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Effect of Zinc oxide and Al-Zinc oxide nanoparticles on the rheological properties of cement paste

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ABSTRACT

This study aims to evaluate the effect of aluminum doped zinc oxide (AZO) and undoped Zinc oxide (ZnO) nanoparticles addition on the superplasticizer adsorption isotherm and rheological properties of cement paste composites. The adsorption isotherm and zeta potential of pastes containing different proportions of ZnO and AZO nanoparticles were also analyzed. The mechanism of superplasticizer adsorption by nanoparticles was found to be a dominant factor which governs the rheological properties. It was found that the amount of superplasticizer adsorbed increases significantly by incorporating nanoparticles which implies that nanoparticles compete with cement particles to adsorb the polymer. Consequently, the addition of both nanoparticles resulted in a considerable increase in saturation point, yield stress and viscosity values relative to plain cement paste. All mixtures containing 0.4 wt % nanoparticles or lower showed excellent workability retention as compared to the reference mix while, the poor workability retention was observed a higher dosage.

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1. Introduction

Nowadays, there is a rapidly growing interest in using nanoparticles in cement and concrete product to tailor materials' mechanical and durability properties [1–6]. The high surface to area ratio of nanoparticles leads to more chemical interactions at the interface, which results in enhanced or novel properties and functions. For instance, the addition of nano SiO_2 and Fe_2O_3 was found to be efficient to improve the mechanical and durability properties of cementitious materials [7–14]. It has been stated that the mechanical properties of high performance concrete can be improved by incorporation of Nano-Al_2O_3 [15]. The addition of Cr_2O_3 nanoparticles can enhance the water permeability resistance of concrete due to refinement of the pore structure [16]. TiO_2 nanoparticles have shown the ability of removing organic pollutants from building facades when exposed to UV radiation [17]. Among the nanoparticles investigated, ZnO has been identified as the most promising one due to its unique materials' photocatalytic and photoluminescence properties [18–21]. ZnO is an inorganic semiconductor compound with a direct band gap of 3.3 eV at room temperature. Similar to TiO_2 as a photocatalyst, the ZnO nanoparticles has been used in self-cleaning applications in concrete structures due to its photocatalytic properties [22–24]. It has been reported that the addition of ZnO improves the reactivity of supplementary cementitious materials, which leads to an increase in the rate of cement hydration and the released heat [25]. Moreover, ZnO addition was found to be effective in reducing the corrosion rate of embedded steel bar in concrete [26]. Although the effect of ZnO nanoparticles on the hydration and hardened state properties of cementitious materials has been explored [27–29], the rheological properties of cement paste containing ZnO has not been investigated. In the present work, attempt has been made to investigate the effect of ZnO nanoparticles on rheological behavior of cement pastes. Adsorption isotherm and zeta potential of pastes containing different proportions of ZnO and AZO nanoparticles were analyzed. In order to compare the results, a plain cement was also considered in the experimental program described ahead. Total organic carbon (TOC) and Zeta potential were measured to further confirm the data.

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2. Experimental program

2.1. Materials

The cement paste mixtures were prepared using the following main constituents: Portland cement type I 42.5 R (C); polycarboxylate ether based superplasticizers (SP); and two different types of ZnO nanoparticles including undoped ZnO nanoparticle (ZnO) and aluminum doped ZnO nanoparticle (AZO). Table 1 shows some physical and chemical properties of cement. The adopted chemical admixture was a polycarboxylic acid based superplasticizer (SP) with the density of 1.108 g/cm^3. The properties of ZnO and AZO nanoparticles are presented in Table 2. The cement pastes were prepared in this study by using a vacuum mixer to reduce the entrapped air voids in the mixes.

Table 3 presents the eleven series of mixtures, prepared with ZnO, AZO and a reference mixture without nanoparticles. Nanoparticles were incorporated as cement replacement by 0.2, 0.4, 0.6, 0.8 and 1 by wt. % of cement. The total content of powder was kept constant in volume. In addition, the water to binder ratio was fixed at 0.35 for all the mixtures.

2.2. Zeta potential measurement

The effect of different dosages of superplasticizer on the zeta potential of cement suspensions was determined with a Colloidal Dynamics Acoustosizer IIs. The systems measure zeta potential using electrophoretic light scattering. Cement suspensions were prepared by mixing 30 g of binder with 160 g of water (solid fraction in the suspension = 0.16). After stirring for 15 min in a magnetic stirrer, the suspensions were placed in a sonicator for 5 min and then in the measuring cell to determine their zeta potential. Polycarboxylate admixture dosages ranging from 0 to 7 mg polymer/g cement were added to these suspensions using an automatic titrator. The zeta potential values were corrected for the pore solution background contribution. Diluted solutions were used in order to study the interaction between PCE-cement from a colloidal chemical point of view.

2.3. Adsorption isotherm

In order to determine the superplasticizer adsorption isotherms, the same mix design for rheology tests were used. The pore solution of the cement paste was centrifuged, the liquid phase was removed through a 0.45 lm Nylon filter by air pressure filtration and the total organic carbon content was found by a SHIMADZU TOC-VCSH/CSN total organic carbon (TOC) analyzer.

2.4. Rheological measurement

The coaxial Anton Paar MCR 302 Rheometer was used to assess the rheological properties of cement pastes. The inner cylinder rotates at different velocities, while the outer cylinder remains stationary. The resulting torque was registered at the inner cylinder. The rheological properties of each cement paste were determined using the following testing procedure. At the start of each test, the cement paste was pre-sheared for 60 s at the maximum shear rate employed during the test, which is 100 s^{-1}. After the pre-shearing period, the cement paste was subjected to a stepwise decrease in shear rate from 100 to 2 s^{-1} in 11 steps. The rheological properties were measured at 15, 45, 75 and 90 min. Also the static yield stress was measured at 28, 43, 58, 73 and 88 min. The testing procedure is illustrated in Fig. 1. The rheological properties of cement-based materials are usually characterized with the Bingham model (Eq. (1)):

$$\tau = \tau_0 + \mu_p \cdot \dot{\gamma} \tag{Eq.1}$$

For this equation, τ is the shear stress (Pa), τ_0 is the yield stress (Pa), μp is the plastic viscosity (Pa s), and $\dot{\gamma}$ is the shear rate (s-1). The yield stress is the stress needed to start the flow. This means that applying a stress lower than the yield stress will not cause any flow in the material. The plastic viscosity is the resistance of the material to an increase in flow rate once the yield stress is exceeded. The yield stress and the plastic viscosity are the two Bingham parameters that characterize the flow properties of the studied materials. When the rheological measurement is performed with a coaxial cylinder rheometer, torque (T) and rotational velocity (N) are measured. Shear stress and shear rate data must be derived from the torque and rotational velocity data. When the torque is at equilibrium at each shear rate step, the rheological properties can be calculated by means of the Reiner-Riwlin equation. If the torque was not at equilibrium at a certain step, the respective data point was eliminated from the results.

The Reiner-Riwlin equation transforms the parameters G and H (Eq. (2)), defining a linear relationship between T and N, into the Bingham parameters (Eqs. (3) and (4)). This assumes a laminar, stable flow and no particle movements in the horizontal or vertical direction and also material, in the entire gap is sheared [30].

$$T = G + H \cdot N \tag{Eq.2}$$

$$\tau_0 = \frac{G}{4\pi h} \cdot \left(\frac{1}{R_i^2} - \frac{1}{R_o^2}\right) \cdot 1/ln(R_o/R_i) \tag{Eq.3}$$

$$\mu_p = \frac{H}{8\pi^2 h} \cdot \left(\frac{1}{R_i^2} - \frac{1}{R_o^2}\right) \tag{Eq.4}$$

where R_i is the inner cylinder (m), R_o is the outer cylinder (m), and h is the height of the cylinder (m).

The static yield stress when a concentric cylinder rheometer is employed, can be calculated using Eq. (5) [31]:

$$\tau_s = \frac{T}{2\pi r^2 h} \tag{Eq.5}$$

where τ_s = static yield stress (Pa) and r = radial parameter (m) and corresponds to the spread between inner radius R_i and outer radius R_o.

Table 1
Chemical composition and physical properties of cement.

Chemical analysis (wt %)	Cement
SiO_2	20.9
Al_2O_3	4.60
Fe_2O_3	3.15
CaO	62.0
MgO	2.00
SO_2	3.60
K_2O	<1
Na_2O	<1
Specific gravity	3.14

3. Results and discussion

3.1. Zeta potential

The stability of the colloidal system is a function of the zeta