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The physical–chemical characterization of mechanically-treated CFBC fly ash

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Abstract

The physical–chemical characteristics of mechanically-treated circulating fluidized bed combustion (CFBC) fly ash, such as 45 μm sieve residue, granulometric distribution, water requirement, specific gravity, pH value, and mineralogical phases, were investigated. It was found that the grinding process can be divided into three stages. The increase in fineness of ground CFBC fly ash is very sharp in the first stage, then slows down in the second stage, and in the last stage it becomes almost invary. The water requirement decreases with prolonged grinding time, and slightly increases during the last stage of grinding. Ground CFBC fly ash shows a higher specific gravity due to the crushing of coarse particles and carbon particles. The pH of ground CFBC fly ash is greater than that of the original CFBC fly ash, indicating that ground samples react more rapidly with water. The mineralogical compositions remain unchanged with grinding, although the intensity of the crystalline phases decreases and the half peak width increases.

Keywords: CFBC fly ash; Mechanical treatment; Physical–chemical characterization

1. Introduction

Circulating fluidized bed combustion (CFBC) is a very effective technology for burning high-sulfate fuels such as lignite, sub-bituminous and high-sulfate petroleum coke [1]. This technology, which has many advantages such as a wide fuel flexibility, low combustion temperatures (typically in the range of 800–900 °C), low NO_x emissions, a high combustion efficiency, a significant desulfurization rate (typically 90%) and so on [2], is being installed and operated in more and more Chinese power plants.

The in situ use of limestone results in CFBC fly ash with a high calcium content. CFBC fly ash usually contains 20–30% (wt.) unreacted CaO because of the low utilization of Ca sorbent [3]. The limestone is calcined to CaO in the furnace, where it reacts with SO_2 and O_2 to form $CaSO_4$. CFBC fly ash contains not only $CaSO_4$, but also CaO. The use and disposal of CFBC fly ash poses challenges, because of its highly exothermic reactions with water, high pH leachates, and excessive expansion of solidified materials [4]. And the dominant particles of CFBC fly ash comprise mainly coarse and angular, flaky, drossy, and irregular particles with a broad particle size range [5]. These particles can result in the need for a high water requirement, which is another reason why the utilization percent of CFBC fly ash is low. The porous and irregular CFBC fly ash particles have a larger specific surface area than spherical particles, which results in the water added to the mortar with CFBC fly ash being increased if the same fluidity is reached. However, the water provided is less than the water needed for the hydration of cement, and the redundant water retained in the mortar which can become the harmful pores after the mortar has hardened. It has been studied that the damaged pores can cause a decrease in the strength of hardenite [6,7], which is the main reason that the utilization percent of CFBC fly ash is low.

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There are three methods to improve the pozzolanic activity of fly ash. The first is heat processing, such as autoclaving and vapor curing; the second is chemical processing, such as adding alkali materials; and the third is mechanical processing, such as grinding [8–14]. As for CFBC fly ash, there have been very few reports about improving its activity, and only the French CERCHAR, has developed a patented technology for hydrating fly ash from processes like fluidized bed combustion (FBC) with high calcium content. This patented hydration technology effectively permits the complete hydration of the CaO component without conversion of the $CaSO_4$ component to gypsum or the formation of compounds like ettringite so that they remain available for cementitious reactions [4,15,16].

Mechanical activation has been used in mineral processing to produce finely ground particles, increase surface area and improve the chemical reactivity of milled materials. A variety of processes take place during grinding such as the generation of a large new surface, the formation of dislocations and point defects in the crystalline structure, phase transformations in polymorphic materials, and chemical reactions [17]. As for CFBC fly ash, mechanical grinding can make the free calcium (f-CaO) distribute homogeneously, and diminish the expansion due to the agglomeration of f-CaO, besides this process can reduce the particle size, increasing the activity of the fly ash.

This paper discusses the effect of grinding on the physical characteristics such as fineness (45 μm sieve residue), granulometric distribution, and specific gravity of CFBC fly ash. The chemical and mineral characteristics of ground CFBC fly ash were also studied.

2. Materials and experimental methods

2.1. Materials for experiment

The chemical compositions and physical properties of CFBC fly ash and Portland cement equivalent to ASTM Type I used in this study are given in Tables 1 and 2, respectively. The fly ash was collected from a commercial CFBC boiler operated by Jinling Electric Power Plant, Nanjing. The CFBC boiler was operated by using a blending fuel consisting of Datong (Shanxi, China) bituminous coal (60%, cal.) and Mideast high-sulfur petroleum coke (40%, cal.), and the resulting SO_2 was captured by the pulverized limestone added in situ.

Fig. 1 shows an SEM photomicrograph of CFBC fly ash. The dominant particles of this fly ash sample comprise mainly coarse and angular, flaky, drossy, and irregular particles with a broad particle size range.

Table 2
Physical properties of cement and CFBC fly ash

Materials	Specific gravity	45 μm sieve residue (%)
Cement	3.11	2.84
CFBC fly ash	2.44	16.08

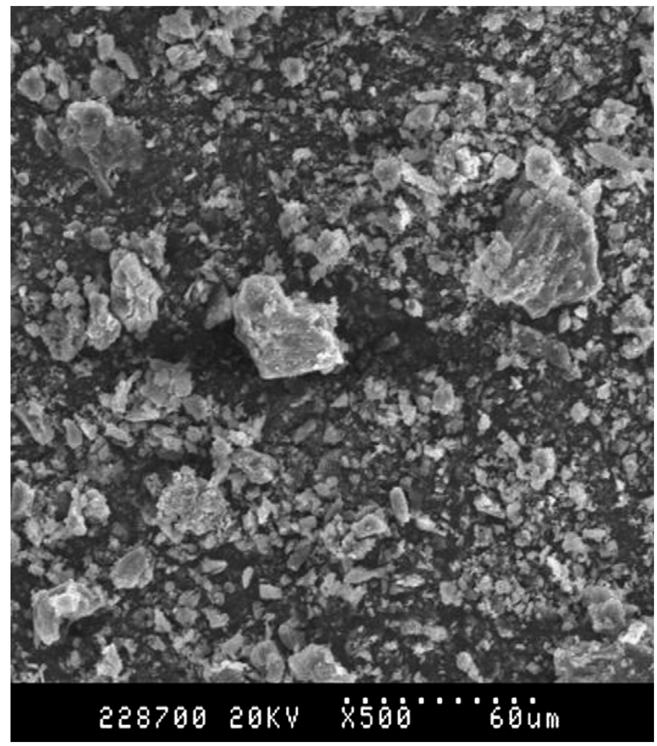

Fig. 1. An SEM photomicrograph of CFBC fly ash (×500).

2.2. Apparatus for experiment

A laboratory ball-mill using ball media as listed in Table 3, was employed for grinding the fly ash samples. Samples (5000 g) of original CFBC fly ash (named as F0) were introduced into the ball-mill and ground for 10, 20, 25, 30, 35, 40, 45, 50, 60, 70 min, yielding the ground CFBC fly ashes F10, F20, F25, F30, F35, F40, F45, F50, F60 and F70, respectively.

Granulometric distributions were performed using a Mastersizer 2000. The pH value was measured with a model 868 pH-meter (Orion, USA). The $Ca(OH)_2$ and

Table 1
Chemical compositions of cement and CFBC fly ash[a] (wt.%)

Materials	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	K_2O	SO_3	LOI
Cement	21.44	4.95	64.3	3.52	0.29	1.39	0.69	2.38	1.59
CFBC fly ash	24.35	15.86	32.00	2.24	0.35	1.84	0.58	7.96	14.73

[a] LOI: Loss on ignition.

Table 3
Grading of ball-mill

Specifications	Numbers	Weight (kg)
∅70 mm	9	12.66
∅60 mm	24	21.67
∅50 mm	37	20.99
∅40 mm	43	13.02
$\varnothing \times L$ (25 mm × 30 mm)	343	42.21

$CaCO_3$ contents were studied with a thermal analyzer (Perkin–Elmer, USA). The mineralogical characterization of ground CFBC fly ash was determined with a model CAD4/PC powder X-ray diffractometer (XRD) (Enraf Noiu, Holland) with CuK_α radiation at 50 kV and 40 mA.

2.3. Methods for experiment

The water requirements of original and ground CFBC fly ashes were determined according to the Chinese standard GB/T 1596-2005. The testing mortar was prepared with 175 g of cement, 75 g of CFBC fly ash, 750 g of International Organization for Standardization (ISO) standard sand, and $w1$ ml of water. The contrast cement mortar was prepared with 250 g of cement, 750 g of ISO standard sand, and $w2$ ml of water. The added water was required when the degree of fluidity of the testing mortar or contrast cement mortar is between 130 mm and 140 mm. The water requirement of fly ash was defined as the ratio of $w1$ to $w2$. The fly ash whose water requirement is less than 100% in concrete can take the effect of decreasing the water content and increasing the strength of the concrete. However, the fly ash whose water requirement is more than 100% causes an adverse effect in concrete.

The f-CaO content of the original and ground CFBC fly ashes was determined according to the glycerin–ethanol method. First, about 0.5 g of sample and 15 ml of glycerin in anhydrous ethanol were heated and boiled for 10 min, and then titrated with standard benzoic acid anhydrous ethanol solution. The f-CaO content was calculated based on the benzoic acid anhydrous ethanol solution quantity used.

3. Results and discussion

3.1. Physical characteristics

Fig. 2 shows the variation of the 45 μm sieve residues of samples with grinding time. It can be seen that the grinding process can be divided into three stages. The first stage is the initial grinding period, in which the increase of fineness is very sharp and the time is about from 0 to 30 min. The second stage is the developing grinding period, in which the increase of fineness slows down and the time is about from 30 min to 50 min. The third stage is the lag period and the time is about from 50 min to 70 min, in which the fineness is no longer increasing or sometimes decreases a little. This occurs because the particles are so fine that they aggregate together by electrostatic forces [18].

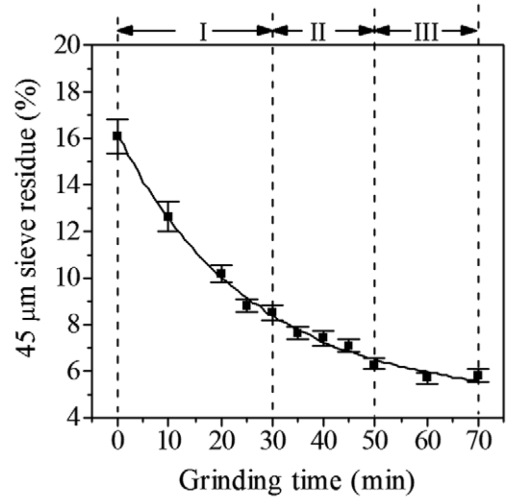

Fig. 2. Variation of 45 μm sieve residue of CFBC fly ash with grinding time (square mesh sieve).

Fig. 3 shows the granulometric distribution determined with a laser granulometer vs grinding time. In the first stage (from 0 to 30 min), the majority of particles with diameter greater than 45 μm have been crushed, which is the reason that the 45 μm sieve residue was drastically reduced during the short grinding period. For grinding times longer than 30 min, the content of particles greater than 45 μm decreased slowly. The percentage of particles less than 10 μm undergoes an increase with increased grinding time. In the third stage, the fineness of the ground samples varies little as the grinding reaches the limit. The percentage of particles with sizes between 10 μm and 20 μm remain unchanged, which means that grinding is invalid for particles with sizes of 10–20 μm in this ball-mill.

The RRSB (Rosin–Rammler–Schuhmann–Bennett) equation can describe the distribution of powder materials. The general RRSB equation is:

$$R(x) = e^{-\left(\frac{x}{\bar{x}}\right)^n},$$

and this can be transformed into another format, which is:

$$\ln \ln R(x) = -n(\ln x - \ln \bar{x}),$$

where $R(x)$ is the screening residues passing x μm; $\bar{x}$ is the position parameter, which is the particle size when the screening residues reaches 36.8%; n is the uniformity coefficient, which can be calculated from the fitting curve of $\ln\ln R(x)$ and $\ln x$.

Table 4 describes the RRSB distribution, the position parameter ($\bar{x}$), and the uniformity coefficient (n) of ground CFBC fly ash. When the particle diameter is more than 1 μm, it can be seen that the particle size distributions of the ground CFBC fly ash follow the RRSB distribution. However, the particle size distributions of the ground CFBC fly ash do not satisfy the RRSB distribution for the whole scope of particle diameters or the scope of diameters less

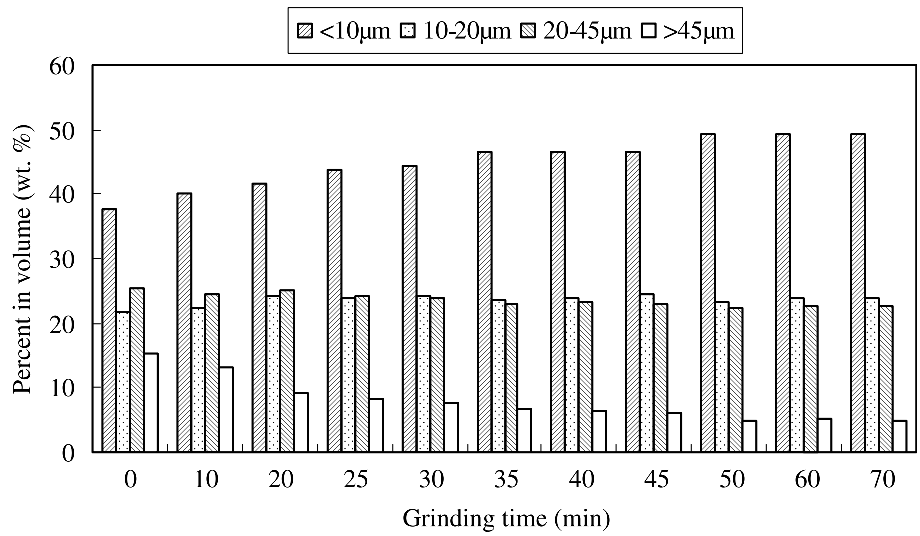

Fig. 3. Variation of granulometric distribution vs the grinding time for CFBC fly ash. (laser granulometer).

Table 4
Variation of fineness parameters of CFBC fly ash with the grinding time

Grinding time (min)	Fineness parameters[a]		Correlation coefficient, R^2
	$\bar{x}$	n	
0	9.42	1.0757	0.9989
10	8.87	0.9448	0.9946
20	8.44	0.9944	0.999
25	7.77	0.9808	0.999
30	7.64	0.9971	0.9993
35	7.35	0.9819	0.9989
40	7.13	1.0011	0.999
45	7.10	0.9947	0.9991
50	6.61	0.9171	0.9974
60	6.47	1.0081	0.9983
70	6.40	0.9577	0.9988

[a] The particle diameter is more than 1 μm.

Table 5
Water added in the testing mortar of the ground CFBC fly ash as a function of grinding time[a]

Grinding time (min)	$w1$ (ml)[b]
0	161
10	156
20	150
25	149
30	146
35	145
40	145
45	143
50	142
60	143
70	143

[a] Water added ($w2$) into the control mortar is 132 ml (average).
[b] $w1$ is average value.

than 1 μm. The reason for this is unknown at the present time. The position parameter decreased with increasing grinding time, which is in accordance with the results of the 45 μm sieve residue. However, the variation of the uniformity coefficient is not regular with grinding time.

Table 5 shows the variation of the water added at the degree of fluidity of the testing mortar is between 130 mm and 140 mm. And Fig. 4 shows the water requirement of the ground CFBC fly ash with grinding time. The water requirement decreases with prolonged grinding time, which reaches a minimum at 50 min, and increases slightly after 50 min.

The water requirement was affected by the characteristics of the fly ash such as the particle size, the specific surface area, and the shape. The reason that fly ash with a water requirement of more than 100% can increase the water content in mortar is as follows. It is studied that the mixing water in mortar includes two parts, filling water which fills the voids between solid particles, and waterfilm water, which packs the solid particles [19]. The filling water decreases because of the decreasing number of irregular particles to form a more homogeneous mixture, and the compacting of the fly ash by grinding. However, the waterfilm water increases due to increases in the specific surface area of the ground fly ash. During the early grinding stage, the influence of the filling water is more than that of the waterfilm water, which is the reason why the water requirement decreases at first. In addition, the water requirement increases after 50 min of grinding, which is due to the influence of the waterfilm water being more than that of the filling water.

The specific gravity of ground CFBC fly ash is illustrated in Fig. 5. During the grinding process, an increase of specific gravity can be observed. It can be seen that grinding for 50 min is a cut-off point, in which before this point the specific gravity increases rapidly, while after it, the specific gravity increases more moderately. Grinding makes the coarse particles and carbon particles finer with a much lower porosity, which is the main reason why the specific gravity increases with prolonged grinding time [10]. However, the specific gravity moderates after 50 min

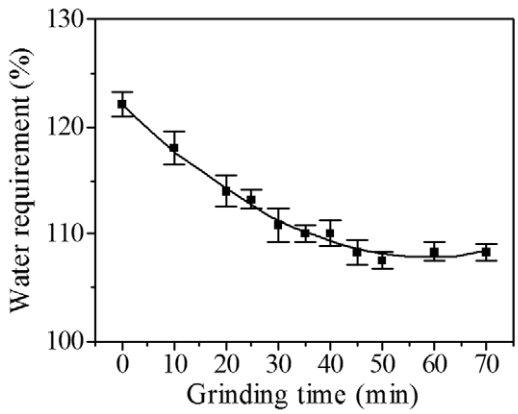

Fig. 4. Variation of the water requirement of ground CFBC fly ash with grinding time.

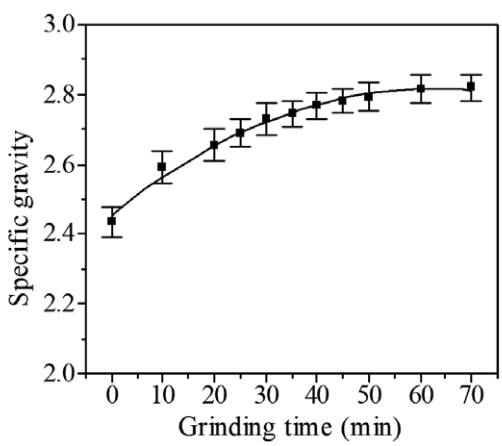

Fig. 5. Variation of the specific gravity of ground CFBC fly ash with grinding time.

grinding, because the fineness of the ground CFBC fly ash eases at this stage.

3.2. Chemical characterization

Fig. 6 shows the variation of pH value of the ground CFBC fly ash with time, where the pH was measured by mixing 10 g of CFBC fly ash with 100 ml of distilled water. It can be seen that the pH value of ground CFBC fly ash is greater than that of the original CFBC fly ash, indicating that ground samples can react more rapidly with water. The CaO present in CFBC fly ash is in the form packed with $CaSO_4$ [20]. Grinding can crush the $CaSO_4$ layer and release CaO, which is the main reason why the pH value of ground CFBC fly ash is more than that of the original CFBC fly ash. Fig. 7 shows the variation of f-CaO vs grinding time. It can be noticed that the f-CaO content increases with increasing grinding time. The ground CFBC fly ash reacted more rapidly with water, because of the larger specific surface area, which is another reason why the pH values of the ground samples are higher than that of the original CFBC fly ash [10].

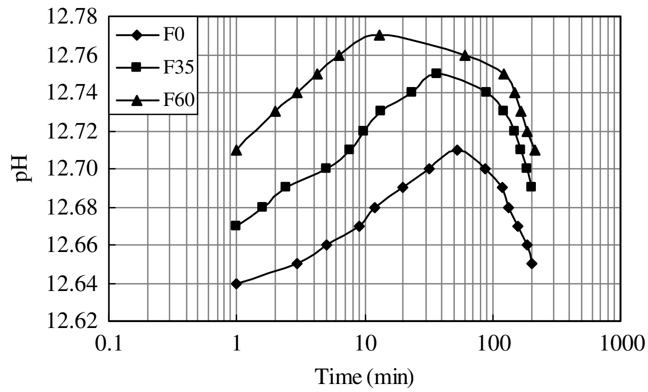

Fig. 6. Variation of pH with time ($L/S = 10$) for CFBC fly ash.

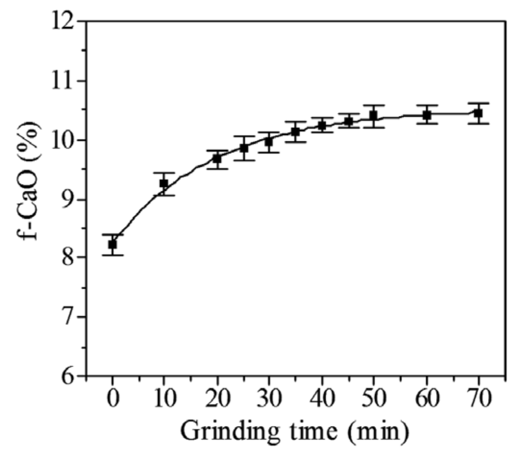

Fig. 7. Variation of f-CaO content in CFBC fly ash with grinding time.

It can also be noticed from Fig. 6 that the pH values of the original and ground CFBC fly ash samples firstly increase and then decrease, which is different from the results reported by Payá et al. [10]. There may be two reasons which account for this difference in pH. The first is that the fly ash used in this paper is CFBC fly ash, which contains more f-CaO and $Ca(OH)_2$ than ordinary Class F fly ash. The dissolving of $Ca(OH)_2$ and f-CaO in CFBC fly ash causes the pH value to increase, while the reaction of $Ca(OH)_2$ with CO_2 in air makes the pH value decrease. It can be noticed from Table 6 that the $CaCO_3$ contents in CFBC fly ash increase markedly after mixed with water for 24 h. The second reason relates to the mixing time, in which Payá reported a mixing time of 100 min, while in this paper

Table 6
Variation of $Ca(OH)_2$, $CaCO_3$, and LOI of CFBC fly ash before and after mixing with water

Samples	CFBC fly ash		CFBC fly ash mixed with water for 24 h	
	$Ca(OH)_2$ (%)	$CaCO_3$ (%)	$Ca(OH)_2$ (%)	$CaCO_3$ (%)
F0	4.09	10.05	5.98	11.54
F35	5.55	10.87	8.93	12.06
F60	5.93	10.92	9.27	12.83

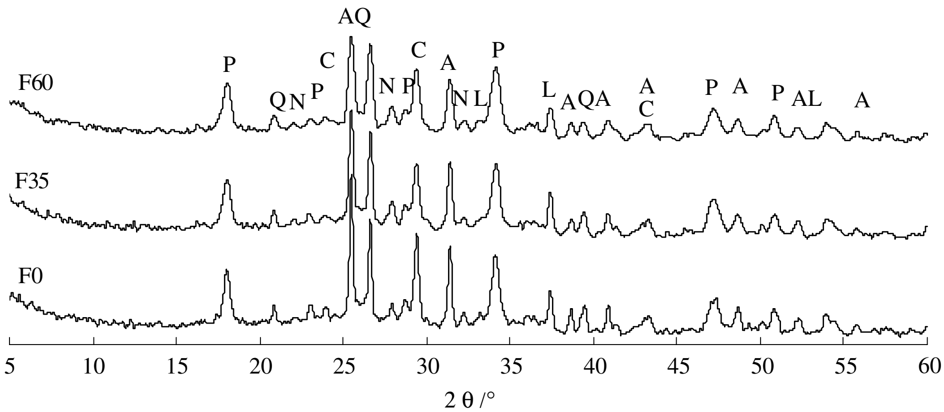

Fig. 8. XRD patterns of ground CFBC fly ash (P – Portlandite, Q – Quartz, A – Anhydrite, C – Calcite, L – lime, N – Unknown).

the mixing time is 200 min. The $Ca(OH)_2$ in CFBC fly ash reacts with CO_2 in air over a prolonged mixing time, which makes the pH value decrease, as illustrated in Fig. 6 and Table 6. And, the content of $Ca(OH)_2$ also increases after mixing with water (24 h), following its generation by the reaction of f-CaO in CFBC fly ash with water.

3.3. Mineral phase

The intensity of the diffraction peaks and the variation in the half peak widths in an XRD chart reveals the size of the particles, the degree of amorphousness, and the lattice deformation of the powder. The reduction in peak height is accompanied by a general broadening of the peaks, which means that the crystalline particle size decreases and the lattice strain increases. Moreover, the crystalline material can become amorphous with prolonged grinding. It is obvious that for fly ash composed of the same minerals, the reactivity of the amorphous phase is larger than that of the crystalline phase, for example, amorphous silica reacts with $Ca(OH)_2$ more easily than quartz does with $Ca(OH)_2$. Generally, the mineralogical composition may remain unchanged during the grinding process, however, the intensity of the crystalline phases decreases and the half peak width increases [21].

Fig. 8 shows the mineralogical phases of CFBC fly ash after different grinding times. It can be observed that the intensity of the main minerals such as portlandite, anhydrite, quartz and calcite, decrease markedly with increased grinding time, which can be clearly seen in Table 7. However, the half peak widths of the main minerals increase with increased grinding time. These observations indicate an increase in the degree of lattice disorder and a decrease in the crystallite size; reducing the symmetry of the unit cell until fractions of some of the minerals which have become amorphous [17]. The content of amorphous minerals increases with prolonged grinding time, which is the reason that the reactivity of the ground sample is more than that of the original sample.

Table 7
Intensity of the main minerals in the ground CFBC fly ash[a]

2θ (mineral)	Grinding time (min)		
	0 min	35 min	60 min
25.461 (A)	13,959	12,525	11,607
26.644 (Q)	13,298	10,682	8566
30.042 (C)	10,466	8675	7274
34.101 (P)	9777	9479	9065
37.469 (L)	6318	4564	4505

[a] P – Portlandite, Q – Quartz, A – Anhydrite, C – Calcite, L – lime.

4. Conclusions

(1) Three stages have been identified in the grinding process, and the variation of fineness of grinding CFBC fly ash is different at each stage. There is no appreciable enhancement in the physical characteristics of fly ash beyond a grinding period of 45–50 min.
(2) The granulometric distributions of ground CFBC fly ash follow the RRSB distribution for particle diameters more than 1 μm.
(3) Grinding can make the water requirement of CFBC fly ash decrease, but the range is limited. Grinding can also make the specific gravity of ground CFBC fly ash increase, thereby improving the compactness of fly ash.
(4) The pH of ground CFBC fly ash is greater than that of original CFBC fly ash, because of the increase in f-CaO content and the larger specific surface. And, the pH of the original or ground CFBC fly ash increases at first, but then decreases later because of the reaction between $Ca(OH)_2$ and CO_2 in air.
(5) The intensity of the crystalline phases of ground CFBC fly ash decreases, while the half peak width of ground CFBC fly ash increases with prolonged grinding time, which means that ground fly ash has a higher reactivity than the original fly ash.

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