

## Article

# Reactivity of Ground Coal Bottom Ash to Be Used in Portland Cement

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**Abstract:** Ground coal bottom ash is considered a novel material when used in common cement production as a blended cement. This new application must be evaluated by means of the study of its pozzolanic properties. Coal bottom ash, in some countries, is being used as a replacement for natural sand, but in some others, it is disposed of in a landfill, leading thus to environmental problems. The pozzolanic properties of ground coal bottom ash and coal fly ash cements were investigated in order to assess their pozzolanic performance. Proportions of coal fly ash and ground coal bottom ash in the mixes were 100:0, 90:10, 80:20, 50:50, 0:100. Next, multicomponent cements were formulated using 10%, 25% or 35% of ashes. In general, the pozzolanic performance of the ground coal bottom ash is quite similar to that of the coal fly ash. As expected, the pozzolanic reaction of both of them proceeds slowly at early ages, but the reaction rate increases over time. Ground coal bottom ash is a promising novel material with pozzolanic properties which are comparable to that of coal fly ashes. Then, coal bottom ash subjected to an adequate mechanical grinding is suitable to be used to produce common coal-ash cements.



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**Keywords:** coal bottom ash; coal fly ash; circular economy; pozzolanicity; coal-ash cement

## 1. Introduction

Carboneras power plant has a power of 1,158,900 kW and currently mainly burns coal from South Africa (90%). This coal presents a low heat value of only 6593 kcal/kg [1] and the ash amount is about 15.75% [2]. A grate boiler was used to burn the pulverized coal. The fly ash/bottom ash ratio was about 6. Coal fly ash is normally used in cement production in Europe. In addition, it is utilized as a supplementary cementitious material (SCM) for concrete not only in America but also in Europe. Coal bottom ash is the coarser ash that falls down and is collected to be handled and disposed of in a landfill [3].

Coal fly ashes use depends on their chemical characteristics and its properties have already been published in many papers [4]. On the contrary, the potential utilization of coal bottom ashes as cement constituent, which is influenced by the physical composition, i.e., particle size distribution (PSD), has not been well studied yet.

The most common use of coal bottom ash has been to replace natural aggregates due to its coarse, fused, glassy texture and, also, due to its low cost [5,6]. It is used as sand replacement in the production of asphalt concrete and as a base in the construction of roads [7]. The porous nature of the coal bottom ash aggregates is believed to be beneficial for reducing the concrete shrinkage [8]; such reduction is achieved thanks to the internal curing obtained as result of the slow release of water from the saturated porous coal bottom ash [9]. Coal bottom ash has also been investigated to replace calcined diatomite and natural clay in fired-ceramic composites and lightweight heat-resistant concretes, respectively [10]. In addition, coal bottom ash is a potentially promising source of rare

earth elements [11]. In some countries, such as India, coal-fired power stations utilize a humid procedure for coal fly ash and coal bottom ash disposal. The first one is collected from the precipitators and the second one is collected from the boilers. These solids are then mixed with water forming a slurry (ponded ash) which is discharged to lagoons. In particular, this mixture is composed by particles with an average size below 75 mm, i.e., about 65% of the total amount of ashes [6]. Therefore, it is not widely used in concrete.

This paper examines the extent to which the ground coal bottom ash (CBA) could be used alone or mixed with the coal fly ash (CFA) produced in the same powerhouse to be potentially valorized as a novel common cement constituent in line with the circular economy principles of resource sharing. Its potential pozzolanic properties will be addressed.

Coal bottom ash is investigated in the present study for its potential pozzolanic properties when used alone or mixed with coal fly ash, both of them produced in the same power station, in order to be potentially valorized for the cement industry in the near future.

The novelty of this research program relies, in particular, on the assessment of ground CBA–CFA mixes to be considered as a novel cement constituent with significant pozzolanic reactivity. We would also like to underline the interest of this investigation of CFA–CBA mixes pozzolanic reactivity which has provided the basis for the potential standardization of new cement types.

## 2. Materials and Methods

### 2.1. Materials

Coal bottom ash (CBA) and coal fly ash (CFA) used in this study were provided by Carboneras power station (Latitude: 36°57'54" N and longitude: 1°53'24" O), located in Almería, in the South of Spain (Figure 1). The power station consumes coal from South Africa (90%) and Colombia (10%). The fineness of the ground coal bottom ash and coal fly ash used in the present work were 3463 m<sup>2</sup>/kg and 3976 m<sup>2</sup>/kg, respectively, measured as Blaine specific surface. A CEM I 42.5 N cement according to the European standard EN 197-1:2011 [12] was employed to prepare the cement mixtures. The Portland cement was supplied by HOLCIM (ESPAÑA), S.A. Table 1 presents the codes (Greek letters) of the ash mixes (coal bottom and fly ashes).



Figure 1. Map of Carboneras in Almería, in the South of Spain.

**Table 1.** Codification of the cement mixes of the coal bottom ash (CBA) with coal fly ash (CFA) and cement (CEM I 42.5 N).

CEMENT MIX	% Material		Coal Fly Ash + Coal Bottom Ash Mix Codification					
			$\alpha$	$\beta$	$\gamma^1$	$\delta^1$	$\lambda^1$	$\Omega$
CEM I	Fly ash	0%	0%					
	Bottom ash		0%					
	Cement	100%	100%					
CEM II/A-V	Fly ash			10%	9%	8%	5%	0%
	Bottom ash	10%		0%	1%	2%	5%	10%
	Cement	90%		90%	90%	90%	90%	90%
CEM II/B-V	Fly ash			25%	22.5%	20%	12.5%	0%
	Bottom ash	25%		0%	2.5%	5%	12.5%	25%
	Cement	75%		75%	75%	75%	75%	75%
CEM IV/A (V)	Fly ash			35%	31.5%	28%	17.5%	0%
	Bottom ash	35%		0%	3.5%	7%	17.5%	35%
	Cement	65%		65%	65%	65%	65%	65%

<sup>1</sup> Mix of CBA and CFA.

## 2.2. Analytical Methodology

The chemical analyses of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, SO<sub>3</sub>, K<sub>2</sub>O, Ti<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub> were performed by XRF with a Bruker S8 Tigger 4 kW model. Loss on ignition (LOI), insoluble residue and chloride ion were determined according to the European standard EN 196-2:2013 [13] and pozzolanicity according to EN 196-5:2011 [14].

## 2.3. Pozzolanic Activity Assessment of the Coal Bottom Ash, Coal Fly Ash, Cement and Their Mixes

Pozzolanic activities of coal bottom ash and coal fly ash mixes were assessed by means of chemical and mechanical testing. The mechanical assessment was performed by means of the compressive strength activity index defined in the European standard EN 450-1 [15]. The compressive strength testing procedure is explained in EN 196-1 [16].

Pozzolanic activity was measured in cement paste (water/cement = 0.5), whereas EDS microanalysis was performed in standard mortars (water/cement = 0.5 and cement/sand = 1/3, according to EN 196-1 [16]). One mixture was used for the pozzolanic activity measurements, and three mortars specimens were made for each composition.

The chemical evaluation was carried out following the procedure given by the European standard EN 196-5:2011 [14]. The CaO and OH<sup>-</sup> concentrations were measured at 1, 3, 7, 14, 28 and 90 days according to EN 196-2 [13]. First at all, pozzolanic activity assessment of coal bottom ash, coal fly ash and cement separately was performed by chemical testing. All of them were immersed in a saturated solution of Ca(OH)<sub>2</sub> at 40 °C for 1, 3, 7, 14, 28 and 90 days. Secondly, both coal ashes were mixed with the cement, in a proportion of 75:25 (cement:ash), and with distilled water (water/cement = 0.5). These mixes were kept at 40 °C for 1, 3, 7, 14, 28 and 90 days.

## 3. Results and Discussion

### 3.1. Characterization of the Coal Bottom Ash, Coal Fly Ash and Cement

The chemical compositions of the coal bottom ash, coal fly ash and cement are given in Table 2. Additionally, the cement physical properties are shown in Table 2.

The calcium oxide content of the coal bottom ash is low (5.9%) and similar to that of the coal fly ash (5.0%). With regard to the sum (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>), it reaches 85.6%. Given that, it is a type F ash according to ASTM C 618-15 [17], as well as the fly ash which reaches 84.4%.

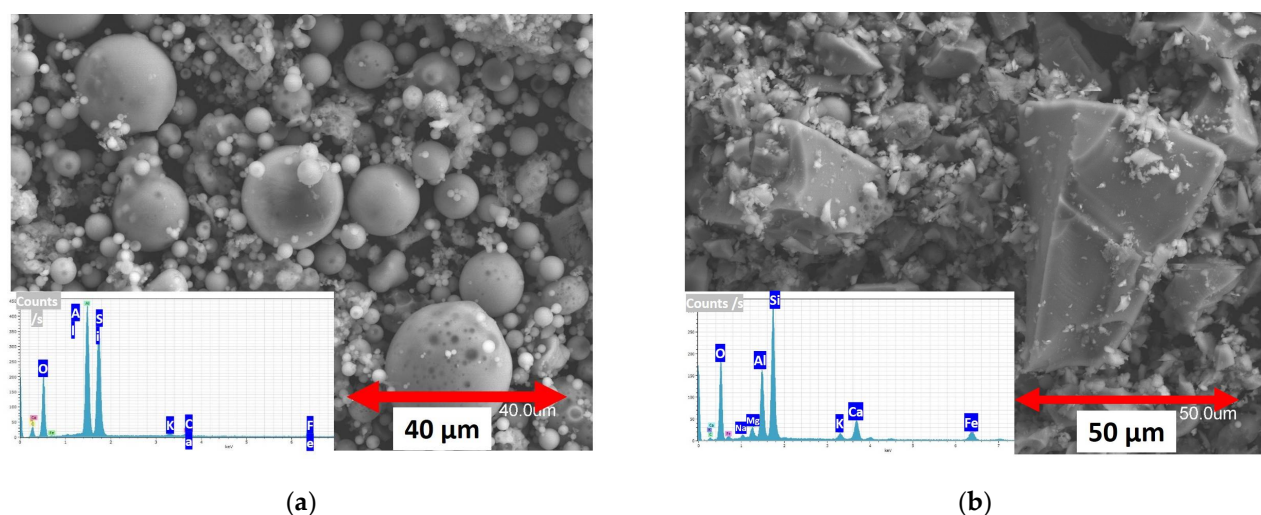
In particular, the silicon and aluminum oxides content ranges from 79.4% (coal bottom ash) to 79.7% (coal fly ash). Figure 2 shows that the highest peaks correspond to these two elements. Accordingly, the coal bottom ash and coal fly ash mixes have similar chemical

compositions to that of pozzolanic materials. The loss on ignition (LOI) in coal bottom ash is primarily because of the carbon content. Therefore, the content of carbon is about 1.9%. With regard to the chloride and sulphate ion amounts, both of them are very low ( $\text{Cl}^- < 0.001\%$  and  $0.13\% \text{SO}_3$ ).

**Table 2.** Chemical composition of the coal bottom ash (CBA), coal fly ash (CFA) and cement (CEM I 42.5 N).

Chemical Composition (%)	Cement	Fly Ash (CFA)	Bottom Ash (CBA)	Physical Properties of Cement	
$\text{SiO}_2$	20.9	50.5	52.2	Specific gravity ( $\text{kg}/\text{m}^3$ )	3.10
$\text{Al}_2\text{O}_3$	4.3	28.9	27.5	Initial setting time (min)	205
$\text{Fe}_2\text{O}_3$	3.5	4.7	6.0	Final setting time (min)	325
$\text{CaO}$	62.7	5.0	5.9	Volume expansion (mm)	0.70
$\text{MgO}$	1.9	1.8	1.7	Blaine Specific surface ( $\text{m}^2/\text{kg}$ )	4050
$\text{SO}_3$	3.4	0.21	0.13	Compressive strength (MPa)	
$\text{K}_2\text{O}$	0.9	0.80	0.57	1 days	13.30
$\text{Ti}_2\text{O}_5$	0.25	1.56	1.53	3 days	19.45
$\text{P}_2\text{O}_5$	0.10	0.76	0.74	7 days	37.95
LOI	3.69	3.6	1.8	14 days	45.25
Insoluble residue <sup>1</sup>	1.04	71.3	75.7	28 days	50.98
$\text{Cl}^-$	0.023	0.001	0.001	90 days	55.55

<sup>1</sup>  $\text{Na}_2\text{CO}_3$  method.



**Figure 2.** Scanning electron micrograph and EDS microanalysis: (a) coal fly ash; (b) ground coal bottom ash.

Chloride content is a critical problem for the reuse of coal fly ash as a raw material in cement in some cases. By contrast, it could be suggested that adding coal fly ash to a concrete can significantly reduce the concentration of free chloride ions. According to the European standard EN 450-1 “Fly ash for concrete—Part 1: Definition, specifications and conformity criteria” [15], the content of chloride, expressed as  $\text{Cl}^-$ , shall not be greater than 0.10% by mass. The reasons for this low chloride content in both ashes is the origin of the coal (South Africa, 90%, and Colombia, 10%).

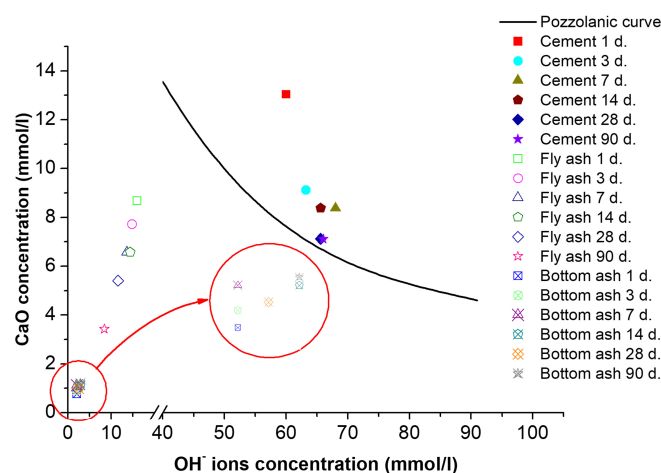
Therefore, a low probability of occurrence of detrimental effects on cement setting, hardening and durability is confirmed. Among the trace elements, higher concentrations of  $\text{P}_2\text{O}_5$  and  $\text{Ti}_2\text{O}_5$  were detected in coal fly ash than in coal bottom ash. Summing up, it can be stated that the chemical composition of CBA and CFA supplied by the same coal-fired power plant is quite similar.

The physical, mechanical and durability properties of the fly ash-bottom ash-common Portland cement mixtures were reported elsewhere [3,18,19]. Finally, the spherical and rounded particles of coal fly ash (CFA) and irregularly shaped grains of ground coal bottom ash (CBA) have been observed by scanning electron microscopy (SEM) analyses

of both ashes (Figure 2). In addition, Energy-Dispersive X-ray Spectroscopy (EDS) was used in conjunction with scanning electron microscopy (SEM) to obtain the chemical differences between both ashes. This chemical microanalysis technique showed their chemical similarity. As shown in Table 2, only calcium and iron are slightly higher in CBA than in CFA. According to McCarthy [20], the ferrous phases are found mostly in crystalline form as magnetite ( $\text{Fe}_3\text{O}_4$ ) or hematite ( $\text{Fe}_2\text{O}_3$ ).

### 3.2. Pozzolanic Activity of Ground Coal Bottom Ash, Coal Fly Ash and Cement Mixes Determined by Chemical Testing

All the raw materials, except the cement CEM I 42.5 N, showed a certain pozzolanic activity (coal bottom ash and coal fly ash), when they were immersed in a saturated solution of  $\text{Ca}(\text{OH})_2$  at  $40^\circ\text{C}$  for 1, 3, 7, 14, 28 and 90 days (Figure 3). CaO concentration decreased with time up to values of 9 mmol/L after 3 days for the cement as result of the hydrated calcium silicates formation, while the  $\text{OH}^-$  concentration remained stable around 65 mmol/L. Such concentrations are quite close to the curve drawn in Figure 3, but they are still slightly above it.



**Figure 3.** Constituents pozzolanicity at 1, 3, 7, 14, 28 and 90 days.

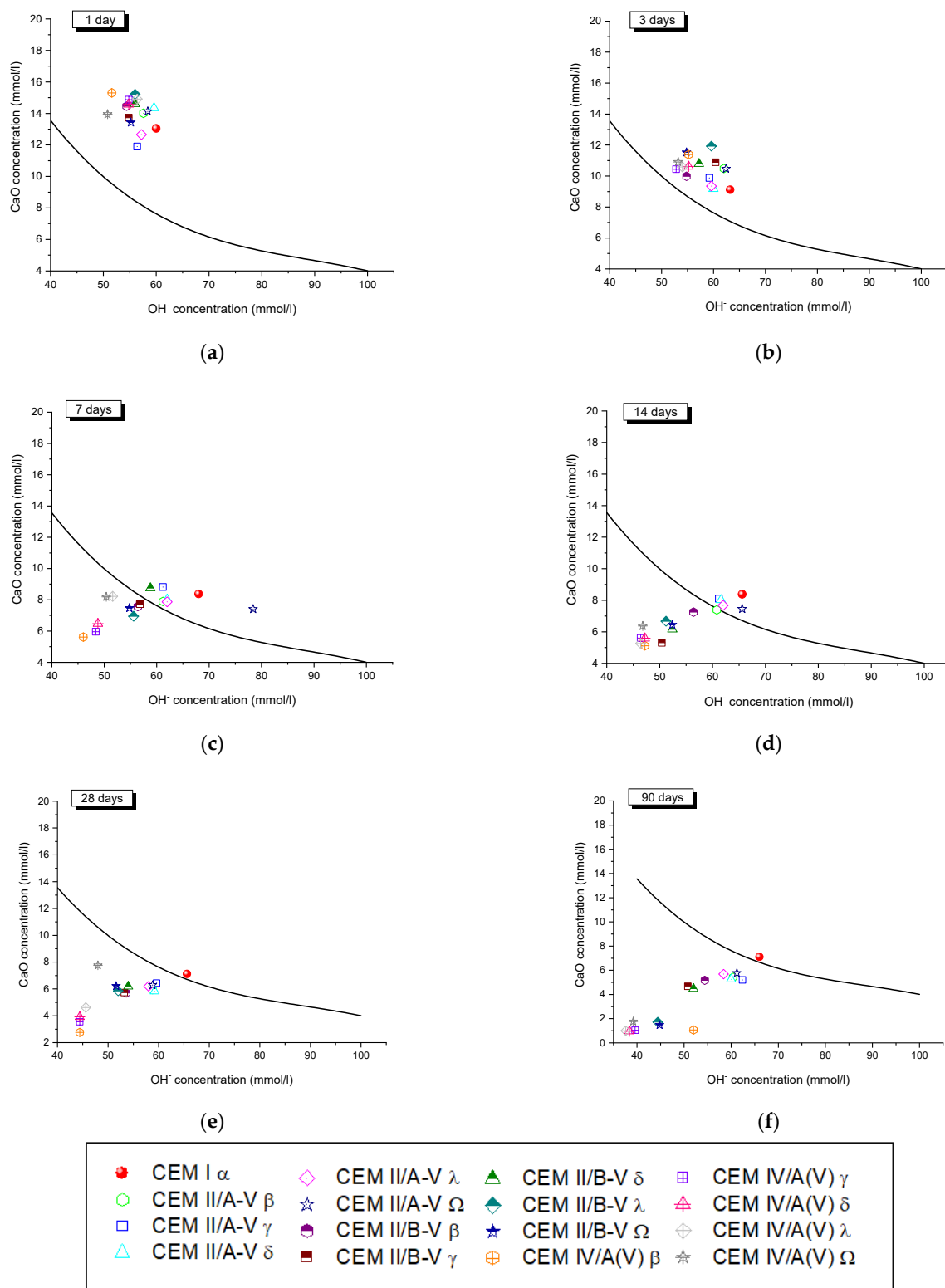
CaO and  $\text{OH}^-$  concentrations for CFA decreased from 9 mmol/L and 15 mmol/L (1 day) to 3 mmol/L and 10 mmol/L (90 days), respectively. Then,  $\text{OH}^-$  concentration changed very little for coal fly ash, e.g., the  $\text{OH}^-$  concentration was 15 mmol/L at 1 day; whereas at 90 days it is 10 mmol/L. On the other hand, the CaO concentration decreases sharply from 9 mmol/L to 3.6 mmol/L during the same period (Figure 3). Apparently, the pair of points defining the CaO and  $\text{OH}^-$  concentrations for coal fly ash in Figure 3 follows a sharp straight line. By contrast, the CaO and  $\text{OH}^-$  concentration points for ground coal bottom ash did not follow any clear trend.

Surprisingly, ground coal bottom ash showed a faster CaO and  $\text{OH}^-$  consumption with values as low as 1 and 3 mmol/L, respectively (Figure 3). These concentrations stayed largely constant for ground coal bottom ash from 1 to 90 days. This fact is attributed to the greater fineness of the ground coal bottom ash and, therefore, larger specific area. The finer the coal ash is, the more reactive a material it will be. In addition, the spherical shape of the coal fly ash provides a lower reactive performance than the angular shape of the ground coal bottom ash. According to Dembas [21], the fineness of the ground coal ashes and the cement used in the mix has an important influence on the performance of the final cementitious material.

Furthermore, pozzolanicity was determined at 1, 3, 7, 14, 28 and 90 days for all the bottom ash-fly ash-cement mixes, as shown in Figure 4. The pozzolanic reaction at  $40^\circ\text{C}$  began at the age of seven days for CEM IV/A (V), i.e., the mix with the largest content of ground coal bottom ash and/or coal fly ash (Figure 4). Thus, the greater increase of ash content showed the higher pozzolanic activity. This fact suggests that the amorphous



aluminous and siliceous phases in both ashes are reactive solids providing a pozzolanic activity to both ashes. This suggestion was evaluated by determining the pozzolanic activity as described in EN 196-5:2005 [14], which revealed that  $\text{Ca}(\text{OH})_2$  consumption, produced by the cement hydration, was performed for all the mixtures.



**Figure 4.** Pozzolanicity for all the mixes measured at several testing times (EN 196-5): (a) 1 day; (b) 3 days; (c) 7 days; (d) 14 days; (e) 28 days and (f) 90 days.

According to Hanehara et al. [22], the pozzolanic reaction at 20 °C of fly ash cement paste begins after 28 days of curing. As the pozzolanic reaction depends strongly on the temperature, pozzolanicity proceeds sooner at 40 °C. Moreover, they found that the coal fly ash reaction rate decreases when coal fly ash replacement increases.

According to Damidot et al. [23], when the coal fly ash is mixed in proportions above 25%, it provides only a filler effect, which corresponds to the suggested strätlingite formation. This fact also indicates that strätlingite has an insignificant contribution in the compressive strength of the cementitious material. In addition, it is well-known that the increase of coal ashes in the cement decreases the pH of the pore solution due to the  $\text{Ca(OH)}_2$  consumption by the pozzolanic reaction and alkalis reduction. This process is responsible for the loss of part of both ashes' reactivity. The alkalinity lowering of the cementitious material is known as self-neutralization [24].

Additionally, pozzolanicity was determined at 1, 3, 7, 14, 28 and 90 days for all the bottom ash-fly ash-cement mixes, as shown in Figure 4. The pozzolanic reaction at 40 °C began at the age of seven days for CEM IV/A (V), i.e., the mix with the highest content of ground coal bottom ash and/or coal fly ash (Figure 4). Thus, the greater increase of ash content showed the higher pozzolanic activity. This fact suggests that the amorphous aluminous and siliceous phases in both ashes are reactive solids providing a pozzolanic activity to both ashes. This suggestion was evaluated by determining the pozzolanic activity as described in EN 196-5:2005 [12], which revealed that  $\text{Ca(OH)}_2$  consumption, produced by the cement hydration, was performed for all the mixtures.

### *3.3. Pozzolanic Activity of Ground Coal Bottom Ash and Coal Fly Ash Mortars Determined by Means of the Strength Activity Index*

In order to compare the pozzolanicity results with the compressive strength activity index for both ashes, cement-ash mortars were made following the procedure described in EN 450-1 [15], replacing 25% of the mass of the reference cement with the coal fly ash ( $\beta$ ) or ground coal bottom ash ( $\Omega$ ). According to Argiz et al. [3], the 28-day compressive strengths obtained in standard mortars were 50.98 MPa (CEM I- $\alpha$ ), 40.78 MPa (CEM II/B-(V)- $\beta$ ) and 43.33 MPa (CEM II/B (V)  $\Omega$ ); whereas the 90-day compressive strengths were 55.55 MPa (CEM I- $\alpha$ ), 50 MPa (CEM II/B-(V)- $\beta$ ) and 60.55 MPa (CEM II/B (V)  $\Omega$ ). Therefore, the calculated strength activity indexes reached 80% and 85% at 28 days, and 90% and 109% at 90 days, for CFA and ground CBA, respectively. These values are over the upper limit established in EN 450-1 [15] of 75% and 85% for 28 and 90 days, respectively. However, higher strength activity indexes were reported in Reference [25].

A better performance of CFA than ground CBA was expected due to its more spherical shape and smooth texture (Figure 2). On the other hand, ground CBA grains have a significantly angular shape in the aftermath of grinding. Ball-shaped CFA and even surfaces enhance low interparticle friction and a significant mobility. As a result, the higher the content of CFA is, the better the plasticity in the cementitious mixture [26]. Conversely, coal fly ash has a higher content of  $\text{SO}_3$  and unburned carbon than ground coal bottom ash, which might boost the water requirement of CFA mortars [27,28]. Moreover, when the fineness of the coal fly ash is greater than that of the cement, such water demand might be increased as a result of the surface area rise. This effect could be the responsible for the compressive strength reduction [29,30].

In addition, coal fly ash cannot always control the consistency and workability of the cementitious material. Sometimes, the porosity, roughened surface and uneven form could be the responsible for a higher water demand in CBA and CFA [31]. Particle size distribution (PSD) is nonetheless one factor affecting the compressive strength of the cementitious products. Ash quality, together with its amount in the mix, also affects this parameter. In any case, and with the aim of using CBA effectively, they must be transformed. Given that, the grinding process is a form of improving the CBA reactivity as shown in Figure 4 [31–35].

Felekoğlu et al. studied the effect of coal fly ash grinding on mortar water demand to obtain a certain workability [36]. They suggested some interactions of the water demand and fineness with the compressive strength.

Jaturapitakkul et al. found that CFA particulates of 90–100 µm presented lower reactivity than the finer ones [37]. Hence, this grain size fraction is not recommended to be used in cementitious materials such as mortars and concretes. Several authors have found that enhancement of the reactivity can be achieved by grinding. Therefore, CFA but also CBA fineness will play an important role in the final compressive strength provided by the mortar or concrete [31]. For instance, high fineness classified coal fly ash has been used to make high-strength concrete [35,38]. Similarly, the grinding process applied to coarse CFA, as well as CBA, will enhance the fineness of the ashes. Thus, their pozzolanic reactivity will be promoted leading to being apt to be utilized in blended cement.

Jaturapitakkul et al. proposed that blended cement with 15%, 25%, 35% and 50% of ground CFA ( $d_{50} = 3.8 \mu\text{m}$ ) could be used to produce concrete with a high strength, whereas 25% of ground CFA achieves the highest compressive strength [37]. In a similar way, CBA could be ground to a controlled size to optimize its use in cement-based materials. Figure 4 provides useful information to come to the conclusion that ground CBA can be utilized to manufacture high-strength concretes.

#### 4. Conclusions

The following conclusions may be drawn from this investigation as regards the potential reactivity of ground coal bottom ash (GCBA):

1. GCBA has a pozzolanic performance in a similar manner to coal fly ash (CFA). Then, partial or total replacement of coal fly ash by ground coal bottom ash in Portland fly ash and pozzolanic cements does not have a significant effect on pozzolanic properties;
2. CFA reacts slowly with lime until 7 days. Reactivity increases at 14 days and, later on, at 28 days, the  $\text{Ca}(\text{OH})_2$  consumption sharply increases;
3. GCBA mixed with CFA is adequate to be standardized as new blended cement. Therefore, it is recommended to standardize the GCBA in the cement standards all around the world;
4. This experimental method provides reliable information about the quality of the coal bottom ash.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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