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Influence of nano-TiO_2 on physical and hydration characteristics of fly ash–cement systems

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HIGHLIGHTS

- Effect of nano-TiO_2 (NT) on fly ash–cement systems properties was investigated.
- Compressive strength of fly ash–cement systems was increased with NT.
- Hydration of fly ash–cement at early ages was promoted by NT.
- Pozzolanic reaction degree of fly ash at early ages was promoted by NT.
- Consumption of CH at early ages was promoted by NT.

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ABSTRACT

This paper presents the effect of nano-TiO_2 (NT) on physical and hydration characteristics of cement-based materials containing different fly ash (FA) contents ranging from 10% to 30% (by weight) as partial replacement of cement. The fluidity of mortars and the setting time of pastes were tested with different NT dosage. The compressive strength of mortars is measured at 3, 7, 28 and 90 days. Results show that NT addition could accelerate initial and final setting and decrease the fluidity, while FA had the opposite effects. Introducing NT would lead to a considerable increase in compressive strength at early ages while it had an adverse effect on the later age strength. However, the positive functions of FA in late strength could offset the negative influence of NT and the optimum contents of NT and FA are 3% and 20%, respectively. Then the influence mechanisms of NT on properties of FA–cement materials are investigated by hydration heat, X-ray diffraction (XRD), differential scanning calorimetry–thermogravimetry (DSC–TG), scanning electron microscope (SEM) and nuclear magnetic resonance (NMR). The results of analyses indicate that incorporating NT promoted the early hydration of cement and accelerated the formation and precipitation of hydration products. Furthermore, in the strength development process, NT could raise the pozzolanic reaction degree of FA and lead to the formation of a C-S-H type with longer chain and higher Al:Si ratio. Also, the interfacial transition zone (ITZ) of FA mortars were improved by NT.

1. Introduction

Concrete is the most widely used construction materials in the world due to its low cost, good plasticity and durability. Ordinary Portland cement (OPC) is the main component of concrete. However, sustainable utilization of cement in concrete has amused extensive attention, which is mainly attributed to the firing process.

In Portland cement production, because of the clinker sintering at 1450 °C [1], quantities of carbon dioxide is discharged into atmosphere, which is roughly 5% of global emissions [2]. Therefore, as an important signal of climate change, global warming is increasing constantly [3]. China, as the world largest cement producer and consumer, takes more than half of the global total, with more than 2400, 000, 000 tons in 2014 alone [4]. Thus this concern has led to the application of supplementary cementitious materials (SCMs), which could partially replace cement.

Fly ash (FA) is one of the SCMs that is widely used as partial replacement of ordinary Portland cement (OPC) in the concrete. It can chemically react with calcium hydroxide (CH) to form C-S-H, which is known as pozzolanic reaction [5]. FA has been widely used because of its many advantages. Firstly, because FA particles are almost a perfect sphere, the workability of

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cement-based materials can be improved significantly with no supplemental water [6]. Secondly, the products of pozzolanic reaction reduce the porosity of cement matrix and by this way the strength and durability are greatly enhanced [7–9]. In addition, FA also has positive effects on sulfuric acid resistance, hydration heat, alkali–silicate reactions and abrasion resistance of cement composites [10–13].

Undesirably, the early strength of FA–cement-based material develops slowly, which goes against its practical application [14,15]. To overcome the disadvantages, many methods of promoting hydration of FA cement have been put forward, including mechanical grinding [16], chemical activator [17], mechanochemical treatment [18] and hydrothermal treatment [19]. But these methods are not only complex, but also costly, being opposite to the direction of green cement industry. In addition, in many studies published today, the performance enhancement of concrete or mortar is accomplished by mixing nanoparticles, proposing an economical and simple way to solve this problem. By far, the work studying nanoparticle admixtures in cement-based materials is mainly concentrated on nano-SiO_2 which possesses certain pozzolanic activity and can increase the compressive strength of the cementitious system [20,21]. It has also been proven that nano-SiO_2 is not only the role of a pore filler and providing nucleation sites, but also the role of modifying the microstructure and an agent to enhance the pozzolanic reaction of FA because of its fairly high surface activity [21–23].

Compared to nano-silica, nano-TiO_2 (NT) has similar effects on cement hydration processes. In addition, nano-TiO_2 is the most generally used photocatalyst in building materials because of its relatively inexpensive, chemically stable, as well as high photocatalytic, and it can also solve the problem of urban air pollutants for its self-cleaning and air purifying properties [24,25]. Therefore, the interactions of nano-TiO_2 with cementitious materials have recently started to be investigated from different points of view. However, as discussed before, TiO_2 is not a pozzolanic material like nano-silica and so the effect of NT on the performance of cement-based materials is greatly related to its high reaction activities and inert filling effect, being different from nano-silica. Chen et al. [26] reported the influences of NT on the hydration and properties of cement paste and they suggested that NT did not participate in pozzolanic reaction and used as the filling particles to accelerate the hydration process. In addition, Nazari and Riahi [27] investigated the physical, thermal and mechanical performances of cement-based materials containing NT, Li et al. and Zhang et al. [28–30] researched the abrasion resistance, flexural fatigue performance, pore structure and chloride permeability of the paving material blending with NT. They proposed that aforementioned performance improvement should be attributed to the filling and nucleation effects of NT.

Although, many researches on the effect of NT on performance of cement-based materials have been reported, very limited results are also available for FA–cement-based materials blending with NT. Thus, in this paper, the influence of NT on the performances (both early ages and late ages) of FA–cement-based materials is studied. The optimal amount of NT is selected. Moreover, the governing mechanisms of NT on properties of FA–cement-based materials are also studied and proved.

2. Experimental

2.1. Materials

Ordinary Portland cement (OPC) CEM I 42.5 produced by Huaxin cement Co. Ltd is used in all mixes. Fly ash (FA) confirming to GB1596-91 produced by Yangluo power plant is used as supplementary cementitious materials [31]. Nano-TiO_2 (NT) with the average particle size of 21 nm is purchased from Degussa Company. Table 1 shows the chemical composition of cement and FA.

Table 1
Chemical composition of OPC and FA.

Chemical analysis	Cement (wt.%)	Fly ash (wt.%)
SiO_2	21.99	52.51
Al_2O_3	5.92	30.78
Fe_2O_3	3.26	3.42
CaO	58.64	4.35
MgO	1.98	0.54
K_2O	0.74	1.01
Na_2O	0.27	0.38
TiO_2	0.4	1.65
SO_3	2.6	1.79
Loss on ignition (LOI)	3.5	2.47

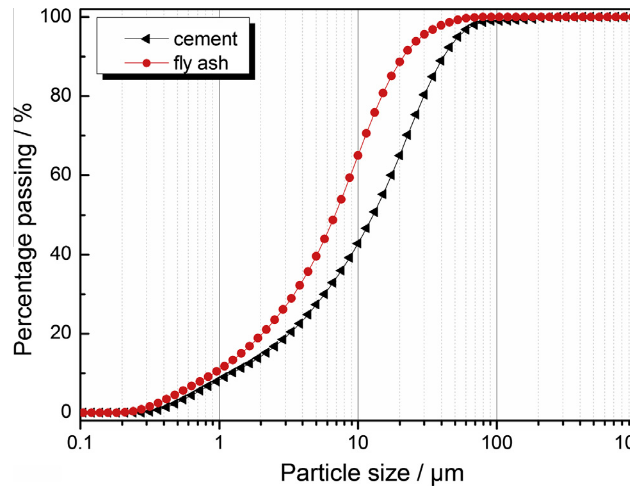

Fig. 1. Particle size distributions of OPC and FA.

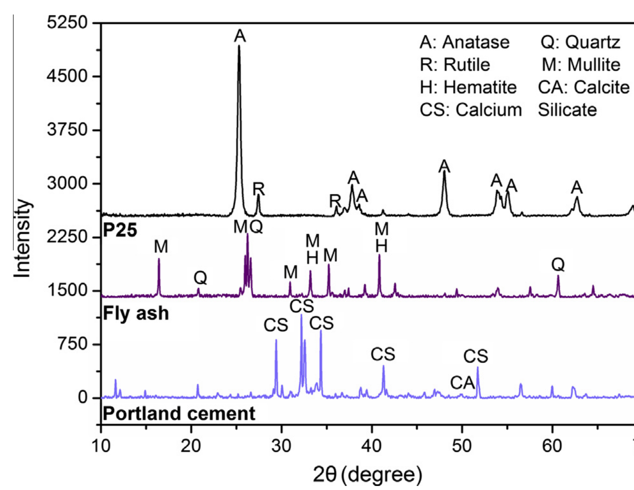

Fig. 2. X-ray diffractogram of OPC, FA and NT (P25).

A particle size analyzer was used to determine the particle size distribution of cement and FA, as shown in Fig. 1. The mineralogical and microstructural properties of the cement, FA and NT were characterized using the XRD, SEM and TEM techniques, respectively. Fig. 2 shows the XRD patterns obtained from these powders whilst Fig. 3(a) and (b) shows selected SEM and TEM micrographs of FA and NT, respectively. It is obvious from Fig. 3 that FA particles were perfectly spherical shape.

Standard sand (SS) in accordance with Chinese specification produced in Xia'men was used as aggregates for mortars. The deionized water was used for all mixtures and experiment.

2.2. Mix proportion and sample preparation

Mix proportions of the pastes and mortars are listed in Table 2.