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Extending the Life Cycle of Cement Binders by Partially Replacing Portland Cement with Different Types Fluidized Bed Combustion Fly Ash

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Abstract: A significant reduction in the CO_2 emission associated with cement production is obtained by partially replacing Portland cement with supplementary cementing materials (SCM's): e.g., siliceous fly ash or granulated blast furnace slag. In the near future, the limited availability of these materials will do more attractive to use ashes from combustion in fluidized bed boilers, which currently are mainly deposited in various landfills. Paper identifies the effect of Fluidized Bed Combustion (FBC) fly ash from both hard and brown coal combustion on the durability of mortars exposed to sodium and magnesium sulfate solution at different curing temperature: 20 and 5 °C. The evaluation was based on the results of long-term linear changes of mortar samples made with Portland cement and different amounts of FBC fly ash addition stored in a corrosive environment, as well as the evaluation of the type of formed corrosion products using XRD and microstructural studies (SEM/EDS). It has been shown that amount of FBC fly ashes used in binders significantly determines sulfate resistance of prepared cements as well as its chemical composition. By using fluidized ashes, the sulfate resistance of cement binders can be achieved with their content even of 15%.

Keywords: blended cement; FBC fly ash; durability of blended cements; cement; concrete; sulfhate resistance; ettringite; thaumasite

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1. Introduction

Portland cement is the most widely used construction material in the world. The consumption of cement in volume is over 4 billion tons per year [1]. Due to the massive production of Portland cement, it is responsible for 5–7% of the anthropogenic CO_2 emissions, which originate mainly from the decomposition of limestone and the intense usage of fossil fuel [1].

With increasing climate changes, the reduction of the CO_2 footprint from cement production represents significant research and industrial challenge. Society's requirements for sustainable cement production can be met using alternative raw materials and more environmentally friendly power supplies. A significant reduction in the CO_2 emission associated with cement production can be obtained by partly replacing Portland cement with SCMs [2]. Additionally, the extensive use of "green" concretes with blended cements in the building/construction industry has a number of further environmental benefits. The most significant benefit next to the ones mentioned above is the extension of the life cycle of these materials through its increased corrosion resistance, which is important with the effect pollution has had on the environment [3–5].

The changes in the procedures of solid fuel combustion in electric and thermal-electric power plants have resulted in the availability of fly ashes from fluidized bed combustion (FBC FA) besides conventional fly ashes (FA) [6]. FBC fly ash does not fulfill the requirements of EN 197-1 Standard for fly ash used as a main component of ordinarily used cements, mainly due to the absence of glassy phase and high water demand, but they are used in the cement industry in a limited way [6–8]. FBC fly ash contains a relatively high amount of calcium sulfate (anhydrite), which serves as a setting time regulator [9]. Additionally, besides SO_3, relatively high CaO content does not meet the requirements of EN-450-1 Standard for fly ash as a concrete additive.

Till now, many experiments have been done to use FBC FA as components of various types of construction materials, the results of which in many cases have proved to be very promising [10–12]. Much attention in the literature has been focused on the possibilities of using FBC FA in materials for stabilization and sub-base of road works [2]. However, these solutions do not completely realize the potential capabilities of FBC FA.

In recent years, much more attention in the literature is concentrated on the search for more effective technologies for the use of FBC FA. Especially many literature reports described trials to use FBC FA in cement production. Mentioned in the literature experiments on cement clinker replacement concern both FBC FA in their original shape, additionally mechanically upgraded, and mixtures of FBC FA with bottom wastes from fluidized bed combustion [11–17]. The degree of cement clinker replacement in the experiments described in the literature ranged from 10–30% by weight for FBC FA alone to 70% for cement clinker replacement with bottom waste from fluidized bed combustion [15].

Moreover, some successful/promising studies on obtaining zero-cement binders with FBC FA, especially alkaline-activated binders (so-called geopolymers), were also burnt kaolin clays apart from FBC FA or ground granulated blast furnace slags can be found [18]. The research on cementless binders with FBC FA is also carried out to obtain synthetic zeolite materials [19] and other cement binders than those commonly used, such as magnesium-sulfate cements [20].

Similarly widely known from the literature are studies on the possibility of using FBC FA in cement concretes [11,21,22]. There are numerous examples of using fluidized ashes in the production of cement concretes with relatively low strength parameters and concretes for so-called non-structural applications, such as vibro-pressed products or rolled concretes [21,23].

Apart from the mentioned applications, there are also examples of trials using FBC FA in the production of autoclaved products, both concrete and bricks/blocks [24,25], although there are also described cases of experiments using FBC FA to produce foamed concrete and non-autoclaved cellular concrete [26].

However, in the literature review, there is no information on the use of such specific highly calcium-alumina FBC FA from brown coal combustion, and even more so in the context of comparing the obtained results with the binders containing FBC FA from hard coal combustion, widely often discussed in the literature.

In this work, the cementitious binders composed of Portland cement CEM I, FBC fly ashes from hard and brown coal fluidized bed combustion mixed at varying proportions were studied. The standard tests of mechanical properties and the other measurements of practical parameters were done. Besides standard methods of testing of functional quality of ashes and cements, different types of analysis have been used such as: XRD phase composition identification and SEM/EDS microstructural observations of hydration and corrosion products. In addition, some attention was focused on the possibilities of thaumasite formation in analyzed materials in the effect of sulfate attack at low and ambient temperatures. The results of experiments give the answer to the question: are the cement binders with various replacements of FBC fly ashes sulfate-resistant (according to PN-B-19707-Polish supplement to the EN 197-1) at ambient and particularly low temperature? Simultaneously results of research show practical limit of the quantity of the FBC fly ash from hard and brown coal fluidized bed combustion installation as a cement and concrete additive.

2. Materials and Methods

2.1. Materials—FBC Fly Ashes Characteristic

In the research, FBC fly ashes from two electric power plants was used, which burn both types of coal (hard and brown) in fluidized bed combustion boilers. The fly ashes under investigation were drawn from both boiler installations at the same time during their stable operation. The chemical composition (calculated on dried material) of the two types of FBC fly ash is presented in Table 1.

Table 1. The chemical composition made according to EN 196-2 procedures of the two types of FBC fly ash obtained from brown and hard coal combustion.

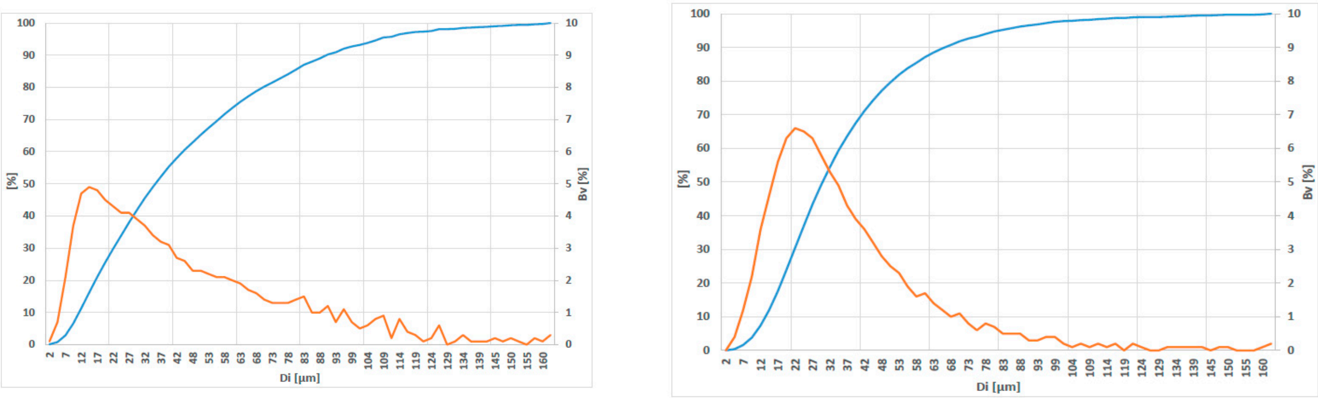
Component	FBC Fly Ash from Brown Coal Combustion (FBC FA BC)	FBC Fly Ash from Hard Coal Combustion (FBC FA HC)
	Wt. %	
LOI, 1000 °C/1 h	2.73	3.40
SiO_2	36.47	47.18
Fe_2O_3	4.40	6.80
Al_2O_3	28.40	25.62
TiO_2	3.84	1.08
CaO	15.95	5.84
MgO	1.65	0.15
SO_3	3.80	3.62
Na_2O	1.64	1.18
K_2O	0.62	2.36
Cl^-	0.03	0.10
CaO_{free}	4.75	0.30

Note: Total sulfhur and bounded sulfhur in the form of SO_4^{2-} was estimated. The determination of free CaO was made with the method according to EN 451-1 Standard.

Additionally, characteristic of FBC fly ashes including physical properties (Table 2), grain size distribution (Figure 1), phase composition (Table 3), the microstructure observations (Figure 2 and the active pozzolan coefficient (Table 4) of both FBC fly ashes were also presented below.

Table 2. Physical parameters of the two types of FBC fly ash obtained from brown and hard coal combustion.

Physical Parameters	Results of the Tests	
	FBC Fly Ash from Brown Coal Combustion (FBC FA BC)	FBC Fly Ash from Hard Coal Combustion (FBC FA HC)
Specific density, g/cm^3	2.75	2.68
BET specific surface, m^2/g	12.1	13.5
Volume median particle diameter, µm	37.3	31.6
Volume mode particle diameter, µm	14.3	22.0
Water/ash ratio for standardized consistency (analog-like for cement-water paste according to EN 196-3)	0.746	0.732



(**a**) (**b**)

Figure 1. Particle size distribution (differential and integral—refer to volume fraction) of FBC fly ash from brown coal combustion (FBC FA BC)—(**a**) and of FBC fly ash from hard coal combustion (FBC FA HC)—(**b**), examined using Malvern MasterSizer 2000, with liquid sample dispergator. Isopropanol was used as dispersing liquid.

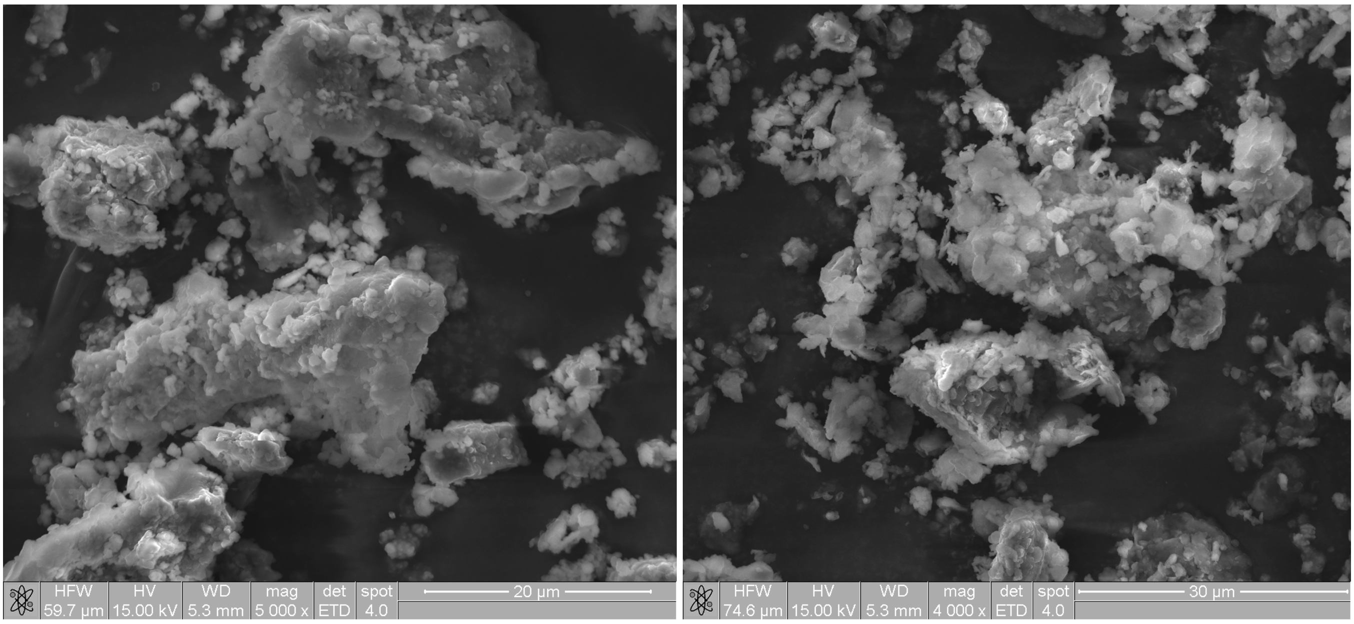
Table 3. Phase composition of the two types of FBC fly ash obtained from brown and hard coal combustion.

Phase	FBC Fly Ash from Brown Coal Combustion (FBC FA BC)	FBC Fly Ash from Hard Coal Combustion (FBC FA HC)
	Wt, %	
SiO_2	1.5	15.0
$CaSO_4$	6.5	6.2
CaO	4.7	0.3
$CaCO_3$	4.5	1.6
Not burned coal	0	1.7
Amorphous phases	82.7	75.2

Note: Relatively low temperature in the fluidized bed (about 850 °C) produces the FBC fly ash that is different from the fly ash produced in a conventional furnace [27,28]. During the fuel combustion process in the fluidized bed, the liquid phase is not produced [27]. The fly ashes are produced weakly sintered and consist mainly of irregular, dehydrated grains of minerals derived from the waste rock with an almost amorphous microstructure.

Table 4. Pozzolanic activity of both types of fly ash according to EN 450-1.

<table>
<tr><th rowspan="2">Composition of Binder in Standard Cement Mortar</th><th colspan="2">Compressive Strength of Mortars after Two Periods of Hardening, MPa</th><th colspan="4">Activity Index: Compressive Strength of FBC Fly Ash-Cement Mortars to Reference Cement Mortar Ratio, %, after:</th></tr>
<tr><th>28 Days</th><th>90 Days</th><th>28 Days</th><th>Requirements</th><th>90 Days</th><th>Requirements</th></tr>
<tr><td>CEM I 42,5R</td><td>45.1</td><td>49.7</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>75%–CEM I 42,5R
25%–FBC FA BC</td><td>53.2</td><td>58.0</td><td>118</td><td rowspan="2">>75</td><td>117</td><td rowspan="2">>85</td></tr>
<tr><td>75%–CEM I 42,5R
25%–FBC FA HC</td><td>57.1</td><td>58.6</td><td>127</td><td>118</td></tr>
</table>



(**a**) (**b**)

Figure 2. Grains of FBC fly ash from brown coal combustion (FBC FA BC)—(**a**) ×5000 and from hard coal combustion (FBC FA HC), ×4000—(**b**).

2.2. Materials—Cement Characteristic

Cement used in the preparation of binders was produced on industrial scale. The characteristic of cement is presented in Table 5. The setting time of cement was tested according to EN 196-3 Standard. The compressive strength of standardized mortars (sand:cement:water as 3:1:0,5 by weight) tests was made according to EN 196-1 after 2 and 28 days of curing.

Table 5. Characteristic of industrial cement: chemical composition (made according to EN 196-2 specific procedures for different types of components) and physical parameters.

Chemical Composition of Used Cement—CEM I 32,5R, wt. %	
SiO_2	18.9
Al_2O_3	5.5
Fe_2O_3	2.9
CaO	63.3
MgO	1.4
SO_3	2.84
Na_2O_{eq}	0.81
Cl^-	0.020
Physical parameters of used cement	
Water demand, %	28.5
Setting time—initial, min	200
Setting time—final, min	270
Compressive strength—2 days, MPa	27.8
Compressive strength—28 days, MPa	41.4

2.3. Methods—Setting Time and Compressive Strength Test

Setting time (initial and final) was determined using the EN 196-3 Standard procedure. The initial setting time is determined by observing the penetration of a needle into cement paste of standard consistency until the distance between the needle and the base plate is (6 ± 3) mm. The final setting time is time in minutes, measured from zero to that at which the needle first penetrates only 0.5 mm into the specimen. The laboratory in which specimens are prepared and tested shall be maintained at a temperature of (20 ± 2) °C and a relative humidity of not less than 50%. Cement, water and apparatus used to make and test specimens shall be at a temperature of (20 ± 2) °C. Samples were tested using handheld Vicat apparatus.

According to methods described in EN 196-1, the compressive strength tests were carried out using 40 mm × 40 mm × 160 mm prismatic samples. Specimens were cast from a batch of plastic mortar containing one part by mass of cement and three parts by mass of standard sand with a water-cement ratio of 0.50. The mortar was prepared by mechanical mixing and was compacted in a mold using a standard jolting apparatus. The specimens in the mold were stored in a moist atmosphere for 24h and then the demolded specimens were stored underwater until strength testing. At the required age (2 days and 28 days), the specimens were taken from their wet storage, broken in flexure into two halves and each half tested for strength in compression. Samples were examined using Controls Automax 5 hydraulic press, with the 500 N/s force increase rate. Each value is the average of six measurements.

2.4. Methods—Linear Changes Test

Mortar prisms (20 mm × 20 mm × 160 mm) for linear change tests were made with prepared FBC fly ash-cement binders. The water-to-cementitious materials ratio was fixed at 0.50. In case mortar samples made from binders containing 30% FBC fly ashes w/c = 0.5 didn't give good workability and the chemical additives were used to obtain established consistency (see Table 6). The high water demand of FBC fly ash-cement mortars resulted mainly from the development of FBC fly ashes specific surface. It gives important information about the limitation of FBC fly ashes as addition to cement and concrete without modifications relies on the addition of an adequate portion of chemical admixtures. Both series of mortars were kept initially for 28 days in water. The test of resistance of mortars containing FBC fly ashes in the amount of 15%, 20% and 30% on sulfate medium reaction was conducted with two sulfate mediums applications: Na_2SO_4 and $MgSO_4$ with concentration SO_4^{2-} = 16.0 g/L. Simultaneously comparative samples were kept in distilled water. Samples were cured in the horizontal position, dipped in 10 mm under the surface of the solution. The solution was changed for 28 days during all periods of investigation. The test was performed according to the method from PN-B-19707. The procedure includes measurement of linear changes of samples stored in corrosion medium to linear changes of samples stored in water every 28 days (four weeks) during 52 weeks. The results of tests are subjected to evaluation according to criteria included in the subjected standard, so verification if the linear changes of the samples after 52 weeks of exposition in sulfate medium do not exceed 5 mm/m value ratio to samples stored in the water (if according to the procedure a solution of Na_2SO_4 is used as the corrosive medium). This criterion is placed for special cements, which are defined as resistant to sulfate corrosion (HSR cement type). The use of magnesium sulfate as a corrosion solution permits an additional evaluation of the resistance of the tested binders in the environment with an additional corrosion factor originating from the presence of magnesium ions.

Table 6. Composition and properties of FBC fly ash-cements binders.

Binders Composition	Setting Time of FBC Fly Ash Cement Binders, min			Compressive Strength [MPa] of Mortars after:	
	W/(C+FBC FA)	Initial	Final	2 Days	28 Days
85%–CEM I 32,5R 15%–FBC FA BC	0.349	200	250	27.4	50.6
80%–CEM I 32,5R 20%–FBC FA BC	0.382	220	275	29.0	53.5
70%–CEM I 32,5R 30%–FBC FA BC (Additionally for mortars –% wt. of binder: 1.5%—Glenium SKY591(BASF) 0.9%—Liquol BV18 (BASF))	0.420	230	340	19.2	52.0
85%–CEM I 32,5R 15%–FBC FA HC	0.340	215	255	28.8	55.2
80%–CEM I 32,5R 20%–FBC FA HC	0.374	230	275	29.0	58.0
70%–CEM I 32,5R 30%–FBC FA HC (Additionally for mortars–% wt. of binder: 0.5%—Glenium SKY591(BASF) 0.9%—Liquol BV18 (BASF))	0.426	275	355	19.3	51.2

Simultaneously, an analogical corrosion test of samples in the same corrosion mediums was performed, but they were conducted at lower temperature conditions: 5 °C. The PN-B-19707 Standard does not predict these conditions of exposition, but they are a significant supplement of this measurement method for the binders containing among other components, this type of industrial waste. Because, in the situation of FBC fly ash usage, it is possible to occur both sulfate and sulfate—carbonate corrosion, especially at low temperature. It could be the consequence of phase composition related to a significant amount of free CaO and $CaCO_3$. The ettringite formed with the aluminate ones at low temperature could next together with the participation of the other components ($CaCO_3$ and $CaSO_4$) transformed to thaumasite [29]. The formation of thaumasite in contrast to ettringite does not cause high expansion, but it leads to a loss in strength and collapse the microstructure by the C-S-H transformation into mush in concretes and mortars [30]. The special objective of this part of the tests is to understand the effect of FBC fly ashes on the durability of mortar exposed to sulfate solution in these specific temperature conditions (e.g., autumn-winter season, early spring season or underground constructions). Each value (independently of binder type and storage conditions), according to the standardized procedure, is the average of three measurements.

2.5. Methods—SEM–EDS and XRD Analysis

SEM observations were performed at 15-kV accelerating voltage using an FEI Nova NanoSEM 200 (Thermo Fisher Scientific, Landsmeer, The Netherlands) ultra-high-resolution instrument equipped with a Schottky type field emission gun, cooperating with an EDAX EDS sanalyzer (EDAX Company, Tilburg, The Netherlands). The samples were mounted on aluminum stubs using double-sided conductive carbon tape and coated with 5-nm thick conductive carbon film prior to analysis. The test of the samples was performed under 60 Pa pressure. The rest of the parameters are shown at the bottom of the figures.

Mineralogical composition was investigated with XRD. Prior to analysis, the dried samples were ground by hand in an agate mortar and then passed through a sieve of 63-μm mesh size. XRD data were collected in the angular range 5°–60° 2θ with a Bragg–

Brentano θ-θ diffractometer [Malvern Panalytical X'Pert Pro X-ray (Almelo, The Netherlands), Cu Ka1 radiation (λ $\frac{1}{4}$ 1.5406 Å)] equipped with a primary curved germanium monochromator (Johansson type). A step size of 0.0080 2θ with scan step time of 1.0 s was employed. To results interpretation, JCPDS-ICDD (Joint Committee on Powder Diffraction Standards—International Center for Diffraction Data) database [31] and mineralogical tables were used.

3. Results

3.1. Physical Properties of FBC Fly Ash-Cements Binders—Setting Time and Compressive Strength

How it was mentioned earlier the FBC fly ash does not comply with EN-450-1 and EN 197-1 Standard requirements, but FBC fly ash, with regard to its chemical composition and properties, must be treated as a complex additive, which contains pozzolanic material, as well as the setting time regulator. The treatment of FBC fly ash as a contributor of anhydrite and pozzolanic additive permits the use of FBC fly ash not as a secondary component but as the main component of CEM II, CEM IV and CEM V types of cement [32,33]. A series of binders containing FBC fly ashes were prepared. The composition of the prepared blended fly ash-cement binders and the results of the tests are shown in Table 6.

3.2. Sulfate Corrosion Resistance of Blended Fly Ash-Cement Binders—Linear Changes Test

The test results after 52 weeks of sample exposition in sodium sulfate medium indicate that FBC fly ashes can significantly increase the corrosion durability in a binder system (Figure 3a). However, it is required to replace the cement with FBC fly ashes in an amount larger than 15%. The comparison test of reference cement mortar indicates an exceeding of critical parameter—linear changes already after 24 weeks of exposition. That is why the cement replacement by FBC fly ashes from brown coal combustion in 20%, or by FBC fly ashes from hard coal combustion in 15% meets the requirements for special sulfate-resistant cements according to the national PN-B-19707 Standard. The group of special high sulfate-resistant cements also includes, among others, Portland cements with mineral additives. It should be noted that this group of cements include Portland cements with addition not less than 25% silica fly ash (FA), while at the same time, the criterion of maximum acceptable linear changes is fulfilled.

The results of linear changes samples stored in $MgSO_4$ solution indicate (Figure 3b) that the magnesium sulfate medium in a larger degree than Na_2SO_4 influenced the appearance of unfavorable effects in mortars, even then, the FBC fly ash content is high. However, the values of relative linear changes after 52 weeks meet the criteria predicted for sulfate-resistant cements, which means they don't exceed the critical value accepted as 0.5%, which means 5.0 mm/m. Visible also is noted out the durability of the mortars containing a higher content of FBC fly ash, hence the conclusion that the content of FBC fly ash in fly ash-cement binders and concrete exposed on magnesium sulfate medium should exceed 20% of binder mass, especially in case of application of FBC fly ashes from brown coal combustion.

The results of linear changes of fly ash-cement binders mortars stored in Na_2SO_4 and also in $MgSO_4$ solutions at 5 °C (Figure 3c,d) indicate considerable similarity in behavior of all types of binders. The largest values of linear changes are noted for mortar samples achieved from reference CEM I cement. The expansion of this material is so large that it provides cracks formation in the samples after 44 weeks of storage in corrosive solutions. In the case of samples stored in Na_2SO_4 solution, the expansion value of beams from CEM I cement after 48 weeks of storage exceeds 5 mm/m value, which is equal to the disqualification of this cement as HSR cement according to requirement national PN-B-19707 Standard for mortar samples (but stored at 20 °C). The rest of the tested binders didn't show such large linear changes. The binders which contain: 85%—CEM I 32,5R and 15%—FBC fly ash from hard coal combustion and 80%—CEM I 32,5R and 20%—FBC fly ash from brown coal combustion stored both in Na_2SO_4 and in $MgSO_4$ solutions after

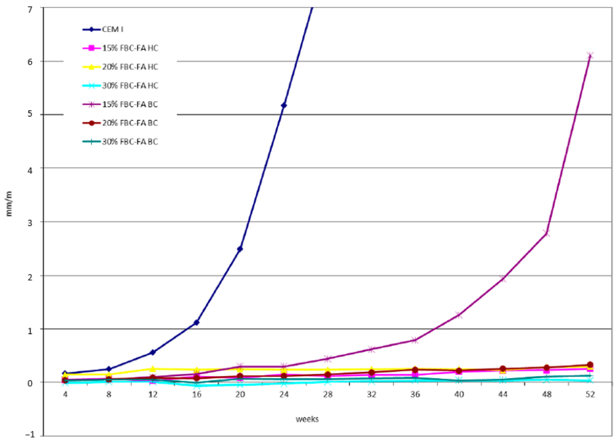
52 weeks showed linear changes ~2 mm/m. The intensity of linear changes of these samples in the last weeks of exposition indicates that further intense expansion is possible. The lowest linear changes were found for binders with 30% content of FBC fly ashes both from hard coal and brown coal combustion. The high ash content especially shows the increase of corrosion resistance in magnesium sulfate medium and gives the lowest expansion index. The results allow assuming that the 15% FBC addition of FBC fly ash from hard coal and the 20% addition of FBC fly ash from brown coal to CEM I cement are the minimum values that meet the sulfate criteria resistance cements described in the Polish Standard. However, larger amounts of these materials should be recommended if resistance is required in this type of environment. The difference in the effectiveness of obtaining sulfate-resistance by the binders containing fluidized ashes may be associated with their different chemical composition, especially with different amounts of pozzolanic components. The results show that the addition of 30% FBC fly ash favors improvement of binder resistance on interactions with sulfate medium. It should be noted that the mortars made with cement +30% FBC fly ash addition had to be modified by chemical additives for the purpose of assurance of proper workability of the mortar on the preparing step. It could also take effect on increase of coating density of tested mortars, simultaneously, and to some degree contribute to increasing their resistance on corrosion mediums activity. However, the interested is the difference in the behavior of CEM I cement in dependence from medium storage. The higher expansion of beams stored in Na_2SO_4 solution in low temperature could be defined mainly by ettringite crystallization in contrast to mortars stored in $MgSO_4$ solution, in which deterioration could relate to another sulfate corrosion product, thaumasite, which caused in hydrated cement paste considerably lower expansion then ettringite.

3.3. Sulfate Corrosion Resistance of Blended Fly Ash-Cement Binders—SEM–EDS and XRD Analysis

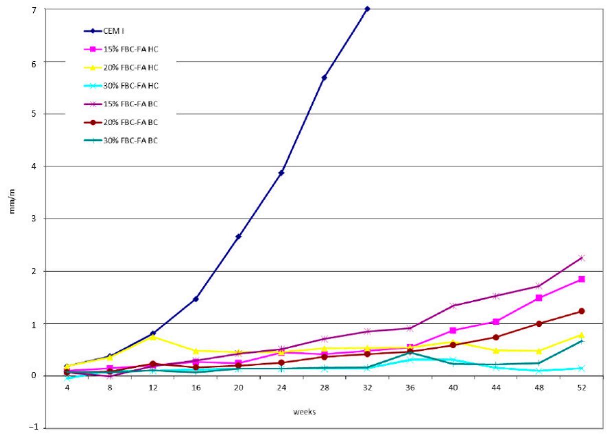
To confirm the evidence of different types of corrosion products in discussed FBC fly ash-cement mortars, SEM-EDS and XRD analysis were carried out on the selected samples stored at low (5 °C) temperature in sulfate solutions. The choice of samples decided the test results of the binders' resistance on the sulfate corrosion (linear changes test) and macroscopic observations of samples. The sampling was made from the undersurface of the beams (up to 5 mm depth), which indicates macroscopic corrosion visual changes. The pictures of FBC fly ash-cement mortar samples morphology are shown in Figures 4 and 5.

To confirm microscopy observation with EDS analysis, the XRD analysis was made on the binder mortar samples stored in corrosion solutions. The results of the selected XRD analysis confirmed evidence of sulfate corrosion products is shown in Figure 6.

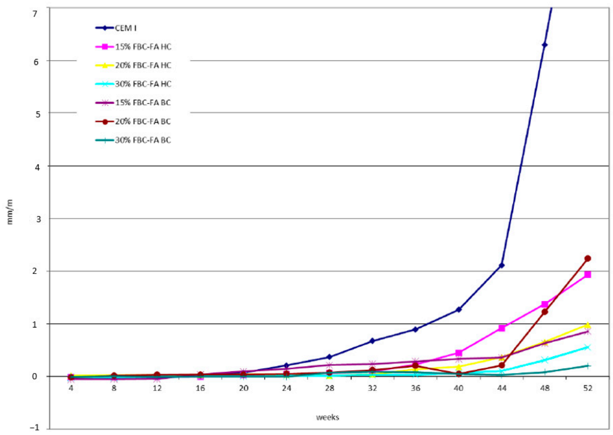
Performed XRD analysis of selected parts of the mortar samples, in all tested materials the identification of the main reflexes characteristic for the quartz (2θ = 26.64; 20.86; 50.14), calcite (29.41; 48.52; 39.42), ettringite (9.14; 15.81; 22.90) and thaumasite (9.24; 16.04; 23.49) were found. Simultaneously, in all tested mortar samples stored in magnesium sulfate solution, high intensity from the gypsum peaks was found (11.59; 20.72; 29.11). Whereas in mortar samples stored in sodium sulfate solution, the intensity of the peaks characteristic for the gypsum is significantly lower, or gypsum was not found (the reference CEM I cement). In these samples, the main sulfate corrosion products were ettringite and thaumasite. In all analyzed samples of the corroded parts of the mortars, no other mineral phases typical for cement hydration products were found. The significant increasing of background in the XRD pattern characterized for cryptocrystalline form of calcium silicate hydrate wasn't identified in mentioned samples. Generally, the results of XRD analysis confirm SEM-EDS microstructural observation of samples.



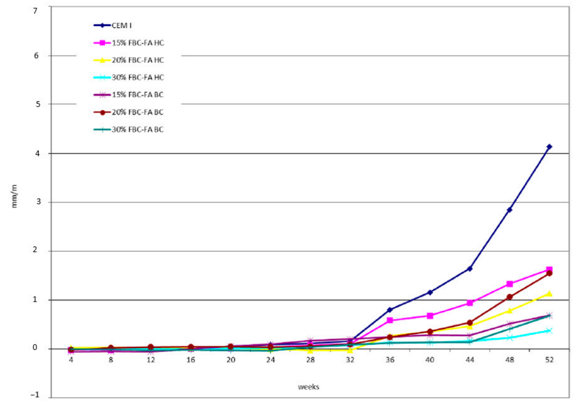
(**a**) mortars stored at 20 °C in Na_2SO_4 medium



(**b**) mortars stored at 20 °C in $MgSO_4$ medium

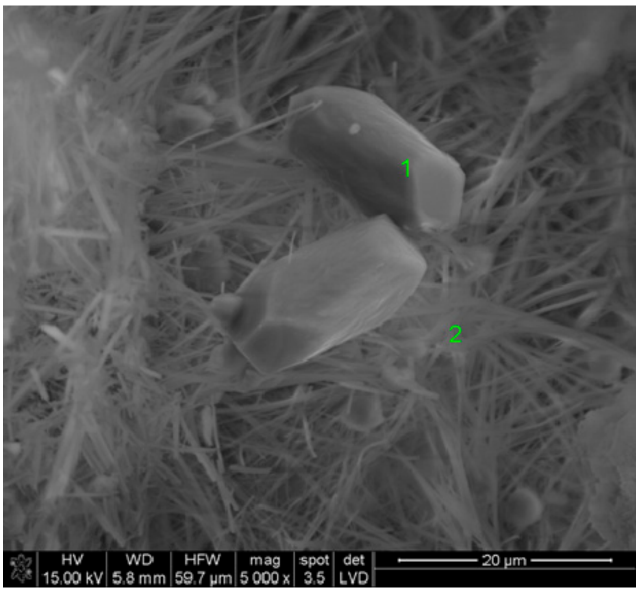


(**c**) mortars stored at 5 °C in Na_2SO_4 medium



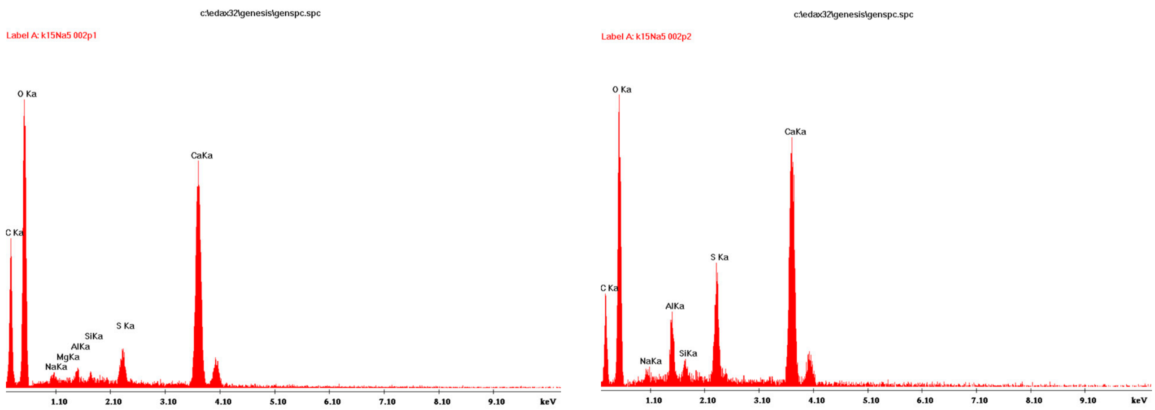
(**d**) mortars stored at 5 °C in $MgSO_4$ medium

Figure 3. Relative linear changes of ash-cement binder mortars with AFBC fly ash from hard (FBC FA HC) and brown (FBC FA BC) coal combustion.



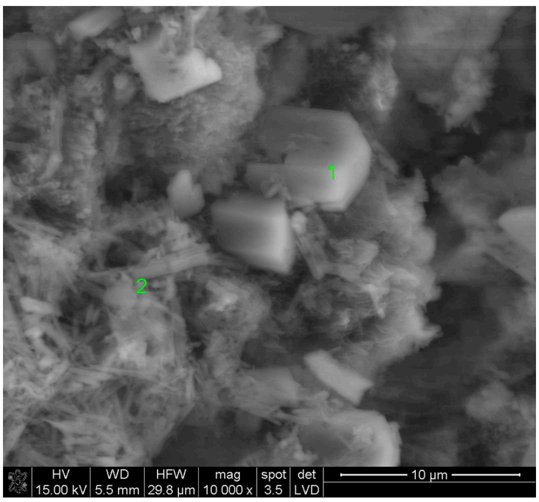
(**a**)

Figure 4. *Cont.*

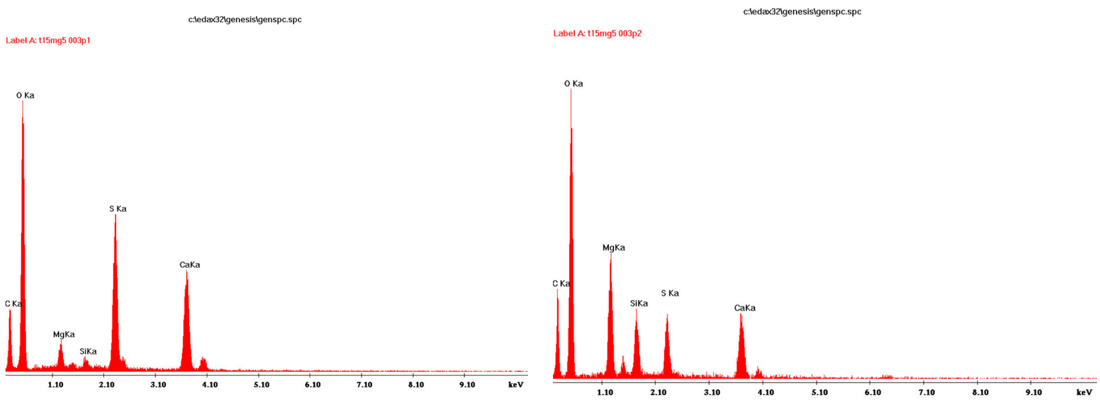


(**b**) EDS – p.1 (**c**) EDS – p.2

Figure 4. (**a**)SEM observation of the mortar sample made with binder of 85%–CEM I 32,5R + 15%–FBC FA HC, stored in 335 Na_2SO_4 solution (5 °C temperature, 360 days, ×5000 magnification). The figure shows a typical view of the sample subjected to observations. In the background, many ettringite crystals with needle section are visible (p. 2) (EDS—Figure 4**c**). In the foreground, well-formed calcite crystals are visible (p. 1) (EDS—Figure 4**b**).



(**a**)



(**b**) EDS – p.1 (**c**) EDS – p.2

Figure 5. (**a**) SEM observation of the mortar sample made of binder 85%–CEM I 32,5R + 15%–FBC FA BC, stored in $MgSO_4$ solution (5 °C temperature, 360 days, ×10,000 magnification). The microscopic observation of the spaces occupied by corrosion products indicates gypsum crystals in the observed sample (p. 1) (EDS—(**b**)) as well as needle form closed to thaumasite (p. 2) (EDS—(**c**)). Attention should be taken to the highest content of the magnesium in the corroded binder mass.

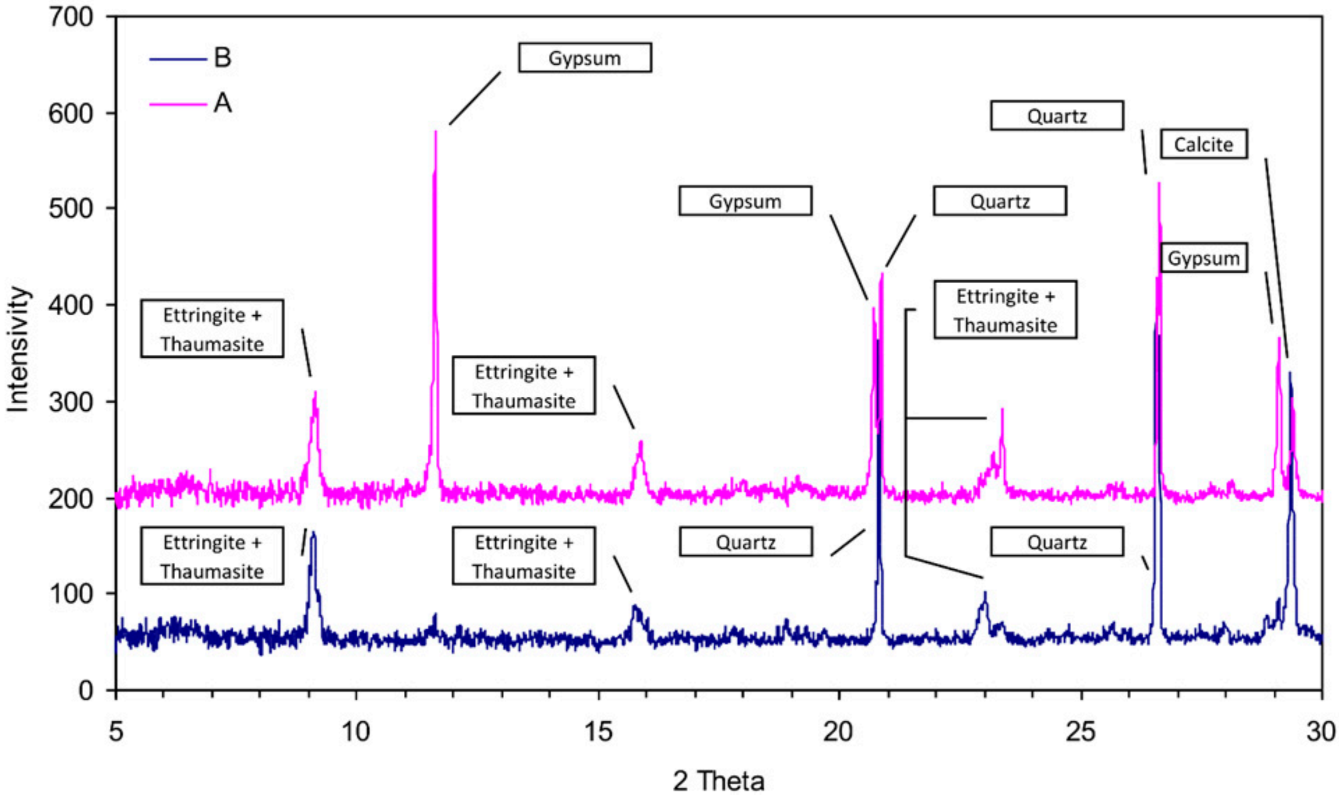


Figure 6. The XRD analysis of the selected mortar samples (5 °C temperature, 360 days), (A)—binder composition: 85%—CEM I 32,5R + 15% FBC FA BC, stored in $MgSO_4$ solution, (B)—binder composition: 85%—CEM I 32,5R + 15% FBC FA HC, stored in Na_2SO_4 solution.

4. Discussion

The experiments demonstrate the influence of the different amount of the FBC fly ash addition to cements obtained from different type of coal on the properties of binders, especially their sulfate-resistance, to assess the possibility of extending their life cycle and reducing their environmental impact by reducing the content of Portland cement in the tested materials using waste substitutes (FBC fly ash). Two separate models of sulfate deterioration had been expected to occur in the sulfate solutions. The first one relates to conventional sulfate attack, which is primarily a reaction between sulfates and the alumina-containing phases of hydrated cement. The products of this reaction are expansive and disrupt and spall the concrete, particularly at corners [29,34]. The second model of affection is the thaumasite form of sulfate attack (TSA), which is an attack on the calcium silicate hydrates that causes the cement paste to lose strength and turn to the 'amorphous mush' [28,35]. The results of the investigation show unambiguously that amount of FBC fly ash, independently apart from the type of coal, used in binders, determines sulfate-resistance of these cements and the presence of a high amount of cement could be the direct reason for deterioration of mortars. The addition of FBC fly ash to cement and concrete relates to the change of SO_3/binder ratio (SO_3/cement). Considering chemical resistance, the presence of sulfate ions, and more precisely, the amount of sulfate ions introduced with FBC fly ash is a very significant factor. Sulfate ions reacted with alumina ions can lead to delayed ettringite formation, also in specified conditions (low temperature) and participation of other mineral phases in cement matrix can lead to thaumasite formation, which can be a direct cause of concrete degradation.

The study of corrosion resistance in sulfate medium indicates beneficial influence when part of the cement is replaced by FBC fly ash. The impact is more effective if more

FBC fly ash is added to mortars. Test results confirm this effect after 52 weeks of sample exposition in sulfate medium.

In the case of the mortars made with 20% FBC fly ash addition (apart of FBC fly ash type), relative linear changes of the mortars do not exceed half of the acceptable value for sulfate-resistant cements (5 mm/m = 0.5%) according to PN-B 19707 Standard for samples stored at 20 °C. Whereas, in the case of binders containing 30% of FBC fly ash addition the expansion rate (<0.7 mm/m) is considerably lower from the acceptable value for HSR cements. The addition of 15% FBC fly ash to tested binders does not indicate so beneficial influence. From the tested brown coal and hard coal ashes, in the case of FBC fly ash from brown coal combustion and his contribution in binder mass on the 15% level, causes that submitted to evaluation mortars do not meet requirements of stability in sodium sulfate medium. Thus, the addition of FBC fly ash from hard coal to cements appears to be more beneficial in this context. This difference can be directly explained by the differences in chemical and mineral composition between the fly ashes used in this study. For an increase in the effectiveness of the protection of binders against sulfate corrosion, it is preferable when the ash contains less CaO and a higher content of SiO_2.

In the case of magnesium sulfate medium, the tendency of linear dimension increasing of all tested samples is pointed out. Despite the results not exceeding the 0.5% value after one year of research, attention should be paid to the possibility of this level of achievement during the next couple of months. Hence, the necessary condition in the case of FBC fly ashes application to concrete mixes exposed to sulfate medium is cement replacement by FBC fly ashes in the amount above 15%.

The tests performed at 5 °C gave concurrent results of stability of mortars containing FBC fly ashes during the test performed at 20 °C. The effect of volume changes of mortars stored in sodium sulfate solution is in connection with ettringite formation, where the mixed crystals of ettringite and thaumasite presence were also found. Whereas in magnesium sulfate solution, the low temperature of the sample storage caused that the linear changes of the samples, especially cement CEM I are delayed in time of the test, but they occur in samples, which test results at 20 °C were also satisfactory, which suggest that observed effects of sulfate and sulfate–carbonate corrosion—especially in lower degree linear change of the mortars resulted from the formation of non-expansive corrosion products (thaumasite).

The non-standard test at 5 °C shows some dependence, which is not required by any domestic or European standard, therefore these test results do not have consequences in the stability evaluation of the cement binder containing FBC fly ash, however, they are useful from the scientific point of view.

The tests of FBC fly ash from both hard and brown combustion, as it was underlined, let to ascertain the possibility of these ashes application to concrete preserving the proper material preparing and monitoring of the chosen physical and chemical parameters of the FBC fly ashes.

5. Conclusions

In summary, the following general conclusions can be drawn from the studies carried out:

1. The experiments demonstrate that the addition of FBC fly ashes obtained from different types of coal to cements strongly influenced the properties of obtained binders, especially their sulfate-resistance.
2. Durability of cement binders in sulfate environment containing a higher amount of FBC fly ash is the more effective, the more fly ash is added into the cement.
3. The cement replacement by FBC fly ashes from brown coal combustion in 20%, or by FBC fly ashes from hard coal combustion in 15% meets the requirements for special sulfate-resistant cements according to Polish PN-B-19707 national standard.
4. The results of sulfate-resistance tests of samples stored in $MgSO_4$ solution indicate that this medium to a larger degree than Na_2SO_4 influences the properties of mortars, even then, when the FBC fly ash content is high.

5. The content of FBC fly ash in fly ash-cement binders exposed on magnesium sulfate medium should not be less than 15% of binder mass, especially in case of application of FBC fly ashes from brown coal combustion.
6. Exposure of mortar samples in Na_2SO_4 or $MgSO_4$ environments at 5 °C generally increases the linear changes of the tested samples, indicating a higher degree of corrosion processes.
7. The bigger expansion of samples stored in Na_2SO_4 solution in low temperature is defined mainly by ettringite crystallization in contrast to mortars stored in the $MgSO_4$ solution, in which deterioration is probably related to other, additional sulfate corrosion product—thaumasite, which caused in hydrated cement paste considerably lower expansion then ettringite.
8. Sulfate-resistance of binders containing FBC fly ashes depends on its chemical composition. The FBC fly ashes with higher SiO_2 content and limited amount of CaO exhibit more beneficial properties.

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References

1. Polish Cement Association. *Neutralność Klimatyczna A Perspektywy Zastosowania Betonu I Cementu W Budownictwie*; II Forum Beton w drogownictwie: Ostróda, Poland, 2020.
2. Gawlicki, M.; Roszczynialski, W. Applicabillity of combustion by-products from fluidized bed as Portland cement components. *Ceramics* **2003**, *80*, 681–686.
3. Sanal, I. Significance of concrete production in terms of carbondioxide emissions: Social and environmental impacts. *Politek. Derg. J. Politech.* **2018**, *21*, 369–378.
4. Minkwan, J.; Kyoungsoo, P.; Won-Jun, P. Mechanical Behavior of Recycled Fine Aggregate Concrete with High Slump Property in Normal- and High-Strength. *Int. J. Concr. Struct. Mater.* **2019**, *13*, 61.
5. Jeong-Eun, K.; Wan-Shin, P.; Young-Li, J.; Sun-Woo, K.; Sun-Woong, K.; Yi-Hyun, N.; Do-Gyeum, K.; Keitetsu, R. Mechanical Properties of Energy Efficient Concretes Made with Binary, Ternary and Quaternary Cementitious Blends of Fly Ash, Blast Furnace Slag and Silica Fume. *Int. J. Concr. Struct. Mater.* **2016**, *10* (Suppl. 3), 97–108.
6. Kumar, P.; Sikder, P.S.; Pal, N. Biomass fuel cell based distributed generation system for Sagar Island. *Bull. Pol. Acad. Sci. Tech. Sci.* **2018**, *66*, 665–674.
7. Uliasz-Bocheńczyk, A.; Mazurkiewicz, M.; Mokrzycki, E. Fly ash from energy production—A waste, byproduct and raw material. *Gospod. Surowcami Miner. Miner. Resour. Manag.* **2015**, *31*, 139–150. [CrossRef]
8. Gazdič, D.; Fridrichová, M.; Kulísek, K.; Vehovská, L. The Potential Use of the FBC Ash for the Preparation of Blended Cements. *Procedia Eng.* **2017**, *180*, 1298–1305. [CrossRef]
9. Chindaprasirt, P.; Rattanasak, U. Utilization of blended fluidized bed combustion (FBC) ash and pulverized coal combustion (PCC) fly ash in geopolymer. *Waste Manag.* **2010**, *30*, 667–672. [CrossRef] [PubMed]
10. Zhang, W.; Choi, H.; Sagawa, T.; Hama, Y. Compressive strength development and durability of an environmental load-reduction material manufactured using circulating fluidized bed ash and blast-furnace slag. *Constr. Build. Mater.* **2017**, *146*, 102–113. [CrossRef]
11. Brandt, A. (Ed.) *Application of CFBC Fly Ash in Structural Concretes*; Collective Work; Polish Academy of Science, Committee of Civil Engineering: Warsaw, Poland, 2010.
12. Abdulmatin, A.; Tangchirapat, W.; Jaturapitakkul, C. An investigation of bottom ash as a pozzolanic material. *Constr. Build. Mater.* **2018**, *186*, 155–162. [CrossRef]

13. Łagosz, A.; Mróz, R. Durability of Building Materials Based on Mineral Binders Modified By Significant Amounts of Fly Ash from Brown Coal Combustion in Fluidized Bed: Reaktywność Ciał Stałych = Reactivity of Solids/Pod Red; Przybylskiego, K., Polska Akademia Nauk—Oddział w Krakowie, Polskie Towarzystwo Ceramiczne—Prace Komisji Nauk Ceramicznych/Polska Akademia Nauk, Oddział w Krakowie. *Ceramika* **2013**, *115*, 259–267.
14. Li, D.; Sun, R.; Wang, D.; Ren, C.; Fang, K. Study on the pozzolanic activity of ultrafine circulating fluidized-bed fly ash prepared by jet mill. *Fuel* **2021**, *291*, 120220. [CrossRef]
15. Lee, B.Y.; Jeon, S.; Cho, C.G.; Kim, H. Evaluation of time to shrinkage-induced crack initiation in OPC and slag cement matrices incorporating circulating fluidized bed combustion bottom ash. *Constr. Build. Mater.* **2020**, *257*, 119507. [CrossRef]
16. Glinicki, M.A.; Jóźwiak-Niedźwiedzka, D.; Dąbrowski, M. The Influence of Fluidized Bed Combustion Fly Ash on the Phase Composition and Microstructure of Cement Paste. *Materials* **2019**, *12*, 2838. [CrossRef] [PubMed]
17. Giergiczny, Z. Fly ash and slag. *Cem. Concr. Res.* **2019**, *124*, 105826. [CrossRef]
18. Osholanaa, T.S.; Dludlub, M.K.; Oboirienc, B.; Sadikua, R. Enhanced reactivity of geopolymers produced from fluidized bed combustion bottom ash. *South Afr. J. Chem. Eng.* **2020**, *34*, 72–77. [CrossRef]
19. Liu, Z.; Li, S.; Li, S.; Wang, J.; Zhou, Y.; Wang, D. One-step high efficiency crystallization of zeolite A from ultra-fine circulating fluidized bed fly ash by hydrothermal synthesis method. *Fuel* **2019**, *257*, 116043. [CrossRef]
20. Xun, X.; Zongyue, H.; Liling, D.; Yudong, Z.; Yulong, X.; Weichao, L. Investigation of high volume of CFBC ash on performance of basic magnesium sulfate cement. *J. Environ. Manag.* **2020**, *256*, 109878. [CrossRef]
21. Zahedi, M.; Jafari, K.; Rajabipour, F. Properties and durability of concrete containing fluidized bed combustion (FBC) fly ash. *Constr. Build. Mater.* **2020**, *258*, 119663. [CrossRef]
22. Zahedi, M.; Rajabipour, F. Fluidized Bed Combustion (FBC) Fly Ash and Its Performance in Concrete. *ACI Mater. J.* **2018**, *116*, 163–172. [CrossRef]
23. Chi, M.; Huang, R. Effect of circulating fluidized bed combustion ash on the properties of roller compacted concrete. *Cem. Concr. Compos.* **2014**, *45*, 148–156. [CrossRef]
24. Song, Y.; Guo, C.; Qian, J.; Ding, T. Effect of the Ca-to-Si ratio on the properties of autoclaved aerated concrete containing coal fly ash from circulating fluidized bed combustion boiler. *Constr. Build. Mater.* **2015**, *83*, 136–142. [CrossRef]
25. Drochytkaa, R.; Helanováa, E. Development of microstructure of the fly ash aerated concrete in time. In Proceedings of the 7th Scientific-Technical Conference Material Problems in Civil Engineering (MATBUD'2015); Procedia Engineering, Kraków, Poland, 22–24 June 2015; Volume 108, pp. 624–631.
26. Xia, Y.; Yan, Y.; Hu, Z. Utilization of circulating fluidized bed fly ash in preparing non-autoclaved aerated concrete production. *Constr. Build. Mater.* **2013**, *47*, 1461–1467. [CrossRef]
27. Glinicki, M.A.; Zieliński, M. The influence of CFBC fly ash addition on phase composition of air-entrained concrete. *Bull. Pol. Acad. Sci. Tech. Sci.* **2008**, *56*, 45–52.
28. Baldermann, C.; Galan, I.; Emmerich, F.; Mittermayr, F. Effect of very high limestone content and quality on the sulfate resistance of blended cements. *Constr. Build. Mater.* **2018**, *188*, 1065–1076. [CrossRef]
29. Sotiriadis, K.; Mróz, R. Simulation of thaumasite sulfate attack on portland cement mixtures using synthesized cement phases. *J. Mater. Civ. Eng.* **2019**, *31*, 1–10. [CrossRef]
30. Haufe, J.; Vollpracht, A. Tensile strength of concrete exposed to sulfate attack. *Cem. Concr. Res.* **2019**, *116*, 81–88. [CrossRef]
31. JCPDS-ICDD (Joint Committee on Powder Diffraction Standards—International Center for Diffraction Data). Available online: https://www.icdd.com/ (accessed on 25 June 2021).
32. Lagosz, A.; Mróz, R. Parameters developed durability of building materials based on mineral binders modified by significant amounts of fly ash from brown coal burnt in zfluidized bed combustion. In Proceedings of the XVI French-Polish seminar on Reactivity of solids, Kraków, Poland, 10–12 December 2012.
33. Brylicki, W.; Małolepszy, J. Properties of cements admixtures with AFBC fly ash. *Ceramics* **2001**, *66*, 370–377.
34. Skalny, J.; Marchand, J.; Odler, I. *Sulfate Attack on Concrete*; Modern Concrete Technology 10; SPON Press: London, UK; New York, NY, USA, 2002.
35. Shi, Z.; Ferreiro, S.; Lothenbach, B.; Geikerd, M.R.; Kunther, W.; Kaufmann, J.; Herfort, D.; Skibsted, J. Sulfate resistance of calcined clay—Limestone—Portland cements. *Cem. Concr. Res.* **2019**, *116*, 238–251. [CrossRef]