

Investigation of Cement Matrix Compositions of Nanosilica Blended Concrete

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Abstract

The use of pozzolanic materials in concrete mixtures can enhance the mechanical properties and durability of concrete. By reactions with pozzolanic materials and calcium hydroxide in cement matrix, calcium-silicate-hydrate (C-S-H) increases and calcium hydroxide decreases in cement matrix of concrete. Consequently, the volume of solid materials increases. The pozzolanic particles also fill spaces between clinker grains, thereby resulting in a denser cement matrix and interfacial transition zone between cement matrix and aggregates; this lowers the permeability and increases the compressive strength of concrete. Moreover, the total contents of alkali in concrete are reduced by replacing cements with pozzolanic materials; this prevents cracks due to alkali-aggregate reaction (AAR). In this study, nanosilica is incorporated in cement pastes. The differences of microstructural compositions between the hydrated cements with and without nanosilica are examined using nanoindentation, XRDA and ^{29}Si MAS NMR. The results can be used for a basic research to enhance durability of concrete slab tracks and concrete railway sleepers.

Keywords: Nanosilica, Cement, Durability, Concrete slab track, Concrete railway sleeper

1. Introduction

It is believed that the maintenance cost of concrete slab tracks is lower than that of ballast tracks. To keep this cost benefit for concrete slab tracks, concrete maintains its required strength and serviceability during the expected lifetime of concrete track system. Therefore, durability of concrete should be assessed for the design of concrete slab tracks. As most chemical causes of deterioration are related to transportation of fluids in concrete, permeability of concrete is considered as a reference of concrete durability [1]. Fluids or gases flow through interconnected capillary pores, having a diameter of 120 nm~160 nm, in cement matrix [1]. Therefore, permeability of concrete is directly proportional to the amounts of interconnected capillary

pores in cement matrix of concrete. By adding pozzolanic materials such as fly ash, silica fume and nanosilica, the permeability of concrete can be reduced. Calcium hydroxide, which is a hydration product of cement, is transformed to calcium-silicate-hydrate (C-S-H) by chemical reaction with pozzolanic materials. The capillary pores in cement matrix are then filled and disconnected by the C-S-H. Moreover, the total alkali contents are reduced by replacing cements in concrete mixtures with pozzolanic materials and alkali-aggregate reaction (AAR), which produce cracks in concrete, can be controlled [2].

C-S-H is the major hydration product that makes up to 67% of the hydrated Portland cement paste [3]. Therefore, it plays the most important role for the mechanical properties of hydrated cements. It is believed that most of the time-dependent mechanical properties of hydrated cement are also controlled by the C-S-H [4,5]. Detailed descriptions of cement hydration and chemical compositions of cement hydration products can be found elsewhere [2,6].

In this study, details for analysis methods and in-depth investigation extended from our previous work presented in post KSR2014S paper [7] were described. 1% wt. (weight) and 3% wt. of cements in concrete mixtures are

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replaced by nanosilica. The differences of microstructural compositions between the hydrated cements with 1% wt. and 3% wt. and without nanosilica are examined using nanoindentation, X-ray diffraction analysis (XRDA) and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR).

2. Experimental Study

2.1 Materials

For the neat and nanosilica incorporated Type II [8] ordinary Portland cement (OPC) paste specimens, water to binder ratio (w/b) of 0.45 was used.

2.2 XRDA

X-ray diffraction analysis (XRDA) is a methodology to characterize crystalline materials in cement chemistry [6]. Using XRD spectra, several compositions in hydrated and unhydrated cement paste such as calcium hydroxide, C-S-H, alite and belite can be detected [9-11]. More information exists on XRD observations of cement hydration products [2, 6].

2.3 Nanoindentation

Indentation tests has been used as non-destructive tests for metals for the last 100 years [12]. The precision of the nanoindentation apparatus is achieved by controlling and recording the time-dependent nanoscale displacement of the indenter tip as it changes with electrical capacitance. The indenter tip penetration depth is measured during loading and unloading with a parallel plate capacitor that has sub-nanometer resolution [13]. The most common indenters include the three-sided pyramid (Berkovich) indenter, spherical indenter [14] and the flat-ended (punch) indenter [15]. The Berkovich indenter was successfully used for extracting the mechanical characteristics of individual microstructural phases in the cement paste [16]. Indentation loading and unloading profiles are used to extract the elastic modulus of individual microstructures such as calcium hydroxide, C-S-H and so on.

Analysis of the nanoindentation data to extract the elastic modulus can be performed following the Oliver and Pharr method [17]. This method recognizes the variation of the indent radius with depth. A power function can be fit to top 60% of the unloading curve and the slope of indentation load-depth curve (dP/dh) will be calculated as the derivative of the power fit relationship. The reduced modulus, E_r is calculated as [13,17]

$$E_r = \frac{1}{2\beta} \frac{\sqrt{\pi} dP}{\sqrt{A} dh} \quad (1)$$

where β is a correction factor to account for the non-symmetrical shape of the indenter tip, which is equal to 1.034 for a 3-sided pyramidal (Berkovich) indenter. A is the contact area of the indenter, which is found by knowing the geometry of the indenter tip as a function of the depth, and the measured depth. For a Berkovich indenter tip, A is equal to

$$A = 3\sqrt{3}(h_p \tan \theta)^2 \quad (2)$$

where h_p is the depth of plastic penetration and θ is the angle the edge of the indenter makes with the vertical. As the reduced modulus E_r is for the elastic modulus including the effect of indenter stiffness, the elastic modulus of the indented material E is calculated from the relationship defined as

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i} \quad (3)$$

where E_i and v_i are elastic modulus and Poisson's ratio of the indenter used respectively 1141 GPa and 0.07.

2.4 ^{29}Si MAS NMR

Nuclear magnetic resonance (NMR) experiments have been proven over the years as an efficient method to examine chemical bonds in different materials [18]. For solid state NMR, the magic-angle spinning (MAS) method is applied in order to avoid large peak broadenings caused by several nuclear interactions. NMR has helped in identifying the nanostructure of silicate composites. ^{29}Si MAS NMR has been used to examine the polymerization of a silicate tetrahedron in C-S-H [19-21]. Silicate polymerization represents the number of bonds generated by the silicate tetrahedron. Using statistical deconvolution of NMR spectra, the corresponding fraction of silicate connections from type Q^0 to Q^4 can be identified. The fraction of a silicate tetrahedron having the number of n shared oxygen atoms is expressed as Q^n where n is the number oxygen atoms. Q^0 represents the fraction of the remaining tricalcium silicate (C_3S) and dicalcium silicate (C_2S) in hydrated cement while Q^1 and Q^2 and Q^3 represent the fraction of C-S-H. Q^4 represents the fraction of the remaining silica rich products such as nanosilica, fly ash and silica fume. From the observed fractions of Q^n s, the average degree of C-S-H connectivity d_{sc} is calculated [22] as

$$d_{sc} = \frac{Q^1 + 2Q^2 + 3Q^3}{Q^1 + Q^2 + Q^3} \quad (4)$$

Higher value of d_{sc} represents higher polymerization of C-S-H. Moreover, the degree of hydration h_c of a hydrated

cement paste is calculated [23] for the absence of Q^4 by silica rich products as

$$h_c = 1 - Q^0 \quad (5)$$

The ^{29}Si chemical shifts are respectively referenced relative to tetramethylsilane $\text{Si}(\text{CH}_3)_4$ (TMS) at 0 ppm, using $\text{Si}[(\text{CH}_3)_3]_8\text{Si}_8\text{O}_{20}$ (Q8M8) as a secondary reference (the major peak being at 11.6 ppm relatively to TMS).

2.5 Statistical deconvolution analysis

The frequency density function of nanoindentation and ^{29}Si NMR MAS spectra were analyzed by statistical deconvolution technique [24]. The frequency density function of nanoindentation and NMR spectra are assumed as a convolution function of n normal distributions such as

$$f(x) = \phi \sum_{i=1}^n g_i \frac{1}{\sigma_i \sqrt{2\pi}} \exp\left(\frac{-(x-\mu_i)^2}{2\sigma_i^2}\right) \quad (6)$$

Here, ϕ is scale factor, which can be the number of nanoindentation tests for the frequency density function or the maximum intensity for NMR spectra respectively. n can be considered as the number of different phases characterized by the property x on abscissa. g_i , σ_i and μ_i represent the volume/surface fraction occupied by the i -th phase, the standard deviation and the mean values of the i -th phase respectively. To properly fit the convolution function in Eq. (6) to the experimental results, the R -squared value needs to be maximized (close to 1.0). The mean, standard deviation, and volume fraction values of n phase are all unknowns and are thus determined by the deconvolution analysis.

3. Results and Discussions

A total of 50 indentations were performed for each cement matrix. The fitted frequency density functions of nanoindentation with the experimental observations for the cement matrix with 1% wt. and 3% wt. nanosilica and without nanosilica are shown in Fig. 1.

The resulted volume fractions of ettringite, LD (low density)-C-S-H, HD (high density)-C-S-H and calcium hydroxide are presented in Table 1.

The ratio of volume fractions for C-S-H to calcium hydroxide in cement matrix without nanosilica is calculated as 2.11 and this agrees with other findings [25]. The volume fraction of HD-C-S-H increases from 15% to 25% by replacing 1% wt. of cements with nanosilica, while it increases from 15% to 20% by replacing 3% wt. of cements with nanosilica. However, LD-C-S-H keeps decreasing by replacing more cement with nanosilica. This

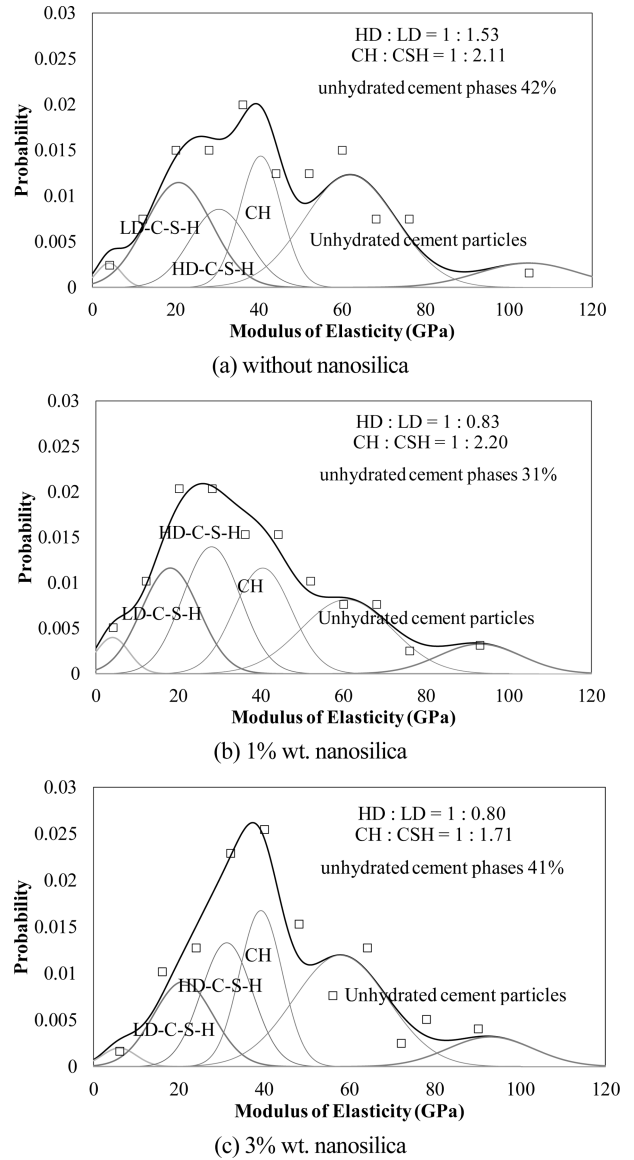


Fig. 1 Frequency density functions with observation of nanoindentation experiments

Table 1 Volume fractions of microstructures determined from nanoindentation experiments

Nanosilica contents	Phase fraction (%)				
	ettringite	LD-C-S-H	HD-C-S-H	Calcium hydroxide	Unhydrated cement particle
0%	2	23	15	18	42
1%	4	20	25	20	31
3%	2	16	20	21	41

observation indicates that there is a threshold replacing contents of cements with nanosilica to enhance durability

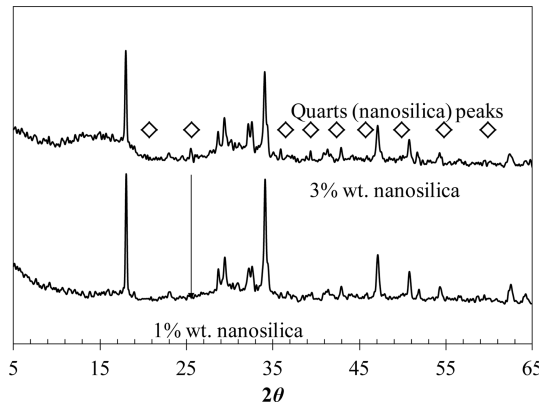


Fig. 2 XRD spectra for the cement matrices incorporated to 1% wt. and 3% wt. nanosilica

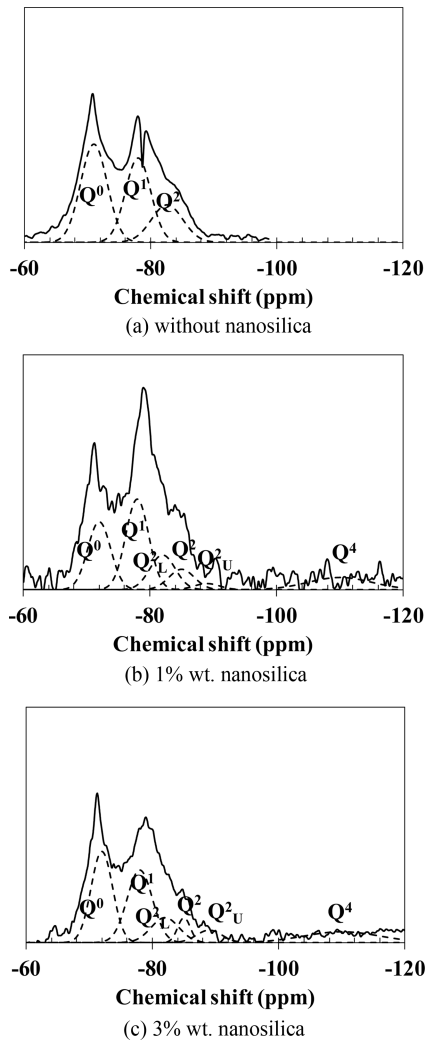


Fig. 3 NMR spectra

of concrete [26,27].

The effects of nanosilica contents on the cement hydra-

Table 2 Q^n intensity determined from ^{29}Si MAS NMR

Nanosilica contents	Q^n (%)				
	Q^0	Q^1	Q^2	Q^3	Q^4
0%	44	36	20	-	-
1%	26	35	26	-	13
3%	33	31	22	-	14

tion and pozzolanic activity were examined using XRDA experiments. The difference in the microstructure of the cement paste according to nanosilica contents 1% wt. and 3% wt. is compared in Fig. 2. By comparing XRD spectra of 1% wt. and 3% wt. nanosilica added hydrated cement matrix, quartz (nanosilica) peaks at 25.7° appear in the XRD spectrum of cement paste incorporating 3% nanosilica while these peaks disappear in cement pastes incorporating 1% nanosilica as shown in Fig. 2. This observation also supports the findings by others [26,27].

The effects of nanosilica on the degree of hydration, and the degree of C-S-H connectivity were examined using the resulting ^{29}Si MAS NMR spectra. The spectra were deconvoluted and the integration results of the Q^n intensities are presented in Table 2. The deconvoluted spectra for hardened cement without and with 1% and 3% nanosilica are shown in Fig. 3.

The Q^4 level of polymerization was shown in hardened cement with 1% and 3% nanosilica and represents the pozzolanic activity. For the effects of nanosilica contents on the degree of hydration of cement, the highest degree of hydration was 61% and occurred with cement paste specimens incorporating 1% nanosilica. For the average degree of connectivity (polymerization), the highest degree of connectivity of 1.43 occurred with cement paste specimens incorporating 1% nanosilica. These observations confirm the aforementioned findings by XRD analysis and nanoindentation about the threshold of nanosilica contents. There is no significant difference in the relative pozzolanic activities (Q^4 intensity) by increasing the nanosilica content from 1% to 3%.

4. Conclusion

The microstructural compositions and the silicate polymerization of the cement pastes without and with 1% and 3% nanosilica hydrated for 7 days were examined using XRDA, ^{29}Si MAS NMR and nanoindentation. The results showed that the optimal contents of nanosilica to enhance the durability and strength of concretes need to be identified. Further research is warranted to correlate these findings to other macroscale strength and durabil-

ity characteristics of hydrated cement paste with and without nanosilica as a basic research to enhance durability of concrete slab tracks and concrete railway sleepers.

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