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Design of a new eco-hybrid cement for concrete pavement, made with processed mixed recycled aggregates and olive biomass bottom ash as supplementary cement materials

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Abstract:	<p>The development of new cements made from waste and by-products as substitutes for traditional raw materials is a necessary approach to mitigate the harmful impacts of the construction industry. These impacts are mainly CO₂ emissions and the consumption of energy and natural resources during construction. In this study, new eco-hybrid cements were formulated with Mixed Recycled Aggregates (MRA) from Construction and Demolition Waste (C&DW) and Olive Biomass Bottom Ash (BBA), processed to a powder fraction. Both MRA and BBA were applied in several mortar mixtures replacing cement. The feasibility of using these recycled materials in a combined way, as supplementary cement material and in substitution of aggregates, can be demonstrated. The study of physical, chemical, mechanical and more types of properties were carried out on the cements, showing the possibility of incorporating both processed waste in relevant percentages. This paper try to match the properties of conventional Portland cements, getting similar properties to CEM II A/L, which is the one commonly used for concrete pavements. An adequate processing applied to both recycled materials and the optimised dosages in which substitution rates were added, resulted in favourable properties. These results have allowed the development of an eco-hybrid cement for the manufacture of both mortar and concrete.</p>
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1 **Design of a new eco-hybrid cement for concrete pavement, made with processed mixed**
2 **recycled aggregates and olive biomass bottom ash as supplementary cement materials.**

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7 **Abstract**

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9 raw materials is a necessary approach to mitigate the harmful impacts of the construction industry.
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11 during construction. In this study, new eco-hybrid cements were formulated with Mixed Recycled
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1. Introduction

Current problems have a high social, economic and environmental impact due to the increasing generation of waste produced by human activity. It is necessary to recover it by including it in new sustainable materials that lead to a Circular Economy [1]. The recycling and reduction of waste generated, as well as the application of efficient measures in its management, respond to a need of utmost importance. This need is due to the high environmental impact as a consequence of the contamination of ecosystems, the excessive use of natural resources and its implications on human health. It is necessary to change the growth model based on the linear sequence "take-manufacture-consume and dispose" towards a circular economy focused on making the most of resources and increasing the useful life span. Currently, this issue is reflected in the application and adaptation of different intervention, information and management policies [2].

The construction industry is challenged to incorporate this model and sustainability in its production processes, either by seeking new raw materials and more environmentally-friendly products and/or by contributing to the reduction of CO₂ in the atmosphere. In current studies, the production of one tonne of CEM I 42.5 produces 845 kg of CO₂ while CEM II 42.5 produces 769 kg of CO₂ [3]. Approximately 5-8% of the world's greenhouse gas emissions are emitted by the cement industry [4].

The use of waste and by-products in this sector represents an important form of recovery and can help to achieve this goal [5] and in order to do so research has been carried out into new building materials that lead to a reduction in CO₂ emissions. This research is grouped along three lines. 1) CO₂ capturing materials [6], 2) production processes with efficient consumption of natural resources and use of cleaner energies [7] and 3) materials made from waste [8, 9]. The use of waste

47 as an alternative supplementary material is a major objective to reduce CO₂ emissions generated
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2 48 by the cement industry [10, 11]. Recycled aggregates, mainly concrete aggregates (RCA), have
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4 49 proven to be waste with high potential for the manufacture of construction materials such as
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7 50 concrete and mortar. Two fractions of RCA have been studied, coarse fraction (CRCA) as a
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9 51 substitute for gravel and fine fraction (FRCA) as a substitute for sand and in the manufacture of
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12 52 mortars [12, 13].

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15 53 Several studies have shown that recycled materials can be applied to the manufacture of concrete
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18 54 with 100% replacement levels, which leads to a 10% reduction in compressive strength. [14, 15].
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20 55 One of the issues to consider when CRCA are used in the manufacture of concrete is that the
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22 56 necessary water must be provided for its correct wetting. In this way, problems derived from drying
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25 57 shrinkage are avoided [16, 17], since this process increases between 10 and 30%, mainly due to the
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27 58 high porosity and water absorption capacity of the CRCA [18].

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31 59 On the other hand, FRCA present worse properties such as higher absorption, porosity or high
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33 60 sulphate content, which limits its use in concrete. For these reasons, the level of replacement of
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36 61 natural sand by FRCA is usually limited to a maximum of 30% [19].
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39 62 The use of waste as new supplementary cementitious materials (SCM) is a growing line of research.
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41 63 The use of ceramic waste from C&DW (residues from bricks, tiles or waste ceramic material) has
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44 64 been tested as alternative pozzolanic material in cement manufacture [20, 21]. High temperatures
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46 65 activate the clay and so these materials can be considered as natural calcined pozzolans [22-24].
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49 66 Previous studies have shown that the addition of these materials in cement manufacture resulted in
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51 67 similar results to the use of silica fume and fly ash [25, 26]. The pozzolanicity of C&DW has been
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54 68 demonstrated to be directly related to its ceramic particle content [20].
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57 69 Powdered ceramic residues have certain advantages as substitutes for cement with replacement
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70 rates of up to 20%, showing a decrease in their mechanical behaviour of less than 5% at an age of
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2 71 90 days [21]. It is recommended to limit the percentage of replacement of ceramic residues between
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4 72 15 and 20% as SCM, to guarantee adequate results of compressive strength in concrete [27-30].
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7 73 Biomass bottom ash (BBA) from biomass calcination in thermoelectric plants has been studied as
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10 74 SCM [31-33]. These studies showed that the composition of the BBA, related to the origin of the
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12 75 biomass that is calcined, significantly influences the properties of the new eco-hybrid cements,
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15 76 which can produce a decrease in mechanical resistance, a greater porosity of the material and
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17 77 therefore a greater demand for water and a delay in the setting time that implies an increase in
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20 78 workability.
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23 79 Previous studies showed that substitutions of 10% to 20% of Portland cement by BBA, met the
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25 80 mechanical requirements established for Type II cement. Furthermore, processing of BBA by
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27 81 crushing, calcination or float removal increases SiO₂ and CaOH values resulting in an increase in
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30 82 positive cementitious capacity [32, 34]. In addition, when BBA is subjected to crushing processes,
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32 83 a higher specific surface area of the material is achieved, and the reactivity of the ashes is increased
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35 84 [35].
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38 85 In this study, the modifications in the properties of the materials due to the treatments carried out
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40 86 to observe the pozzolanic reactions that occur in eco-hybrid cements were analysed. The effect of
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42 87 the use of these residues on the mechanical properties, the hydration process and the microstructure
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45 88 was studied. It has been studied using MRA and BBA processed as supplementary cementitious
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47 89 material in variable percentages of substitution, between 8 and 25%, and combining different levels
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50 90 of substitution. Specifically, different processes on BBA and MRA were studied, comparing the
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52 91 application of mixed recycled aggregate powder (pMRA), pulverised olive biomass bottom ash
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55 92 (pBBA) and BBA subjected to a process of spraying, washing and heating (phwBBA), to
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57 93 significantly reduce and improve its properties as a supplementary cementitious material.
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2. Materials

2.1 Characterisation properties of materials

In the present study, mixed recycled aggregates and olive biomass bottom ash that were processed with different treatments were evaluated as a material in the manufacture of new cements. Three processed materials were obtained (Figure 1). The MRA and BBA were subjected to a crushing process using a jaw crusher; subsequently, they were introduced into an impact mill and the resulting material was screened through a 0.125 mm sieve, obtaining two materials (pMRA and pBBA).

Additionally, due to the high K content present in the BBA, a processing of this material was carried out in which it was subjected to a washing with a 1/3 water/solid ratio for 24 hours; subsequently, the material was heated at 600 °C for 4 hours and then it was sieved through the 0.125 mm sieve, obtaining the phwBBA material.

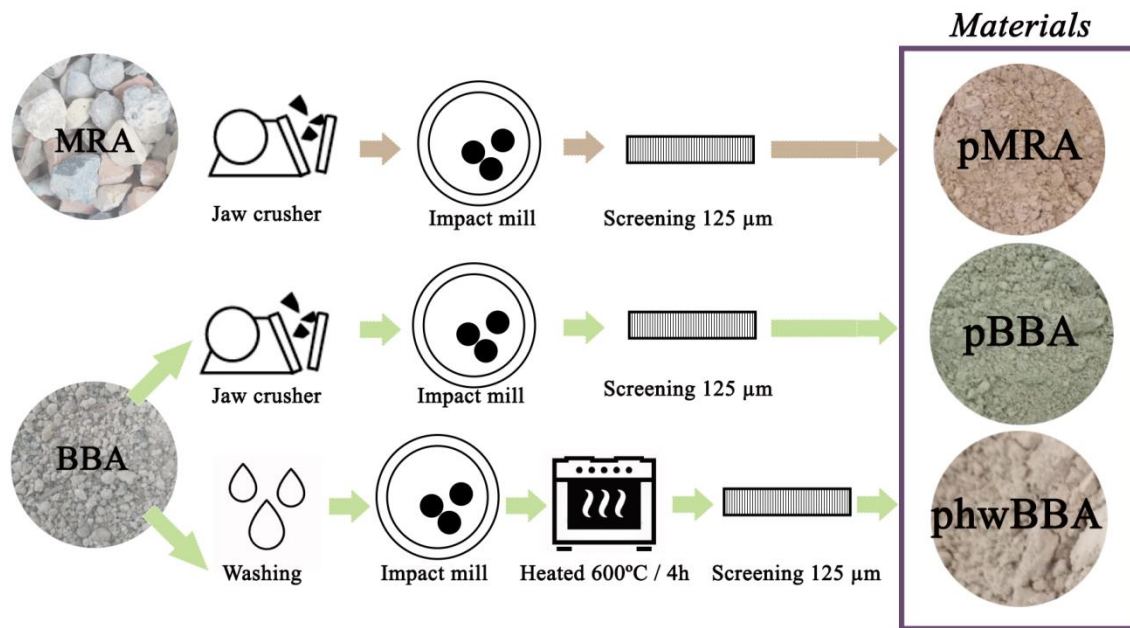


Figure 1. Treatments carried out and materials obtained

To evaluate the influence of these materials as a partial cement substitute, they were compared with the properties of a Portland cement type CEM I and CEM II. The main reason for comparing these new eco-hybrid cements with CEM II A/L, which include limestone filler, is because this OPC is the one commonly used for concrete pavements.

The physical and chemical properties of the materials were analysed before and after processing. Additionally, the 3 resulting materials were analysed using advanced characterisation techniques.

Analytical methods such as laser grain size, Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) were used to analyse the material properties.

2.1.1. Cement: CEM I and CEM II A/L

The cements used in this research were two types: ordinary Portland Cement CEM I 42.5 R with

rapid hardening and CEM II A/L 42,5, with properties according to EN 197-1:2011. The reason for using CEM II A/L 42,5 as reference cement is because this cement is the one commonly used for pavement concrete. Since the general objective of the study is the optimised design of pavement concrete and the execution of the experimental concrete pavement, the properties of CEM II A/L are the ones to be matched. The main chemical composition of each of the cements used is shown below.

Table 1. Physicochemical properties of Cement

	FRX (%)										EN 196-6
	CaO	SiO ₂	SO ₃	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	Density (kg/m ³)	
CEM I 42.5R	66.22	17.95	5.44	4.25	2.89	1.36	1.12	0.39	0.19	3.11	
CEM II/AL 42.5	67.05	18.11	4.43	4.24	2.65	1.71	1.07	0.40	0.19	2.97	

2.1.2 Powdered Mixed Recycled Aggregates (pMRA)

The aggregate used came from the GECORSA company, the waste management plant located in Cordoba, Spain. Mixed recycled aggregate from GECORSA has been classified according EN 933-11 normative. The concrete values (Rc) are 43.7%, aggregates values (Ru) are 33.8% and ceramic values (Rb) are 20.9%. A study of the physical and chemical properties of the waste after crushing and screening and processes was carried out and the results are shown in Table 2.

The chemical composition varies according to the place of origin and the type of treatment given at the plant. Previous studies showed C&DW powder with high Al₂O₃ and Fe₂O₃ content [36]. The MRAs analysed in this study resulted in lower values of both components, as shown in the study by Medina et al. [37].

Table 2 shows physicochemical characterisation of the recycled materials included in this work.

Properties	CHARACTERIZATION POWDER OF MRA AND BBA					
	Size	Results			Test Method	
		pMRA	pBBA	phwBBA		
Density-SSD (kg/m ³)	0 – 0.125 mm	2.93	2.85	2.95	EN 1097-6	
Water Absorption (%)	0 – 0.125 mm	8.95	21.02	18.15		
Sulfates (% SO ₄)	0 - 0.125 mm	Acid	0.68	0.30	0.16	ISO 11048
		Water	0.20	0.30	0.13	
Chlorides	0 - 0.125 mm	0.08	0.23	0.052	EN 1744-1	
Organic Content (%)	0 - 0.125 mm	0.23	2.49	0.42	UNE 103204	
Composition (%)	0 - 0.125 mm	SiO ₂ (%)	45.74	33.91	31.48	FRX
		CaO (%)	33.05	31.71	35.59	
		Al ₂ O ₃ (%)	9.972	6.62	6.29	
		Fe ₂ O ₃ (%)	3.42	3.02	3.00	
		MgO (%)	2.90	5.05	5.42	
		K ₂ O (%)	1.94	15.37	13.56	
		SO ₃ (%)	1.62	0.51	0.24	
		Na ₂ O (%)	0.58	0.34	0.27	
		TiO ₂ (%)	0.48	0.26	0.61	
		P ₂ O ₅ (%)	0.15	3.05	3.36	
MnO ₂ (%)	0.12	0.143	0.11			

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Regarding the content of sulphates and chlorides, the standards determine that the amount of sulphates and chlorides must be less than 4% and 0.1% [36]; The pMRA analysed showed results below these limits in contrast to results obtained in other studies [36]. The lower the sulphate and chloride content, the better the quality of the cementitious powder. The density of phwBBA is higher than that of pBBA. Calcining and washing the biomass bottom ash powder removes part of

146 the organic matter content (from 2.49% to 0.42%). The organic matter makes the powder less dense,
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247 so the removal of organic matter makes phwBBA have a higher density [32].
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6148 **2.1.2. Powdered Olive Biomass Bottom Ash (pBBA)**

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9149 In this study, biomass bottom ash from Linares biomass combustion power plant was studied,
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12150 which is situated in the Andalusia region (Spain) in which there is a high concentration of olive
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14151 orchards.
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17152 The physicochemical properties of this processed material are shown in Table 2. The density of
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19153 pBBA was 2.85 kg/m³, which is important for the design of mortar mixes. The BBA used as
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22154 cementitious powder has been studied by Eliche-Quesada et al. [38] giving similar compositional
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24155 results to the results obtained in this study showing that pBBA is mainly composed of SiO₂, CaO,
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27156 K₂O and Al₂O₃.
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30157 **2.2.1 Powdered, Heated and Washed Biomass Bottom Ash (phwBBA)**

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34158 The high content of alkaline salts such as K₂O and MgO that pBBA might contain directly affects
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36159 the durability of cement or concrete made from these wastes [39]. For this reason, the washing and
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38160 calcination process was implemented to obtain better results. To quantify the K₂O and MgO
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40161 removed during washing, the pre-wash and post-wash waters were chemically analysed. The
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42162 content of alkaline salts such as K₂O and MgO influences the hydration processes of mortars. The
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44163 hydration process is directly related to setting time, rheology and mechanical strength. Therefore,
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46164 an increase in these elements causes the setting time to increase, in addition to an instability
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48165 dimensional changes due to a lack of hydration of the cement phases. In addition, the hydration of
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51166 alkalis such as potassium phases causes the reaction products resulting from hydration to modify
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53167 the internal structure of the mortar [40].
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55168 There are few previous studies that have applied washing as a treatment. James et al. [41] based
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57169 their study on the fact that ash washing could reduce the content of some metals and Cl, leading to
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170 an improvement in the final properties of the BBA. Regarding the composition, high values of SiO₂
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2 171 and CaO were observed, which makes us think that this material would be a cementitious material.
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4 172 In previous studies, such as B. Carrasco [42], it was found that the amount of SiO₂ was 27.87%
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7 173 and CaO was 29.96%. In this study the amount of Al₂O₃ was also analysed, which was 4.34%. The
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9 174 phwBBA showed higher values than previous studies [42] and, compared with pBBA, we can
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12 175 observe that the quantity of these components decreased.
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15 176 Another good factor found in the washing, heating and grinding process is the amount of chlorides
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17 177 and organic matter. We can see how these values were considerably reduced; the amount of organic
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20 178 matter by 83% and the amount of chlorides by 77%.

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23 179 Table 3. Chemical analysis of prewashing and postwashing water used for washing olive BBA.

Element	Per kg of raw material (%)	Eliminated by washing per kg of material (%)
K	7.61	1.01
Si	9.95	0.04
S	0.07	0.03
Na	0.14	0.01
Cl	0.04	0.01
Al	2.25	0.00
Ca	22,65	0.00

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48 181 In order to determinate the quantity of Potassium that could have been eliminated by washing, the
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51 182 wash water was analysed before and after the process. We can observe that the amount of potassium
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53 183 precipitated in the wash water was of great magnitude. Washing the material led to a 1.01%
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56 184 reduction in K (Table 3).
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2. Advanced characterisation of the materials

2.2.1. X-ray diffraction

X-ray diffraction is based on the optical interference that occurs when monochromatic radiation passes through a slit of a thickness comparable to the wavelength of the radiation. X-rays have wavelengths of Angstroms, of the same order as the interatomic distances of the components of crystal lattices. When irradiated on the sample to be analysed, the X-rays diffract at angles that depend on the interatomic distances. The analytical method consists of irradiating a sample consisting of a multitude of crystals randomly placed in all possible directions with X-rays. For this, Bragg's Law is applicable: $n\lambda = 2d \cdot \sin\theta$, where "d" is the distance between the interatomic planes that produce the diffraction. The fundamental application of X-ray diffraction is the qualitative identification of the mineralogical composition of a sample.

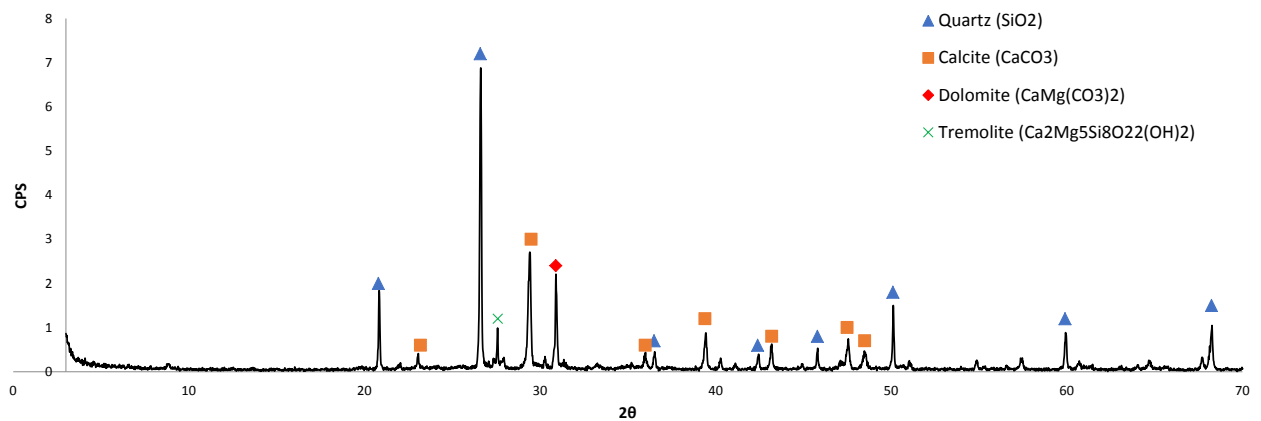
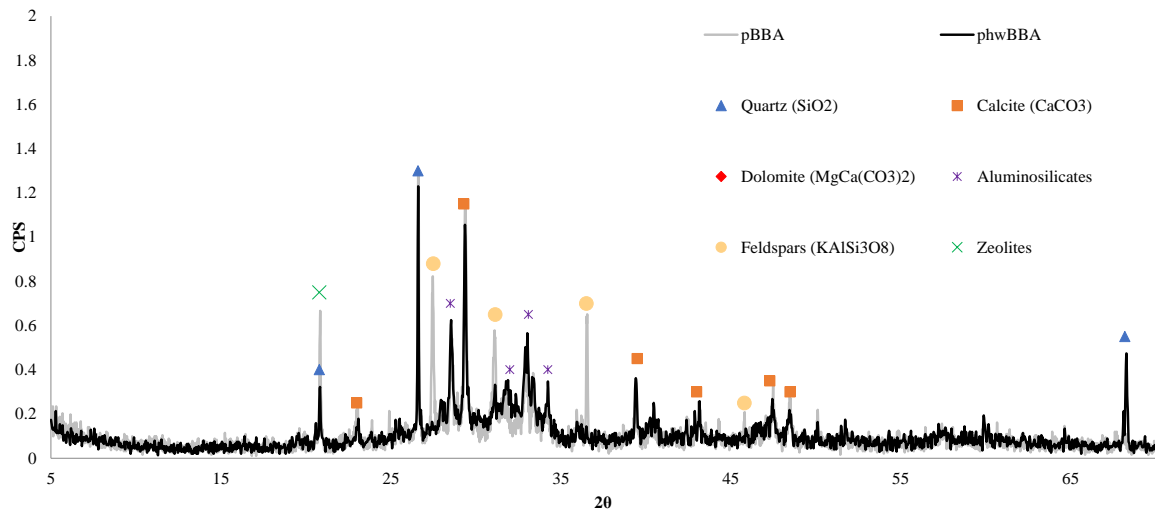


Figure 2. DRX of pMRA

The X-ray diffraction study of each of the waste showed that the diffractogram of pMRA (Figure 2) had a complete crystalline structure, while pBBA and phwBBA (Figure 3) resulted in a diffractogram with a slightly more amorphous structure. However, it is important to note

204 that comparing these mineralogical results with biomass fly ash, BBA showed a high
1 crystallinity, as its diffractogram did not show a significant amorphous halo as is generally
205 the case for fly ash [43-45].
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207 The mineralogy of the pMRA showed mainly calcite, quartz and dolomite. Analysis of MRA
8 from different origins showed similar mineralogy to that obtained in this study [46].
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210 Figure 3. DRX of pBBA and phwBBA
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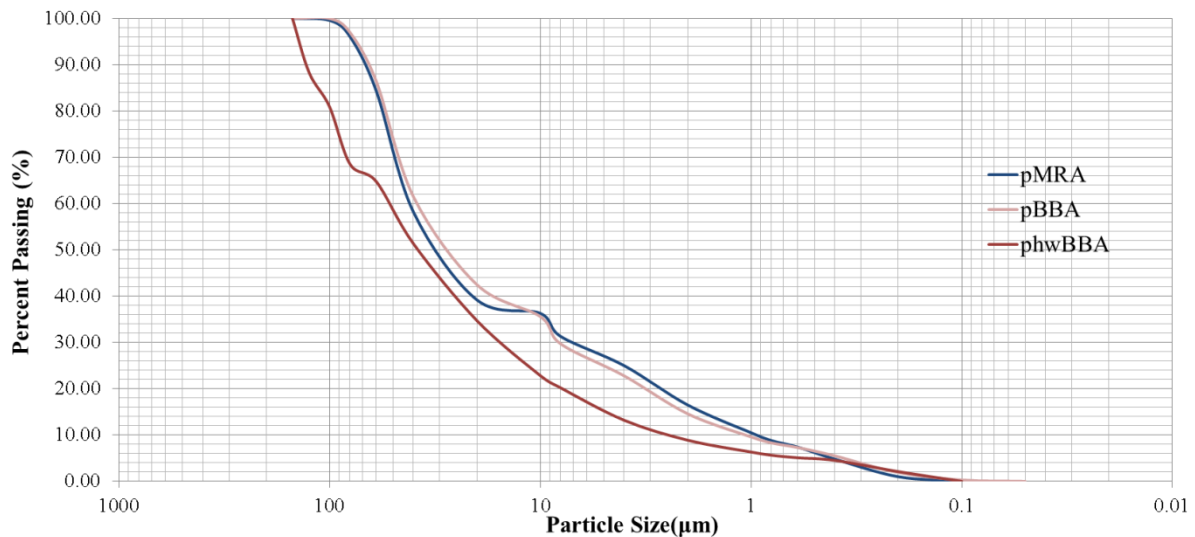
212 The composition of BBA does not change according to the treatment it has been subjected to;
213 it is mainly composed of calcite minerals, quartz and aluminosilicates. This composition was
214 previously shown by other authors who analysed olive BBA [47-51]. The high amount of
215 quartz and calcite indicates biomass burnt at high temperature [52]; the high content of
216 aluminosilicates in the ash favours the setting reaction of the cement, resulting in a particularly
217 strong mixture and demonstrates that the presence of this mineral leads to an improvement in
218 pozzolanic properties [53].
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220 However, as observed in Figure 3, the BBA subjected to washing and heating processes
221 (phwBBA) showed a different mineralogy than the unprocessed BBA (pBBA). In the latter
222 material, peaks of mainly potassium feldspars were observed, which were reduced by
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222 subjecting the material to washing and heating. This reduction of potassium feldspar
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223 contributes to an improvement in the durability properties of the manufactured cement or
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224 concrete [50].
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225 2.2.2. Particle size analysis using Laser particle size distribution 8 9

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11 226 Advanced characterisation of the physical properties of the materials was carried out by particle
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14 227 size distribution analysis of pMRA, pBBA and phwBBA; this property was determined by wet
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16 228 laser diffraction (Malvern Mastersizer). The particle size of the material is shown in Figure 4.
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230 Figure 4. Particle size distribution
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233 All materials showed a continuous particle size distribution. pMRA and pBBA showed a similar
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235 particle size distribution, which shows the effectiveness of the developed crushing and screening
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237 treatment, resulting in materials with similar particle size properties.
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240 The washing, heating and crushing process led to a decrease in particle size, as can be seen in
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242 Figure 4. The washing and heating of the material resulted in a decrease in organic matter (Table
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244 2); these elements are difficult to crush; therefore, their removal prior to crushing leads to a finer
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246 particle size of the resulting material.
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2.2.3. Thermogravimetric analysis (TGA)

This test determines the amount of mass that volatilises when the material is subjected to a temperature gradient. Thanks to this we were able to determine some of the elements that made up the tested material. In Figure 5, thermogravimetric analysis, we can observe the percentage of mass remaining in the sample as we increased the temperature.

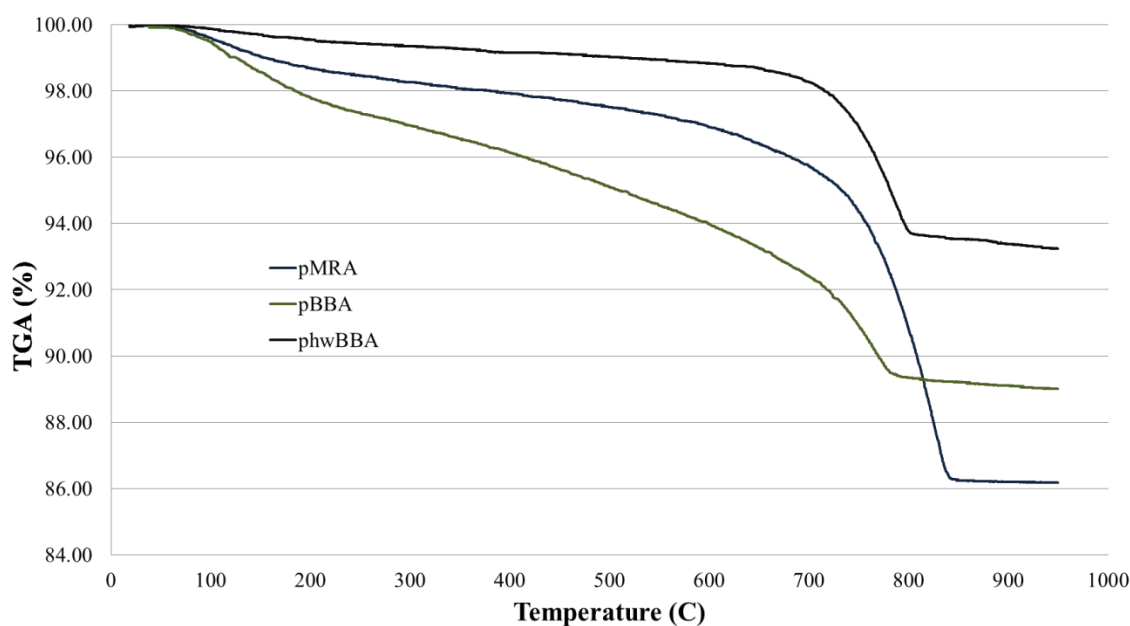


Figure 5. Thermogravimetric analysis

It can be seen that for pBBA, there is an accentuated loss between 170°C and 250°C, which may be due to the loss of organic matter it may contain. In contrast, for the same material but with previous treatment of washing and calcination (phwBBA), it is observed that this loss is less accentuated, even more so than the loss that occurs in pMRA.

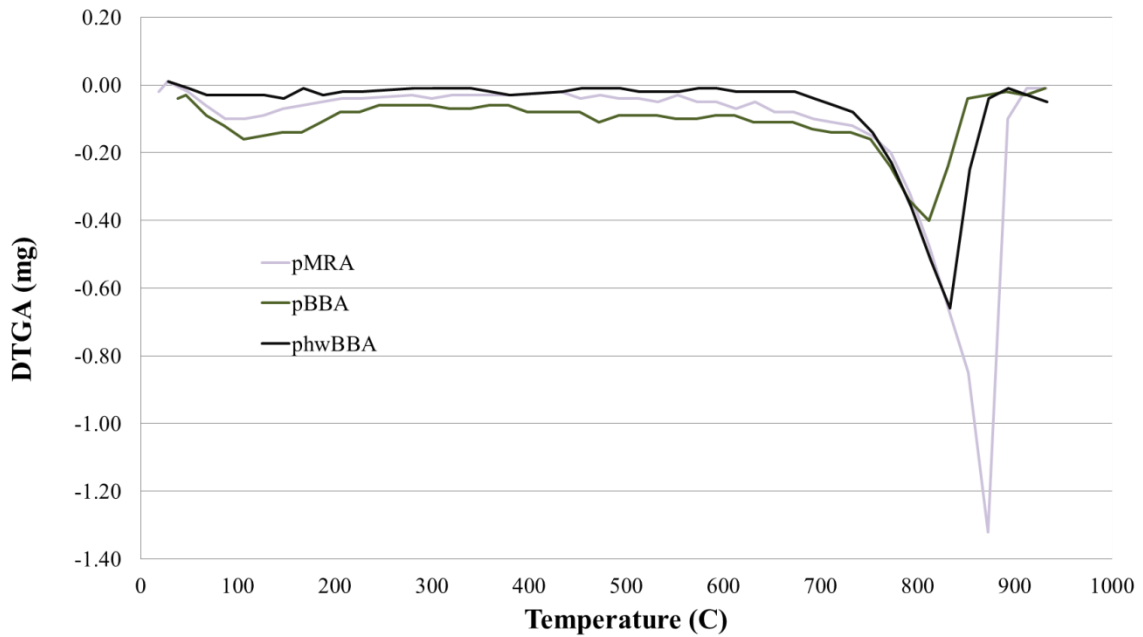


Figure 6. Derivative Thermogravimetry analysis

For phwBBA, the organic matter was removed through the washing and calcining treatment.

For the marked mass loss of the three materials between the temperatures of 770°C and 850°C, it was analysed in differential terms with respect to the previous hour. In Figure 6, Derivative Thermogravimetry analysis shows these results.

2.2.4. Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy shows the absorption of infrared rays of different wavelengths. Thanks to this analysis, we were able to corroborate the minerals that made up the analysed material. In Figure 7, FTIR spectra for pMRA, pBBA and phwBBA shows the results. After the analysis of the figure, we find important peaks that provide a comprehensive analysis of the results, whose main peaks are shown in Table 4. We can see that the peaks in the graph are very similar, with small differences between the pMRA and the powders from the BBA.

Table 4. Principal infrared absorption bands

	Wavenumbers cm^{-1}										
pMRA	1418	1004	847	795	778	728	712	694	643	519	445
pBBA	1413	962	873	711	686	641	440				
phwBBA	1409	930	872	710	691	442					

For pMRA, we found peaks at 1418, 847 and 712, which are representative of Calcite. The occurrence of a cluster of peaks between 800 and 700 indicates the presence of Kaolin minerals, coupled with hydroxyl OH groups [54]. In pBBA and pMRA, we found a small peak at the wavenumber of 3600, which is representative of aluminosilicate [55].

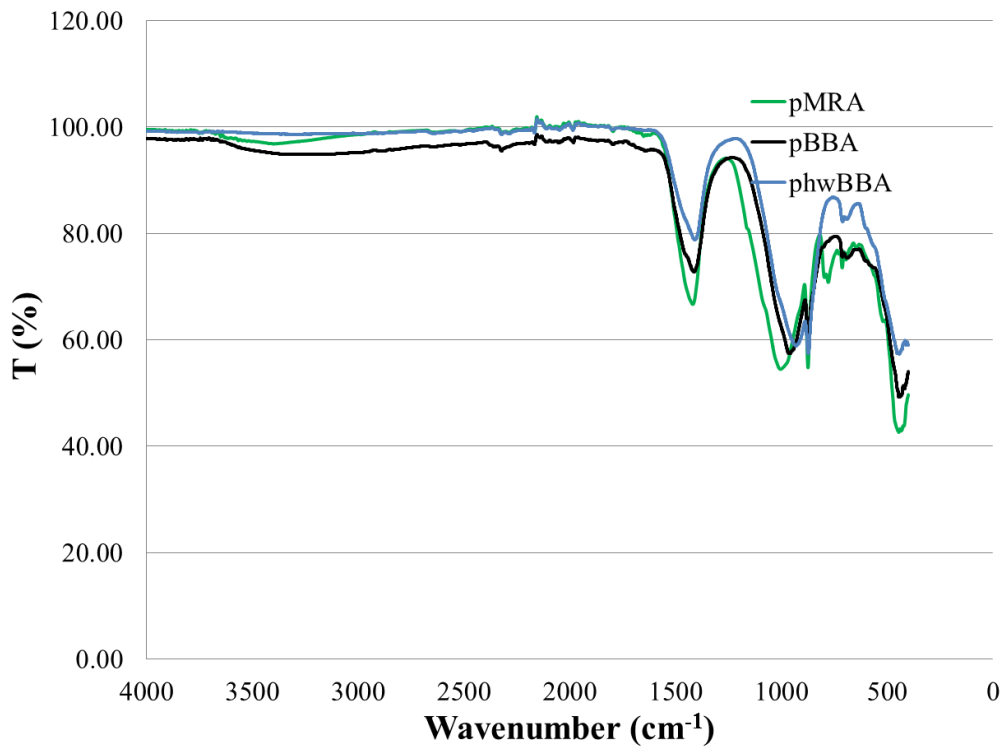


Figure 7. FTIR spectra for pMRA, pBBA and phwBBA

2.2.5. Pozzolanic activity: Saturated lime solution test

The evaluation of the pozzolanic activity in the material was carried out using an accelerated

276 method, in which the reaction of the material with a saturated lime solution was studied over time.
 1
 277 The calcium fixed by the sample, expressed as calcium oxide (mm/l), was obtained by the
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 278 difference between the concentration of the initial saturated lime solution (17.68 mm/l) and the
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 279 CaO present in the solution in contact with the sample, at the end of each present period (3,7,28
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 8
 280 and 90 days). Table 5 shows the results obtained.
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 10
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 12

13
 14 Table 5. Concentration of calcium oxide fixed
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Material	Calcium oxide fixed (%)			
	Age (days)			
	3	7	28	90
pMRA	27.7	37.9	50.6	61.0
pBBA	49.5	56.6	67.8	86.3
phwBBA	39.2	46.8	56.4	70.2

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282 After 90 days, pMRA set a lime rate of 60%. However, this lime rate was higher for pBBA which
 283 reached 86% and these values are similar to a standardised pozzolan such as silica fume (-90%)
 284 [56].

285
 286 As shown in previous studies [57], pBBA fixed lime at rates comparable to non-standardised
 287 materials that have been studied for use as a supplementary cementitious material, such as sanitary
 288 waste [58] or tile waste [59]. It should be noted that the pMRA analysed in this study does not show
 289 the usual lime fixation in wastes from ceramic materials (85%).

290 The pozzolanic activity of the washed and heated BBA was similar at 90 days to that of the BBA
 291 not subjected to washing and heating processes (Table 5). This is related to the results shown
 292 previously in the mineralogy study (Figure 3 and Figure 4) where it can be observed that the
 293 crystalline phases of both wastes were similar and no significant differences were shown in their
 294 mineralogy. The non-influence of calcination procedures on the pozzolanic activation of the
 295 biomass has already been studied by other authors [57]. A high temperature heat treatment would

296 have been reflected in the mineralogical composition leading to devitrification and crystallisation
1
297 of the material, which would have an adverse effect on the pozzolanicity of the material [60]. Thus,
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4
298 it is observed that heating to 600°C does not produce any adverse effect on the pozzolanicity of the
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299 material.

2.2.6. Scanning Electron Microscopy (SEM)

300
301 Using the scanning electron microscope, a magnified image of the surface of the sample to be
302 analysed was obtained, allowing the morphology of the sample to be studied. The operation was
303 based on scanning the sample with a beam of highly concentrated electrons, which can be scattered
304 from the sample or cause the appearance of secondary electrons. These electrons were collected
305 and connected by means of an electronic device, so that the more electrons collected, the brighter
306 the image of the sample. As the electron beam swept the entire sample, the complete image of the
307 sample was represented, allowing the observation and surface characterisation of the sample,
308 providing information on morphological aspects of microscopic areas. The equipment used was a
309 Hitachi S-4800 (Scanning electron microscope (SEM)) equipped with Bruker EDX (Energy
310 dispersive X-ray analyser).

311 An analysis of the internal structure of the processed samples was carried out after they were
312 subjected to the saturated lime solution test. The powder resulting from the test, once dried, was
313 analysed by SEM. The results at different ages are presented below (Figure 8 and Figure 9) and the
314 resulting pozzolanic activity products are shown in the images.

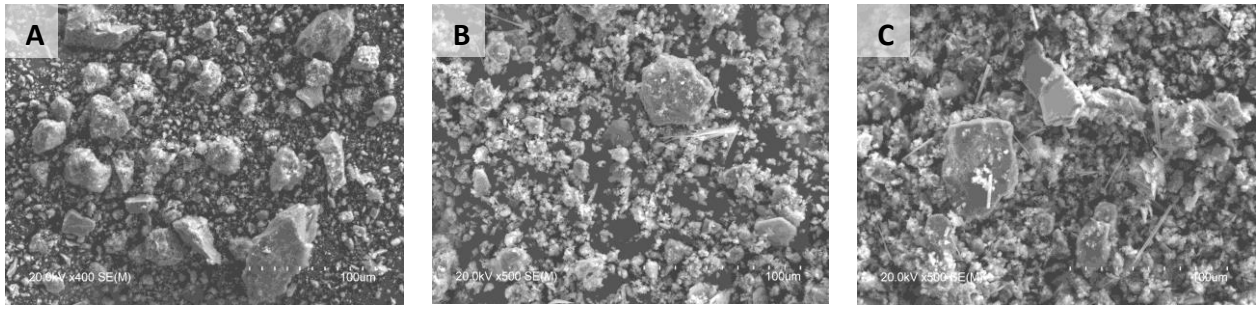


Figure 8. SEM image pMRA. A) Non hydrated pMRA; B) pMRA hydrated with saturated lime solution at 3 days; C) pMRA hydrated with saturated lime solution at 28 days.

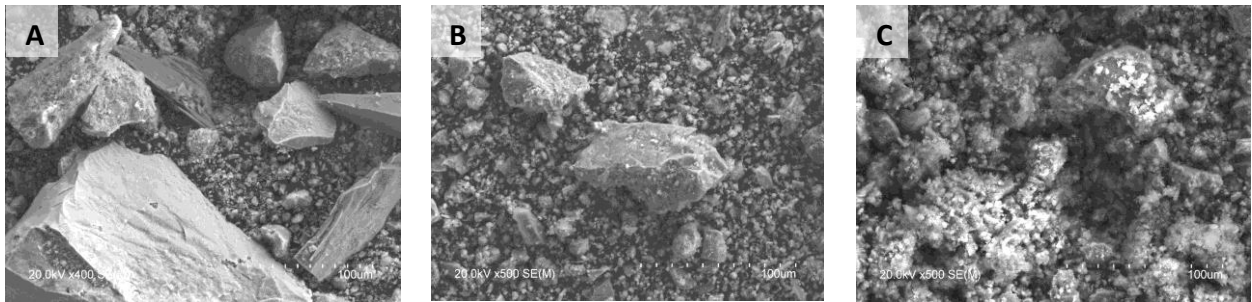


Figure 9. SEM image pBBA. A) Non hydrated pBBA; B) pBBA hydrated with saturated lime solution at 3 days; C) pBBA hydrated with saturated lime solution at 28 days.

SEM study of pMRA showed the appearance of hexagonal stone-shaped C_4AH_13 28 days after lime hydration of the material, as shown in Figure 8C. This phase is related to the presence of calcium aluminate [61].

Additionally, the formation of amorphous C-S-H phases was observed in both residues, this formation being more predominant in pBBA, as shown in Figure 9C. The formation of the C-S-H gel in the form of small equal grains in BBA after pozzolanic reaction with $Ca(OH)_2$ forms on the surface of the residue as demonstrated by previous studies [57, 62]. This type of gel is classified as type III gels, according to the classification proposed by Diamond et al [63]. The formation of it is due to the reaction between Si-O and Al-O bonds that break upon attack by hydroxy ions (OH^-) and as a result of the reaction between silicon and aluminium anions and Ca^{2+} cations [60].

3. Methods and Results

The different mixes manufactured in Series 1 were subjected to 4 blocks of analysis.

Firstly, the eco-hybrid cement powder produced was analysed by advanced characterisation.

Subsequently, the manufactured mortar pastes were analysed by means of workability, hydration

and mechanical tests; a study of the micro properties of the manufactured mortars was carried out

and the environmental impact of leaching was analysed. In addition, the mechanical properties of

the mortars manufactured in Series 2 were also analysed. A detailed experimental scheme of the

study carried out in this work is shown in figure 10.

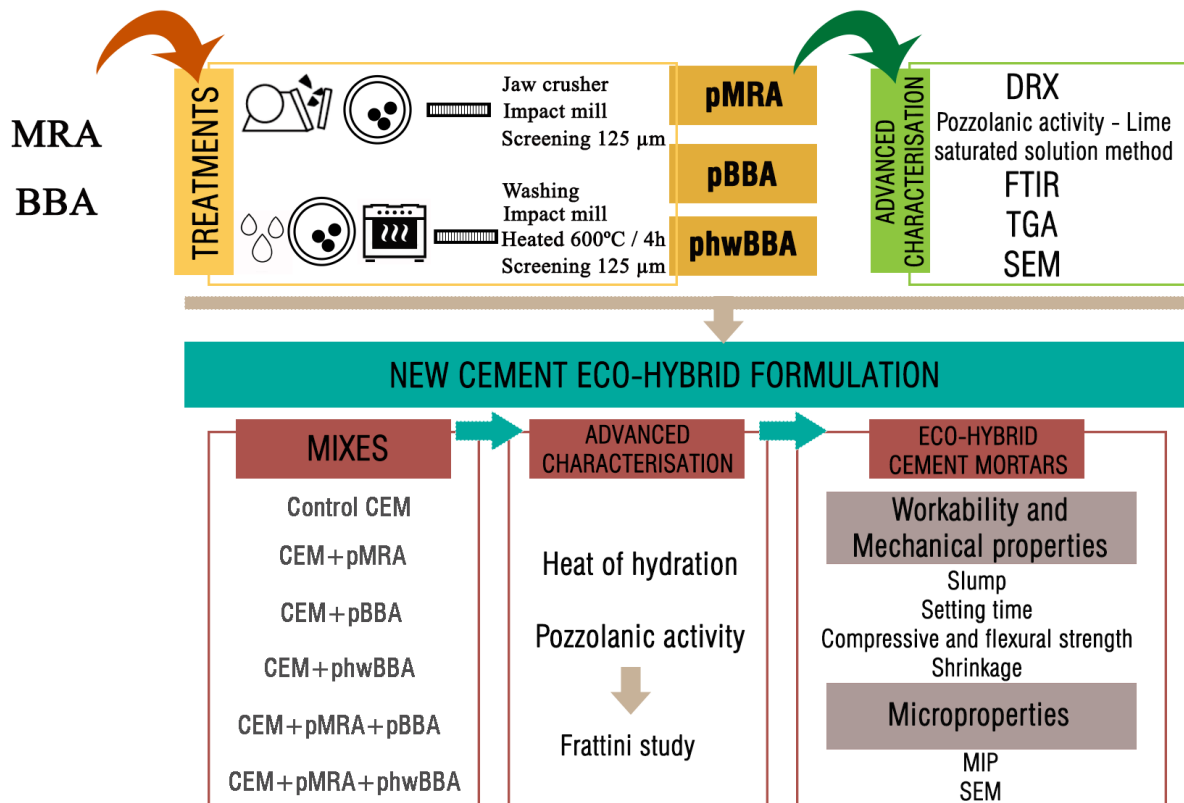


Figure 10. Experimental programme

3.1. Mixture proportions

Two series of cement mortar production were carried out and one series of Control. In Series 1 cement was partially replaced by pMRA, pBBA and phwBBA with different combinations and substitution ratios. These substitution ratios have been made on a volume basis. The new eco-hybrid cement was evaluated by means of advanced characterisation, workability, hydration and mechanical tests and by means of tests that analyse the micro-properties of the new eco-hybrid cement.

Table 6 presents the reference dosages for Control Serie. Table 7 presents dosages for mortar with cements containing substitution products.

Table 6. Control Serie dosages

		DOSAGE –Control Serie (g)							
NAME	DESCRIPTION	SNS	pBBA	phwBBA	pMRA	Cement	Water	Water Absortion	Additive
REF1	Control 1 – CEM I	1350	-	-	-	450	225	-	0
REF2	Control 2 - CEM II A/L	1350	-	-	-	450	225	-	0

Table 7. Mortar mix proportions Series 1 (cement replacement)

		DOSAGE –Serie I (g)							
NAME	DESCRIPTION	SNS	pBBA	phwBBA	pMRA	Cement	Water	Water Absortion	Additive
30M	30% pMRA	1350	-	-	127	315	225	5	1
20M	20% pMRA	1350	-	-	85	360	225	3	0.5
30B	30% pBBA	1350	124	-	-	315	225	7	1
10B	10% pBBA	1350	41	-	-	405	225	4	0.5

1	10phwB	10% phwBBA	1350	-	41	-	405	225	1	0.3
2										
3	10B/20M	10% pBBA & 20% pMRA	1350	41	-	85	315	225	5	1
4										
5										
6	8B/17M	8% pBBA & 17%pMRA	1350	33	-	72	337	225	3	0.3
7										
8										
9	8B/22M	8% pBBA & 22% pMRA	1350	33	-	93	315	225	2	0.4
10										
11										
12	8phwB/22M	8%phwBBA & 22%pMRA	1350	-	33	93	315	225	2	0.3
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17 354 **3.2 Workability and setting time**

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21 355 **3.2.1 Slump (EN 1015-3:2000)**

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25 356 This consists of determining the consistency or fluidity of the fresh mortar using a shaking table.

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28 357 The consistency is determined by measuring the flow rate (mean value of the diameter) of a sample

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32 358 of the fresh mortar being tested. For this purpose, the truncated cone-shaped mould which is placed

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35 359 on a circular shaking table is filled and, once the mould is removed from the table, the fresh mortar

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38 360 is subjected to a certain number of vertical shakes (it is first raised to a certain height and then

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41 361 allowed to fall freely), and the average diameter of the fresh mortar is measured.

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45 362 **3.2.2 Setting time (EN 196-3:2005)**

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49 363 This parameter is determined by means of a test that measures how the consistency of a paste

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52 364 (cement + water) evolves over time, but the EN 196-3:2005 standard sets the environmental

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55 365 conditions (Temperature and relative humidity), and defines what the water/cement ratio

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366 (consistency) should be, so that the setting times depend only on the desired factors, i.e., the type
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 367 and composition of the cement. In this way the results obtained with different types of cement can
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 368 be compared.

369 Table 8. Workability and setting time of new cement eco-hybrid mixes

		<i>Slump (mm)</i> <i>EN 1015-3</i>	<i>Setting time (minutes)</i> <i>EN 196-3</i>	
			<i>Initial</i>	<i>Final</i>
Control	REF1	19.5	90	165
	REF2	18.8	105	165
Series 1 (cement replacement)	30M	19.5	110	150
	20M	18.9	105	160
	30B	19.3	135	225
	10B	19.2	125	200
	10phwB	19.8	100	170
	10B/20M	18.8	135	215
	8B/17M	18.8	130	200
	8B/22M	19.1	135	225
	8phwB/22M	19	115	190

370 Table 8 shows the workability and setting time of the mixes analysed. No significant differences
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 371 were observed in the slump of each of the mixes, because additive was used to obtain workability
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 372 similar to the control, as shown in Table 6 and Table 7.

373 Regarding setting time, it was observed that the addition of BBA and MRA in the cement mixtures
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 374 resulted in an increase in the initial and final setting time, as occurred in previous works [64-66].

375 A higher replacement rate resulted in a longer delay in setting time. The delay in setting time
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 476 relative to the OPC reference cement may be due to several factors. Previous studies showed that
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 777 the substitution of BBA for cement reduced the C3A content, which is an essential compound in
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 1078 the first hours of cement hydration [67, 68].
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 1479 As is showed in Table 2, pBBA had more organic content than phwBBA. Other studies showed
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 17380 that organic content of BBA was directly correlated with water absorption [69]. The water
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 20381 absorption of BBA and MRA; produced a reduction in the portion of water available for cement
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 2482 hydration and therefore, the setting time was delayed.
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3.3 Mechanical properties - Compressive and flexural strength

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 3284 The method for determining the compressive and flexural strength of mortars is defined in the EN
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 3585 1015-11:2007 standard. For testing, they are used six prismatic specimens of 40x40x160 mm per
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 3886 flexural strength result and six prismatic specimens of 40x40x80 mm per compressive strength
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 41387 result. After 1 day, the specimens were removed from their moulds and stored in damp rooms until
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 4588 the time of testing. Compressive strength tests were carried out at different ages of 7, 28 and 90
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 4889 days. Table 9 shows the results obtained for flexural and compressive strength.
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5190 Table 9. Flexural and Compressive Strength of hardened mortars

	Flexural strength (MPa)								Compressive strength (MPa)							
	7D		28D		90D		% 90D – 28D	7D		28D		90D		% 90D – 28D		
	Res	Dev	Res	Dev	Res	Dev		Res	Dev	Res	Dev	Res	Dev			
REF1	7.52	0.28	9.34	0.18	10.21	0.57	9.31%	51.8	3.69	61.4	2.52	65.1	4.86	6.03%		

REF2	7.18	0.44	8.72	0.69	9.44	0.41	8.26%	47.2	1.19	51.6	2.05	56.4	3.71	9.30%
30M	6.12	0.36	7.64	0.32	8.12	0.29	6.28%	42.1	2.78	49.8	4.67	53.6	4.73	7.63%
20M	7.29	0.40	8.55	0.71	8.97	0.66	4.91%	49.8	3.68	54.7	3.05	58.7	3.12	7.31%
30B	4.73	0.46	5.32	0.33	6.43	0.39	20.86%	32.0	2.71	34.8	4.81	41.1	3.41	18.10%
10B	5.91	0.19	6.19	0.37	7.22	0.45	16.64%	37.9	2.08	40.7	3.46	47.1	2.39	15.72%
10phwB	7.46	0.29	8.94	0.15	9.86	0.90	10.29%	50.1	4.64	57.8	2.95	62.8	4.51	8.65%
10B/20M	5.73	0.53	6.86	0.19	7.94	0.54	15.74%	38.7	2.55	45.0	4.62	49.9	3.39	10.89%
8B/17M	5.94	0.45	6.48	0.17	7.29	0.65	12.50%	40.4	3.07	45.7	3.58	49.8	3.16	8.97%
8B/22M	5.28	0.42	7.24	0.29	8.03	0.33	10.91%	39.1	4.34	45.1	4.42	49.7	2.56	10.20%
8phwB/22M	6.49	0.61	7.7	0.49	8.41	0.61	9.22%	42.3	3.61	47.9	3.93	52.1	3.49	8.77%

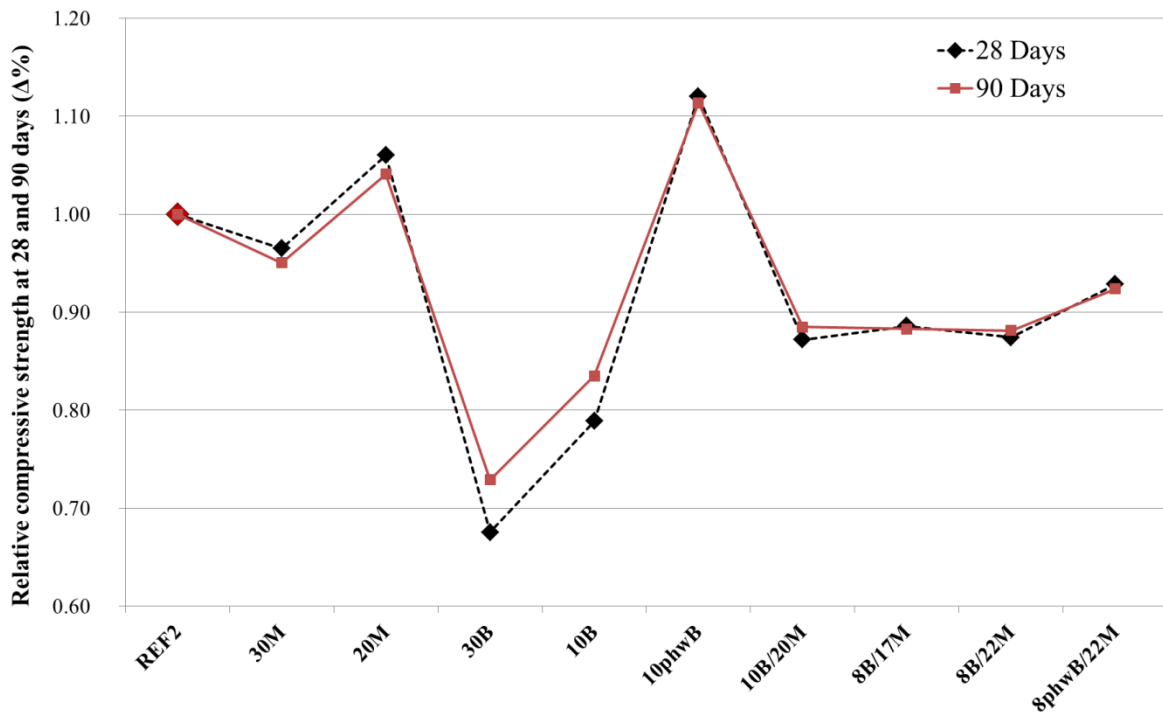
According to the results shown in table 9, the compressive strength for the mortars studied exhibited 28-day strength > 42.5 MPa, regardless of the percentage of addition, except for the 30B and 10B series.

This behaviour may be due to two main factors: the pozzolanicity of the new additions, which do not compensate for the decrease of clinker in the manufactured mortars [57], and the higher porosity [70]. Rosales et al., [32] obtained similar results when the substitution was 20% of processed and washed BBA. They reported that the strength decreased if the light material of the BBA was not crushed or removed.

Although the flexural strength also decreased, the loss was less intense than that observed for the compressive strength. The explanation for these observations lies in the more rapid increase, in the pozzolan-containing materials (pBBA and pMRA in this case), of the flexural strength than the compressive strength, producing more elastic cement-based materials [71, 72].

403 The increase in long-term compressive strength of biomass-based mortars is noteworthy. For the
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 404 mixture with maximum substitution of pBBA (30B), an increase in strength from 28 to 90 days of
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 705 approximately 19% was obtained, compared to the 6-9% increase in strength of the reference
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 406 mortars.

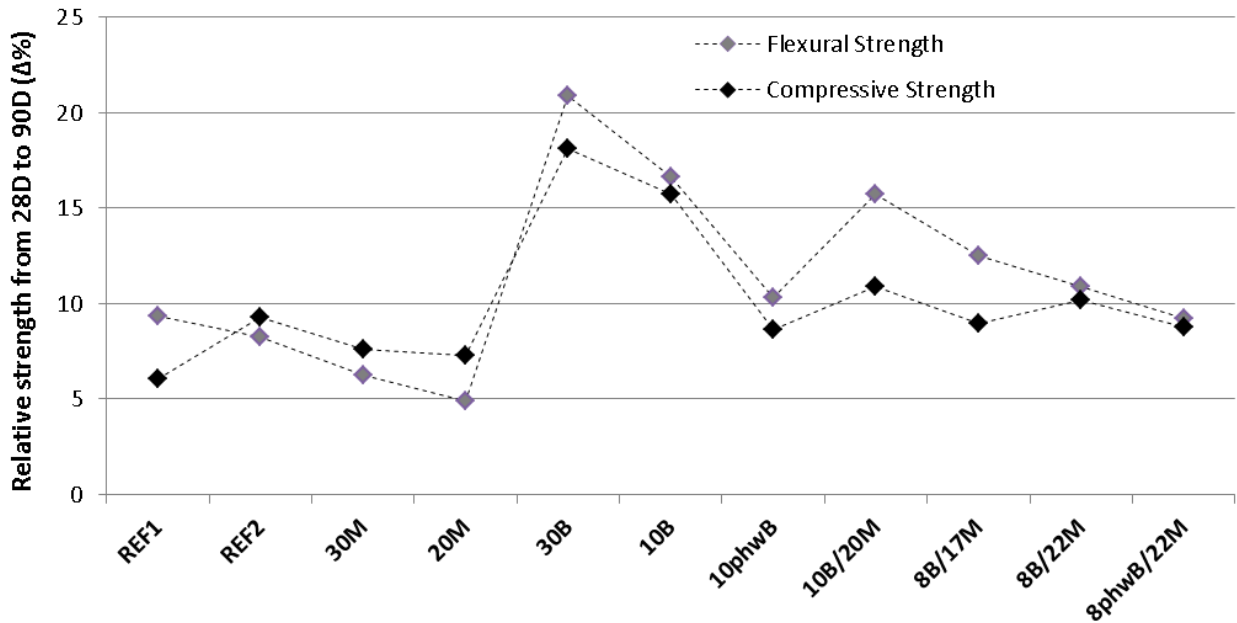
14
 15
 407 Figure 11 shows the relative compressive strength in percent per 1 at 28 days of each of the mortars
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 17
 408 manufactured in series 1 compared to a Reference mortar manufactured with CEM II (Ref 2).



409
 410 Figure 11. Relative compressive strength of cement mortars at 28 days versus control

411 It was observed that 20M and 10phwB mortars made with 20% pMRA and 10% pBBA respectively
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 412 resulted in higher 28-day compressive strengths than the reference mortar. This strength increased

413 more at 90 days, as shown in Figure 12. Mortars made with BBA increased the relative compressive
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 414 strength in the long term (90 days) more than in the medium term (28 days).
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 Figure 12. Relative strength from 28 days to 90 days

3.4. Heat of hydration (EN 196-9/2011)

418 This test was carried out in accordance with the EN 196-9/2011 standard and consists of measuring
 419 the heating of a mass of mortar in comparison with a reference, i.e., once the mortar has been
 420 kneaded, 1575 ± 1 g are introduced into a jar, which is then covered and hermetically sealed with
 421 the help of a small hammer. The rod that is inserted into the mortar is filled with approximately 2.5
 422 cm³ of oil, in order to improve the contact and the MRA transmission between the mortar to be
 423 tested and the probe in charge of recording the temperature during the hydration of the mortar.

424 Once the can is hermetically sealed, it is placed in the calorimeter (isotherMAL-Dewar container),

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425 covered, and the probe in charge of recording the temperature variations is inserted.

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426 The temperature variations are collected and compared at all times with the temperature of the

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427 reference (inert aluminium cylinder, which does not show temperature variations and which is

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428 inside another contrast calorimeter). At this point, and with the help of the specific software,

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429 WinLect32), data collection begins. At the end of the test, the data corresponding to the heating of

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430 the mortar mass during the period of 41 hours as indicated in the standard is obtained.

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431 The heat of hydration ($J.g^{-1}$) is obtained from the following mathematical expression:

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$$Q = \frac{c}{m_c} \theta_i + \frac{1}{m_c} \int_0^t \alpha \cdot \theta_t \cdot dt$$

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29

433 Where:

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434 t: hydration time (h)

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435 c: total heat capacity of the calorimeter ($J.K^{-1}$)

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436 m_c : mass of cement contained in the test specimen (g)

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437 α : heat loss coefficient of the calorimeter ($J.h^{-1}.K^{-1}$)

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438 θ_t : increase in temperature of the mass of mortar at time t (K)

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439 The results obtained from the heat of hydration test are shown below (Figure 13), followed by three

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440 graphs for the different stages of hydration of the mortar.

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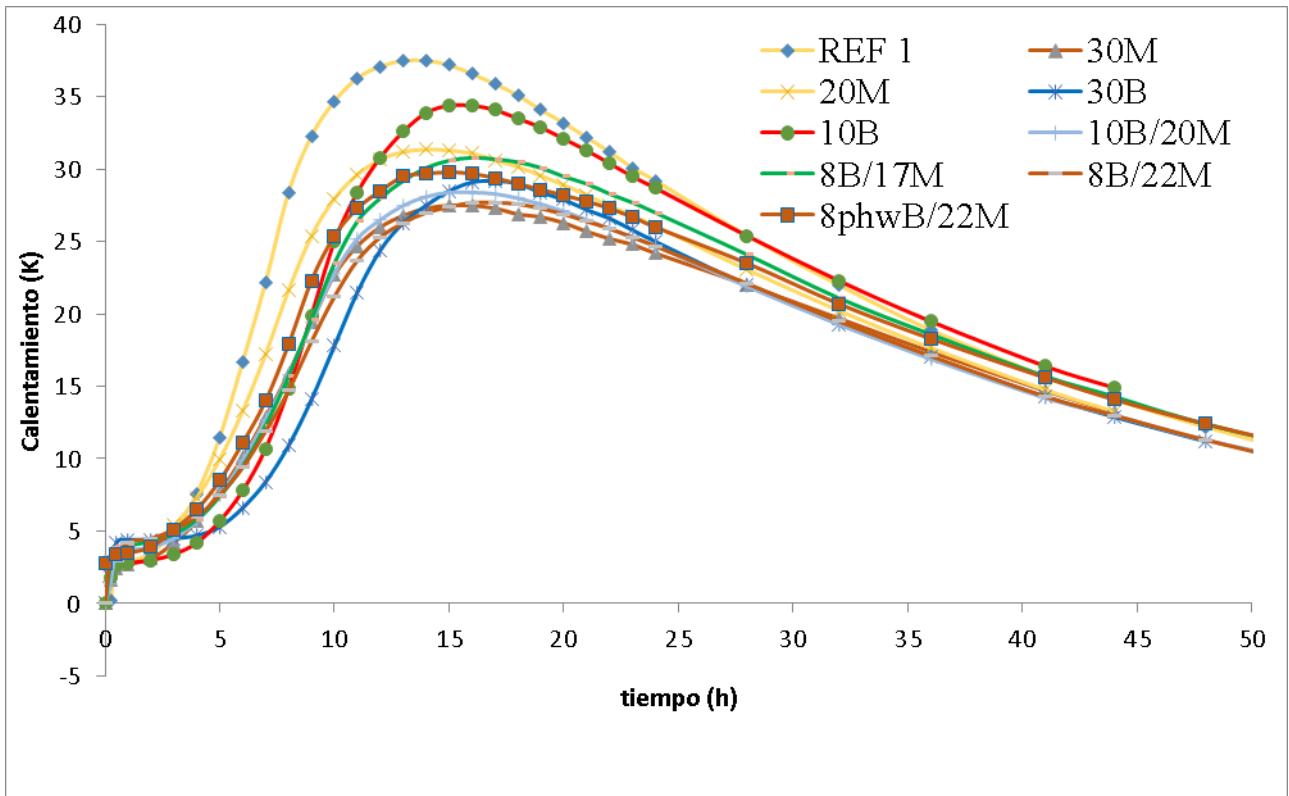


Figure 13. Heating (K) in mortars

In this study, the amount of heat dissipated during the setting of the mortar was determined. It was observed that the mixtures with by-products as cement substitute heated up less than the reference mortar with CEM I. It was observed that the mixture with the lowest substitution (10B 10%pBBA substituting cement) was the one that acquired the highest temperature of all the new cements studied. It should be noted that, comparing 30M with 30B in which they had the same percentage of substitution, although the former with pMRA and the latter with pBBA, we found differences both in the maximum setting temperature and in the time elapsed to reach that peak. We observed that the 30B mix reached higher maximum temperatures while this peak was delayed with respect to mix 30.

452 Furthermore, in the comparisons between the same substitute materials but in different percentages,
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 453 we observed that among the mixes with pMRA, 20M had a peak temperature of 27K, higher than
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 754 30M 32K, being 30M a 30% substitution and 20M 20%. For the mixes with pBBA cement
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 10455 substitutes, we found that 30% substitution placed the maximum temperature at 29K, while at 10%
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 13456 substitution we found the peak temperature at 34K. The same trend was observed in the work of
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 16457 Asensio et al. [73] in which cement was replaced by different percentages of pre-treated C&DW.
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 20458 In this test, we found results in which the heat of hydration decreased as the percentage of
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 23459 substitution increased from 10% to 70%.

27460 Table 10. Energy dissipated by Hydration Heat.

Energy dissipated by hydration heat (J/g)								
REF1	30M	20M	30B	10B	10B/20M	8B/17M	8B/22M	8phwB/22M
320.88	268.93	290.3	259.47	300.56	259.47	282.19	264.38	282.12

36461 These mixtures are classified by European standards as low heat of hydration or very low heat of
 37
 38
 39
 40462 hydration cements. To be classified as such, the heat of hydration must be less than 270 J/g. Table
 41
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 43463 9. Energy dissipated by Hydration Heat shows that 30M, 30B, 10B/20M, 8B/22M can be classified
 44
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 46464 as low heat of hydration [74].

50465 Analysing this test in the first three hours, we found that cements with additions had a higher heat
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 53466 of hydration. This fact is related to the study by Sanchez de Rojas et al. [75] in which different
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 56467 additions were made to the cement to test its heat of hydration. This study provides information in
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468 the three first hours of hydration that that is very similar to the results obtained. The cements with
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 469 additions show a strong increase in temperature compared to the 100% OPC mix. This may be due
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 470 to the fact that the substituents are nucleation sites where the formation of post-hydration products
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 471 is favoured and, given the exothermic nature of the reaction, the temperature increases more than
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 472 in the mixes made with 100% OPC as 30M.

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 473 From 15h to 65h, we can observe how the mixtures with substituents, after the temperature peak,
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 474 started to outperform the OPC. This may be due to the reactions that occurred between pMRA,
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 475 pBBA and porlandite during the exothermic reaction of the OPC [76]. Regarding a comparison
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 476 between the same amount of cement substitution but different recycled by-product (pBBA,
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 477 pMRA), we can observe that the heats of hydration of mix 30M (30% pMRA) was lower than mix
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 478 30B (30% pBBA). This was directly related to the pozzolanic activity of these materials. The pBBA
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 479 had higher pozzolanicity, as the hydration heat of mixtures that this material contained was higher.

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3.4.1. Analysis of high increase of heating stage - Heat of hydration

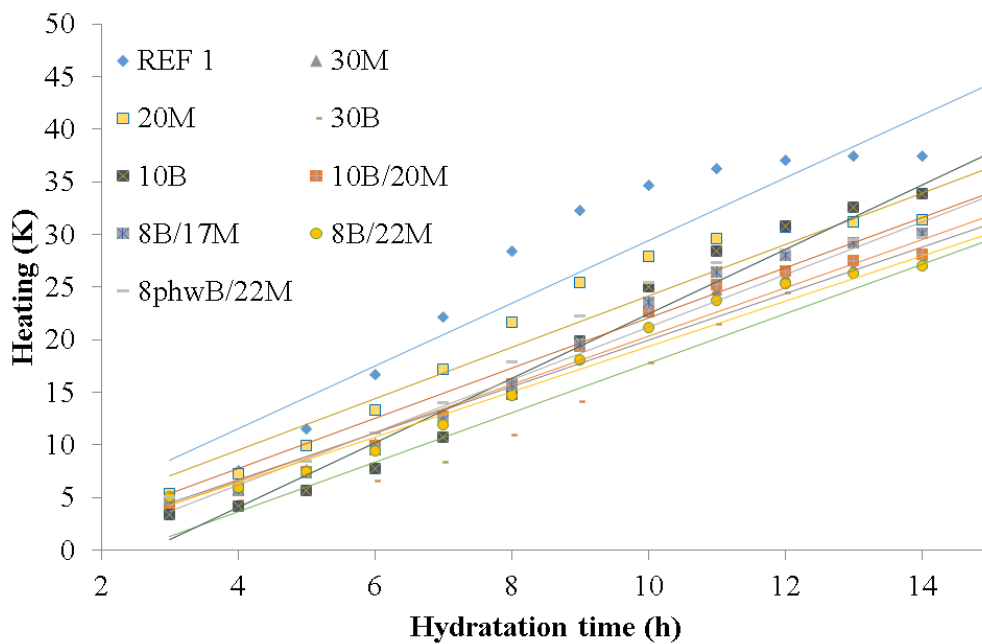


Figure 14. Heating during the high increase of heating stage (3–15 h)

Table 11: Linear regression ($y = m \cdot x + n$) values for mortar heating during the high increase of heating stage

Linear regression functions			
Cement	m [K·h ⁻¹]	N [K]	R ²
REF1	2.9802	-0.3604	0.8841
30M	2.2104	-2.1324	0.9593
20M	2.439	-0.2306	0.9227
30B	2.3544	-5.665	0.9659
10B	3.0588	-8.1753	0.9685
10B/20M	2.2923	-2.6308	0.9642
8B/17M	2.5	-3.8154	0.9694
8B/22M	2.1527	-2.1747	0.971
8phwB/22M	2.3874	-1.8247	0.9473

We can observe from table 10: Linear regression ($y = m \cdot x + n$) values for mortar heating during this stage, that the heating rate (m, slope of the regression line) of the mixtures with substitutes was lower than that of the OPC. Furthermore, it was observed that the heating rate increased as the amount of substituted cement decreased. We found that for 30M and 20M mixes the heating rate was 2.2104 K·h⁻¹ and 2.439 K·h⁻¹ respectively, which were 30% and 20% OPC substitutions for pMRA respectively. The same was true for the substitutions of cement by pBBA. We found that the heating rate for a 30% replacement was 2.3544 K·h⁻¹ and for the 10% pBBA cement replacement mix it was 3.0588 K·h⁻¹.

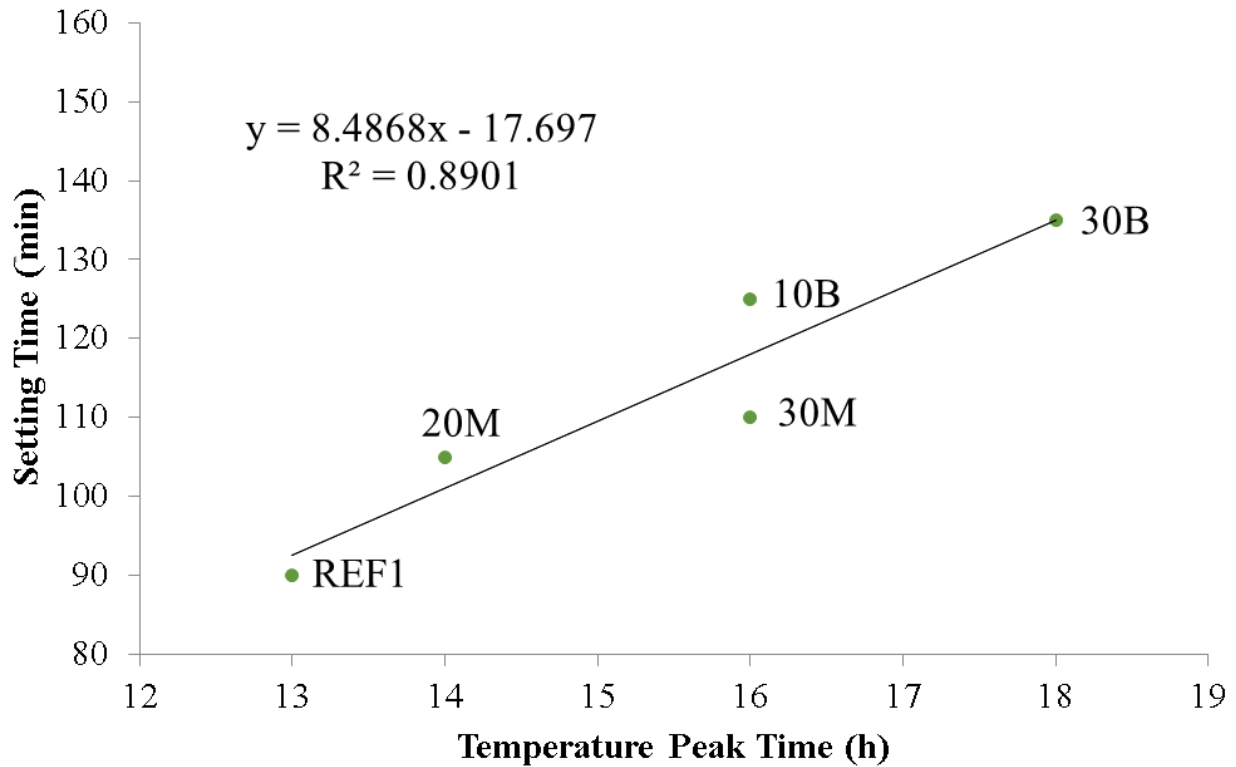


Figure 15. Correlation between setting time and heat of hydration of mortar manufactured with pMRA and pBBA

A correlation between the heat of hydration and the setting time showed that the temperature peaks of the mixtures with substituents were delayed with respect to the OPC. In addition, the temperature peaks of mixtures containing pBBA were later than those of mixtures containing pMRA.

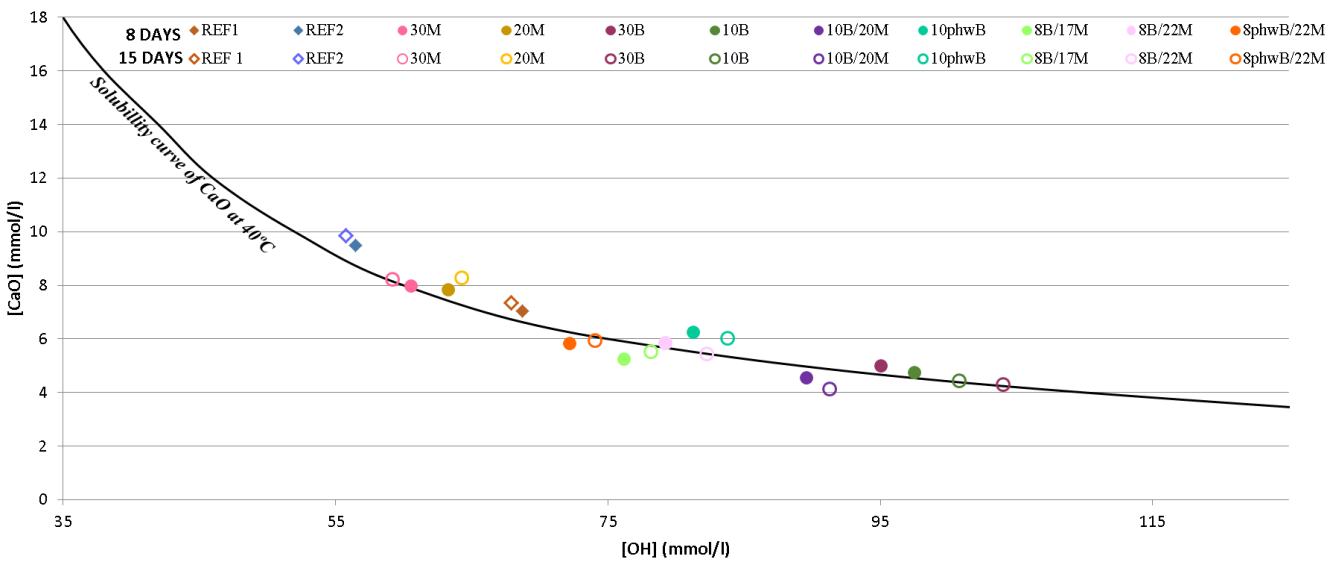
3.5. Pozzolanic activity (Frattini study). EN 196-5:2011

The pozzolanicity test according to Frattini was carried out in accordance with EN 196-5:2011. Pozzolanicity is determined by comparing the concentration of calcium ion, expressed as calcium hydroxide, in the aqueous solution in contact with the hydrated cement, after a fixed period of time,

504 with the amount of calcium ion capable of saturating a solution of the same alkalinity. The cement
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 505 is considered to comply with the test, i.e., to give a positive result, if the concentration of calcium
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 506 ion in the solution is less than the saturation concentration.

507 Figure 16 shows the results obtained for the [CaO] and [OH-] concentrations of each of the mixtures
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 508 analysed after 8 and 15 days according to the standardised test. The results were compared with the
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 509 portlandite solubility curve.

510 The cement or material tested is considered to comply with the test, i.e., to be pozzolanic, when the
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 511 concentration of calcium ions is lower than the saturation concentration indicated by the reference
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 512 curve.



513
 514 Figure 16. Result of Frattini test at 8 and 15 of different mixes

515 In Figure 16 it was observed that the reference cements (CEM I 42.5 and CEM II 42.5 A/L), not
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416 being pozzolanic cements, were above the reference line, indicating non-pozzolanicity. The
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717 incorporation of waste in the manufacture of the new eco-hybrid cements resulted in mixtures
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1018 manufactured with BBA being below or very close to the solubility curve. 10phwB, 8B/17M,
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1319 8phwB/22M are classified as pozzolanic cements. These results are related to the high pozzolanic
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1620 activity shown by pBBA and phwBBA (Table 8). Previous studies showed similar results, where
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1921 the incorporation of 20% bio-ash was sufficient to develop pozzolanic cements, this factor being
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2322 directly related to the pozzolanicity of the material obtained by the saturated lime solution test [61].
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2723 The pozzolanic activity of BBA ash is slow, compared to the more reactive coal fly ash. All 3
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3024 residues processed contained fairly high amounts of CaO, as shown in Tab. 5-Tab. 7. However, the
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3325 mixes made with pMRA are located in the non-pozzolanic zone of the pozzolan, and some of the
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3626 mixtures made with pBBA and phBBA are located in the pozzolanic zone, this may be due to the
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4027 low reactive SiO₂ content [77].
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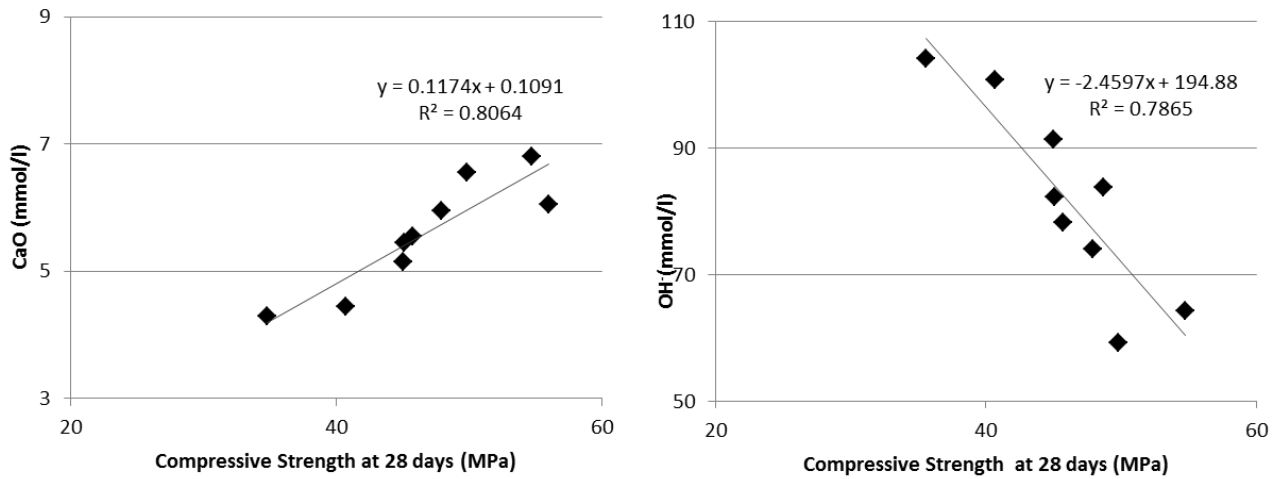


Figure 17. Correlation between compressive strength of cement mortars at 28 days and CaO-OH⁻ content

The compressive strength obtained at 28 days in the manufactured mortars is related to the pozzolanic activity of the mixes, as shown in Figure 17.

3.6 Dimensional changes. Dry and under water conditions.

The methodology for the determination of shrinkage is specified in the UNE 83831:2021 Standard and basically consists of the preparation of mortar specimens of special dimensions (25x25x287 mm), with calibration pins inserted, which allow length measurements to be taken on a length comparator throughout the curing process. Figure 18 shows the dimensional variations obtained in mortars cured under water (UW) and dry chamber (DC).

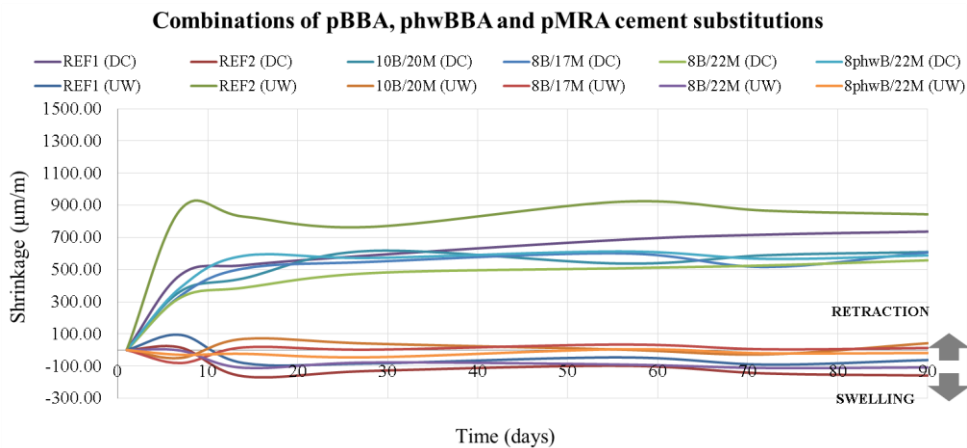
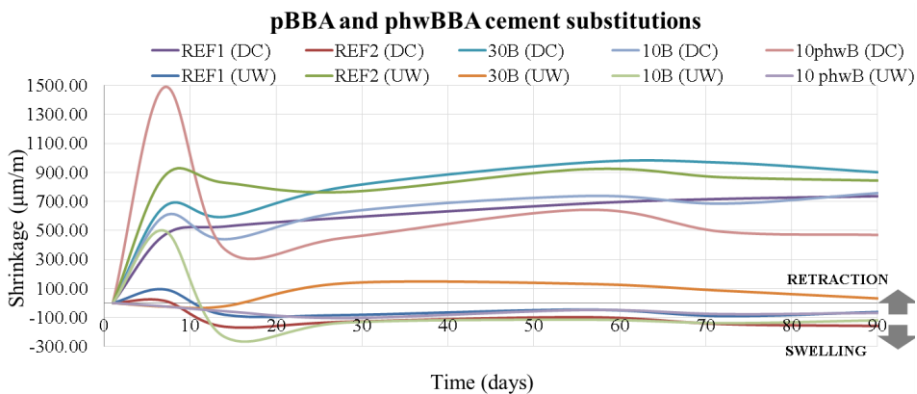
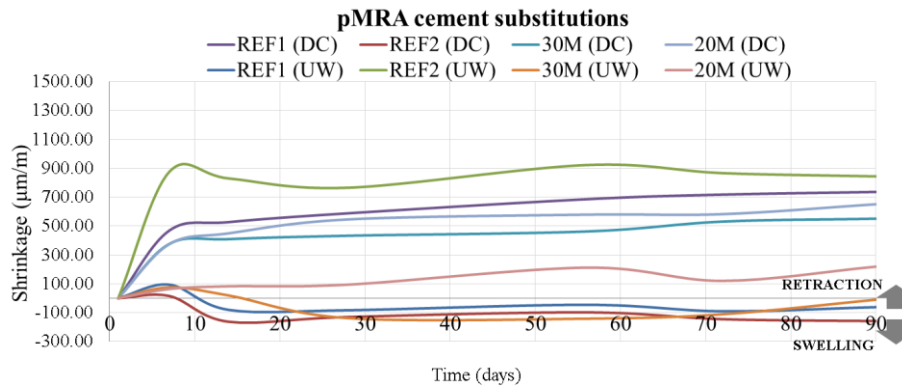
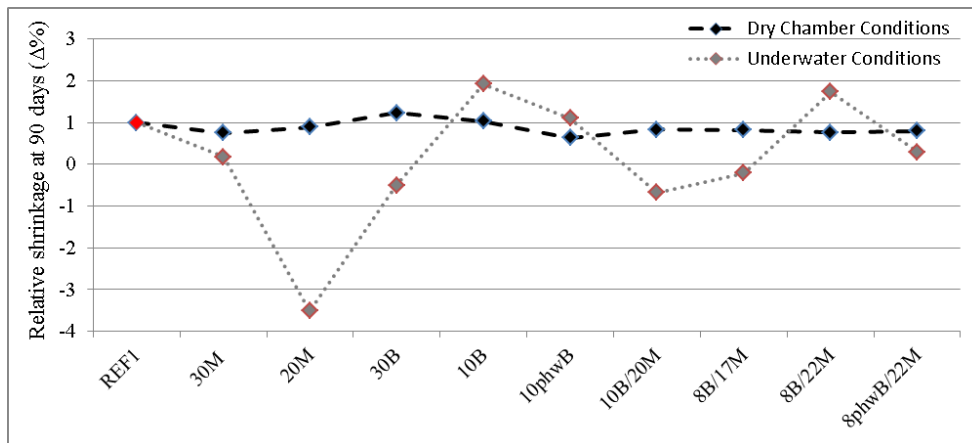


Figure 18. Dimensional changes of hardened cement mortars under two curing conditions

The mortar behaves differently depending on its age: in the first hours it behaves in a similar way to a fluid with high viscosity, a few hours later it behaves like a semi-solid and at about 10 hours it is already a solid in which the reactions of the cement with the water are present and it is acquiring

546 strength. From day 28 onwards, the mortar can be considered as mature, but dimensional changes
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 547 continue to occur throughout its useful life. The phenomena that occur in each of the stages through
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 548 which the mortar passes condition its behaviour and the application throughout its useful life.
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 11 549 During the production of the mortar, water is added to the mixture, partly to make it workable and
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 14 550 partly to react with the cement. The water that does not react with the cement slowly leaves the
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 17 551 mortar, which results in the final volume of the ingredients to be less than the initial volume,
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 21 552 resulting in a volumetric decrease, or shrinkage, in the mortar specimen. In addition to the above
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 24 553 loss of volume, there is another loss of volume due to the cooling of the mortar. The reaction of
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 27 554 cement with water is exothermic, the mortar mass in the first hours of life will be hotter than it will
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 30 555 be in the long term and therefore it will also have a higher volume at early ages compared to what
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 33 556 it will have in the long term.



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 54 558 Figure 19. Dimensional changes of hardened cement mortars under two curing conditions
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559 From day 28 onwards the mortar can be considered as mature and stable, but dimensional changes
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 560 continue to occur throughout its service life. Figure 19 shows the dimensional changes in two
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 561 curing environments at the age of 90 days. It can be observed that the mortars cured in a dry
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 10 562 chamber present similar values in all the mixtures under study, while those cured under water
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 13 563 present more alterations due to the constant hydration, which produces the different chemical
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 16 564 reactions that cause the dimensional changes.

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 21 565 **3.7 Microproperties of hardened mortars**

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 25 566 **3.7.2 Mercury Intrusion Porosimetry (MIP)**

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 29 567 Mercury intrusion porosimetry (MIP) is a technique used for the evaluation of porosity, pore size
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 32 568 distribution and pore volume (among others) to characterise a wide variety of solid and powdered
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 35 569 materials. The instrument, known as a porosimeter, uses a pressurised chamber to force mercury
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 38 570 into the voids of a porous substrate. When pressure is applied, the mercury fills the largest pores
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 41 571 first. As the pressure increases, the filling proceeds to smaller and smaller pores. With this
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 45 572 technique, both interparticle pores (between individual particles) and intraparticle pores (within the
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 48 573 particle itself) can be characterised.

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 51
 52 574 Table 12. Volume of total porosity in mortar mixes at 90 days.

Volume of total porosity	
Mortar mix	Total Porosity (% Vol.)
REF1	9.361

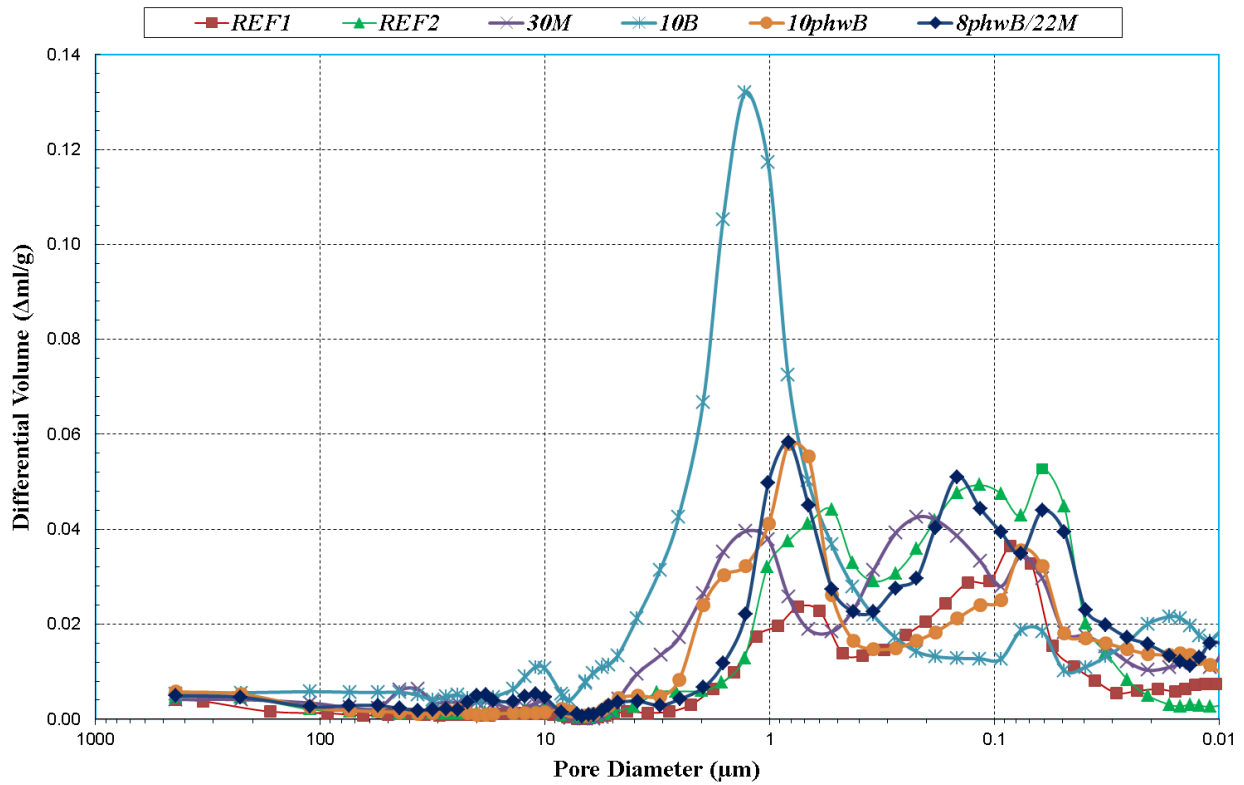
REF2	14.8973
30M	15.3344
10B	21.1278
10phwB	13.8501
8phwB/22M	16.148

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The pore analysis test was carried out on the combined maximum substitution mix that performs mechanically remarkably well in addition to our reference mixes. It should be noted that the test was carried out on the mortar specimens 90 days after the test was performed.

It can be seen that in the eco-hybrid cement mix studied, the volume of pores increases with respect to the reference mixes. This may be due to the fact that the degree of fineness of the phwBBA and the MRA is less than that of the cement, which may lead to a greater number of pores. This amount of pores reduces the density of the hardened mortar, as well as reducing the thermal conductivity, as can also happen in concretes with the same qualities [78]. On the other hand, previous studies have shown that the porosity of the mortar is related to the density of the material [79] as happens with phwBBA and pMRA in comparison with the density of the cement, or even comparing CEM I with CEM II. Other works such as that of Rosales et al. [47] show concordant results that a porous material makes its derived mortars porous as well. It should be noted that a certain amount of water necessary for the hydration of phwBBA or pMRA was added at large substitutions (30% cement

589 substitution). Previous studies show that this water also fills voids, creating pores during the
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 490 hardening stage [80].
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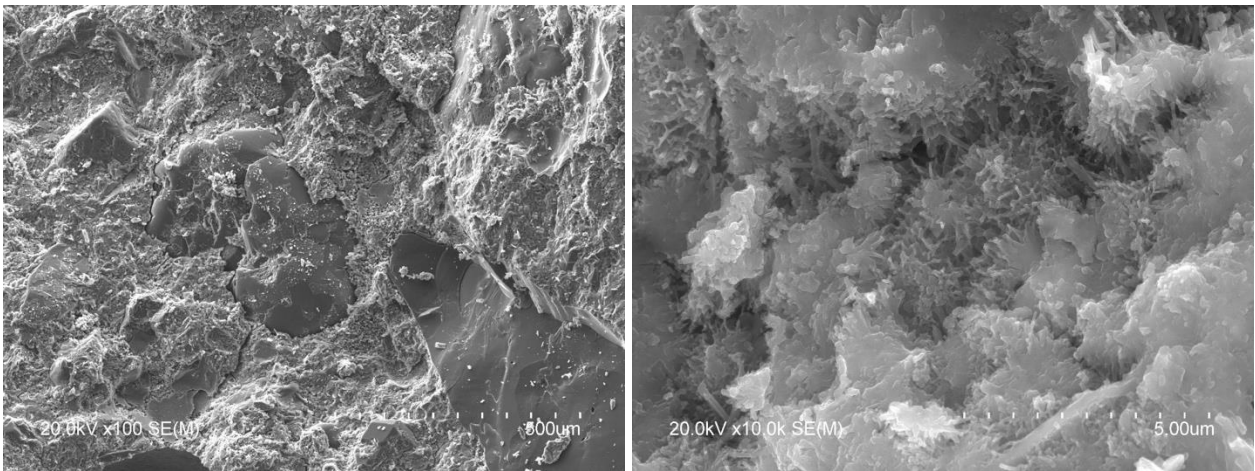
591
 592 Figure 20. Differential Volume intrusion in function of Pore Diameter at 90 days.
 593

593 It is observed that the eco-hybrid cement mixture studied shows similarities in the number and size
 594 of the pores with CEM II mixture. There are peaks in the number of pores of 1 μm, 0.2 μm and
 595 0.05μm in diameter for the CEM II mortar and for the eco-hybrid cement mortar. However, the
 596 critical pore size of our CEM II reference cement mortar, REF 2, is 0.06 micrometers when in the
 597 8phwB/22M mix the critical pore size is 0.8 micrometers. This fact may cause the durability of the
 598 8phwB/22M mortar mixes to be lower, and there may be an early deterioration [81].
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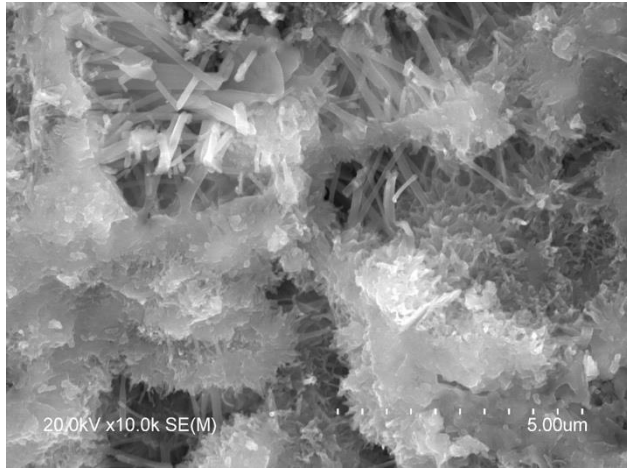
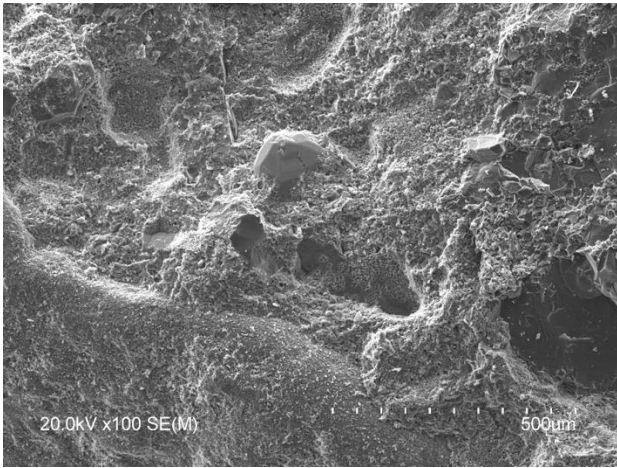
599 **3.8 Scanning Electron Microscopy (SEM)**

600 Scanning Electron Microscopy (SEM) provides three-dimensional images of the external
601 morphology of a sample, allowing the observation and characterisation of organic and inorganic
602 materials, by means of topographic or compositional contrast. The range of sizes observable by
603 SEM (between a few millimetres and a few nanometres) makes it a suitable instrument for the study
604 of the structure and ultrastructure of a sample.

605 Cement mortars at 90 days versus control with calibration pins inserted, which allow length
606 measurements to be taken on a length comparator throughout the curing process. Scanning Electron
607 Microscopy (SEM).

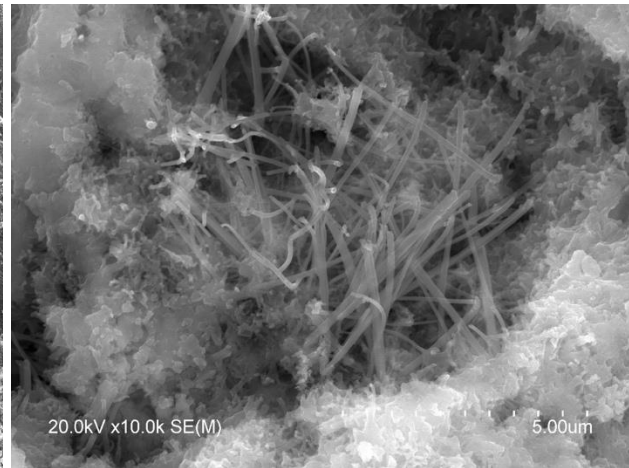
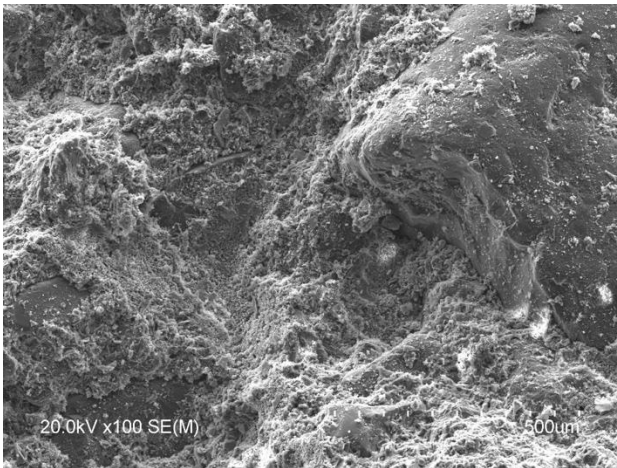


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609 Figure 21. SEM image REF1 mortar. A) REF1 mortar at 90 days scale 500µm; B) REF1 mortar at
610 90 days scale 5µm.



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Figure 22. SEM image REF2 mortar. A) REF2 mortar at 90 days scale 500um; B) REF2 mortar at 90 days scale 5um.



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Figure 23. SEM image 8phwB/22M mortar. A) 8phwB/22M mortar at 90 days scale 500um; B) 8phwB/22M mortar at 90 days scale 5um.

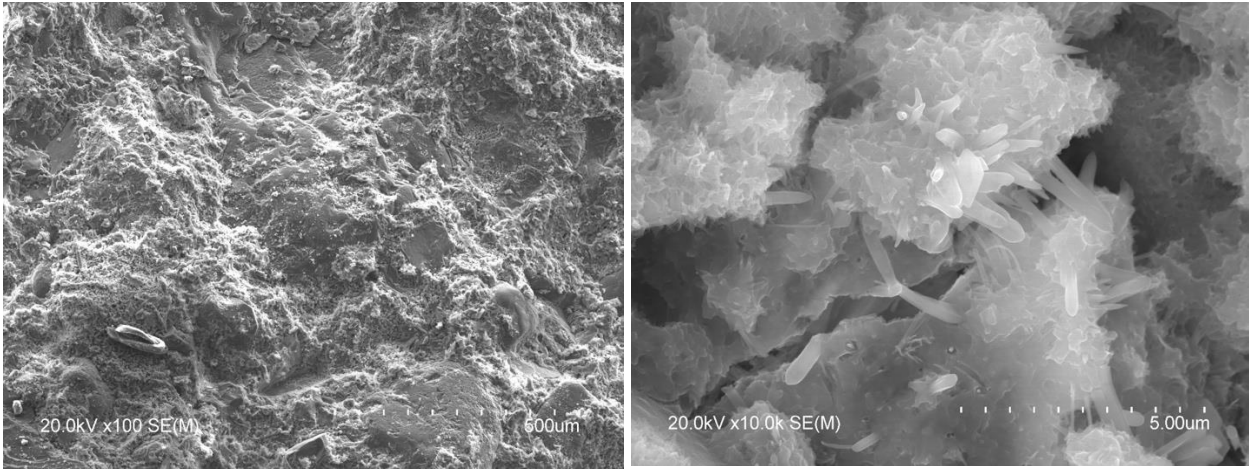


Figure 24. SEM image 10phwB mortar. A) 10phwB at 90 days scale 600µm; B) 10phwB at 90 days scale 5µm.

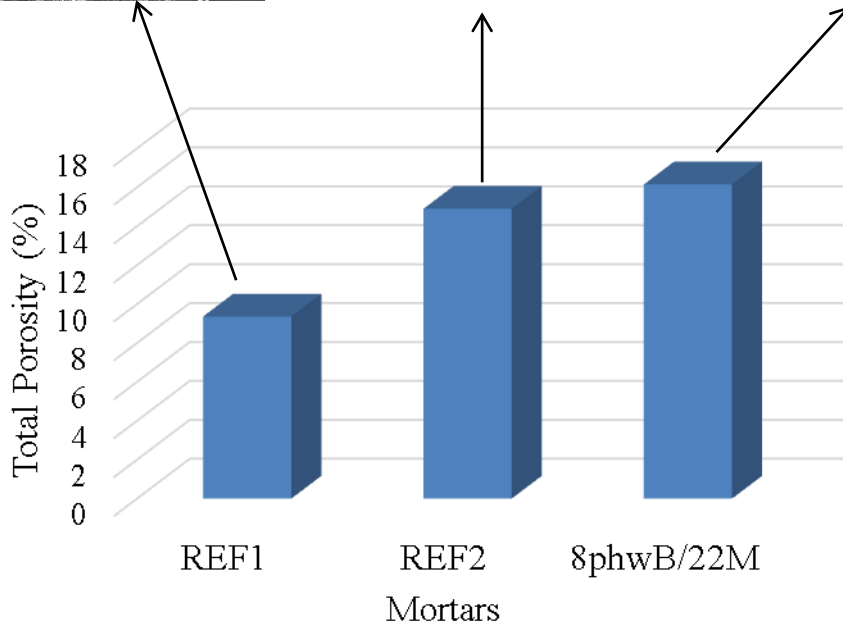
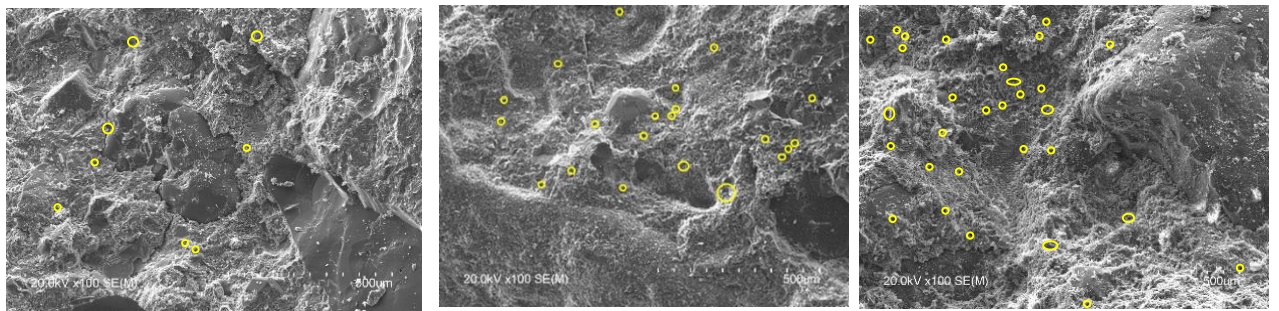
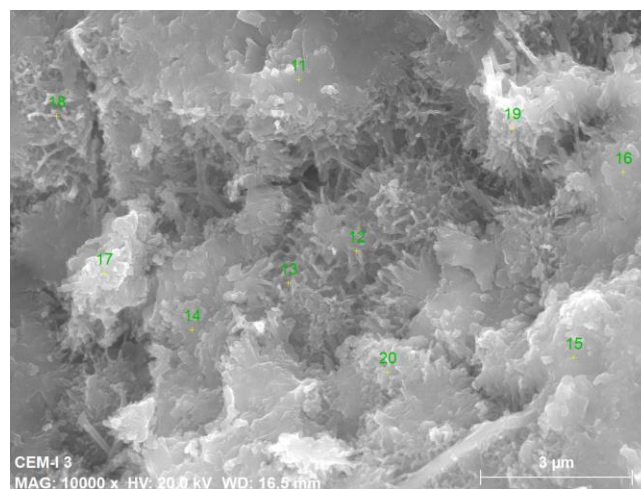


Figure 25. Comparative between MIP and visual pore distribution with SEM

626 Analyzing the images provided by the microscope, we can observe how the number of pores in the
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627 mortar specimens increases as we modify the amount of clinker in the cement used. In REF1 we
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628 find that the number of pores is small, being this cement 100% Clinker. As we increase the number
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629 of additions to the Clinker (REF2 is a CEM II A/L with limestone filler and 8phwB/22M has a 30%
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630 replacement of Clinker by recycled by-products) we observe how the number of pores increases
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631 both in the MIP test and in the microscope images. It is worth noting that the number of pores and
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632 their distribution is similar between the REF2 mortar and the designed eco-hybrid cement. Since
13
633 CEM II A/L is used for concrete pavements and the eco-hybrid cement under study in this paper is
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634 for future use in this type of application, it is a positive point that the mortars made with CEM II
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635 A/L and those made with the eco-hybrid cement behave similarly on this point.
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637 Figure 26. SEM image REF1 mortar with element analysis

638 In the picture we can observe that the C-S-H gels are very present, for example in pins 13, 15, 17
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639 and 20. In the analysed points we do not find stringite formation as the sulphur quantities are low
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640 for an element whose main composition is sulphur oxide. The CaO/SiO₂ ratios for these gels are
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641 3.5.
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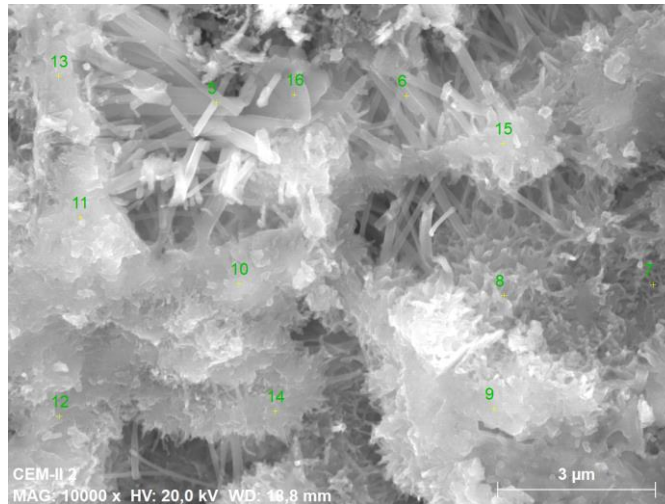


Figure 27. SEM image REF 2 mortar with element analysis

In Figure 27 and with the help of the elemental analysis in which the average CaO is 67.55%, it can be observed that hydrated calcium gels are very present. Furthermore, in pins 6 and 12, due to their high amount of calcium CaO (72.67% and 80.62% respectively), we can say that they are Portlandite. Pin 7 has a large amount of Magnesium MgO (25.70%) in a punctual way. This may be due to the occurrence of dolomite, although given the resolution of microscopy this cannot be fully determined. The CaO/SiO₂ ratios for these gels are 5.2.

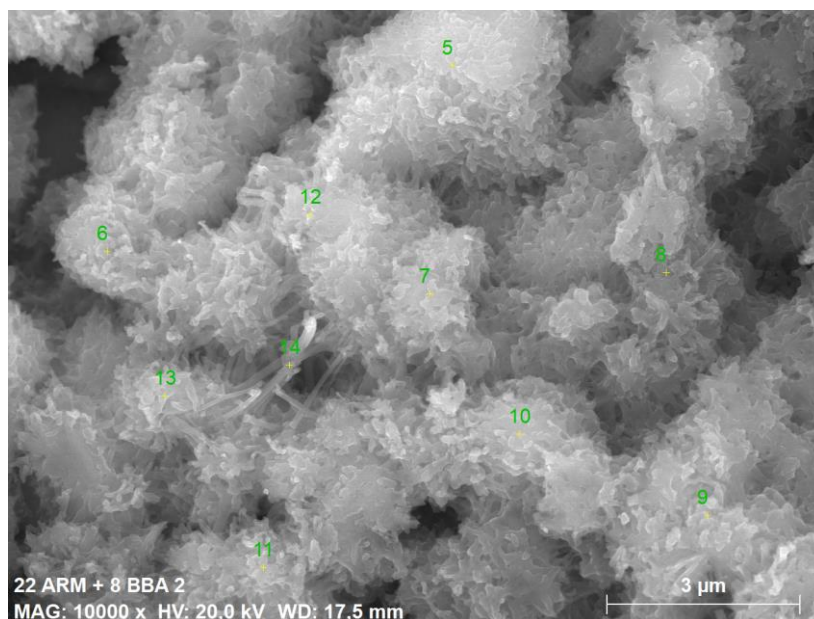
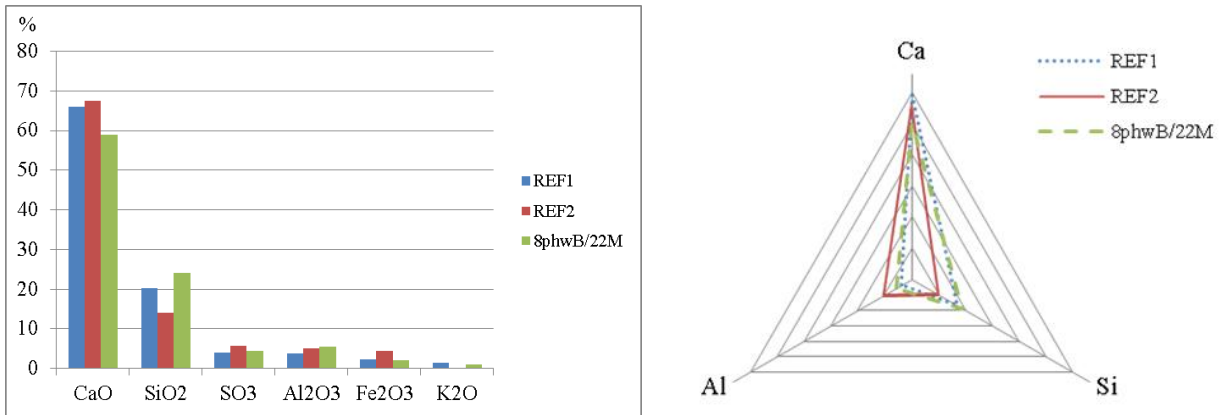


Figure 28. SEM image 8phwB/22M mortar with element analysis

652 Calcium silicate hydrated gel is very present in the mortar made with eco-hybrid cement. We found
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 653 that they are in amorphous phases. The CaO/SiO₂ ratios for these gels are 2.5. The low sulphur
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 654 content, at most pin 15 with 5.12%, makes us think that there is no ettringite, although pin 14 seems
 6
 655 to contain ettringite by looking at the fibrous material in figure 28.



a)

b)

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 658 Figure 29. a) Average values of oxide elements in SEM; b) Ternary plot correlating pure elements
 659 Figure 29a shows how the large amount of calcium oxide and silicon oxide form the Calcium
 660 silicate hydrated gels. The amounts of potassium are negligible and the sulphur content is
 661 remarkable to note.

662 4. CONCLUSIONS

663 The eco-hybrid cements developed in this work are intended for use as pavement cement. The
 664 widespread use of CEM II A/L for this application makes(allows) the studied properties of eco-
 665 hybrid cements to be compared with the properties of CEM II A/L. CEM II A/L has limestone filler
 666 additions between 6% and 20%. By reaching additions of 30% with recycled materials such as
 667 pMRA or phwBBA, the number of additions established to achieve a CEM II A/L is exceeded,
 668 reducing the amount of natural material considerably and adding recycled material that was
 669 originally waste. The following conclusions emerge from this study:

- 670 - By processing the waste, it is found useful as SCM by-products. Due to the shredding and
 1 screening of the mixed recycled aggregates, it has been increased their specific surface area.
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 3 671
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 5 672 Moreover, as it contains a considerable number of ceramics, this by-product acquires
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 7 673 cementitious properties. The treatment on the Biomass bottom ash causes a similar effect,
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 9 674 visible in the results derived from the 10B mix. However, if a washing and calcination
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 12 675 treatment of this powder (phwBBA) has also been carried out; better results are achieved
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 14 676 with the combination of an increase in the specific surface area and the elimination of
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 17 677 undesirable components such as potassium in from 9.18% to 8.15%.
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 19 678 - With respect to the heat of hydration, mixtures of good mechanical strength and high
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 22 679 substitutions such as 20M or 8phwB/22M show a very low hydration heat, which is
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 24 680 beneficial to avoid potential thermal cracking, in addition to the fact that their durability is
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 27 681 high. Compared to CEM I, these hydration heats are lower by 16.2% and 12.1%
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 29 682 respectively. In fact, the 20M mix undergoes a maximum shrinkage of 600 $\mu\text{m}/\text{m}$ and the
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 31 683 8phwB/22M mix shrinkage of 500 $\mu\text{m}/\text{m}$, both in the curing chamber. These are less than
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 33
 34 684 the maximum dimensional change of CEM I of 700 $\mu\text{m}/\text{m}$ and slightly greater than the CEM
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 36 685 II A/L maximum swelling of 200 $\mu\text{m}/\text{m}$. We can observe that eco-hybrid cement mixes are
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 38
 39 686 generally not pozzolanic through the Frattini test. It must be considered that eco-hybrid
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 41 687 cement is composed of a part of CEM I and a part of substitutes. Being a hydraulic cement,
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 44 688 its pozzolanicity through Frattini is not very high, as shown by the results of CEM I and
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 47 689 CEM II.
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 49 690 - Mixtures with MRA and BBA substitutes cause, both at 8 days and 15 days, this eco-hybrid
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 51 691 cement to be located on the borderline between being pozzolanic and not. However,
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 53
 54 692 combined substitutions of MRA and BBA (10B/20M, 8B/17M) or MRA and phwBBA
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 56 693 (8phwB/22M) are considered pozzolanic eco-hybrid cements both in the 8 days and 15 days
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 58 694 test.

- 695 - The setting times of the eco-hybrid cements (20M, 30M and 8phwB/22B) are delayed
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2696 compared to the hydraulic cements CEM I and CEM II. This is because the by-products
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4697 pMRA, pBBA and phwBBA need to absorb water until saturated. Congruencies between
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6798 the heat of hydration and setting time tests have been found. In them it can be observed that
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8699 the cementitious reaction is delayed compared to hydraulic cements.
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12700 - With respect to the hardened mortars, the porosity of the 8phwB/22M mix is slightly higher
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14701 than the mortar with CEM II A/L, 0.44% less pores. In addition, it should be noted that the
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16702 washing and calcining treatment of the BBA reduces the number of pores. The mortar made
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18703 with a 10% substitution of BBA powder has 7.28% more pores than the mortar made with
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20704 the same substitution of washed and calcined BBA powder.
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24705 - Below, the following mechanical conclusions are included of this investigation, in which
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26706 processed BBA and MRA were studied as SCM:
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29707 ○ Mixtures with BBA have poorer mechanical strengths but, in the long term (90d),
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31708 they still increase their cementitious capacities; precisely, the percentage increase
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33 of 30B is 18.10% from 28 days to 90 days, highest of all mixes. This long term
34709 performance is important, but this mixture is not strong enough to match CEM II
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36710 A/L, the reference cement.
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39711 ○ It can be observed that, a washing and calcining treatment makes the mechanical
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41712 strengths of BBA considerably higher. Mixtures with 10% substitution with
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43713 phwBBA compared with mixtures with 10% pBBA, is 42% higher at 28 days.
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46714 ○ Finally, there are mixtures that outperform the reference mixture with CEM II A/L
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48715 in terms of strength. 20M by 4%, 10phwB by 11%. However, mixtures with high
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50 substitutions (30% of cement) such as 30M, 10B/20M, 8B/22M and 8phwB/22M
51716 fall by only 5%, 11%, 12% and 7%. This last mixture could be considered as useful
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53717 cement for the execution of works.
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1720 **Acknowledgements**

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