Construction and Building Materials 84 (2015) 269–276

Contents lists available at ScienceDirect

Construction and Building Materials

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

Effect of nanosilica addition on the fresh properties and shrinkage of mortars with fly ash and superplasticizer

M. Sonebi [a], E. García-Taengua [a,*], K.M.A. Hossain [b], J. Khatib [c], M. Lachemi [b]

[a] School of Planning, Architecture and Civil Engineering, Queen's University of Belfast, Northern Ireland, United Kingdom
[b] Dept. of Civil Engineering, Ryerson University, Toronto, ON, Canada
[c] School of Architecture and Built Environment, University of Wolverhampton, United Kingdom

HIGHLIGHTS

- Fresh and hardened properties of cement mortars with nS, FA and SP are modeled.
- Mortar flowability is affected by nS content and SP dosage, but not by FA content.
- Higher nS contents require higher SP dosages to maintain acceptable flowability.
- Increasing nS content significantly reduces plastic shrinkage.
- The optimum nS content appears to be 1.7% over cement weight.

ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form 3 February 2015
Accepted 21 February 2015
Available online 23 March 2015

Keywords:
Fly ash
Mortar
Nanosilica
Superplasticizer

ABSTRACT

The ongoing use of various mineral additions along with chemical admixtures such as superplasticizers justifies the need for further research. Understanding and quantifying their effects and possible synergies on the fresh and hardened properties of cement-based materials is necessary, especially if some of these components are known to have a pozzolanic effect. This paper describes and models the fresh and hardened properties of cement mortars including nanosilica and fly ash, and relates their properties to the proportioning of these materials and the superplasticizer dosage. Mini-slump, Marsh cone and Lombardi cone tests were used to examine the properties of the fresh mortars, and to assess density, plastic shrinkage, and drying shrinkage up to 20 days. The equations presented in this paper make it possible to optimize mortar proportionings to the required levels of performance in both fresh and hardened states.

1. Introduction

1.1. Nanosilica as a supplementary cementitious material

The use of active and inert powders as materials for concrete production has been prompted by two main factors: (1) an increasing interest in high-performance cement-based materials such as high-performance grouts, self-compacting concrete, or ultra-high strength concretes that typically include significant amounts of powders other than cement [1–4], and (2) the demand for sustainable construction and for the reduction of energy consumption associated with cement production [5].

As a response to these two factors, cement replacement materials, also known as supplementary cementitious materials, have attracted much interest from researchers and industry. These terms refer to raw materials such as fly ash (FA), silica fume (SF), ground granulated blast-furnace slag (GGBS) and limestone powder (LSP) that are generated as by-products of other industries and added to concrete.

Nanosilica (nano-SiO_2 or simply nS) can be considered as one of these supplementary cementitious materials [6] but it also falls into the category of nanomaterials or nanoparticles. The nanoparticles most commonly used in cement-based materials are nS, TiO_2, Al_2O_3 and carbon nanotubes [7]. Most of the research published to date has dealt with nS [8], and it is reportedly the most widely used variety of nanoparticles nowadays [9]. Nanoparticles in general have attracted considerable interest as a result of their ability to improve concrete properties by modifying the structure of the cementitious matrix at the micro and nano levels [10,11], despite the fact that their market price is still higher than that of fly ash or silica fume [6].

---

* Corresponding author.
E-mail address: e.garcia-taengua@qub.ac.uk (E. García-Taengua).

http://dx.doi.org/10.1016/j.conbuildmat.2015.02.064

Nanosilica consists of ultra-fine particles of amorphous silica, which is usually distributed and used in aqueous solution, in the form of a slurry or hydrosol [12]. It can be produced via several methods, and the production method affects its properties by determining the degree of dispersion in the slurry or gel [13]. This variable, along with the impact of fineness and particle size on nanosilica performance as a supplementary material, highlights the convenience of referring to "types" of nS when comparing different results [10].

1.2. Mechanisms of action

The reactivity of nS is attributed to two main factors: its high purity in terms of SiO_2 content and its high specific surface area [11]. The effect of nS on the enhancement of fresh and hardened properties of cement-based materials is exerted through a variety of simultaneous mechanisms:

- Filler effect or pore-filling effect. As a result of the extremely reduced size of nS particles, they function as a filler in the cementitious matrix, improving its microstructure [11]. As nS particles fill the voids between cement grains, they potentially increase the packing density when correctly dosed and dispersed [9].
- Acceleration of cement hydration through nucleation effect. Nanosilica particles, when dispersed in the pore solution during cement hydration, act as highly efficient nucleation sites for the silica units released from cement particles [14] and also for the first C–S–H seeds [8,11]. The hydration products accumulate not only on the surface of cement grains but also around these additional nucleation sites dispersed in the pore solution. As a result, upon good dispersion of nS particles, the production of the C–S–H phase also takes place in voids between grains, producing a potentially more compact matrix [9].
- Pozzolanic effect. Calcium hydroxide in the pore solution forms as a by-product of cement hydration and eventually forms portlandite, a crystalline phase that has no relevant contribution to strength [9]. The maximum concentration of calcium hydroxide in the liquid phase is reached during the dormant period of cement hydration [15]. Nanosilica particles react very quickly with the calcium hydroxide, which is a product of cement hydration, to form additional C–S–H. This was confirmed by monitoring the evolution of the free portlandite content through time in cement pastes, which was significantly decreased in mixes with nS.
- Synergy between the acceleration of cement hydration and the pozzolanic effect. Calcium hydroxide in the pore solution results from the hydration of C_3S and C_2S. Besides, since cement hydration is accelerated by the nS particles as a result of the nucleation effect, the rate of C_3S consumption is accelerated [11,14]. As a result, the rate of calcium hydroxide release is also accelerated. This means that the nucleation effect and the consequent acceleration of cement hydration provoked by nS particles makes the calcium hydroxide more readily available, thus favoring the pozzolanic effect of nS. In consequence, the induction period of cement hydration is shortened when nS is present, as a result of this accelerated release of calcium ions and their rapid consumption by the pozzolanic action of nS [13].

1.3. Influence of nanosilica on the properties of cement-based materials

Nanosilica has been extensively reported to be a material that potentially enhances density, strength development and the mechanical properties of cement-based materials in general [9,16–19]. However, contradictory results are found in literature in relation to the following two key concerns: whether or not the use of nS implies substantial improvement, and the advisable range for the nS contents.

Two main factors contribute to these discrepancies. One is the fact that the nanosilicas used in different studies are of different types, have a different particle size, a different specific surface, or have been produced by different methods [13]. The second is the difficulty of dispersing nS particles in the fresh cement grout, paste, mortar or concrete [6].

The dispersion of nS particles cannot be completely explained on mechanistic grounds. It is true that varying the mixing energy can affect the initial aggregation or dispersion state of these particles in a pure water solution [20]. However, even if nS particles are stable and well dispersed in their original slurry or hydrosol form, once they come in contact with the pore solution of a cement-based material they tend to aggregate as a result of the presence of ions such as Ca^{2+}, Na^{+} and K^{+} released into the pore solution by cement upon contact with water. The high concentration of these ions in the liquid phase compresses the double layer [21] surrounding the nS particles, and the adsorption of Ca^{2+} ions onto the surface of nS particles causes a reduction in their negative electrostatic charge. Furthermore, these ions have a bridging effect, agglomerating silica units according to the pattern (SiO^{-})–(Ca^{2+})–(SiO^{-}) [13]. All of these mechanisms tend to destabilize the distribution of nS particles in the pore fluid and prevent their homogeneous dispersion.

The rheology of cement pastes and mortars with nS presents another issue: the introduction of nS potentially affects the compatibility between the cement and superplasticizers or any other chemical admixture or mineral additions [6,22]. In these systems, increasing nS contents results in significantly higher yield stress values [22], and using superplasticizers at dosages higher than the saturation point has been reported as a convenient way of obtaining better performance in the fresh state [18].

Different conclusions concerning the effect of nS have been reported with respect to the compressive strength of mortars. Some studies have found that it has a limited or negligible impact on compressive strength [12]. In other cases, increasing nS contents increased compressive strength values up to a certain dosage, with further increases causing a reduction in compressive strength, leading to the determination of an intermediate optimum dosage for nS [18,23]. There is no consensus regarding this optimum nS dosage, as the values reported are not congruent. However, even though nS contents of 10% over cement weight or even higher have been considered in some studies, it appears that a rule-of-thumb maximum dosage acceptable for nS has been established as 5% over cement weight [6].

2. Objectives and research significance

The aim of this study was to evaluate the effects of different contents of nS, FA and different SP dosages on the fresh properties and plastic and drying shrinkage of cement mortars. A series of cement mortars was produced and tested, and the experimental results were analyzed and modeled in a semi-empirical manner following a statistical approach. Key parameters and synergies with a statistically significant impact on the rheology and shrinkage of the mortars were detected, and their effect quantified. The equations obtained can be used to evaluate the potential influence of the proportioning of the different components, and to adjust their dosages to ensure the stability of mortar proportionings that include nS and FA. These tools can facilitate the protocol needed to optimize mortar with a given set of performance criteria.