

# ÎMBUNĂȚIREA PROCESULUI DE ÎNTĂRIRE A CENUȘII REZULTATE LA ARDEREA ÎN PAT FLUIDIZAT A TURBEI ȘI LEMNULUI PRIN ADĂUGAREA DE ACTIVATOR ALCALIN ȘI CIMENT PORTLAND

## IMPROVING THE HARDENING OF FLY ASH FROM FLUIDIZED-BED COMBUSTION OF PEAT AND WOOD WITH THE ADDITION OF ALKALINE ACTIVATOR AND PORTLAND CEMENT

JANNE PESONEN<sup>1</sup>, JUHO YLINIEMI<sup>1</sup>, TOIVO KUOKKANEN<sup>2</sup>, KATJA OHENOJA<sup>1</sup>, MIRJA ILLIKAINEN<sup>1\*</sup>

<sup>1</sup>Faculty of technology, Fibre and Particle Engineering research group, P.O. Box 4300, 90014 University of Oulu, Finland

<sup>2</sup>Research Unit of Sustainable Chemistry, P.O. Box 3000, 90014 University of Oulu, Finland

*Combustion affects the physical and chemical characteristics of fly ash. Peat and biomass are typically combusted using fluidized-bed combustion (FBC) technique, which causes the fly ash to have a low chemical reactivity. Especially low-Ca FBC ashes have very weak hardening properties, which reduce their utilization potential in many applications. This study examined the effect of adding alkaline activator and Portland cement on the hardening of two peat-wood fluidized bed combustion fly ash samples—one of high-calcium fly ash (24.9 % Ca) and the other low-calcium fly ash (9.7 % Ca). The reactive components of the raw materials, the mineralogical compositions, and compressive strengths of the resulting mortars were studied. Significant improvement to strength development was achieved. The addition of Portland cement proved necessary for low-Ca ash to harden at all. The ash cannot be considered solely as a filler material, since the reactive component (Ca, Si, Al, and S) contents of the ash, especially the Ca content, affect the strength development. Strength development of the mortars can be partly explained by the Ca/(Si + Al + S) ratio and the sum of the reactive components.*

**Keywords:** fly ash, biomass, peat, Portland cement, alkaline activation, fluidized bed combustion

### 1. Introduction

Sustainable growth is a main priority in the current European Union (EU) growth strategy (Europe 2020) [1]. This strategy focuses on building a more competitive low carbon economy, protecting the environment, and the development of new green technologies. Key targets for sustainable growth include a 20% reduction in greenhouse gas emissions and 20% increases in both renewable energy sources and energy efficiency by the year 2020. In practice, this means that the EU will increase combustion of renewable biomass and therefore, the amount of produced biomass fly ashes will increase.

On the other hand, the European Waste Framework Directive (2008/98/EC) requires more efficient use of waste materials [2]. This directive introduced the concept of a waste hierarchy into European legislation. This waste hierarchy consists of five levels, or goals. The first level is preventing waste. If this is not possible, the next step is reuse, followed by recycling, and then energy recovery. Waste disposal is the last option—resorted to only if none of the previous steps are feasible. Thus, the waste produced in combustion of biomass and other fuels should be effectively used in different applications.

Combustion affects the physical and chemical

characteristics of fly ash [3,4] significantly, altering its potential for use in other applications. For coal, the most common technique is pulverized coal combustion (PCC) [5]; this involves a combustion temperature higher than 1200°C. When combined with a fast cooling process, this technique gives the fly ash a high chemical reactivity (i.e., pozzolanic activity) [4,5]. In contrast, peat and biomass are typically combusted using fluidized-bed combustion (FBC), which combusts at 800 to 1000°C. Thus, the ash from FBC combustion is considered to have less pozzolanic activity than PCC ash [6,7].

The high pozzolanicity of fly ash from PCC is well suited for concrete and alkaline-activated structures. Coal fly ash can be used to create structures that are as hard, or even harder, than those made with Portland cement [8–12]. Recent studies of the alkaline activation of coal fly ash and Portland cement blends [13] demonstrate that these gels are very complex. The products of ordinary Portland cement reactions (mainly calcium silicate hydrate, i.e., C-S-H gel) and alkaline-activation reactions (mainly amorphous alkaline aluminosilicate hydrate, i.e. N-A-S-H gel) do not form as separate gels but interact and change in structure and composition during the process [14].

Due to the low pozzolanic reactivity of biomass and peat FBC fly ashes, they are not well suited for high-strength concretes or geopolymers.

\* Autor corespondent/Corresponding author,  
E-mail: mirja.illikainen@oulu.fi

However, their high calcium content gives them self-hardening properties [15,16]. A common application of self-hardening is the granulation of biomass fly ash to reduce dust formation and improve the handling of ash fertilisers. Thus FBC biomass fly ashes proves a potential replacement material for soil stabilization [17–19].

Current soil-stabilization techniques rely on granular (gravel and sand) or cementitious materials (Portland cement and lime). Future development, however, focuses on partially substituting cementitious materials that fulfill the requirements of the specific soil through the use of industrial by-products. Because the self-hardening strength of FBC ashes is highly dependent on the fuels used it can vary significantly [16], however adding an alkaline activator or cement can increase its hardening. Few studies have been made concerning alkaline activation of FBC peat-wood ash [20,21]. Tyni et al. [21] characterized only the reaction products of alkaline-activated peat-wood ashes and did not study the strength development; Rajamma et al. [20] used only high-Ca wood ash, and not the peat-wood ashes used here. Neither of these studies tested the addition of Portland cement.

This study examined hardening improvements of two peat-wood FBC fly ash samples: High- (24.9 % Ca) and low-calcium fly ash (9.7 % Ca). In a previous study concerning self-hardening properties of these ashes, the strength of hardened high-Ca ash was quite low and the low-Ca ash did not harden at all [16]. This study evaluated whether the hardening of these low reactivity ashes could be increased by alkaline-activation and cement addition. Cement addition of 20 and 30 % was used, with sodium hydroxide used as an alkali activator and the reactive

components of the raw materials, the mineralogical compositions, and compressive strengths of the resulting mortars were studied.

## 2. Material and methods

### 2.1. Materials

The first of the two peat/wood fly ash samples used here came from a pulp and paper mill that uses bubbling fluidized-bed combustion (BFB) technique (WP ash) and the second from a thermal power plant that uses a circulating fluidized-bed (CFB) technique (PW ash).

Table 1 details the origin of the fly ash samples. No limestone is added in either plant, except that, in the first case, paper mill sludge containing CaCO<sub>3</sub> is periodically fed into the boiler. The exact proportion of the peat content in each case is not known but in the pulp and paper mill the approximate ratios are 30% peat and 70% (forest residue) wood (WP); in the thermal power plant the proportions are 70% peat and 30% wood (PW). The samples were collected from the first field of the electrostatic precipitators in 50 l containers.

The alkaline solution (SiO<sub>2</sub>/Na<sub>2</sub>O = 0.67, ρ = 1.2 g cm<sup>-3</sup>) used for the alkaline activation of fly ash was manufactured using a sodium silicate solution (27 % SiO<sub>2</sub>, 8 % Na<sub>2</sub>O, ρ = 1.35 g cm<sup>-3</sup>, Merck KGaA, Germany), NaOH pellets (p.a. ≥ 99 % Merck KGaA, Germany) and deionized water. The cement used in the mortars was white Portland cement (CEM I; Finnsementti, Finland).

The formulae for the alkaline solution and the fly ash mortars were adapted from those quoted by Palomo et al. [13] and Garcia-Lodeiro et al. [22]. Table 2 presents the formulae for the mortars containing 0–30% cement and 70–100%

Table 1

Fly ash sample names and details of the origin of the samples.

	WP	PW
Boiler type	BFB	CFB
Boiler capacity	246 MW	96 MW
Boiler bed temperature	854 °C	840 °C
Electrostatic precipitator unit	First	First
Approximate fuel mixture	70 % wood 30 % peat	70 % peat 30 % wood

Table 2

Formulae for the mortars. The abbreviations used are: WP = wood-peat fly ash; PW = peat-wood fly ash; PC = Portland cement; AA = alkaline activated; H = heat-treated.

Sample name		Fly ash (%)	Portland cement (%)	Alkaline activator	Water/binder ratio
Without heat treatment [22°C]	With heat treatment [60°C]				
WP100AA	WP100AA(H)	100	0	Yes	0.45
WP80PC20AA	WP80PC20AA(H)	80	20	Yes	0.45
WP70PC30AA	WP70PC30AA(H)	70	30	Yes	0.45
WP80PC20	WP80PC20(H)	80	20	No	0.47
PW100AA	PW100AA(H)	100	0	Yes	0.58
PW80PC20AA	PW80PC20AA(H)	80	20	Yes	0.58
PW70PC30AA	PW70PC30AA(H)	70	30	Yes	0.58
PW80PC20	PW80PC20(H)	80	20	No	0.62

fly ash; in some of these the alkaline activator was replaced with water (WP80PC20, WP80PC20(H), PW80PC20, PW80PC20(H)). The mortars were prepared by first mixing the dry matter thoroughly. This dry mixture was then slowly added to the liquid solution (alkaline solution + deionized water) while stirring continuously for 5 minutes. The amount of alkaline-activation solution was kept constant in every case and the amount of deionized water was chosen for good workability of the mortars. The fast setting of these mortars prevented studying their rheology. Directly after mixing the mortars were packed into cubic molds (35 x 35 x 35 mm) that were then placed in a closed curing chamber for 24 hours. The temperature of the curing chamber was either 22 or 60°C. The samples were then removed from the molds and stored in the curing chamber (at 22°C) for 7 or 14 days.

## 2.2. Methods

The sizes of the fly ash and Portland cement particles were measured with a Beckman Coulter LS 13320 and reported based on their volumetric-based median size ( $d_{50}$ ). Specific surface area measurements of the fly ash were based on the physical adsorption of gas molecules to a solid surface using a Micrometrics ASAP 2020 device and the results were reported as Brunauer–Emmett–Teller (BET) isotherms. The main chemical components of the fly ash and Portland cement were determined by X-ray fluorescence (XRF) in a melt-fused tablet produced from 1.5 g of fly ash melted with 7.5 g of X-ray Flux Type 66:34 (66%  $\text{Li}_2\text{B}_4\text{O}_7$  and 34%  $\text{LiBO}_2$ ). The hydraulic reactivity of the fly ash was assessed by a selective dissolution method, in order to determine the fraction of each component that is available for short-term hardening reactions. The reactive calcium, silica and aluminum were determined as the amounts found to be soluble in an ethylenediaminetetraacetic acid and triethanolamine solution having a pH of  $11.6 \pm 0.1$ . The Ca, Si and Al contents of the solution were determined using the inductively coupled plasma (ICP) technique [23–25]. Compressive strength was measured according to European cement standard EN 196–1 [26] using a Zwick Z100 Roell test machine with TestXpert II software. Compressive strengths were measured after 7 and 14 days of curing and the average of three individual measurements was taken in each case. The main crystalline phases of the powdered samples were identified with a Siemens 5000 X-ray diffractometer using  $\text{CuK}\alpha$  radiation (40 mA and 40kV) and a graphite monochromator. The step interval, integration time and angle interval used were  $0.04^\circ/\text{step}$ , 2.5 s/step, and  $10\text{--}60^\circ$ , respectively. X-Ray diffraction analysis was performed on the starting materials and on the

mortars after 14 days of curing. The International Centre for Diffraction Data (ICDD) database was used to identify the crystalline phases [27].

## 3. Results and discussion

### 3.1. Characterization of the ash and Portland cement

Table 3 shows the compositions of the ash and Portland cement. There is a clear difference in the compositions of the two ashes combusted with different fuel mixtures. The WP ash from the power plant burning forest residues in the BFB boiler produced higher Ca and S content and higher reactive Si, Al, and Ca content. The amount of reactive Ca in the WP was almost five times that in the PW. The Si and Al were mainly in unreactive forms in both ashes. The Portland cement contained mainly Ca and Si, which were, as expected, entirely in a reactive form, as was the Al. The reactivity of the Portland cement proves the suitability of the method chosen for testing reactivity of the ash. The average particle size ( $d_{50}$ ) in white Portland cement was close to 10  $\mu\text{m}$ , whereas in both fly ashes it was close to 20  $\mu\text{m}$ .

Table 3

Chemical composition and physical properties of the ash and white Portland cement samples.

	WP	PW	White Portland cement
$d_{50}$ ( $\mu\text{m}$ )	21.2	18.6	9.8
Surface area (BET) ( $\text{m}^2 \text{g}^{-1}$ )	4.6	4.6	
CaO (%)	25.8	9.7	68.1
$\text{SiO}_2$ (%)	29.5	47.9	23.7
$\text{Al}_2\text{O}_3$ (%)	11.6	9.7	2.0
$\text{Fe}_2\text{O}_3$ (%)	16.6	24.2	0.4
$\text{Na}_2\text{O}$ (%)	1.9	1.1	0.2
$\text{K}_2\text{O}$ (%)	2.0	1.3	0.1
MgO (%)	3.2	1.7	0.6
$\text{P}_2\text{O}_5$ (%)	3.6	2.5	0.2
$\text{TiO}_2$ (%)	0.3	0.2	0.0
$\text{SO}_3$ (%)	3.9	1.6	2.1
Cl <sup>-</sup> (%)	0.30	0.06	0.0
Reactive Si (%)	2.2	1.5	11.1
Reactive Al (%)	0.8	0.3	0.5
Reactive Ca (%)	14.4	3.1	48.6

### 3.2 Compressive strengths

The compressive strengths of the sample mortars are shown in Figure 1. High-Ca WP ash mortars provided better compressive strength. The strength increments in all mortars were quite small during second week of curing, except in mortar WP80PC20, which also had by far the highest 14-day compressive strength (13.6 MPa). Increasing the amount of Portland cement from 20% to 30% made a slight improvement in the 14-day compressive strengths. Mortar PW100AA, which contained no Portland cement, did not harden.

Oven treatment clearly reduced the strength of the mortars made from high-Ca WP

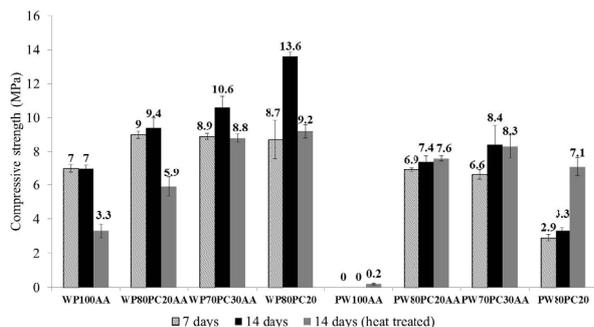


Fig 1 - Compressive strengths after 7 and 14 days of curing (MPa).

ash, but showed no effect on the compressive strengths of low-Ca PW mortars. On the other hand, the strength of mortar PW80PC20(H) more than doubled following oven treatment, which suggests that the heat treatment enhanced the cement reactions in the mortar. Heat treatment usually increases the mechanical strength of alkaline-activated coal fly ash [28,29], although Temuujin et al. [30] reported that adding Ca improved the mechanical strength of geopolymers cured at room temperature, but reduced this strength at elevated temperatures. They suggested that Ca reacts to form a calcium (aluminum) silicate hydrate phase at room temperature, which improves the dissolving of fly ash by increasing the pH, and thereby ensuring better geopolymerization. At elevated temperatures, rapid dissolving of calcium could cause it to become part of the aluminosilicate structure, which could reduce the mechanical strength of the structure. The difference in the reaction paths between room and elevated temperatures may explain the differences among the high-Ca mortars in our study. García-Lodeiro et al. [22] also suggested that the N-A-S-H gel interacts with Ca over time, leading to the formation of a C-A-S-H gel, which requires a sufficient amount of Ca.

Our compressive strengths compare favorably to the results obtained by Rajamma et al. [20], who studied the alkaline activation of biomass ashes (6.65–11.69 MPa), but they are clearly lower than those for coal ash (20 MPa and over) [13, 22, 30]. This was expected, since the ash from FBC combustion is generally considered to have less pozzolanic activity than coal ash from PCC [6,7]. The compressive strength of self-hardened samples (mixed only with water) prepared from these same types of fly ashes was much lower: 0.06 MPa for PW fly ash and 2.6 MPa for WP fly ash. Thus, adding cement and alkaline activation provided a significant improvement [16]. The PW ashes did not harden in the self-hardening study. These new results show that the addition of Portland cement is needed to get low-Ca PW ash to harden at all.

The strengths of the mortars (14 days) as a function of reactive Ca, Si, Al, and S are shown in

Figs. 2–5. A strong correlation was found with the compressive strength of reactive Ca (Fig. 2). The reactive Si content exhibited a moderate positive correlation with the compressive strength, and reactive Al showed a quite strong positive correlation. The total S content showed a moderate positive correlation. Compressive strengths (14 days) of sample mortars as a function of the ratio between reactive Ca and the sum of the reactive (Al + Si + S) are shown in Figure 6. The strong positive correlation with the reactive component ratios demonstrates that, as the amount of reactive Ca increases (compared to the other reactive components) the compressive strength increases. There is probably some optimum value to this ratio after which the compressive strength starts to decrease. In Portland cement the ratio between Ca and other reactive components is almost 4. In our study, the ratio for the mortar with the highest compressive strength (WP80PC20) was close to 3.5. However, the total sum of reactive components (Fig. 7) also influences the strength development of the mortars. For example, the one clearly abnormal result (PW20PC80), shown in Figure 6, is explained by the low sum of the reactive components in the mortar (Fig. 7). So, in addition to having the reactive components in correct proportions, there must be a sufficient quantity of the reactive components in the mortars.

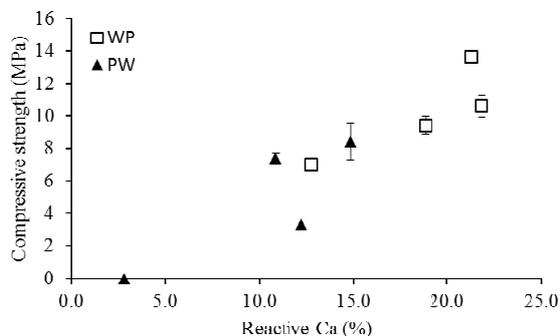


Fig. 2 - Compressive strengths (14 days) of sample mortars as a function of reactive Ca.

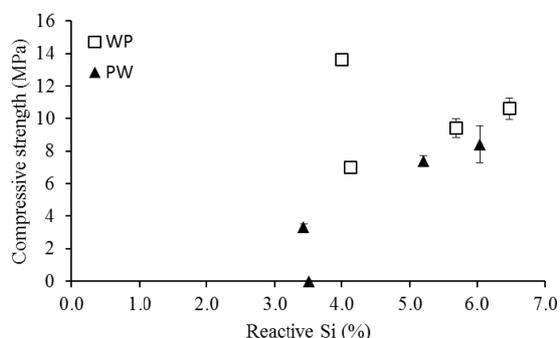


Fig. 3 - Compressive strengths (14 days) of sample mortars as a function of reactive Si.

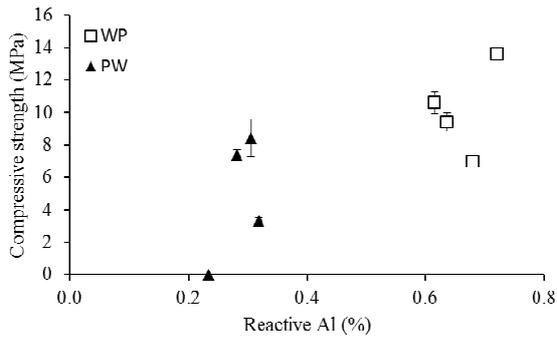


Fig. 4 - Compressive strengths (14 days) of sample mortars as a function of reactive Al.

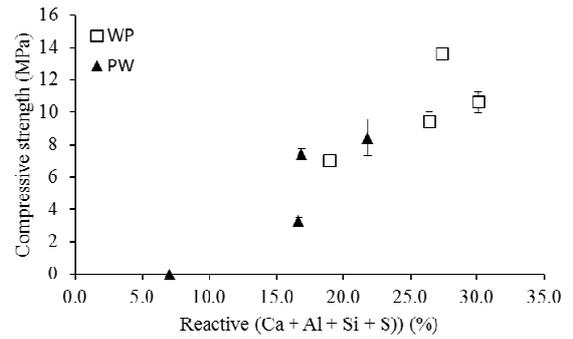


Fig. 7- Compressive strengths (14 days) of sample mortars as a function of the sum of reactive components (Ca + Al + Si + S).

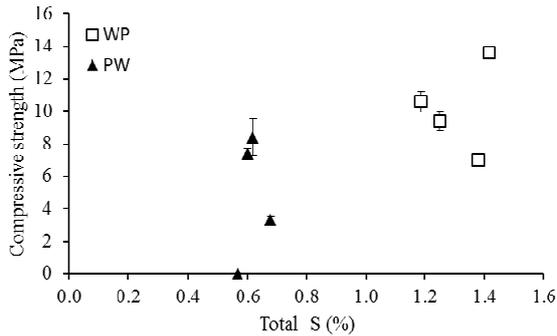


Fig. 5 - Compressive strengths (14 days) of sample mortars as a function of total S.

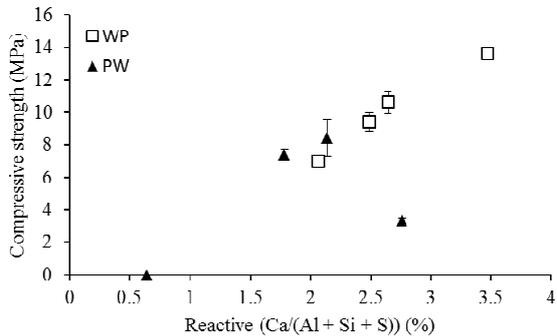


Fig. 6- Compressive strengths (14 days) of sample mortars as a function of the ratio reactive (Ca/(Al + Si + S)).

The mortars studied here are complex. The reactive components come from three different sources (ash, Portland cement, and alkaline activator) and it is difficult to predict how these precursors interact with each other and which reaction products are formed during the hardening process. Still the strength development of the mortars can be explained, at least to some extent, by simple correlation plots. Also the hardening of both low- and high-Ca FBC fly ash can be improved by adding Portland cement and alkaline activator. Note that the addition of Portland cement and alkaline activator do not entirely explain the strength development, as the reactive components in the ash, especially Ca, affect the strength development. The ash cannot be considered solely as a filler material. Also note that the alkaline activator solution used was highly basic (pH over 14) compared to the pH (11.6) of the solvents used for reactive component determinations. The high alkalinity probably allows the alkaline activator solution to dissolve more Ca, Al, and Si than is indicated by the reactive component determinations, which could affect these correlation plots.

### 3.3. XRD analysis

Figure 8 shows examples of the XRD diffractograms. Most of the binders produced in

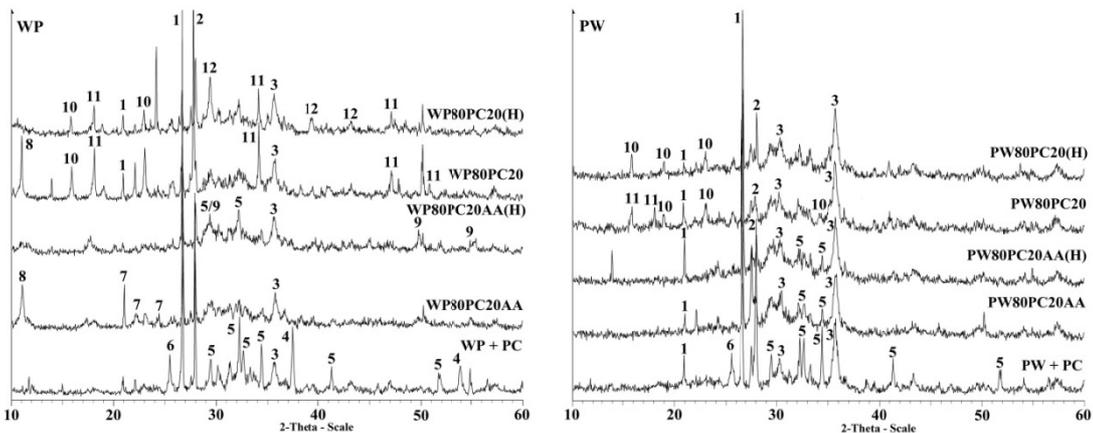


Fig. 8 - XRD diffraction data for fly ash + Portland cement (PC) mixes and the sample mortars after 14 days of curing: 1 = quartz, 2 = anorthite, 3 = maghemite, 4 = lime, 5 = alite 6 = anhydrite, 7 = sodium aluminum sulfate, 8 = hydrated calcium aluminat (AFm), 9 = calcium silicate hydrate (CSH), 10 = ettringite, 11 = portlandite, 12 = calcite.

this study contain a high percentage of amorphous to semi-crystalline materials, which are difficult to identify with XRD method.

The crystalline phases identified in the mixtures of fly ash (WP and PW) and Portland cement (PC) were quartz, anorthite, maghemite, anhydrite, and alite. Lime was also found in the mixture of WP and PC. A small halo, indicating amorphous material, was detected between 25° and 38° in both ash types.

After 14 days of curing, anhydrite, lime, and alite were mostly consumed from the high calcium WP mortars. In mortar WP80PC20 we detected sodium aluminum sulfate and some form of hydrated calcium aluminate (AFm). This AFm phase also appeared in mortar WP80PC20AA. The AFm phase is a typical reaction product in hydrated cement, but due to the low crystallinity, polytypism, and variations in composition, it proves difficult to analyze [31] and the exact form of the species could not be confirmed. The AFm phase was detected only in the mortars treated at room temperature, including sample WP100AA, which did not contain any Portland cement. This suggests that this phase formed as a result of a self-hardening reaction of the high-Ca ash.

In the oven-treated mortar WP80PC20(H), some crystalline CSH was detected. Ettringite and portlandite were detected in mortar samples WP80PC20AA and WP80PC20AA(H), and calcite was also detected in mortar WP80PC20AA(H).

A halo between 26° and 37° was detected in all WP sample mortars after 14 days of curing, indicating the formation of amorphous phases. This halo was roughly the same size in all cases. The N-A-S-H gel in geopolymers is usually detected as a broad halo between 20° and 40°, whereas in cement the C-S-H and C-A-S-H signals are a broad peak at 30° [32-34]. No clear C-S-H/C-A-S-H signal was found in the present WP mortars; instead, the halo was broadly distributed, indicating geopolymer phases.

Most of the anhydrite and alite phases were consumed from the low-calcium PW mortars after 14 days of curing. No product signals were detected in the alkaline-activated mortars (PW80PC20AA, PW80PC20AA(H)). Ettringite was detected in mortars PW80PC20 and PW80PC20(H), and portlandite in PW80PC20. A visible halo, between 25° and 38°, was detected in all PW sample mortars, indicating geopolymer phases. The halos were approximately the same size in all mortars.

Ettringite, portlandite, and calcite were only detected in the mortars without any alkaline activator content. All these phases typically form during the self-hardening of fly ash and cement hydration, so their presence was expected [16,35-37]. Their absence in the mortars containing alkaline activator suggests that the presence of the activator prevents their formation. Mainly

amorphous phases were detected in hybrid cements of coal fly ash in the experiments of Garcia-Lodeiro et al. [22] and Palomo et al. [13]. Martinez-Ramirez and Palomo [38] concluded that highly alkaline media retard normal Portland cement reactions. This could partly explain why the strength of high-Ca WP ash mortars decreases with the addition of alkaline activators. However, the ratio between Ca and other reactive components also changes, and this could be a reason for the decrease in strength. Furthermore, mortars based on FBC ashes differ significantly from PCC fly ash or slag based mortars, which consists almost entirely of reactive components. In this study, the addition of Portland cement and sodium silicate solution increased the amount of reactive components in the mortars, increasing the strength. Thus, observations made from the behavior of those reactive precursors do not necessarily apply to these less reactive FBC ashes. The component that contributes the most to increasing the strength of Portland cement is the CSH gel and, in geopolymers, the NASH gel, which are difficult to recognize in XRD diffractograms. NASH gel does not include any Ca, which the compressive strength data suggests plays a significant role in the strength development of the studied mortars. This means amorphous CSH gel should be produced, even though it cannot be detected from the diffractograms. There could also be other Ca-containing amorphous phases formed.

#### 4. Conclusions

Adding Portland cement and alkaline activator can significantly improve the strength development of both low- and high-Ca FBC peat-wood fly ashes. For low-Ca ashes it is necessary to add Portland cement for it to harden at all. Portland cement and alkaline activator addition do not entirely explain the strength development, as the reactive components in the ash, especially Ca, affect the strength development. Thus, the ash cannot be considered solely as a filler material. The strength development of the mortars can be explained, at least to some extent, by the Ca/(Si + Al + S) ratio and the sum of the reactive components.

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