Pergamon

Cement and Concrete Research 29 (1999) 1387–1391

CEMENT AND CONCRETE RESEARCH

Pozzolanic properties of pulverized coal combustion bottom ash

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Received 16 July 1998; accepted 22 April 1999

Abstract

The pozzolanic properties of a coal combustion bottom ash were investigated. Plain pastes containing equal amounts of calcium hydroxide and bottom ash were prepared and analyzed at different ages for their strength and the calcium hydroxide consumption. At early ages, bottom ash does not react with calcium hydroxide. Its pozzolanic reaction proceeds slowly and accelerates gradually to become very interesting after 28 days and especially after 90 days. The strength activity indexes measured on mortars are sufficiently important to allow the use of bottom ash in concrete. When ground for 6 h in a laboratory ball mill, the 28-day strength activity index of bottom ash is increased by 27%.

Keywords: Bottom ash; Blended cement; Grinding; Pozzolan; Strength; Thermal analysis

1. Introduction

The Brazilian company Eletrosul's Jorge Lacerda power station currently burns a coal that has a heat value of only 4500 kcal/kg and an ash content as high as 42%. In utilizing such low-quality coal it should be realized that increasing amounts of ash are being handled and disposed of. The power station produces on average approximately 1.2 million metric tons of ash by burning 2.9 million metric tons of coal per annum. Coal is pulverized and burned in a grate boiler. Fly ash is collected in a proportion of 60% and is easily valorized in concrete and cement production. The remaining 40% of coarser ash falls down on a belt conveyor to be milled and water-cooled before transportation to a lagoon. This type of ash is called "bottom ash" in the present study and has been investigated for its potential pozzolanic properties. Until now, it has not yet been valorized in the cement industry.

The properties of pulverized fly ash have been extensively reported in the literature [1]. The utilization potential of fly ash is mainly controlled by its chemical composition (although fineness is also an important consideration), whereas the utilization potential of bottom ash is determined more by its physical characteristics such as grain-size distribution, soundness, staining potential, and color. The normally coarse, fused, glassy texture of bottom ash makes it an ideal substitute for natural aggregates [2]. It is often used as a low-cost replacement for more expensive sand in the production of concrete blocks and in many countries it is used as a base in road construction [3–6]. High-performance lightweight concrete can be produced using sintered fly ash coarse aggregates, bottom ash fine aggregates, and fly ash mineral admixture in combination with Portland cement and water [7]. Densities of 1800 kg/m^3 and compressive strengths of 55 MPa are obtained. In the 1980s, Wisconsin Electric issued a research contract to the University of Wisconsin-Madison to study the use of bottom ash for amending heavy clay agricultural soils in southeast Wisconsin [2,8]. It appears that the addition of bottom ash to such soils can serve to supplement commercial fertilizer applications and may positively increase crop yields. In India, most of the thermal power plants use a wet system for disposal of ash. The bottom ash from the boilers and the fly ash from the precipitators are mixed together and pumped off in the form of slurry to lagoons. Such ash, referred to as ponded ash, is not widely used in concrete but some size fractions can be regarded as pozzolanic, and especially the particles below 75 μm (about 65% of the ponded ash) [9].

This paper examines the pozzolanic activity of a Brazilian bottom ash and a way that allows for an improvement of its reactivity.

2. Experimental

2.1. Characterization of the bottom ash

The chemical composition of the bottom ash is given in Table 1. The calcium content is very low ($<1\%$) and the

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PII: S0008-8846(99)00098-8

Table 1
Chemical composition of the bottom ash

Oxides (wt%)									
SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	LOI
56.0	26.7	5.8	0.6	0.8	0.2	2.6	1.3	0.1	4.6

sum (SiO_2 + Al_2 O_3 + Fe_2O_3) reaches 88.5%, which means that this ash belongs to ASTM Type F ash. For this bottom ash, the loss on ignition (LOI) is mainly due to carbon. The amount of carbon was found to be 3.8%, which gives 13.9% CO_2, while the measured quantity of CO_2 was 14%. The remaining LOI (0.8%) is certainly due to combined water in residual clays.

The X-ray diffractogram of the ash (Fig. 1) shows the presence of a glassy phase with two major crystalline phases of quartz and mullite. This low-calcium ash shows diffused halo maxima at 20–27°2θ (Cu Kα radiation).

The scanning electron micrograph of the ash (Fig. 2) shows both spherical and rounded particles, and irregularly shaped grains. The specific gravity measured by the pycnometer method was 2.0. This low value suggests that hollow particles, such as cenospheres or plerospheres, are present in significant proportions in the ash. The particle size distribution of bottom ash as received was measured using a laser granulometer. Of the particles, 100% were smaller than 100 μm and 2% were smaller than 1 μm. The average diameter of the particle size distribution was 35 μm.

2.2. Evaluation of the pozzolanic activity of the bottom ash

Evaluation of the pozzolanic activity of ash and other pozzolans falls into three categories: chemical, physical, and mechanical. The chemical evaluation, which is the method of the International Organization for Standards (ISO) recommendation R 863-1968, measures the reduction of calcium ions when a pozzolan is suspended in a saturated lime solution. The X-ray diffraction technique has been used to monitor the progress of the lime uptake in pozzolan-Portland cement containing fly ash and rice-husk ash [10].

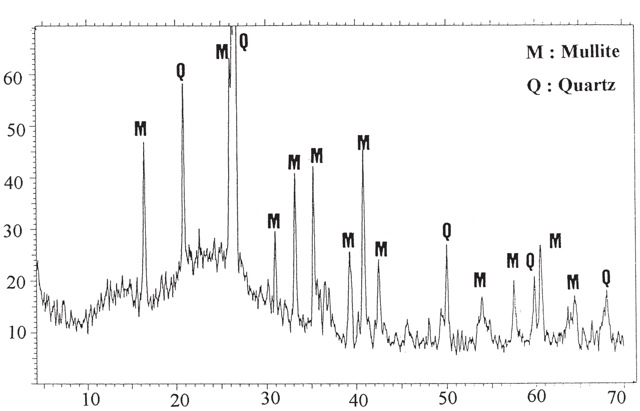

Fig. 1. X-ray diffractogram of the bottom ash.

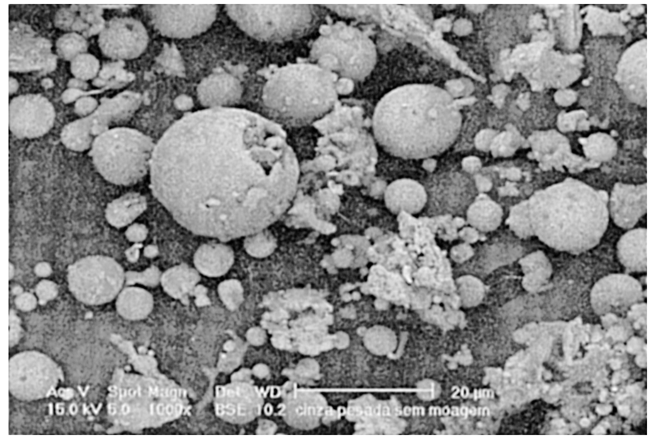

Fig. 2. Morphology of the bottom ash.

The results obtained by this method indicated good correlation between the lime combined in the reaction and the compressive strength of mortars at 6 months and 1 year.

The mechanical methods assess the strength properties of concretes containing fly ash and pozzolans, and ASTM C 311 describes the strength activity with Portland cement and with lime. For both, the compressive strength of the control mixture is compared with the strength of pozzolan-containing mixture at ages of 7 or 28 days.

In the present study, both mechanical and chemical assessments of the pozzolanic activity with lime were performed. Plain paste containing 50% bottom ash (BA) and 50% calcium hydroxide (CH) was prepared at standard consistency. The water-to-solid ratio was 0.42. The paste was placed into cylinders (Ø = 50 mm, h = 100 mm), kept in molds for 6 days, then cured in water until 13, 27, and 89 days of hydration. Before testing the samples were dried at 50°C for 1 day. The cylinders were subjected to compressive strength tests at 7, 14, 28, and 90 days.

At the same ages, the calcium hydroxide consumption was measured by the following method, previously developed by Ambroise et al [11] to study the pozzolanic activity of metakaolin. The measurement was done by differential thermal analysis on 600 mg of powder ground to be smaller than 100 μm. The surface area of the residual calcium hydroxide peak was measured and compared to that of a paste containing 50% calcium hydroxide and 50% ground silica, which acts as an inert material. The ratio between these two peaks gave the relative calcium hydroxide consumption of bottom ash compared to an inert filler.

Table 2
Pozzolanic activity of bottom ash with lime

	Age (days)			
Characteristic	7	14	28	90
Compressive strength (MPa)	1.8	3.2	6.4	17.3
Calcium hydroxide consumption (%)	5	15	37	60

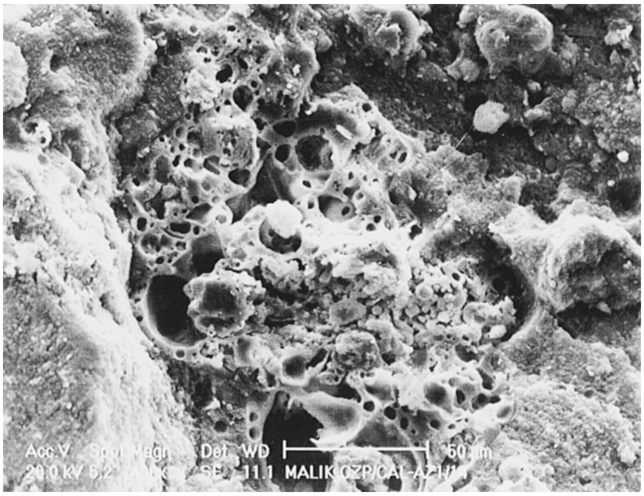

Fig. 3. Scanning electron micrograph of hydrated bottom ash-calcium hydroxide mixture at 14 days. Unattacked ash particles.

The microstructure of the different pastes was also investigated by scanning electron microscopy associated with energy-dispersive X-ray analysis, using a Philips XL30 microscope (Philips, The Netherlands).

2.3. Strength activity of bottom ash

The strength activity of bottom ash was determined according to the European standard EN 450. The strength activity index is the ratio of the compressive strength of standard mortar bars, prepared with 75% reference cement plus 25% ash by mass, to the compressive strength of standard mortar bars prepared with reference cement alone, when tested at the same age. If these indexes are higher than 0.75 at 28 days and 0.85 at 90 days, the ash is allowed to be used in concrete.

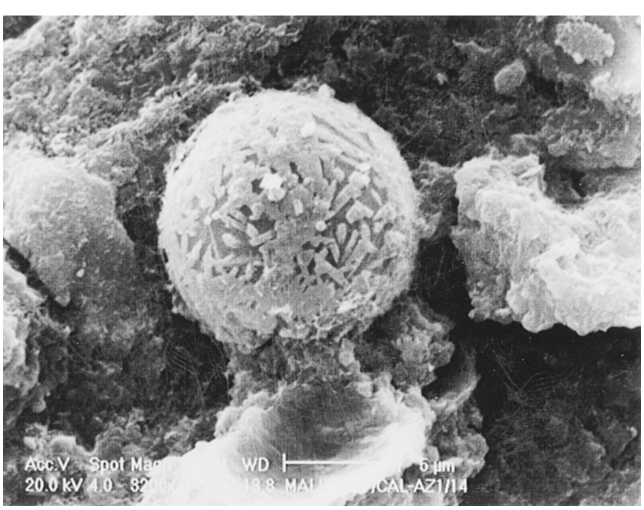

Fig. 4. Scanning electron micrograph of hydrated bottom ash-calcium hydroxide mixture at 14 days. Particles starting to react with $Ca(OH)_2$.

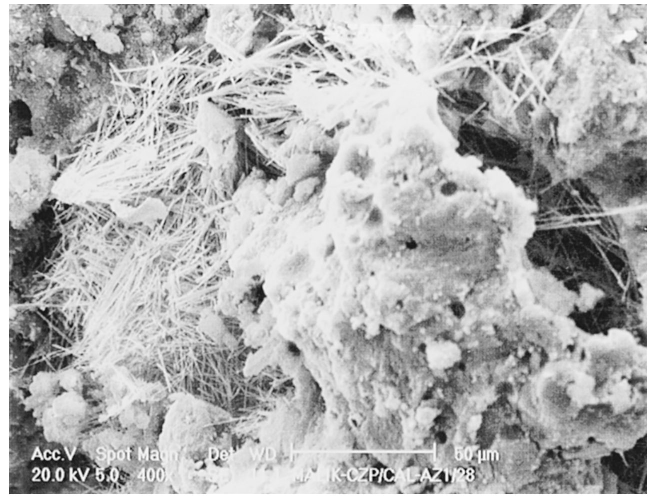

Fig. 5. Scanning electron micrograph of hydrated bottom ash-calcium hydroxide mixture at 28 days. Formation of C-S-H.

3. Results and discussion

3.1. Pozzolanic activity of bottom ash with lime

The strength and calcium hydroxide consumption of BA/CH pastes up to 90 days of hydration is given in Table 2. The results obtained show that bottom ash slightly reacts with calcium hydroxide at early ages. The pozzolanic reaction starts after 14 days: the strength is gradually improved and the calcium hydroxide consumption compared to an inert filler is important after 90 days of hydration. These results are in good agreement with those reported by Ghgafoori and Buchole [12].

The low strength observed after 14 days of hydration is due to the fact that many of bottom ash particles remained unattacked by calcium hydroxide, especially those presenting a slaglike morphology, as shown in Fig. 3. At the same age, Fig. 4 shows that spherical particles began to be covered by hydrates but were not yet disintegrated.

After 28 days of hydration, bottom ash particles reacted with calcium hydroxide, resulting in the formation of C-S-H gel and needles (Fig. 5).

3.2. Strength activity of bottom ash with Portland cement

The strength activity indexes of bottom ash at different hydration times are reported in Table 3. The strength index is higher than 0.75 (0.764) after 14 days of hydration, which also proves the pozzolanic activity of the ash. It reaches 0.88 after 28 days and 0.97 after 90 days of hydration. These values are higher than those required by the European

Table 3
Strength activity of bottom ash with portland cement (according to EN 450)

	Age (days)			
	7	14	28	90
Activity index	0.72	0.764	0.88	0.97

Table 4
Physical properties of ground bottom ash

Time of grinding (h)	0	1	2	3	4	6
Specific gravity	2.00	2.02	2.11	2.14	2.21	2.25
Average particle-size diameter (μm)	35	33	25	20	16	13
Particles <1 μm (%)	2	2	5	8	12	15

standard ENV 450, and it can be concluded that this bottom ash is suitable for use in concrete.

3.3. Improvement of bottom ash reactivity

The mechanical treatment by grinding of fly ash alters physical, mineralogical, morphological, and chemical fly ash properties. J. Payá et al. [13] have pointed out an increase in pozzolanic activity with grinding of fly ash. On another hand, Chengzhi et al. [14] have analyzed the filling role of pozzolanic material. From theoretical analyses and experimental results, they have concluded that the addition of pozzolanic material influences the packing state and decreases the amount of filling water. This role depends on the fineness of pozzolanic materials.

In order to improve the reactivity of bottom ash, it was ground in a laboratory mill for 1–6 h. The physical properties of ground bottom ash are reported in Table 4.

As shown in Table 4, during the milling process an increase of specific gravity was observed: +12.5% for a 6-h grinding time. The same phenomenon was observed by Payá et al [15] when grinding fly ash. They concluded that it was due to crushing cenospheres and porous carbon particles. The average particle size diameter decreased from 35 μm to 13 μm after 6 h of grinding and the quantity of particles smaller than 1 μm increased from 2 to 15%.

The pozzolanic activity of the ground ash was determined according to the Brazilian standard NBR-5752. Standard mortars were prepared at equivalent consistency with a sand-to-binder ratio of 3.00. The binder was either plain cement or a mixture of 65% cement and 35% ground ash.

After casting, samples were kept in molds for 24 h, then demolded and cured at 38°C for 26 days. The compressive strength was measured at 28 days. The pozzolanic activity index is defined as the ratio between the strength of the mortar containing the blended cement and that of the mortar cast with plain cement The results obtained are shown in Table 5. Table 5 points out that the higher the grinding time is, the higher the pozzolanic activity of bottom ash is, according to NBR-5752.

Table 5
Strength activity index (28 days) of ground bottom ash (according to NBR-5752)

Time of grinding (h)	0	1	2	3	4	6
Water-to-binder ratio	0.62	0.60	0.58	0.58	0.57	0.57
Activity index	0.81	0.81	0.92	0.93	0.95	1.08

Table 6
PER values for mortars

Time of grinding (h)	0	1	2	3	4	6
S_f	1	1	1.14	1.15	1.17	1.33
F	1	1.04	1.06	1.05	1.05	1.05
PER = S_f/F	1	0.96	1.08	1.09	1.11	1.27

3.4. Pozzolanic effectiveness ratio

In order to estimate the pozzolanic activity of ground bottom ash by another method, the pozzolanic effectiveness ratio (PER) proposed by Berry et al. [16] and Ramyar et al. [17] was calculated. Based on Feret's law, which establishes a relationship between strength (f) and absolute volumes of water (w), cement (c), and air (a), this PER parameter is the value of S_f/F, as shown in Eq. (1):

$$F = \frac{f_i}{f_o}\left[\frac{c_o + w_o}{c_i + w_i} \cdot \frac{c_i}{c_o}\right]^2 \qquad (1)$$

where S_f is the experimental strength ratio s_i/s_o, s_i is the compressive strength of the mortar containing ground ash, and s_o is the strength for the mortar containing the starting ash. Eq. (1) shows the calculated strength ratio based on mixture proportion.

Table 6 shows PER values for mortars after 28 days of hydration. Except when the bottom ash is ground for 1 h, PER values are greater than unit and, consequently, an increase of pozzolanic activity of bottom ash due to grinding can be assumed. But, as the water to binder ratio decreases with grinding time, the filling role of ground bottom ash cannot be neglected [14].

4. Conclusion

From this limited investigation, the following conclusions can be drawn:

1. This particular ash, very poor in CaO (0.8%), presents a certain similarity to class F fly ash.
2. The pozzolanic activity of bottom ash with lime is very low till 14 days of hydration. Pozzolanic activity starts at 28 days and the calcium hydroxide consumption is very important at 90 days.
3. The strength activity indexes with Portland cement determined on standard mortars according to the European standard ENV450 reach 0.88 at 28 days and 0.97 at 90 days. Such values allow the use of bottom ash in concrete.
4. An adequate grinding improves the pozzolanic activity of the bottom ash. The filling role of ground ash is also interesting and the 28-day strength index of ash is increased by 27% when it is ground for 6 h in laboratory ball mill.

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