A Comparative Study on the Pozzolanic Activity between Nano-SiO$_2$ and Silica Fume[*]

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Abstract: The pozzolanic activity of nano-SiO$_2$ and silica fume was comparatively studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and the compressive, bond and bending strengths of hardened paste and concrete were also measured. Results indicate that the compressive strength development of the paste made from Ca(OH)$_2$ and nano-SiO$_2$, the reaction rate of Ca(OH)$_2$ with nano-SiO$_2$ and the velocity of C-S-H gel formation from Ca(OH)$_2$ with nano-SiO$_2$ showed marked increases over those of Ca(OH)$_2$ with silica fume. Furthermore, the bond strength at the interface between aggregate and hardened cement paste, and the bending strength of concrete incorporated with 3% NS increased more than those with SF, especially at early ages. To sum up, the pozzolanic activity of nano-SiO$_2$ was much greater than that of silica fume. The results suggest that with a small amount of nano-SiO$_2$, the Ca(OH)$_2$ crystal at the interface between hardened cement paste and aggregate at early ages may be effectively absorbed in high performance concrete.

Key words: Ca(OH)$_2$; interaction; nano-SiO$_2$; pozzolanic activity; silica fume

1 Introduction

The technology of nano-structured material is being developed rapidly and will be applied extensively with many materials. For instance, raw materials of ceramics or polymer incorporated with some nano-SiO$_2$ (NS) content, their toughness was 2-10 times over that of ordinary ceramics or polymer[1-4]. Although cement is a common building material, its main hydrate C-S-H gel is a natural nano-structured material[5-9]. Many researchers have applied slag, fly-ash and silica fume (SF) to improve the properties of hardened cement paste (HCP) and cement based materials, and have achieved great successes, such as HPC and reactive powder concrete and so on. SF belongs to the category of highly pozzolanic materials because it consists essentially of silica in non-crystalline form with a high specific surface, and thus exhibits a great pozzolanic activity. But the pozzolanic activity of SF at early ages is low according to the literatures[10-13]. Putting SF into saturated calcium hydroxide (CH) solution, Mitchell et al[10] found that the XRD pattern of SF changed little up to 7 days and extensive C-S-H formation had occurred after 120 days. Li et al[13] showed that only 75% of SF was consumed in a cement paste after 90 days of hydration. Hjorth[14] found that in the Portland cement paste with 10% SF replacement and w/s ratio of 0.45, the maximum CH content was 11.2% at 10 days and 8.3% at 180 days. In this paper, with nano-technology for ceramics and polymer served as reference, the interaction

of CH with NS or SF was studied in order to absorb CH effectively at the interface between HCP and aggregate at early ages and thus improve the microstructure of HCP by this technology.

2 Experimental

2.1 Raw materials

Calcium hydroxide (CH) powder used in this study was analytical reagent grade and its specific surface was 340 m^2/kg (Blaine's fineness). NS (nano-SiO$_2$) was a commercially available undensified material supplied by Mingri Nano-material Ltd in China. SF was a commercially available undensified material supplied by Zunyi Ferroalloy Ltd in China. Both NS and SF were amorphous substances. A commercial ordinary Portland cement (OPC) (42.5 grade, Blaine specific surface 310 m^2/kg) complying with the Chinese standard (GB 175-99) was used and its composition (wt%) was 82 % clinker, 13 % slag and 5 % gypsum. The coarse aggregate (G, 6/25 mm) was crushed limestone. The fine aggregate (S) was river sand with fineness modulus of 2.5. The superplasticizer (SNF) used was a commercial sulphonated naphthalene formaldehyde polymer with water reduction up to 20 %. The water (W) used was tap water. The chemical composition and physical properties of NS and SF are shown in Table 1.

Table 1 Chemical composition and physical properties of NS and SF

Raw material	SiO$_2$ /%	Physical properties			
		Average of diameter /nm	Specific surface /m$^2 \cdot$g^{-1}	Density /g$\cdot$cm^{-3}	Loose density /g$\cdot$cm^{-3}
NS	99.9	15	160	2.12	0.22
SF	94.1	180	21.5	2.22	0.21

2.2 Procedures

In order to form C-S-H gel ($3CaO \cdot 2SiO_2 \cdot nH_2O$), the mix proportion of CH -NS or SF-water was designed as shown in Table 2. CH with NS or SF was fully mixed under dry process conditions in advance. Paste samples at standard consistency in accordance with that of cement paste were mixed by means of a cement paste mixer (ISO 9597:1989). The mixing process involved a total of 2.0 min at a paddle speed of both 62 rpm (revolution) and 140 rpm (rotation), a 15 second stop and a total of 2.0 min at a speed of both 125 rpm (revolution) and 285 rpm (rotation).

The fresh paste was cast into cubic moulds 25 mm × 25 mm × 25 mm on a vibrating table, cured at (20 ± 2) ℃ and above 90% r. h. moisture. The cubic specimens were demoulded after the final setting time, and then were stored in water at (20 ± 2) ℃ till test. Three cubes were tested for each sample at the given age, by a hydraulic press with 0-20 kN capacity and 0.25 MPa/s loading speed. Each strength value is an average of three specimens.

2.3 Preparation

The cement pastes containing NS or SF were prepared using a planetary mixer (ISO). For the paste, a cement with NS or SF: water: superplasticizer ratio of 1: 0.23: 0.01 was used, as shown in Table 3. Cement with NS or SF was fully mixed under dry process conditions befosehand. The mixing procedure was the same as the above preparation.

The fresh cement paste was cast into square-bar moulds of 40 mm × 40 mm × 160 mm on a vibrating table, and then a glass plate (39.8 mm × 39.8 mm × 3 mm) was set into the middle of the square-bar specimens with the plate parallel to the bar cross section. Specimens, which were cured at (20 ± 2) ℃ and above 90% r.h. moisture, were demoulded after 24 hours and then stored in water at (20 ± 2) ℃ till test. Three specimens were tested for each sample at the given age. The span for bending test and the compressed area for compressive strength were 100 mm and 40 mm × 40 mm, respectively.

At 28 days, when the glass plate was split apart between glass and hcp after the above flexural strength determinations, the fracture surface (interface) of the hcp was analyzed by SEM immediately in order to observe the orientation, size and morphology of CH crystal at! the interface.

The bending and compressive strength of concrete were tested according to Chinese Standards GB 81 and 82. For the concrete, a cement with NS or SF: water: fine aggregate: coarse aggregate: superplasticizer ratio of 1: 0.25: 1.08: 1.75: 0.01 was used, as shown in Table 4. Cement with NS or SF was fully mixed under dry process conditions beforehand. A compulsive concrete mixer (J50 type) was used for concrete mixing. The fresh concrete was cast into 100 mm × 100 mm × 400 mm square-bar moulds and 100 mm × 100 mm × 100 mm cubic moulds. Three square-bar specimens were tested for bending strength, the span being 300 mm; and three cubic specimens were tested for compressive strength at the given ages. And the specimens, which were demoulded after 24 hours, were cured at (20 ± 3) ℃ and above 90% r.h. moisture.

Table 2 Mix proportions and compressive strengths of pastes made from CH and NS or SF

Paste sample	Mix proportion /wt%				Compressive strength /MPa						
	CH	NS	SF	W	1/2 d	1 d	3 d	7 d	14 d	28 d	60 d
ANS	100	54	/	80	2.3	7.4	9.5	11.8	12.3	14.1	16.5
ASF	100	/	57	60	0	0	0	3.4	7.4	11.3	16.3

Table 3 Variation in flexural strength of the pastes with glass plate made from cement and NS or SF with time

Cement paste sample	Mix proportion /wt%					Flexural strength /MPa		Compressive strength /MPa	
	C	NS	SF	W	SNF	7d	28d	7d	28d
BCO	100			23	1	5.1	5.8	65.0	80.1
BNS	97	3		23	1	6.6	10.0	82.5	102.2
BSF	97		3	23	1	5.0	6.7	70.2	94.2

Table 4 Variation in bending strength of the concrete made from cement and NS or SF with time

Concrete sample	Mix proportion /kg·m⁻³							Slump /mm	Bending strength /MPa			Compressive strength/MPa		
	C	NS	SF	W	S	G	SNF		3 d	7 d	28 d	3 d	7 d	28 d
CCO	600			150	650	1050	6	200	7.99	9.05	10.9	53.2	67.0	89.5
CNS	582	18		150	650	1050	6	175	10.5	13.4	17.1	69.4	84.6	109.3
CSF	560		40	150	650	1050	6	205	9.94	12.0	15.0	59.9	75.9	96.1

2.4 Determination

X-ray diffractometer: D/Max-3B type, CuKα radiation, tube electric current 40 mA and tube voltage 40 kV, and scanning speed 2°/min. Scanning electron microscope: Hitachi S570 type, whose energy spectrometer is EDAX-9900. Differential scanning calorimeter: DSC-7, Perkin Elmer (USA), using about 8.0 mg sample and heated at 10 ℃/min in an argon atmosphere.

With the above pastes, the paste samples which were ground to have a specific surface of 300-350 m²/kg

(Blain) were analyged immediately by XRD in order to determine the degree of reaction between CH and NS or SF.

The degree of the pozzolanic reaction of NS or SF can be estimated by the reduction of CH content in paste made from CH and NS or SF by DSC[15]. Paste samples were cured under the same conditions as above. The DSC curves were obtained using about 8.0 mg sample, which was dried in an oven at (105 ± 5) ℃ by advance, in a differential scanning calorimeter (DSC-7). The sample
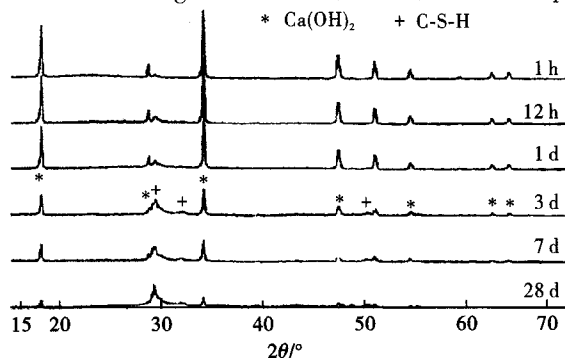

Fig.1a　XRD powder patterns of CH-NS-H₂O system with time

3　Results and Discussion

3.1　Strength development of hardened paste made from CH and NS or SF

Table 2 shows the compressive strength development of hardened pastes in the systems of CH-NS or SF-H₂O. The strength development of the paste sample ANS made from CH and NS, as compared with the paste sample ASF made from CH and SF was very different. At the age of 1 day sample ANS, which hardened before the age of 6 hours, had a considerable strength (7.4 MPa), and during the period from 1 day to 60 days the paste strength developed very well. However, sample ASF did not harden until the age of 3 days, and had only a low strength (3.4 MPa) at 7 days. During the period from 7 days to 60 days the strength of sample ASF returned slowly and gradually to normal. For example, the strength of sample ASF at 14 days was only equal to that of sample ANS at 1 day. To sum up, the strength development of the paste sample ANS was much quicker than that of paste sample ASF. The results seem to indicate that the reaction rate of CH

was heated at 10 ℃/min in an argon atmosphere with aluminium crucibles (with lid) as the reference material. The amount of energy absorbed by the endothermic reaction due to dehydration of CH in the temperature range of 420-510 ℃ was computed for each sample. The quantity of CH present in each sample was then calculated using the energy absorbed by the 480 ℃ DSC peak. The level of CH content in a sample can be used as an estimate of the percentage of pozzolanic reaction.
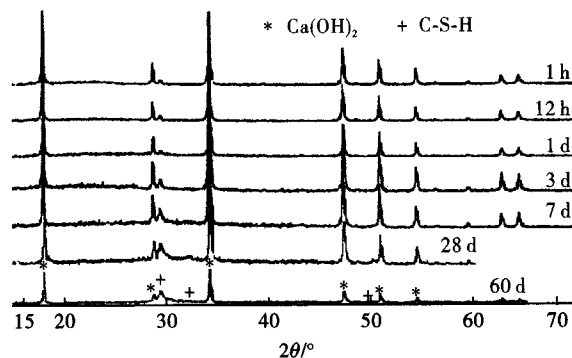

Fig.1b　XRD powder patterns of CH-SF-H₂O system with time

with NS was much quicker than that of CH with SF.

3.2　Degree of interaction of CH with NS or SF

Fig.1a, Fig.2a and Table 5 show the degree of reaction of CH with NS characterized by XRD powder patterns and DSC curves, respectively. During the period from 1 hour to 28 days, the diffraction peak intensity of CH (especially at $2\theta = 18.0$ °, $d = 0.490$ nm) in the paste sample ANS decreased quickly, and the DSC endothermic peak of CH (at 480 ℃) also decreased quickly. At the ages of 1, 3 and 28 days the CH content in the paste sample ANS was 33%, 20% and 13%, respectively, when estimated by DSC. Fig.1b, Fig.2b and Table 5 show the degree of interaction of CH with SF determined by XRD powder patterns and DSC curves. The diffraction peak intensity of CH in paste sample ASF did not decrease until the age of 3 days, and during the period from 3 days to 60 days the intensity decreased slowly. At the ages of 1, 3, 28 and 60 days the CH content was 63%, 60%, 19% and 15%, respectively, when estimated by DSC. The results indicate that the pozzolanic activity of NS was much higher than that of SF.
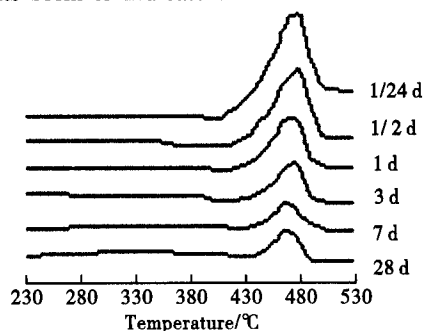

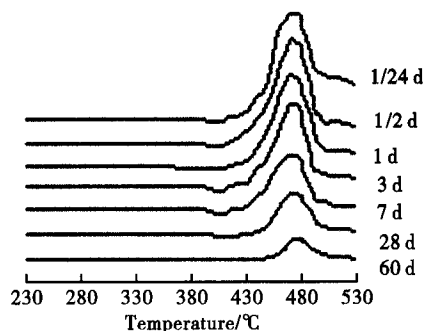Fig.2a　Varation of CH content in the pastes made from CH and NS with time determined by DSC curves

Fig.2b　Varation of CH content in the pastes made from CH and SF with time determined by DSC curves

Table 5   Variation of CH content in the pastes made from CH and NS or SF with time by DSC

Paste sample	CH content/%								
	0 d	1/24 d	1/2 d	1 d	3 d	7 d	28 d	60 d	
ANS	(65)	51	46	33	20	17	13	/	Estimated by DSC
ASF	(65)	65	64	63	60	46	19	15	
ANS	(65)	48	45	39	18	15	6	/	Estimated by QXRD
ASF	(65)	65	65	65	60	55	20	15	

3.3 Hydration products in pastes made from CH and NS or SF

Fig. 1 and Table 6 show hydration products in pastes made from CH and NS or SF. C-S-H (I) gel, one of the main hydrates of ordinary Portland cement, was the main hydrate in samples ANS and ASF, with the data of main diffraction peaks at 0.304, 0.280 and 0.182 nm (Cu Kα radiation)[16]. At the ages of 12 hours and 1day respectively, peaks of C-S-H gel in sample ANS were very weak but could be found, and during the period from 3 days to 28 days the peaks were obvious. But peaks of C-S-H gel in sample ASF had not been found until the age of 7 days, and the peaks were obvious at the ages of 28 days and 60 days. The results appear to indicate that C-S-H gel was formed by the reaction of CH with NS or SF, but the rate of C-S-H gel formation from CH with NS showed a marked increase over that from CH with SF, particularly at early ages.

Table 6   Variation of intensity of C-S-H (I)diffraction peak in the pastes made from CH and NS or SF with time

Paste sample	Diffraction peak intensity of C-S-H (I) ($d = 0.280$ nm)/CPS						
	1/24 d	1/2 d	1 d	3 d	7 d	28 d	60 d
ANS	0	Trace	Trace	323	325	434	
ASF	0	0	0	0	Trace	210	310

3.4 Flexural strength of cement paste incorporated with NS or SF

Table 3 shows the variation of bending strength of cement pastes with a glass plate made from cement and NS or SF with time. At the ages of 7 and 28 days bending strengths of paste sample BNS containing 3% NS were 6.6 MPa and 10.0 MPa, respectively and were 29% and

72%, respectively higher than that of sample BCO, and were 32% and 49%, respectively higher than that of sample BSF. Similarly to the bending strength, compressive strengths of sample BNS were 27% and 28% higher than that of sample BCO, and were 18% and 8% higher than that of sample BSF. The results indicate that the bond strength at the interface between aggregate and hcp incorporated with 3% NS increased obviously, especially at early ages.

3.5 Observation of CH images at the glass-cement paste interface incorporated with NS or SF

SEM images of CH gathered at the glass-cement paste interface with NS or SF added at 28 days are presented in Fig. 3. The CH image at the interface between glass and paste without NS and SF added, namely sample BCO, is shown in Fig. 3a, in which many hexagenal plates of CH crystal with the c-axis were perpendicular to the glass surface. The edges of the hexagonal plates were clear when the crystal size was big, and the size of the biggest CH crystal was up to 10 μm in the SEM image. At the interface of sample BNS the CH image is shown in Fig. 3b, where the big CH plates with the c-axis were also normal to the glass surface. However, the edges of hexagonal plates with eroded phenomenon were unclear when the crystal size was big, and the size of the biggest crystal CH was up to 4 μm in the SEM image. The CH image at the interface of sample BSF is shown in Fig. 3c, in which the big CH plates with the c-axis were also perpendicular to the glass surface. The edges were similar to those in sample BCO when the crystal size was big, and the size of the biggest CH crystal was up to 7 μm.

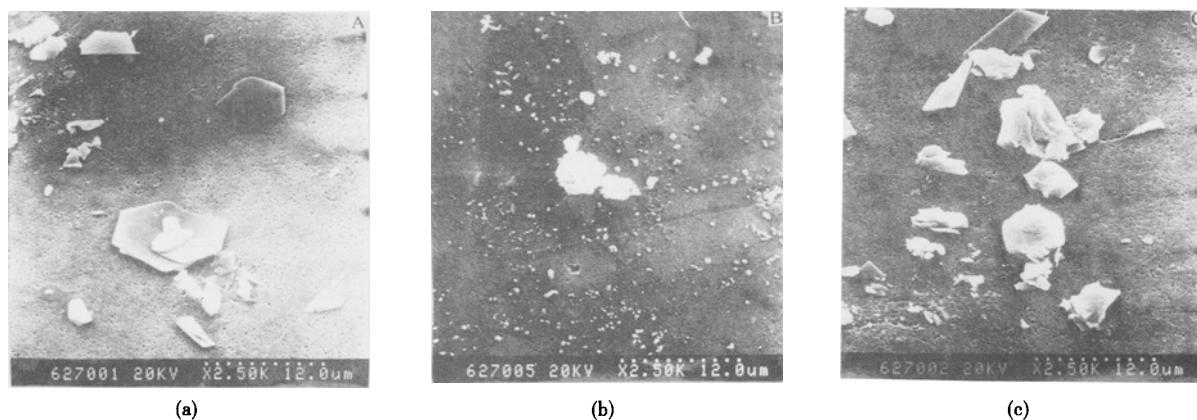The results indicate that NS can reduce the size of CH crystal gathered at interface more effectively than SF.

(a)   (b)   (c)

Fig. 3   SEM images of CH crystal at the interface between aggregate and paste made from cement and nano-SiO$_2$ at 28 days (a) without NS and SF (b) with 3% NS (c) with 3% SF

3.6 Bending strength of concrete incorporated with NS or SF

Table 4 shows the variation of bending strength of concrete blended with NS or SF with time. At the ages of

3, 7 and 28 days bending strengths of the concrete sample CNS containing 3% NS were 10.5 MPa, 13.4 MPa and 17.1 MPa, respectively and were 31%, 48% and 57%, respectively higher than that of sample CCO, and were

6%, 12% and 14%, respectively higher than that of sample CSF. Similarly to the bending strength, compressive strengths of sample CNS were 69.4 MPa, 84.6 MPa and 109.3 MPa, respectively and were 30%, 26% and 22%, respectively higher than that of sample CC0, and were 16%, 11% and 14%, respectively higher than that of sample CSF. The results indicate that the bending strength of concrete blended with 3% NS increased, especially at early ages.

3.7 Improvement of HPC by a small amount of nano-SiO₂

It is a common knowledge that SF has a high pozzolanic activity and is normally the best mineral addition used for concrete up to now. However, the pozzolanic activity of SF at early ages is low according to the aforementioned literatures[8-11]. Judged from our study, the pozzolanic activity of NS is much greater than that of SF. In high performance concrete containing SF, or fly ash or slag, if again with the addition of 2-3% NS, we hope to produce a new high performance concrete with much better properties. Because NS can fill in small pores, NS can act as nucleation sites for cement hydration at early ages and NS has a higher pozzolanic activity than SF, it can improve the microstructure of hardened cement paste better. Because the reaction rate of CH with NS is much greater than that of CH with SF, a small amount of NS can effectively digest CH crystals at the interface between hardened cement paste and aggregate at early ages in high performance concrete. So, using a small amount of NS can enhance the durability and the mechanical properties of cement based materials.

4 Conclusions

a) The compressive strength development of cement paste made from $Ca(OH)_2$ and nano-SiO₂ was incomparably superior to that from $Ca(OH)_2$ and silica fume. The strength of the latter at 14 days was only equal to that of the former at 1 day.

b) The pozzolanic activity of nano-SiO₂ was much greater than that of silica fume. The reaction rate of Ca $(OH)_2$ with nano-SiO₂ and the velocity of C-S-H gel formation from $Ca(OH)_2$ with nano-SiO₂ were much quicker than that of $Ca(OH)_2$ with silica fume.

c) The bond strength at interface between aggregate and hcp, and the bending strength of concrete containing 3% NS increased obviously, especially at early ages. The size of CH crystals gathered at the aggregate-cement paste interface containing 3% NS was reduced more effectively than that containing SF.

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