Cement & Concrete Composites 49 (2014) 84–91

Contents lists available at ScienceDirect

Cement & Concrete Composites

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

Effect of sodium silicate- and ethyl silicate-based nano-silica on pore structure of cement composites

Kyoung-Min Kim [a], Young-Sun Heo [b,*], Suk-Pyo Kang [c], Jun Lee [d]

[a] Architectural Technology Research Team, Daewoo Institute of Construction Technology, 60 Songjuk-Dong, Jangan-Gu, Suwon 440-210, Republic of Korea
[b] Fire Research Center, Korea Institute of Construction Technology, Hwaseong 445-861, Republic of Korea
[c] Department of Architecture & Interior Design, Woosuk University, Samnye-Eup, Wanju-Gun 565-701, Republic of Korea
[d] Korea Conformity Laboratories Daejeon & Chungnam Testing Lab., 60-4 Jang-Dong, Yuseong-Gu, Daejeon 305-343, Republic of Korea

ARTICLE INFO

Article history:
Received 26 November 2011
Received in revised form 6 December 2013
Accepted 17 December 2013
Available online 27 December 2013

Keywords:
Nano-silica
Silica fume
Cement composites
Pore structure
Compressive strength

ABSTRACT

This study proposes using sodium silicate-based nano-silica (SS) in cement composites. The effect of the addition of the proposed nano-silica on cement composites was compared to that of conventional ethyl silicate-based nano-silica (ES) and silica fume (SF). This study found that the inclusion of SS in cement composites has mainly two effects on their properties: one is a fast pozzolanic reaction, and the other is a pore-filling effect in a cement matrix. As a result, SS dramatically improves the early-age strength of cement composites by up to 184% and 152%, compared to a control specimen and the specimen with ES inclusion, respectively. Calorimetry, X-ray diffraction (XRD), scanning electron microscope (SEM) and mercury intrusion porosimetry (MIP) tests were conducted to monitor the effects of these nano-silicas.

1. Introduction

Mineral and chemical admixtures for concrete have been widely used to satisfy the design requirements of building constructions [1–3]. In recent years, it has been found that a partial replacement of cement with nano-sized mineral admixtures significantly improves the performance of concrete [4–7]. In the literature, there are a number of studies reporting the effects of nano-sized materials with different types (such as SiO_2, Fe_2O_3, Al_2O_3, ZnO_2, TiO_2, $CaCO_3$ and Cr_2O_3) on the properties of concrete. Of these nano-sized materials, spherical nano-silica (SiO_2) added to concrete has been extensively investigated. One study examined the effect of single and combined nano-sized materials on the compressive strength of cement mortar and found that using combinations of nano-sized materials was not as effective as using a single nano-sized material [8]. Oltulu and Şahin [8] have conjectured that this is because the interaction between nano-particles in binary and ternary combinations leads to certain negative effects on the physical and mechanical properties of the mortars. Hence, to optimize the effect of nano-sized materials on the performance of concrete, a single type of nano-silica is generally recommended.

In general, nano-silica consists of particles between 1 nm and 500 nm, and is defined as a highly reactive siliceous colloidal material consisting of an amorphous SiO_2 core with a hydroxylated surface [9]. In the review of the literature, adding nano-silica to cement composites improves their durability and mechanical properties. This is because the nano-size of the silica particles improves the interface of the cement paste and aggregate [10]. Nazari and Riahi [11] have demonstrated that nano-sized materials fill the voids between the cement grains, resulting in the immobilization of free water. Atahan and Dikme [12] have compared the effect of mineral admixtures that include nano-silica on the properties of concrete and found that admixtures with only a 2% replacement ratio of nano-silica can produce very high sulfate resistance, much the same effect as using blast furnace slag at 40–60% replacement ratios.

Important characteristics of nano-silica that improve the performance of concrete are its size, specific surface area, and particle size distribution [11–13]. In particular, the high specific surface area of the nano-silica is a key parameter for a thorough reaction contributing to a rapid hydration of the cement [14]. A sol–gel process that includes hydrolysis and condensation using tetraethylorthosilicate (TEOS) is widely used to synthesize nano-silica. A number of researchers [15,16] have hypothesized that the concentration of TEOS, the ratio of water to TEOS, the feed rate of ammonia, the concentration of solvent, and the reaction temperature are the five critical parameters to control the nucleation, growth, size, and specific surface area of the nano-silica. Rahman et al. [15] observed that the particle size of the nano-silica increased as the

* Corresponding author. Tel./fax: +81 31 369 0551.
E-mail address: retona.heo@gmail.com (Y.-S. Heo).

0958-9465/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.cemconcomp.2013.12.009

concentration of TEOS and ammonia increased, and decreased when the concentration of water increased, the temperature increased, and the feed rate of ammonia decreased.

However, ethyl silicate-based nano-silica produced using TEOS can cause several problems when used in cement composites. For example, using ethyl silicate can result in a large mean size of the nano-silica, which obviously deteriorates its benefits in cement composites. Thus, it is very important to inhibit the particle growth of the nano-silica to produce a more effective admixture material. A previous study [17] introduced a new sol-precipitation method that reduced the particle growth of nano-silica by adding an electrolytic additive (sodium iodide). In the study, it was found that the addition of sodium iodide reduced the particle size by up to 50%. However, it should be noted that this reduction was only achievable when the amount of the sodium iodide was controlled optimally, and thus, this result may not be reproducible with variable starting materials. In addition, this method required a high concentration of ethyl silicate, which can significantly increase costs in a production line. Therefore, this study used sodium silicate as a primary material for producing nano-silica. The cost of sodium silicate is generally four times less than that of ethyl silicate in Korea, due to its lower purity, and it is expected to be reproducible with a small particle size. The aim of this study is to investigate the effect of the proposed nano-silica on the properties of cement composites.

2. Experimental program

2.1. Experimental procedure

To investigate the effect of the proposed material, sodium silicate-based nano-silica (SS), on the pore structure and other fundamental properties of cement composites, the mineral admixtures of conventional ethyl silicate-based nano-silica (ES) and silica fume (SF) were prepared for comparison purposes. A mortar mixer was used to prepare the specimens. After demoulding the specimens, they were moved to a water curing tank where they were cured until the experimental tests were conducted.

To provide evidence for the true effect of SS, ES and SF on the properties of cement composites, hydration heat, chemical composition, hydration products and pore size distribution of the cement paste were examined. Finally, to quantify the effect of nano-silica, this study examined the compressive strength of mortar specimens for an indication of whether or not the addition of SS improves the mechanical properties of cement composites relative to those made with conventional ES and SF.

Table 1 shows the mixture proportions of the cement composites. The percent of SS, ES and SF replacements of cement was 5% by mass for cement paste specimens and 5% and 10% for mortar specimens. The water to binder ratio of the cement composites was fixed at 0.5 by mass for all mixtures. It should be noted that, as can be seen from Table 1, the calculated water volume fraction (relative to the binder) decreases as the replacement ratio of nano-silica or silica fume increases. This reduction in mass and volume of water in the cement pastes is to offset the increased volume of binder (SS, ES, or SF) that is caused by the low densities of the silica additives. Similarly, the mass and volume ratios of sand decrease when one of SS, ES, and SF replaces cement—its mass ratio dropping from its highest value of 2.5:1.0 (sand:cement) in the control mortar (compressive strength: 35 MPa at the age of 28 d)—leading to the reduction of the water volume fraction relative to the binder (Table 1).

It is generally accepted that in a cement paste condition, with the addition of partial replacements (low or high density), the mass ratio of water changes to balance their proportion in the mixture at a given volume of cement paste. In a mortar or a concrete condition, however, the mass ratio of aggregate (not water) changes for the same reason. Hence, in this study, it is expected that upon the addition of low density replacements, the resulting reduced water volume fraction relative to binder in cement composites can partly contribute to both a decrease in the slump and an increase in the strength of the cement composites, compared to the control cement composites.

2.2. Methods

The hydration heat release of nano-silica and silica fume blended cement pastes were measured by monitoring the heat flow in an isothermal calorimetry test. A Twin conduction type calorimeter manufactured by Tokyo Riko was used. As for the sample preparation, the control and silica-blended powders were separately placed in sample cups in the calorimeter and allowed to equilibrate to 25 °C. Water was also equilibrated at a temperature of 25 °C in a water tube in the calorimeter, before being injected into the pre-prepared cement powder, which was subsequently mixed. The ambient temperature in the calorimeter was maintained at 25 °C. Finally, the data acquisition system was operated to record the rate of heat evolution during the first 45 h of hydration. An X-ray diffraction (XRD) analysis was conducted at the age of 1 d. A MINIFLEX diffractometer (Cu Kα radiation, Ni filter) produced by Rigaku was used for analyzing the chemical variation. The operating power of the X-ray generator was 25 kV and 20 mA in 3°/min detector's scan speed, and data collections were carried out over the 5–70° (2θ range) with a counting time of 14 s/step. A scanning electron microscope (SEM) was used to observe the hydration products of control and nano-silica-blended cement pastes. SEM analysis was conducted at the ages of 1 d and 3 d. The porosity and pore size distribution of the cement pastes were measured by mercury intrusion porosimetry (MIP), according to ISO 15901-1. The pressure of mercury was fixed at 30000 psi, and contact angle was 130°. The test was carried out at the age of 28 d. The flow and compressive strength of the mortars were tested in accordance with ASTM C230/C230M and ASTM C109/C109M, respectively. For testing the compressive strength, three specimens were prepared for each batch and the average values of the test results were reported.

2.3. Materials

Ordinary Portland cement (density: 3140 kg/m^3 and fineness: 346 m^2/kg) and fine aggregate (type: river sand, density: 2600 kg/m^3 and absorption: 0.6%) were used. ES, SS, and SF were the mineral admixtures incorporated into the cement composites. The properties of both nano-silica products are given in Table 3. The density, fineness, and loss on ignition of SF were 2200 kg/m^3, 20,000 m^2/kg, and 1.5%, respectively.

3. Synthesis of nano-silica

Since Stöber et al. [18] first studied the synthesis of silicon oxide, the sol–gel process has been popular for producing fine powders, owing to its many advantages for controlling their purity and size [15,19,20]. In the present study, this sol–gel process was selected to synthesize both SS and ES. It is well known that the power input and the concentration of the starting material significantly influence the particle nucleation and growth of silicon oxide [16]. Therefore, to single out the effect of the starting material (ethyl silicate and sodium silicate) on the resulting nano-silica and the properties of the resulting cement composites, the mixing speed (500 rpm), impeller diameter (100 mm), feed rate