Construction and Building Materials 78 (2015) 250–259

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Ultrafine grinding of fly ash with grinding aids: Impact on particle characteristics of ultrafine fly ash and properties of blended cement containing ultrafine fly ash

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HIGHLIGHTS

- Grinding aid (GA) improves the particle characteristics of ultrafine fly ash (UFFA).
- Pozzolanic reaction degree and activity index of UFFA are also improved by GA.
- Properties of blended cement containing UFFA with GA are better than without GA.
- UFFA with GA improves the hydration process and microstructure of blended cement.

ARTICLE INFO

Article history:
Received 21 August 2014
Received in revised form 28 December 2014
Accepted 4 January 2015
Available online 16 January 2015

Keywords:
Ultrafine fly ash
Grinding aids
Particle characteristics
Pozzolanic reaction
Blended cement property
Hydration product

ABSTRACT

This paper presents the ultrafine grinding performance of fly ash with grinding aids (GA) and effect of GA on the particle characteristics, pozzolanic reaction degree of ultrafine fly ash (UFFA) and properties of blended cement containing UFFA. The experimental results indicate that GA can improve the particle characteristics of ground fly ash. The specific surface area of UFFA with 0.05 wt% GA is higher by 104 m^2/kg than control sample. The particle size distribution of UFFA with GA becomes narrow and particle content of less than 16 μm is obviously increased. Additionally, the fluidity and loose bulk density of UFFA have also been improved. For pozzolanic reaction degree, 3-day, 7-day and 28-day hydration degree of UFFA with GA is increased by 1.2%, 2.3% and 4.6%, respectively; and 3-day, 7-day and 28-day activity index of UFFA with GA is also increased by 6%, 8% and 9%, respectively. For properties of blended cement containing UFFA, enhancement effect of UFFA with GA on the strength of blended cement containing 20 wt%, 30 wt% and 40 wt% fly ash are significant, and 3-day strength is increased by 12.6%, 6.6% and 6.6%, respectively, 28-day strength is increased by 6.5%, 9.3% and 10.5%, respectively. In this study, the hydration degree and microstructure of blended cement containing UFFA paste are also analyzed by SEM, XRD, IR and TG-DTA. The studies show that improvements such as hydration degree, products quantity, uniformity and compactness of products structure of blended cement containing UFFA are attributed to finer particle size and better particle size distribution caused by the addition of GA.

1. Introduction

Fly ash is a pozzolanic materials containing aluminosilicate glass formed after the burning of pulverized coal [1]. It is rich in SiO_2, Al_2O_3 in chemical composition, accounting for about 80% of the total mass. Moreover, mineral phase of fly ash is mainly composed of spherulitic glass phase which accounts for more than 50% of the total mass; and crystalline phase is also present in the fly ash, including mullite, α-quartz, β-C_2S, calcite and anorthite, etc. [2–4]. Based on the composition characteristics of fly ash, it has pozzolanic activity [5–10]. For a long time, fly ash as a supplementary cementitious material was widely used in the cement and concrete industries. However, the relatively large particles size, low hydration activity and hydration rate of ordinary fly ash, the early strength of cement and concrete containing fly ash is low and the development of strength is also slow, meaning that the amount of fly ash in cement or concrete materials is limited to a certain range and its engineering applications are also subject to certain restrictions [11–21]. Research shows that the smaller the particles size of fly ash, the higher its hydration activity and hydration rate. Therefore, in order to make better use of fly ash, it is usually refined by mechanical grinding methods [22–29].

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http://dx.doi.org/10.1016/j.conbuildmat.2015.01.025
0950-0618/

Research results on blended cement and concrete containing ultrafine fly ash (UFFA) with an average particle size of less than 10 μm or specific surface area of more than 700 m^2/kg exhibit improved performance over a comparable control mixture. These improvements include filling role, water-reducing role, pozzolanic reaction, and improvement roles of mechanical and durability properties [30–34]. Therefore, application effects and utilization ratio of fly ash will be improved by using UFFA as supplementary cementitious materials of cement and concrete.

However, it also has some problems such as disproportionate high energy consumption and relatively easy agglomeration of fine particles in the mechanical grinding preparation process of UFFA. In recent years, organic grinding aids (GA) are used to improve the grinding efficiency of solid materials such as cement, slag, fly ash and others. These organic molecules can be adsorbed in the particles and then cause a change in the physical and chemical properties of particle surface in the grinding process, thus play the dispersion and grinding role so that reduce the grinding energy consumption [35–38]. The ground powder particles with GA have fine sphericity, uniform particle size distribution and excellent dispersibility. In addition, some GA molecules (such as triethanolamine, triisopropanolamine and the like, etc.) adsorbed on ground fly ash particles also have chemical activation effect on the activity of fly ash, improving the properties of cementitious materials containing fly ash [39,40]. Therefore, it is a good choice to use GA in the preparation process of UFFA by mechanical grinding for many UFFA manufactures to improve preparation efficiency and hydration activity of UFFA.

Based on this, this thesis described the ultrafine grinding characteristics of fly ash with GA from fineness, particle size distribution, angle of repose and loose bulk density. The effects of UFFA with GA on the properties of blended cement with regard to strength, water requirement of normal consistency, setting time, and hydration degree were discussed. Microscopic properties of UFFA were analyzed by X-ray diffraction (XRD) and infrared spectroscopy (IR). The hydration degree and microstructure of blended cement containing UFFA paste were also analyzed by scanning electron microscopy (SEM), XRD, IR and thermogravimetry differential thermal analysis (TG-DTA).

2. Experimental study

2.1. Raw materials

(1) The fly ash used was supplied from Shijingshan Thermal power plant of Beijing Jingneng Thermal Power Co. Ltd. in China. Its chemical composition was listed in Table 1. (2) The GA used was prepared by mixing triethanolamine and ethylene glycol (the mass ratio between the two was 1:1), and the effective content of GA was 99 wt%. Triethanolamine and ethylene glycol were both chemically pure, produced by Beijing Chemical Reagent Factory of China. (3) The cement used was Portland cement with the strength grade of 52.5 (similar to ASTM I cement) from Beijing Cement Plant of China, and its chemical composition was listed in Table 1. (4) The sand used in the mortar mixtures was the China ISO standard sand and produced according to the ISO696 and EN196-1 standard by Xiamen ISO Standard Sand Co., Ltd. (5) Both CaO and NaOH reagents were chemically pure, produced by Beijing Chemical Reagent Factory of China.

Table 1
Chemical composition of fly ash and cement (wt%).

Chemical composition	Fly ash	Cement
CaO	4.65	65.74
SiO_2	50.52	21.17
Al_2O_3	35.48	5.65
Fe_2O_3	2.78	2.73
MgO	0.65	1.75
K_2O	1.12	0.92
Na_2O	0.06	0.24
SO_3	0.22	1.08
Loss	4.24	0.62

2.2. Methods

2.2.1. Ultrafine grinding of fly ash

The grinding experiment of fly ash was carried out by using laboratory ball mill. The type of the ball mill is Φ500 mm × 500 mm, 48 r/min and closed circuit, and the grinding media is composed by 60 kg steel balls (Φ40 mm, Φ50 mm, Φ60 mm and Φ70 mm) and 40 kg small steel forgings (Φ25 mm * 35 mm). The weight of materials for each grinding experiment was 5 kg. In order to determine the ultrafine grinding time of fly ash, a pre-grinding experiment was carried out by selecting four grinding periods: 15 min, 30 min, 45 min, and 60 min, respectively. The relationship as shown in Fig. 1 between the fineness of ground fly ash and the grinding time was obtained. As seen from Fig. 1, the specific surface area of ground fly ash is more than 700 m^2/kg when the grinding time is 60 min, so 60 min grinding time was determined as ultrafine grinding time of fly ash. GA was not mixed in the blank control group, while 0.05% GA of the total materials was mixed in the experimental group.

2.2.2. Particle characteristics of UFFA

(1) The specific surface area and sieve residue of UFFA were measured according to the Chinese National Standard GB/T8074-2008 and GB/T1345-2005, respectively.
(2) The particle size distribution of UFFA was measured according to the Chinese Industry Standard JC/T721-2006.
(3) The angle of repose was tested according to the Chinese National Standard GB/T11986-1989, as follows: UFFA was poured into funnel, and UFFA samples from the funnel fell on and coated the disc below the funnel, then the height, h, of powder layer and the radius, R, of the disc were measured, thus the angle of repose, θ, of UFFA was obtained according to the formula ($\tan\theta = h/R$).
(4) Loose bulk density of UFFA was measured by the following method: UFFA was injected into a certain weight, W_0, and volume, V, of container, and the total weight, W, of the container and the powder was weighed after UFFA filling up the container, then the loose bulk density, ρ, of UFFA was measured by according to the formula:

$$\rho = (W - W_0)/V$$

(5) The microscopic properties of UFFA particles were analyzed by XRD and IR. The XRD measurement was conducted with a D6000 diffractometer using nickel-filtered Cu Ka radiation (=1.5405 Å, 40 kV and 40 mA) from Shimadzu company of Japan; the IR analysis was conducted with a Nicolet iS10 Fourier transform infrared spectrophotometer, in the range of 4000–400 cm^{-1} with 200 successive scans. The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector and with an attenuated total reflectance (ATR) unit, and the spectra rationed against a potassium bromide (KBr) background.

2.2.3. Pozzolanic reaction degree of UFFA

The pozzolanic reaction degree of UFFA was measured by the following method [41,42]: the UFFA paste was first prepared from 90 wt% UFFA, 10 wt% CaO and simulated solution (0.2 mol/L NaOH solution) by stirring uniformly, and the water–binder ratio (W/B) of paste was 0.4. When the paste specimens were cured at temperature about 20 ± 1 °C and >95% humidity for 3 days, 7 days and 28 days, respectively. The middle portions of specimens were obtained at the age of 3 days, 7 days and 28 days, respectively, broken and soaked in absolute ethanol to suspend hydration. Then, the reaction degree of UFFA paste was determined by the

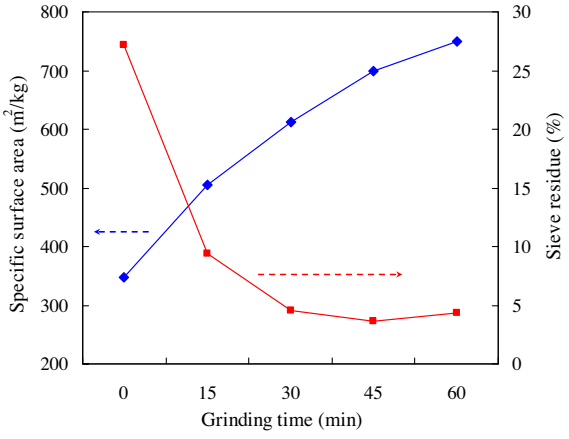

Fig. 1. Change of fineness of ground fly ash with grinding time.