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POSSIBILITIES OF UTILIZING SOLID RESIDUES FROM PRESSURED FLUIDIZED BED COAL COMBUSTION (PSBC) FOR THE PRODUCTION OF BLENDED CEMENTS

J. Havlica,* J. Brandstetr,* and I. Odler[1]†
*Technical University Brno, 63700 Brno, Czech Republic
†Technical University Clausthal, 38678 Clausthal-Zellerfeld, Germany

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ABSTRACT

Solid residues produced in pressurized fluidized bed combustion differ in their chemical and phase composition from those produced under atmospheric pressure and even more from conventional fly ashes. They usually exhibit distinct hydraulic/pozzolanic properties and thus may be used, in combination with Portland clinker, as constituents of blended cements. Due to their high SO_3 content, the addition of gypsum to such binders has to be adjusted accordingly. *© 1998 Elsevier Science Ltd*

Introduction

The combustion of solid fuels will be the main source of energy for the production of electricity at least for the few next decades. In conventional power plants the combustion of fuel takes place at temperatures between 1150°C and 1750°C. The process is associated with the generation of variable amounts of sulfur dioxide that has to be removed from the flue gas for environmental purposes. The required desulfurization units are costly, and frequently there is insufficient space for their installation, especially in existing power plants.

In recent decades, a variety of "clean" technologies has been developed for the combustion of solid fuels, and it may be expected that some of them will be widely applied in newly-built power plants. So far, technologies based on fluidized bed combustion at temperatures of about 850°C and at atmospheric pressure have found the greatest acceptance. Here, ground coal is burnt after being blended with limestone or dolomite, which acts as a sorbent of sulfur dioxide formed in the combustion (1,2). It has been reported that in Germany already 7% of the generated electricity is produced by this atmospheric fluidized bed combustion (AFBC) process (3). The solid residues formed under these conditions differ distinctly from those generated in conventional power plants; they may be used as constituents of blended cements or mortars, as fertilizers, as raw materials for the production of ceramic bricks or autoclaved lime-silica products, and in other applications(1–9).

In recent years, a new fluidized bed combustion technology has been developed by ABB Carbon (Finsong, Sweden) in which the combustion takes place at elevated, rather than at

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[1] To whom correspondence should be addressed.

TABLE 1
Chemical composition of the studied materials.

	PFBC bed ash A	PFBC cycl. ash A	PFBC filt. ash A	PFBC bed ash B	PFBC cycl. ash B	PFBC bed ash C	PFBC cycl. ash C	AFBC bed ash D	AFBC e.sep. ash D	PC clinker
SiO_2	35.4	37.1	38.5	34.2	31.1	18.2	24.1	27.2	29.5	21.1
CaO	23.5	20.2	10.1	25.9	25.3	28.7	25.8	37.7	35.5	66.8
MgO	1.6	2.7	2.7	5.6	6.4	22.9	16.9	2.2	3.0	1.0
Al_2O_3	12.9	15.6	23.4	12.8	15.0	6.3	13.8	13.6	17.0	5.0
Fe_2O_3	3.3	6.0	6.9	6.6	6.0	4.1	5.4	3.6	5.1	3.0
TiO_2	0.6	0.8	1.4	0.8	0.9	0.2	0.5	0.5	0.7	0.2
Na_2O	0.6	0.9	1.8	n.a.	n.a.	0.4	0.6	n.a.	n.a.	0.1
K_2O	1.6	1.6	2.1	1.5	1.4	0.8	0.9	1.1	1.4	1.4
C	n.a.	n.a.	n.a.	1.8	3.7	n.a.	n.a.	1.5	1.2	–
SO_3	10.6	5.6	11.6	8.3	9.0	n.a.	n.a.	12.2	9.3	0.6
L.O.I.	8.3	6.1	0.8	5.9	7.2	7.7	7.8	5.2	3.5	0.4
CaO free	0.3	0.6	0.0	1.4	1.0	n.a.	n.a.	20.0	16.3	1.0

PFBC, pressurized fluidized bed combustion; AFBC, atmospheric fluidized bed combustion; bed ash, ground bed ash; cycl. ash, cyclone fly ash; filt. ash, hose filter fly ash; e.sep. ash, fly ash from electrostatic separator; PC clinker, Portland cement clinker; n.a., not available.

A, PFCB pilot plant (Finspong, Sweden), sorbent: limestone; B, PFBC power plant (Värtan, Sweden), sorbent: limestone; C, PFBC power plant (Värtan, Sweden), sorbent: dolomite; D, AFBC power plant (Leykam, Austria), sorbent: limestone.

atmosperic pressure. The advantages of this pressurized fluidized bed combustion (PFBC) technology include increased efficiency of the process and savings in the amount of sorbent required. Five units of different capacities based on this technology are presently in operation in different countries of the world and it may be expected that additional ones will follow. So far there are no published data on the composition and properties of the combustion residuals formed under these conditions.

In our work, we analysed a series of ashes produced in pressurized fluidized bed combustion (PFBC) and studied the possibilities of using them as constituents of inorganic binders. These ashes were supplied to us from two power plants located in Sweden. In this study, we also included ashes from an atmospheric fluidized bed unit existing in Austria, for comparison.

Composition of the Studied Materials

In Table 1, the chemical compositions of the studied materials are shown. These include both PFBC and AFBC ashes obtained directly from the fluidized bed, ashes collected in cyclones as well as those collected from a hose filter and an electrostatic precipitator. It should be noted that different coals with different contents and compositions of the inorganic fraction were utilized in the different power plants from which the ashes were obtained. The table also includes the composition of the clinker employed in the experiments. Figure 1 shows the x-ray diffraction (XRD) patterns of three of the PFBC ashes studied.

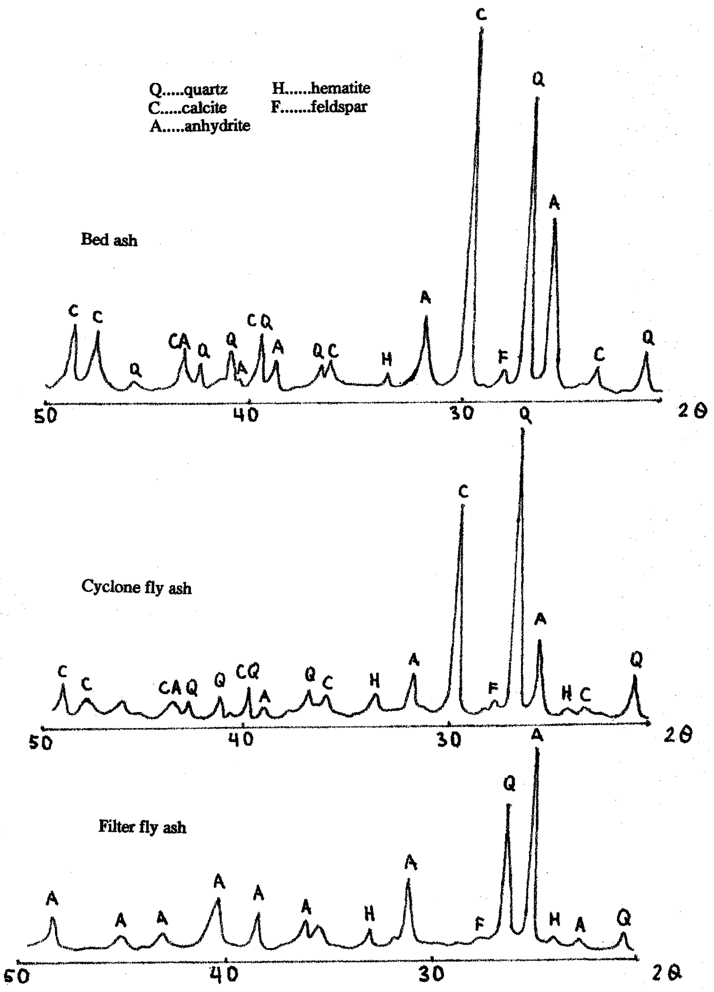

FIG. 1.
XRD patterns of PFBC ashes.

Most fluidized bed ashes contain relatively high amounts of CaO, which originate in part from the inorganic fraction of the employed coal and in part from the added limestone or dolomite. In the combustion process, a significant fraction of the CaO combines with SO_2 and the primary formed $CaSO_3$ is subsequently oxidized further to yield anhydrite ($CaSO_4$). The studied AFBC ashes also contained significant amounts of free lime (CaO), whereas the amount of this constituent was very low in the PFBC ashes. This is due to the fact that the amount of limestone/dolomite that must be added to the fuel is lower in the PFBC than in the AFBC process. In addition, in the PFBC process the CaO in the combustion residue tends to stay in the form of calcite, rather than in the form of lime, due to the higher CO_2 partial pressure in the combustor. The higher MgO content in two of the PFBC ashes is due to the use of dolomite, rather than limestone, as the SO_2 sorbent. Fluidized bed ashes may also contain variable amounts of x-ray amorphous material formed in the thermal decomposition of clay minerals present in the original

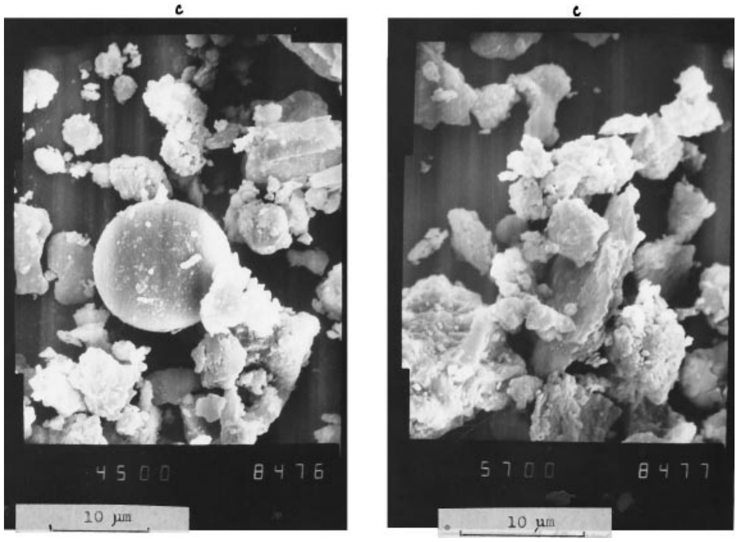

FIG. 2.
SEM micrograph of a PFBC cycone fly ash.

coal. Some residual non-decomposed clay minerals may also be present. Unlike conventional fly ashes, neither AFBC nor PFBC ashes contain a glass phase or mullite, as the employed maximum burning temperature is too low to allow their formation. For the same reason, any free CaO found in fluidized bed ashes is present in highly reactive form, as "hard-burnt" or "dead-burnt" lime cannot be formed under these conditions.

The coarseness of the ashes depended greatly on their origin. The bed ashes were coarsest and had to be preground to be used as constituents of experimental cements. The cyclone ashes were distinctly finer, yet still required moderate pregrinding before being used in the experimental mixes. Contrary to that, the obtained hose filter ash was extremely fine, with a medium particle size of 3.5 µm. The BET_{N2} specific surface areas of all analyzed PFBC ashes were similar and ranged between about 4 and 7 m^2/g, indicating a rather large internal surface of these materials.

Figures 2 and 3 show the secondary electron images of two of the ashes. Unlike typical fly ashes, the individual particles appear irregularly shaped with coarse surfaces, indicating the absence of a history of melting. Only very rarely are spherical particles also found; such particles are rich in alkalies and their presence indicates a local melt formation at temperatures present in the combustor.

Figure 4 shows a typical DTA + TG recording of a PFBC ash. Here two distinct endothermic peaks at around 750°C and 1150°C, associated with weight losses, predominate. They are due to the thermal dissociation of calcium carbonate and calcium sulfate. Two weak exothermic peaks at around 550°C and 1200°C can be attributed to the oxidation of residual carbon and to the crystallization of non-crystalline phases present.

Hydraulic Properties

To assess their hydraulic reactivity, the strength activity index of selected ashes was determined by a modified ASTM C 311/EN 450/1994 method. In the original procedure the

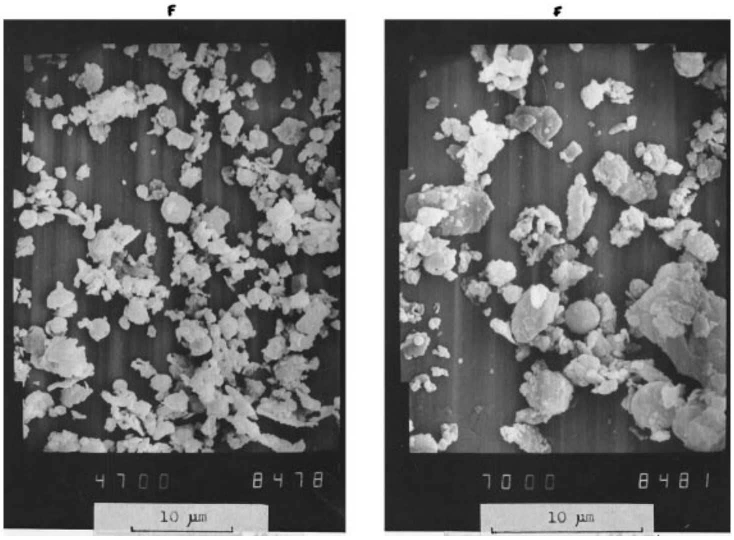

FIG. 3.
SEM micrograph of a PFBC hose filter ash.

strength of a mix, in which 20% (or 25%) of cement was replaced by the tested ash, is compared with that of one containing just Portland cement. This procedure had to be modified in our experiments to avoid excessive amounts of SO_3 in some of the mixes containing fluidized bed ash. To do so, blends of preground clinker, gypsum, and ash were prepared, which had a constant SO_3 content, i.e., 3.50%. Their strength was compared with that of a similar blend containing just gypsum and clinker, which served as a reference. To eliminate the effect of fineness, both the clinker and ashes (except filter ash) were preground

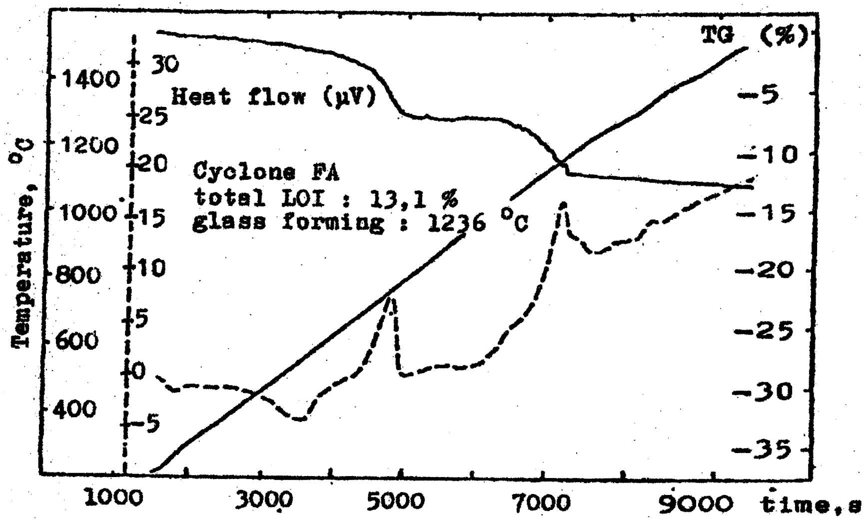

FIG. 4.
DTA + TG recording of a PFBC cyclone fly ash.

TABLE 2
Strength activity index of selected ashes (modification of ASTM C 311).

sample	ref.	1	2	3	4	5
MIX COMPOSITION (in g)						
Portland clinker	466	392	383	385	393	386
PFBC filter ash	0	100	0	0	0	0
PFBC bed ash B	0	0	100	0	0	0
PFBC cyclone ash	0	0	0	100	0	0
AFBC bed ash D	0	0	0	0	100	0
AFBC cyclone ash	0	0	0	0	0	100
gypsum	34	8	17	15	7	14
consistency [cm]	13.7	14.0	13.8	13.1	11.3	10.1
density [kg/m^3]	2334	2336	2320	2325	2338	2285
compr. strength [MPa]	81.5	83.3	68.9	67.4	75.5	70.3
activity index (28 d.) [%]	100.0	102.2	84.5	82.7	93.6	86.2

w/c = 0.45; total SO_3 = 3.5%.

to the same fineness, i.e., to 300±10 m^2/kg (Blaine). Test specimens 40 times] 40 × 160 mm prepared from a standard mortar mix (sand/binder = 3.00; w/c = 0.50) were demolded after 24 h of moist curing and subsequently stored in saturated lime water. The strength activity index was established as the ratio of compressive strengths of the ash-substituted and ash-free samples determined after 28 days of curing at 20°C. Because the water-binder ratio of the mixes was kept constant, the effect of the ash addition on the rheology could be determined. In separate experiments, the consistencies of the fresh mortar mixes were determined using a flow table in which the diameter of a predetermined amount of mortar (10 cm cone) placed on a plain glass plate, was measured after allowing the plate to lift and then fall 10 mm for 15 times.

The strength and consistency results from testing a series of PFBC and AFBC mixes are shown in Table 2. Of the analyzed ashes only the available filter ash, a material of extreme fineness, exhibited an activity index higher than 100, indicating a 28-day bonding capacity greater than that of the reference Portland cement. However, all other PFBC and AFBC ashes tested yielded results that indicate a hydraulic reactivity of these materials similar to, or greater than that of most conventional fly ashes. As to their effect on rheology, none of the three PFBC ashes altered the consistency of the mortar distinctly, whereas the presence of the two AFBC ashes caused a moderate worsening of the flow properties.

Table 3 shows the strength development of mortars made from cements with variable amounts of ash and gypsum, yet with a constant overall SO_3 content. The highest amount of ash that could be interblended into the cement without exceeding the preset overall SO_3 content was given by the amount of SO_3 present in the ash. After 180 days of curing, the compressive strength of all blended cements exceeded that of pure Portland cement, with the single exception of one cement, in which 55% of the clinker was replaced by the PFBC cyclone ash. It is especially remarkable that cements containing fluidized bed ashes exhibited high strengths after short hydration times, typically after just 3 days, unlike blended cements containing conventional class C fly ash.

TABLE 3
Strength development of cements.

sample	ref.	1	2	3	4	5
Cement composition						
Portland clinker	93	70	71.1	45	85.6	70
PFBC bed ash A	0	30	0	0	0	0
PFBC cycl. ash A	0	0	25	55	0	0
PFBC filt. ash A	0	0	0	0	10	30
gypsum	7	0	3.9	0	4.4	0
totoal SO_3	3.6	3.5	3.6	3.3	3.6	3.7
density [kg/m^3]	2310	2308	2320	2296	2332	2304
Compressive strength [MPa]						
1 day	26.3	19.1	21.6	10.0	25.7	20.6
3 days	34.9	37.2	36.7	21.1	44.0	40.6
7 days	41.3	46.9	45.2	28.2	53.5	53.6
28 days	51.8	54.2	59.5	42.6	64.7	72.8
90 days	60.5	65.7	74.2	56.0	73.6	82.8
180 days	65.7	72.6	76.9	61.0	77.1	93.0
180 days [%]	100.0	110.5	117.0	92.8	117.3	141.7

Hydration Mechanism

The hydration reactions of PFBC ashes were studied on pastes without the added clinker or gypsum, which were allowed to hydrate for up to 540 days at ambient temperature. After that, the following phases could be identified in the material by X-ray diffraction: main constituents: quartz, calcite, and gypsum; minor constituents: anhydrite and hematite; and traces: ettringite.

DTA + TG investigations revealed the presence of gypsum, ettringite, calcite, and some C-S-H or C-S(A)-H in the hydrated material. The pH value of the pastes was around 8 to 10 right after mixing, and declined moderately as the hydration progressed. These relatively low pH values may be explained by the absence of more than traces of free lime in the original PFBC ashes. Test specimens produced from plain pastes exhibited setting and hardening, with 28 day compressive strengths of up to 12 MPa.

In separate experiments, the hydration was studied after interblending the ashes with variable amounts of calcium hydroxide. The amount of formed ettringite and C-S-H increased under these conditions, apparently due to an enhanced pozzolanic reaction, which requires the presence of sufficient amounts of free $Ca(OH)_2$. At the same time the resultant strength values also increased distinctly.

Discussion

Fluidized bed combustion ashes differ from conventional fly ashes in many respects. Due to the calcium carbonate interblended with the fuel, these ashes are relatively high in their overall CaO content and contain virtually the entire amount of sulfur originally present in the coal as anhydrite. Due to the reduced combustion temperature, fluidized bed combustion ashes contain neither a glass phase nor mullite. Instead, the clay minerals, originally present in the fuel, undergo a partial thermal decomposition, thus attaining a distinct pozzolanicity. The ashes may also contain variable amounts of residual carbon, whose amount depends on the efficiency of the combustion process; excessive amounts of it may adversely affect the performance of the ash in blended cements. The amount of added calcium carbonate needed for an effective desulfurization of the flue gas generally must be above that required by stoichiometry; however, this excess may be lower in the PFBC than in the AFBC process. One significant difference between both types of fluidized bed ashes is the fact that in PFBC ashes the fraction of CaO that was not consumed in a reaction with sulfur dioxide is present predominantly or exclusively in the form of CaCO3, whereas in AFBC ashes free CaO predominates. Thus, the amount of calcium hydroxide that must be supplied from an external source for the formation of equal amounts of C-S-H or ettringite will be higher in PFBC ashes. Ashes in which dolomite, rather than calcite, had been used as the sorbent may also contain significant amounts of MgO, mainly in the form of free oxide, but also in the form of sulfate or carbonate. Such ashes are barely suitable to be used as constituents of blended cements, due to a slow and expansive MgO hydration that may cause unsoundness of the hardened cement paste, due to the inability of $MgO/Mg(OH)_2$ to convert into phases with cementing properties, and due to a high solubility of magnesium sulfate.

The hydraulic/pozzolanic reactivity of fluidized bed ashes appears to be due to the presence of thermally decomposed clay minerals. They act as a source of SiO_2 for the formation of a C-S-H phase in a reaction with calcium hydroxide, and as a source of Al_2O_3 for the formation of ettringite in a reaction with calcium hydroxide and calcium sulfate. In AFBC ashes, significant amounts of calcium hydroxide may be readily formed in a reaction of the present calcium oxide with water. This reaction progresses rather fast, as the calcium oxide is present in a reactive form due to the relatively low temperature in the combustor. Contrary to that, the amount of available free lime in PFBC ashes is usually small and a significant formation of a C-S-H phase only takes place if calcium hydroxide from an external source is available. The rate of ettringite formation in PFBC ashes, just as in AFBC ashes, is usually determined by the amount and reactivity of the available SO_4^{2-} source, i.e., anhydrite; however, the limited availability of calcium hydroxide in PFBC ashes may also play a role. Usually, distinct amounts of anhydrite will remain in unhydrated form even after long curing times, though some of it will eventually hydrate to gypsum in a reaction that may also contribute to setting and hardening. Due to a higher degree of dispersion and thus a greater reactivity of the clay mineral decomposition products, the hydration and strength development of blended cements containing fluidized bed ashes progresses faster than that of cements containing conventional fly ash in which a glass phase that is more compact and less reactive acts as the main hydraulic/pozzolanic constituent.

Available data suggest the possibility of using most PFBC ashes, in combination with Portland clinker, as constituents of blendeed cements, in a similar way as AFBC ashes. PFBC ashes not suitable for this purpose include those with too much MgO, or residual carbon. In using fluidized bed ashes, care has to be taken to keep the overall SO_3 content in the final blended cement within limits considered safe with respect to volume stability. This will require reducing the amount of SO_3 introduced in the form of gypsum, or eliminating the addition of gypsum alltogether. A serious legal obstacle for the use of these materials as cement constituents may be that current specifications, such as the European prestandard 197–1, do not include fluidized bed combustion ashes among materials admissible as constituents of blended cements. An ammendment of such standards may be indicated, to eliminate this problem.

Conclusions

1. Pressurized fluidized bed combustion (PFBC) ashes formed at relatively low temperatures and elevated pressure, with limestone added to the fuel as a sorbent of sulfur dioxide, differ distinctly from conventional fly ashes. They contain neither a glass phase nor mullite among their constituents. Instead, they contain products of thermal degradation of clay minerals that may serve as sources of active SiO_2 and Al_2O_3, if allowed to react with calcium hydroxide. The sulfur, originally bound within the fuel, is present in the ash mainly in the form of anhydrite. Unlike ashes produced in atmosperic fluidized bed combustion, calcium oxide that was not consumed in a reaction with sulfur dioxide remains present mainly in form of calcium carbonate, rather than free lime.
2. Pastes made from PFBC ashes by mixing them with water may exhibit setting and hardening, yielding a C-S-H phase, ettringite, and gypsum as products of hydration. In the absence of an external calcium hydroxide source, the extent of this reaction will be limited by the amount of free lime present in the ash.
3. Blended cements produced by combining PFBC ashes with Portland clinker tend to exibit a relatively fast initial strength development, indicating a rather high hydraulicity/pozzolanicity of this type of ashes. Because a substantial fraction, or all of the needed calcium sulfate in these cements is introduced with the ash, a separate addition of gypsum to these binders may be not necessary, or may be reduced.

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