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Effects of nano-silica and nano-limestone on flowability and mechanical properties of ultra-high-performance concrete matrix

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HIGHLIGHTS

- Higher NS and NC replacement amounts lead to lower flowability of UHPC matrix.
- There are optimal contents of NS and NC for UHPC matrix to obtain highest strengths.
- The improvement in mechanical strengths incorporating NS and NC become higher with lower W/B ratio.
- Compared to standard curing, NS and NC can accelerate cement hydration more effectively by combined curing.

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ABSTRACT

The effects of nano-silica/SiO_2 (NS) and nano-limestone/$CaCO_3$ (NC) on the flowability, strengths and microstructure of ultra-high-performance concrete (UHPC) matrix under different curing conditions were investigated in this study. The NS and NC were incorporated at different ratios as partial mass replacements for cement. On the microstructure aspect, the results verify that the NS acts as an effective filling material, which reduced porous areas and accelerated the cement hydration process by pozzolanic effect. On the other hand, the NC acts mainly as an inert filler material that created a denser microstructure, but accelerated the cement hydration process through boundary nucleation growth effect. On the mechanical properties aspect, a threshold value of the NS and NC contents were found so that the compressive, flexural strengths and flexural to compressive strength ratio of the UHPC matrix were found to increase as the NS and NC contents increased towards the threshold content, and then to decrease with the increase of NS and NC contents when the threshold was surpassed. Corresponding to the highest measured mechanical strengths of UHPC matrix, the optimal contents of NS and NC are around 1.0% and 3.0%, respectively. The research concluded that the NS and NC contents are critical to the performance of UHPC matrix.

1. Introduction

Compared to conventional concrete, ultra-high performance concrete (UHPC) contains much higher content of cementitious materials, such as silica fume, slag and fly ash. Park and Kang [1], Richard and Cheyrezy [2] and Granger et al. [3] found that incorporation of these materials into UHPC not only fulfills the economic requirement, but also brings other advantages such as lowering the shrinkage and improving the mechanical properties and durability of concrete. More importantly, cement substitution contributes to the recycling of industrial waste and the reduction of cement consumption, which reduces carbon dioxide emission and makes the material environmentally friendly.

Compared to the other pozzolanic materials [4], Senff et al. [5] showed that the pozzolanic reaction of silica fume is fast and could more effectively promote the strength development of concrete due to its high specific surface area. The recent developments of nanotechnology guarantee that various forms of nanosized amorphous silica, e.g. nano-silica/SiO_2 (NS), can be produced, which have higher specific surface areas and activities compared to conventional silica fume as reported by Senff et al. [6] and Lin et al.[7]. NS is produced synthetically, in the form of a water emulsion of ultrafine amorphous colloidal silica with sizes of 1–50 nm [8]. It

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has been utilized in many applications of concrete technology [9,10]. Sobolev et al. [11], Hou et al. [10,12] and Kawashima et al. [13] found that with the incorporation of NS in paste or concrete, even at small dosages, the NS can significantly improve the mechanical properties of the materials. When incorporating NS in ordinary cement paste, the NS content, water-to-binder ratio (W/B), and curing time were found to be critical to increase the compressive strength by many researchers [14–16]. Dolado et al. [17] reported that the compressive strength increase progressively with the increase of NS content within the range from 0.2% to 12% by mass of cement. With respect to pastes not containing NS, it was found that strength gains up to 65% higher could be achieved. In contrast, Shih et al. [18] found a maximum strength gain of 43% for cement pastes with 0.6% NS by mass of cement, while the strength gain reduced to 19% as the NS content was increased from 0.6% to 0.8% by mass of cement.

Limestone powder, as the other commonly used supplementary material, is primarily used as a filler material to improve rheological property of concrete. While limestone powder has also been shown to influence hydration of cement, Green et al. and Gurney et al. [19–21] showed that limestone powder can accelerate early-age hydration, and provide nucleation sites for calcium silicate hydrate (C–S–H), and react with calcium aluminates and tricalcium silicate to produce calcium carboaluminates and calcium carbosilicate hydrates, respectively. Most of the previous studies focused on micro-sized limestone powders, but nano-limestone/$CaCO_3$ (NC) has not been as widely investigated. Camiletti et al. [22], Gurney et al. [23] and Sato et al. [24] showed that NC has the potential in offsetting the negative effects of fly ash on the early-age properties, even at high replacement ratio. These findings show that the seeding effect of the NC particles and the nucleation of C–S–H cause the enhanced strength development for cement-based materials [22,24]. It has also been concluded that the early cement hydration is significantly accelerated by the NC, and the higher the amount of NC, the greater is the accelerating effect.

In terms of previous researches [25,13], silica fume and limestone powders can be used together for reinforcing cement-based materials. It was shown that for fiber reinforced cement composites, 8% of Kraft fibers (by the cement mass) in conjunction with 3% of silica fume and 10% limestone powder gave the highest flexural strength and the greatest ductility [26]. However, limited research has done to investigate the effect of blended NS and NC in UHPC, its benefits and potential applications.

In this study, the effects of incorporating NS and NC, both individually and blended, as partial mass replacements for cement on the properties of ultra-high-performance concrete (UHPC) matrix without fiber reinforcing were examined. The emphasis is on the difference in the pozzolanic and boundary nucleation growth effects induced by NS and NC, respectively and their contributions to the flowability, different mechanical strengths and microstructure characteristics of UHPC matrix.

2. Experimental program

2.1. Materials and mixture proportions

In this study, ordinary type I Portland cement (OPC, P.O 52.5), fly ash and silica fume were used as binders (Co., Ltd, China). The chemical compositions of the various binders are listed in Table 1. According to the suggestions of references [27,28], coarse aggregates were not used in UHPC matrix, silica sand having a particle size in the range of 0.9–2.0 mm was used instead. Silica flour has a density of 2.626 g/cm^3 and average particle size of 50.1 μm was also used. A polycarboxylate-based high-range water-reducing admixture (HRWRA) was used at a ratio of 0.15% by mass of cement. NS having 20 nm average particle size and NC sized in the range of 15–80 nm were incorporated at ratios of 0.5%, 1.0%, 1.5% and 2.0% for NS and1.0%, 2.0%, 3.0% and 4.0% for NC as partial mass replacement for cement, respectively. A TEM image of the used NS and an SEM image of the NC powders are shown in Fig. 1, respectively. The mix proportions of the control UHPC matrix are listed in Table 2. For the modified UHPC matrix with single nano-material (either NS or NC), W/B ratios varying from 0.16 to 0.22 were used. For the modified UHPC matrix with blended nano-materials (both NS and NC), only W/B ratio of 0.16 was used. The mix proportions for the modified UHPC matrix are listed in Table 3. Water from the HRWRA was included in the specified water-to-binder ratio (W/B). In Table 3, the mixtures are labeled with respect to their dosage: NS#–NC#, For example, NS1.0–NC3.0 represents a mixture with 1.0% nano-$SiO_2$and 3.0% nano-$CaCO_3$, together partially replacing 4.0% of cement by mass. Before mixing the UHPC matrix, NS and NC particles were dispersed in the mixing water using the ultrasonic dispersion method proposed by Kawashima et al. [29]. Mixing procedures were carried out in a rotary mixer according to the method presented in a previous works [30,31]. First, the OPC, silica flour, silica fume and fly ash were added to the mixer and mixed at medium speed (80 rpm) for 5 min. Silica sand was then added gradually to mix for another 3 min. After that, progressive incorporation of water containing the superplasticizer was added and mixed at high speed for additional 2 min. The mixture was allowed to rest for 1.5 min and then mixed for 5 min at a high speed.

Table 1
Chemical composition of raw binder materials.

Materials	Cement (P.O 52.5)	Fly ash	Silica fume
SiO_2 (%)	23.3	42.52	93.90
Al_2O_3 (%)	7.2	32.62	–
Fe_2O_3 (%)	3.1	9.35	0.59
SO_3 (%)	3.0	1.21	–
CaO (%)	59.6	8.63	1.85
MgO (%)	1.7	0.73	0.27
K_2O	–	2.16	0.86
Na_2O	–	0.59	0.17
Total	97.90	97.81	97.64

2.2. Test methods and sample preparation

The workability of each mixture was evaluated based on the flowability test (spread in mm) according to ASTM C 1437 (standard test method for flow of hydraulic cement mortar). The strengths of the UHPC matrix were measured based on ASTM C109/C109M-02 (standard test method for compressive strength of hydraulic cement mortars) and ASTM C78/C78M-10e1 (standard test method for flexural strength of concrete), respectively. Flexural strength tests were conducted on 40 mm × 40 mm × 160 mm UHPC matrix prisms and the compressive strength tests were done on 50 mm cubes using a three-point bending testing machine (DKZ-500) and a 200-ton compression testing machine (innovative instruments), respectively. Two curing regimes were used in this research: standard curing condition (20 ± 2 °C and RH of 95%) and heat curing condition (placed into a lime bath at 90 °C). For standard curing, two curing ages (7 days and 28 days) were used; for combined curing, the curing age was first 2 days heat curing and then 26 standard days curing. Three replicate UHPC specimens were used for all the tests. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (FEI Quanta 200 FEG) was used for microstructural evaluations.

3. Results and discussions

3.1. Flowability

Fig. 2 plots the changes in flowability for UHPC matrix incorporating different contents of NS and NC, with the added percentage increased from 0.5% to 1.5% and 1.0% to 4.0%, respectively. Generally, all UHPC matrix incorporating NS or NC exhibited lower flowability compared to that of the control mixture as shown in Fig. 2(a) and (b). Fig. 2(c) plots the change in flowability when both NS and NC were used. It can be seen that the flowability decreased as NC was incorporated to mixtures with constant amounts of NS. For instance in mixtures with 1.0% NS, incorporating 1.0% and 3.0% NC led to 20% and 34% decrease in the flowability, respectively. Similarly, UHPC matrix became less flowable as the NS content increased at constant NC replacement ratios. For example, mixtures with 3.0% NC had a decrease in flowability of 23% and 35% when NS content was increased to 0.5–1.5%, respectively. Therefore, greater cement replacement amounts achieve lower flowability. This phenomenon is due to the fine particle sizes of the nano-materials, which have much higher surface areas that absorb water, leaving less free water to contribute to the flowability [14,32].