Activation of fly ash through nanomodification

Shiho Kawashima, Pengkun Hou, Kejin Wang, David J. Corr, and Surendra P. Shah

Synopsis: Due to the high carbon emissions that result from cement production, it is desirable to limit the cement content of concrete to make it a more sustainable material. This is possible through substantial replacement of cement with supplementary materials, such as fly ash. The positive effects of this approach are twofold. First, reducing the cement content of concrete will reduce its carbon footprint. Second, fly ash is a coal combustion by-product, so essentially a waste material, which must be stored in landfills and enclosures if unused. Therefore, the productive use of fly ash by incorporating it into building materials at high volumes can help alleviate a waste storage issue. This paper is a summary of studies performed at the Center for Advanced Cement-Based Materials - Northwestern University, in collaboration with Iowa State University, relating to the activation of fly ash through nanomodification. Through seeding effects and increased reactivity, nanoparticles can accelerate cement hydration and subsequently the production of calcium hydroxide (CH), which can help activate the pozzolanic reaction of fly ash particles. Two types of nanoparticles are discussed in this summary paper: silica (SiO_2) and calcium carbonate ($CaCO_3$). The study on $CaCO_3$ nanoparticles addresses the issue of dispersion, which is critical for nanomaterials, and the resultant effects on the hardening and early-age properties of fly ash-cement pastes. And the study on nano SiO_2 focuses on determining the mechanisms underlying the effect of the pozzolanic nanoparticle on the early-age and long-term compressive strength gain of fly ash-cement mortars.

Keywords: fly ash; nanoparticles; nanosilica; calcium carbonate; pozzolanic, microstructure; dispersion

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INTRODUCTION

Given that cement production is high in carbon emissions and that concrete is so widely utilized in construction, it is necessary to make concrete a greener infrastructural material. This is possible through substantial replacement of cement with supplementary cementitious materials, such as fly ash. The positive effects of this approach are twofold. First, reducing the cement content of concrete will reduce its carbon footprint. Second, fly ash is a coal combustion by-product, so essentially a waste material, which must be stored in landfills and enclosures if unused. Therefore, the productive use of fly ash by incorporating it into building materials at high volumes can help alleviate a waste storage issue. Although fly ash can introduce a number of beneficial rheological and long-term mechanical properties to concrete, it has effects on the early-age properties that are undesirable from a constructability standpoint. Due to its pozzolanic nature, at higher replacement levels fly ash can lead to significantly lower rate of hydration, slowed setting, and low early-age compressive strength gain.

In order to facilitate the use of fly ash, it is necessary to develop strategies to produce fly ash-cement concrete that still exhibits properties comparable to cement concrete. Numerous studies have focused their efforts on activating fly ash to improve the early-age properties, including mechanical and chemical methods (Pay· et al. 1997; Fan et al. 1999; Qian et al. 2001; Goñi et al. 2003; Wang et al. 2004; Kumar et al. 2007). In the studies presented in this summary paper, the approach of nanomodification is explored. The use of nanoparticles can introduce a number of effects, such as seeding and increased reactivity, due to their fine size and corresponding high specific surface area. Therefore nanoparticles can accelerate cement hydration and subsequently the production of calcium hydroxide (CH), which can help activate the pozzolanic reaction of fly ash particles. This summary paper will highlight the results of two studies performed at Northwestern University's Center for Advanced Cement-based Materials, in partnership with Iowa State University, on calcium carbonate ($CaCO_3$) nanoparticles and nanosilica (nanoSiO_2). The study on $CaCO_3$ nanoparticles addresses the issue of dispersion, which is critical for nanomaterials, and the resultant effects on the early-age properties of fly ash-cement pastes. And the study on nanoSiO_2 focuses on determining the mechanisms underlying the effect of the pozzolanic nanoparticle on the early-age and long-term compressive strength gain of fly ash-cement mortars.

CALCIUM CARBONATE NANOPARTICLES

$CaCO_3$, or limestone, powders have been found to accelerate early-age hydration, provide nucleation sites for calcium silicate hydrate (C-S-H), and produce additional hydration products (Péra et al. 1999; Heikal et al. 2000; Irassar et al. 2000; Kakali et al. 2000; Bonavetti et al. 2001). And a few studies have also demonstrated the potential of $CaCO_3$ nanoparticles in offsetting the retarding effects of fly ash on the early-age properties (Sato and Beaudoin 2011; Bentz et al. 2012; Gurney et al. 2013). With the use of any additive, dispersion within the cement matrix is important to achieve and it becomes increasingly more difficult with decreasing particle size. To improve the early-age properties of fly ash-cement systems with nanoparticles, it is necessary to achieve sufficient dispersion. In this study, the influence of mechanically and chemically dispersed $CaCO_3$ nanoparticles on the setting behavior and early-age compressive strength gain of fly ash-cement pastes was investigated. The degree of dispersion of $CaCO_3$ in aqueous suspension was quantitatively measured through spectrophotometry.

Experimental methods and materials

Materials – Type I Portland cement and tap water were used in all mixes, with a Class F fly ash being used in select mixes. The specific gravity of the cement and fly ash were 3.15 and 2.51 g/cm^3, respectively. The chemical composition is presented in Table 1 and particle size distribution is presented in Figure 1. The $CaCO_3$ nanoparticles were in dry powder form and had a particle size range of 15 – 40 nm (0.59 – 1.58 μin) according to their manufacturer.

In this referred to study, a number of surfactants were tested to determine their suitability for dispersing and stabilizing $CaCO_3$ nanoparticles in aqueous solution. These surfactants included naphthalene- and polycarboxylate-based superplasticizers, anionic, amphiphilic surfactants, and nonionic, amphiphilic block copolymers. The surfactant discussed in this summary paper will be a polycarboxylate-based superplasticizer (PC).

Figure 2a shows a scanning electron microscopy (SEM) image of $CaCO_3$ nanoparticles treated with PC that were stirred in water. It is apparent that they were aggregated to the micron level, exceeding 20 μm (787 μin) in size. Therefore, it was necessary to mechanically break up the aggregates through sonication. Both horn and bath sonication was implemented, depending on the batch size necessary. Dry nanoparticles and surfactant were added to the water, then sonicated at a set amplitude and duration to produce the suspension. Figure 2b shows how sonication aids in dispersion. Whereas large aggregates were present in the mechanically stirred suspension (Figure 2a), none were present in the sonicated suspension (Figure 2b).

All paste samples had a water-to-binder (w/b) ratio of 0.35 and were prepared in a small upright mixer. Cement was replaced with fly ash on a mass basis. When nano$CaCO_3$ was used, it was added as a suspension, which contained part or all of the mixing water, to the dry ingredients.

Table 1 – Chemical composition of cement and fly ash.

Materials	Type I Cement	Type F Fly Ash
SiO_2	20.2	46
Al_2O_3	4.7	17.8
Fe_2O_3	3.3	18.2
SO_3	3.3	2.59
CaO	62.9	8.4
MgO	2.7	0.95
Na_2O	/	0.59
K_2O	/	2.16
LOI	1.1	1.49
Total	98.2	98.2

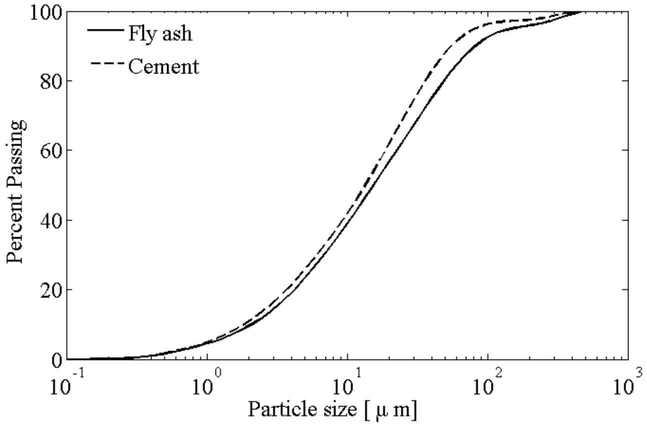
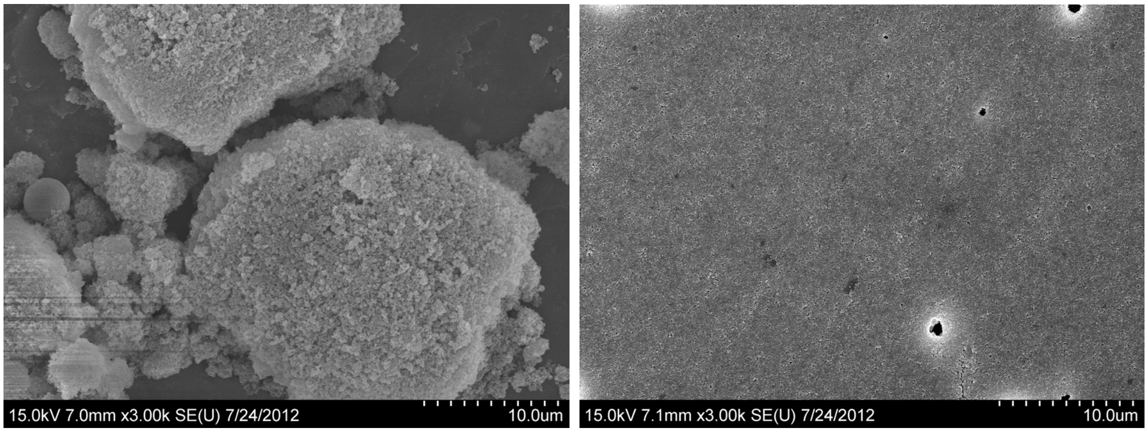


Figure 1 – Particle size distribution of cement and fly ash.



a b

Figure 2 – SEM image, approximately 40 μm x 30 μm (1575 μin x 1180 μin), of PC-treated nano$CaCO_3$ that were a) mechanically stirred in water and b) bath sonicated (Kawashima 2012).

Methods – To obtain a quantitative measure of dispersion, the absorbance spectra of centrifuged nano$CaCO_3$ aqueous suspensions were measured by a spectrophotometer. It is expected that nanoparticles that are dispersed will remain in suspension, while any aggregated particles will settle to the bottom. By recording the decrease in optical density of samples before and after centrifugation, it was possible to deduce the extent of sedimentation, which is an indicator of the quality of dispersion. Absorbance spectra readings were taken between wavelengths 380 and 800 nm (15 and 31 μin) for each sample and the absorbance at 550 nm (31 μin) was compared between samples. The details of the method can be found elsewhere (Kawashima 2012). The absorbance spectra were measured for the supernatant of nanoCaCO$_3$ suspensions after centrifugation and suspensions obtained immediately after sonication. The latter served as a reference point, at which the majority of nanoparticles were expected to be suspended.

Setting times of pastes were measured using the Vicat needle test, based on ASTM standard C191-08. Compressive strengths of 50 mm (2 in) cube paste samples were measured at 1, 3, and 7 d in accordance to ASTM standard C109/C109M-08.

Results

Dispersion – The influence of surfactant type and dosage, and sonication amplitude and duration on dispersion were evaluated. Here, the results of CaCO$_3$ nanoparticles treated with different concentrations of PC are presented. Sedimentation is defined by the following expression:

$$100\% - \frac{Abs_C}{Abs_{t=0}} \times 100\%$$

where Abs$_{t=0}$ was the measured absorbance at 500 nm (31 μin) before centrifugation and Abs$_C$ was the corresponding absorbance after centrifugation. The results of sedimentation are shown in Table 2 for PC-treated CaCO$_3$ nanoparticle suspensions. All suspensions had a concentration of 0.02 % nanoCaCO$_3$ by mass of water and were horn sonicated at 40 % amplitude for three hours. The concentration of nanoCaCO$_3$ was selected to yield the desired mix proportion of cement paste samples for performance testing. The results show that at 7% PC content by mass of nanoCaCO$_3$, almost all the particles settle, indicating poor dispersion. However, at 17% PC, dispersion is improved. And this also marked a threshold value, from which further increase in PC content did not improve dispersion. The PC content of the paste mixes in the following tests was selected based on these results.

Table 2 – Sedimentation of CaCO$_3$ suspensions that were horn sonicated for 3 hours at 40% amplitude. Effect of PC content.

PC content (% by mass of nanoCaCO$_3$)	Sedimentation (%)
7	99.9
17	92.3
33	92.1

Setting – The setting time of plain cement pastes were compared against pastes with 30% cement replacement with fly ash (FA), and 1% nanoCaCO$_3$ addition (1nC). The nanoCaCO$_3$ suspensions were treated with 17% PC by mass of nanoCaCO$_3$, based on the preceding dispersion results, and prepared either by horn sonication or mechanical stirring, each for 3 hours. The latter is a much milder method than sonication. This allowed for the effect of nanoCaCO$_3$ and method of dispersion to be observed. The equivalent PC dosage was added to all mixes.

The results are shown in Figure 3. It is apparent that the addition of nanoCaCO$_3$, both stirred and sonicated, accelerated setting of the fly ash-cement paste. Further, sonication enhanced the accelerating effect, where it offset the delay in initial and final setting caused by the fly ash by approximately 75%. This can be attributed to improved dispersion, which likely gave rise to a seeding effect to accelerate percolation (setting). Even at relatively low additions of 1%, nanoCaCO$_3$ can significantly shorten setting, where its effectiveness can increase with dispersion.

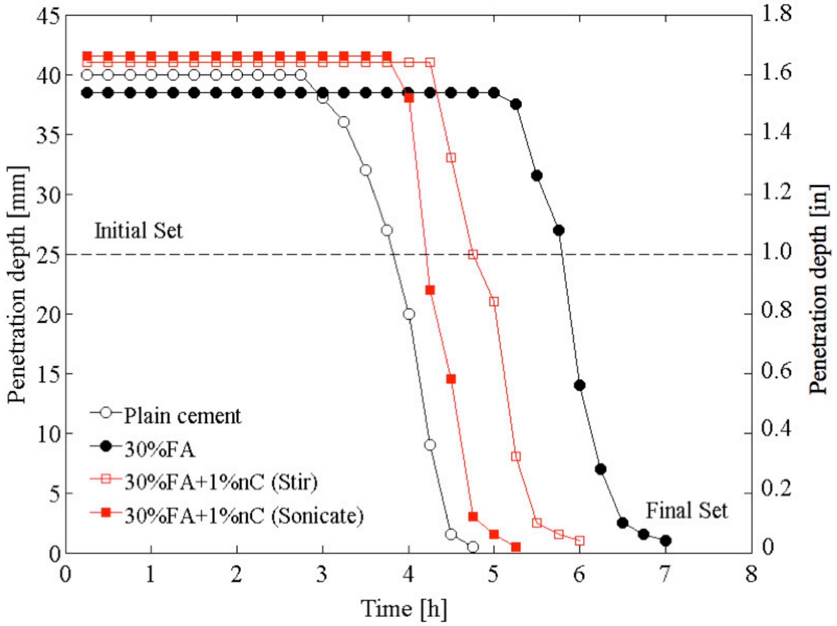


Figure 3 – Setting time of plain cement paste compared to 30% fly ash-cement paste (30%FA) with 1% nano$CaCO_3$ addition (30%FA+1%nC), where nano$CaCO_3$ was either stirred or sonicated in suspension (Kawashima 2012).

Early-age compressive strength gain – The 1, 3, and 7 d compressive strength gain of 30% fly ash-cement pastes with 0, 1, 2.5 and 5% addition of nano$CaCO_3$ by mass of binder were compared. All suspensions were prepared by bath sonication of mixing water, nano$CaCO_3$ and PC for 6 hours. The mixture proportions are given in Table 3 and the results are shown in Figure 4. By 7 d, the nano$CaCO_3$ improved strength at all additions, where 2.5% led to the most enhanced effect with 20% increase compared to the control (0%nC). This can be tied to seeding and/or filler effects, of which the latter would reduce the porosity of the samples. However, 5% addition led to the smallest increase in strength at 7 d and even a slightly detrimental effect at 1 d. This can be attributed to issues of dispersion.

Recalling back to the results of the dispersion tests through photospectroscopy, Table 2, sedimentation at PC additions of 17 and 33% by mass of nano$CaCO_3$ were lower than at 7%, indicating improved dispersion at the higher PC addition levels. Looking at the PC content as % by mass of nano$CaCO_3$ (last column of Table 3), 5%nC only contained 7% PC. Since PC is a dispersant, the addition level was limited by the rheology of the paste sample, where excess amounts would have resulted in segregation. The lower rate of strength gain of 5%nC compared to both 1%nC and 2.5%nC, thereby, can be tied to issues of dispersion due to the insufficient amount of PC, limited by paste mix design, to treat the particles. Also, dispersion becomes increasingly more difficult at higher concentrations. Both of these factors explain the apparent threshold value that exists for nano$CaCO_3$ dosage in the compressive strength results.

Table 3 – Mix composition of paste samples for compressive strength testing.

Mix	Cement, g (lb)	Fly ash, g (lb)	Water, g (lb)	Nano$CaCO_3$, g (lb)	PC	
					g (lb)	% by mass of nC
0%nC	525 (1.16)	225 (0.50)	262.5 (0.58)	0	2.5 (0.0055)	--
1%nC				7.5 (0.017)	2.5 (0.0055)	33
2.5%nC				18.8 (0.041)	3.1 (0.0068)	17
5%nC				37.5 (0.083)	3.1 (0.0068)	7

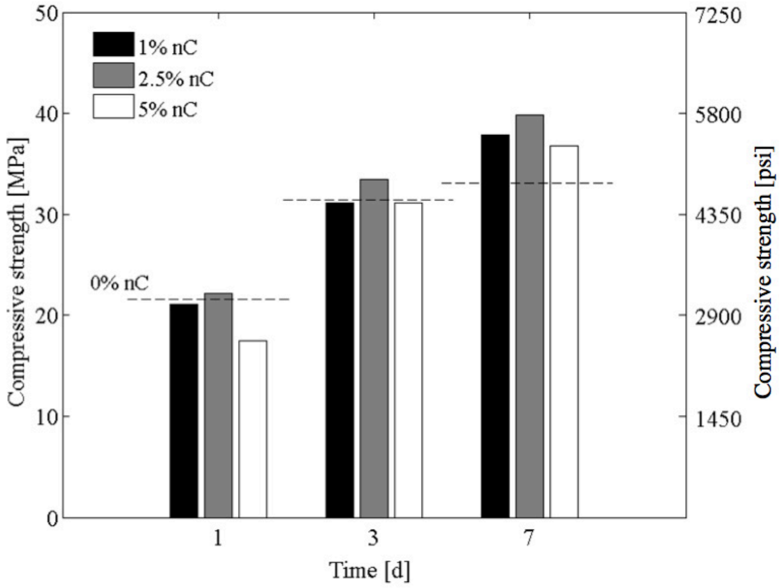


Figure 4 – Compressive strength results of fly ash-cement pastes with different nanoCaCO$_3$ (nC) additions compared to the control (0%nC), indicated by the dotted line. All paste samples had 30% fly ash replacement of cement (Kawashima 2012).

NANOSILICA

Numerous studies have demonstrated that nanosilica can accelerate rate of hydration of cementitious materials through seeding effects and increased pozzolanic reactivity (Björnström et al. 2004; Shih et al. 2006; Thomas et al. 2009; Gundogdu et al. 2010). Therefore, nanosilica is a good candidate to improve the hardening and early-age mechanical properties of fly ash-cement systems. However, it is important to know the effect of nanosilica on later-age strength gain, which has not been thoroughly investigated. In the study discussed here, an in-depth investigation on the mechanisms underlying the effect of nanosilica on the early-age and long-term strength gain of fly ash-cement systems was performed.

Experimental methods and materials

Type I Portland cement and tap water were used in all samples, with Class F fly ash being used in select mixes. Pastes had a w/b ratio of 0.4; and mortars had a w/b ratio of 0.5 and sand-to-binder ratio of 3. The nanosilica came in colloidal form; therefore the issue of dispersion was not investigated. The colloidal nanosilica (CNS) had an average particle size between 10 nm (0.39 µin) and 20 nm (.088 µin).

Compressive strength of 50 mm (2 in) mortar samples were measured in accordance to ASTM standard C109/C109M-08. Thermogravimetric analysis (TGA) was implemented to monitor CH content – the weight loss between 400°C (752°F) and 510°C (950°F) was considered to be the decomposition of CH. And SEM with energy dispersive spectroscopy (EDS) was performed to analyze the morphology and elemental composition of paste samples.

Results

Compressive strength gain – The compressive strength of mortars with 40% replacement of cement with fly ash and 0, 2.5 or 5% nanosilica addition by mass of binder were compared. The results are shown in Figure 5. At early age (7 d), nanosilica increased compressive strength, where strength increased with addition level. This agrees with the results of most studies, and can be attributed to the seeding effect and increased pozzolanic reactivity of the CNS. However, at 90 d, there is little measurable effect at 2.5% CNS addition and a slight reduction in strength at 5%. Therefore the results indicate that the nanosilica enhanced the early-age strength but led to a reduction in rate of strength gain over time, where the reduction was greater at higher additions, in the tested fly ash-cement systems. To explain this, the CH content and SEM-EDS results will be discussed.

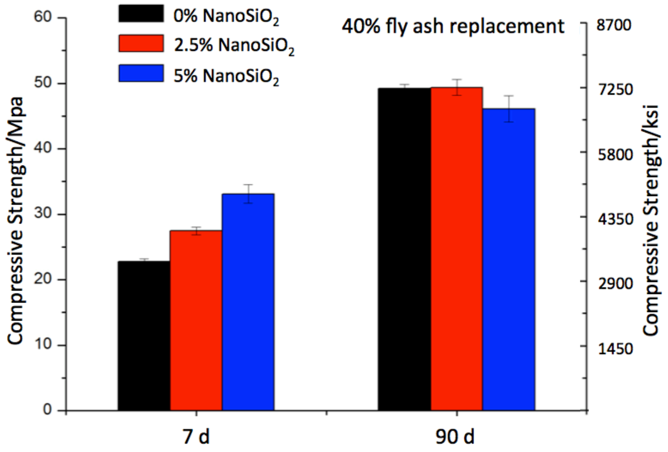
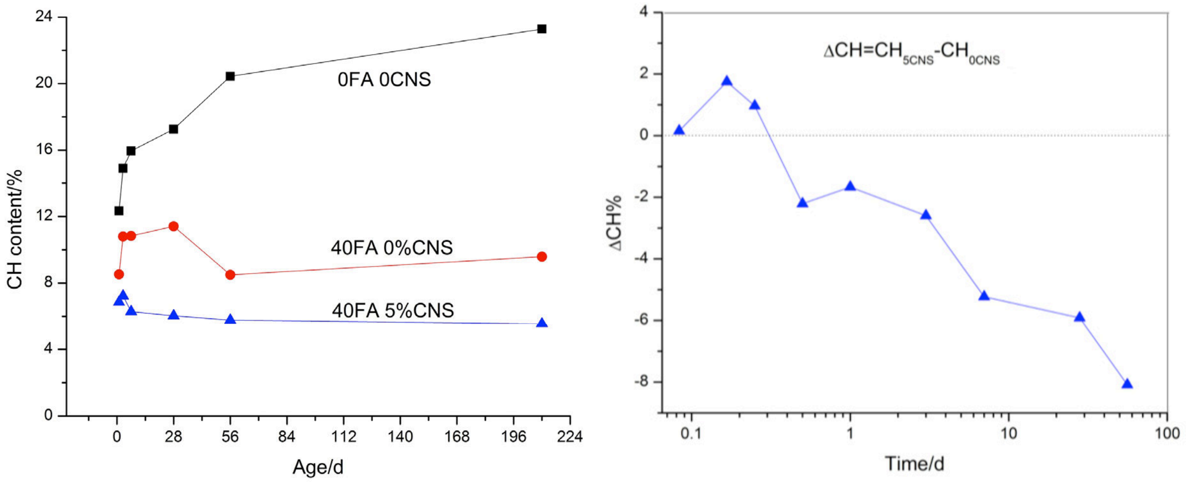


Figure 5 – Compressive strength gain of 40% fly ash-cement mortars with different CNS additions (Hou et al. 2012).

<u>TGA</u> – In a nanosilica-modified fly ash-cement system, both nanosilica and fly ash participate in pozzolanic reactions. Therefore, they will essentially be in direct competition with each other for CH. To observe this, the CH content over time of 40% fly ash-cement pastes with and without a 5% CNS addition were compared against that of plain cement paste. The results are shown in Figure 6a. As expected, 40% replacement of cement with fly ash (40FA 0%CNS) resulted in a substantial decrease in CH compared to the plain cement paste (0FA 0%CNS) due to reduction in cement hydration. 40FA 0%CNS exhibited an increase in CH early on, up to 28 d, but was followed by a decrease by 56 d, which can be attributed to CH consumption by fly ash. With the addition of 5% CNS (40FA 5%CNS), the overall CH content decreased even further and there was no initial increase. This can be attributed to the CH consumption by the CNS, which occurs at a higher rate than fly ash due to its increased reactivity (smaller particle size). This could also be a contributing factor for the reduction in rate of strength gain of the CNS-modified fly ash-cement mortars presented in the preceding section – the higher rate of CH consumption by CNS left less CH for the fly ash to consume to sustain long-term strength gain that is typically characteristic of fly ash-cement systems.

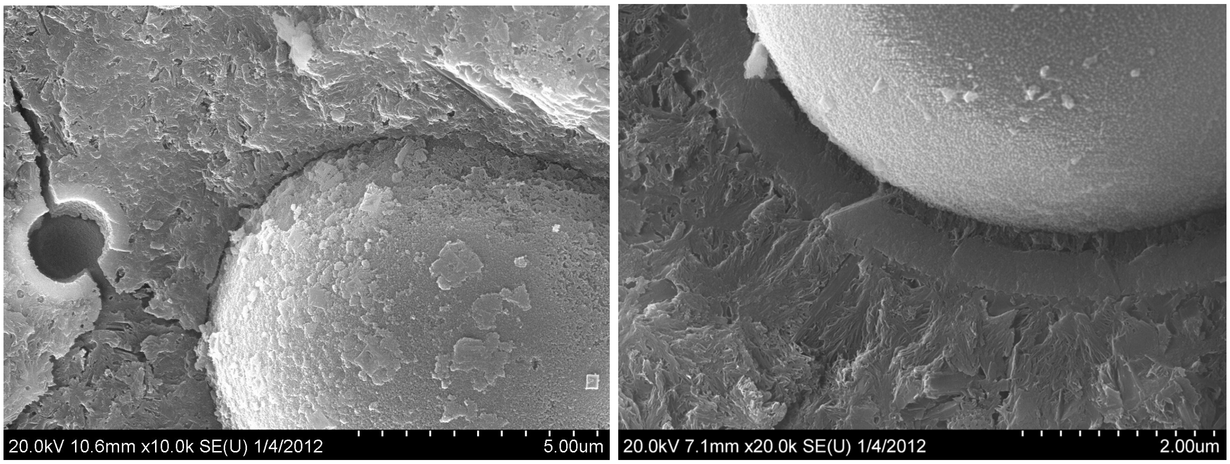
Figure 6b shows the difference in CH content between cement pastes with 5% and 0% CNS in a logarithmic scale to capture the CH content very early on, within 24 h. There is an initial spike that is apparent within the first few hours, which indicates that the 5% CNS addition led to accelerated rate of cement hydration. This can be tied to the seeding effect. Then the CH content drops dramatically – that can be attributed to the pozzolanic reactivity of the CNS. Both of these phenomena explain the increase in early-age compressive strength (7 d) measured in mechanical testing.



a) b)

Figure 6 – TGA results: a) CH content of plain cement paste (0FA 0CNS) and 40% fly ash-cement paste (40FA) with 0% and 5% CNS (Hou et al. 2013) and b) difference in CH content between cement pastes with 5% CNS and 0% CNS additions (Hou et al. 2013).

SEM-EDS – The compressive strength gain of the fly ash-cement mortars (Figure 5) suggest that the hydration mechanisms of nanosilica-modified systems may be different from those of control pastes. Figure 7 presents SEM images of the microstructure of 7 month old fly ash-cement pastes with and without CNS. There was an apparent coating around the fly ash in the sample with CNS (Figure 7b) that was not present in the control paste (Figure 7a). EDS results at 15 different areas of the compacted coating structure revealed an average Ca/Si ratio of 1.38, which was smaller than that of the adjacent C-S-H gel of 1.66. It has been reported that C-S-H gel with a low Ca/Si ratio is less permeable (Garrault and Nonat 2001). And in other work, nanosilica hydration gel has been observed to seal off C_3S particles from the pore solution and stop hydration (Thomas, Jennings et al. 2009). Thus, it was deduced that the outer layer of compacted hydrates, which was formed by the pozzolanic reaction of nanosilica and CH, hindered ion diffusion and thus hindered fly ash hydration at later ages. This can, thereby, partially explain the reduction in rate of strength gain exhibited by the nanosilica-modified fly ash-cement mortars.



a) b)

Figure 7 – SEM images of 7 month old fly ash-cement samples with (a) and without (b) CNS (Hou, Wang et al. 2012).

CONCLUSIONS

This was a summary paper that discussed two studies pertaining to the use of nanoparticles to facilitate the replacement of cement with fly ash to lead to a greener infrastructural material. It was demonstrated in each of these studies that nanoparticles, such as $CaCO_3$ and SiO_2, can help to offset the retarding effects fly ash has on the hardening and early-age compressive strength by contributing to seeding effects and increased reactivity. The effect of nano$CaCO_3$ was enhanced through dispersing the particles in aqueous solution through chemical and mechanical methods. And the results of mechanical testing agreed well with the dispersion results obtained through photospectroscopy. It may be possible to further enhance dispersion by tailoring the architecture of the polycarboxylate-based superplasticizer (i.e. alter the number of repeatable units in the anionic backbone and length of side chains) for $CaCO_3$ nanoparticles, which can be the topic of future work. Also, although early-age properties were the focus of the present work, later-age strength development should be investigated to determine the long-term effects of $CaCO_3$ nanoparticles. The mechanisms underlying the effect of nanosilica on fly-ash cement systems were investigated. Increase in early-age compressive strength was attributed to the seeding effect and high rate of CH consumption by the nanosilica, while the decrease in rate of strength gain over time was attributed to a compact coating of calcium silicate hydrate gel that forms around fly ash particles and hinders their subsequent ability to participate in pozzolanic reactions.

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