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Effects of the addition of nanosilica on the rheology, hydration and development of the compressive strength of cement mortars

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ABSTRACT

This paper examines the rheology, hydration kinetics and development of the compressive strength of cement mortars including nanosilica and fly ash. The contents of these materials and the superplasticizer dosage are related to different rheological and strength parameters. Effects on rheology were analysed through yield stress and viscosity. Calorimetry tests were carried out to assess the variations in cement hydration kinetics, and the maximum and minimum heat release rates were analysed. Compressive strength was evaluated at different ages up to 56 days. The equations presented in this paper make it possible to optimize mortar proportionings that fulfil required performance levels in both fresh and hardened states.

1. Introduction

The terms 'cement replacement materials' and 'supplementary cementitious materials' refer to raw materials that are generated mostly as by-products of other industries and added to cement-based materials as powders, such as: silica fume, fly ash (FA), ground granulated blast-furnace slag (GGBS), or limestone powder. They have attracted much interest from researchers and industry due to an increasing interest in high performance concretes that typically include important amounts of powders other than cement [1–4].

FA has long been used as a supplementary cementitious material. FA particles are round in shape, and as a result their addition to cement-based materials increases their workability and cohesion [5,6]. Furthermore, due to high vitreous silica and alumina contents, FA reacts with portlandite or calcium hydroxyde, although this pozzolanic effect is not noticeable until two or three months after mixing [5].

Nanosilica (nano-SiO_2 or simply nS) is a nanomaterial which can also be considered a supplementary cementitious material [7]. Most research published so far concerning nanotechnology and construction materials has dealt with nS [8] and it is reportedly the most widely used variety of nanoparticles [9], although its market price is still higher than that of FA or silica fume [7]. Nanosilica consists of ultra-fine particles of amorphous silica, usually distributed in aqueous solution, in the form of a slurry or hydrosol [10]. It can be produced using several methods, and the production method affects its properties as it determines the degree of dispersion in the slurry or gel [11].

Nanosilica has been extensively reported to be a material that potentially enhances density, strength development and mechanical properties of cement-based materials [9,12–15]. Its reactivity is attributed to its high purity in terms of SiO_2 content and its high specific surface area [16,17]. Different simultaneous mechanisms are involved in the enhancement of fresh and hardened properties of cement-based materials by nS particles:

- Filler effect or pore-filling effect. As a result of the extremely small size of nS particles, they function as a filler in the cementitious matrix, improving its microstructure [16] and

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potentially increase the packing density when correctly dosed and dispersed [9].

- Acceleration of cement hydration through nucleation effect. During cement hydration, nS particles act as nucleation sites for the silica units released from cement particles [18] and also for the first C–S–H seeds [8,16]. This way, the hydration products accumulate not only on the surface of cement grains but also around these additional nucleation sites dispersed in the pore solution, creating a potentially more compact matrix [9].
- Pozzolanic effect. Calcium hydroxide in the pore solution is the result of the hydration of C_3S and C_2S. It reacts very quickly with nS particles to form additional C–S–H is formed. The maximum concentration of calcium hydroxide in the liquid phase is reached during the dormant period of cement hydration [19]. As hydration is accelerated by nS particles due to the nucleation effect, the rate of C_3S consumption is also accelerated [16,18] and, as a result, so is the rate of calcium hydroxide release. This means that the nucleation effect and the consequent acceleration of cement hydration caused by nS particles make the calcium hydroxide more readily available, thus favouring the pozzolanic effect of nS. In consequence, when nS is present, the induction period of cement hydration is shortened as a result of this accelerated release of calcium ions and their rapid consumption by nS [11]. The pozzolanic activity of nS has been found to be higher than that of other active additions, especially at early ages [20].

The literature shows contradictory results around two key aspects: whether the use of nS offers substantial improvement of the mechanical properties of cement-based materials, and the recommended range for nS contents. There are two main sources that contribute to these discrepancies. First, the nanosilicas used in different studies are of different types, different particle size, different specific surface, or produced by different methods [11]. And second, the difficulty of dispersing nS particles in the fresh cement grout, paste, mortar or concrete [7], which is an issue that cannot be completely explained on mechanistic grounds. Even if they are well dispersed in their original slurry or hydrosol form, once in contact with the pore solution of a cement-based material they tend to aggregate due to the presence of ions such as Ca^{2+}, Na^+ and K^+ released by cement upon contact with water. These ions have a bridging effect, agglomerating silica units according to the pattern (SiO^-)–(Ca^{2+})–(SiO^-) [11,21], which tends to destabilize the distribution of nS particles in the pore fluid and prevents their homogeneous dispersion.

The introduction of nS potentially affects compatibility between the cement, superplasticizers and any other chemical admixture or mineral additions [7,22], and as a consequence the rheology of cement pastes and mortars is affected. In these systems, increasing nS contents tend to significantly increase yield stress values [22].

With respect to the effect of nS on the compressive strength of mortars, different conclusions have been reported. Some studies have found that it has a limited or negligible impact on compressive strength [10], while some others have reported different trends finding an intermediate optimum nS content [14,23]. Some authors have reported higher gains in compressive strength by achieving a better dispersion of the nanoparticles using a defoamer in addition to the water reducing agent [24]. However, there are also studies that have reported a moderate decrease in compressive strength when nS is used at dosages up to 5% [25]. Therefore, there is no consensus regarding the most appropriate range for nS contents, as the values found in current literature are not congruent. It appears that a rule-of-thumb maximum nS content would be 5% over cement weight [7], but other authors have reported that this maximum is 2% over cement weight when the particle size is between 15 nm and 80 nm [26].

2. Research objectives

The aim of this study was to evaluate the effects of different nS and FA contents and different superplasticizer (SP) dosages on the rheology, cement hydration and development of compressive strength of cement mortars. A series of mortars were produced and tested, and the experimental results were analysed and modelled by means of multiple linear regression. The key parameters and synergies with a statistically significant impact on the rheology, cement hydration kinetics and compressive strength of mortars were identified, and their effect quantified.

Different equations modelling the relationships detected were obtained. They constitute a useful tool to evaluate the influence of the different mortar components, which makes it possible to adjust their dosages in order to ensure the stability of mortars that include nS and FA. Furthermore, these equations have been used in a multiobjective optimization to find the most effective nS, FA, and SP contents that fulfil certain performance criteria. Such a multi-objective approach can provide a basis to reconcile discrepancies in literature as to the definition of optimum nS contents.

3. Experimental investigation

3.1. Factors and levels considered

The factors considered in this research as well as their levels are summarized in Table 1:

- nS added to the mortar. Its solid weight, expressed as percentage of the cement weight in the mortar, was varied between 0.5% and 3.0%.
- FA, as partial replacement of cement. It was used in amounts between 5% and 20% over the weight of cement.
- SP dosage was varied between 0.3% and 0.9% over total binder weight, that is over total weight of cement and FA.

3.2. Materials

The materials used to produce the mortars were tap water, cement, FA, nS, SP, and sand. Table 2 presents the equivalent oxides composition of cement and FA as well as the composition of the solid fraction of the colloidal nS, with all values expressed as percentage relative to total mass. Table 3 gives informs about relevant physical properties of these materials.

The cement was Portland cement type CEM I 42.5N, as specified by the standard EN 197-1:2000 [27], FA conformed with the standard EN 450-1:2005 [28], and nS was a commercially available colloidal form, being an aqueous solution with an SiO_2 content of 50% by mass. The SP used was a commercially available modified

Table 1
Factors and levels considered.

Factor	Levels (*)
Nanosilica addition, nS (solid content)	0.5% o/c 2.0% o/c 3.5% o/c
Fly ash, FA (cement replacement)	5.0% o/c 12.5% o/c 20.0% o/c
Superplasticiser dosage, SP	0.3% o/b 0.6% o/b 0.9% o/b

(*) o/c: over cement weight.
(*) o/b: over binder weight (cement + FA).