Construction and Building Materials 52 (2014) 422–427

Contents lists available at ScienceDirect

Construction and Building Materials

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

Microstructure and performance of fly ash micro-beads in cementitious material system

Hui Li [a,b,*], Delong Xu [a,b], Shaohang Feng [a], Boming Shang [a]

[a] Institute of Powder Engineering, College of Materials & Mineral Resources, Xi'an University of Architecture & Technology, Xi'an 710055, China
[b] Shaanxi Province Key Laboratory of Construction Technology, Xi'an University of Architecture & Technology, Xi'an 710055, China

HIGHLIGHTS

- We found that fly ash beads possess a very special internal micro-constitution.
- Inert micro crystal and active glassy phases inside fly ash play different roles in cement.
- Super-fine grinding release nano-spheres of fly ash, enhance active and micro-aggregate effects.
- Super-fine grinding develop reinforcing fibre effect and enhance flexural strength of materials.

ARTICLE INFO

Article history:
Received 29 August 2012
Received in revised form 1 November 2013
Accepted 12 November 2013
Available online 8 December 2013

Keywords:
Fly ash micro-beads
Microstructure
Superfine grinding
Micro-crystal

ABSTRACT

To exploit the advantages of fly ash in cementing materials to the full, in this study, the micro-constitution of fly ash beads was investigated; the effects of micro crystalline and non-crystalline phases inside fly ash on the performance of cementing material were discussed, also including technical ways to bring these advantage effects into play. It was found that the sinking beads, were hollow and containing a mass of smaller round spheres or even nano-spheres. A large quantity of interlaced nano micro-crystal fibers constitute the basic frame work of the bead wall, and the active silicon–aluminum matrix fills the gaps among the micro-crystal fibers. The silicon and aluminum matrix is active, which could react with $Ca(OH)_2$ produced during the hydration of cement clinker minerals, while nano-crystals that fly ash particles containing are inert. Super-fine grinding can break the out-shell of fly ash beads, releasing the nano-spheres and really improving the active and micro-aggregate effects of fly ash micro-beads. Meanwhile, the reinforcing fiber effect of micro-crystals inside fly ash particles will be developed and enhancing the flexural strength of cementing materials at later age.

1. Introduction

Fly ash is a typical pozzolanic material, high in SiO_2 and Al_2O_3, possessing little cementing property when simply blended with water [1], but it could be activated by OH^-. It will become sufficiently reactive as the mixture of fly ash with water and CaO. At ordinary temperature C–S–H forms in the terminal system and thereby acts as hydraulic cementitious material [2,3]. Currently, blending cement with fly ash, and using fly ash in concrete or in roller compacted concrete for pavement and dam applications are widespread in practice. It was reported that fly ash helps to modify the properties of concrete in both the fresh and hardened stated, with improved workability, acceptable early-age strength, high long-term strength, low drying-shrinkage and creep and excellent durability, compared with Portland cement (PC) concrete with similar strength [4–7].

Many researchers devoted themselves to the application and the action mechanism of fly ash in cementing material system in the past 70 years, and the hypothesis of "fly ash effects" was put forward, including three effects of fly ash in concrete, i.e., morphological, active and micro-aggregate effects [8–11]. It is indicated that in the early stages, fly ashes have the physical effect of space filler and are involved in the formation of ettringite(Aft). In the long-term, they are involved in the hydration reaction mainly as silicon–aluminum binders [12]. At later ages, the fly ash has a two-fold effect: it strengthen the contact between particles and also consume $Ca(OH)_2$ to reduce the flaws associated with it [13,14]. As most of the ash particles remain un-reacted even after a long period cure, high-volume fly ash pastes can be considered as a composite material with the ash particles serving as reactive micro-aggregate [15].

* Corresponding author. Tel.: +86 18591882128; fax: +86 029 85535724.
E-mail address: sunshineli@vip.sina.com (H. Li).

0950-0618/$ - see front matter
http://dx.doi.org/10.1016/j.conbuildmat.2013.11.040

The above studies have provided considerable information on the effect of fly ash in the cementing material system. However, most of them focused on the macroscopic chemical reactivity and physical space filling, seldom paid attention on the microstructure of fly ash particles. Fly ash contains a lot of fine spherical micro-beads, largely glassy particles and also existed in crystalline phase. According to the difference in density, micro-beads from fly ash can be classified as sinking beads and floating beads. After the pre-separation in power plants, the fly ash used as pozzolan to partially replace Portland cement in cementing material system is mainly comprised by sinking beads, which consist of magnetic beads and multiple vitreous beads high in SiO_2 and Al_2O_3. In this paper, the physical micro-constitution of fly ash beads was investigated; the effects of micro crystalline phase and glassy non-crystalline phase inside fly ash beads on the performance of cementing material were discussed, as well as the technical ways to bring the advantage of these effects into play.

2. Experimental

2.1. Materials

A type low calcium fly ash(FA) from the combustion of bituminous coals, and Portland cement (PC) were used in the present study. The chemical composition and physical properties of Portland cement and fly ash are given in Table 1. The total amount of the major components SiO_2, Al_2O_3, Fe_2O_3 and CaO in fly ash is 91.09%, the content of CaO is less than 7%, and the loss on Ignition (LOI) is less than 5%. Some elementary characters of fly ash for using in cement and concrete are listed in Table 2. According to the Chinese standard GB/T1596-2005, this fly ash could be ranked as II grade. The particle size distribution of FA is shown in Fig. 1, and the XRD pattern of FA is given in Fig. 2. It reveals that FA consists of a glassy matrix with crystalline phases like quartz, mullite, lime, sillimanite, and magnetite.

2.2. Separation of different micro-beads in FA

Sink/float process was used to separate the very few floating beads from sinking beads, then wet magnetic drum separation was introduced to separate magnetic beads from sinking beads. Table 3 gives the content of different micro-beads in FA.

2.3. Preparation of cement pastes

Fly ash was used to replace Portland cement at different rate separately, by weight of binder. The ratio of water to binder (W/B) was constantly 0.45 throughout the investigation. The pastes were mixed in a mechanical mixer and then were cast in $4 \times 4 \times 16$ cm steel prism models (according to the Chinese standard GB/T 17671-1999) and compacted by tamping rod, and were sealed by plastic to prevent water loss. 24 h after casting, specimens were removed from the molds and cured in water at 20 ± 3°C until the time of testing.

2.4. Microstructure observation

To observe the insider microstructure of different fly ash beads, the floating beads, magnetic beads and sinking beads with high silicon and aluminum were softly grinded in an agate mortar respectively by hand. Then the microstructure of cracked beads was examined using a Jeol JSM-6510LV scanning electron microscope (SEM) accompanied by a Philip QUANTA200 energy spectrum and a Jeol JEM-200CX transmission electron microscopy (TEM). On the other hand, the separated floating beads, magnetic beads and sinking beads with high silicon and aluminum were etched with the hydrofluoric acid (HF) of 50% mass concentration for 15 minutes respectively. The residues were washed to acid-deficient with distilled water and dried for the microstructure examination under SEM and XRD. The results were compared with the microstructure of fly ash micro-beads inside the pastes after 365 days of curing.

Table 2
Elementary characters of fly ash.

45 μm sieve residue (%)	16.37
Water demand ratio (%)	95
Strength activity index (%)	92.4
Water content (%)	0.93

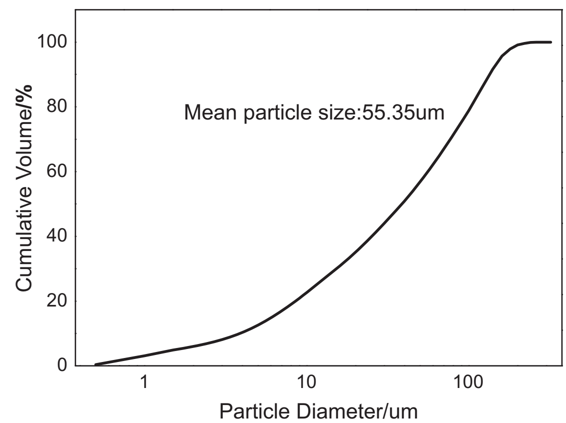

Fig. 1. Particle size distribution of FA.

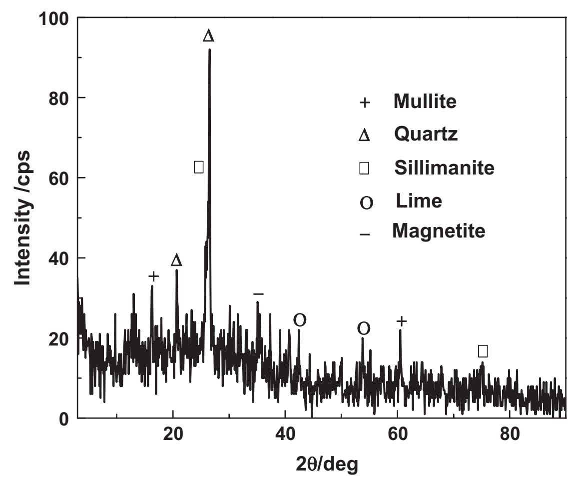

Fig. 2. X-ray diffraction patterns of FA.

Table 3
Content of different micro-beads in FA (on weight).

Type of micro-beads	Sinking beads		Floating beads
	Magnetic beads	Sinking beads high in silicon, aluminum and calcium	
Content (%)	7.12	92.50	0.38

Table 1
Chemical and physical properties of PC and FA.

Chemical composition (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	SO_3	Na_2O	LOI	Blaine fineness (m^2/kg)	Specific gravity
PC	20.74	3.68	3.16	62.6	0.17	1.77	0.86	0.50	1.34	350	3.2
FA	48.2	29.8	6.49	6.60	1.20	0.559	1.47	0.532	3.02	–	2.44