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The effect of nanosilica addition on flowability, strength and transport properties of ultra high performance concrete

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ABSTRACT

The experimental study herein presented was conducted aiming to evaluate the influence of nanosilica (nS) addition on properties of ultra-high performance concrete (UHPC). Thermo gravimetric analysis results indicated that nS consumes much more $Ca(OH)_2$ as compared to silica fume, specifically at the early ages. Mercury intrusion porosimetry measurements proved that the addition of nS particles leads to reduction of capillary pores. Scanning electron microscope observation revealed that the inclusion of nS can also efficiently improve the interfacial transition zone between the aggregates and the binding paste. The addition of nS also resulted in an enhancement in compressive strength as well as in transport properties of UHPC. The optimum amount of cement replacement by nS in cement paste to achieve the best performance was 3 wt.%. However, the improper dispersion of nS was found as a deterrent factor to introduce higher percentage of nS into the cement paste.

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1. Introduction

Ultra-high performance concrete (UHPC) is one of the most promising types of concrete, which has been developed in the last decade [1–3]. This innovative high-tech material is characterized by a dense microstructure, which presents both ultra-high compressive strength and ultra-high durability [4–5]. The main composition of UHPC contains a large amount of cement, usually between 800 and 1100 kg/m³, which is around three to four times more than the quantity of cement in normal concrete [5]. Therefore, the blending of cement with high pozzolanic fine materials, such as nanosilica (nS), can be a suitable option to reduce the high volume of cement in the UHPC proportioning.

Nevertheless, the efficiency of UHPC is particularly dependent on its density. In fact, by optimizing the particle packing, an ultra-high consolidation of the concrete matrix can be reached. This can be obtained through an almost 'perfect' grain size distribution, by incorporating a homogeneous gradient of fine and coarse particles in the mixture. In this scope, the use of nS as pozzolanic addition is highly effective. Actually, due to its extremely small size particles, nS can fill the voids between cement and silica fume particles, leading to higher packing level ("filler" effect) and also generating a denser binding matrix, with more calcium silicate hydrate (C-S-H). Consequently, a

E-mail addresses: ghafari@dec.uc.pt (E. Ghafari) hcosta@isec.pt (H. Costa) ejulio@civil.ist.utl.pt (E. Júlio) atp@eq.uc.pt (A. Portugal) luisa@eq.uc.pt (L. Durães). significant improvement on both durability and mechanical properties is obtained. Li et al. [6] showed that both the compressive and flexural strengths of concrete can be enhanced by incorporating nS. A concrete with addition of silica fume, fly ash and nS was also studied by Collepardi et al. [7]. It was concluded that concrete with this ternary combination has a better performance, in terms of both strength and durability, than those just with fly ash, but similar to those just with silica fume. Li [8] also found that an addition of nS results an increase in both early-age strength and long-term strength. Aly et al. [9] reported that incorporation of a hybrid combination of colloidal nS and waste glass into the cement mortars led to an enhancement of the mechanical properties in comparison with plain mortar.

Additionally, it has been proved that the incorporation nS also improves the durability properties of concrete. He and Shi [10] studied the chloride permeability and microstructure of Portland cement mortar with different types of nano-materials. This study confirmed that an addition of nS and nano-clay significantly improves the chloride penetration resistance as well as the general ionic permeability of cementitious mortar. An experimental study performed by Ji [11] showed that the addition of nano-SiO₂ to the mixture improves the water permeability resistance of concrete.

Moreover, well-dispersed nano-particles act as centers of crystallization of cement hydrates, therefore accelerating the hydration [12]. Qing et al. [13] stated that the pozzolanic activity of nano-SiO₂ is much higher than that of silica fume. It was found that the bond strength of the paste-to-aggregate interface, incorporating nS, is higher than that of specimens with silica fume. A research also showed that the pozzolanic activity of fly ash significantly increases after incorporating

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| Table 1 | |
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| Chemical composition and physical properties of cement and silica fume | |

| chemical composition and physical properties of cement and sinca fume. | | | |
|--|--------|-------------|--|
| Chemical analysis (%) | Cement | Silica fume | |
| SiO ₂ | 20.9 | 93.6 | |
| Al ₂ O ₃ | 4.60 | 1.3 | |
| Fe ₂ O ₃ | 3.15 | 0.90 | |
| CaO | 62.0 | 0.4 | |
| MgO | 2.00 | 1 | |
| SO ₂ | 3.60 | 0.4 | |
| K ₂ O | <1 | 1.52 | |
| Na ₂ O | <1 | <1 | |
| Specific gravity | 3.14 | 2.17 | |

nS [8].

There are several studies on incorporation of nS in concrete proportioning but most of them have focused on using SiO2 nanoparticles on mixtures with high values of water/cement ratio [8–17].

The present study aims to give a contribution in this field. In this scope, the pozzolanic activity of nS in UHPC mixture with very low water/cement ratio was studied. Pozzolanic activity of nS in cement pastes was studied as compared with silica fume using conductivity analysis, x-ray diffraction (XRD) and thermo gravimetric analysis (TGA).

Additionally, the mechanical properties of several UHPC mixtures were characterized, namely by measuring the compressive strength. The evaluation of the fluid and gas transport properties of concrete specimens, including the water absorption, capillary water sorption, and gas permeability, was also performed. Mercury intrusion porosimetry (MIP) tests were conducted to characterize the size distribution of capillary pores in the UHPC specimens. Moreover, the microstructures of those were analyzed by scanning electron microscopy (SEM).

2. Experimental study

2.1. Materials and mixtures proportions

Portland cement type I 52.5R was used. An addition of silica fume (SF) presenting a specific area of 18.41 m²/g and an addition of nS with an average particle size of 15 nm were adopted. Table 1 shows some physical and chemical properties of cement and silica fume and Table 2 summarizes the properties of nS. The SEM micrographs of nS particles are also presented in Fig. 1, where it can be seen that nS particles exhibit a spherical shape. The aggregate used was siliceous sand with 0.6 *mm* of maximum aggregate size. The adopted admixture was a polycarboxylic acid based superplasticizer (SP) with solids content between 28.5 and 31.5 wt.% and density between 1.067 and 1.107 g/cm³.

In order to study the pozzolanic behavior of nS, three series of cement pastes with a very low water/cement ratio were considered. The cement pastes were designed and produced considering a water/ cement ratio of 0.2, in which 3% of cement was replaced by nS and SF. A control paste, containing only cement, was also produced to serve as reference paste. The properties of the cement pastes are shown in Table 3.

In addition, five series of UHPC mixtures containing different percentages of nS were prepared for this study. An optimized mixture proportion of UHPC, which was obtained through previous studies, was selected to serve as reference mixture [18–20]. Then, nS was incorporated as cement replacement by 1, 2, 3 and 4 by wt.% of cement. The large difference between the density of nS and silica fume resulted in an increase in the paste volume. The total content of powder was kept constant in volume. In addition, the water/powder ratio was kept constant for all mixtures. Table 4 shows the five series of mixtures, prepared with nS and a reference mixture without nS.

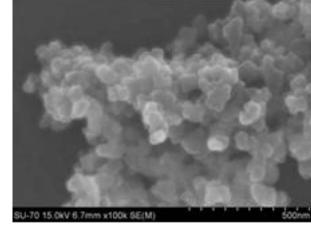


Fig. 1. SEM micrograph of nS particles.

The mixing procedure involved several steps. First, in order to prevent agglomeration and also to promote uniform distribution of very fine particles, all powders and siliceous sand were mixed dry for 5 minutes at low speed. To incorporate dry nS would not have been possible, due to its very low density, causing particles to disperse in the air. Therefore, nS was first dissolved in water, the latter already containing the superplasticizer, and then gradually added to the mixture. After 5 minutes, the mixture became fluid. After mixing, the concrete was poured into the molds and, 24 hours later, it was demoulded. Then, the specimens were cured in water immersion at 20 °C until the day of the test.

2.2. Experimental test

The experimental program of this study is divided into two main parts: first the pozzolanic activity of nS as compared with SF was studied by different methods; then, the effect of nS on fresh and hardened states and transport properties of UHPC was studied.

2.2.1. Determination of pozzolanic reactivity of nS and SF in cement pastes

Several techniques have been developed to study the pozzolanic activity of the materials but the determination of pozzolanic activity still presents considerable uncertainty being thus a complex problem [21–22]. In general these techniques can be classified into four main groups: electrical conductivity, quantitative X-ray diffraction analysis (XRD), thermo-gravimetric analysis (TGA) and chemical extraction.

The electrical conductivity method is a fast technique for evaluating the pozzolanic activity of materials. Raask and Bhaskar [23] applied this method for evaluating the pozzolanic activity of fly ash. This method allows the measuring of the amount of silica dissolved in a solution of hydrofluoric acid in which the active material is dispersed. This method requires 10 minutes for obtaining the pozzolanic index. Luxan et al. [24] proposed a faster method and pozzolanic index, given by the variation between the initial and final electrical conductivity of a calcium hydroxide pozzolanic suspension. The reaction between the calcium hydroxide and the pozzolanic material leads to a reduction in the electrical conductivity of the suspension, which can be attributed to the fixation of dissolved calcium hydroxide by pozzolanic particles.

Recently, Paya et al. [25] proposed a method for evaluating the pozzolanic activity of fly ash, in which the pozzolanic activity of the material was calculated as the percentage of loss in conductivity at different reaction times (100, 1000 and 10000 s). In the study herein described, a method similar to the one proposed by Paya [25] was used to evaluate the pozzolanic activity of both nS and SF. An unsaturated

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