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Hydration characteristic, thermal expansion and microstructure of cement containing nano-silica

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HIGHLIGHTS

- NS increases the water demand and consequently retards the setting process.
- The values of pH and free lime decrease with increasing NS% content.
- Chemically combined water contents increase with increasing NS% content, due to the pozzolanic reaction of NS.
- Microstructure and mechanical properties improved with increasing NS up to 3.0% and then slightly up to 5%.
- Thermal expansion coefficient of hydrated cement pastes containing 3% NS increases with curing time.

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ABSTRACT

The effect of nano-silica (NS) on the hydration characteristics, thermal expansion and microstructure of cement pastes and mortars was studied. OPC was replaced with NS up to 6.0%. The presence of NS increases the required water of standard consistency and elongated the setting times. The results of chemically combined water, free portlandite, pH, bulk density, compressive strength and thermal expansion showed that NS contents up to 5.0 mass% improve the physico-chemical and mechanical properties of cements. NS behaves not only as filler to improve the microstructure, but also as an activator to promote the pozzolanic reaction, which enhances the formation of hydrated products. It was concluded that partially substitution of OPC up to 5 mass% NS improves the mechanical and microstructural characteristics in comparison with the neat OPC paste up to 90 days.

1. Introduction

Recently, nanotechnology has attracted a considerable scientific interest due to the new potential uses of particles in nanoscale, which can change the concrete world. Nano-materials improve the concrete characteristics [1,2].

Nano-particles (NPs) showed unique physical and chemical properties different from those of the conventional materials [2]. There is a great interest in replacing NPs in concrete structure to improve the chemical and physico-mechanical properties of concrete [1,3].

NPs were used either to replace part of the cements [1,2]. The addition of NPs improves the performance of cement, in fresh mixtures, an improvement of rheological properties has been recorded and in the hardened state, the compressive strength was increased [4]. Nano-silica act as nuclei for promoting the hydration of cement phases (i.e., β-C_2S and C_3S), it acts as a nucleation site, which accelerates the cement hydration [5,6].

The greater reactivity of NPs is attributed to the high purity and high specific surface area. Some researchers have recorded an increased in the water demand for mixing of the cements and concretes to give the same workability [7–9].

The most common NPs used in cement production are nano-sized SiO_2 (NS), TiO_2 (NT), Al_2O_3 (NA), Fe_2O_3 (NF), ZnO_2 (NZ), and carbon nano-tubes [10,11].

The role of the NPs can be summarized as follows: (i) NPs not only act as fillers to improve the microstructure, but also as an activator to promote pozzolanic reactions [12], (ii) act as a nucleation site for

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C–S–H seeds which then accelerate the cement hydration [5], (iii) NPs (NS) accelerated the consumption of C_3S and the formation of portlandite (small sized CH) crystals and homogeneous clusters of CSH composition [5], and (iv) NPs improve the microstructure of the interfacial transition zone between aggregates and cement pastes [3]. NS improves the mechanical properties of cement, mortars and concrete [12,13]. The strengths on compressed samples developed from reactive power concretes ranging from 200 to 800 MPa by the application of densified system containing uniformly dispersed ultra-fine particles with superplasticizer [14,15].

Thermal expansion (TE) phenomenon has an important role in numerous engineering applications. Thermal expansion (TE) is a consequence of the change in the average distances between the atoms in an object [16]. Thermally induced cracks are formed among the main forms of deterioration of concrete if the structures are exposed to the elevated temperatures in a short period [17]. The hardened cement paste and aggregates in concrete have different thermal expansion properties, which leads to different volumetric changes, if the concrete is rapidly heated or cooled. Internal stress is thus generated, causing cracking of concrete in the micro- or macro-scale [18–20]. Typical values of thermal expansion coefficients (TEC) of hardened cement pastes (HCP) about $15–20 \times 10^{-6}$/°C, which are approximately two times of that of the normal coarse aggregates [21]. The solid composition, the amount of water and the pore structure are the main factors acting on the TEC value of HCP [22]. Thermal expansion coefficients are affected by the water contents in HCP, especially the free water (W_e) in contents. Hence, the presence of large amount of W_e is the main reason for the high TEC of cement paste at early hydration ages [23]. TEC of a compacted material is smaller than that of a porous material [24]. It has been reported that, the physical properties of hydration products such as density play an important role in the thermal dilation of cement pastes.

Replacing Portland Cement with micro and NS reduce the total amount of CH through pozzolanic reaction and change the porosity of the paste. The consumption of CH due to pozzolanic reaction lowered thermal dilation rate (TDR) and TEC [17].

This work aims to study the effect of nano-silica (NS) on the physico-chemical, mechanical, thermal expansion and microstructure of superplasticized blended cement pastes.

2. Materials and experimental techniques

2.1. Materials

The starting materials used in this work were Ordinary Portland Cement (OPC), nano-silica (NS) and polycarboxylate superplasticizer. OPC (Type I) was provided from Beni-Suief Portland Cement Company, Egypt. The results of chemical analysis of OPC and NS are given in Table 1. Blaine surface area of OPC and NS were 3050 and 95 m^2/g respectively. The average particle size of nano-silica (NS) was 15 nm; supplied from nanotechnology Lab, Faculty of Science, Beni-Suief University, Beni-Suief, Egypt. The amorphous nature of NS-particles was verified using XRD, TEM and SEM (Figs. 1 and 2). The superplasticizer (Conplast SP-610) based on polycarboxylate superplasticizer was derived from Fosroc Company, 6 October City, Egypt. It is opaque light yellow liquid, with density 1.08 g/ml and chloride content <0.1 mass%.

2.2. Experimental techniques

2.2.1. Preparation of cement pastes and mortars

OPC was substituted with NS up to 6 mass%. The OPC–NS cement blends were mixed in a rotary mixer. NS particles are not easy to disperse uniformly due to their high surface energy. NS particles are not easy to disperse uniformly. Accordingly, the mixing was performed as follows: (i) NS was stirred with water/binder ratio of 0.25 in the presence of 1.0% superplasticizer at high speed of 120 rpm for 2 min, (ii) the cement and the residual amount of mixing water were added to the mixer and mixed at medium speed (80 rpm) for another 1 min, and (iii) the mixture was allowed to rest for 90 s and then mixed for 1 min at high speed (120 rpm). For preparation of mortars, the sand was added gradually and mixed at medium speed for additional 30 s, then (ii). The mortars were prepared by mixing 1 part of cement and 2.75 parts of standard sand proportion by weight with water content sufficient to obtain a flow of 110 ± 5 with 25 drops of the flow table [25]. Freshly prepared cement mortars were placed into 50 × 50 × 50 mm cubic moulds in two approximately equal layers manually, compacted and pressed until a homogeneous specimen was obtained. The moulds were vibrated for a few minutes to remove any air bubbles and better compaction. The mix compositions of the prepared blends are shown in Table 2.

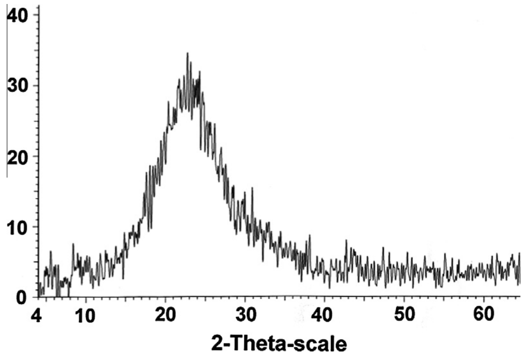

Fig. 1. XRD diffraction patterns of NS.

2.2.2. Determination of the water of standard consistency and setting times

The required water of standard consistency gives a paste which permitted the settlement of the Vicat plunger (10 mm in diameter) to a point 5–7 mm from the bottom of the Vicat moulds. It was measured to get all specimens having the same workability. The required water of standard consistency and initial and final setting times for each mix were determined according to ASTM specification [26].

2.2.3. Curing and stopping of hydration

The specimens were cured in 100% RH chamber at a constant temperature 23 ± 1 °C for the first 24 h and then immersed in tap water until the time of testing (3, 7, 14, 28 and 90 days). The hydration of cement pastes was stopped by pulverizing 10 g of representative sample in a beaker containing 1:1 (v/v) methanol–acetone mixture, then mechanically stirred for 1 h. The mixture was filtered through sintered glass G_4, after washing two times with the stopping solution and diethyl ether, then dried at 70 °C for 1 h, then collected in polyethylene bags; sealed and stored in desiccators for analysis [27].

2.2.4. Determination of combined water content

The combined water content is considered as the percent of ignition loss of the dried sample (on the ignited weight basis). Approximately 2 g of the pre-dried samples were ignited up to 1000 °C for 1 h soaking time. The results of combined water contents were corrected for the water of free portlandite present in each sample [28].

2.2.5. Portlandite determination

Free portlandite contents of the hydrated cement pastes can be thermally determined. 0.5 g sample of the hardened cement was placed in a porcelain crucible introduced into a cold muffle furnace (room temperature). The temperature was increased up to 390 then to 550 °C at heating rate of 3 °C/min. The loss of weight occurred between 390 and 550 °C with soaking time of 15 min is equal to the weight of water of calcium hydroxide. Therefore, the free portlandite can be calculated [29].

Table 1
Chemical analysis of OPC and NS (mass %).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	Total
OPC	21.40	3.67	5.05	64.73	1.50	2.05	0.30	0.22	2.60	99.70
NS	98.61	0.01	0.01	0.01	0.01	0.29	0.3	0.045	0.71	99.99