Mechanical Activation of the Ca-Rich Circulating Fluidized Bed Combustion Fly Ash: Development of an Alternative Binder System

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Abstract: Mechanical activation of the calcium-rich fly ash formed in circulating fluidized bed combustion (CFBC) boilers was investigated to enhance the compressive strength performance of the pastes. We studied the effect of the activation on the physical, chemical, and mineral characteristics of fly ash and its pastes. Our study shows that already a short mechanical activation yields a 10-fold improvement in the compressive strength of the pastes, reaching 60 MPa after 90 days of curing without any chemical activation or blending. Mechanical activation caused fragmentation of large porous aggregates in the raw ash enhancing the physical properties and reactivity of fly ash particles. Similarly to calcium sulfoaluminate cements, the mechanical strength was provided by the formation of abundant ettringite and possibly C-(A)-S-H gel-like phase that created a highly compact microstructure. Our findings suggest that mechanically activated Ca-rich CFBC fly ash can be successfully used as an alternative binder.

Keywords: fly ash; grinding; compressive strength; ettringite; calcium-silicate-hydrate (C-S-H); waste utilization

1. Introduction

Notwithstanding the increasing pressure to reduce cement clinker production, the second largest industrial CO₂ emitter [1], the demand for cement and concrete remains high in general construction practices and is predicted to grow by more than 20% in the coming decades [2]. To overcome these issues, research and innovation in the cement and concrete field has been aimed at making radical changes towards sustainable concrete usage and to find suitable less greenhouse gas-intensive replacements [3]. There are several ways to reduce classical cement clinker usage, including its partial or full replacement with supplementary cementitious materials and/or the development of alternative binders with smaller CO₂ footprint than that of cement clinker production [1,4]. Fly ash, along with granulated blast furnace slag, has been a widely used supplement to cement clinker [5] with high potential for reduction of greenhouse emissions [6]. Over 90% of granulated blast-furnace slag produced worldwide is recycled in cement and concrete, but the utilization rate for fly ash is only 30%, mainly due to its largely variable properties resulting from the use of different fuels and firing technologies [7].

Siliceous-glass rich low-calcium fly ash (also known as Class F ash) with considerable pozzolanic properties upon hydration is the main supplement used in blends with cement [5,6], but it can also be used as a raw material for alkali activated materials with a potential to substitute cement clinker [8]. High-calcium fly ashes (Class C ash) that form mostly by firing of lignite or sub-bituminous coal are characterized with high free CaO content and show both pozzolanic and self-cementitious properties, also being a suitable additive in
composite cements [9,10]. However, Class C ashes have a highly variable chemical and phase composition [11], that thus impedes their usability in the construction field.

The phase composition of fly ash that largely determines its activity, depends on the raw fuel composition and on the combustion temperature [12]. Additionally, during fluidized-bed combustion, in most cases also desulfurization additives are used, which affect the chemical and mineral composition of the ash [12]. The conventional high temperature (in excess of 1200 °C) pulverized combustion boilers have gradually been replaced worldwide by the more energy efficient low SO\textsubscript{2} and NO\textsubscript{x} emission circulating fluidized bed combustion (CFBC) boilers operating at 750–900 °C since the 1990s and early 2000s [13–15]. More than 14 million tons of fluidized bed combustion fly ash is generated annually in United States [16] whereas in Europe only in Estonia utilizing calcareous oil shale in power plants ca. 6–7 million tonnes of CFBC ash is produced annually [17]. CFBC technology allows efficient firing of low quality Ca and S rich fuels, but the variability of their chemical and phase composition as well as lower pozzolanic activity and the high content of free CaO and SO\textsubscript{3} limits the wider use of CFBC ash in cement and concrete composition [5,10,12,14,18–21].

Nevertheless, the evergrowing need for supplementary cementitious materials [22] drives the interest in the beneficiation of potentially cementitious materials such as CFBC ashes that do not meet the desired specifications, but the properties of which can be improved, for example, by blending, classification-separation, chemical passivation, and thermal beneficiation [23]. In addition, the mechanical activation of fly ash by grinding is one of the simplest measures increasing its surface area and thereby causing a surge in fly ash reactivity [24–26]. The aim of this contribution is to study the effect of mechanical activation on the cementitious properties the Ca-rich CFBC fly ash. We show that only even a short period of mechanical activation results in a nearly tenfold increase in the uniaxial compressive strength of the pastes made with Ca-rich oil shale fly ash.

2. Material and Methods

2.1. Circulating Fluidized Bed Combustion Ash

Fresh unhydrated fly ash material was obtained from the ash separation system at Balti Thermal Power Plant CFBC boiler No. 8 in Estonia, which uses oil shale as primary fuel. This CFBC boiler replaced the earlier pulverized combustion boilers in 2004. Approximately 60% of the total ash is separated as fly ash, most of it at electrostatic filters.

The Estonian energy sector relies mainly on thermal power plants fueled with large quantities of oil shale (>10 Mt annually). Oil shale is a Ca-rich solid fuel of low calorific value with ca. 40–50 wt% of the processed shale remaining as Class C ash, majority of which (≈98%) becomes landfilled [17]. Fly ash from the earlier pulverized combustion boilers was successfully used as an additive to Portland cement, but the low temperature oil shale CFBC ashes do not meet the required criteria because of weak pozzolanic and self-cementitious properties [27–29]. Raw oil shale ashes have been also studied for alkali activated material design in recent years but without significant success [30–34].

2.2. Mechanical Activation

The mechanical activation of fly ash was done in a dry state with a planetary ball mill (RETSCH PM100), using ten 20-mm size steel grinding balls in a 500 mL steel grinding jar. Ash was dry milled for 2, 3, 4, 6, and 8 min at a rotation speed of 500 rpm in 0.5 kg batches. The efficiency of the grinding process in the ball mill decreased with milling times exceeding 6 min as the material started to clump to the grinding balls and the sides of the containers.

Particle size analysis was performed with raw and milled (for 2, 4, and 8 min) ash samples using a laser diffraction particle size analyzer (Malvern Mastersizer 3000 + Hydro EV). Ethanol was used as a dispersant and the samples were continually ultrasonicated during measurements. Specific surface area was measured by BET analysis (Micrometrics Flex3) of raw, 4 and 8 min milled fly ash.
Pastes of raw ash and milled ash were mixed with different water/ash ratios (0.35, 0.4, 0.45, 0.5, and 0.55), poured into 50 × 50 × 50 mm molds in three replicas and placed on a vibrating plate for 1 min. At water/ash ratios < 0.35 the workability of pastes was not sufficient to allow the homogenous mold filling. The mixing was performed in a laboratory environment at the average ambient temperature of 22 °C and relative humidity of 50–60%. The samples were then left to cure under the same conditions in an open air environment for 7 days for all samples and 28 and 90 days for ash mixtures activated for 4 min.

2.3. Uniaxial Compressive Strength Test

The uniaxial compressive strength of pastes was measured under continuous loading (20 kPa·s⁻¹) until the specimen broke. Compressive strength was measured in three replicas after 7 days for all samples and, in addition, after 28 and 90 days of curing for raw ash paste and pastes made of ash milled for 4 min. Relative standard deviation (RSD) of compressive strength measurements for replicas was typically <5%.

2.4. X-Ray Fluorescence Spectrometry Analysis

The chemical composition of the raw ash was determined by means of X-ray fluorescence spectrometry on a Rigaku Primus II XRF spectrometer using the SQX quantification model with RSD better than 5%. The thermogravimetric (TGA) and differential thermal analysis (DTA) of raw ash, ash pastes of raw ash, and ash milled for 4 min and cured for 90 days was performed on an STA 449 F3 Jupiter thermal analyzer in Al₂O₃ crucibles by heating to 1000 °C at 10 °C min⁻¹.

2.5. Infrared Spectroscopy Analysis

The Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) patterns of raw ash, pastes of raw ash, as well as ash milled for 4 min and cured for 28 and 90 days were measured by using a “Smart Orbit” diamond ATR-microanalyzator attached to a Thermo Scientific Nicolet 6700 FT-IR spectrometer with CsI optics and DLaTGS detector. Transmittance IR spectra were collected from 225–4000 cm⁻¹ at a resolution of 4 cm⁻¹ with 256 scans per sample.

2.6. X-Ray Diffraction Analysis

The mineral composition of raw ash and pastes after 7, 28, and 90 days was determined in selected samples by means of X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer in randomly oriented pressed powder samples, using Ni-filtered CuKα radiation and LynxEye linear detector over the 2–70° 2θ region. The mineral composition of samples was interpreted and modeled using the Rietveld algorithm based code Topaz 4.0. Amorphous phase (glass) content was determined by spiking the samples with 10 wt% ZnO prior to measurement. The amorphous phase content was calculated from the difference between the added and measured ZnO spike, assuming that the apparent lower ZnO content is caused by the adsorption of X-rays by the amorphous phase. The relative error of quantification was better than 10% for major phases (>5 wt%) and better than 20% for minor phases (<5 wt%).

2.7. Electron Microscopy Analysis

The microstructure and chemical composition of raw ash and pastes were investigated using Zeiss EVO15MA SEM with Oxford X-MAX energy dispersive detector. Samples were investigated in freshly broken surfaces in high vacuum mode with 4–5 nm thick Pt coating, and in polished slabs with 10 nm thick carbon coating.

3. Results

3.1. Grain Size and Specific Surface Area of Raw and Activated Ash

The characteristic grain size distribution patterns of raw ash and activated ash as a function of milling time are shown in Figure 1. The average specific surface area of the raw and mechanically activated ash is given in Figure 2. The raw ash is characterized by
a nearly normal grain size distribution with mean grain size of 43 µm (average $d_{10}$ 10 µm, $d_{50}$ 43 µm, $d_{90}$ 115 µm). Under scanning electron microscope (SEM) the raw CFBC ash is fine–medium grained with particle sizes typically less than 100 µm (Figure 3A,B). The material is dominated by irregular-flaky porous lumps and aggregates of 50–80 µm. Spherical cenospheres scattered throughout the material are typically 1–20 µm in diameter, although spherical particles of up to 50–100 µm are occasionally found (Figure 3A). In some larger lumps the surface is covered in (fused) crusts, few µm thick (Figure 3B).

Grinding in a planetary ball mill causes the breaking up of easily friable large lumps into sub-µm fine particles. However, most of the small (<10 µm) cenospheres retain their integrity and only the large sized lumps are shattered into irregular pieces (Figure 3C,D). Milling causes a rapid shift in favor of finer particles in grain size distribution, resulting in a twofold reduction in coarser particles (>20 µm) and a substantial increase in particles <1-µm size (average $d_{10}$ 0.25 µm, $d_{50}$ 7.2 µm, $d_{90}$ 7.06 µm). The particle size reduction
increased slowly with milling time (Figure 1) but larger particles (aggregates) started to appear at milling times exceeding 6 min due to particle agglomeration in ground ash material [35]. The loss in milling efficiency is also evident from the changes in ash-specific surface area showing only a slight increase (less than 5%) in the specific surface area with 8 min milling time compared to 4 min. The specific surface area increases from 2.5 m² g⁻¹ in raw ash to 4.7 and 4.9 m² g⁻¹ after 4 and 8 min, respectively (Figure 2). Though the larger particles form in prolonged milling the total BET surface still remains higher than in raw ash probably because these agglomerated large lumps are still internally microporous.

![Figure 3. SEM backscattered electron images of the raw ash (A,B) and 8 min milled ash (C,D). White triangles indicate dense Ca-sulfate crusts on some particles.](image)

3.2. Chemical and Mineral Composition of the Raw and Activated Ash

The chemical composition of raw and mechanically activated fly ash is dominated by SiO₂ and CaO, on average constituting 35.1 and 29.8 wt%, respectively (Table 1). The average content of MgO, Al₂O₃, and Fe₂O₃ in raw ash is 5.1, 8.5, and 4.0 wt%, respectively. Similarly to all CFBC ashes, fly ash shows high sulfur content, expressed as SO₃ (an average of 6.7 wt%).

The mineral composition of the crystalline phases of fresh and activated fly ash (Figure 4) is dominated by terrigenous primary silicate phases remaining largely unaltered during firing: quartz (16 wt%), K-feldspar (11 wt%), and K-mica (7 wt%). Incomplete decarbonation characteristic to CFBC ashes [36] is indicated by the presence of residual calcite (10 wt%), although dolomite that starts to decompose at >550 °C [37] was not detected. Instead, periclase (MgO) and lime (CaO) are present on average 4 and 8% wt%, respectively. The content of Ca-sulfate mineral anhydrite is ca. 9 wt%, whereas the content of secondary Ca- and Ca-Mg silicates (belite [C₂S], akermanite and merwinite) is 8, 5, and 3 wt%, respectively. The estimated amount of amorphous silicate glass phase varies in raw and activated
ash between 15 and 20 wt%, with the average of 17 wt%. Mechanical activation does not show any significant effect on the mineral composition of the ash and the intensity and the shape of diffraction peaks on X-ray diffraction patterns of raw and activated ash match to each other (Figure 4).

![Figure 4](image)

**Figure 4.** Representative XRD patterns of the raw and 4 min mechanically activated ash and activated ash pastes after 28 and 90 days of curing. Legend for major peaks: Ak—akermanite; Anh—anhydrite; Ca—calcite; C2S—belite; Et—ettringite; Hem—hematite; Kfs—K-feldspar; L—lime; P—portlandite; Per—periclase; Q—quartz; Z—zinc oxide. ZnO spike was added to estimate the amorphous phase content.

Table 1. The chemical composition of raw and mechanically activated ash, wt%. L.O.I.—Loss on ignition at 950 °C.

|       | SiO₂ | Al₂O₃ | TiO₂ | Fe₂O₃ | MnO | CaO | MgO | Na₂O | K₂O | P₂O₅ | SO₃ | L.O.I. |
|-------|------|-------|------|-------|-----|-----|-----|------|-----|------|-----|-------|
| Raw   | 35.19| 8.47  | 0.49 | 3.98  | 0.06| 29.81| 5.07| 0.11 | 4.25| 0.15 | 6.74| 4.71  |
| Activated | 35.12| 8.49  | 0.44 | 3.93  | 0.06| 29.87| 5.04| 0.10 | 4.25| 0.14 | 6.77| 4.94  |

3.3. Uniaxial Compressive Strength

The uniaxial compressive strength of the ash pastes of raw ash and milled ash mixed at different water/ash ratios (0.35, 0.4, 0.45, 0.5, and 0.55) and cured for 7 days are shown in Figure 5. The compressive strength of raw fly ash pastes and the pastes made with ash grinded for 4 min and cured for 7, 28, and 90 days is shown in Figure 6 and Table 2.
Figure 5. Uniaxial compressive strength of the ash pastes of raw ash mixtures and pastes made with milled ash for 2, 3, 4, 6, and 8 min mixed at different water/ash ratios (0.35, 0.4, 0.45, 0.5, and 0.55) and cured for 7 days. Note a significant drop in compressive strength in the pastes with activated ash at higher water/ash ratios.

Figure 6. Compressive strength of raw fly ash pastes and the pastes made with ash grinded for 4 min, mixed at different water/ash ratios (0.35, 0.4, and 0.45) and cured for 7, 28, and 90 days. The mechanical activation shows a significant positive effect on compressive strength of the pastes already after 7 days of curing. The relative increase in compressive strength is more pronounced after 28 days. Further increase by 90 days of curing is less than 10% of the final strength.
Table 2. Compressive strength (MPa) of the activated (M) and raw (R) ash mortars after 7, 28, and 90 days of curing. The value after the dash in sample name indicates the water/ash ratio.

|        | Activated Ash | Raw Ash |
|--------|---------------|---------|
|        | M-0.3         | M-0.35  | M-0.4 | R-0.4 | R-0.45 | R-0.5 |
| 7 days | 11.4          | 29.2    | 17.9  | 1.8   | 2.1    | 1.7   |
| 28 days| 20.5          | 54.2    | 44.4  | 4.8   | 4.9    | 4.6   |
| 90 days| 17.5          | 62.2    | 48.0  | 7.1   | 8.4    | 9.5   |

The uniaxial compressive strength of raw ash mixtures after 7 days of curing varied between 1 and 2.4 MPa on average, with slightly higher compressive strength corresponding to higher water/ash ratios (Figure 5). A mechanical activation period of only 2 min in a planetary ball mill improved the compressive strength of ash pastes by an order of magnitude reaching 20.3 MPa in the mixture with water/ash ratio of 0.35. The pastes with the same water/ash ratio but different grinding time achieved compressive strengths 22.4, 29.2, 28.1, and 25.0 MPa for 3, 4, 6, and 8 min grinding time, respectively (Figure 5). Similarly to ordinary cement, the compressive strength of ash–water mixtures is sensitive to water/ash ratio, with compressive strength values dropping exponentially with higher water content. However, even at the highest water/ash ratio (0.55) the compressive strengths of mechanically activated pastes are at least twice as high as those of raw ash pastes. The highest compressive strength was obtained with ash milled for 4 min, whereas the value was lower in ashes milled for 6 and 8 min. This is evidently due to the loss in milling efficiency and the formation of large agglomerated particles at longer milling times, noticed in grain-size analysis.

The compressive strength of raw ash pastes remained low with only a slight increase (on average 4.9 MPa) after 28 days of curing (Figure 6). In contrast, the strength in pastes made with ash activated for 4 min continued to increase significantly, on average yielding values of 44.4 and 54.2 MPa in mixtures with water/ash ratios 0.4 and 0.35, respectively (Figure 6). The mixture with 0.35 water/ash ratio achieved uniaxial compressive strength of 62.2 MPa after 90 days of curing. A similarly slight increase in compressive strength values was observed in the activated ash mixture with the water/ash ratio 0.4 between 28 and 90 days. The maximum compressive strength in raw ash pastes yielded 9.5 MPa after 90 days (Figure 6).

3.4. Phase Composition and Microstructure of Ash—Water Pastes

The phase composition of raw and activated ash in pastes is significantly different from the initial raw ash (Figure 2) due to a series of hydration reactions. Upon hydration, the lime CaO free disappears and Ca(OH)₂ phase (portlandite) appears after curing for 7 days. The 8.5 wt% anhydrite content of fresh raw ash disappears completely in activated ash mixtures already after 7 days of curing, but persists in raw ash mixtures in a small amount (ca. 1–2 wt%) for 90 days (Figure 7). The dissolution of anhydrite is accompanied by the formation of the secondary hydrous Ca-Al sulfate phase—ettringite. The content of ettringite after 7 days of curing reached ca. 15–17 wt% and remained nearly at the same level for 90 day curing period. A significant change occurred in the estimated amorphous phase content. In fresh raw ash, the content of the amorphous phase is 15 wt% on average, increasing to nearly 40 wt% in raw ash mixtures after 7 days, but dropping to 30 wt% and further to about 12 wt% after 28 and 90 days of curing, respectively (Figure 7). In mechanically activated mixtures the share of amorphous phase increased to a maximum of 45 wt% after 28 days of curing, decreasing to about 32 wt% after 90 days.

ATR-FT-IR spectra of raw and activated ash, and raw ash and activated ash—water pastes after 28 and 90 days are shown in Figure 8. ATR-FT-IR spectra are characterized by a prominent band at around 1411 cm⁻¹ representing C-O stretch, a band at 876 cm⁻¹ corresponding C-O out-of-plane bend, and a 712 cm⁻¹ band representing C-O in-plane bend in CO₃²⁻ ion, respectively, suggesting the presence of calcite, which is also evident in the XRD analysis of the studied materials. The emerging shoulder at 1101 cm⁻¹ and the low
intensity but distinctive bands at 594, 611, and 670 cm\(^{-1}\) in the raw ash spectrum correspond to the stretching and bending of S–O bond in SO\(_4^{2-}\) ion in Ca-sulfate mineral anhydrite [38]. The bands between 400 and 1200 cm\(^{-1}\) indicate Si functional groups in silicate mineral phases. The bands at 796 and 777 cm\(^{-1}\) correspond to Si-O vibrations of quartz. The broad band with the maximum around 973 cm\(^{-1}\) in the raw and activated ash spectrum is a combination of Si-O vibrations from different silicate phases present in the material. It can be associated with Si–O–Si (Si–O–Al) asymmetric stretching vibrations in SiO\(_4\) tetrahedra [39], possibly representing Q\(^2\) silicon sites.

**Figure 7.** Mineralogical composition of raw ash and ash and water mixed raw ash and mechanically activated (4 min) pastes after 7, 28, and 90 days of curing. Terrigenous minerals—quartz, K-feldspar, mica/muscovite; calcite; lime; portlandite; Ca/Mg-silicate—C2S, merwinitie, akermanite; ettringite; anhydrite; others—hematite, gypsum, anhydrite.
Figure 8. Representative ATR-FTIR spectra of raw and mechanically activated ash and ash pastes made with raw ash and activated ash (4 min) after 28 and 90 days of curing.

ATR-FT-IR spectra of ash–water pastes after 28 and 90 days (Figure 8) show remarkable changes, when compared to raw ash. Bands occurring at around 3300–3400 and 1640 cm\(^{-1}\) correspond to O–H stretching and bending vibrations in water molecules, while the sharp band at ca. 3640 cm\(^{-1}\) is characteristic of O–H stretching in portlandite [Ca(OH)\(_2\)]. This band also appears in activated ash spectrum indicating beginning of the lime hydration in samples kept under open air conditions. The dissolution of anhydrite in hydrated pastes is indicated by the absence of characteristic anhydrite bands near 595, 611, and 680 cm\(^{-1}\). Instead, the broad and intense band at about 1090 cm\(^{-1}\) appears, constituting a combination of Si–O stretching vibrations from silicate phases associated with Q\(_3\) silicon sites \([40]\) and S–O vibrations in SO\(_4^{2-}\), arising from different sulfate minerals such as gypsum and most probably ettringite, also detected in XRD analysis. In addition, the formation of ettringite is confirmed by the presence of Ca–O and Al–O vibrations originating from the columnar arrangement of Al(OH)\(_6\) octahedrons and CaO\(_8\) polyhedrons in ettringite at ca. 540 and 615 cm\(^{-1}\). A broad band at 973 cm\(^{-1}\) in raw ash resulting from the vibrations of Si–O–Si grows in intensity and sharpens in pastes with mechanically activated ash (Figure 8). The position of this band shifts to lower the wavenumbers at 958–960 cm\(^{-1}\) in all pastes after 28 and 90 days of curing. This indicates that the initially formed structures possibly deformed in time, resulting in the replacement of the bridging oxygen atoms in the initial alumina-silicate phase with two nonbridging oxygen atoms with a negative charge. It could also indicate that Al is possibly substituted into the silicate network \([41]\).

The TG analyses of raw and activated ash and pastes with raw and activated ash agree with the XRD and ATR-FTIR data. The thermal effects in raw and activated ash (Figure 9) are associated with the evaporation of minute amounts of free water and with the decomposition of calcite at 600–850 °C \([42]\). The calcite decomposition starts at ca. 20–25 °C lower temperature in activated ash compared with raw ash that is probably due to
a finer grain size in the latter. In pastes made with raw ash and the activated ash the TGA lines with higher mass loss at temperatures over 100 °C can be associated with the decomposition of ettringite [43], whereas the mass loss is slightly higher in pastes made with raw ash (Figure 9). The characteristic mass loss at around 400–450 °C is associated with the dehydroxylation of Ca(OH)$_2$, which is higher in the paste made with raw ash as well. The mass losses at around 700 °C can be assigned to CO$_2$ escape, mainly from calcite [43,44]. While the identification of C-S-H-type phases is complicated in TGA analysis due to the multitude and overlapping phases in ash pastes, the mass loss without clear peaks between temperatures 125–275 °C could be tentatively attributed to C-S-H or other possible X-ray amorphous phases [43,45].

![Figure 9. Representative curves of thermogravimetric (TGA) analysis of raw and mechanically activated ash and pastes with raw ash, and activated ash (4 min) after 90 days of curing.](image)

The SEM analysis of raw ash pastes shows a granular and porous aggregate with large pore space partly filled with well-developed hexagonal portlandite crystals embedded in fine meshes of submicron-sized needle-shape crystallites of ettringite (Figure 10A,B). The microstructure of pastes made with mechanically activated ash is significantly different from that of raw ash pastes (Figure 10C–G). The material is compact and gel-like to very fine-grained masses fill the area between unreacted ash and glassy cenospheres and their fragments. The occasional pores (e.g., broken cenospheres, Figure 10E) are filled with lath-shaped ettringite crystals. Glassy cenospheres show thin alteration rims of only a few to 10 µm (indicated by white arrows in Figure 10F). The matrix between unreacted particles is filled with submicrometer masses. The EDS analysis (Figure 10G) shows that the matrix is composed of Ca-silicate material with high amounts of Al, Mg, and S, the latter probably together with Ca in ettringite (Figure 10H).
Figure 10. SEM backscattered electron images of pastes made with raw ash (A,B) and mechanically activated ash after 90 days of curing (C–G). Images A–D are broken surfaces. Images F and G are polished surfaces. Note a thin, few to 10 µm thick, alteration rims on glassy cenospheres (F). Energy dispersive spectrum (H) of the area in image G. P—portlandite, Et—ettringite.
4. Discussion

Mechanical activation without changing the materials’ chemical composition is mostly used to improve their bulk and surface reactivity by increasing the particles surface area and altering their surface and crystal structure properties, that can collectively enhance their hydration and dissolution rates [24,46]. Marjanovic et al. [47] has shown more than 10-fold increase in the compressive strengths of geopolymers made of mechanically activated thermal power plant fly ash, when compared to geopolymer made of raw ash precursor. Similarly, cement-free activation of Ca-rich fly ash, combining mechanical activation and blending with silica fume and flue gas desulfurization gypsum as a grinding aid, and/or polycarboxilate ether based plasticizer additive and NaOH alkali activation, was reported to yield ca. 35% increase in compressive strength, topping at 46 MPa in 28 days, compared to blends without mechanical activation [48]. Our results show, however, that significant, nearly an order of magnitude improvement in compressive strength both in terms of final strength (60 MPa after 90 days) as well as the strength development (30 MPa in 7 days) is achieved in Ca-rich CFBC fly ash pastes by means of even a short period of mechanical activation without any chemical activation or blending.

During the grinding of fly ash, the particles are broken up, which increases the fineness and specific surface area of the ash but also generates crystalline defects, leading to an increase in the amorphous phase and enhancing the overall reactivity of the ash [46]. In the studied CFBC fly ashes, however, the specific surface area increase after milling is less than twofold, when compared to raw ash that does not scale with the significant increase in mechanical properties of the ash–water pastes. This suggests that the effect of the short mechanical activation on CFBC fly ashes resides not in the fine milling per se, but rather in the fragmentation of large irregular flaky porous lumps and aggregates into sub-µm-sized constituents (Figure 3). The agglomerated ash particles and the significant reduction in fineness is a particular feature of CFBC boilers, where SO₂ is effectively removed from the circulating boiler system by flue gas reaction, with calcined limestone forming relatively large particles composed of dense CaSO₄ shells on unreacted CaO cores [49,50]. The breaking of the hard and impermeable anhydrite shells also has an immediate effect on the anhydrite dissolution rate, causing it to disappear from mechanically activated CFBC fly ash already after 7 days of curing, whereas in pastes made with raw ash anhydrite remains detectable for 90 days.

Another important effect of the fly ash grinding is concerned with the final compactness of the paste microstructure (Figure 10B,D). In pastes made with raw ash, the intact aggregates form a highly porous microstructure, bridged only at tangential grain contacts by ettringite, calcite, and portlandite precipitates. However, in pastes made with activated fly ash the entire space between unreacted particles is filled with dense sub-µm ettringite fibrous aggregate webs and possibly a (semi)-amorphous calcium-silica-hydrate (C-S-H) phase providing the high compactness of the paste (Figure 10E). The dynamics of the estimated amorphous phase content in pastes suggests that in the first stages of hydration the most reactive phases form X-ray amorphous gel-like phase, the content of which increases over 28 days of curing, but showing a decrease after 90 days which indicates recrystallization into stable crystalline phases, in this case calcite, hydrocalumite and ettringite.

The cementitious properties of the activated ash, but also of raw ash pastes are controlled by the formation of abundant crystalline ettringite (Ca₆Al₄(Al₃Si₃O₁₄)(SO₄)₁₂·26H₂O), In addition, the dissolution of Ca- and Ca-Mg silicates C₂S (belite) and merwinite/akermanite, continuing over the full length of the hydration period, possibly produces a heterogeneous C-(A)-S-H gel-like phase, with additional crystalline portlandite Ca(OH)_2 forming also by the hydration of lime. In this sense the activated Ca-rich CFBC fly ash behaves similarly to calcium sulfoaluminate (CSA) cement, which is considered as one of the low-CO₂ alternatives of ordinary Portland cement [51]. In CSA hydration, strength development is provided by the hydration of the ye’elimite (Ca₆Al₄(SO₄)₂) in the presence of gypsum (CaSO₄·2H₂O), producing ettringite and nanocrystalline Al(OH)_3, and depending on cement
composition other phases as monosulfate, C-S-H phase, strätlingite, or hydrogarnet [52–54]. In Ca- and S-rich CFBC ashes, ettringite is formed by the reaction of the anhydrite/gypsum and Al-bearing phases.

The availability of Ca-sulfate is typically considered as the limiting reactant for ettringite formation in hydrated CFBC ashes [55]. However, the Ca-rich CFBC ash is low in reactive silica and aluminum, but rich in Ca-sulfate, and it can precipitate with ettringite concurrent gypsum [27,56]. It is, therefore, the presence and availability of dissolved Al species, rather than sulfate, which limits the ettringite formation in Ca-rich CFBC ash. This is further supported by the absence of excess Al-hydroxide precipitation, characteristic in CSA cements, even though the Al-hydroxide precipitation is also suppressed by the presence of Ca(OH)₂ [51,53] that is abundant in hydrated Ca-rich CFBC fly ashes. In Ca-rich oil shale CFBC ashes the main readily available Al sources are the amorphous Ca-Si-Al-(K) cenospheres and/or residual dehydroxylated aluminosilicate clays. However, at the early stages of the hydration the Al(OH)₃ ions’ diffusion from Al-bearing phases into the pore space is inhibited in the presence of lime and gypsum [57]. On the other hand, due to retarded Al mobility the interfaces of Al-phases become supersaturated in respect to ettringite, causing an explosive formation of small nano-crystallites at high nucleation rate [56]. This, in turn, provides the early strength in hardening pastes, whereas ettringite recrystallizes into larger and well-crystalline form with progressing hydration providing the concurrent development of C-(A)-S-H gel-like phase at the expense of the dissolution of glassy cenospheres and the firm bonding of their fragments in the activated Ca-rich CFBC ash pastes.

5. Conclusions

- Fly-ash-based binders are considered to be viable alternatives for CO₂-extensive cement clinker systems. While low calcium fly ashes rich in siliceous glass are mostly used in blends with ordinary cement or in alkali activated binders, the use of high calcium fly ashes, particularly those produced in circulating fluidized bed combustion (CFBC) boilers with high content of free CaO and CaSO₄ is hindered, mainly due to their variable composition and poor cementitious properties.

- Results of our study show that even a short period of mechanical activation of the Ca-rich CFBC fly ash yields a nearly 10-fold improvement in the compressive strength of hydrated fly ash pastes, topping at 60 MPa after 90 days without any chemical activation or blending. The mechanical activation facilitated the fragmentation of large irregular flaky porous lumps as well as aggregates characteristic to CFBC ashes, improving their physical properties and reactivity (finer grain size, larger surface area, and disintegration of compact CaSO₄ shells on unreacted CaO cores).

- The cementitious properties of Ca-rich CFBC ash are controlled by the formation of crystalline ettringite (Ca₆Al₂(SO₄)₃(OH)₆·26H₂O) and possibly a heterogeneous C-(A)-S-H gel-like phase. In mechanically activated fly ash pastes the enhancement of mechanical strength is achieved by a significantly more compact microstructure where pore space between unreacted particles is completely filled with dense webs of ettringite crystallites and a gel-like Ca-Al-Si phase.

- The phase development in activated Ca-rich CFBC fly ash is similar to that in calcium sulfoaluminate (CSA) cements where the strength development is provided by the hydration of ye’elimite in the presence of gypsum, producing ettringite and nano-crystalline Al-hydroxide. Ettringite forms in Ca- and sulfate-rich CFBC ashes by the reaction of the anhydrite/gypsum and Al-bearing phases (glass, clay minerals, feldspars), being possibly limited by the availability of reactive Al phases.

- Our findings suggest that mechanically activated Ca-rich CFBC fly ashes can be successfully used as an alternative to CSA type binders, providing mechanical strength comparable to common concrete systems. Further studies should be aimed at (1) the influences of additives and/or alkali activation to create a binder with properties.
exceeding those of one-component systems, and (2) testing durability to reveal the performance of ash pastes in different environments.

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