



Article Characteristics of Ordinary Portland Cement Using the New Colloidal Nano-Silica Mixing Method

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Abstract: This study applies a new method of mixing colloidal nano-silica (CNS). Previous studies have used powdered nano-silica or colloidal nano-silica and applied a binder weight substitution method. In this study, we tried to use ordinary Portland cement (OPC) as a binder and replace CNS with weight of mixing water. CNS was replaced by 10%, 20%, 30%, 40%, and 50% of the mixing water weight. The flow value, setting time, compressive strength, hydration reactant (X-ray diffractometer; XRD), pore structure (mercury intrusion porosimetry; MIP), thermal analysis, and scanning electron microscopy (SEM) analysis were performed. Experimental results show that the new substitution method improves the mechanical and microstructural properties through two effects. One is that the weight substitution of the mixing water shows a homogeneous dispersion effect of the nano-silica particles. The other is the effect of decreasing the w/b ratio when the CNS is substituted because the CNS is more dense than the mixing water. Therefore, we confirmed the applicability of mixing water weight replacement method as a new method of mixing CNS.

Keywords: colloidal nano-silica; mixing water; ordinary Portland cement; mechanical and microstructural properties

1. Introduction

Studies in the field of advanced construction materials, such as the use of nanoparticles as cement admixture, have reported significant improvements in the properties of traditional building products. In previous research, various nanoparticles were mixed with cement, and their performance was evaluated [1–4]. Nanoparticles, such as nanoclay, Al₂O₃, Fe₂O₃, TiO₂, and CaCO₃ were evaluated; however, SiO₂ was the most commonly studied [5–18].

Nano-silica denotes that small particles comprise an amorphous SiO_2 core with a hydroxylated surface, which makes the substance insoluble in water. The size of the particles can vary between 1–100 nm; therefore, they are small enough to remain suspended in a fluid medium without settling. Parameters, such as specific surface area, particle size, and size distribution can be controlled using the synthesis technique [3]. Nano-silica particles have a high surface area to volume ratio that provides high chemical reactivity. They behave as nucleation centers, contributing to the development of the hydration of ordinary Portland cement (OPC) or cementitious materials [19].

The addition of nano-silica into mortar and concrete mixtures accelerates the hydration process, improving the strength and microstructure characteristics of the OPC [8,13,19–25]. The increase in the initial hydration rate caused by the pozzolanic reaction increases the amount of calcium-silicate-hydrate (C-S-H) gel [26–28]. Cement-based materials containing nano-silica particles demonstrate an improved performance due to the combined effects of the filler, nucleation, and pozzolanic reaction [29,30].

Most of the previous research have focused on the powdered nano-silica (PNS) replacement percentages of less than 5% by binder weight [8,9,21,22,31], whereas a few studies have increased this fraction to reach 12% [27]. The binder weight replacement method was used, which displayed a significant decrease in fluidity due to the high specific surface area of the PNS. A large amount of mixing water and/or superplasticizer was required to counteract this effect and ensure sufficient fluidity [19,22,24,32,33]. Therefore, previous studies using PNS and the binder weight replacement method are difficult to apply with a high substitution rate of more than 12% due to the ensuing rapid decrease of fluidity. Some studies have reported the results of binder weight replacement using CNS instead of PNS [7,19,26,28,34]. As a result, the mechanical behavior of OPC with higher percentages of PNS has not been well-reported. A study on the mixing method and mechanical and microstructural characteristics for replacing CNS by 15% or more is still insufficient. Therefore, a new mixing method, the next step will be to study the mechanical and microstructural characteristics of the matrix of high CNS replacement rates.

Therefore, for the development of cement using nano-silica particles and various nano-particles, a mixing method that can apply various substitution ratios is needed. In particular, a method to improve sudden initial fluidity degradation using nano particles is more important. This is important for solving problems such as a reduction in mechanical performance and durability degradation due to rapidly decreased fluidity.

Binder weight replacement of nano-silica reduces the amount of binder. This may also affect the formation of hydration reactants and the pore structure. In addition, the rapid decrease in fluidity due to the mixing of nano-silica forms a dense matrix together with the binder reduction effect caused by the binder replacement method. Therefore, there is a need to consider how to apply the effects of nano-silica without reducing the amount of binder. In addition, it can be expected to be a more effective compounding method if it is considered together with methods to alleviate or improve the problem of abrupt fluidity reduction. The weight change method of mixing water to be applied in this study does not change the binder weight. In addition, because the liquid type of CNS is used, it is possible to replenish a part of the mixed water which is reduced by substitution. The CNS used in this study, rather than powdered nano-silica, is pre-mixed with mixed water, making it easier to stir nano-silica, and the dispersing effect of particles is excellent. Therefore, the new mixing method is expected to remedy the above-mentioned problem of rapid fluidity reduction. We will attempt to apply a higher mixing ratio of nano-silica particles through weight replacement of mixing water. This process can be used as basic research data to investigate the effect of high concentration of nano-silica particles of OPC.

This study examines the mechanical properties of the OPC paste using CNS. The replacement method for the weight of mixing water was used instead of the binder replacement method, which was appropriate to be applied in the PNS. Additionally, the water-binder ratio was assumed to be 0.5 without the addition of superplasticizer.

2. Materials and Methods

2.1. Materials

A commercial-grade CNS was used, which exhibited a mean particle size of 20 nm, a density of 0.0012 g/mm^3 , and an aqueous solution having an alkaline pH of 10. The SiO₂ content in the aqueous solution was 30%, while the viscosity was reported to be not greater than 20 cps at 20 °C. The chemical properties of the OPC that is used in this study are summarized in Table 1, as determined by X-ray fluorescence (XRF) analysis.

Chemical Components (%)							Density	Fineness	L.O.I	
	SiO ₂	Al ₂ O	Fe ₂ O	MgO	CaO	K ₂ O	SO_3	- (g/mm ³)	(m²/kg)	(%)
OPC	20.51	5.27	3.64	2.86	62.58	0.69	2.72	0.00315	330	0.76

Table 1. The chemical properties of ordinary Portlandite cement (OPC).

2.2. Experiments Methods

In this study, a replacement method was developed based on the replacement of mixing water weight rather than binder weight. Mixing CNS with mixing water is an attempt to increase the homogeneous dispersion of nano-silica particles.

The water-to-binder ratio (w/b) of all the paste mixtures was 0.5; further, because a superplasticizer was not used, corrections to w/b were unnecessary. Six OPC mixtures with incremental CNS replacement ratios (0%, 10%, 20%, 30%, 40%, and 50% of the mixing water weight) were prepared by combining CNS with the mixing water that was followed by mechanically stirring prior to paste mixing. Table 2 shows the substitution ratio and water-binder ratio of CNS according to mixing water and the binder weight substitution method. CNS has a higher density than mixing water. Therefore, substitution of CNS for the weight of mixing water reduces the w/b ratio.

	CNS Substitution Ratios			
w/b Ratios of Considering water including CNS	Mixing Water Weight (%)	Binder Weight (%)		
0.5	0	0		
0.485	10	5		
0.47	20	10		
0.45	30	15		
0.44	40	20		
0.425	50	25		

Table 2. Summary of w/b ratios and the mixing ratio of colloidal nano-silica (CNS).

The flow value was measured according to ASTM C230 [35] and the setting time was ASTM C266 [36] when using the Gillmore needle method. Paste mixing was performed by following the procedures described in ASTM C305 [37]. After mixing, the six different paste mixtures were kept in a temperature and humidity control chamber for 24 h at a temperature of 23 ± 2 °C and a relative humidity (RH) of $90 \pm 5\%$. The mold that was formed on the mixtures was then removed, and the mixtures were placed back in the chamber under identical humidity and temperature conditions until the age of measurement was reached. Compressive strengths were measured at 1-, 3-, 7-, and 28-days. The compressive strength of three specimens was measured and the mean value was used.

The compressive strength was measured according to ASTM C109 [38] using a $50 \times 50 \times 50$ mm cube mold. After measuring the compressive strength, the fractured pieces were immersed in acetone for 12 h and were then dried in a vacuum desiccator for 24 h. Thereafter, the samples were pulverized into fine particles and passed through a 7.5 µm sieve; further, the samples were analyzed with an X-ray diffractometer (XRD, Empyrean, PANalytical, Almelo, Netherlands). The purpose of this analysis was to investigate the type and morphology of hydration reaction materials by CNS using XRD analysis. The generator settings are 40 mA and 45 kV. The measurement range is from 5° to 60° (20) and the step size is 0.017° (20). XRD was performed for 1-day and 28-day samples.

Separate specimens comprising small broker or cut pieces were also prepared after 28-days of aging for porosity analysis using mercury intrusion porosimetry (MIP, AutoPore IV 9500, Micromeritics, Norcross, GA, USA). The average contact angle was 130.0 degrees, the Hg surface tension was 485.0 dynes/cm, and the Hg density was 13.5291 g/mL. The microstructures were observed using scanning electron microscopy (SEM, SUPRATM 40, ZEISS, Oberkochen, Germany) after conducting the fracture toughness measurement. Measurements were made using a high vacuum mode using an

accelerating voltage of 15 kV. Further, thermogravimetric (TG) and differential thermal analysis (DTG) were performed on specimens at 28-days of age. Finally, a thermal analyzer (DSC800, Perkin Elmer, MA, USA) was used to evaluate the weight loss associated with water at 30 °C to 800 °C at 20 °C/min in a N₂ gas environment.

3. Results and Discussion

3.1. Flow and Setting Times

The measured flow values of the paste according to the substitution ratio of CNS are shown in Figure 1. The 0% CNS sample without CNS substitution overflows the flow table due to the high w/b ratio. However, from 10% CNS paste, flow rate decreases steeply as the substitution ratio of CNS increases. In particular, the 50% CNS sample showed a low flow value of 127.5 mm. This substitution of CNS promotes the hydration reaction of OPC and reduces the flow. This is similar to the flow characteristics of previous studies using PNS.



Figure 1. Flow values by CNS replacement rate.

In a previous study using most nano-silicas, a superplasticizer was used. This is due to the heterogeneous dispersion due to the high specific surface area of the nano-silica particles and the sudden drop in fluidity. Particularly, in the case of powdered nano-silica, since the fluidity is seriously deteriorated, a lot of experiments using the superplasticizer are performed. This study used CNS with relatively homogeneous dispersibility than PNS. And a high w/b ratio of 0.5 was chosen to exclude the effect of the superplasticizer. However, as shown in Figure 1, the abrupt decrease in fluidity is due to a decrease in the w/b ratio with an increasing CNS replacement ratio.

The results of measuring the setting time according to the Gillmore needle method are shown in Figure 2. As the substitution rate of CNS increased, initial and final setting time decreased. Chithra et al. [19] also showed the setting times of colloidal nano-silica substituted for OPC by 0.5%, 1%, 1.5%, 2%, 2.5%, and 3%. As the CNS replacement rate increases, the setting time decreases. In particular, the reduction of the final setting time is more steep than before. Decreasing the setting time can be thought of as being caused by two reasons in this study. One is the pozzolanic reaction and nuclear effects of nano-silica particles. This is a known effect from previous studies [8,19,21,26,39,40]. The other is the effect of w/b reduction due to the mixing water weight substitution of CNS.



Figure 2. Setting time of the CNS replacement rate.

3.2. Compressive Strength

Figure 3 shows the results of compressive strength measurements according to the ages of the test specimens. As the replacement rate of CNS increased from 0% to 50%, the strength was observed to increase at all the measurement ages in Figure 3a. The 1-day strength increased from 15.04 MPa for 0% CNS to 33.37 MPa for 50% CNS, while the 3-day strength increased from 30.51 MPa for 0% CNS to 50.69 MPa for 10% CNS; the 7-day strength increased from 33.72 to 61.33 MPa, followed by a 28-day increase from 40.48 MPa of 0% CNS to 75.41 MPa of 10% CNS.

Replacement of CNS exhibited a significant effect on the improvement in strength, and the effect was further increased according to the CNS substitution ratio. In previous PNS studies, the strength enhancement effect of nano-silica particles in the early stages of hydration is already known [6,20,22]. In the present study, in which CNS was applied as a weight substitution method for mixing water, the initial strength improvement effect was consistent with previous PNS studies. This is because nano-silica particles promote the hydration of cement and act as a nucleation site in the formation of hydration products [5,20,26,41]. This nucleating effect contributes to the improvement in strength by generating dense hydration products during the early stage of hydration [20,42,43]. In addition to the improvement of the microstructure due to the filler effect, the pozzolanic reaction promotes the hydration of the cement, thereby improving the strength [5,7,44].

Figure 3b shows the compressive strength results of previous studies using mixing water weight substitution method and binder weight substitution method. Said et al. [7] used colloidal nano-silica with mean particle size of 35 nm, 50% SiO₂ contents, and pH of 9.5. Two kinds of binders, OPC and OPC + Fly ash, were used, and the compressive strengths of 3-day and 7-day were measured by adding CNS to each binder (not the substitution method). Both the OPC and OPC + Fly ash binding materials increased in 3-day and 7-day compressive strength as the weight substitution rate of CNS increased to 0%, 6%, and 12%. Chithra et al. [19] used a CNS with a particle size of 5–40 nm, 40%–41.5% SiO₂ contents, and a pH of 10. CNS was replaced by 0.5%, 1%, 1.5%, 2%, 2.5%, and 3% of the OPC and the 3-day, 7-day, and 28-day compressive strengths were measured. Experimental results show that as the concentration of CNS increases from 0% to 2%, the compressive strength increases at all ages. The highest compressive strength occurs at 2% CNS, after which the strength decreases until 3% CNS concentration is reached. Nikravan et al. [45] is the result of compressive strength using CNS with pH 10.23, mean particle size 2.1 nm and the specific gravity 1.21. CNS replaced 0%, 1.5% and 3% of

cement weight. The 1-day, 3-day, 7-day, and 28-day compressive strengths increased with increasing concentrations of CNS.



Figure 3. CNS replacement ratio and compressive strength according to age (**a**) this study, (**b**) compared with previous studies.

In previous studies using CNS, binder mass displacement methods have increased compressive strength as the concentration of CNS increases [7,45]. In other studies, however, there was a specific concentration of CNS that produced the highest compressive strength [19]. The specific CNS concentration with the highest intensity is the point where the nano-silica particles achieve a homogeneous dispersion and the pozzolanic reaction, nucleation effect and filler effect are optimal. However, exceeding the optimal CNS concentration, the compressive strength decreases due to the

drastic loss of fluidity due to uneven dispersion of nano-silica particles and lack of units due to high specific surface area.

Figure 4 shows the relative strength increase ratios for each CNS replacement ratio as compared to the strength of the 0% CNS specimen. As the substitution rate of the CNS increases, the rate of relative strength increase increases. In Figure 4, the highest relative strength growth rate varies with age and CNS substitution rate. The 10% CNS sample had the highest relative intensity increase of 7-day, the 20% CNS sample was 28-day, and the 30% to 50% CNS sample was 1-day. If the CNS substitution rate was less than 20%, it affected the strength of late age from 7-days to 28-days, and the CNS substitution rate from 30% to 50% greatly affected the initial 1-day strength increase rate.



Figure 4. Compression strength increase rate according to the CNS replacement ratio.

In particular, the 1-day relative strength increase rates were 174.5% at a 30% CNS replacement rate, 205.3% at a 40% CNS replacement rate, and 221.8% at a 50% CNS replacement rate. The 1-day intensity increase of the 40% and 50% CNS replacement rate samples is about twice the increase compared to the sample that did not replace the CNS. If the substitution rate of the CNS exceeds 30%, the rate of increase in the daily strength is then sharply improved. The compressive strength results of previous studies using PNS are consistent with reports that nano-silica particles have a significant effect on the initial strength improvement [6,21,22,43,46]. However, after a rapid increase in intensity at 1-day, the rate of increase in strength from 3-days to 28-days decreases significantly. The decrease in strength increase after 1-day is similar to the trend in strength change shown in previous studies using PNS [26]. Therefore, the strength-improving effect of nano-silica particles is known to have the greatest effect at the beginning of hydration within 1-day [28]. As a result, as shown in Figure 4, the strength increase rate of 30% to a 50% CNS substitution rate was highest at 1-day. However, the remaining 3-, 7-, and 28-day strength increase rates were significantly lower than those at 1-day.

Chithra et al. [19] analyzed the compressive strength increase rate of the CNS with 0.5%, 1%, 1.5%, 2%, 2.5% and 3% replacement of the binder mass. As a result, the 1-day strength increase rate is the largest and decreases in the order of 3-days, 7-days, and 28-days. Also, as the substitution rate of CNS increases, the rate of the increase in strength increases. Therefore, the rate of increase of strength is high under the condition of early age and high CNS replacement rate. This is consistent with the tendency of increasing the compressive strength of this study.

Studies have also showed that, if the nano-silica particles are excessively mixed, the compressive strength decreases [27]. Therefore, the excess SiO₂ nanoparticles can leach out without any further

chemical reaction and serve only as filler and can no longer effectively contribute to the compressive strength of binary blended concrete. This situation can also occur due to the fact that the excess of silica can transform the original C-S-H gel (lower Ca/Si ratio) into tobermorite, which exhibits lower strength properties and increases the extent of silicate polymerization [47,48]. It may also be due to the defect in the dispersion of nano-silica particles that causes weak zones [22]. However, the weight replacement method of mixing water used in this study did not result in decreased strength, even with 50% CNS replacement ratio. This is because the dispersion of nano-silica particles is enhanced by liquid CNS.

Compared with the previous studies using PNS, the strength improvement effect was excellent for the CNS ratios that were tested. In addition, the method of this study, which substituted CNS for the weight of mixing water instead of replacing the weight of the existing binder, meant that as the substitution ratio of CNS increased, the strength was improved because there was no weight change of the binder.

In this study, the weight water substitution method of mixing water has the effect of reducing the w/b ratio according to the density difference of mixing water and CNS. Therefore, as the substitution ratio of CNS increased, the decrease of w/b ratio affected the increase of compressive strength.

3.3. Hydration Products

Figure 5 shows the XRD results for the 0% CNS and 50% CNS specimens. Representative reaction products included portlandite, calcite, ettringite, and C-S-H gel. 0% CNS hydration reactants are portlandite, ettringite, C-S-H gel, calcite, quartz, and gypsum. The hydration reactants of 50% CNS were similar to 0% CNS. The 50% CNS samples showed little change in peak size, for portlandite, ettringite, and C-S-H gel, which are major hydration reactants in the 1-day and 28-day periods. The gypsum was observed in the 0% CNS specimen; however, it was not observed in the 50% CNS specimen. The nano-silica particles were not observed in 50% CNS gypsum because gypsum and portlandite were consumed by the formation of ettringite by the pozzolanic reaction [8,20,27,31]. The pozzolanic reaction is further promoted as the number of nano-silica particles increased [49–52]. However, as shown in Figure 5b, there was no change in the size of the C-S-H peak from 1-day to 28-days, even in case of the 50% CNS specimen. This is because the reaction between CNS and OPC occurs mostly before 1-day, which is the initial hydration stage, and then the hydration reaction proceeded very slowly. The reason why the initial hydration reaction is performed rapidly is explained as follows.

It is known that the particles in CNS are characteristically composed of mono-dispersed spherical particles consisting of an amorphous SiO₂ core with a hydroxylated surface, making them small enough to remain suspended in a liquid medium without settling [39,53,54]. Additionally, the nano-silica particles exhibit a high surface energy, which is known to react easily with other substances. Therefore, the pozzolanic reaction of nano-silica particles is improved during the initial hydration reaction step [6]. This affects the reduction of flow value and setting time as the amount of CNS increases, as in the results already mentioned in Figures 1 and 2. In addition, the increase in the relative compressive strength shown in the Figure 4 is also markedly increased in the 1-day period, so that the initial hydration reaction promoting effect can be confirmed.

Figure 5c shows the XRD results after 28-day according to the CNS replacement percentages that ranges from 0% to 50%. The amount of portlandite decreased as CNS increased to 50%. The gypsum has the highest peak at 10% CNS and then decreases to 50% CNS. Thus, gypsum peaks are rarely observed in 50% CNS. Peaks of ettringite from 0% to 50% CNS showed no significant change in size and were almost similar. The decreasing tendency between the ettingite and gypsum peaks is similar. At a substitution rate of less than 20% CNS, nano-silica particles promotes the formation of ettringite and C-S-H gel by the action of pozzolanic reaction and nucleation effects [5–7,20,22,26,34,55]. However, at replacement rates above 20% CNS, nano-silica particles have a major impact on filler effects [5,6]. Thus, there is little change in ettringite or C-S-H peaks in XRD above 20% CNS. The pozzolanic reaction of these nano-silica particles is most apparent during the initial stage of hydration, which reduces the

coagulation time and improves the initial strength [8,19,21,26,39,40]. The effect of these nano-silica particles has already been mentioned in the flowability (Figure 1) and setting time (Figure 2).



Figure 5. Cont.



Figure 5. XRD results after 1-day and 28-day: (**a**) 0% CNS, (**b**) 50% CNS, (**c**) compared XRD with CNS, P: portlandite, E: ettringite, G: gypsum, C: calcite, M: magnesium oxide, S: quartz, A: alite, B: belite, CSH: calcium silicate hydrate.

A previous study related to PNS reported that portlandite decreased rapidly during the first 7-day, which then declined slowly after 7-days. This indicates that most of the pozzolanic reactions occurred during the first 7-days [29]. There is almost no change in the ettringite and C-S-H peaks from 3-days to 28-days, as shown in Figure 5b. However, CNS has a faster hydration reaction effect than PNS.

Previous studies using CNS have shown that the generation of C-S-H gel is accelerated in the initial hydration stage before 12 h [28]. This means that the initial hydration reaction of CNS is much faster than the PNS. In view of the changes in these reactants, CNS accelerates hydration more rapidly as compared to the powdered nano-silica particles in previous studies. Therefore, the substitution of CNS during the initial hydration stage before 1-day reacts with portlandite to cause a rapid pozzolanic reaction. Therefore, portlandite consumption is accelerated during the first 1-day, and the reaction with nano-silica particles gradually slows as the amount of portlandite decreases. The peaks of ettringite and C-S-H did not show a sharp increase, even when the mixing ratio of CNS increased from 0% to 50%. This is because the amount of OPC (the main source of calcium and aluminum) required to form ettringite, and C-S-H does not change. Therefore, most of the portlandite is consumed in the initial hydration stage and the amount of hydration reactant changes little as the age increases.

These results are supported by previous studies that have reported that the hydration acceleration caused by the PNS exhibits a high correlation with sufficient calcium-adsorption ability [39,42]. In the present study, CNS and mixing water weight substitution methods show little change in the hydration reactant peak in XRD analysis after 1-day due to the rapid hydration reaction in the initial hydration stage.

3.4. Pore Structure

Figure 6 shows the pore structure of the specimens with 0%, 30%, and 50% CNS by MIP analysis at 1-day and 28-days. Figure 6a shows the pore structure analysis of the 1-day samples. As the amount of CNS increases, the graph gradually moves to the left. This indicates that the diameter and amount of pores gradually decrease. The 28-day samples in Figure 6b also show pore changes that were similar to that for 1-day. In addition, the MIP results shown in Figure 6 confirm that the CNS mixing method applied in this study has the effect of reducing the diameter and amount of pores.



Figure 6. MIP results, (a) 1-day, (b) 28-day.

Previous researchers have reported that fine nano-silica particles form a dense matrix by filling pores between hydration reactants, thereby improving mechanical performance [5,6]. The results of this study applying the new mixing-method using CNS show the same effect as the previous studies. This is because nano-silica particles reduce the porosity of the matrix through the nucleation effect, pozzolanic reaction, and filler effect in cement hydration reaction. This effect is further enhanced with increasing amounts of nano-silica particles [7,8,21,29–31,43,44,56]. Figure 6 also shows that as the amount of CNS increases, the pore size and amount decrease due to the effects mentioned above.

There are various studies on the mechanism and effect on the change of pore structure of nano-silica particles. Once a small amount of nano-silica particles is homogeneously mixed with the cement paste, the cement hydration products can react with these particles due to their ultra-large surface area and high energy, and a continuous solid mass forms around the nano-silica particles. The nano-silica particles that were embedded in the cement paste can further promote and accelerate the hydration process due to their ultrahigh reactivity, causing the formation of a compact microstructure with uniformly distributed mass [22]. Therefore, the pores in the reaction products are reduced.

However, increases in the amount of trapped air can be expected in PNS that contain pastes in fresh state conditions. Substitution of nano-silica particles has implications for adversely affecting the pores reduction effects. This is due to the fact that nano-silica particles introduce a high gelling tendency, thereby increasing the entrapped air content, as observed through experimental results in Senff et al. [32]. This increase in porosity is caused by the non-uniform dispersion of the nano-silica particles and the abrupt decrease of the fluidity due to the lack of mixing water as the amount of nano-silica particles increases. Therefore, the use of CNS reduces the rapid deterioration of fluidity and induces dispersion of nano-silica particles better than PNS.

Mindess et al. [57] classified the pores of cement paste into large capillary pores (10-0.05 μ m), medium capillary pores (0.05-0.01 μ m), and gel pores (<0.01 μ m). The gel pores represent the intrinsic porosity of C-S-H gel. That is, an increase in gel pores means an increase in C-S-H gel, indicating that a dense hydration matrix has been produced.

Table 3 summarizes the pore size distribution in the 0%, 30%, and 50% CNS specimens in Figure 6. As the amount of CNS increases, the large capillary pores gradually decrease, while the middle capillary pores and the gel pores increase. This is due to the hydration promoting action and the filler effect associated with the pozzolanic reaction of CPC and OPC particles. On the 28-day, large capillary pores decreased and gel pores increased than 1-day. Thus, the CNS forms a dense OPC mixture matrix. These results are consistent with those observed in previous studies using PNS [29,30,43,56] or CNS [7,34].

			CNS C	Contents		
	0%		30%		50%	
	1-Day	28-Day	1-Day	28-Day	1-Day	28-Day
Large capillary pores (10-0.05 μm), (%)	61.51	48.33	67.25	42.72	32.65	26.2
Medium capillary pores (0.05-0.01 μm), (%)	18.55	19.94	11.6	23.51	33.09	32.65
Gel pores (<0.01 µm), (%)	19.91	31.73	21.15	33.77	34.26	41.16
Total porosity, (%)	22.21	19.95	17.79	16.43	17.1	14.11

Table 3. Pore size distribution according to the CNS replacement ratio.

The total porosity also decreased as the amount of CNS increased, with 28-day total porosity being smaller than 1-day. Said et al. [7] reported the total porosity of samples with 0%, 6%, and 12% addition of CNS to OPC and OPC + Fly ash weights. As a result, OPC samples decreased to 10.13%, 6.91%, and 6.44%, and OPC + Fly ash samples decreased to 12.56%, 9.30%, and 8.21%, respectively. The total porosity decreased with increasing amount of CNS, consistent with the results of this study.

3.5. Thermal Analysis

The results of thermal analysis of the 0% CNS and 50% CNS specimens are showed in Figure 7. The TG/DTG results for the 0% CNS specimen are presented in Figure 7a. The weight loss in the temperature range of 50 °C–200 °C [58] or 120 °C–145 °C [2] was due to the water loss of the C-S-H gel. The weight loss observed at 80 °C–130 °C [59] or 110 °C–150 °C [60] was due to the water loss of ettringite. As the age gradually increased to 1-, 3-, and 28-days, weight loss also increased. This indicates that the formation of ettringite and C-S-H gel were increased with the increasing age.

At 100 °C–200 °C [61], the weight loss of gypsum was confirmed. This was supported by the gypsum peak observed in the XRD of Figure 5a. In Figure 5a, the gypsum peak showed a larger peak height at 28-days than at 3-days. In Figure 7a, 28-days shows more weight loss than 3-days. This means that the hydration of OPC particles continues to 28-days.

The weight loss at 400 °C–450 °C [62] is due to the water loss of portlandite. In the 0% CNS specimen, as the age increased, the weight loss rate of portlandite also increased. This indicated that the cement particles were continuously hydrating after the initial hydration stage and that the weight loss at 665 °C–800 °C [63] or 720 °C–760 °C [64] was due to the water loss of calcite.

Figure 7b shows the results of TG/DTG analysis of the 50% CNS specimen. The weight loss of C-S-H gel was observed at 50 °C–200 °C [58] or 120 °C–145 °C [64]. Water loss of ettringite was also observed at 80 °C–130 °C [59] or 110 °C–150 °C [58]. However, the weight loss of gypsum (100 °C–200 °C [61]) observed in Figure 7a did not occur. Unlike the 0% CNS sample, the weight loss rate due to water loss of portlandite observed at 400 °C–450 °C [62] was similar at 1-, 3-, and 28-days. Further, the weight reduction rate of portlandite in the 50% CNS specimen was less than that of the 0% CNS specimen. This indicates that most of the portlandite was consumed in hydration and that pozzolanic reacted during the early stage of hydration (initial 24 h). This is consistent with the observations of Björnström et al. [28] that colloidal nano-silica rapidly forms the C-S-H gel within 12 h. Therefore, the replacement of CNS with the weight of mixing water accelerates the hydration of cement particles, and this phenomenon is mostly completed during the initial 24 h.



Figure 7. Cont.



Figure 7. Thermal analysis: (a) 0% CNS, (b) 50% CNS.

When the CNS is replaced by the mixing water weighing method of this study, portlandite is rapidly consumed before 1-day to form a dense hydration reaction matrix. Therefore, it is a mixing method that can improve the mechanical performance sufficiently compared with the PNS and binder weight substitution method used in the previous research.

3.6. Microstructure

Figure 8 shows the SEM images of the specimens with 0%, 30%, and 50% CNS replacement. The presence of ettringite and C-S-H gel observed in the XRD results of Figure 5 was confirmed.



(a)

Figure 8. Cont.



Figure 8. SEM images at 28-day: (a) 0% CNS, (b) 30% CNS, (c) 50% CNS.

The CNS-substituted specimens exhibit a needle-like shape ettringite in the reaction products [26]. As shown in Figure 8a, this ettringite is also observed inside the pores. However, when the CNS replacement rate increased to 30%, a thin bed ettringite was rarely observed, as shown in Figure 8b. As showed in Figure 8c, little ettringite was observed in 50% CNS specimens. However, the reaction product matrix exhibited a dense state with almost no pores. The increase in the CNS substitution rate promoted the formation of hydration reactants, such as C-S-H gel, by the reaction of nano-silica particles with portlandite. Therefore, the nano-silica particles of CNS improved the microstructure dencification by increasing the reactivity with the cement particles using the filler effect and the pozzolanic reaction [22,31].

Figure 9 shows the Ca/Si and Al/Si ratios by performing energy dispersive spectroscopy (EDS) analysis on the hydration products that are exhibited in Figure 8. The Ca/Si ratio of the reaction product C-S-H gel was 2.76, 2.31, and 1.68 in the 0%, 30%, and 50% CNS specimens, respectively. As the substitution ratio of CNS increased, the nano-silica particles increased, and the Si of C-S-H gel also increased. As a result, the Ca/Si ratio of the reactants decreased. Previous studies with PNS have shown that the Ca/Si ratio decreases with increasing nano-silica concentrations [21,29,34]. Furthermore, in the previous study, the increase in the amount of nano-silica increases the Al/Ca ratio of the hydration

reactant [27] and the tendency of increasing the Al/Ca ratio shown in Figure 9 is similar. The method of substituting CNS for the weight of mixing water in this study showed that the Ca/Si and Al/Ca ratios of the hydration reactants were similar to those of the previous studies using PNS or CNS.



Figure 9. Atomic ratios of the hydration products.

4. Conclusions

The experimental data that was evaluated as a part of this study led to the following conclusions. As the substitution rate of colloidal nano-silica (CNS) increased, flow value and setting time decreased. Also, the compressive strength increased at all measurement ages. Especially, the pore structure increased the amount of gel pores and affected the increase of large capillary pore. This tendency was clearly evident at a CNS replacement rate of 50%. CNS promoted the hydration of cement and affected the ettringite, calcium-silicate-hydrate (C-S-H), gypsum and portlandite. In particular, portlandite showed a tendency to decrease as the substitution rate of CNS increased. Through the thermal analysis (DT/DTG), it was confirmed that the amount of ettringite and C-S-H gel was increased and the portlandite was changed as the amount of CNS was increased. The SEM showed a long needle type ettringite and a dense hydration reactant. The EDS analysis showed a decreasing tendency of the Ca/Si ratio.

The effects of CNS mixing water weight replacement method applied in this study are summarized as being caused by two main reasons. One is that the substitution of the CNS with the weight of the mixing water promotes the homogeneous dispersion effect of the nano-silica particles, promoting the pozzolanic reaction, the nucleation effect, and the filler effect. The other is the reduction effect of w/b caused by replacing the dense CNS than the mixing water. This results in a decrease in w/b by reducing only the mixing water without changing the amount of binder. As a result, the CNS was able to replace up to 50% of the mixing water. This substitution rate was at a permissible level at up to 25% of the binder weight.

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Abbreviation

CNS	colloidal nano-silica
OPC	ordinary Portland cement
PNS	powdered nano-silica
XRD	X-ray diffractometer
MIP	mercury intrusion porosimetry
SEM	scanning electron microscopy
TG/DTG	thermogravimetric/ differential thermal analysis
C-S-H	calcium-silicate-hydrate
EDS	energy dispersive spectroscopy

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