive strength was measured in an Ele Auto Test press (with a capacity between 5 to 110 kN) (Figure 3.23). The flexural strength was determined by three points loading of hardened mortar prism samples to failure (Figure 3.23) and calculated by Equation 15. The mortar's compressive strength was determined in two parts resulting from the flexural strength test. The compressive strength was calculated as the maximum load carried by the specimen divided by its cross-section area. For each mortar formulation, three mortars were prepared and tested and the results are the average of the three samples. The mechanical tests were done at 2, 7, 28, 56, 90 and 180 days of curing.

$$f = 1.5\frac{Fl}{bd^2} \tag{15}$$

Where,

f is flexural strength, (MPa);

F is the maximum load applied to the specimen, (N)

l is the distance between the axes of the support rollers, (mm);

b is the width of specimen, (mm)

d is the depth of the specimen, (mm).

Figure 3.23 – Flexural and compressive strength tests

3.4.7 Water Absorption by Capillarity

The water absorption by capillarity was done according to EN 1015-18:2002 [362]. Before the test, all mortar sample parts were dried at 60±5 ºC. After drying, the face, which was the result of the flexural strength test of the specimen, was immersed in 5 mm of water and the increased mass was determined and registered until no change in two consecutive mass measurements (i.e. the measures did not differ by more than 0.1% by mass) is achieved. To ensure that the water goes to the sample by capillarity forces, the sample was covered with silicone (Figure 3.24 (a)), with the exception of the test face and the opposite face (Figure 3.24 (b)). Several weight measures were made: 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 coefficient of water absorption by capillarity ((Figure 3.24 (c))) is defined by the representation of a straight line linking the points of the measures carried out between 10 and 90 minutes and calculated based on Equation 16.

$$C = 0.1(M1-M0) \tag{16}$$

Where,

C is the coefficient of water absorption, (kg/(m^2.min$^{0.5}$));
M1 is the mass (g) of the specimen after soaking for 90 min;
M0 is the mass (g) of the specimen after soaking for 10 min.

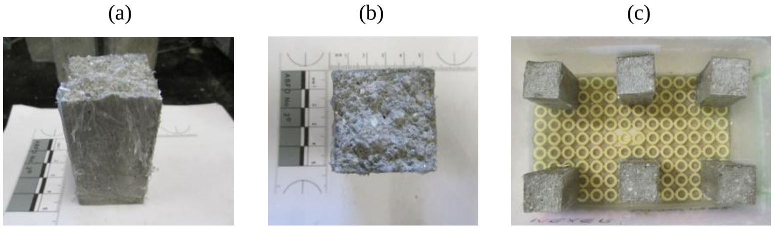


Figure 3.24 – Water absorption capillarity test: (a) sample covered with silicone, (b) test face and (c) test apparatus.

3.4.8 Carbonation Resistance

The carbonation test was done in three samples for each mortar formulation with the dimensions of 40x40x160 mm^3, cured in a wet chamber (at approximately 87% of relative humidity and 21 ºC of temperature) and also cured in water, for a period of 28, 90, 180, 270 and 360 days. After curing, the cured samples were preconditioned in an isolated container subjected to constant temperature and relative humidity (88.0±4.0% and 17.5±1.6 ºC) for 14 days, to ensure the stabilisation 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 CO_2, 43.7±16.2% RH and 20.0±0.0 ºC). To measure the carbonation depth, the cross-sections were sprayed with a phenolphthalein indicator, based on the procedure described in [354,355]. The procedure was performed until the samples were completely carbonated.

3.4.9 Shrinkage Test

The total shrinkage test was done to the mortar formulations that presented the most promising results, in terms of mechanical strength after 28 days of curing and for each level of cement replacement. To measure the shrinkage and weight loss, three prisms with 25x25x250 mm^3 for each mix were moulded. The moulds for this experiment have a system that allows the application of stainless-steel bolts in the specimen tips (Figure 3.25 (a), (b) and (c)). Shrinkage was determined on the specimens after being demoulded (after 24 h). After that time, the mortars were put in a climatic chamber with a temperature and relative humidity control (temperature 20 ºC and moisture content of 60%), where the shrinkage measuring equipment was also stored (Figure 3.25 (d), (e) and (f)). Measurements were taken every day for a period of 60 days.

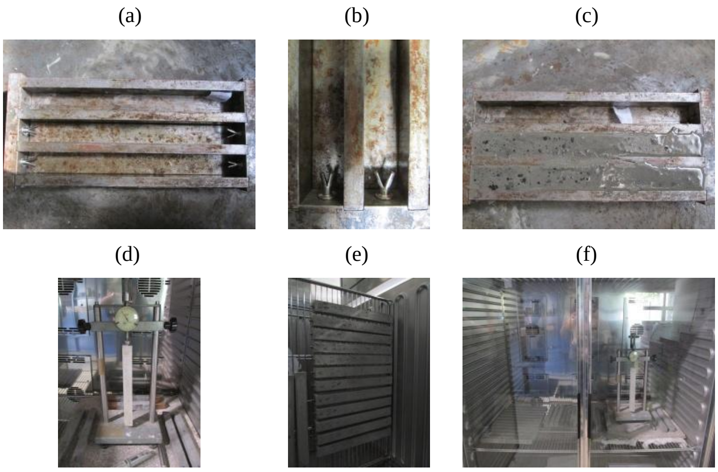


Figure 3.25 – Shrinkage procedure.

3.4.10 Leaching Test

For the leaching test, three mortars for each mix with non-standardized dimensions (20x43x64 mm^3) were moulded. The mix preparation, casting and curing were prepared according to what was described for the mortars subjected to mechanical strength tests. The leaching test was done at the age of 28 days, according to the EN 12457-2 standard [363], with a liquid to solid ratio (L/S) of 10 l/kg. After leaching, the eluates were analysed in terms of: pH value, conductivity and chemical composition. Ca, Na, K, Mg were analysed by flame atomic absorption/emission spectroscopic and heavy metals by inductively coupled plasma. In addition, to the chemical composition of the mortar eluates, the leaching test included a blank test. For that purpose, the chemical composition of the eluates from blank tests was deducted from the chemical compositions of the mortar formulations.

3.5 Concrete

Mortars were prepared and tested with the intent of evaluating the effect of using BFA on the properties of HVFAC. Mortars instead of concrete were made since it allows the study of a large group of formulations with different compositions and a large group of tests and analysis without consumption of a large amount of raw materials. Based on the results obtained in mortars, the formulations that provided better results in terms of quality, durability and sustainability were chosen to produce the concrete formulations studied and presented in Table 3.12.

Table 3.12 – Concrete formulations

Nomenclature	% of binder				w/b	SP
	C	CFA	BFA	HL		
REF2	100.0	0.0	0.0	0.0	0.5	0.0
CFA50	50.0	50.0	0.0	0.0	0.35	0.5
CFA49.5HL0.5	50.0	49.5	0.0	0.5	0.35	0.3
CFA49.5BFA0.5	50.0	49.5	0.5	0.0	0.35	0.7
CFA48.8BFA1.3	50.0	48.8	1.3	0.0	0.35	0.7
CFA45BFA5	50.0	45.0	5.0	0.0	0.35	0.2
CFA48.8BFA0.6HL0.6	50.0	48.8	0.6	0.6	0.35	0.1

The main goal of this study is to find a concrete composition with similar or higher mechanical strength, but more durable and with better sustainability performance, than a plain cement concrete, using a lower amount of cement and water in concrete production. The dosage of binder was 350 kg/m^3, which is the usual content of binder in a conventional concrete. Three aggregates (described before) and two water/binder ratios (0.5 and 0.35) were used. In the mixes with a w/b of 0.35, a superplasticizer was used to ensure a good workability The concrete formulations were compared with a reference mix, produced using just cement as binder and with a w/b ratio of 0.5 (in this mix no superplasticizer was used). The results of a HVFAC with 50%wt of cement replacement by CFA with a w/b of 0.35 were also studied and used to compare with those of the formulations with BFA and HL, since it was observed in mortar formulations that this formulation gives similar results to those of a plain cement mortar, mainly in terms of mechanical strength and also because it is known that this type of concrete with low amount of cement, with high CFA content and low amount of water can be a solution for conventional concrete and is used at industrial level [362,364]. The amount of each material used for the preparation of the different concrete mixes is presented in Table 3.13.

Table 3.13 – Material dosages per m^3 of concrete for each mix

Nomenclature	kg/m^3								L/m^3
	C	CFA	BFA	HL	Sand	Gravel (4-8mm)	Gravel (6-12mm)	SP	Water
REF2	350.0	0.0	0.0	0.0	738.1	165.6	803.6	0.0	175.0
CFA50	175.0	175.0	0.0	0.0	804.5	186.8	857.5	8.8	122.5
CFA49.5HL0.5	175.0	173.5	0.0	1.9	768.6	188.2	860.8	5.3	122.6
CFA49.5BFA0.5	175.0	173.5	1.9	0.0	795.2	188.2	860.8	11.4	122.6
CFA48.8BFA1.3	175.0	170.6	4.4	0.0	842.8	188.2	861.9	11.4	122.5
CFA45BFA5	175.0	160.0	17.8	0.0	838.9	189.1	860.4	3.9	123.4
CFA48.8BFA0.6HL0.6	175.0	170.6	2.2	2.2	832.9	191.3	875.9	2.5	122.5

Aggregates were used as received (not dry) and for that reason the humidity of aggregates was taken into account for the amount of water added to the mix. The amount of each aggregate was determined by the Faury method (Table 3.13).

The mixes were prepared according to the following procedure: i) gravel (6-12), gravel (4-8) and sand were added to the mix, respectively by that order (Figure 3.26 (a, b and c)); ii) aggregates were mixed together for 3 min (Figure 3.26 (d)); iii) the mixing stopped and cement, coal fly ash, biomass fly ash and hydrated lime were added to the mix (Figure 3.26 (e)); iv) mixing for 3 more min; after this time and without stopping mixing, water and superplasticizer were added to the mix (Figure 3.26 (f, g and h)); and v) mixing for 3 more min. The slump test of the fresh mixes was done to ensure the workability of concrete (Figure 3.26 (i)). The samples were prepared in standard moulds (Figure 3.26 (j)) according to what is specified in [365]. After 24 h, the samples were demoulded and cured. Two curing types were studied for each concrete formulation: water curing and a hydrated lime solution curing. Hydrated lime curing was made, due to the fact that is known that in water curing, concrete lose alkalinity by leaching, which leads to a pH decrease and consequently a decrease of carbonation resistance. The use of this curing has the main goal of minimizing or inhibiting the loss of alkalinity, but without affecting the rest of the concrete properties. For this reason, all tests were replicated for the samples cured in water and in lime solution, to verify the effect of the two curing types on the concrete properties.

All concrete formulations were tested for fresh properties (slump test) and hardened properties: compressive strength, water absorption (by immersion and by capillarity), resistance to carbonation and chloride penetration for samples with 7, 28, 90 and 180 days. The results are expressed as an average of three samples for each concrete formulation.

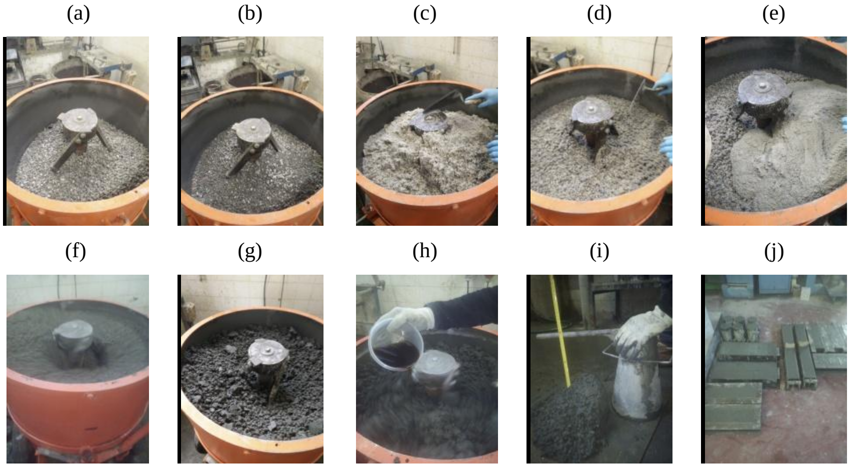


Figure 3.26 – Concrete mixing and casting.

3.5.1 Slump Test

The concrete slump test measures the consistency of fresh concrete before it sets. It is done to evaluate the workability of freshly made concrete. The fresh concrete is compacted inside the Abram´s cone. When the mould is removed by elevating it, the slump establishes a consistency measure, which is determined by measuring the height difference between the higher part of the mould and the highest point of the sample (Figure 3.27) [366].

Figure 3.27 – Slump test.

3.5.2 Mechanical Strength

The mechanical strength test done in this study was the compressive strength according to EN 12390-3:2003 [367]. For the compressive strength test, three samples with 100x100x100 mm^3 for each concrete formulation and for each curing age (28, 90 and 180 days) were prepared. The samples were moulded, demoulded and cured according to [368], immersed in water and in a hydrated lime solution at approximately 21 ºC. After curing, the specimens were tested in a compressive machine (Elle with range between 50-3000 kN) until rupture (Figure 3. 28). The maximum force was registered and the compressive strength was calculated according to Equation 17.

Figure 3. 28 – Compressive strength test.

$$f_c = \frac{F}{A_c} \tag{17}$$

Where,

f_c is the compressive strength, (MPa);

F is the maximum applied load, (N);

A_c is the cross-sectional area of sample where the force is applied, (mm^2).

3.5.3 Water Absorption by Immersion

The water absorption by immersion was performed according to LNEC E 394:1993 [369] in samples cured in water and in hydrated lime solution for 28, 90 and 180 days. The test was carried out at atmospheric pressure and the samples (100x100x100 mm^3) were immersed in water for 24 h. After this period, the surface of the specimen 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 did not differ by more than 0.1 %wt. The water absorption was determined according to Equation 18.

$$A_i = \frac{m_1 - m_3}{m_1 - m_2} \times 100 \tag{18}$$

Where:

A_i is the water absorption, (%);

m_1 is the mass of the water saturated specimen, (g);

m_2 is the mass of the saturated specimen immersed in water, (g);

m_3 is the mass of specimen (g).

3.5.4 Water Absorption by Capillarity

The water absorption by capillarity was done according to LNEC E 393:1993 [370]. For this test, three samples were prepared for each concrete formulation and for each curing period, with

100x100x100 mm^3. The process of preparation of samples, procedure and calculation of water absorption capillarity coefficient is similar to the one described in 3.4.7.

3.5.5 Chloride Migration Coefficient from Non-Steady-State Migration Experiments

Chloride migration coefficient was determined by a non-steady-state migration test according to a specification of LNEC (*Laboratório Nacional de Engenharia Civil* – National Laboratory of Civil Engineering) E 463:2004 [371]. In this method, the diffusion coefficient is computed from the measurement of resistance to chlorides penetration of concrete.

Cylindrical specimens of concrete with a diameter of 100 mm and a thickness of 50 mm, sliced from cast cylinders with length of 200 mm were prepared. For each test, three samples of each concrete formulation were used.

An external electrical potential was applied axially across the sample and forces the chlorides ions outside to migrate into the specimen. After the test period, the sample was axially split 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 (Figure 3.29). The coefficient was calculated according to Equation 19:

$$D = \frac{RT}{zFE} \cdot \frac{x_d - \alpha\sqrt{x_d}}{t} \tag{19}$$

Where,

$$E = \frac{U-2}{L} \tag{20}$$

$$\alpha = 2\sqrt{\frac{RT}{zFE}} \cdot erf^{-1}\left(1 - \frac{2c_d}{C_0}\right) \tag{21}$$

D is the non-steady-state migration coefficient, (m^2/s);

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

F is the Faraday constant, F=9.648×10^{4}J/(V.mol);

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

R is the gas constant, R=8,314J/(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);

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:

$$D = \frac{0.0239(273+T)L}{(U-2)t}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right) \tag{22}$$

Where:

D is the non-steady-state migration coefficient, x10^{-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, (ºC);

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);

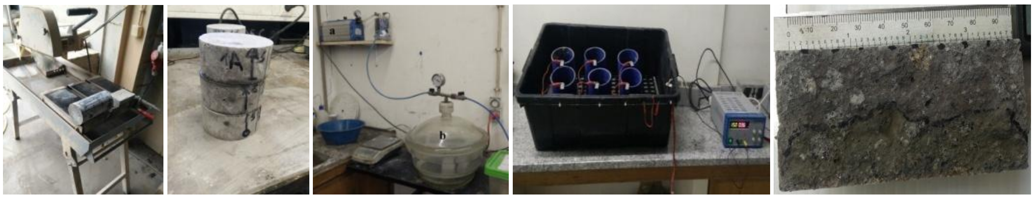


Figure 3.29 – Chloride migration test apparatus.

3.5.6 Carbonation Resistance

The carbonation test was done as described in section 3.4.8. For concrete, the samples used were cubes with 100 mm edge (for samples tested after 28 days of curing) and prisms with 100x100x855 mm^3 (for samples tested at 90 and 180 days). The carbonation depth (Xc), was evaluated over time and the carbonation coefficient (Kc) was determined. The carbonation coefficient was determined by the linear regression between the depth penetration coefficient and the square root of time.

Chapter 4

Pastes and Mortars:

Results and Discussion

4.1 Introduction

The main goal of this work was to evaluate whether using biomass fly ash (BFA) as cement replacement allows the minimization of the issues related with high volume fly ash concrete (HVFAC). Therefore, an extensive experimental program was developed, to understand the effect of BFA on the hydration, fresh and hardened properties of HVFAC.

As the main difference between a plain cement concrete and a HVFAC is the binder, which in the first one is just cement, and in the second one is composed of cement plus coal fly ash (CFA), and in the case of this study, plus biomass fly ash. The study of the effect of BFA on the hydration compounds was done in a group of cement pastes (binder plus water, without aggregates), using TGA and XRD analysis. In these pastes, the carbonation resistance was also studied using TGA analysis and the accelerated method. During the study, a comparison between pastes containing BFA as partial replacement of cement (25 and 50%wt) or/and pastes with CFA (25% and 50%wt) and plain cement past (100%wt) was carried out. The main goal was to understand whether BFA had a typical behaviour of a pozzolanic material in a HVFAC (although it has been previously seen that it does not meet the requirements for use as pozzolanic material and has a low reactivity – chapter 3.2.2) and whether its effect on the cement hydration was similar, for example to the most used pozzolan worldwide, CFA.

It was important to find some HVFAC with BFA incorporation that had a similar behaviour to that of a plain cement concrete, but with the minimization of the issues related to that type of concrete and with higher durability and a better environmental performance. It was necessary to study a large group of formulations, with different percentages of cement replacement by BFA, alone or mixed with CFA and to study a large group of tests to understand its effect on the fresh and hardened properties of HVFAC. Since it was such a large study, it was decided to use mortars, instead of concrete, because of raw materials and time consumption needed in concrete preparation. However, the preparation of the mortar compositions was based on the composition of a plain cement conventional concrete (binder equal to 350 kg/m^3, sand equal to 750 kg/m^3 and a water/binder ratio of 0.5).

The study in mortars was divided into two main objectives: (1) production of mortars using 20%, 40% and 60%wt of BFA and blends of biomass and coal fly ash as a replacement of cement and the study of its effects on the fresh, hardened and leaching properties; and (2) the study of the effect of using BFA in 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 to its worst carbonation behaviour. As BFA are more alkaline than CFA, an experimental study was carried out concerning the use of BFA in 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, since it was shown in other studies [372] that the introduction of lime minimises the issues related with pH decrease by preventing the loss of alkalinity. Small amounts of HL (0.5, 1.3 and 5%wt) were studied since in other studies it was seen that the best results were achieved when small amounts were used, as e.g. the highest carbonation resistance was observed for samples with 2.5 and 5%wt of hydrated lime [373].

4.2 Pastes

Four different cement pastes were set, using CFA and BFA as supplementary cementitious materials (Table 3.9). The reference mix designated 100C, two mixes with 50%wt of cement replacement with BFA and with CFA, 50C-50BFA and 50C-50CFA, respectively, and one mix with 50%wt of cement replacement with a blend composed of the two fly ashes, with 25%wt of each ash (50C-25CFA-25BFA). A constant water-binder ratio of 0.5 was used for all mixes. The selection of these quantities was due to the fact that this study focused on the effect that the BFA can have on the part corresponding to the binder of HVFAC, and for the determination of the quantities a conventional concrete was considered (with 350 kg/m^3 of binder and with a w/b of 0.5).

4.2.1Thermal Analysis

Figure 4.1 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 4.1, where the values obtained in pastes at 28 and 90 days are shown.

Table 4.1 - Mass losses at 28 and 90 days

Sample	Uncombined water		$Ca(OH)_2$ (wt%)		$CaCO_3$ (wt%)		Total mass loss	
	at 28days	at 90days	at 28days	at 90days	at 28days	at 90days	at 28days	at 90days
100C	9.66	11.78	3.46	3.32	6.34	7.16	27.00	31.44
50C-50CFA	10.21	9.97	1.30	0.67	7.16	13.75	23.23	26.30
50C-50BFA	8.27	11.62	2.32	1.27	6.75	15.52	22.33	29.70
50C-25CFA-25BFA	5.80	8.83	1.88	0.84	6.77	17.31	18.65	26.63

The first peak observed in the graphs of TG/DTA was related to the loss of free water that occurs between 0 and 105 ºC. The water in the large pores evaporated for temperatures up to 35 ºC. Above this temperature, the retained water is released by capillarity tension in the capillarity pores [212]. The water that is not chemically combined is not used for the calculation of the level of hydration [212,353,374].

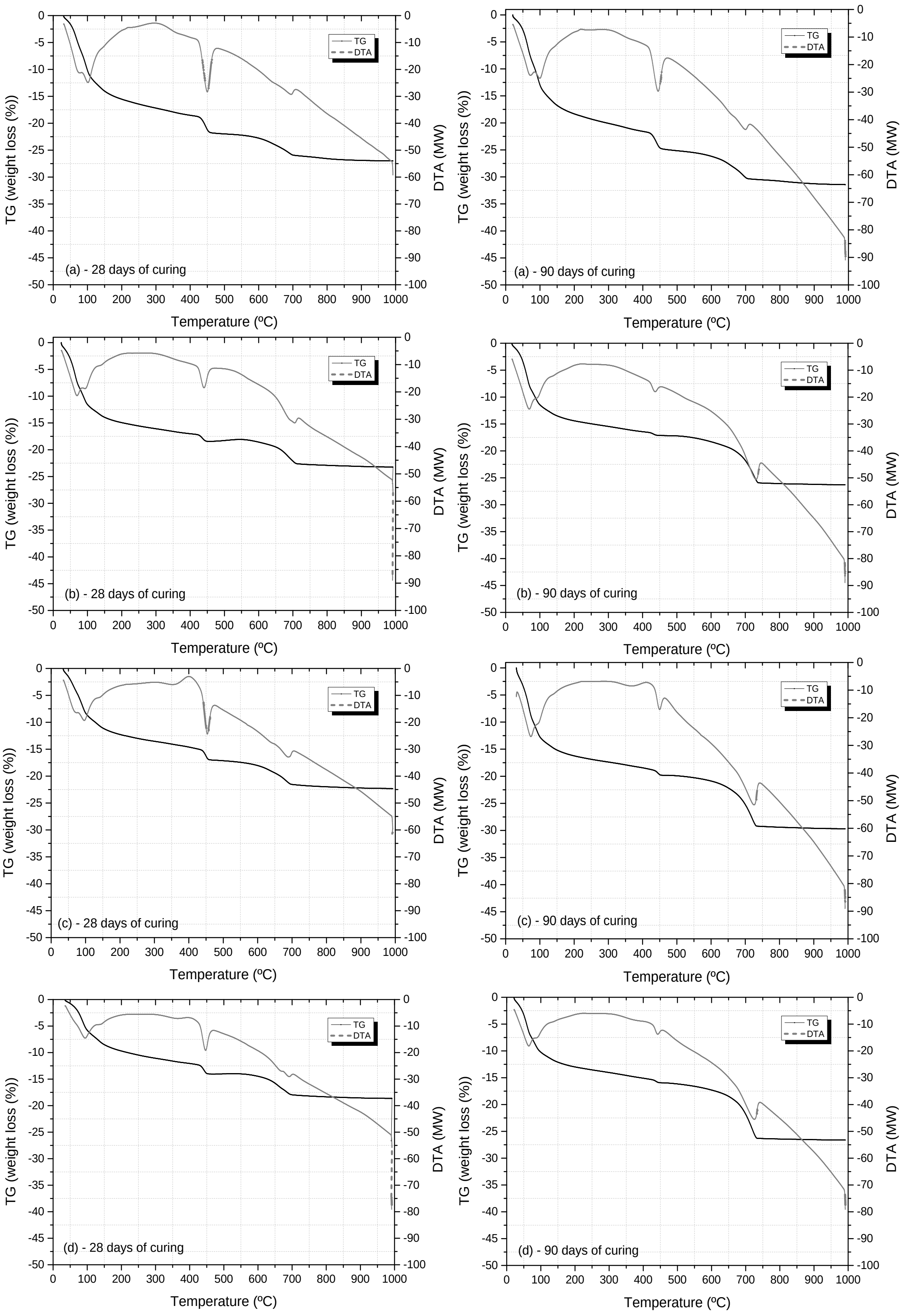


Figure 4.1 - Thermogravimetric analysis of the 100C (a), 50C-50CFA (b), 50C-50BFA (c) and 50C-25CFA-25BFA (d) specimens.

A weight reduction of samples was observed for temperatures between 150 and 400 ºC (Figure 4.1). This is due to the evaporation of the physically combined water from the reaction products (for example C-S-H gel and aluminosilicate gel) [132,375,376].

Figure 4.2 shows the chemically combined water found in the hydrated pastes after 28 and 90 days. 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. The hydration degree (α) was calculated, which is the weight fraction of original cement that has become completely hydrated (0≤α≤1) [63], as observed in Equation 23.

$$\alpha = \frac{W_n}{W_\infty} \tag{23}$$

Where:

α is the hydration degree;

W_n is the combined water content (%) at a presented curing age;

$W\infty$ 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 completely hydrated [63,377].

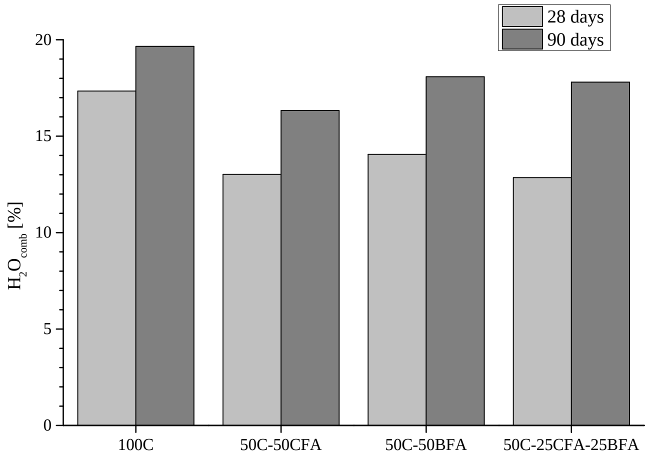


Figure 4.2 - Chemically combined water content after 28 and 90 days

The degree of hydration obtained for the hardened cement pastes can be found in Table 4.2. 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 those of the reference sample.

Table 4.2- 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 $Ca(OH)_2$ content for the different pastes is presented in Table 4.1. This compound is formed during the hydration of dicalcium silicate (C_2S) and tricalcium silicate (C_3S) contained in the cement. Some authors showed that for cement CEM I 42.5, this is formed at 3 days of curing [378]. One of the most noted peaks in the TG/DTA curve (Figure 4.1) corresponds to the mass related with the dehydroxylation of calcium hydroxide, which occurs between the temperatures of 410 and 480 ºC [101]. The content of free calcium hydroxide is an important parameter to assess the hydration, is shown in Figure 4.3, and was calculated according to Equation 10.

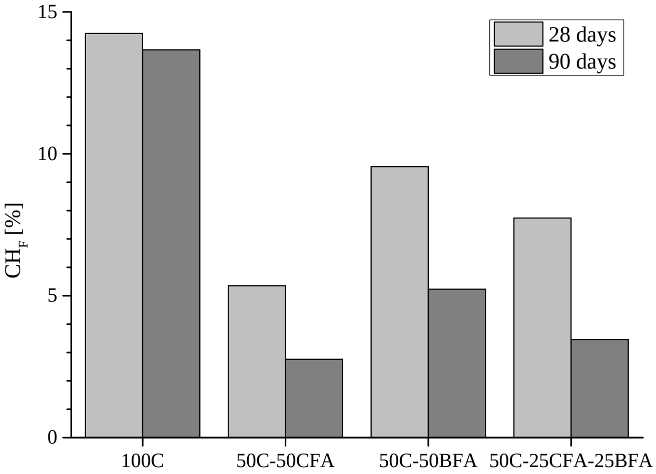


Figure 4.3 - Content of CH_F in pastes after 28 and 90 days

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 [212]. A 50%wt cement replacement was studied for each paste sample. If the ash contributed nothing to the pozzolanic reaction, the $Ca(OH)_2$ present 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 (Figure 4.1). The results showed that BFA did not have a significant contribution to 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 [80,129]. 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 [190,196,203].

The last peak observed in the thermogravimetric analysis was related with calcium carbonate (650-800 ºC) (Figure 4.1). Similar results were observed in various studies [132,375,376,379]. The $CaCO_3$ analysis is very important because it is related to the carbonation phenomena and can consequently affect the corrosion of the concrete reinforcement. The $CaCO_3$ content for different pastes is presented in Figure 4.4 and was determined by the results expressed in Figure 4.1 and the values obtained by Equation 14. As can be seen, the content of calcium carbonate was higher for pastes with the two types of fly ash than for pastes containing cement only. The content of $CaCO_3$ 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 CO_2 concentration in the atmosphere and the physical characteristics of materials, which allow some resistance to CO_2 penetration [195]. In terms of total loss mass (Table 4.1), an increase of mass loss was observed with the increase of the curing age. This is related to the increase in $CaCO_3$ content at 90 days.

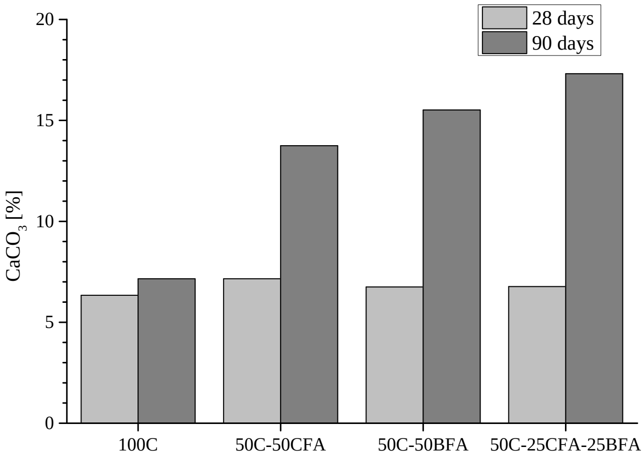


Figure 4.4 - Content of $CaCO_3$ in pastes at 28 and 90 days

4.2.2Mineralogical Analysis

Figure 4.5 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 [80] and are part of the chemical composition of Portland cement [57]. The presence of C_2S peaks for pastes with fly ash can be observed for both ages that show the presence of unhydrated cement grains. C_3S peaks were not observed and this was expected, since this compound has a higher reaction rate with respect to C_2S [212].

It was verified that the intensity of the portlandite ($Ca(OH)_2$) peak was significantly higher for the plain cement mix (Figure 4.5) and similar results were observed in [67]. This indicates higher hydration and corroborates the values obtained from chemically combined water obtained by TG/DTA (Figure 4.2).

A significant increase in the C-S-H 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 C-S-H peak. It is possible that the amount of C-S-H was derived from the introduction of BFA of compounds that reacts and increases the hydration.

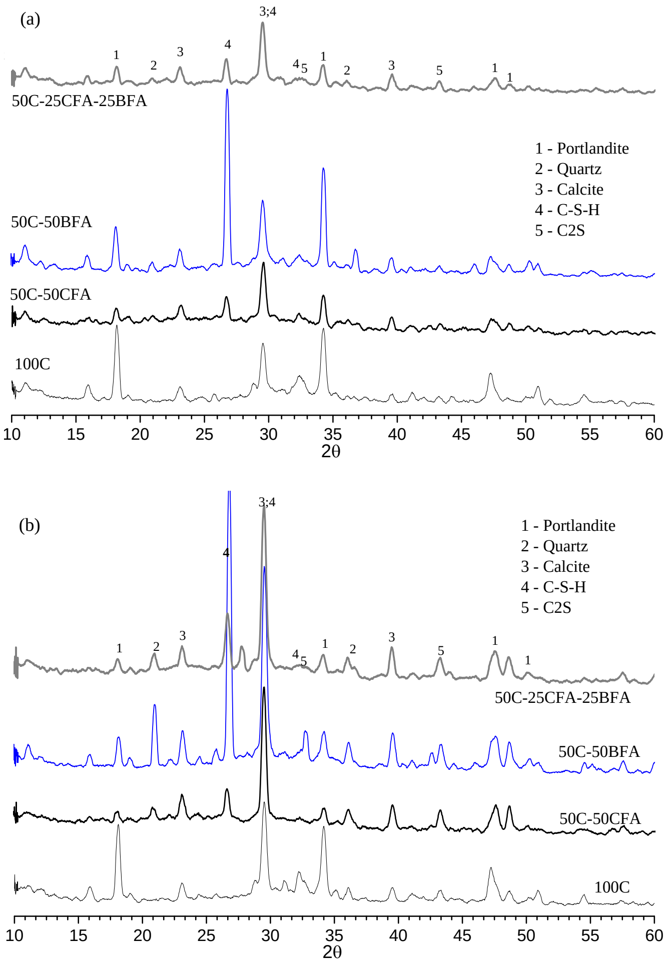


Figure 4.5 - XRD patterns for pastes with: (a) 28 days and (b) 90 days

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 Figure 3.5. As was 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.

4.2.3Accelerated Carbonation Test and pH Measurement

The results for the carbonation depth at the two curing ages during the test period are presented in Figure 4.6. No initial carbonation was observed for any pastes before being exposed to CO_2 at the two curing ages. The reference paste showed very slow progress in 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 [18,21,90,92,207,380] and this is due to the consumption of calcium hydroxide and the consequent decrease in pH [21,324,381].

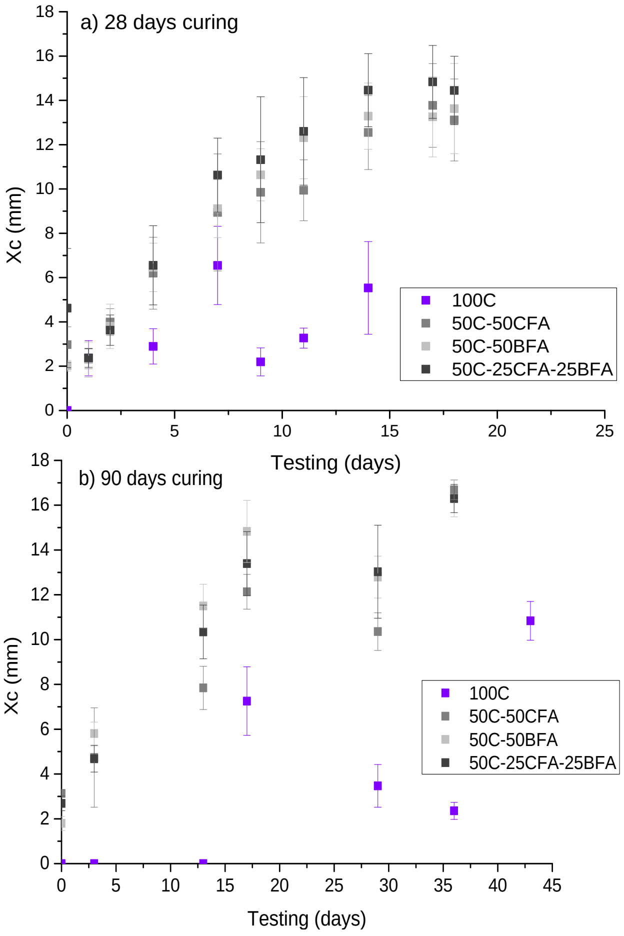


Figure 4.6 - Variation of carbonation depth for the different pastes

The test was carried out until the sample did not show a colour change, when sprayed with phenolphthalein, which means that the sample is totally 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 total carbonation of the samples after 36 days of testing and at this age the cement paste presented low values of carbonation depth. No significant differences between the values of carbonation depth were observed in the pastes with fly ash and this confirmed the results shown in the TGA analysis (Table 4.1). As observed in Table 4.1, 50C-25FA-25BFA presented the highest values of calcium carbonate at 28 days of curing. At 90 days, the 50C-50BFA sample presented higher values of carbonation depth, but at the end of the test the results were similar for all paste samples (Figure 4.6).

In Table 4.3, 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 [83]. There was an increase in the pH during hydration at 28 and 90 days of curing, when compared with the fresh sample.

Table 4.3 - Values of pH measured in pastes

Samples	After demoulding	28 days		90 days	
		After curing	After total carbonation (20 days)	After curing	After total carbonation (36 days)
100C	12.24	12.69	11.65*	12.44	12.50*
50C-50CFA	12.35	12.70	9.94	12.07	10.27
50C-50BFA	12.34	12.72	9.90	12.23	10.00
50C-25CFA-25BFA	12.38	12.71	9.89	12.16	9.97

*the pH value is the value that cement paste had at the time when the samples of pastes with ash are totally carbonated

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 were totally carbonated (Table 4.3). This decrease is diagnosed to result from carbonation [380]. The pH analysis of solid samples after the carbonation test was in agreement with the phenolphthalein indicator, which shows colour changes around 9.

4.3 Effect of Cement Replacement by Biomass Fly Ash on Mortar Properties

A group of 16 formulations of mortar (Table 3.10– Group A of tests) was set using BFA as the cement replacement and use of the same ash but blended with CFA. In those formulations, a CEM I 42.5R (Outão, Secil) cement was used and a commercial river rolled sand 0/4 mm was used as aggregate. Three levels of cement replacement were studied: 20, 40 and 60%wt. All mortar mixes were made with 1 wt. part of binder (considered the sum of cement and fly ash): 2.5 wt. parts of aggregate and water-binder ratio (w/b) of 0.5. For each mortar mix, three samples were produced. All mortar formulations were cured in a controlled humidity chamber, with approximately 87% of relative humidity and 21 ºC of temperature.

4.3.1 Fresh Properties

The flow spread results obtained are presented in Figure 4.7, expressed as an average of three samples and it was possible to observe that there was no significant dispersion for the three samples of each mortar. The values obtained for the studied formulations showed that mortars with fly ashes had lower spread value than the reference mortar (REF1). However, the differences were, in general, not relevant, except for mortars made without CFA and with BFA replacement percentages higher than 40%wt. The incorporation of CFA only did not present a significant influence on the flow spread when compared with cement. On the other hand, a decrease in the flow spread value was observed with the increase of cement substitution with BFA (alone or blended with CFA) when compared with the reference mortar. The lower value was observed in the mortar with 60%wt of cement substitution by BFA. These results are explained by the physical characteristics, mainly the irregular shape of particles and in the high specific surface area. Furthermore, the presence of a significant organic matter content can support the adsorption of water molecules [22], leading to the flow spread value decrease.

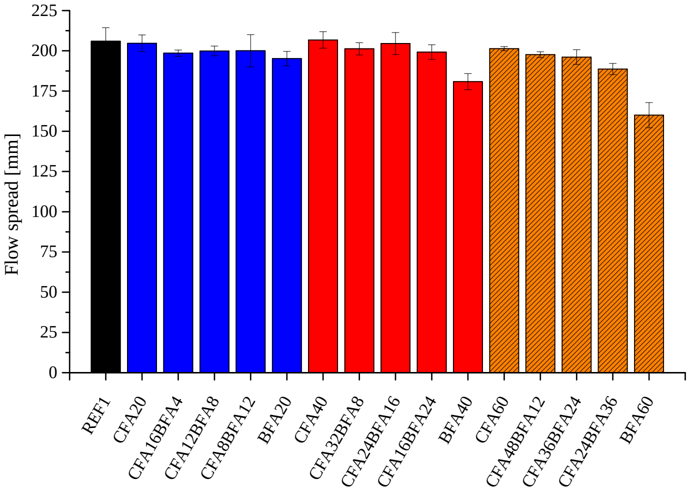


Figure 4.7 - Values of flow spread of mortars prepared with different fly ashes incorporations

4.3.2 Mechanical Strength

The flexural strength values of mortars containing BFA or/and CFA and of the reference mortar are shown in Figure 4.8. As can be seen, the values of the flexural strength of all mortars made with BFA and/or CFA at 2 curing days were lower than that of the reference mortar and a significant decrease was observed in all mortars with 60%wt of cement substitution. In mortars with 20%wt of cement replacement and at 2 curing days, an increase was observed with the BFA increment, and the highest value was observed in mortars with 20%wt of cement replaced with BFA. For the other curing periods, the flexural strength values of the mortars with 20%wt of cement substitution (CFA20 to BFA20) were slightly lower than that of the reference mortar, with the exception of BFA20 at 90 days that presented a higher value than the reference mix, and the best values were observed in BFA20. For the other cement replacement percentages, the flexural strength values were lower than that of the reference mix, and the highest values were again observed in mortars with cement replaced with BFA.

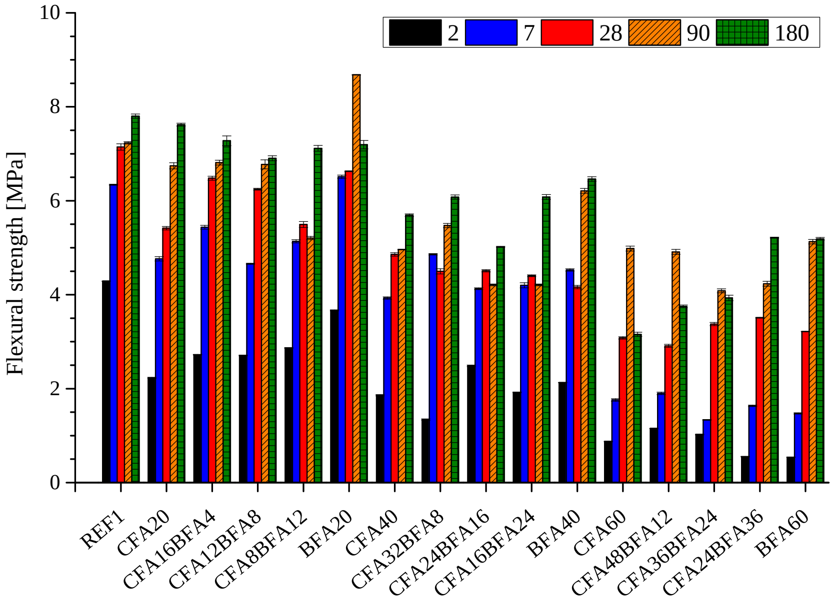


Figure 4.8 - Evolution of the flexural strength values of mortars up to 180 days of curing

The values for compressive strength of mortars are shown in Figure 4.9. As can be seen, the compressive strength values of all mortars with BFA or CFA and at the different curing periods showed lower values than the reference mortar, with the exception of CFA16BFA4 at 180 curing days.

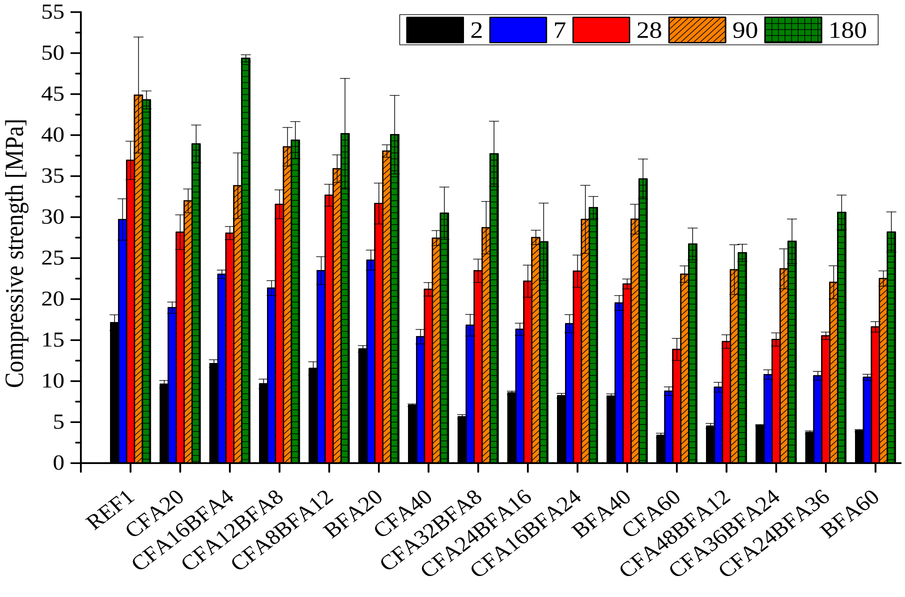


Figure 4.9 - Evolution of the compressive strength values of mortars up to 180 days of curing

The values increased with curing time and this is related with the fact that pozzolanic materials show low early strength and a higher development of strength with age [382]. Mortars with 20%wt of cement replacement presented better results when compared with the reference mortar, at all curing times. It was observed that an increase in the biomass fly ash content allows an increase of compressive strength, for mixes with 20%wt of cement replacement.

For the other percentages of substitution, no significant differences were observed between mortars with CFA, blended of CFA and BFA and BFA only. However, in the three percentages of substitution, and for all curing periods, the best results were found in mortars with BFA, followed by the mortars with more content of BFA in the blends with CFA. The lower values of compressive strength of mixes with coal and/or biomass fly ash compared to the ones made without cement replacement can be due to its particle geometry/dimensions. BFA particles are coarser than those of coal fly ash and this may lead to an increase of the porosity of mortars [80].

4.3.3 Water Absorption and Dry Bulk Density

The influence of the presence of fly ashes on the water absorption by capillarity of mortars (after 28 days curing) is shown in Figure 4.10 and Figure 4.11. Mortars with 20%wt of cement replacement and with high BFA content (CFA8BFA12 and BFA20) showed lower values of water absorption when compared with the reference mortar (REF1).

Mortars with 40%wt of cement replacement with CFA (CFA40) exhibited higher values than the reference mix. However, 40%wt of BFA led to capillary water absorption similar to that observed in plain cement mortar (BFA40). Formulations with 60%wt of cement replaced presented higher values of water absorption by capillarity when compared with the reference ones, with the exception of BFA60 formulation.

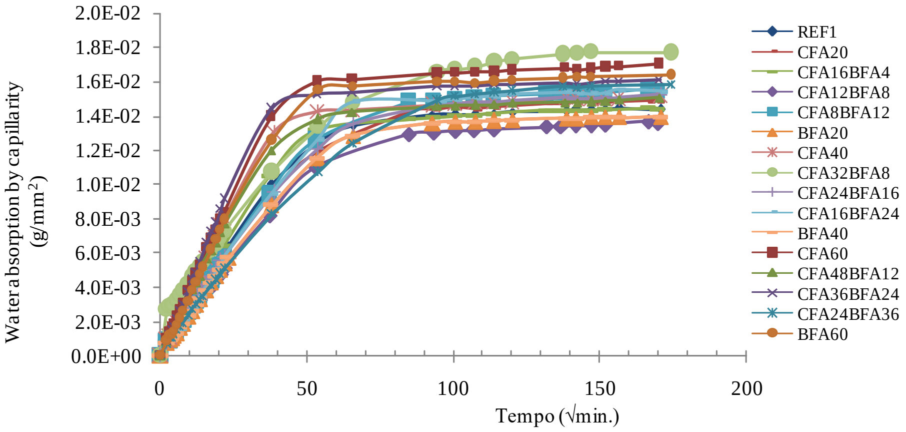


Figure 4.10 - Water absorption capillarity evolution of the different formulations

Figure 4.12 and Figure 4.13 show the values of open porosity and the volume (determined by Equation 16) obtained from the water absorption by immersion test for all mortar formulations. All mortars exhibited higher values of water absorption when compared with the reference mortar. The presence of BFA seems to have a slight positive effect when compared to the values obtained in CFA mixes.

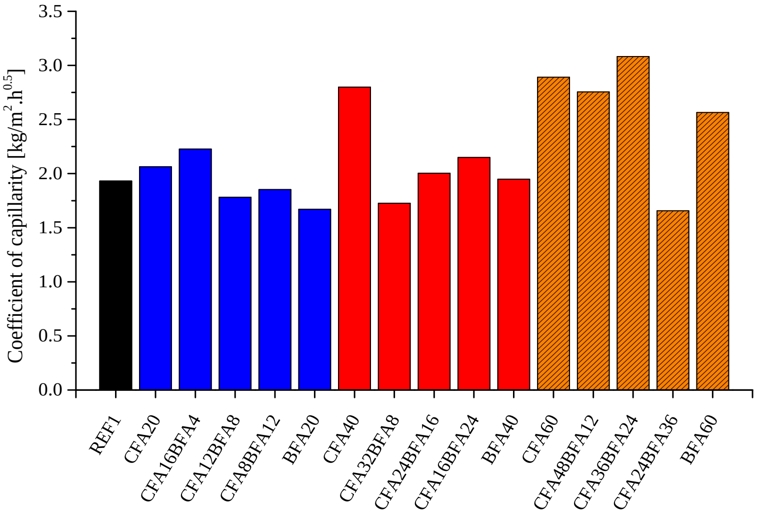


Figure 4.11 - Water absorption capillarity coefficient of the different formulations

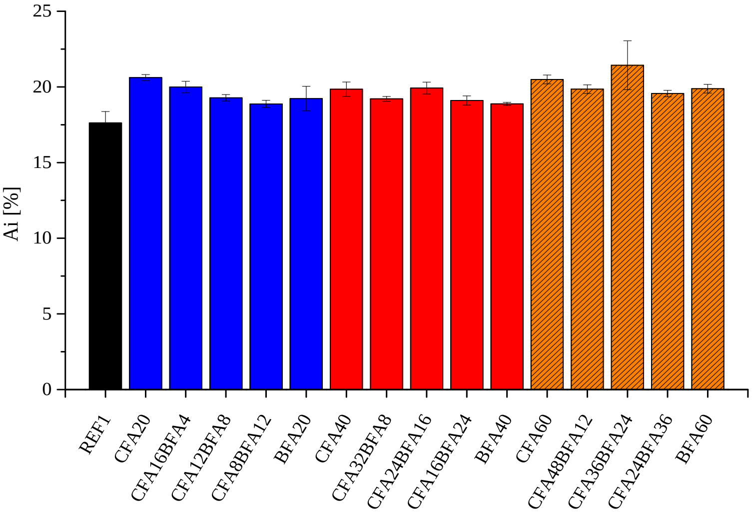


Figure 4.12 - Values of the water absorption by immersion (expressed in %) of each mortar formulations

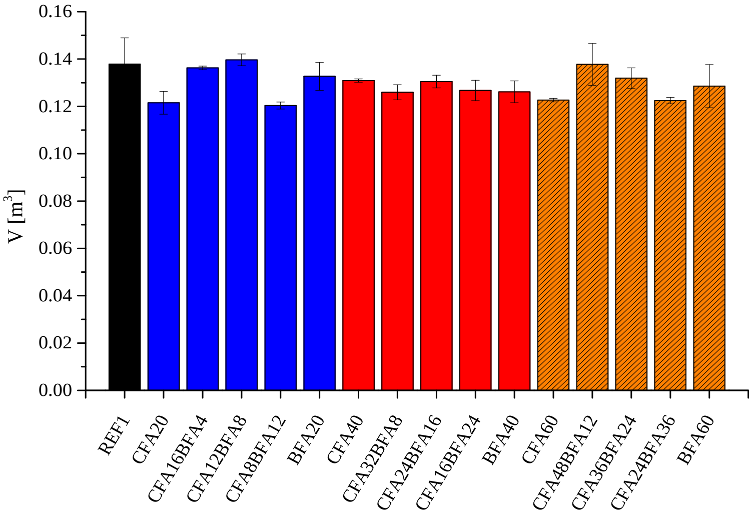


Figure 4.13 - Values of water absorption by immersion expressed in terms of volume (expressed in m^3) for each mortar formulations, determined by Equation 16

4.3.4 Shrinkage

The shrinkage behaviour of mortars over time and with different contents of the selected fly ashes is presented in Figure 4.14. A higher shrinkage rate was observed in the first 14 days. After that period, the shrinkage values were still growing but at a lower rate. The incorporation of fly ashes reduced the shrinkage of mortar at a later age and all values were lower than in the reference mortar. Similar results were found in [311].

The weight loss was similar for the different mortars at early ages, but after approximately 5 days differences could be observed. The mortar with higher content of fly ashes and with a higher percentage of cement replacement exhibited the highest weight loss values. These results showed that even though the formulations with high content of fly ashes presented higher weight loss values, this did not lead to higher shrinkage values. This could be related to the fact that shrinkage was possibly affected by other parameters in addition to weight loss, such as porosity. Plain cement mortar presented a finer pore structure, and this could lead to the shrinkage values increase [383]. Another explanation for this could be related to the different types of shrinkage. The decrease in cement content in mortars with fly ash could reduce the effect of autogenous shrinkage and thus the drying shrinkage becomes more significant.

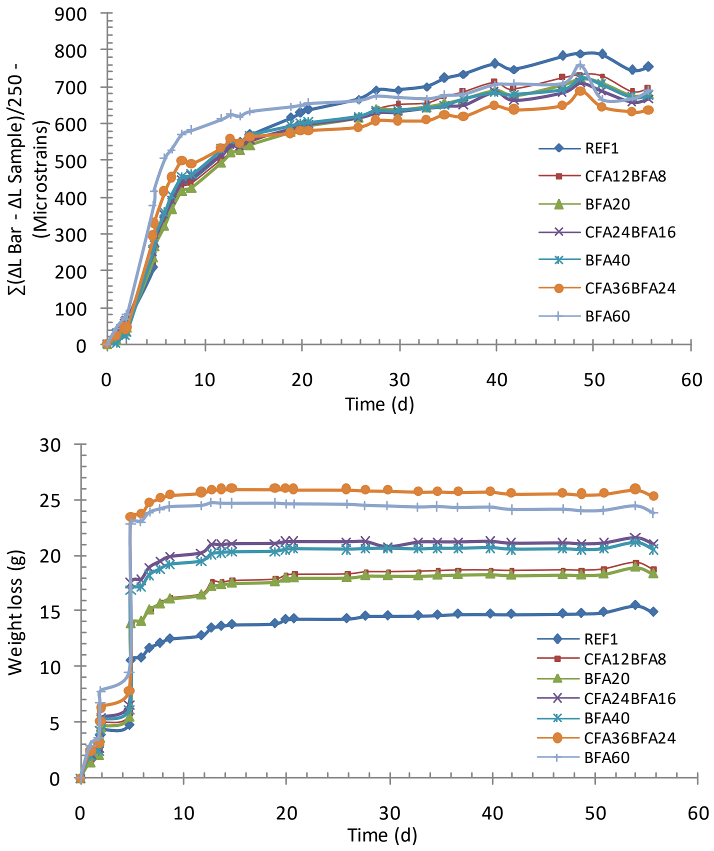


Figure 4.14 - Average values for total shrinkage and weight loss with time of the different mortars formulations

4.3.5 Water Leaching

The pH, conductivity and chemical elements after water leaching are given in Figure 4.15 and Figure 4.16. The pH of the leaching solutions was measured at a temperature of 25.4±1.2 ºC. The water leaching of samples originates alkaline solutions, with pH in the range of 10.5 to 11.8. The pH decreased with the increase of cement substitution, being the lowest values observed for mortars with 60%wt of cement replacement.

The conductivity of mortars varied in the range of 341 to 1761 µS/cm. The highest value was observed in the mortar containing only cement (REF1) and the lowest value in the mortar with 60%wt of cement substitution (CFA36BFA24). The conductivity is related with the concentration of dissolved ions, among those the ions derived from alkali elements such as Na, K, Ca, and also ions derived from Cl and S (Figure 4.16). Higher conductivity reveals a higher ionic strength of the solution and this is associated with higher concentration of ions, thus reflecting a higher solubility of alkali elements, chloride and sulphur [264].

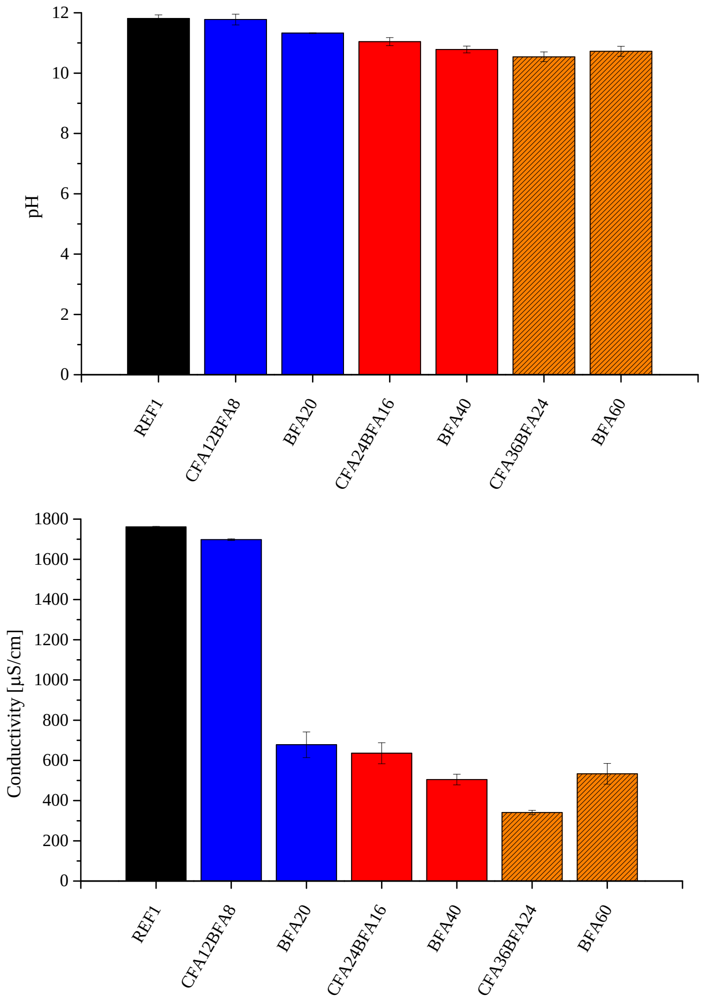


Figure 4.15 - pH and electrical conductivity of the mortars' leaching solutions

Calcium was the element present in higher concentration in the leaching solution of the mortar made with cement only (Figure 4.16). In the other formulations, potassium was the major chemical element with higher concentration. This can be caused by the high calcium content of cement (Table 3.3) and with the substitution of this material by BFA. A decrease in its content in mortars is expected and during leaching the calcium content solubilized was lower. An increase of the potassium released was also observed with the increase of BFA content, and this can be explained by the fact that this BFA presented a higher content of this major chemical element (Figure 3.5).

The concentration of heavy metals in the leaching solutions of mortars is fairly low, and in some mortars, it was below the limit detection. Aluminium presented concentration values higher than 7 mg/kg for all formulations, but the other chemical elements had concentrations below 0.6 mg/kg. This leads to the conclusion that the presence of these elements in mortars was in very low concentration and/or these elements are not very solubilized in water. This is an important parameter in terms of environmental performance.

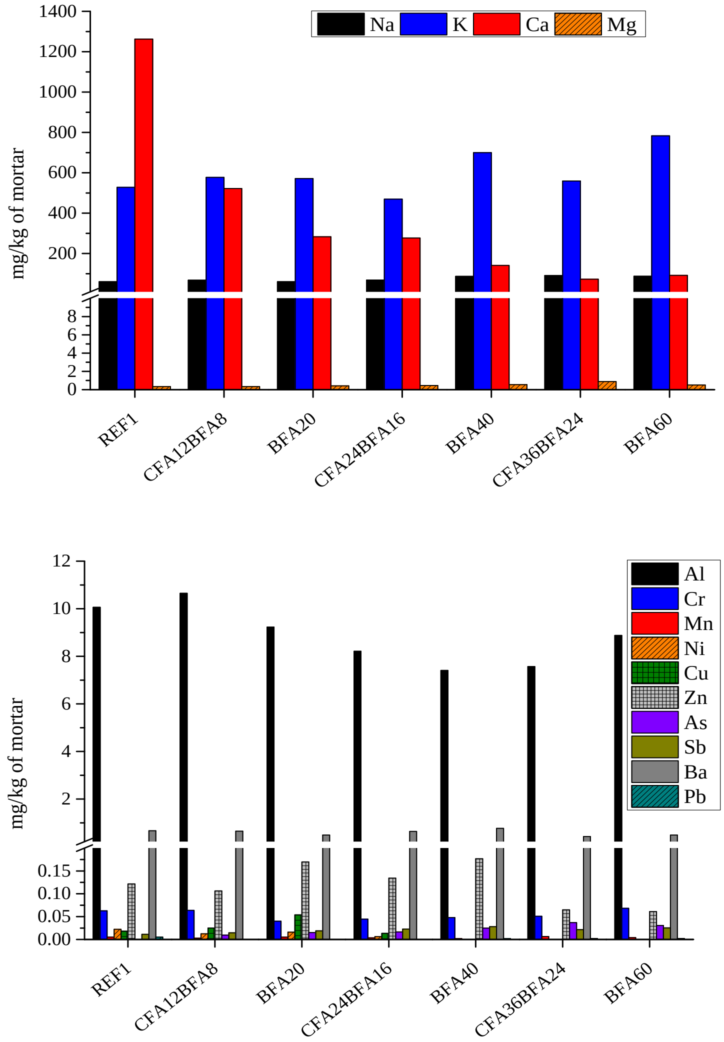


Figure 4.16 - Water soluble chemical elements in solution after 24 h leaching, expressed per mg of chemical element per kg of mortar

4.4 Effect of Biomass Fly Ash on High Volume Fly Ash Mortar Properties

A set of mortar formulations (Table 3.10 – Group B) was studied to understand the effect on the quality, durability and sustainability properties of mortars that use high volume of BFA as cement replacement and to understand whether slight amounts of hydrated lime (HL) or BFA (an alkaline waste) contribute to solve the problems of alkalinity found in the mortars with a high amount of cement replaced with CFA.

In the preparation of all high volume fly ash mortar mixes, the main goal was to reduce the cement content in order to increase the environmental performance, while maintaining the quality and durability properties. The powder materials used in the mixes were Portland cement CEM I 42.5R, CFA, BFA and HL. The aggregate used was a commercial river rolled sand 0/4 mm. All mixes were produced with 1 mass basis (wt.) part of binder (taken as the sum of cement, fly ashes and hydrated lime): 2.5 wt. parts of aggregate. Two water/binder ratios (w/b), 0.5 and 0.35, were studied, and the proportion of cement replacement was 50% by weight. Additionally, a commercial polycarboxylic ether superplasticizer (Glenium Sky 617), was used for the mixes with w/b=0.35. No further chemical admixtures were used. The characteristics of each material are described in Chapter 3.

The experimental procedures include, for each mix, the evaluation of the flow spread, bulk density, air content, flexural and compressive strength, water absorption and carbonation. The tests were conducted to assess the workability, mechanical strength and durability properties.

4.4.1 Workability, Density and Air Volume Content

The flow spread values obtained for each mortar formulation are shown in Figure 4.17. For mortars with a w/b of 0.5 it was observed that all mortars presented higher values than the reference one, with the exception of mortars with 49.5%wt and 48.8%wt of BFA and 0.5%wt and 1.3%wt of HL. Those mortars showed lower values than the reference mix. These results are in accordance with those achieved in [27,255]. The incorporation of CFA in the mixes, alone or blended with BFA or/and HL, increased the value of spread flow when compared with the reference mix and with the mixes containing BFA only, with the exception of the 45BFA5HL mix. The mixture with 50%wt of BFA presented lower values for flow spread than the mix with 50 %wt of CFA. This behaviour was also verified before in the mixes with 40 and 60%wt of cement replaced by those two fly ashes (Figure 4.7).

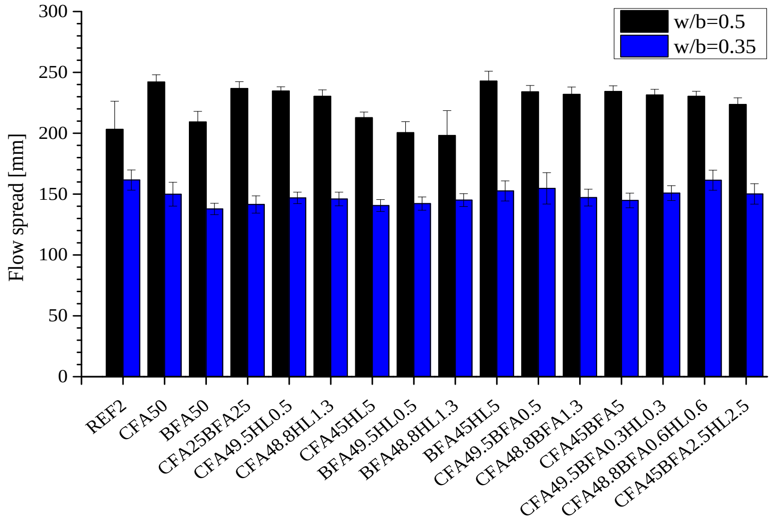


Figure 4.17 – Flow spread determined in each mortar formulation for the two water/binder ratios

Mortars with 0.35 (w/b) presented values lower than mortars with 0.5 of w/b in all batches. This was expected, since a decrease of the water content leads to a decrease of the workability of mortars [384]. All mixes with the two fly ashes and with hydrated lime had lower values than the reference mix, which uses cement only as binder, but it is important to refer that this mix had a higher SP content than the others (3% - Table 3.10). This is the result of a cement replacement with supplementary cementitious materials and because of that a superplasticizer was added to the mixes to keep a good workability. The dosage of superplasticizer was adjusted to obtain a flow spread between the class ranges of 140-160 mm. Mortars with BFA presented the lowest diameter values. It seems that the superplasticizer was less effective in the mixes with BFA than in those with CFA, and this explained a higher content of SP used in the mixes with BFA to maintain the workability (Table 3.10). These results were due to the fact that BFA presents a heterogeneous distribution of particles, with irregular shape and fineness, that determines the high specific surface area and controls the compactness of the mixes [27,297]. Besides that, the high organic matter (Table 3.3) leads to an adsorption of water molecules, which leads to a decrease of the free water available for workability purposes [27,30,255].

In terms of density of the fresh mix, no significant differences were observed between the different mixes for the two water/binder ratios (Figure 4.18). However, a slight increase is noted of the density values in the mixes with 0.35 of w/b, for some mixes.

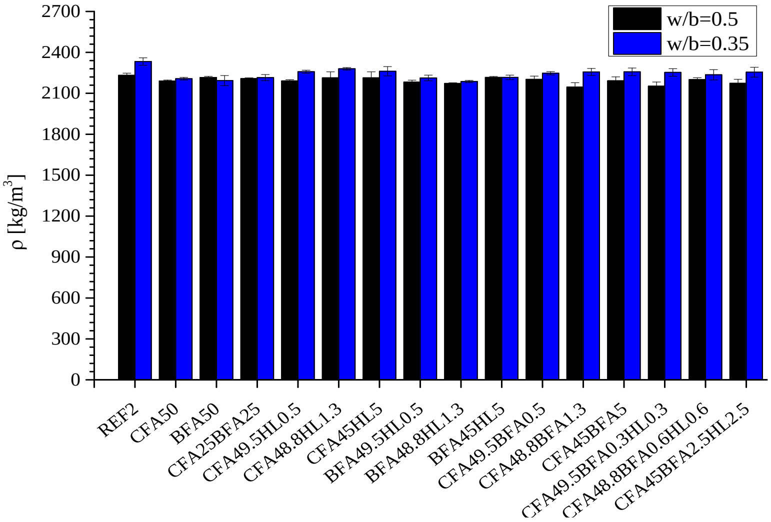


Figure 4.18 – Density of fresh mixes determined for the two water/binder ratios

Significant differences were observed in the amount of air content (Figure 4.19) between the mixes with 0.5 and 0.35 of w/b. For mortars with 0.5 of w/b, the reference mix presented more voids (almost 3% of air content) than the other mixes. Once again, the mixes with high content of BFA mixed with low HL content presented a similar behaviour when compared with the reference mix. Mixtures with high content of CFA presented lower values (below 1%). Similar results were found in others studies [47,385–388]. The results can be explained by the smooth surface characteristics and the spherical shape of CFA which improved the fresh properties of concrete [385]. One important observation was that the decrease of the water/binder ratio and the incorporation of two fly ashes and/or hydrated lime led to an increase of the air voids content (Figure 4.19) but it is difficult to define any tendencies with these results.

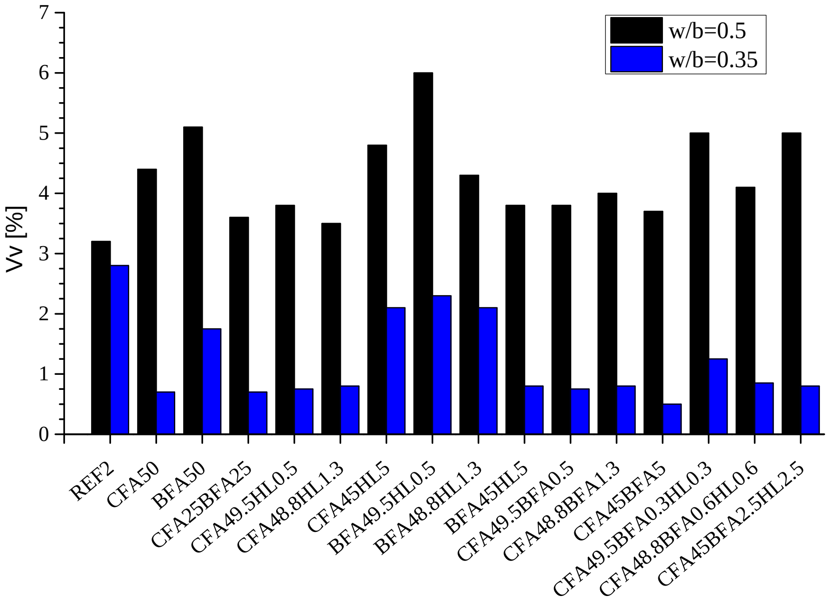


Figure 4.19 – Air volume of fresh mixes determined for the two water/binder ratios

4.4.2 Electrical Resistivity

The electrical resistivity was measured over time (2, 7, 28, 56, 90 and 180 days) to understand the hydration process [27] of mortars and the results are presented in Figure 4.20. Mortars have electrical conductivity mainly due to the fact that ions can propagate in their volume. Electrical resistivity is directly dependent on mortars' permeability. In more permeable mortar, the propagation of ions in the medium is easier. By increasing the number of ions in the pore solution, a decrease on the electrical resistivity can be observed [389].

An increase of the electrical resistivity with the decrease of the w/b ratio was registered (Figure 4.20). This is due to reducing the amount of w/b that leads to an increase of the densification of the cement paste, which results in a reduction of the mortar's permeability and conductivity [389].

The electrical resistivity's evolution was similar in all mortar formulations and for the two w/b ratios, increasing with the curing period. At the early ages, the reference mortar presented higher resistivity values in comparison with the mortars containing the two fly ashes. Similar results were found in other research and this behaviour can be explained by the fact that a higher content of cement leads to a faster setting [27]. The time needed for pozzolanic reaction between CFA or BFA and $Ca(OH)_2$ resulting from cement hydration leads to longer setting periods in these mortars [40]. Besides, there was a delay in the gain of resistivity in mortars with fly ashes at the early ages. The values observed after 28 days of curing (for the two w/b ratios) were higher than those registered in the reference mortar (Figure 4.20).

Mortars with CFA alone or blended with BFA and/or HL presented a higher electrical resistivity and similar results were found in other studies with pozzolanic materials [219,390]. These results showed that the lack of cement was compensated by the synergetic effect between CFA with BFA [390]. This increase in the electrical resistivity can be related to the fact that a decrease in the conductivity of the pore solution occurs by means of reducing in OH^- ion, which is one of the most important parameters in the conductivity properties of the pore solution [391,392] and with a higher compactness of those mixes [21]. Furthermore, mortars with BFA alone or blended with HL presented the lowest values of the electric resistivity, which can be explained by the fact that these mixes are less dense and have a porous cementitious matrix. Besides that, it is important to note that these mortars seem to be less permeable than the Portland cement mortars (REF2).

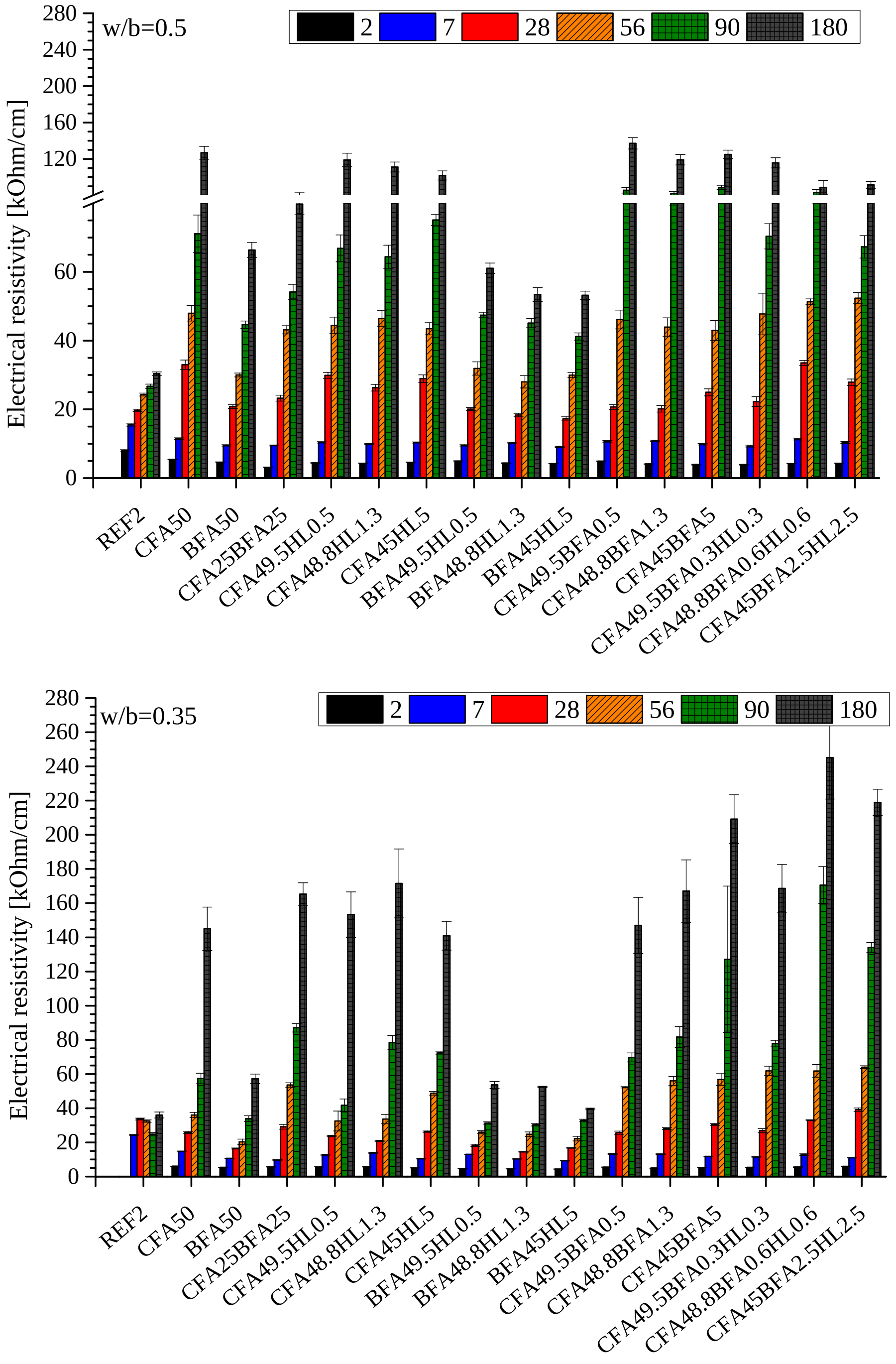


Figure 4.20 - Electrical resistivity evolution of mortars for the two water/binder ratios

4.4.3 Mechanical Strength

In Figure 4.21, the average values obtained for the flexural mechanical strength of the different mortars, for the two w/b ratios, can be observed.

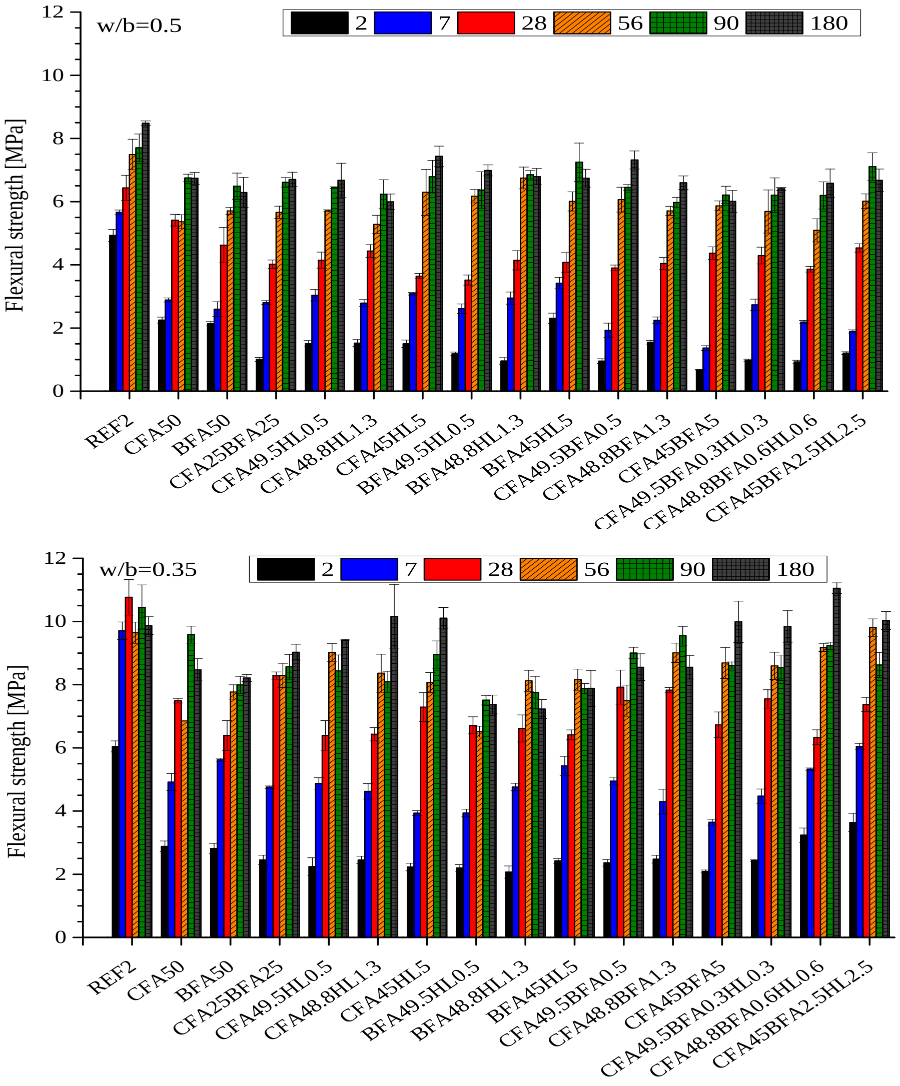


Figure 4.21 - Evolution of the flexural strength values of mortars with the curing period for the two w/b ratios

In general, the values of the flexural strength increased with the increase of the curing period. The decrease of the water/binder ratio led to mortars with higher values of flexural strength. This result was expected, as it is well known that a decrease of the water/binder usually leads to a gain in strength [384].

The replacement of cement with CFA, BFA or/and a blend of the two ashes led to a decrease of 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 contribute to decreasing the strength of materials, despite the pozzolanic reaction, not sufficient to offset the lack of cement [30,31,246,324,393,394].

In terms of the utilization of HL, in mortars with CFA and BFA, the best results were observed in the composition with the highest hydrated lime content. However, when BFA was used in mortars with CFA, the mortars with lower BFA content presented the best results for w/b=0.5

and with higher BFA content for w/b=0.35. Using the two ashes and HL had different effect 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 4.22). A significant decrease was observed with the incorporation of ashes and HL as cement replacement in the compressive strength, when compared with the reference mix. The introduction of fly ashes leads to a delay of the hydration process, which leads to a retardation of the compressive strength increase [22]. An increase in the compressive strength with the curing age was also observed and similar results were found in [68,246,280,281,342,395,396].

The use of BFA as cement replacement material led to a mortar with lower strength than that with CFA (Figure 4.21) and was more notorious in samples with w/b of 0.35. Several studies showed that the use of BFA as partial cement replacement in concrete leads to a decrease of the compressive strength [30,31,255,276,294]. Besides that, it is important to note that BFA did not present a high pozzolanic activity index (Table 3.5), and this shows that this material does not have a behaviour similar to a pozzolanic material. When it is used to replace high amounts of cement, it has a negative effect on the mechanical strength. Contrary to the results obtained for mortars with 40 and 60%wt of cement substitution with a w/b of 0.5 (Figure 4.9), higher values of compressive strength at later ages were not observed in BFA mortars than in mortar with CFA. This may be due to the fact that BFA lost some of its properties during the conditioning, since mortars with 50%wt of cement replacement were prepared later than the other mortars. BFA is quite sensitive to conditioning since it can hydrate and carbonate in contact with air, over time, which may lead to a decrease in its alkalinity and, since these ashes do not have a high reactivity (Table 3.5), this may have led to the production of mortars with a lower compressive strength.

Using HL and CFA in mortars increased the compressive strength the early ages, but it did not have a significant influence with the increase of the curing time. 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 silicates hydrates [397]. Nevertheless, its introduction in mortars with BFA led to an increase of the mortar strength, being the cement substitution of 1.3%wt with HL the content that provides the best results at the different curing ages, when compared with mortars with BFA only.

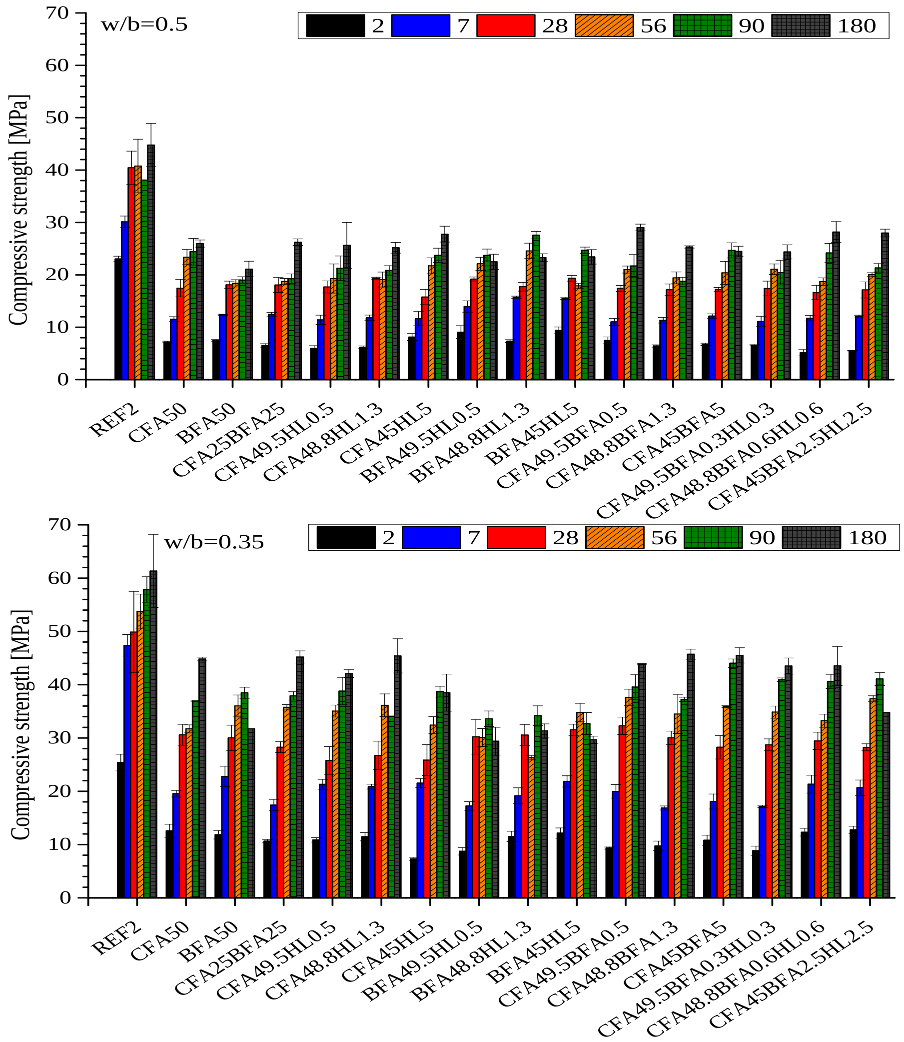


Figure 4.22 - Evolution of the compressive strength values of mortars with the curing period for the two w/b ratios

The introduction of BFA as a reserve of alkalinity of 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 and similar results were observed when the two fly ashes were used together with HL, for the formulations with w/b of 0.5. It was verified that with the increase of the curing period, an increase in the CH in pastes with BFA was observed (Figure 4.1), minimising the consumption of this compound by the pozzolanic reaction. Taking into consideration the cement replacement by the two materials, studied in cementitious pastes, it is possible to determine the content of $Ca(OH)_2$ consumed in pozzolanic reaction (Table 4.4) and the excess given by BFA. To determine the content of $Ca(OH)_2$ consumed by fly ashes during the pozzolanic reaction it was necessary first to calculate the content of $Ca(OH)_2$ in Portland cement. The $Ca(OH)_2$ content was calculated on the basis of the mass loss in the TG curve (400-500 ºC - Figure 4.1), which corresponds to the endothermic effect in the DTA curve. After this, it was necessary to take into account the dilution effect of Portland clinker in fly ash blended cement, which means that it was considered that the portlandite in fly ash Portland cement was (100-%of fly ash)x$Ca(OH)_2$.

Table 4.4 - $Ca(OH)_2$ content consumed in pozzolanic reaction during hydration of fly ash pastes (values obtained using the results expressed in Figure 4.1)

Sample	$Ca(OH)_2$ consumed in pozzolanic reaction(wt%)	
	at 28 days	at 90 days
50C-50FA	0.22	0.11
50C-50BFA	-0.35	-0.46
50C-25FA-25BFA	-0.18	0.09

$Ca(OH)_2$ is one of the products formed during the hydration of Portland cement. In the presence of ashes, calcium hydroxide decreased as a consequence of the pozzolanic reactions. At 28 days of curing, the content of $Ca(OH)_2$ consumed in pozzolanic is very low for the paste with coal fly ash, and this is due to the progress of hydration of cement and simultaneous delay of the pozzolanic reaction at early ages of hydration [80]. Pastes with biomass fly ash presented negative values and this means that biomass fly ash did not react as fast as fly ash at early ages. At 90 days, the calcium hydroxide consumed in the pozzolanic reaction is around 0.1% for the pastes with coal fly ash (alone or blended with BFA) and -0.5% for the pastes with BFA, showing that BFA gave some calcium hydroxide to the paste mix, or that with time some chemical reactions can occurs that allow BFA to act as alkalinity reservoir, and this justified the results shown in Figure 4.22.

In mortars with w/b of 0.35, mortars with CFA blended with low BFA content led to higher values of compressive strength than when CFA only was used as cement replacement material. However, with HL, a similar behaviour was observed for the mortar with 1.3%wt of HL. The improvement of compressive strength can be due to CFA particles breaking down at high calcium hydroxide content and the inner silicate phase becoming suitable for the reaction and the production of more calcium silicates hydrates [397]. In terms of mixes with coal fly ash, biomass fly ash and hydrated lime, up to 90 days of curing, the values observed for compressive strength were similar or higher than those of mortars produced with cement only and coal fly ash. At 180 days, mortars with 0.3%wt of BFA and 0.3%wt of HL and 0.6%wt of BFA and 0.6%wt of HL presented values of compressive strength similar to those of mortars with 50%wt of CFA.

4.4.4 Water Absorption

Water absorption by immersion can assess the open porosity of mortars. These results are shown in Figure 4.23 and similar results were observed for the two water/binder ratios. All mortars containing fly ashes have a higher water immersion coefficient than the plain cement mortar. Similar results were found in [398]. BFA mortars have a behaviour in terms of water absorption similar to that of CFA mortars. In general, the porosity decreased with curing age. This was due to the increase in hydrated compounds content and the latent hydration during the pozzolanic reaction of fly ashes in the presence of calcium hydroxide [98].

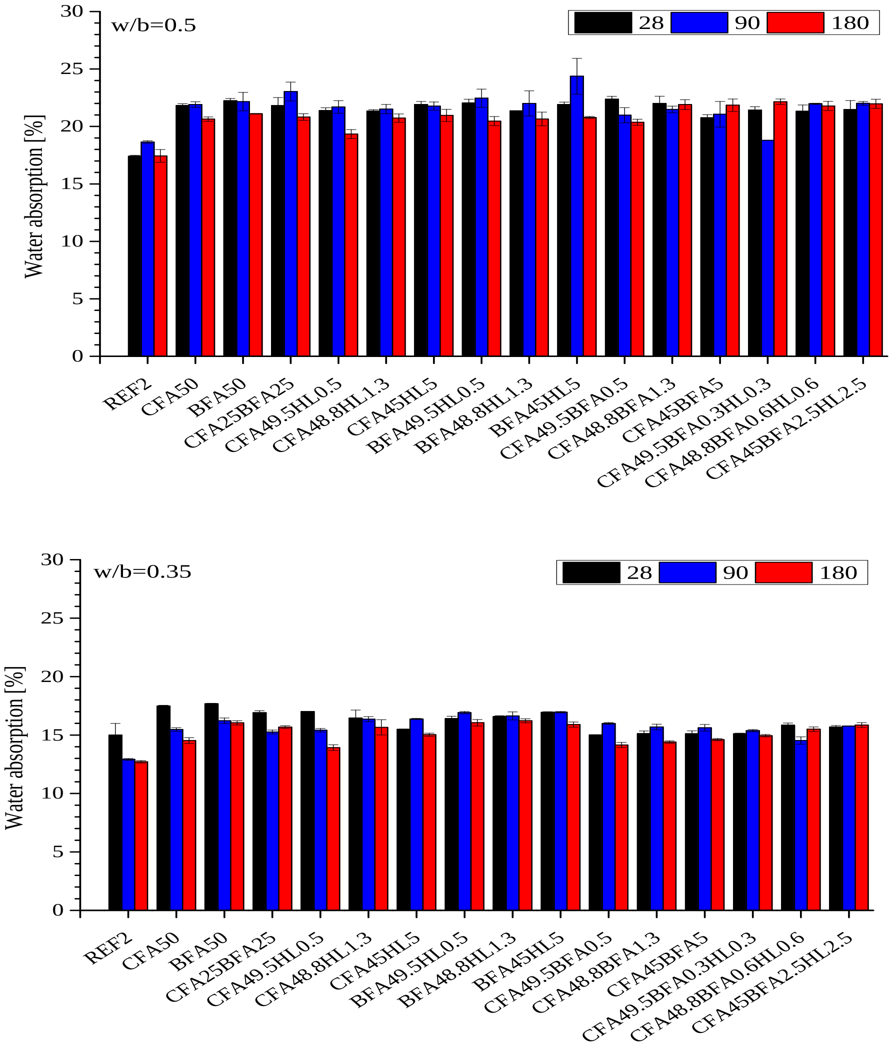


Figure 4.23 - Total porosity of the mortar samples (for the two w/b ratios) determined by water absorption

The introduction of HL in mortar with CFA did not have a different effect on the water immersion coefficient, at the early ages, when compared with the mortar containing CFA only. However, for 180 days curing, the coefficient for mortar with 0.5%wt HL had a lower value than that observed in the mortar with CFA, but still higher than that of the reference one. On the other hand, the introduction of lime in mortars with BFA did not have a different effect on the open porosity when compared to the mortars made with BFA only.

The substitution of cement with 0.5%wt of BFA in mortars with CFA led to a decrease in the open porosity for mortars with 90 and 180 days of curing, when compared to mortars made with cement and CFA only. The other replacements did not lead to an improvement of the open porosity when compared with the mortar containing CFA. Using the two fly ashes and HL together did not allow an improvement in the open porosity of mortars when compared to the reference one or with mortars containing only one fly ash or the two fly ashes.

The capillarity absorption curves are shown in Figure 4.24 and Figure 4.25, for the w/b ratios of 0.5 and 0.35, respectively. The coefficient of capillarity absorption for all studied formulations is shown in Table 4.5.

Table 4.5 - Coefficient of water absorption by capillarity of mortars for the two w/b ratios

Samples		**w/b=0.5**			**w/b=0.35**	
	28 days	**90 days**	**180 days**	**28 days**	**90 days**	**180 days**
		$g/(cm^2.min^{0.5})x10^{-4}$			**$g/(cm^2.min^{0.5})x10^{-4}$**	
REF2	1.75	0.83	1.10	1.07	0.70	0.60
CFA50	1.07	1.01	0.76	1.06	0.90	0.50
BFA50	3.24	1.11	1.10	1.12	0.91	0.85
CFA25BFA25	2.46	1.69	1.43	0.60	0.65	0.24
CFA49.5HL0.5	1.64	1.25	1.24	0.95	0.67	0.48
CFA48.8HL1.3	1.59	1.28	1.23	1.08	0.62	0.50
CFA45HL5	1.62	1.06	1.07	0.82	0.71	0.25
BFA49.5HL0.5	1.74	1.68	2.17	0.94	1.37	0.76
BFA48.8HL1.3	1.25	2.05	1.34	1.25	1.01	0.84
BFA45HL5	2.53	2.06	1.52	0.95	1.09	0.75
CFA49.5BFA0.5	2.08	1.91	1.40	0.77	0.52	0.52
CFA48.8BFA1.3	1.67	1.40	1.33	0.91	0.60	0.43
CFA45BFA5	1.74	1.24	1.44	0.96	0.79	0.34
CFA49.5BFA0.3HL0.3	1.73	1.59	1.33	0.85	0.59	0.45
CFA48.8BFA0.6HL0.6	1.97	1.22	1.39	0.46	0.43	0.32
CFA45BFA2.5HL2.5	1.96	1.39	1.52	0.68	0.45	0.36

In general, the coefficient of water absorption decreased with the curing age and this was expected due to the fact that during curing, the reaction of hydration occurs, leading to a decrease of the voids and the physical structure of mortars. Similar results were found in [399]. For mortars with w/b=0.5, it was observed that mortars with 50%wt of CFA had lower capillarity coefficient than that of the reference mortar. Besides that, mortars with 50%wt of BFA had higher coefficient than the reference and 50%wt of CFA mortars, at all curing ages. It was observed that CFA mortars with HL had higher values of the coefficients (Table 4.5) than mortars made with cement and CFA only. The higher results were achieved in mortar with higher HL content. An important observation was that blends of CFA or/and BFA with or without HL led to more porous mortars than the reference one.

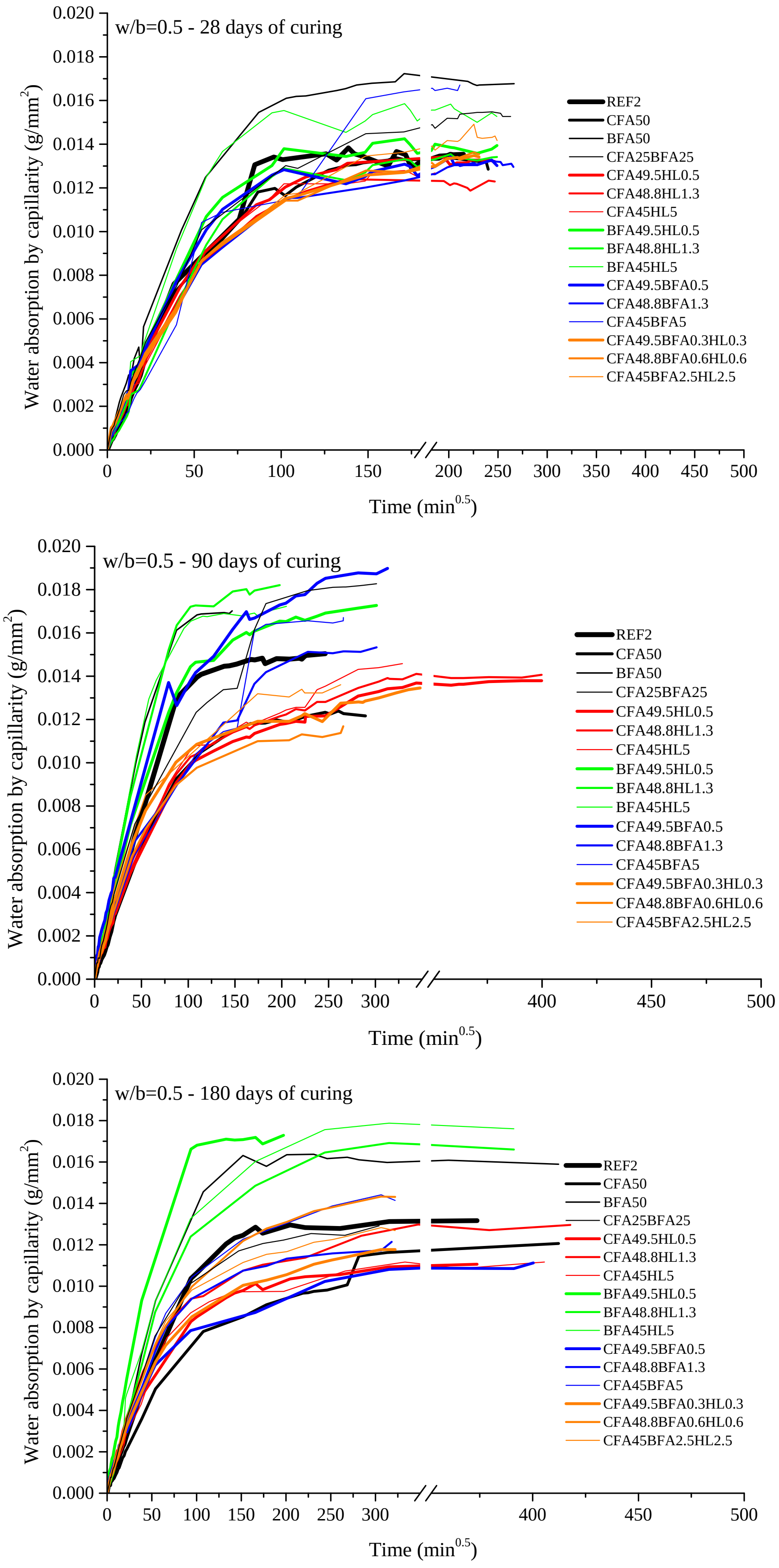


Figure 4.24 - Curves for the capillary absorption of mortars with 0.5 of w/b ratio

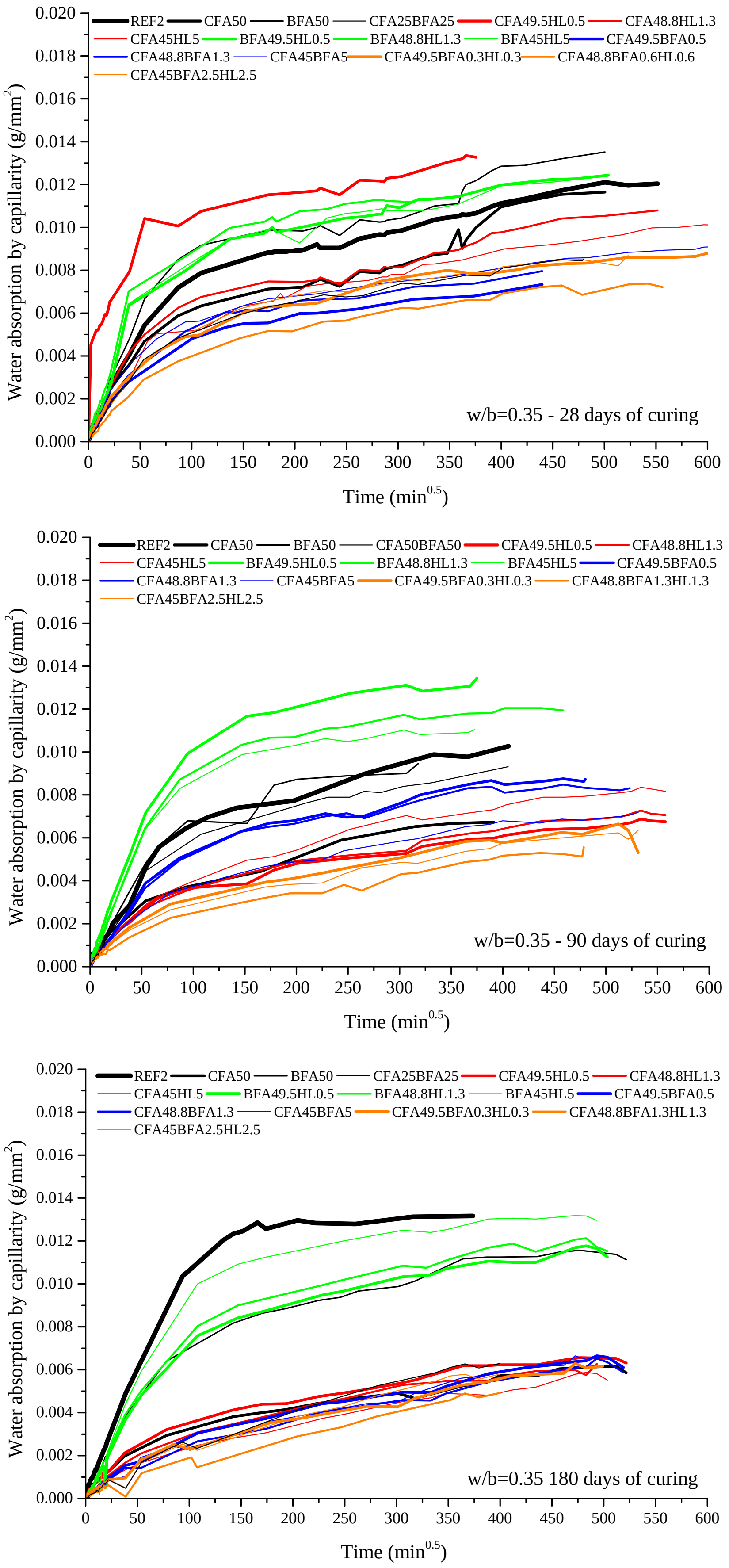


Figure 4.25 - Curves for the capillary absorption of mortars with 0.35 of w/b ratio

The results of mortars with w/b of 0.35 showed that the capillarity absorption was influenced by the water/binder ratio and by the binders used in the production of mortars, since the values registered in these mortars were lower than those of mortars with 0.5 of w/b. A higher water/binder ratio leads to a production of a more porous material [400]. Once again, the replacement of cement with 50%wt of BFA ash did not lead to a better result in terms of capillarity absorption, when compared with mortars with CFA.

However, when the two fly ashes were used together as cement replacement, the produced mortars presented the lowest values of the water absorption capillarity tests. This reduction of the values is due to the CFA is inclusion and its synergic effect with BFA. The synergic effect of CFA with other pozzolanic materials and its effect on porosity was also observed in other studies [400].

The introduction of HL in mortars with BFA did not have a positive effect on the water absorption. However, in mortars with coal fly ash and hydrated lime, lower values for water absorption were observed and the saturation condition was achieved later than in mortars with BFA and HL.

The introduction of small quantities of BFA in mixes with cement and CFA led to mortars with lower absorption values, which showed that these mortars have a higher bulk density than mortars containing CFA only. Similar results were observed when small quantities of BFA and HL were used in CFA mortars. The use of fly ashes in construction materials delays the cement hydration reaction and, during curing time, calcium hydroxide dissolved in the water present in the mortar reacts with the fly ashes to form solid reaction products that will partially or completely fill the capillary pores. The blocking of those pores by physical actions due to the new products of the pozzolanic reaction results in lower permeability mortars [102,401].

4.4.5 Accelerated Carbonation Test

In Figure 4.26, Figure 4.27, Figure 4.28 and Figure 4.29, the depth of carbonation of the studied mortar formulations at 28, 90, 180, 270 and 360 days of curing, for mortars with w/b of 0.5 and 0.35, respectively, is presented. As shown, the depth of carbonation increased with the duration of the carbonation test. For all curing ages and for the two w/b ratios, it is evident that the cement replacement with the two fly ashes led to an increase in the rate of carbonation. This might be due to the consumption of calcium hydroxide in the pozzolanic reaction, which occurs even before the initiation of carbonation. Due to the consumption of hydrates, the alkalinity of pore solution of mortars decreased [326].

The results related with the carbonation depth in each formulation have been fitted to the classical expression, which relates carbonation depth with the square root of time, to obtain the carbonation rate constant [402] (Table 4.6), according to Equation 24.

$$Xc = V_{CO_2}\sqrt{t} \tag{24}$$

It is important to take into account, that this expression does not consider other factors that affect the penetration of the carbonation front, such as the relative humidity and temperature [402,403], because in this study they were constants during all test period.

Table 4.6 – Carbonation rate coefficient of the different mortar formulations, for the two w/b ratios, for the different curing periods

Samples	w/b=0.5					w/b=0.35				
	28 days	90 days	180 days	270 days	360 days	28 days	90 days	180 days	270 days	360 days
	mm/days$^{0.5}$					mm/days$^{0.5}$				
REF2	0.77	0.77	0.68	0.77	0.76	-	0.18	0.08	-	-
CFA50	3.23	2.29	1.97	1.99	1.95	1.40	1.59	1.34	1.31	1.31
BFA50	3.24	2.42	2.26	1.93	2.93	2.19	1.88	1.66	1.66	1.98
CFA25BFA25	2.85	2.74	2.33	2.49	2.49	1.61	1.86	1.41	1.48	1.40
CFA49.5HL0.5	3.35	2.53	2.17	2.10	2.43	1.40	1.28	1.29	1.30	1.41
CFA48.8HL1.3	3.06	2.52	2.21	1.92	2.49	1.43	1.33	1.27	1.38	1.54
CFA45HL5	3.06	2.43	2.58	1.75	2.16	1.35	1.28	1.19	1.21	1.13
BFA49.5HL0.5	3.16	2.55	2.29	1.96	2.56	1.74	1.61	1.71	1.97	1.68
BFA48.8HL1.3	2.63	2.51	2.19	2.21	2.09	1.89	1.69	1.86	1.47	1.61
BFA45HL5	3.10	2.67	2.30	2.39	2.37	1.73	1.49	1.47	1.52	1.56
CFA49.5BFA0.5	2.51	2.37	2.13	2.52	2.36	1.34	1.39	1.25	1.26	1.21
CFA48.8BFA1.3	3.05	2.63	1.86	2.36	2.37	1.43	1.46	1.23	1.34	1.26
CFA45BFA5	3.09	2.59	2.24	2.28	2.38	1.48	1.32	1.24	1.28	1.37
CFA49.5BFA0.3HL0.3	2.74	2.59	2.20	2.30	2.31	1.50	1.32	1.22	1.34	1.27
CFA48.8BFA0.6HL0.6	2.79	2.71	2.67	2.45	2.40	1.33	1.28	1.25	1.26	1.30
CFA45BFA2.5HL2.5	2.40	2.42	2.32	2.07	2.11	1.39	1.33	1.36	1.44	1.33

The results for mortars with w/b ratio of 0.5 showed that the plain cement reference mortar presented the lowest carbonation depth values of all studied mortars. All mortars presented an increase in the values of carbonation depth along the test period. As it can be seen, mortars with BFA and HL and CFA with HL or/and BFA presented lower values of carbonation depth ratio at 28 days of curing, than the mortar with 50%wt of CFA. However, for the other curing periods, mortars with 50%wt of CFA presented lower values than the other mortars with ashes and HL. It is noted that the utilization of BFA in high amount did not lead to an improvement of mortars in terms of carbonation resistance. However, its utilization in small amounts blended with CFA led to a better behaviour than when CFA only was used as cement replacement material, showing that the synergic effect of the two ashes allows the production of more resistant mortars. Using small amounts of BFA seems to give the alkalinity needed for a better carbonation resistance of HVFAC.

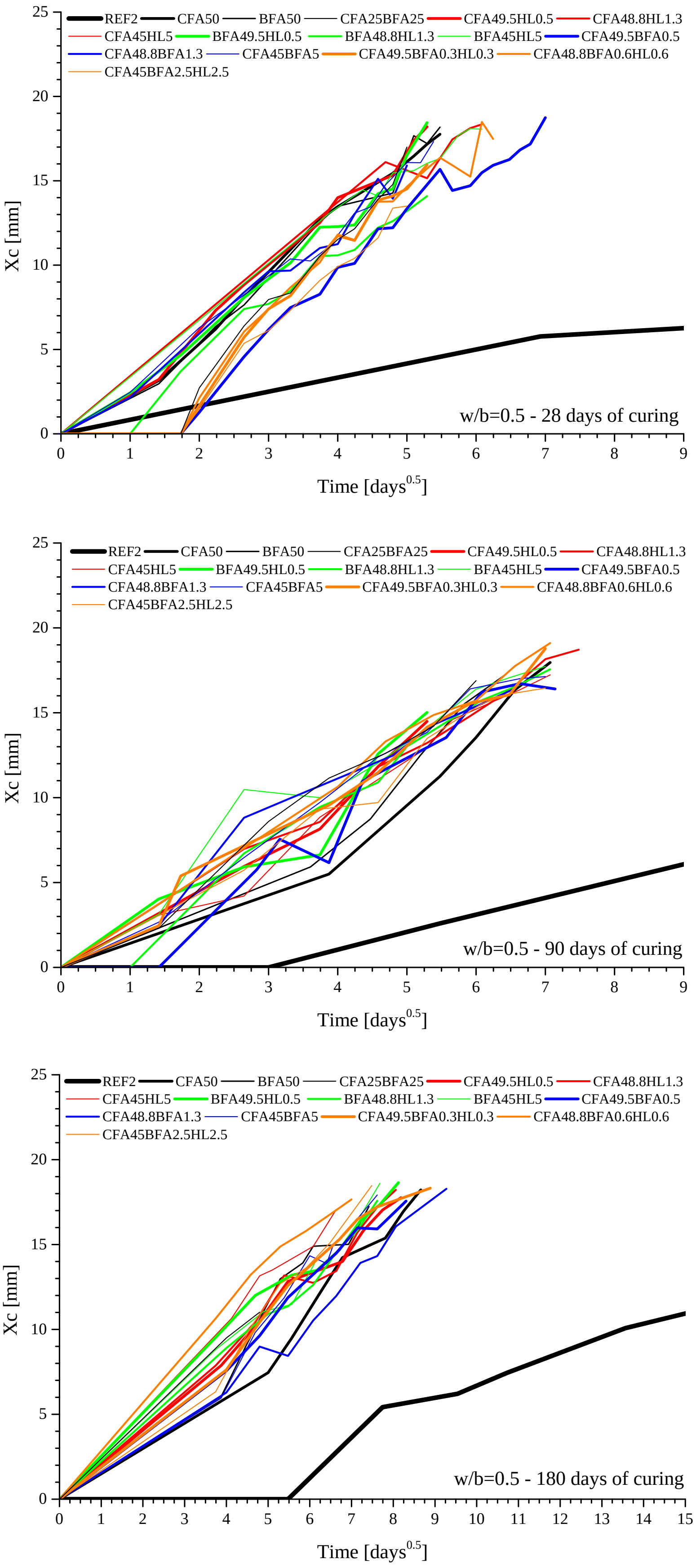


Figure 4.26 - Carbonation depth measured in mortars, with w/b of 0.5, for 28, 90 and 180 days of curing

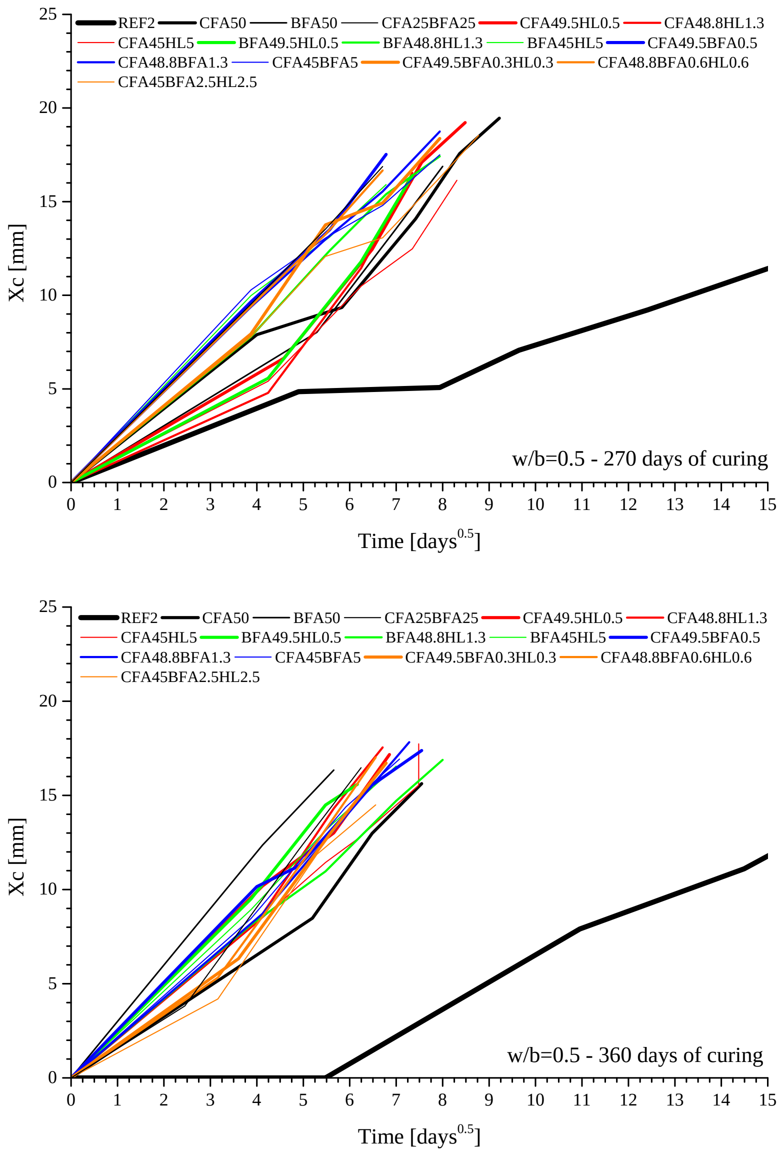


Figure 4.27 - Carbonation depth measured in mortars, with w/b of 0.5, for 270 and 360 days of curing

As can be observed in Table 4.6, the behaviour of mortars with a w/b ratio of 0.35 presented slight differences from that of mortars with w/b of 0.5. In this case, the values registered for the carbonation depth rate were lower and this is mainly due to the fact that lower water content led to the production of mortars with less porosity and for that the penetration of CO_2 takes more time. It was observed in Figure 4.29 that the reference mortar presented the lowest carbonation constant rate at all curing ages. This is due to the fact that cement mortars are less permeable than mortars with fly ash and because those mortars presented a lower calcium hydroxide amount that was consumed during the pozzolanic reaction. Mortars with pozzolans have a higher consumption of CH and this leads to a decrease of the alkalinity of mortar. The decrease in alkalinity is one of the conditioning parameters to the development of the carbonation reaction [373,404].

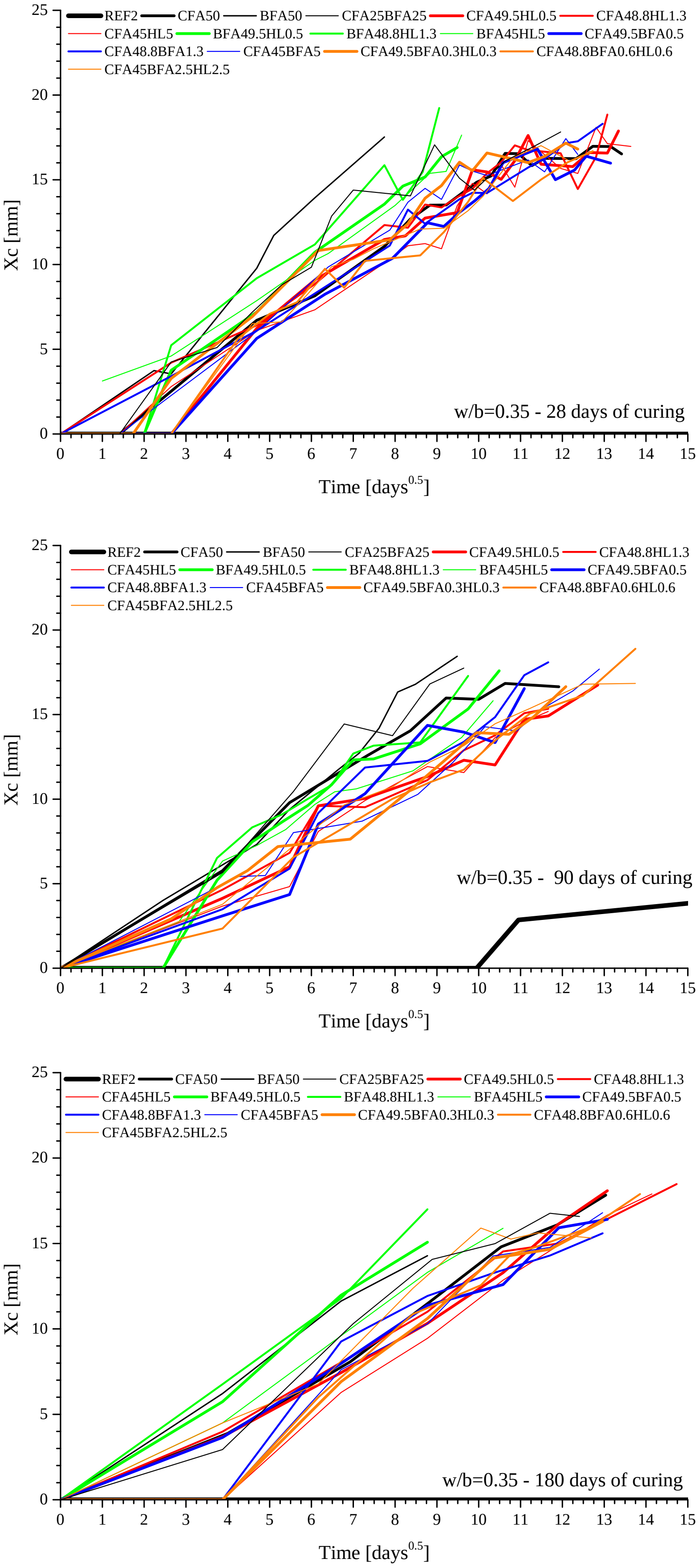
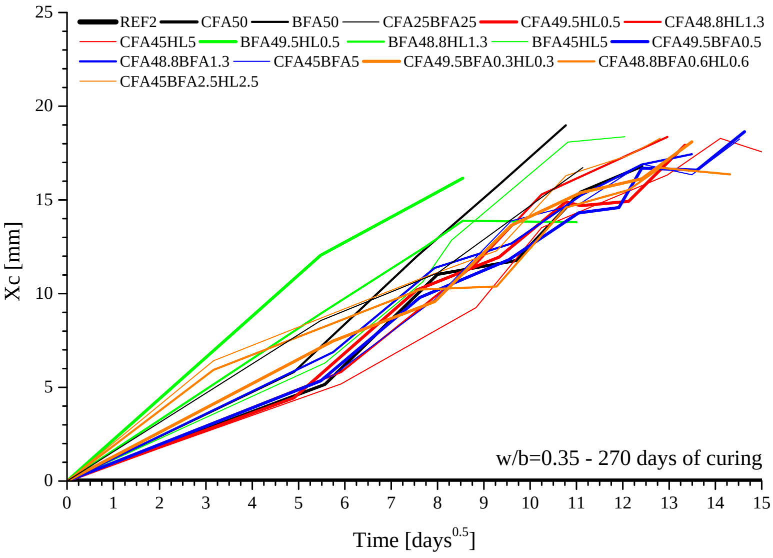


Figure 4.28 - Carbonation depth measured in mortars, with w/b of 0.35, for 28, 90 and 180 days of curing



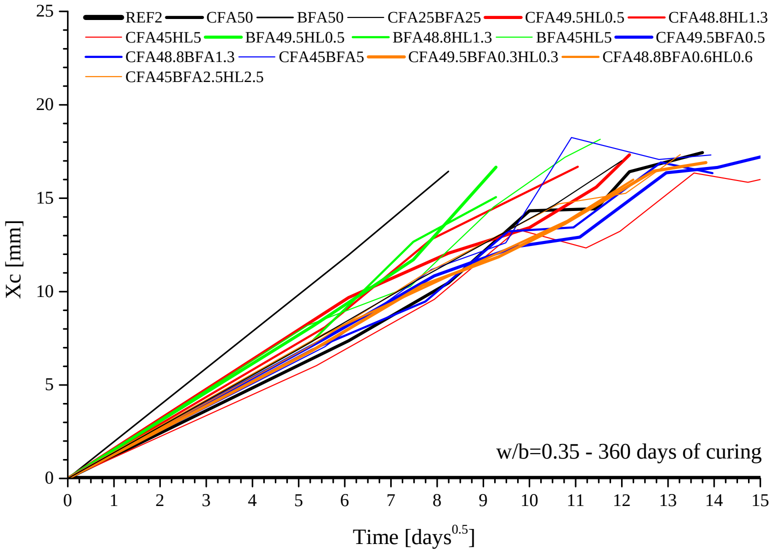


Figure 4.29 - Carbonation depth measured in mortars, with w/b of 0.35, for 270 and 360 days of curing

In general, mortars with CFA and with HL and BFA presented a decrease in the carbonation coefficient with the increase of the curing age. A longer exposure time to humidity curing leads to: a higher hydration of cement, a smaller porosity, a reduced permeability and consequently a more compact microstructure. In this case, the velocity of carbonation penetration is reduced [405]. Once again, it was noted that the utilization of 50%wt of BFA alone or blended with HL did not lead to an improvement of the carbonation resistance when compared with the mortars with same amount of CFA. Mortars with BFA or/and HL mixed with CFA presented lower values than mortars with CFA. It is noted that the introduction of BFA or HL led to an increase of the alkalinity of mortars and had a good synergy with CFA, which was reproduced in a lower carbonation rate and in the production of mortars with higher durability than the mortars with CFA and cement as a binder.

4.5 Conclusions

Pastes with 50%wt of cement replacement by coal/biomass fly ash as cement replacement 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. However, this result was expected since these mixes presented 50%wt of cement content reduction. The XRD analysis corroborates this achievement and suggests that the pozzolanic reaction is still occurring.

The results show that pastes with BFA promote mixes with higher alkalinity reserves and probably the BFA 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 CFA, even at 90 days of age.

In terms of calcium carbonate formation, no significant differences were observed between using CFA or BFA, which indicated similar resistance to carbonation, for the cement replacement percentage under study (50%wt). However, a higher consumption of calcium hydroxide during the carbonation mechanism of CFA paste was observed. The use of BFA seems to have a similar behaviour to that of the use of CFA in terms of carbonation.

In terms of mortars, the results presented in this chapter were divided in two main objectives. First, the effect of the cement replacement with biomass fly ash (20, 40 and 60%wt of replacement) on mortar properties was presented and compared with a plain cement mortar and with mortar with cement replacement with CFA.

Mortars with BFA exhibited slightly less workability than the reference one. A decrease was observed of the flow spread diameter with the increase of cement substitution by BFA. Mortars with 20% of cement substitution presented better results for all curing time, in terms of mechanical strength and water absorption. However, in the three percentages of substitution and for all curing periods the best results were found for mortars composed with BFA. The replacement of cement by CFA and/or BFA benefitted and mitigated the total shrinkage of the mortars. In terms of water leaching analysis, a decrease of the calcium solubilisation in water was observed with the increase of biomass content in mortars. This could be an interesting result, mainly in terms of a possible solution for the carbonation phenomena that is observed in concrete with CFA addition. Furthermore, in terms of heavy metals, the concentration of those elements in water was very low and this has good implications in terms of environmental sustainability. The results, for all parameters studied at the levels of 40 and 60%wt of cement replacement, were similar to the results observed when CFA was used as binder.

Briefly, these results showed that it could be possible to use BFA as partial cement replacement, despite the fact that BFA characterization showed that this material is not considered by the standard as a pozzolanic material (results presented in chapter 4). These results showed that maybe the utilization of BFA could be important to mitigate the issues related to HVFA content. The second part of this chapter was focused on the study of the effect of BFA as an addition and also tries to understand whether slight amounts of HL or BFA (an alkaline waste) have a contribution to the problems related to mortars with a high amount of cement replaced with CFA, mainly the carbonation issue. However, in this study the effect of two/water binder ratios of those mortar formulations was also studied, since the main goal of this thesis is the production of eco-efficient materials. The introduction of BFA in cement-base materials had an influence on its fresh and hardened properties. Once again, and as it was observed before, BFA had an influence on the workability, more noticeably in mortars with a w/b of 0.35 and to maintain a similar flow spread it was necessary to increase the superplasticizer’s dosage.

Mortars with BFA presented a higher electric resistivity and were more heterogeneous than cement mortars. However, its utilization in a blended mix with coal fly ash presented a higher electric resistivity.

The replacement of cement with the two fly ashes led to a decrease of the mechanical strength and to a retardation on the gain of mechanical strength for the two w/b ratios. The best strength values for HL mortars were obtained in mortars with the highest content. However, when BFA was used in CFA mortars, the mortars with the lowest BFA content presented the best results. It is important to note that the utilization of BFA and hydrated lime in the same mix does not lead to mortars with good mechanical performance.

The replacement of cement with BFA did not lead to an improvement of the open porosity, at all curing ages. The use of BFA or/and HL in mortars with CFA led to results similar to those observed in CFA. The addition of small quantities of BFA, in mixes with cement and CFA, produced mortars with lower water absorption by capillarity values, which showed that these mortars have lower porosity than the mortars with CFA only, and these findings were observed for the two w/b ratios.

Cement replacement with fly ashes led to an increase in the rate of carbonation for all curing periods and this was observed for the two w/b ratios. The results for mortars with w/b ratio of 0.5 showed that the 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 and HL and CFA with HL or/and BFA presented lower values of carbonation depth ratio at 28 days of curing than the mortar with 50%wt of CFA. However, for the others curing periods, the mortar with 50%wt of CFA presented lower values than the other mortars with ashes and hydrated lime. Mortars with a water/binder ratio of 0.35 showed that mortars with BFA/HL mixed with CFA presented similar or lower values than mortars with CFA. It is noted that the introduction of BFA led to an increase of the alkalinity of mortars and had a good synergy with CFA, which was reproduced in a lower carbonation rate.

So, one of the solutions to minimize the problems of high volume of fly ash mortar seems to be the utilization of a small amount of biomass fly ash blended with coal fly ash. The use of small amounts of biomass fly ash in mortars with high volume of coal fly ash leads to the production of mortars with similar quality properties to those of mortars with coal fly ash, showing a good synergy between the two ashes. BFA blended with CFA seems to have a positive contribution on the durability of those mortars when compared with mortars with coal fly ash only as supplementary cementitious material.

Chapter 5

Concrete: Results and Discussion

5.1 Introduction

In view of the research gap that has been identified and described before, about the use of biomass fly ash (BFA) as cement replacement material in high volume fly ash concrete (HVFAC) and as an alkaline material, a group of mortar formulations was produced and the influence of biomass fly ash on these two points was studied, and the results were shown in the last chapter. Based on these results, it was chosen as the concrete formulations to study the ones with low content of BFA (0.5, 1.3 and 5%wt of cement replacement) blended with coal fly ash (CFA) (49.5, 48.8 and 45%wt of cement replacement). These formulations were compared with a typical plain cement concrete and with a HVFAC with 50%wt of CFA (Table 3.12).

In mortar formulations, it was observed that the 49.5%wt of CFA and 0.5%wt of BFA seems to produce the material with better quality, durability and sustainability, and therefore this mix was also compared with two mixes with the same percentage, but in this case using hydrated lime and coal fly ash (0.5%wt of HL+49.5%wt of CFA) and a mix with hydrated lime blended with coal fly ash and biomass fly ash (0.3%wt HL+49.5%wt CFA+0.3%wt BFA).

The main goal of this experimental campaign was to assess the effect of using BFA in the fresh and hardened characteristics of concrete. To achieve this goal, the workability, quality, and durability performance of the concrete studied were evaluated. Workability was evaluated by the slump test, whereas the analysis of the hardened concrete consisted in evaluating the compressive strength (after 7, 28, 90 and 180 days of curing), water absorption, resistance to chloride ions penetration and resistance to carbonation (after 28, 90 and 180 days of curing).

It is known that one of the problems of concrete with high volume fly ash (HVFA) is the curing sensitivity, because of the leaching of alkaline materials during curing, mainly in water curing, that leads to a decrease of the pH of concrete and consequently to a lower resistance to the carbonation phenomenon. So, taken into account this issue, two different curing were studied: plain water curing and a curing in a water solution saturated with hydrated lime. As the second curing is a solution with a pH of around 14, a higher pH than the pH of concrete, the leaching of alkaline materials is not expected. Therefore, the results obtained for the different tests for samples cured in water were compared to this hydrate lime solution curing.

The analysis carried out for those concretes allow understanding the effect of each formulation on the concrete characteristics, analysing the formulations that reached the best behaviour in the different tests, curing periods, types of curing, and to understand the obtained results, to understand whether it is possible to produce concrete with a better performance with the incorporation of BFA blended with CFA. Namely, in the aspects related with sustainable development, with the increase of the quality and durability of concrete, and with the production of a material with initial low cost, making an economic competitive material.

5.2 Fresh Properties: Slump

The fresh concrete is a transitional state, but it is important to understand its characteristics and conditions, which are mostly affected by the compaction degree. The concrete consistence showed the facility of concrete transportation, placing and compaction and also the resistance to segregation [33]. In Table 5.1, the values relative to the slump test observed for each concrete formulation are showed. It is important to remember that the reference mix was related to a plain cement conventional concrete (with 350 kg/m^3 of binder and a w/b ratio of 0.5) and the other concrete formulations had also the same content of binder, but with low cement content, with a w/b equal to 0.35 and with superplasticizer (Table 3.12).

Table 5.1 - Slump values and classes

Nomenclature	Slump (cm)	Class of slump [406]
REF2	7.5	S2
CFA50	23.0	S5
CFA49.5HL0.5	18.0	S4
CFA49.5BFA0.5	21.0	S4
CFA48.8BFA1.3	22.5	S5
CFA45BFA5	20.5	S4
CFA48.8BFA0.6HL0.6	20.0	S4

The slump values for concrete with fly ashes are significantly higher than for the reference mix (REF2) (Figure 5.1). This is due to the fact that concrete with ashes presented a w/b ratio of 0.35 and the reference presented a w/b ratio of 0.5. In the formulations with a w/b of 0.35, it was necessary to use superplasticizer, which led to an increase of the slump values. It is important to note that the use of BFA did not have a significant effect on slump. These results were expected since authors that studied the incorporation of BFA in concrete showed that the values of slump are affected by high cement replacements, decreasing the values of slump with the increase of the BFA content [294,307].

Figure 5.1 – Slump test of the reference mix (left side) and of CFA45BFA5 (right side)

5.3 Compressive Strength

In Figure 5.2, the values obtained in the compressive strength test after 7, 28, 90 and 180 days are presented, for the concrete samples cured in water and cured in the hydrated lime solution. The values are an average of 3 samples for each concrete formulation and for each curing period. Concerning the compressive strength at 7 days, the CFA49.5BFA0.5 mix showed the highest values for the two curing solutions, followed by CFA50, CFA48.8BFA1.3, REF2, CFA49.5HL0.5, CFA49.5BFA0.3HL0.3 and CFA45BFA5. A decrease in the compressive strength with the increase of the content of BFA was observed. As was observed in the characterisation of BFA, this ash was less reactive than CFA, and despite the two ashes exhibiting a good synergy, the increase in the BFA content leads to less quantity of material that can react and gain strength. However, is important to note that mixes with 0.5 and 1.3%wt of BFA presented higher values than concrete with cement only as binder that can be also due to the filler effect that BFA can induce in the concrete, which led to a better compactness of the concrete. The presence of HL, at early ages, led to a decrease of the compressive strength, showing that its use does not lead to an improvement of the concrete behaviour at early ages. This can be attributed to the low amount of alite presented in the binder [407].

At 28 days, two mixes cured in water presented higher values and similar values, CFA50 and CFA49.5BFA0.5, 56.6 MPa and 55.8 MPa, and 55.1 MPa and 57.0 MPa, respectively for water curing and hydrate lime curing. However, the CFA48.8BFA1.3 and CFA49.5HL0.5 mixes also presented higher values than the reference mix (plain cement concrete) for the two curing. A decrease of the compressive strength was observed with the increase of the BFA content and the introduction of HL led also to a decrease of the values of compressive strength. In concrete with hydrated lime, the decrease of the values is consistent with the hydration of belite that is slower and with the pozzolanic reaction ongoing, that continued after 28 days of curing [407].

For 90 and 180 days, concrete with 0.5%wt of BFA, cured in water and in hydrated lime solution, had the highest values of compressive strength when compared with the other formulations. There was stagnation in the evolution of compressive strength in the mix with cement only (REF2). This is due to the fact that cement has faster hydration reaction, resulting in the gain of strength at early ages. At these ages, the introduction of HL did not lead to a significant effect on the compressive strength. In the case of CFA49.5HL0.5, the values were higher than for the mix with CFA only. For these two periods, all concrete formulations with ashes presented higher values than the plain cement concrete. Concrete produced with HVFA content has a compressive strength development slower than a plain cement concrete. This is due to the pozzolanic reaction of fly ashes that is slower and leads to a retardation of the gain of strength [14].

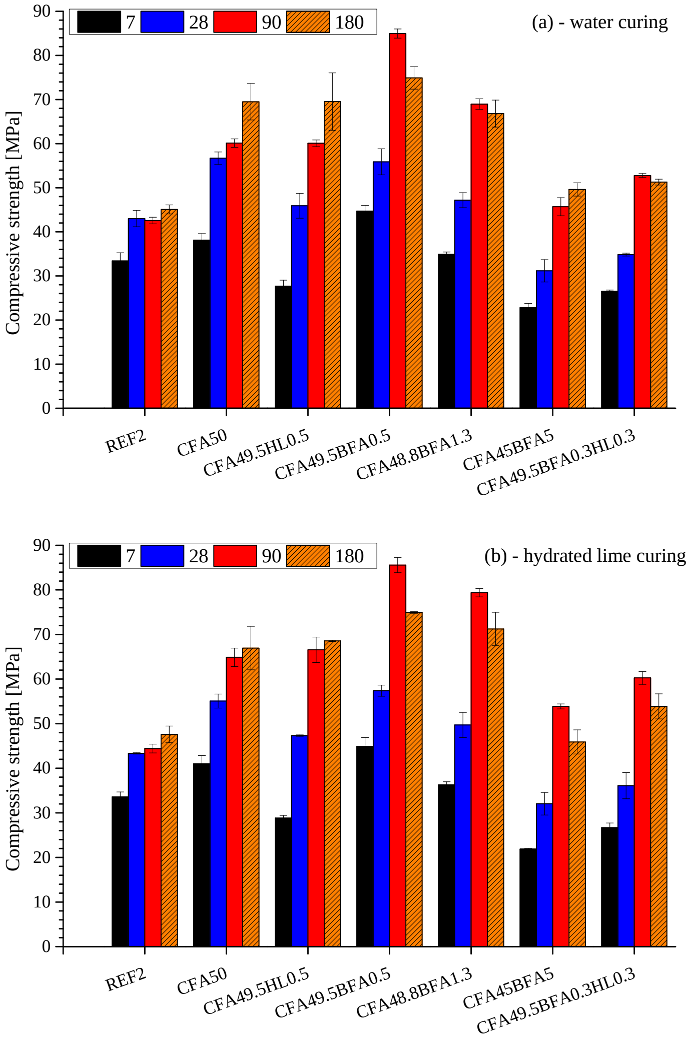


Figure 5.2 – Compressive strength of the concrete samples for the two studied curing types

The results showed that, out of all formulations with ashes, CFA49.5BFA0.5 obtained the more satisfactory compressive strength values at all curing periods and for the two curing types. This result can be related with the physical effect of the CFA particles that filled the voids of cement paste and resulted in a more dense cement paste. While the chemical effect is the reaction of the BFA with the hydrated cement compounds, for which the development of resistance is lower than the cement and CFA [276]. BFA are alkaline with pH in the range of 11 and 13 [264] and have silicium and calcium carbonate as major phases. Furthermore, they have portlandite and lime in higher amounts than CFA (Figure 3.7). So, these ashes act as an alkaline reservoir, resulting in a good synergy between the two fly ashes [31].

It is important to remember that these HVFAC formulations were based on the results achieved in the mortar formulations, and the formulations that give similar compressive strength than the reference (that corresponding to a composition of a conventional plain cement concrete) (Figure 4.22) were chosen. An important observation was that the same concrete formulations, at later ages of curing, showed higher values for compressive strength than the reference mix, and the behaviour of those compositions in concrete was better than that observed in mortars.

With regard to the effect of the two curing types on the compressive strength values of each concrete formulation is presented in Figure 5.3. It can be observed that the effect of curing with an alkaline solution depends on the concrete formulation. In relation to the mix with cement only as binder (REF2), it can be observed that with the increase of the curing period, the values of compressive strength for specimens cured in hydrated lime solution were higher than for samples cured in water, achieving results higher by5.6% at 180 days of curing.

In the CFA50, CFA49.5HL0.5 and CFA49.5BFA0.3HL0.3 mixes, it was observed that, until up to 180 days of curing, the values for samples cured in a hydrated lime solution were higher than for samples cured in water. However, at 180 days in the two formulations, the samples cured in hydrated lime presented similar or slightly lower values than samples cured in water.

With respect to the CFA49.5BFA0.5 mix, at all curing times, the differences in compressive strength between the specimens of the two types of curing were relatively small, but the lime curing of specimens yielded slightly higher results. For the CFA48.8BFA1.3 mix, at 7 and 28 days of curing, the lime curing specimens obtained values higher by 4.1% on average in relation to the water cured test specimens; at 90 and 180 days of curing, the lime curing samples obtained values 15.1 and 6.6%, respectively, higher than the water cured test specimens. Regarding the CFA45BFA5 mix, at 7 and 28 days of curing, the differences in compressive strength between the test specimens of the two types of curing were relatively inferior, but at 90 days of curing, the hydrated lime curing test results were higher on average by about 17.9% than the water curing test. However, at 180 days the value obtained for compressive strength on the specimen cured in water was higher than that cured in hydrated lime solution.

Curing concrete with a saturated hydrated lime solution generally resulted in values of the compressive strength higher than water curing. This aspect is justified because of the hydration of cement, over time, the occurrence of the dissolution and the leaching of CH in the water curing environment, which is greater than in the lime saturated curing environment. Higher leaching and dissolution of CH leads to increased porosity of the cement matrix and thus results in lower strength. Another reason is the reduction of the Ca^{2+} ions in the water curing environment, which does not favour the pozzolanic reaction, and therefore, reduces the compressive strength of concrete [408]. The curing of the concrete test pieces in solution of saturated water of lime brings benefits, in the case of compression strength.

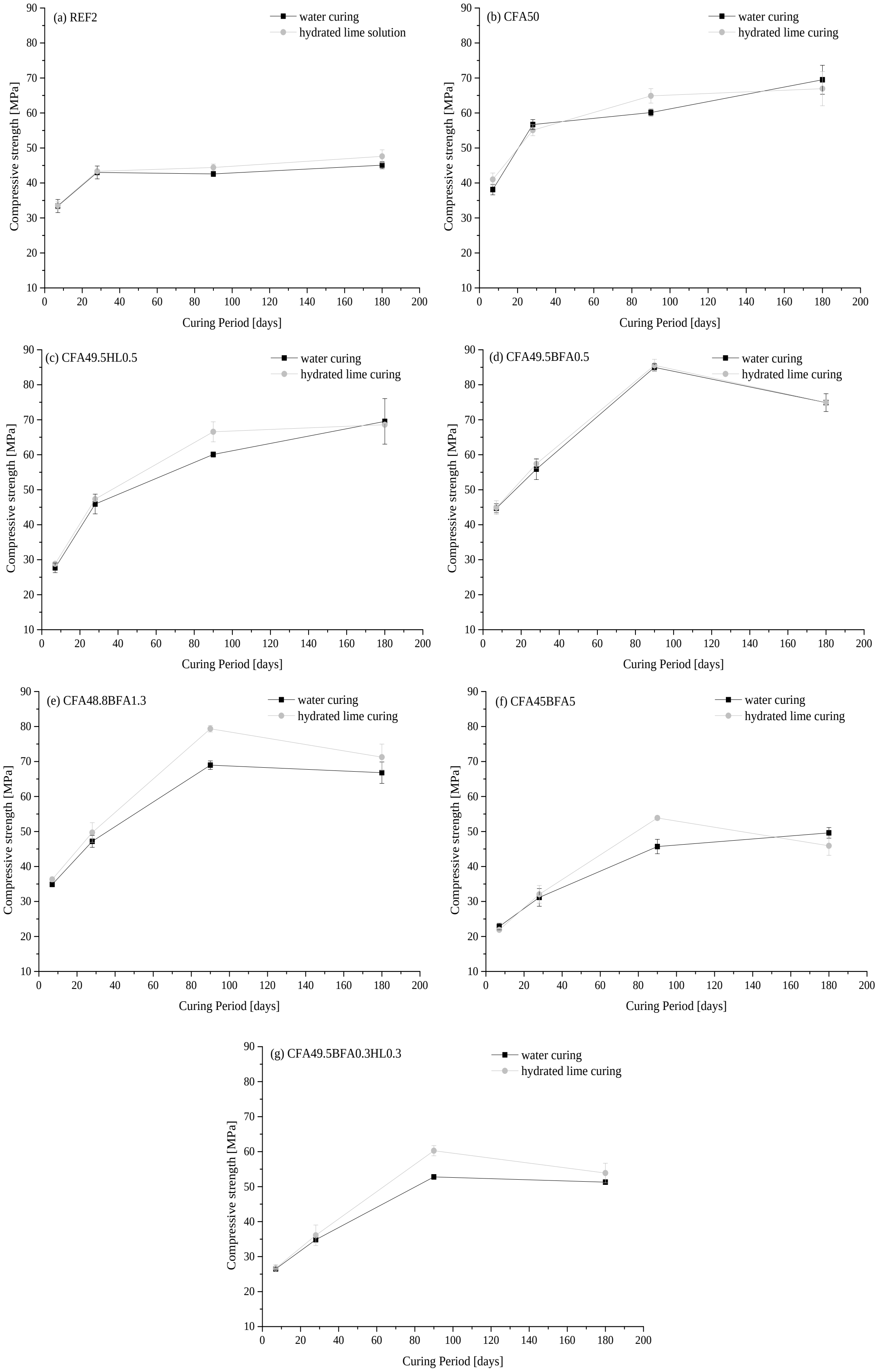


Figure 5.3 – Comparison of the effect of curing in water or in hydrated lime solution on the compressive strength for each concrete formulation

5.4 Water Absorption by Immersion

The water absorption by immersion gives a measurement of the pore volume or porosity in the hardened concrete that is occupied by water in saturated condition [283]. Figure 5.4 shows the results obtained for the water absorption by immersion at atmospheric pressure for the samples cured in water and in a hydrated lime solution, at room temperature. Concerning water curing, at the three curing periods, the mix with 0.5%wt of BFA showed the lowest values of water absorption, followed by CFA50 and CFA48.8BFA1.3. The reference mix presented the highest values. These results were expected because they were also observed in the mortar formulations (Figure 4.23). The results observed in plain cement concrete were related with the water/binder ratio of this mix, since the other mixes presented a w/b of 0.35. It is known that with the increase of the water/binder ratio there is an increase of the volume of pore in concrete [70]. The lowest values observed for the CFA49.5BFA0.5 and CFA48.8BFA1.3 mixes were also found by others researchers that observed that for low percentages of BFA incorporation the water absorption was lower, and are related to the amorphous silica dioxide that increases the strength of concrete by reducing the porosity of the matrix [409]. Furthermore, CFA is composed of finer particles than BFA and cement, and this leads to the production of a denser concrete [283]. An important observation is that, with the increase on the BFA content, an increase of the water absorption percentage is also observed. This is due to the fact that BFA have hygroscopic properties, and with their increase on the concrete mix, the absorption of water also increases [283].

The introduction of hydrated lime, with coal or/and biomass fly ash, in the mix did not correspond to the production of a less porous concrete than a CFA concrete. However, the values for the two concrete formulations and for all curing periods were lower than for the plain cement concrete and for the concrete with 5% of BFA. A decrease of the porosity of concrete with fly ash and hydrated lime is due to an increase in homogeneity and dense microstructure. Some researchers [410] showed that a formation of more C-S-H gel is observed in mixes containing CFA and HL, than in a plain cement concrete. Due to the formation of more C-S-H gel and filling of the boundaries of the aggregate, micro gaps occur along the boundaries leading to a decrease of porosity and increasing the homogeneity.

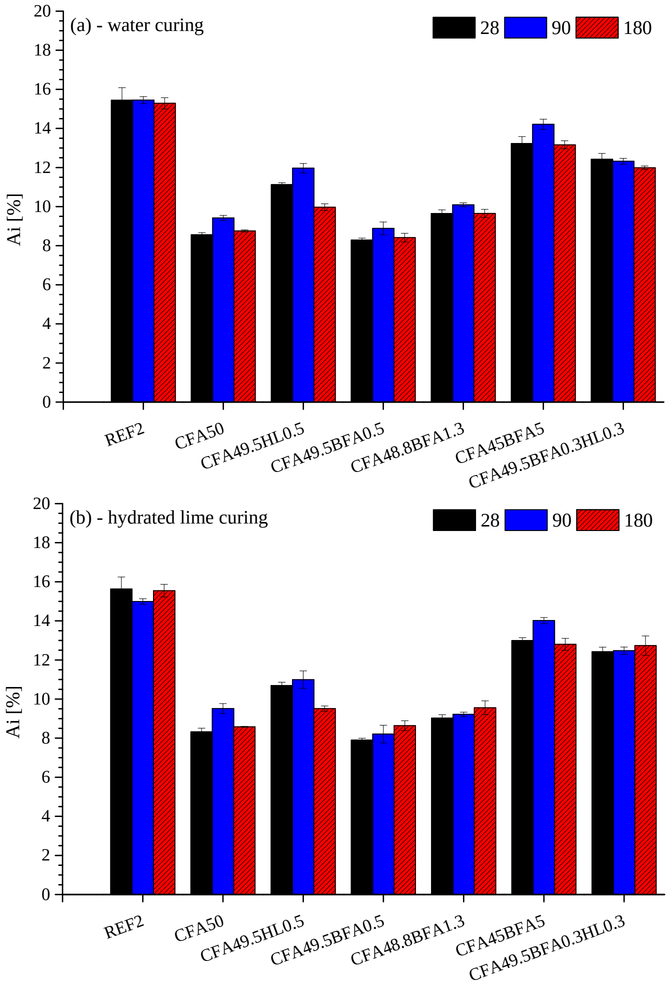


Figure 5.4 – Water absorption by immersion results of the concrete samples cured in water and in a hydrated lime solution

Similar results to those observed for water curing samples were observed for hydrated lime curing. Once again, higher values for the reference concrete and lower values for the CFA49.5BFA0.5 and CFA50 were registered. It was therefore very important to verify the influence of the curing, in water or in hydrated lime solution, on the porosity of concrete, and the results are described in Figure 5.5.

It can be observed that for the reference and for the concrete composed of 50%wt of CFA, the porosity did not have a significant influence of the curing mode. However, the mixes with BFA and with HL were affected by curing in terms of water absorption by immersion, being noticed a decrease of the porosity in the samples cured in hydrated lime, showing less than almost 1% of water absorption. On the other side, the mix with HL and the two fly ashes presented higher values of water absorption with curing in a hydrated lime solution. In term of water absorption, the curing process did not have a significant influence on the values but it is noted that, depending on the concrete composition, curing in a hydrated lime solution can promote a concrete with less porosity.

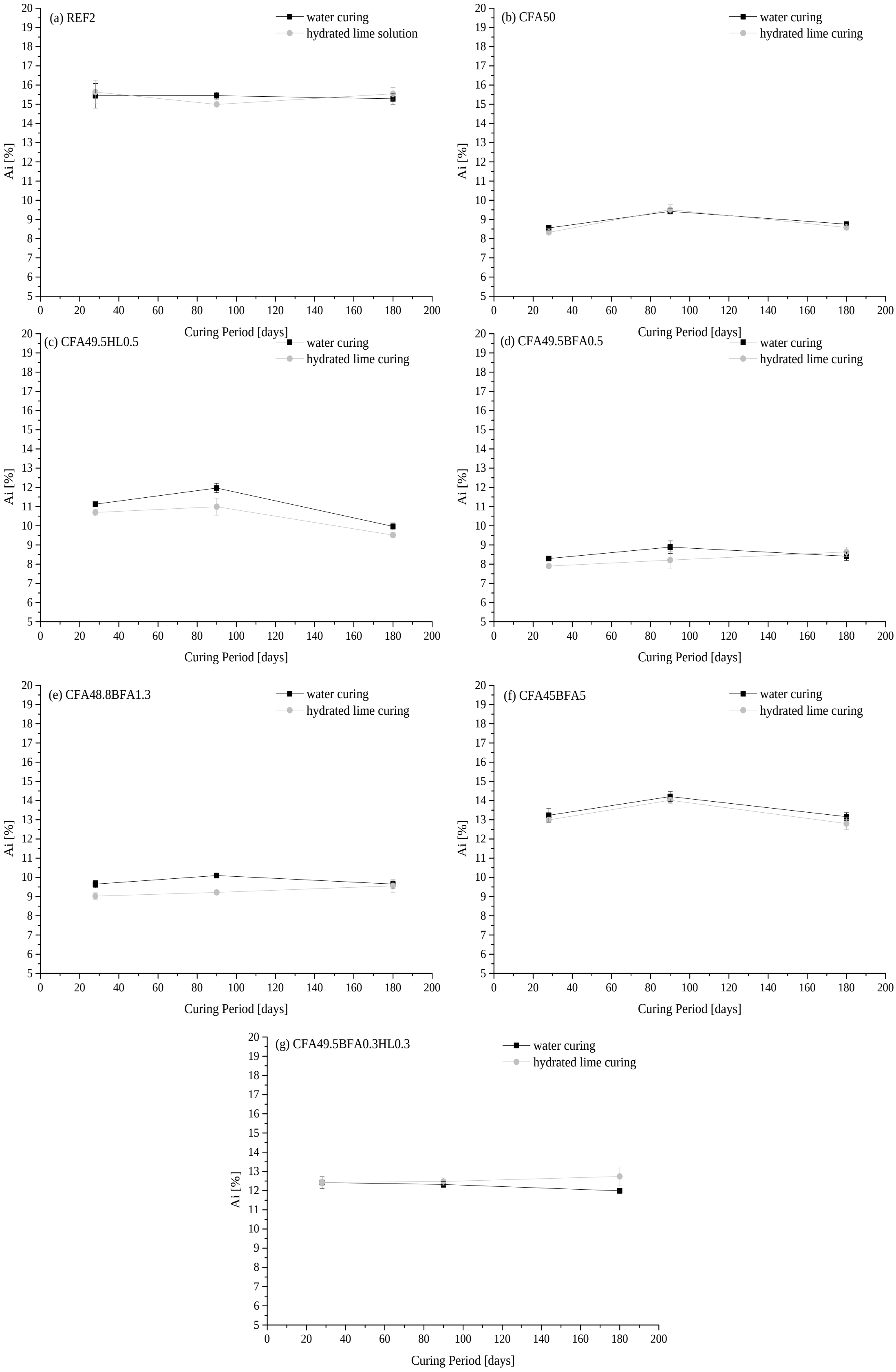


Figure 5.5 - Comparison of the effect of curing in water or in hydrated lime solution on the water absorption by immersion for each concrete formulation

5.5 Water Absorption by Capillarity

The water absorption by capillarity test allows quantifying the capillary absorption coefficient. This index refers to the relation between the absorbed water mass per unit area as a function of the square root of time [21]. Figure 5.6 shows the average results of the water absorption by capillarity coefficients of samples cured in water and in a hydrated lime solution.

It is possible to classify qualitatively the concrete based on the coefficient of water absorption by capillarity, using the classification proposed by Browne, 1991 [411].

Table 5.2 - Quality class of concrete in function of its coefficient of water absorption by capillarity

Coefficient of water absorption by capillarity	Quality Class
≥ 0.2 mg/(mm^{2}xmin$^{0.5}$)	Reduced
0.1-0.2 mg/(mm^{2}xmin$^{0.5}$)	Normal
≤0.1 mg/(mm2xmin$^{0.5}$)	High

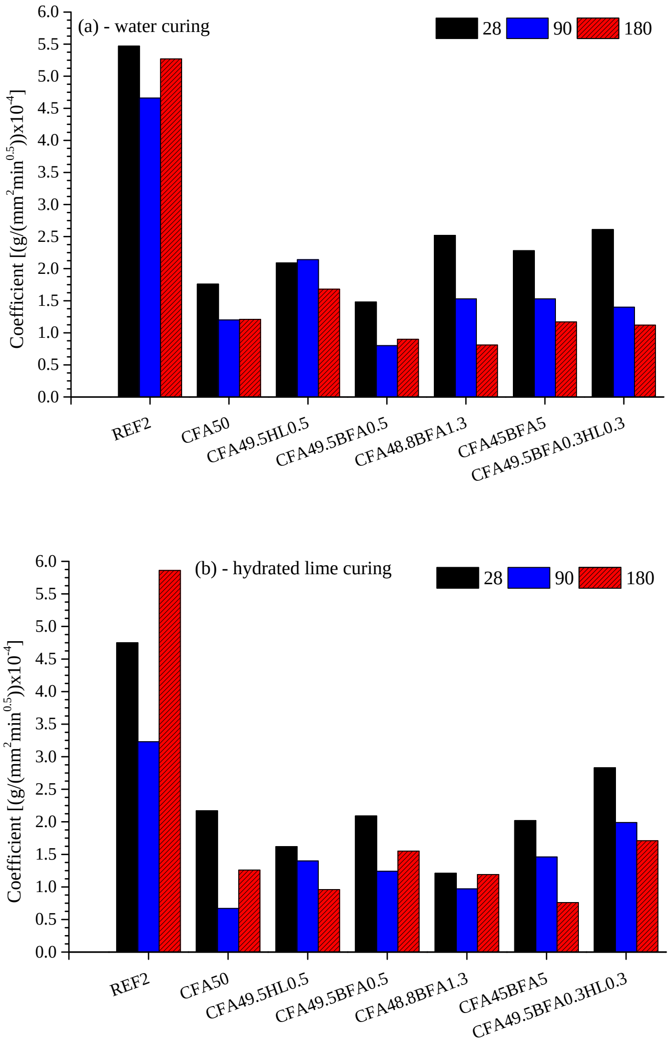


Figure 5.6 – Coefficient of water absorption by capillarity

As it can be seen (Figure 5.6), for concrete cured in water, the reference mix was considered a concrete with reduced quality and the concrete with 50%wt of cement replaced with CFA presented a normal quality. The formulations that presented HL in their composition also presented a normal quality. CFA49.5BFA0.5, after 28 days of curing, presented a high quality. CFA48.8BFA1.3 presented a normal quality after 20 days of curing and a high quality after 180 days of curing. The replacement of 5%wt of cement with BFA resulted in a normal quality in function of capillarity the coefficient after 28 days of curing.

For samples cured in a hydrated lime solution, the reference mix was also considered a concrete of reduced quality and the others in general were considered concretes of normal quality.

Figure 5.7 shows the representative kinetic curves for the capillarity water absorption in function of the test time for samples with 28, 90 and 180 days cured in water and in a hydrated lime solution. With respect to the samples cured in water, it was observed at 28 days that the CFA49.5BFA0.5 mixture presented the lower water absorption coefficient by capillarity (Figure 5.6), and is the mixture with highest resistance to the absorption of water by capillarity, followed by CFA50 and CFA48.8BFA1.3 (Figure 5.7). These mixes presented lower absorption of water during all test period, mainly due to the synergetic effect of the two ashes that led to the production of a denser material with a better pozzolanic activity [31,283]. The introduction of HL did not cause an improvement of the resistance to water absorption when compared with CFA mixes but better results were observed when compared with a plain cement concrete. However, the 49.5CFA0.5HL mix presented the second lowest value of the coefficient for absorption by capillarity. This can be due to the finer CFA particles and to the HL, which led to a endothermic dehydration of C-S-H and C-A-H, existing in the mixes with cement and HL, originated by the dissociation of portlandite and calcite [412].

At 90 days of curing, it was also the mix with 5%wt of cement replacement by BFA that presented the lowest water absorption capillarity coefficient, followed by CFA50. At 180 days, this mix presented the second lowest value, after the sample with 1.3%wt of BFA. Once again, the reference mix presented the lowest water absorption resistance, as was observed at 28 and 180 days of curing. This is due to the fact that the reference mixes presented a higher w/b ratio, and it is known that the increase of the w/b ratio leads to an increase in the volume of voids and porosity of concrete [413]. It was observed that the increase in the BFA content leads to a decrease in the water absorption resistance (Figure 5.7). This is mainly due to the fact that BFA is an hygroscopic material, which leads to a higher absorption of water by the samples with higher BFA content [279]. However, the synergetic effect with CFA results in a good pozzolanic activity and allows the production of concrete with good results [31,283].

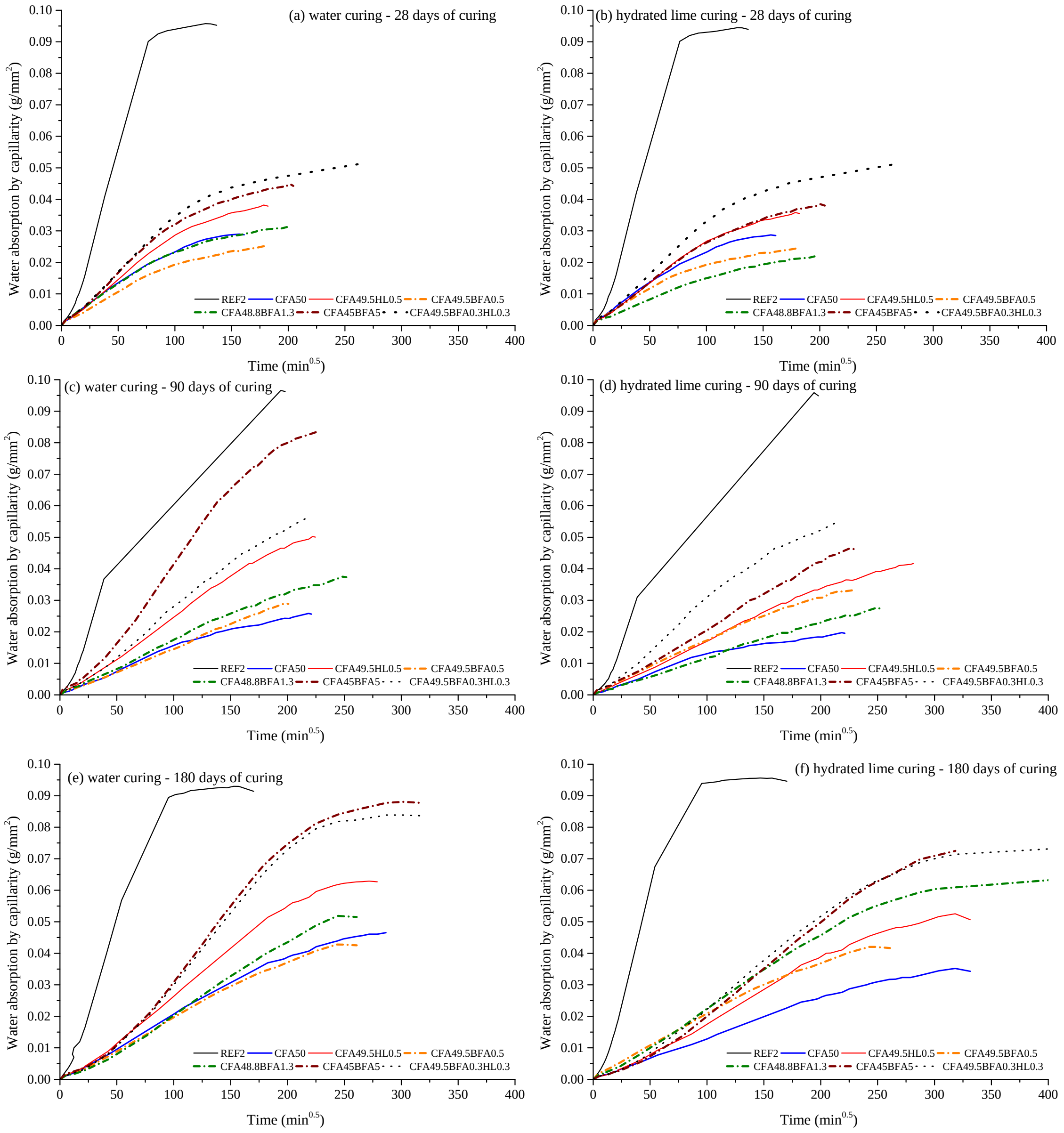


Figure 5.7 – Water absorption by capillarity of the different concrete formulations after 28, 90 and 180 days of water and hydrated lime curing

The results of samples cured in a hydrated lime solution were different from those of samples cured in water. At 28 days of curing, the CFA48.8BFA1.3 mix obtained the lowest value, followed by CFA49.5HL0.5. At 90 and 180 days, it was observed that CFA50 and CFA45BFA5 presented the lowest values, respectively (Figure 5.6). However, as was observed in the samples cured in water, the samples with 0.5 and 1.3%wt of BFA presented the lowest absorption of water during the test period similar to that observed in the CFA50 sample (Figure 5.7). As was expected, even for curing with hydrated lime, the reference concrete presented the highest absorption of water by capillarity, since this absorption is not because of curing but due to the higher w/b ratio.

Usually, the water absorption by capillarity of samples cured in hydrated lime was lower than that of samples cured in water (Figure 5.7). This could be related with two factors: i) the leaching of some alkaline compounds (essentially Ca) for water, in water curing. At the early ages, CH is an important compound, which accelerates the cement hydration, and for later ages it contributes to the pozzolanic reaction. The lower concentrations of Ca^{2+} presented in the water curing, especially in an early hydration phase, produces low pozzolanic reactivity. The dissolution and the leaching of CH increases the porosity inside the cement system, decreasing the level of pH, and consequently compromises the resistance and the durability of concrete [408]; ii) the presence of a more alkaline environment in curing because of the hydrated lime saturation, the pH and the alkaline compounds are higher in the environment than in the concrete pores, and instead of an occurrence of leaching, there is a migration of the calcium compounds to inside of concrete to maintain the chemical equilibrium. The entrance of lime into the concrete pore, essentially in the pores near the surface, leads to a filler effect like a protective surface layer, which decreases the water absorption of samples cured in the hydrated lime solution.

5.6 Accelerated Carbonation Test

Carbonation is a chemical attack, where the aggressive agents are the atmospheric gases compounds, mainly carbon dioxide, sulphur dioxide and hydrogen dioxide. Usually, these gases are widespread in the gas form into the porous system, in the cracks existent in the interfacial transition zone between the cement paste and the concrete aggregate, neutralizing the alkaline compounds, resulting in a pH decrease, to values lower than 9, leading to the destruction of the passivation protection layer and allowing reinforcement corrosion [21]. The carbonation analysis consists in an accelerated test with the main goal of measuring the resistance to CO_2 penetration of the hardened concrete.

In Figure 5.8, the results of the accelerated carbonation test of concrete samples cured in water and in hydrated lime for 28, 90 and 180 days during the test period are shown. The depth of carbonation can be expressed in function of the square root of exposition time resulting in a linear tendency, and it is possible to determine the carbonation coefficient as expressed in Table 5.3.

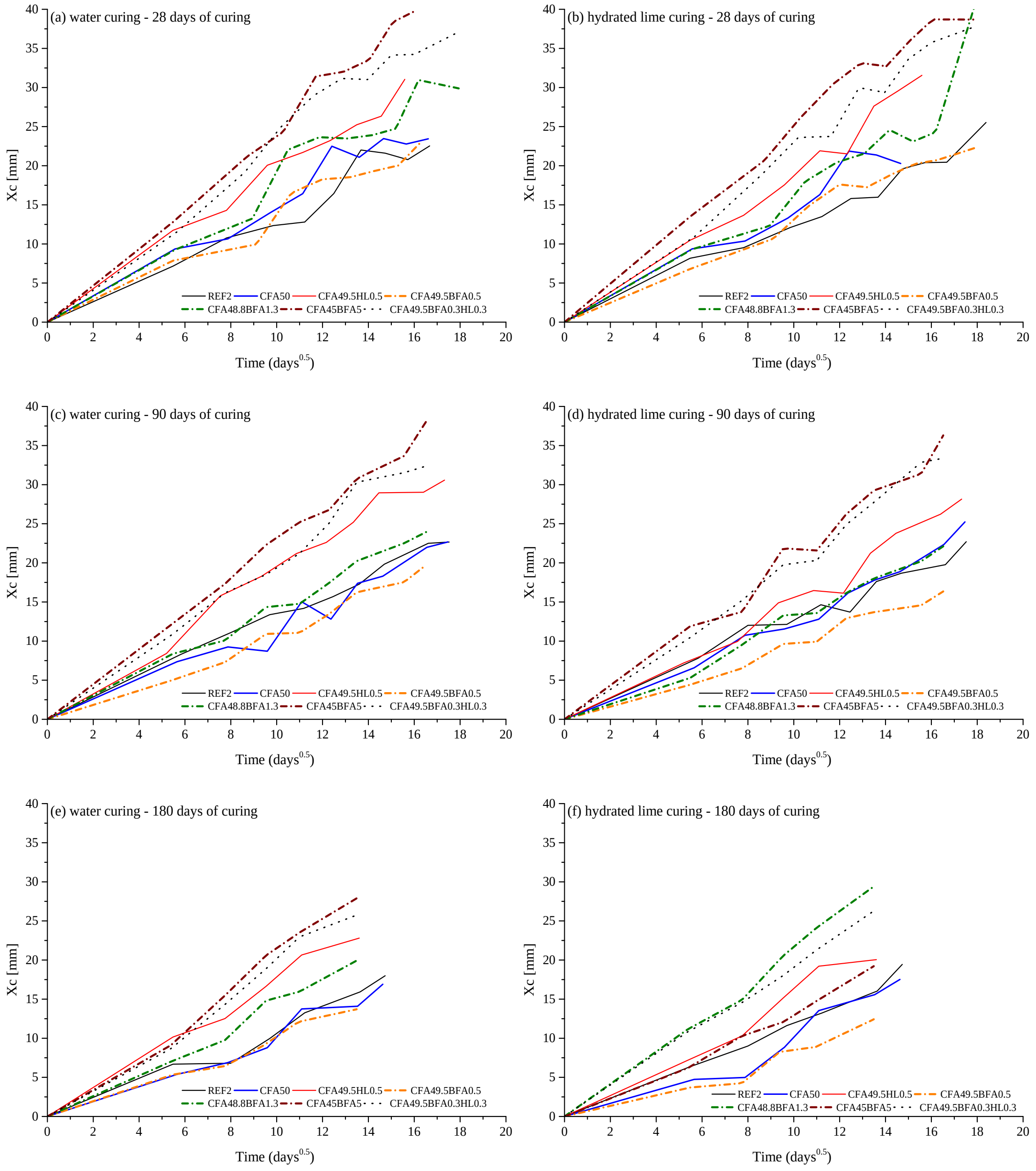


Figure 5.8 – Carbonation depth of samples cured in water or in a hydrated lime solution for 28, 90 and 180 days

For all curing periods and for the two curing process, the mix CFA49.5BFA0.5 presented the lowest value of penetration coefficient (Table 5.3), followed by REF2 and CFA50 and it is also observed in Figure 5.8 that these three samples presented the lowest values of penetration during the whole period of testing. The result observed for the reference concrete was expected since in the hydration of cement, the compounds alite and belite react with water to form C-S-H and CH. In the presence of pozzolanic additions (CFA), the consumption of CH in the pozzolanic reaction decreases the alkalinity of concrete, the susceptibility to carbonation increases, and accelerates the consumption of CH [21]. With these results, it seems that the utilization of BFA, which is a more alkaline material, restores the alkalinity that is lost during the partial cement replacement by CFA and the concrete with 0.5%wt of BFA had a higher carbonation resistance.

Table 5.3 – Coefficient of accelerated carbonation test (Kc in mm/days$^{0.5}$)

Nomenclature	Curing	28 days		90 days		180 days	
		$X_c = K_c \times \sqrt{t}$	R^2	$X_c = K_c \times \sqrt{t}$	R^2	$X_c = K_c \times t$	R^2
REF2	Water	y=1.37x	0.99	y=1.32x	1.00	y=1.14x	0.99
CFA50		y=1.52x	0.99	y=1.24x	0.99	y=1.08x	0.99
CFA49.5HL0.5		y=1.92x	1.00	y=1.87x	1.00	y=1.74x	1.00
CFA49.5BFA0.5		y=1.39x	0.99	y=1.12x	0.99	y=1.00x	0.99
CFA48.8BFA1.3		y=1.77x	0.99	y=1.44x	1.00	y=1.45x	1.00
CFA45BFA5		y=2.48x	1.00	y=2.25x	1.00	y=2.07x	1.00
CFA48.8BFA0.6HL0.6		y=2.24x	1.00	y=2.03x	1.00	y=1.94x	1.00
REF2	Hydrated lime	y=1.28x	1.00	y=1.26x	1.00	y=1.22x	1.00
CFA50		y=1.51x	0.99	y=1.32x	1.00	y=1.09x	0.97
CFA49.5HL0.5		y=1.95x	1.00	y=1.56x	0.99	y=1.53x	0.99
CFA49.5BFA0.5		y=1.30x	1.00	y=0.97x	1.00	y=0.82x	0.97
CFA48.8BFA1.3		y=1.74x	0.97	y=1.30x	1.00	y=2.14x	1.00
CFA45BFA5		y=2.39x	1.00	y=2.11x	1.00	y=1.35x	1.00
CFA48.8BFA0.6HL0.6		y=2.18x	1.00	y=2.03x	1.00	y=1.93x	1.00

However, the use of BFA seems to improve the resistance to carbonation penetration. This is true just for 0.5%wt, because with the increase of the BFA content, a decrease of the resistance to carbonation penetration occurs, being the values registered in the samples with 1.3 and 5%wt of BFA higher than in the reference mix or the CFA50 mix, most probably due to the fact that an increase of cement replacement with BFA, where more amorphous silica minerals are available to react with calcium hydroxide, produced by cement hydration, forming a calcium silica hydrated gel, leaving less content of calcium hydroxide in the hardened mix, and consequently decreasing the resistance to carbonation [311]. These results were not expected since these formulations were chosen because in the results obtained for mortars, these formulations presented a greater carbonation resistance than the mortar with 50%wt of cement replaced with CFA (Figure 4.28 and Figure 4.29).

The mixes with HL obtained poor results. This may be due to the fact that the vitreous silica of the CFA cannot react with all available lime, so that excess lime, even if it contributes to the maintenance of pH, are not contributing to the production of C-S-H and consequent densification of the matrix [311].

The values of the carbonation depth for the two types of curing, water curing and hydrated lime curing, showed differences that must be taken into account in order to understand their origins. It has been observed that, in general, curing with calcium hydroxide improves the resistance to carbonation. The best results for mixing with hydrated lime can be justified by reducing the alkaline gradient between the samples and the curing solution, avoiding the leaching compounds [311].

5.7 Chloride Penetration Resistance

The migration of chlorides was tested in the concrete samples cured in water and cured in the hydrated lime solution, according to [371]. After the test, the samples were broken into two equal parts and pulverized with a solution of silver nitrate, which allowed the measurement of the penetration of chlorides' depth, as can be seen in Figure 5.9.

Figure 5.9 – Concrete samples after the migration chloride test

In Figure 5.10 and Table 5.4, the average results of the chloride diffusion coefficients are shown. Analysing the obtained results, it was verified that, for the three curing periods and for the two types of curing processes, all the compositions presented a better behaviour than the reference composition, which showed that the addition of fly ash led to concrete with higher resistance to penetration of chlorides. This better performance is more significant for samples with 90 and 180 days of curing, as a decrease of more than 80-90% in the diffusion coefficient of the chlorides migration was observed for all samples. This result was expected since the reference mix had a higher water/binder ratio. It is known that the chloride migration is influenced by the porosity of matrices and for that reason as an increase in the water/binder ratio leads to more porous concrete, a higher diffusion coefficient is observed [371].

Table 5.4 – Diffusion coefficient from the chloride migration test

	Water curing			**Hydrated lime curing**		
Nomenclature	**28d**	**90d**	**180d**	**28d**	**90d**	**180d**
	D·(10^{-12}m^2/s)					
REF2	20.33±0.43	19.32±1.11	21.28±1.86	18.83±0.43	19.02±0.89	20.75±1.84
CFA50	14.54±0.58	2.08±0.21	1.02±0.07	13.30±0.31	2.01±0.15	1.09±0.14
CFA49.5HL0.5	19.03±1.92	3.61±0.20	1.48±0.08	14.27±0.84	1.61±0.08	1.35±0.03
CFA49.5BFA0.5	14.31±0.30	2.32±0.15	0.88±0.07	10.76±0.89	1.29±0.16	0.88±0.13
CFA48.8BFA1.3	15.53±0.16	2.47±0.19	1.99±0.56	11.93±0.14	1.32±0.01	1.28±0.19
CFA45BFA5	18.55±0.00	3.20±0.16	1.51±0.09	12.52±0.77	1.57±0.13	1.66±0.10
CFA48.8BFA0.6HL0.6	14.51±1.19	2.67±0.25	1.40±0.12	10.13±0.93	1.52±0.01	1.22±0.15

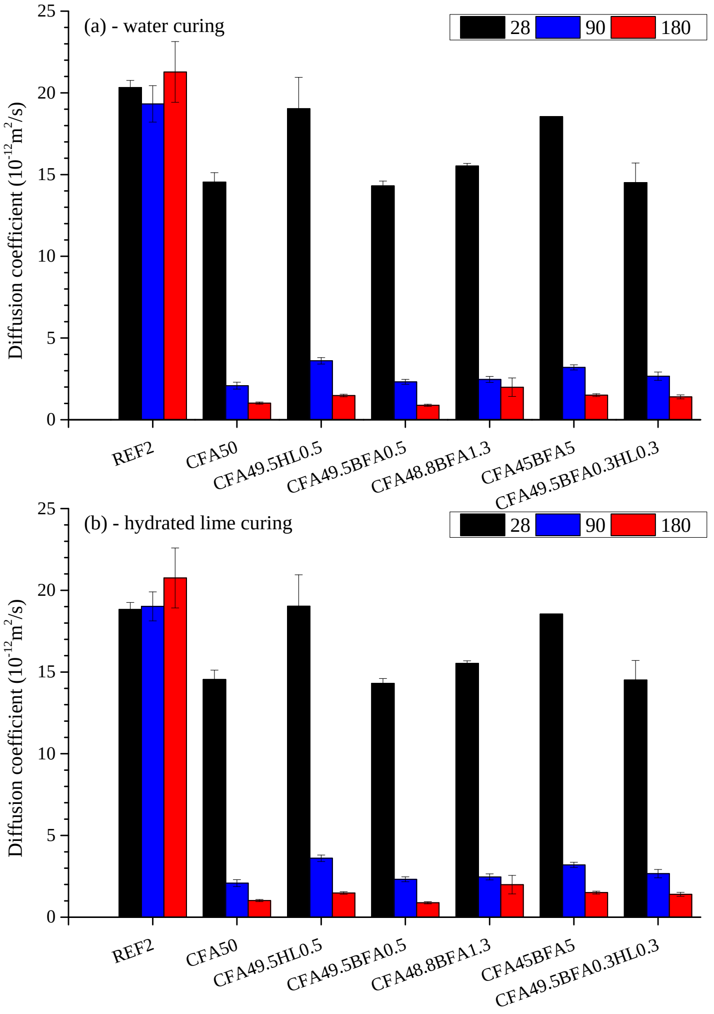


Figure 5.10 – Diffusion coefficient of chlorides migration for samples cured in water and in a hydrated lime solution

The results showed that the CFA49.5BFA0.5 and CFA50 mixes presented the lowest values of samples cured in water. This can be caused by the fact that the two fly ashes presented a good synergy, in this level of cement replacement, and could happen because a higher quantity of aluminates present in concrete with fly ashes leads to a better behaviour against chlorides' penetration, which leads to its fixation and reduction of the content of free chloride ions capable of migrating into concrete, leading to the decrease of the diffusion coefficient [371]. Despite the good synergy presented in this mix (CFA49.5BFA0.5), an increase in the diffusion coefficient was observed with the increase in the BFA content. However, the values were inferior to those of the reference one.

In samples cured in water, the introduction of hydrated lime into the mix did not lead to a better behaviour of these concrete mixes against chlorides diffusion when compared with concrete with 50%wt of coal fly ash. Therefore, all values, for three curing periods, were lower than those observed for plain cement concrete.

The results obtained for the diffusion coefficient of the chlorides for the samples cured in hydrated lime solution showed a slightly different behaviour to those observed in curing in water. In general, for the three curing periods, the samples with BFA (CFA49.5BFA0.5, CFA48.8BFA1.3, CFA45BFA5 and CFA49.5BFA0.6HL0.6) were the ones that presented the lowest values of the diffusion coefficient, with an exception at 180 days where CFA50 presented the second lowest value. This shows that the addition of BFA, together with a curing in an alkaline environment led to an improvement in the performance of concrete in terms of chloride diffusion. This showed once again that the synergy between CFA with BFA or/and HL was good, being the durability of concrete produced with these materials together better than that of concrete with CFA only or plain cement concrete.

It is important to note that curing in a hydrated lime solution led to values of chloride diffusion coefficients lower than the values obtained for curing in water (Table 5.4 and Figure 5.10). This can be due to the fact that this curing does not lead to the leaching of the alkali elements of concrete for the curing solution, since this solution is very alkaline and also because of the pozzolanic reaction of the cement, i.e. the cement particles initiate hydration and C-S-H with thorny form is formed, at the same time as calcium hydroxide is formed as a by-product of hydration. The pH of pore water increases as calcium hydroxide accumulates and dissolves in pore water. When the pH of the pore water increases and exceeds a pH threshold, the pozzolanic reaction is activated. The fly ash particles react with calcium hydroxide and additional C-S-H is formed, which fills the interstitial pores. Due to the physical effect of void filling by pozzolan reaction products that cause pore refinement and reduce microcracks in the transition zone, further improvements of the ion diffusion properties are achieved because in curing in lime saturated water there is a larger amount of calcium hydroxide that will react with the fly ash particles [37,414,415]. The curing of the concrete test samples in a solution of saturated water of lime brings benefits, in the case of the resistance to the penetration of chloride ions.

5.8 Conclusions

Through the results obtained from the present work as from the analysis performed, several conclusions can be drawn. Concerning the compressive strength, increasing the dosage of biomass ash reduces the compressive strength of concrete. However, concrete with 0.5%wt and 1.3%wt of BFA presented higher or similar values of compressive strength to concrete with 50%wt of CFA. With the incorporation of HL in the concrete composition, there was a strong delay in the adjustment time of the mix and with this a reduction of strength at the initial ages occurs without affecting the final compressive strength of concrete.

Concrete with HVFA had a slower strength development than concrete with a low volume of fly ash, or with cement only as a binder. Concrete with cement as a binder reached its final compressive strength at around 28 days and at later ages its mechanical strength practically stagnated. CFA slows the hydration of the binder and, at early ages, concrete had a lower strength than concrete with cement only. However, over time, the strength of the high volume fly ash concrete overcomes that of concrete with cement only as a binder, without stagnation of the evolution of the strength. The curing of the concrete in a solution of water saturated with lime results, in general, in values of the compressive strength higher than those of samples cured in water. Taking into account the results obtained, one may conclude that it is possible to produce HVFAC, incorporating BFA or not, and fulfilling the common requirements related to the mechanical strength of conventional concrete.

In the immersion water absorption test, concrete with cement only as a binder obtained the highest absorption of water by immersion, a sign of a greater open porosity. CFA causes concrete to improve its performance with respect to the absorption of water by immersion. The incorporation of HL in concrete in relation to the absorption of water by immersion showed mediocre results. Thus, concrete compositions with the amounts of HL tested are not ideal in order to obtain less porous concrete. Increasing the BFA dosage led to an increase in the absorption coefficient of water by immersion, but once again 0.5%wt of BFA led to lower values of water absorption by immersion. This is related to the amorphous silica dioxide that increases the strength of concrete by reducing the porosity of the matrix [409].

In relation to the water absorption by capillarity, with the increase in the water/binder ratio of the mix, the porosity also increased and, with this, the water absorption coefficient by capillarity. The introduction of CFA and low content of BFA blend with CFA in the mix improves the performance of concrete, reducing its coefficient of water absorption by capillarity. The increase in the BFA dosage in the mix leads to the increase in the water absorption by capillarity coefficient. The incorporation of HL in the blend seems to lead to a better performance in water absorption by capillarity when mixed with only CFA and cement, while the addition of BFA with HL did not demonstrate good performance. The curing of concrete samples in a hydrated lime saturated solution showed that the concrete samples were sensible to the curing process and water leaching of some alkaline compounds occurs along curing period and this affects the hydration of the concrete matrix and its porosity.

In the presence of pozzolanic additions, the consumption of CH in the pozzolanic reaction causes a decrease of the alkalinity of concrete. Thus, the susceptibility to carbonation increases. Therefore, the REF mix shows good results in the various measurements, over time. Regarding the dosage of biomass fly ash, carbonation increased along with the increase in biomass fly ash content. The introduction of hydrated lime in the blends obtained poor results. The incorporation of small amounts of a more alkaline ash such as biomass ash seems to provide concrete with a higher resistance to corrosion by carbonation. The carbonation depths of the test specimens subjected to curing in hydrated lime were generally lower that of the water curing test samples.

Taking into account the resistance to chloride penetration, the addition of a pozzolan such as CFA improved the strength of concrete especially after 28 days of curing. Plain cement concrete presented the lowest resistance to chlorides' penetration. The incorporation of HL in the blend when mixed with cement and CFA did also not show good results. However, the incorporation of HL when mixed with cement, CFA and BFA resulted in a good resistance to chloride ions penetration. With regard to the dosage of BFA, the resistance to chloride penetration decreases with increasing biomass ash dosage. The mixes that have BFA in their composition showed good performance in terms of resistance to penetration of chlorides, mainly for low contents.

The durability of the compositions with HVFA, with or without BFA, has generally proved to be superior to that of the REF composition, with cement only as a binder, except for the carbonation resistance which, however, has been particularly improved with the inclusion of a reduced amount of BFA.

Another parameter in the analysis of the different concrete compositions, besides the results obtained of the strength, workability, volume of voids and durability, is the eco-efficiency of the concrete. The replacement of large quantities of cement with fly ash can be beneficial from an economic point of view, also from energy efficiency, durability, ecological and environmental approach. A considerable amount of forest biomass received by the pulp and paper industries is not suitable for pulp and paper production. The most common destination of these forest residues is their thermal recovery through combustion, since the energy content is sufficiently high for energy recovery. Thus, the BFA can be more eco-efficient than CFA concrete.

The studied concrete mixes have only 50%wt of cement in terms of the total weight of the binder and a lower w/b ratio than the plain cement concrete mix. The mix that showed the best performance in the various concrete analysis parameters was CFA49.5BFA0.5 mix. The studied concrete formulations were chosen, because in the mortars formulations they were the ones that presented similar compressive strength to the reference mix. Nevertheless, it was seen, that the CFA49.5BFA0.5 concrete presented higher compressive strength than the reference one, but also less water absorption and higher resistance to accelerated carbonation and chloride ions penetration. The CFA49.5BFA0.5 blend could be one of the most eco-efficient blends studied in this work, with the reduction of 50% of the cement in the total weight of binder, maintaining a good quality and also a better durability. Even with the use of superplasticizer in the blend, the reduction of the water/binder ratio justifies its use from an economic and ecological point of view. Taking into account all that has been shown, the CFA49.5BFA0.5 mix allowed obtaining a high efficiency concrete, which can be a solution for conventional plain cement concrete. Is important to point out that even though mix CFA48.8BFA1.3 does not present the best results, it showed good results for most of the studied parameters and therefore can be also a good alternative to conventional mixes.

Chapter 6

Environmental Life-Cycle Analysis of Biomass/Coal Fly Ash Concrete

6.1 Introduction

The development of low carbon footprint concrete with the aim of reducing the environmental impact of Portland cement production was one of the most important goals of the work developed in the PhD. As seen previously, biomass fly ash (BFA) has an effect on the concrete quality and durability, and in some cases concrete with BFA presents similar or better results than plain cement concrete. Even though, some concrete mixes with BFA presents a positive benefit in terms of quality and durability, it is also important that those mixes are economically competitive and present a good environmental performance, to be considered a more sustainable material than plain cement concrete.

Therefore, it is important to analyse and compare the potential environmental impacts related to the production of plain cement concrete and the impacts resulting from the production of a concrete that uses BFA (alone or blended with coal fly ash (CFA) or/and hydrated lime (HL)) as raw material substitution. One of the best approaches to develop this type of study is to use the life cycle assessment (LCA) method [416]. This method enables the quantification of the potential environmental impacts of products or services. It quantifies both the input flows, such as energy, water and materials, as well as the output flows, such as CO_2 emission, solid wastes and liquid wastes [12,417]. LCA allows estimating the potential impact on humans and nature and enables identifying areas with improvement potential [12].

Based both on the abovementioned context and methodological approach, a quantification and comparison of potential environmental impacts resulting from the production of 1 m^3 of concrete was made, using different types of binder: i) Portland cement; ii) Portland cement and CFA or/and BFA, iii) Portland cement and CFA and HL; and iv) Portland cement, CFA, BFA and HL.

6.2 Concrete Formulations

This study compares the environmental performance of concrete mixes with incorporation of BFA, CFA or a blend of the two ashes with or without HL (with equal mass content) as cement substitution in a typical concrete (reference). The compositions studied were those studied for the quality and durability properties, described in the last chapters.

Once again a plain cement concrete with a water-binder (w/b) ratio of 0.5 and a binder content of 350 kg/m3 was studied as reference. The other studied formulations were those that in terms of mechanical strength gave the best results and similar or higher when compared to a plain cement concrete and are presented in Table 6.1, in this case the formulations were prepared with a w/b ratio of 0.35 with a binder content of 350 kg/m^3, but with a cement replacement by the three materials of 50%wt. To understand whether this high cement replacement content allows obtaining concrete with a better environmental performance three concrete with 20, 40, 50 and 60%wt of cement replacement by CFA or/and BFA and one with 50%wt of cement replacement by CFA with a w/b of 0.35 were also studied. Those four concrete formulations presented also a binder content of 350 kg/m^3 and a w/b of 0.5. These values were chosen because several studies showed good results in terms of mechanical and durability properties for concretes with up to 60%wt of cement replacement by coal and/or biomass fly ashes [176,279–281].

Table 6.1 - Binder fraction and water/binder ratio used in the concrete formulations

Concrete mix ID	%wt				w/b
	Cement	Biomass fly ash	Coal fly ash	Hydrated Lime	
REF2	100.0	0.0	0.0	0.0	0.50
CFA20	80.0	0.0	20.0	0.0	0.50
BFA20	80.0	20.0	0.0	0.0	0.50
CFA40	60.0	0.0	40.0	0.0	0.50
BFA40	60.0	40.0	0.0	0.0	0.50
CFA50	50.0	0.0	50.0	0.0	0.50
CFA50b	50.0	0.0	50.0	0.0	0.35
BFA50	50.0	50.0	0.0	0.0	0.5
CFA60	40.0	0.0	60.0	0.0	0.5
BFA60	40.0	60.0	0.0	0.0	0.5
CFA49.5HL0.5	50.0	0.0	49.5	0.5	0.35
CFA49.5BFA0.5	50.0	0.5	49.5	0.0	0.35
CFA48.8BFA1.3	50.0	1.3	48.8	0.0	0.35
CFA45BFA5	50.0	5.0	45.0	0.0	0.35
CFA48.8BFA0.6HL0.6	50.0	0.6	48.8	0.6	0.35

6.3 Methodology

6.3.1 Goal and Scope

The main goal of this study was to evaluate the environmental performances of the various concrete formulations using fly ash as a cement replacement. The method used in this study followed the phases of a LCA. The use of LCA is done according to the ISO 14040 standard, which provides a consensual framework, terminology and methodological phases [12]. The implementation of this method is based on four major phases: i) goal and scope definition; ii) inventory analysis; iii) impact assessment; and iv) interpretation [12,417]. The goal and scope express the purpose, objectives, product system, boundaries and functional unit. In the inventory analysis, the data necessary to analyse the life cycle of the product is collected. In the impact assessment, the life cycle inventory (LCI) flows are classified, characterized and normalized, using one of many possible Life Cycle Impact Assessment (LCIA) methodologies to estimate the potential environmental impacts. The last phase, interpretation, is very important to : i) identify, quantify and evaluate the information that results from the last two phases; ii) communicate the information in a correct way; and iii) recommend improvements within the analysed system [12,30].

The comparative analysis and the aggregation of indicators were developed using the multi-criteria decision support Methodology for the Relative Sustainability Assessment of Building Technologies (MARS-SC) [418,419]. The MARS-SC methodology is based on three groups of sustainability categories: environmental, functional and economic [419]. Since this research aimed at assessing the environmental performance of different concrete formulations, only the environmental category of MARS-SC was considered.

The MARS-SC methodology is processed in five steps (Figure 6.1): i) definition of the sustainability indicators; ii) quantification of the indicators (including the life cycle inventory); iii) normalization of the indicators; iv) aggregation of the indicators; and v) sustainable score calculation and global assessment [418,419].

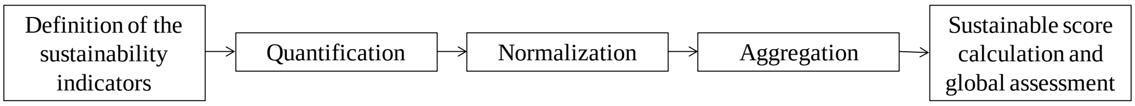


Figure 6.1 - Structure of the MARS-SC methodology for the environmental sustainability indicator adapted from [418]

6.3.2 Functional Unit and System Boundaries

In this study the object of analysis is concrete. The MARS-SC methodology allows assessing all different life-cycle stages [418,419]. However, the boundaries of this work mark the embodied environmental impacts (cradle-to-gate) of the different concrete compositions as well as the environmental impacts that result from the transportation of the materials to the concrete plant and their mixing. The choice of limiting the study to the cradle-to-gate stage is justified by the fact that, in the studied compositions, the use and disposal of concrete will result in similar environmental impacts. The declared functional unit is dependent on the goal of life cycle analysis and therefore constitutes 1 m^3 of concrete in this case.

Figure 6.2 displays in a simplified way the processes that are included in the LCA analysis and the boundaries of the study. The system presented was adapted according to the mix in question.

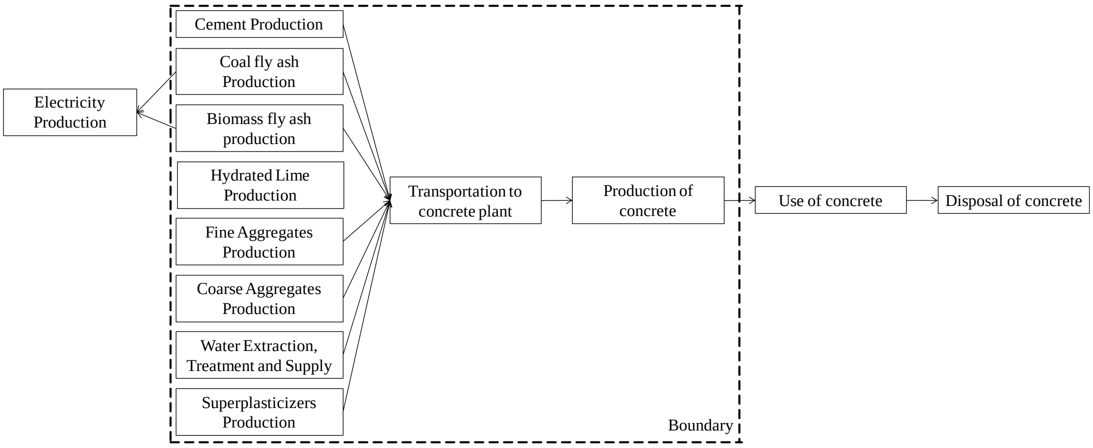


Figure 6.2 - Processes considered in the environmental analysis of the different concrete formulations

6.3.3 Inventory Analysis

To quantify the sustainability indicators, it is necessary to first develop the inventory analysis [419]. The inventory is used to quantify the inputs (e.g. energy, materials and chemical) and outputs (e.g. emissions and wastes) of the product system [420]. As mentioned before, in this study the production of raw materials, their transportation to the concrete plant and the production of concrete were included in the inventory.

Table 6.2 shows the inventory of the materials and transportation considered for each concrete formulation. This inventory took into consideration the specific context of the Portuguese concrete industry. The life cycle analysis software SimaPro 7.3.3 was used to facilitate the quantification of the impact categories.

In this study, the specific consumption of raw materials, energy and fuels and the emissions released to air, water and soil during the cement production of an important Portuguese cement plant, located in the south of Portugal, was considered. The figures used are described in the public Environmental Declaration [421] of this cement plant. For this research, it was taken into account that this plant supplied the cement used for the preparation of the different concrete formulations. It was necessary to quantify the impact categories, since the environmental declaration did not cover all impact categories necessary for this study, being limited to those mandatorily declared according to Portuguese environmental legislation. Using the inventory listed in the enviornmental declaration, the SimaPro software was used to assess the potential environmental impacts of the used Portland cement.

Regarding each type of fly ashes, it was necessary to make the allocation of flows of the power plant according to the place of production. Allocation is necessary in the case of joint co-production, where the processes cannot be sub-divided, as is the case in fly ashes production [422]. Allocation shall respect the main purpose of the processes studied, appropriately allocating all relevant products and functions. Since the main purpose of a thermal power plant is to produce electricity and since the difference in revenue between the electricity and the fly ashes is high, it is not possible to use an allocation process based on physical proprieties (e.g. mass and volume). Therefore the allocation process used in this research was based on economic values.

Table 6.2 - Inventory results of the material and transportation inputs for each concrete (figures per m^3 of produced concrete)

Formulations	PC*	Gravel	Sand	Water	SP*	CFA	BFA	HL
	Material Input (kg)							
REF2	350.0	969.2	738.1	200.0	0.0	0.0	0.0	0.0
CFA20	280.0	982.1	756.7	149.5	0.0	70.0	0.0	0.0
BFA20	280.0	985.3	759.1	149.4	0.0	0.0	70.0	0.0
CFA40	210.0	973.0	749.6	149.7	0.0	140.0	0.0	0.0
BFA40	210.0	979.3	754.5	149.5	0.0	0.0	140.0	0.0
CFA50	175.0	968.4	745.1	149.8	0.0	175.0	0.0	0.0
CFA50b	175.0	1044.3	804.5	88.4	8.8	175.0	0.0	0.0
BFA50	175.0	976.3	752.2	149.6	0.0	0.0	175.0	0.0
CFA60	140.0	963.8	742.5	149.9	0.0	210.0	0.0	0.0
BFA60	140.0	973.3	749.9	149.7	0.0	0.0	210.0	0.0
CFA49.5HL0.5	175.0	1049.0	768.6	91.5	5.3	173.5	0.0	1.9
CFA49.5BFA0.5	175.0	1049.0	795.2	91.5	11.4	173.5	1.9	0.0
CFA48.8BFA1.3	175.0	1050.1	842.8	35.5	11.4	170.6	4.4	0.0
CFA45BFA5	175.0	1049.5	838.9	42.4	3.9	160.0	17.8	0.0
CFA48.8BFA0.6HL0.6	175.0	1067.2	832.9	36.9	2.5	170.6	2.2	2.2
Transportation (tkm)								
REF2	14.5	357.6	272.4	-	-	-	-	-
CFA20	11.6	362.4	279.2	-	-	12.4	-	-
BFA20	11.6	363.6	280.1	-	-	-	10.2	-
CFA40	8.7	359.0	276.6	-	-	24.8	-	-
BFA40	8.7	361.4	278.4	-	-	-	20.3	-
CFA50	7.3	357.3	274.9	-	-	31.0	-	-
CFA50b	7.3	385.3	296.9	-	2.9	31.0	-	-
BFA50	7.3	360.3	277.6	-	-	-	25.4	-
CFA60	5.8	355.6	274.0	-	-	37.2	-	-
BFA60	5.8	359.1	276.7	-	-	-	30.5	
CFA49.5HL0.5	7.3	387.1	283.6	-	1.7	30.7	-	0.2
CFA49.5BFA0.5	7.3	387.1	293.4	-	3.8	30.7	0.3	-
CFA48.8BFA1.3	7.3	387.5	311.0	-	3.8	30.2	0.6	-
CFA45BFA5	7.3	387.3	309.6	-	1.3	28.3	2.6	-
CFA49.5BFA0.6HL0.6	7.3	393.8	307.3	-	0.8	30.2	0.3	0.3

*PC –Portland Cement; SP - Superplasticizer

Due to the environmental report [423] from a major Portuguese coal power plant (located in the centre of the country), it is possible to known how many tons of coal are consumed to produce 1 kWh of electricity as well as the quantity of CFA produced during coal combustion. In Portugal, the commercial value of CFA is about 18€/ton and the value of the electricity is 0.16€/kWh. Therefore, the economic allocation coefficient of 0.17% is applied to the impacts of the extraction, transportation and combustion of the coal from that power plant. As with the cement plant, this environmental report only covered the impact categories that are mandatory according to Portuguese environmental legislation. As a result, all the flows (inputs and outputs) declared in this report were introduced in the SimaPro software, taking into consideration the quantified economic allocation coefficient of 0.17%.

Regarding BFA, it is important to highlight that in Portugal this kind of fly ash is considered a waste product and therefore they do not provide an economic value. Because of this fact and according to the allocation rules presented in ISO 14040, no flows from the thermal power plant are allocated in the production of BFA.

With respect to the life-cycle inventory of the other used materials (gravel, sand, water and superplasticizer), generic data was used. Since the development of specific environmental information for products is very time and cost consuming, initial LCA studies, whose main goal was to compare different design scenarios, are normally based on generic (average) data [419]. For this reason and due to the lack of publically available specific data for the abovementioned materials, this information was gathered from one of the most internationally accredited generic environmental databases of the Ecoinvent report V2.2 [424]. This database covers the average inventory data of the main building materials and processes in different regional contexts [419]. The nearest context to the Portuguese one was considered for this study. Since the energy consumed during the manufacturing process is the parameter that most influences the life-cycle environmental impact [71] and since the Portuguese energy mix is different from the European average [425], a contextualization of the energy used in each process was developed. This means that all used processes from the Ecoinvent database were edited and all energy input flows were changed to take into account the Portuguese energy mix.

In the inventory of the transportation processes, the study took into account the distances between the Portuguese places of raw material extraction or raw materials storage facilities and the concrete mixing plant in question. The distance between the raw materials production facilities and concrete production was considered for this study. The kilometres considered as the transportation distance of cement (Secil Group), sand and gravel (MIBAL - Minas de Barqueiros, S.A.), coal fly ashes (Pegop-energia Eléctrica Sa), biomass fly ash (Altri), superplasticizer (BASF) and hydrated lime (Lusical-companhia Lusitana De Cal Sa) to the concrete industry considered in this study were 41.5, 369, 177, 145, 329 and 117 km, respectively.

The inventory related to the production of concrete was quantified taking into account the Environmental Product Declaration (EPD) of a specific Portuguese concrete plant [426], where the different concrete formulations are supposedly produced. From this EPD, only the flows related to the concrete mixing phase were considered.

6.3.4 Impact Assessment

The life cycle inventory data was converted into potential environmental impact, using the life-cycle impact assessment (LCIA) methods.

In MARS-SC, the definition of the sustainability indicators depends, above all, on the type of analysed product or building element and on the aims of the study. In this method, the environmental performance assessment is based on the following six environmental impact categories (Table 6.3): i) Global warming; ii) Ozone depletion; iii) Acidification of soil and water; iv) Eutrophication; v) Photochemical ozone creation; and vi) Depletion of abiotic resources-fossil fuels. Compared with the list of impact categories found in the EN15804:2012 [427] standard, MARS-SC does not consider the Depletion of abiotic resources-elements as an impact category.

Table 6.3 - Indicators, units and quantification methods

Environmental indicators	**Units**	**LCIA Methods**
Global warming (GWP100)	[kg CO_2 eq]	CML 2 baseline 2000 V2.05
Ozone layer depletion (ODP)	[kgCFC-11 eq]	CML 2 baseline 2000 V2.05
Acidification potential (AP)	[kg SO_2 eq]	CML 2 baseline 2000 V2.05
Eutrophication potential (EP)	[kg PO_4 eq]	CML 2 baseline 2000 V2.05
Formation potential of tropospheric ozone (POCP)	[kg C_2H_4 eq]	CML 2 baseline 2000 V2.05
Abiotic depletion potential of fossil resources (ADP_FF)	[MJ eq]	Cumulative Energy Demand V1.08

6.3.5 Normalization

In order to avoid the scale effects in the aggregation of parameters of the different indicators and in order to minimize the possibility that some of the parameters are of the type “higher is better” and others “lower is better”, it was necessary to normalize the indicators [419]. The normalization was done using the Diaz-Balteiro [428] (Equation 25).

$$\bar{P}_i = \frac{P_i - P_{*i}}{P_i^* - P_{*i}} \ \forall_i \qquad (25)$$

In this Equation, P_i is the value of i^{th} parameter. P_i^* and P_{*i} are the best and worst value of the i^{th} sustainability parameter among the analysed products. Normalization converts the values into a scale bounded between 0 (worst value) and 1 (best value) and turns the value of each indicator dimensionless [419].

6.3.6 Aggregation and Global Assessment

Equation 26 calculates the aggregation of each environmental indicator in terms of a global indicator, describing the overall environmental performance (ND_A).

$$ND_A = \sum_{i=1}^{n} w_i . \bar{P}_i \tag{26}$$

The global indicator ND_A results from the weighting average of each normalized indicator $\bar{P}_i$, while w_i is the contribution of the i^{th} indicator for the overall environmental performance. The sum of all weights must be equal to 1 [419]. For aggregation purposes, this study considers the weights (Table 6.4) set in a study developed by the US Environmental Protection Agency's Science Advisory Board (SAB) [429]. Reasoning for this is that there are no specific studies in Portugal or in a nearby regional context regarding the relative importance of each environmental impact category in the quantification of the global environmental performance. According to the MARS-SC, this is the approach recommended for the Portuguese context and one of the most accepted by the international scientific community in the field [418]. In the application of this methodology to a different context, if there are specific weights, they should be used in the assessment of the global environmental performance.

The results are also presented in a "radar" or Amoeba diagram, also known as a sustainable profile. In the diagram, the number of rays is equal to the number of indicators that are analysed. In each sustainable profile, the global performance of a respective concrete with fly ash is monitored and compared with that of the reference concrete.

Table 6.4 - Weight for each environmental indicator [418]

Indicator	Weight (%)
GWP	38
ODP	12
AP	12
EP	12
POCP	14
ADP_FF	12

6.3.7 Sensitivity Analysis

In the inventory of BFA, their transportation from the power plant to the concrete plant was the only parameter considered (Scenario 1), due to the fact that, as described above, the BFA do not have market value. Nevertheless, it is important to understand the effects that a possible evolution of the market value of BFA might have on the obtained results.

In this life cycle analysis study, two additional scenarios were thus considered: one assuming that the biomass ashes gain a market value that is half that of the CFA value (9 €/ton) – Scenario 2; and another assuming the same market value to that of the CFA (18 €/ton) – Scenario 3. As there is no publically available environmental declaration for biomass power plants, in Portugal, the inventory of the considered plant is based on the generic data presented in the Ecoinvent report V2.2 on cogeneration biomass power plants. However, the Ecoinvent process was edited and thereby adjusted to the Portuguese context. In Portugal, biomass is mostly used as a raw material in the pulp and paper industries. During the preparation of biomass for the process of manufacturing, some residual biomass is produced (mainly during the wood log peeling/shelling/stripping processes) and this waste is used to produce energy in cogeneration power plants located within the pulp and paper industries. Because the biomass used to produce energy is a waste product, its economic value has no significance in terms of allocation rules. Therefore, the flows related to the supply of biomass were deleted from the considered Ecoinvent process. Additionally, the energy inputs were changed so as to comply with the Portuguese energy mix. Using the Ecoinvent report, it is also possible to relate the quantity of energy produced to the quantity of biomass fly ashes. Therefore, in the abovementioned Scenarios 2 and 3, the environmental impact of BFA production was considered, using the allocation process previously described for the CFA. The allocation coefficients were 0.03% and 0.05%, for Scenarios 2 and 3 respectively.

6.4 Results and Discussion

6.4.1 Environmental Impacts

Table 6.5 presents the results of the quantification of the potential environmental impacts related with the production of 1kg of different types of binder, according to the Portuguese context.

Table 6.5 - Quantification of the environmental impact categories related with the production of 1kg of binder (specific values for Portugal)

Impact Category	Unit	Cement	Coal Fly Ash	Biomass Fly Ash		Hydrated Lime
				Scenario 2*	Scenario 3	
GWP100	kg CO_2 eq	8.70E-01	2.86E-03	2.20E-03	3.67E-03	8.58E-01
ODP	kg CFC-11 eq	2.53E-08	1.88E-10	2.69E-09	4.48E-09	3.13E-08
AP	kg SO_2 eq	1.57E-03	1.86E-05	5.68E-06	9.47E-06	1.43E-03
EP	kg PO_4 eq	4.20E-04	7.40E-05	-7.09E-06	-1.18E-05	3.20E-04
POCP	kg C_2H_4 eq	5.78E-03	7.74E-07	4.78E-03	2.39E-06	5.88E-05
ADP_FF	MJ eq	3.34E+00	4.56E-01	3.46E-02	5.76E-02	4.26E+00

Potential environmental impact resulting from the production of BFA (Scenario 1) was not considered (as described in before)

Table 6.6 summarizes the values obtained in the quantification of the environmental impacts categories, related with the production of the different concrete mixes, taking into consideration Scenario 1. Analysing the results, it was possible to verify that the concrete that uses cement only as binder presents the highest values of CO_2 emission. The high emission of CO_2 is a result of the chemical reactions (calcination) that occur during clinker production [279,430,431].

Table 6.6 - Values obtained for the different environmental impacts

Formulations	GWP100 kg (x10^{2})	ODP kg (x10^{-5})	AP kg	EP kg (x10^{-1})	POCP kg (x10^{-2})	ADP_FF kg (x10^{3})
REF2	4.02	2.67	1.00	2.53	4.00	2.71
CFA20	3.44	2.55	0.91	2.32	3.64	2.56
BFA20	3.44	2.55	0.91	2.27	3.64	2.53
CFA40	2.83	2.38	0.80	2.08	3.23	2.36
BFA40	2.83	2.38	0.80	1.98	3.22	2.30
CFA50	2.53	2.30	0.75	1.96	3.02	2.26
CFA50b	2.88	2.69	0.90	2.41	3.97	3.10
BFA50	2.53	2.29	0.75	1.83	3.01	2.18
CFA60	2.23	2.21	0.69	1.84	2.82	2.16
BFA60	2.23	2.21	0.69	1.69	2.80	2.07
CFA49.5HL0.5	2.75	2.53	0.84	2.22	3.55	2.77
CFA49.5BFA0.5	2.96	2.77	0.94	2.51	4.20	3.31
CFA48.8BFA1.3	2.99	2.85	0.95	2.54	4.26	3.36
CFA45BFA5	2.75	2.59	0.85	2.22	3.57	2.73
CFA48.8BFA0.6HL0.6	2.73	2.57	0.83	2.18	3.46	2.64

When compared with typical concrete, the incorporation of the two fly ashes allows a reduction in all environmental impacts. The potential environmental impacts decrease with increasing cement substitution, regardless of the type of fly ashes used. But it is more noticeable for mixes with high cement replacement by BFA. At this stage, it is necessary to highlight the effect of the allocation step on the obtained results. In Portugal, BFA are considered a waste product without economic value [23] and therefore there are no flows from the biomass power plant allocated to its production. The same does not happen with CFA, as they have a market value and consequently a percentage of the power plant's flows is allocated to their production [432].

The use of concrete mixes with combination of the two types of ashes and HL or CFA with HL led to a decrease in the environmental impacts when compared to the reference concrete.

The results also show that the values for the concrete mixes with CFA mixed with small amounts of BFA (0.5, 1.3%wt) decreased the environmental impact related with the CO$_2$ emissions but an increase on the values of the others environmental indicators was observed. This is a not result of the incorporation of BFA, since this result is not noted in the mixes with 5, 20, 40 and 60%wt, but it is due to the fact of these two mixes presented a higher superplasticizer content. It was concluded in other studies [338,433] that superplasticizer had high influence on e.g. ODP and ADP_FF impact categories, but did not have an significant influence on GWP that most influences the overall environmental impact concrete with ashes, which confirm the results achieved in this study.

The normalization of the values obtained for each environmental impact category was obtained and the results are presented in Table 6.7. This enables a better perception of which of the concretes has a better environmental performance. It is observed that, among all concrete formulations analysed, the concrete in which 60% of cement was replaced by BFA (BFA60) had the best environmental performance, being REF2 and CFA48.8BFA1.3 the mixes that presented the lowest environmental performance.

Table 6.7 - Normalized values of the studied environmental impact categories

Formulations	GWP100	ODP	AP	EP	POCP	ADP_FF
REF2	0.00	0.24	0.00	0.01	0.18	0.50
CFA20	0.32	0.44	0.30	0.26	0.42	0.62
BFA20	0.32	0.44	0.31	0.32	0.43	0.65
CFA40	0.66	0.72	0.65	0.54	0.71	0.78
BFA40	0.66	0.72	0.65	0.66	0.71	0.82
CFA50	0.83	0.86	0.82	0.68	0.85	0.85
CFA50b	0.64	0.20	0.32	0.16	0.20	0.20
BFA50	0.83	0.86	0.83	0.83	0.86	0.91
CFA60	1.00	0.99	0.99	0.82	0.99	0.93
BFA60	1.00	1.00	1.00	1.00	1.00	1.00
CFA49.5HL0.5	0.71	0.47	0.52	0.37	0.49	0.46
CFA49.5BFA0.5	0.59	0.09	0.21	0.04	0.04	0.03
CFA48.8BFA1.3	0.58	0.00	0.17	0.00	0.00	0.00
CFA45BFA5	0.71	0.37	0.50	0.38	0.47	0.49
CFA48.8BFA0.6HL0.6	0.72	0.41	0.54	0.42	0.55	0.56

6.4.2 Sustainability Analysis

Table 6.8 and Table 6.9 present the sustainability profiles and the overall environmental performances. In the profiles, the shadowed area represents the performance of each concrete analysed. At the level of each impact category, the best concrete is the one that has the value closest to one. It is verified that the BFA60 concrete presented the best environmental performance (ND_A = 1.00) and plain cement concrete (REF2) presented the worst performance (ND_A=0.12).

Therefore, these results allow the conclusion that using a high content of BFA significantly increases the environmental performance of concrete production, since the overall environmental performance of concrete is improved. Additionally, the usage of these materials contributes to a better compatibility between the construction sector and the goals of Sustainable Development.

The results of the sensitivity analysis show that, regardless of the potential market value of the BFA, the results will remain similar to the ones presented in Scenario 1. This conclusion is underlined by the fact that, although in Scenarios 2 and 3 the impacts related to biomass combustion are considered, the largest part of this impact can be attributed to the energy production, due to its much higher economical revenue. As a result, the impact attributed to the fly ashes is very small when compared to other system flows, and therefore it does not affect the environmental performance of concrete.

Table 6.8 - Normalized values that describe the sustainability profile

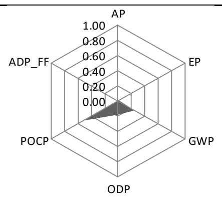
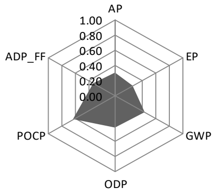
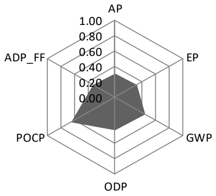
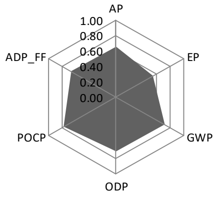
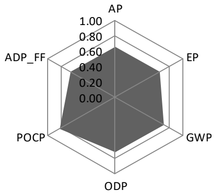
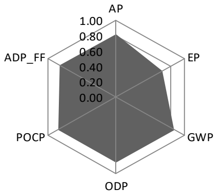
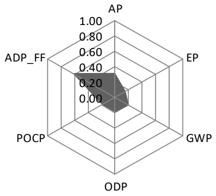
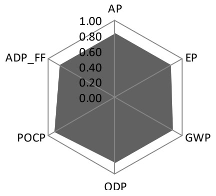
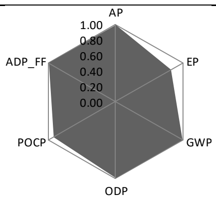
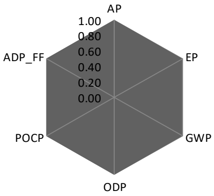
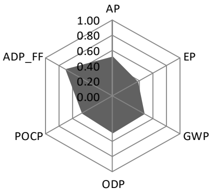
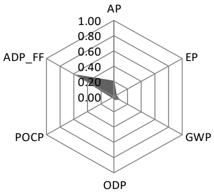
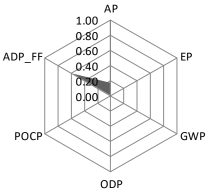
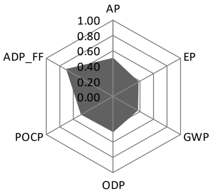
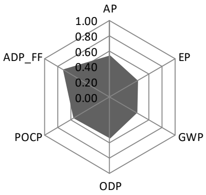
Formulation	Sustainable Profile	Performance ND		
		Scenario 1	Scenario 2	Scenario 3
REF2		0.12	0.12	0.12
CFA20		0.38	0.38	0.38
BFA20		0.39	0.38	0.38
CFA40		0.67	0.68	0.68
BFA40		0.69	0.68	0.68
CFA50		0.82	0.82	0.82
CFA50b		0.38	0.38	0.38
BFA50		0.85	0.83	0.83

Table 6.9 - Normalized values that describe the sustainability profile (continued)

Formulation	Sustainable Profile	Performance ND		
		Scenario 1	Scenario 2	Scenario 3
CFA60		0.97	0.97	0.97
BFA60		1.00	0.97	0.97
CFA49.5HL0.5		0.56	0.56	0.56
CFA49.5BFA0.5		0.27	0.27	0.27
CFA48.8BFA1.3		0.24	0.24	0.24
CFA45BFA5		0.54	0.54	0.54
CFA48.8BFA0.6HL0.6		0.58	0.58	0.58

To complement the results presented in the LCA analysis, showing that pozzolanic concrete presents better environmental performance, it is important to take into account some parameters that are also relevant in the design of concrete products, such as compressive strength and durability. This is crucial since, according to other studies, these parameters can limit the cement substitution ratio [434]. However, it is important to refer that all concrete formulations were chosen because present values for mechanical strength are similar to or higher than those of a plain cement concrete, and those characteristics were verified in chapter 6. Therefore, the LCA analysis showed that it is possible to produce concrete with high cement replacement with good quality (Figure 5.2) and durability (Figure 5.8 and Figure 5.10), but also with a good environmental performance. Since all cement replacement percentages allow a significant improvement of the environmental performance when compared with the plain cement concrete (REF2).

Besides the good results observed, it is important to refer that the concrete formulations with 0.5 and 1.3%wt of cement replacement by BFA presented a low environmental performance, but better than the plain cement concrete. Being these two concrete formulations with higher compressive strength (Figure 5.2) and with a better durability for the concrete formulations studied in this thesis, it is important to understand why their environmental performance is not so good as expectable. Since it was observed that the use of BFA allows a better environmental performance, being the best formulation of all studied the BFA60. The environmental issues related with these two concrete formulations are due to the use of a higher content of superplasticizer when compared with the others formulations (Figure 5.1). The effect of superplasticizer on the environmental indicators is known and some studies showed an influence on e.g. ODP and ADP_FF [338,433]. As seen in Figure 5.1, it is possible to slightly reduce the content of SP, without having a significant effect on the workability, maintaining the values similar to the concrete formulation with 5 %wt of cement replacement by BFA. The decrease on the content of SP has an important contribution to the improvement of environmental performance of these two concrete mixes.

6.5 Conclusions

The concrete formulations studied in the experimental campaign, whose results were discussed before, were studied and compared with a plain cement concrete. The results showed that the potential environmental impact of concrete, mainly the part related with CO_2 emissions, is due to the Portland cement content. This justifies the higher value observed in the reference concrete, and the increase of environmental performance with the decrease of cement percentage. CFA and BFA used alone or blended displayed a capability to reduce the environmental impacts of concrete, when compared to conventional concrete. The results showed that the best concrete is the one in which 60% of cement is replaced with BFA. The results also show that it is possible to produce concretes with low Portland cement content, i.e. with improved environmental performance, achieving satisfactory expected compressive strength, thus being a promising alternative to plain cement concrete.

Besides the good results observed, it is important to refer that the concrete formulations with 0.5 and 1.3%wt of cement replacement with BFA presented a low environmental performance, but better than that of plain cement concrete. The environmental issues related with these two concrete formulations are due to the use of a higher content of superplasticizer when compared with the other formulations. The effect of superplasticizer on the environmental indicators is known, but the results showed that it is possible to slightly reduce the content of SP, without having a significant effect on the workability, maintaining the values similar to those of the concrete formulation with 5%wt of BFA. The decrease of the content of SP has an important contribution on the improvement of environmental performance of these two concrete mixes.

Chapter 7

Conclusions and Further Developments

7.1 General Highlights

The study developed within the scope of this thesis was aimed at evaluating the possibility of producing an eco-efficient high volume fly ash concrete (HVFAC), using biomass fly ash (BFA) for the mitigation of the issues related with this type of concrete. For this purpose, an experimental program was designed that involved the characterization of pastes, mortars and concrete. A number of compositions were developed and the incorporation of BFA from a Portuguese pulp and paper industry and coal fly ash (CFA) from *Pego* thermoelectric power plant was evaluated. All materials were used as received, i.e. they were not subjected to any type of treatment that would improve their characteristics, such as sand washing or particle size separation of fly ash.

The laboratory tests were carried out in order to allow the evaluation of the overall performance of the produced mixes, focusing on the most relevant characteristics of concrete performance: workability, mechanical behaviour, durability and sustainability.

In this chapter the main conclusions resulting of the experimental analysis and the possible relationship between the characteristics of the concrete produced are presented. Future developments that involve aspects not described or that have not been completely clarified throughout the present study and that can contribute to deepen the knowledge of the theme approached in this thesis are also suggested.

7.2 Main Conclusions

The work developed, in particular the analysis of the tests carried out and the results obtained, highlights that is possible to produce concrete with low cement content but with similar compressive strength to that of a conventional plain cement control mix. This low-cement content concrete is more durable and more sustainable than the tested plain cement concrete. During this study, it was possible to conclude that BFA had an effect on the hydration of concrete, but in some cases it leads to the production of a material with higher mechanical strength than the plain cement concrete. The durability of the compositions with high volumes of fly ash, with or without biomass ash, has generally proved to be superior to that of the reference composition, containing only cement as a binder, except for the carbonation resistance which, however, has been particularly improved with the inclusion of a reduced amount of biomass fly ash.

The results show that biomass fly ash promotes mixes with higher alkalinity reserves, since it was observed that the utilization of BFA minimizes the decrease in the calcium hydroxide content of high volume fly ash concrete due the pozzolanic reaction of the CFA.

It was noticeable that the replacement of cement with BFA only, was possible only for percentages of replacement of about 20 %wt. High volume biomass fly ash concrete did not have a significantly different performance than a high volume coal fly ash concrete. However, in terms of sustainability, those concrete mixes presented less leaching of chemical compounds for the environment and a better environmental performance. Thus, the results showed that it could be possible to use BFA as partial cement replacement despite the fact that BFA characterisation showed that this material is not considered by the standard as a pozzolanic material. However, using a high amount of BFA alone did not show significant improvement on the properties of the produced concrete.

Since, it was concluded that the replacement of cement by BFA only is not a good technical solution, an alternative solution was explored. Its incorporation in HVFAC was studied, in small amounts and the performance of this mix was compared with HVFAC containing small amounts of hydrated lime, since the literature review indicated its utilization has a benefit to concrete properties. One of the main conclusions of the tests was that, even when using small amounts of BFA, high amounts of BFA content leads to a mechanical strength decrease, increases the porosity, decreases the resistance to carbonation and decreases the resistance to chloride ion penetration of concrete. However, 0.5 %wt and 1.3%wt of BFA presented higher or similar values for compressive strength than concrete containing 50%wt of CFA. Concrete with cement as a binder reached its final compressive strength at around 28 days and at later ages its mechanical strength practically stagnated. CFA slows the hydration of the binder and, at early ages, concrete has a lower strength than concrete containing cement only. However, over time, the strength of HVFAC overcomes that of concrete with cement only as a binder, without stagnation of evolution of the strength, due to the good synergy of the two fly ashes. Taking into account the results obtained, one may conclude that it is possible to produce HVFAC incorporating BFA or not, and to fulfil the common requirements related to the mechanical strength of conventional concrete.

It was also observed that 0.5%wt of BFA led to lower values of water absorption by immersion, indicating a lower porosity of this concrete. The introduction of CFA and low content of BFA blend with CFA in the mix improves the performance of concrete, reducing its coefficient of water absorption by capillarity.

In the presence of pozzolanic additions, the consumption of CH in the pozzolanic reaction causes a decrease of the alkalinity of concrete; thus, the susceptibility to carbonation increases. Therefore, the reference mix shows good results in the various measurements, over time. The incorporation of a more alkaline ash such as BFA, in the composition of the mixes in small amounts seems to provide concrete with a higher resistance to corrosion by carbonation. Furthermore, mixes that have BFA in their composition showed good performance against chlorides penetration, mainly for low contents.

The concrete formulations studied, whose results were discussed before, were compared with those of a conventional cement concrete in terms of sustainable performance. Coal and biomass fly ashes used alone or blended displayed a capability to reduce the environmental impacts of concrete, when compared to conventional concrete. The best results were obtained when 60% of cement was replaced with BFA. The results also show that it is possible to produce concrete with low Portland cement content, i.e. with improved environmental performance, achieving satisfactory expected compressive strength, thus being a promising alternative to plain cement concrete

CFA49.5BFA0.5 could be one of the most eco-efficient concretes studied in this work, with a reduction of 50% of the cement in the total weight of binder, maintaining a good quality and exhibiting higher durability. Even with the use of superplasticizer in the blend, the reduction of the water/binder ratio justifies its use from an economic and ecological point of view. Taking into account all that has been shown, the CFA49.5BFA0.5 mix allowed obtaining a high efficiency concrete, which can be a solution to replace conventional plain cement concrete. It is important to point out that even though the CFA48.8BFA1.3 mix did not present the best results, it showed good results for the majority of the studied parameters and therefore can be also a good alternative to the conventional mixes.

Thus, one of the solutions to minimise the problems of HVFAC can be the utilization of small amount of BFA blended with CFA. Since the use of small amounts of BFA with high volume CFA content leads to concrete with similar quality or better properties than concrete with CFA, showing a good synergy between the two ashes. BFA blended with CFA seems to have a positive contribution on the quality, durability and sustainability of concrete when compared with concrete made CFA only as supplementary cementitious material or when compared to a plain cement concrete.

7.3 Further Developments

The thematic approach in this study will continue to develop in the future, and for this reason some topics are suggested that can contribute to fill some existing gaps in the current knowledge regarding the characteristics and properties of high volume fly ash concrete with biomass fly ash incorporation.

During the present research, it was not possible to analyse all the aspects related to the subject under study, namely the durability and mechanical strength in the most advanced curing ages of concrete, workability and void volume of concrete with high volume of fly ash. Thus, the work developed in this thesis can be complemented in order 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, electric resistivity, freeze-thaw resistance, porosity and leaching tests. Those tests can be important to complement the study on concrete with high volume of fly ash and the incorporation of biomass ash and to have a better understanding about its benefit and applicability.

Other possible work to be carried out is to understand the origins of the solubility of the incorporation of fly ash of coal fly ash, biomass fly ash and hydrated lime in the composition of concrete mixes. Analyse and understand the effects of the solubility of these binders on the concrete performance is necessary to understand the link between the solubility and the synergy of CFA, BFA and HL, as well as the effect of these materials on concrete and their applicability.

During this work, it was possible to verify that these BFA provides some alkalinity to the materials (pastes, mortars and concretes) when it was used in small amounts. However, it was not possible to verify the optimum dosage, and for that reason an important study to carry out is the evaluation of the amount of CH that is needed by adding BFA.

Finally, it should be noted that all experimental work has been developed with BFA from the same source. In order to make it possible to generalize the behaviour of concrete with BFA incorporation, it will be advantageous to compare the performance of concrete made with BFA from different origins, with different chemical and physical characteristics and analyse its influence on the concrete properties. In this study the materials were used as received, but maybe it is important also to study the influence of changing some characteristics of BFA on the concrete fresh and hardened properties, as for example: reducing the unburned material content present in the ash or decreasing the average particle size of BFA by grinding and sieving.

In order to widespread the use of these new eco-efficient HVFAC, it is necessary to update knowledge in existing standards, which are very conservative and restrictive, and thus hinders its application. Therefore, it is necessary to develop a proposal for updating knowledge in EN 206-1 and Eurocode 2 taking into account specific characteristics of these concrete, incorporating of other wastes/by-products than coal fly ash.

Chapter 8

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