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Effect of fly ash microsphere on the rheology and microstructure of alkali-activated fly ash/slag pastes

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ABSTRACT

The highly viscous property of alkali silicate-activated cements is one of the critical challenges that hinder their wide application. The present study focuses on ameliorating the rheological performance of sodium silicate-activated fly ash/slag pastes by using fly ash microsphere (FAM), which are highly spherical particles collected from fly ash with electrostatic adsorption classification technology. The FAM particles work as 'ball-bearings' in the pastes to reduce the internal friction between fly ash and slag grains, and meanwhile mitigate the agglomeration of flocs and fragmentation to release the locked water. The interrelationship between the FAM particle geometry and plastic viscosity of the paste is well described by the Krieger-Dougherty equation, which supports the proposed mechanisms of 'ball-bearings' effects. FAM can work as an inorganic dispersing agent to improve the workability of alkali-activated cement products for a variety of application aspects.

1. Introduction

The highly viscous property of alkaline silicate activators used to produce the alkali-activated cements (AAC) impairs workability of the AAC concretes. It has become one of the critical challenges that hinder their wide application, especially for the pumping and onsite casting works [1–4]. This drives an urgent demand for developing effective methods of improving the workability of AAC products.

The common practice is to use water reducing admixtures or superplasticizers (vinyl copolymers, polycarboxylates, naphthalene- and melamine-based) to improve the dispersion and workability of Portland cement concretes [5]. These polymers adsorbed on the surface area of cement grains results in the inter-particle electrostatic repulsion and steric hindrance, which are helpful in releasing the water trapped in the agglomeration of flocs and assisting movement of the grains in sheared systems [6]. Previous studies evaluated the effectiveness of these common superplasticizers in the AAC products, and the results showed that their fluidizing role clearly depends on the admixture type, activator type and concentration [7–10]. Among them, naphthalene-based superplasticizer is the only chemically stable candidate, but exhibits limited effectiveness in ameliorating the flowability of NaOH-activated cements [8,11]. In the sodium silicate-activated systems, all these superplasticizers lose their fluidizing function [8,11]. The incompatibility of superplasticizers in alkali silicate-activated systems could be explained in two aspects: (1) the highly concentrated alkalis destroy the molecular of superplasticizers through the reaction between OH^- and functional groups such as $-COO^-$ and $-R-OH$, and thus the steric hindrance from these additives is impaired; (2) the concentrated colloidal silicate species in the activating solution extremely degrade the electrical double layer formed on the surface of solid particles [12,13]. From this point of view, it is difficult, if not impossible, to improve the workability of AAC concretes by using these common chemical additives. Alternative approaches, such as the development of totally new superplasticizers and rheological control through physical effects, have to be considered in this situation.

Previous studies have revealed that the particle geometry, including the particle shape and size distribution, plays a significant role in determining the rheological properties of cement pastes [14–16]. One of the well-known mechanisms is the 'ball-bearings' effects of spherical fly ash particles, which could improve the rheology of cementitious suspensions [17]. The fly ash spheres mitigate the interparticle surface friction of angular cement grains mitigate, and meanwhile reduce the

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potential for agglomeration to release water trapped within flocs [16]. However, the usual coal combustion process brings some impurities into the fly ash, such as the coarse grain consisting of a cluster of microspheres and the unburned carbon with porous structure [18]. The impurities with high surface area will increase the water demand during wetting process, and thus depress the fluidizing role of fly ash in the cementitious suspensions, especially in the AAC system with high viscosity. To solve the problem, this study focuses on controlling the workability of AAC pastes by using fly ash microsphere (FAM). FAM is a class of superfine spherical-shaped particles collected from fly ash with a particle separation process to remove the impurities [19]. Kwan et al. [20,21] and other researchers [19] reported that FAM could fill into the interstitial voids in cement grains to release the entrapped water, and thus improved workability of the cement mortar and concrete. Herein, it is proposed that FAM may also be a suitable material for such usage in AAC system. In this study, the sodium silicate-activated fly ash-slag pastes with different fly ash replacement by FAM are prepared for the yield stress and plastic viscosity measurements. The effects of FAM on rheology and microstructure of the pastes are evaluated.

2. Experimental

2.1. Materials

2.1.1. Solid precursors

Ground granulated blast-furnace slag and class F fly ash were supplied by Xuzhou Guohua Power Station (Xuzhou, China). Fly ash microsphere (FAM), supplied by Sika Ltd. (Suzhou, China), was by-product collected from the exhaust smoke of coal combustion in the furnace at around 1800 °C. This temperature is higher than that (800–1500 °C) of usual coal combustion process, where the common Class F and C fly ashes are produced, and is helpful to eliminate the unburned flocculent organic matters, such as the carbon particles, sulfates and bio-contaminations [22,23]. These impurities have porous structure and high specific surface area (SSA), demanding high water/solid in wetting [22]. An electrostatic adsorption classifier was used to screen the fly ash particles collected from a bag filter for the purpose of achieving a nearly 100% granulation rate. Wang et al. [19] reported that when the collected fly ash particles were put through ceramic dust tubes firstly, they could also be screened by a wind separator to get the FAM. Therefore, the electrostatic adsorption technology used in this work is more cost efficient.

2.1.2. Alkaline activators

Alkaline activators were prepared by blending sodium hydroxide pellets (≥96 wt% purity) with sodium silicate solution (SiO_2 = 30.3 wt %, Na_2O = 12.8 wt%) and deionized water to reach desired modulus of Ms = 1.4 and 1.8 (molar ratio SiO_2/Na_2O), and a constant concentration of 30 wt% ($Na_2O + SiO_2$). The activating solutions were equilibrated at room temperature for 24 h before using.

2.2. Characteristics of the raw materials

2.2.1. Morphology

SEM images in Fig. 1 show the morphologies of the slag, fly ash and FAM particles (test conditions shown in Section 2.4.4). The slag particles exhibit typical angular shape. In the fly ash, a large amount of spherical particles are observed, including solid ash particles and cenospheres with a shell structure. The coarse grains consisting of a cluster of microspheres are formed due to the microsphere capture occurred in the combustion zone, and the irregular porous particles are unburned carbon [24]. The FAM particles exhibit smooth surface and high sphericity.

2.2.2. Physical properties

Fig. 2 shows the particle size distribution (PSD) analysis of the slag, fly ash and FAM as determined by laser diffraction based on the assumption that all particles are spherical. The slag is comparable in size to the fly ash, while the FAM is markedly finer than them. The mean particle sizes (D_{50}) of the slag, fly ash and FAM are 13.79 μm, 14.20 μm and 1.89 μm, respectively.

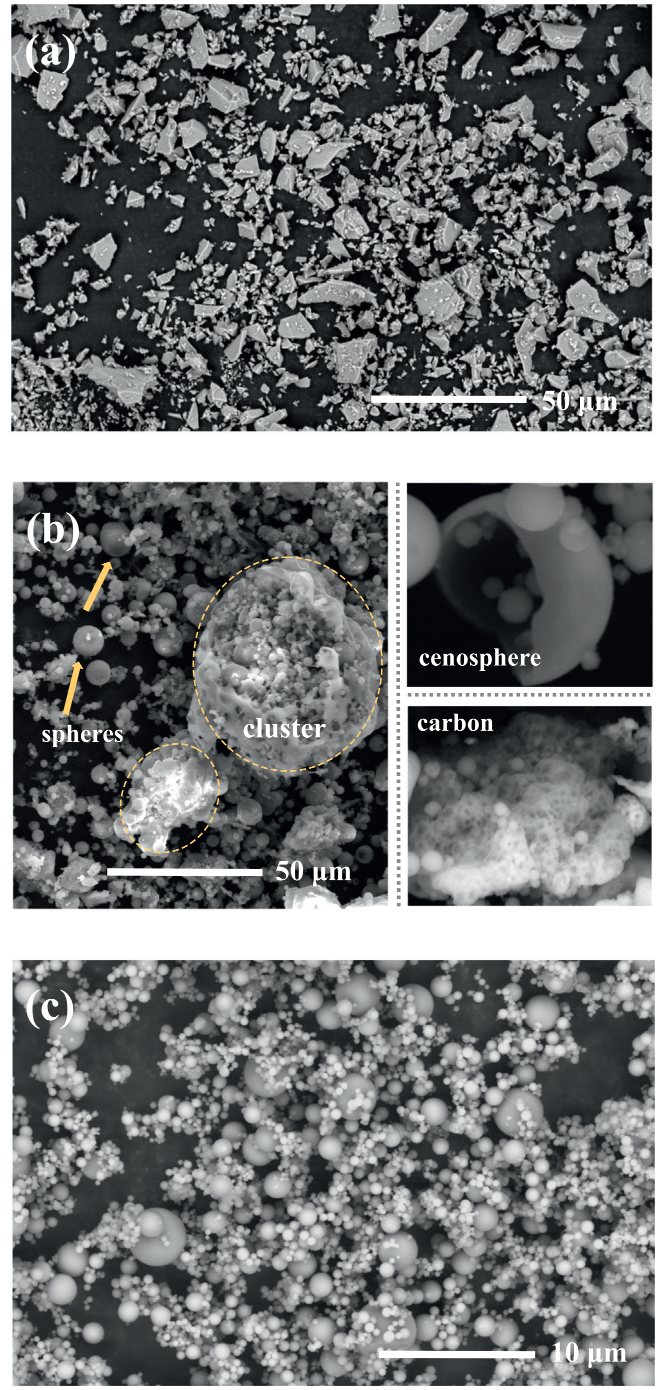

Fig. 1. SEM images of (a) slag, (b) fly ash and (c) FAM.

The physical properties of solid precursors are listed in Table 1, including the mean particle sizes (D_{50}), particle density and specific surface area (SSA). Particle density was tested using the Archimedes method with kerosene as the liquid medium, and three replicate tests were conducted to obtain an average value. The densities of fly ash (2.22 g/cm^3) and FAM (2.44 g/cm^3) are close. The SSA of solid precursors, defined as the surface area per unit volume, was measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption