

Scientific paper

Effect of Nano-CaCO₃ on Compressive Strength Development of High Volume Fly Ash Mortars and Concretes

Steve W. M. Supit¹ and Faiz U. A. Shaikh²

Received 20 March 2014, accepted 31 May 2014

doi:10.3151/jact.12.178

Abstract

This paper presents the experimental results on the effect of nano-CaCO₃ on compressive strength development of mortars and concretes containing high volume fly ash (HVFA). The effect of various nano-CaCO₃ contents such as 1, 2, 3 and 4% (wt.%) as partial replacement of cement on the compressive strength of mortars are evaluated in the first part. The nano-CaCO₃ content which exhibited the highest compressive strength above is used in high volume fly ash mortars and concretes containing 40% and 60% class F fly ash. The results show that among four different nano-CaCO₃ contents, the addition of 1% nano-CaCO₃ increased the compressive strength of mortars and concretes. The addition of 1% nano-CaCO₃ also increases the early age and 28 days compressive strengths of HVFA mortars and concretes. The X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis results also support the above findings.

1. Introduction

Currently, supplementary cementitious materials (SCMs) are being increasingly used in concrete around the world to reduce the amount of cement and improve its properties. The commonly used SCMs such as, fly ash, silica fume, metakaolin and slag are widely used due to their availability and significant contribution in improving the concrete properties. In the context of sustainability, the replacement of cement by SCMs in concrete is employed to produce environmentally friendly “green concrete” at low cost.

Fly ash acts as pozzolan that reacts with Calcium Hydroxide (CH) due to the presence of amorphous SiO₂ and Al₂O₃ and forms additional Calcium Silicate Hydrate (CSH) gel. This pozzolanic reaction improves the properties of concrete and mortar. However, the use of fly ash as partial replacement of cement in concrete is limited to around 15-20% by mass of cement which is not adequate to make the concrete more sustainable. Therefore, researches have investigated the use of high volume fly ash as partial replacement of cement in concrete that has enormous impact in reducing the cost and improving its sustainability. Several studies have reported that the use of high volume fly ash in concrete provides higher durable properties than ordinary concretes in low water-cement ratio (Dhir 1999; Tahir 2005; Crouch 2007; Chalee *et al.* 2009). However, although high volume fly ash (HVFA) concretes show promising performance compared to concrete, yet its low early age strength development is still a concern for wide struc-

tural application (Aggrawal 2010; Guo-qiang 2010; Murali 2012).

The use of nano particles has recently been researched to overcome the deficiency of low early age compressive strength in HVFA concretes. Nano material is defined as a very small size particle in a scale of 10⁻⁹ meter, produced from modification of atoms and molecules in order to produce large surface area (Mann 2006). The addition of nano particles in concrete is more effective than micro size particles and is recognized as a means to improve the strength and durability properties of concrete or mortar. Much of the work to date with nanoparticles has been done using nano silica (SiO₂), nano iron (Fe₂O₃), nano titanium oxide (TiO₂), nano alumina (Al₂O₃), and nano clay particles. It is suggested that the nanoparticles act as a nuclei for cement to accelerate the cement hydration and densify the microstructure of the matrix and the interfacial transition zone (ITZ), thereby reduces the permeability of concrete (Sanchez 2010).

In recent years, limited studies have been conducted on the additions of nano calcium carbonate (nano-CaCO₃) as partial replacement of cement in concrete on the hydration and compressive strength behaviour. Calcium carbonate can be found in limestone, marble, chalk or produced artificially by combining calcium with CO₂ (Camiletti *et al.* 2013). Although the use of calcium carbonate was first considered as filler to partially replace cement or gypsum, studies have shown some advantages of using CaCO₃ in terms of strength gain, accelerating effect and economic benefits as compared to cement and other supplementary cementitious materials. Chemically, the presence of CaCO₃ increases the rate of hydration reaction of tricalcium aluminate (C₃A) to form a carboaluminate compound (Pera *et al.* 1999). In addition, it also reacts with tricalcium silicate (C₃S) and accelerates the setting and early strength development (De Weerd *et al.* 2011). As a result of the formation of

¹PhD student, Department of Civil Engineering, Curtin University, Perth, Australia.

²Senior Lecturer, Department of Civil Engineering, Curtin University, Perth, Australia.
E-mail: S.Ahmed@curtin.edu.au

higher volume of hydrates, the increase in hydration degree compensates the dilution effect of the binder thus compensates the low initial strength (Goergescu 2009). In terms of durability properties, it was revealed that replacement of cement with limestone powder had significant effect on the resistance of sulphate attack and water absorption which is related to the filler effect, heterogeneous nucleation and the dilution effect of limestone powder (Ramezaniyanpour 2010).

Elsewhere, Sato and Beaudoin (2011) carried out an investigation on the incorporation of micro- and nano- CaCO_3 with high volume of supplementary cementitious materials. In that experiment, cement was replaced with 50% fly ash and 50% slag and incorporated with 10 and 20% of micro- and nano- CaCO_3 by weight of the binders. It was found that the replacement of cement

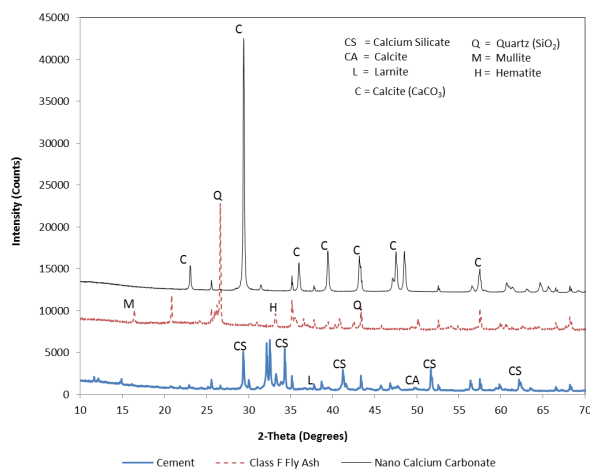


Fig. 1 X-ray diffractogram of cement, class F fly ash and nano- CaCO_3 .

Table 1 Chemical composition and physical properties of cementitious materials.

Chemical Analysis	Cement (wt. %)	Fly Ash (wt. %)	Nano CaCO_3 (wt. %)
SiO_2	20.2	51.80	-
Al_2O_3	4.9	26.40	-
Fe_2O_3	2.8	13.20	0.02
CaO	63.9	1.61	-
MgO	2.0	1.17	0.5
MnO	-	0.10	-
K_2O	-	0.68	-
Na_2O	-	0.31	-
P_2O_5	-	1.39	-
TiO_2	-	1.44	-
SO_3	2.4	0.21	-
CaCO_3	-	-	97.8
Physical Properties			
Particle size	25 - 40% $\leq 7 \mu\text{m}$	40% of 10 μm	15 - 40 nm
Specific gravity	2.7 to 3.2	2.6	-
Surface area (m^2/g)	-	-	40
Loss on ignition (%)	2.4	0.5	-

with nano- CaCO_3 accelerated the early hydration of cement and enhanced the early development of modulus of elasticity as the amount of nano- CaCO_3 was increased. The presence of nano- CaCO_3 particles has been suggested to have a significant effect on the hydration kinetics of C_3A and C_3S which may cause acceleration of setting and early strength development. On another study, Sato and Diallo (2010) reported the seeding effect of nano- CaCO_3 where the rapid growth of CSH is obtained on the surface of the C_3S particles. This view is supported by Kawashima *et al.* (2013) who provided a basis for understanding the mechanical properties of high volume fly ash when incorporated with calcium carbonate nanoparticles. It was shown that the 5% nano CaCO_3 with 30% fly ash-cement paste samples tested at 1, 3 and 7 days showed progressive development of compressive strength compared to control fly ash-cement paste. While the above investigations evaluated the effects of nano- CaCO_3 on the hydration, setting, microstructure and compressive strength of fly ash pastes, there has been limited progress on the effect of nano- CaCO_3 in HVFA mortars and concretes. Therefore, the objectives of the present work are to study the effects of nano- CaCO_3 on workability and early age compressive strength development of HVFA concretes and mortars. Likewise, the microstructure and crystalline phases of paste samples are also investigated by SEM and XRD analysis to support the findings.

2. Experimental program

2.1 Materials

Ordinary Portland Cement Type I (PC), Class F Fly Ash (FA) and nano- CaCO_3 (NC) are used in all mixes in this study. The nano- CaCO_3 is obtained from Skyspring Nanomaterials, Inc. of USA with average particle diameter of 15-40 nm. The X-ray Diffraction (XRD) spectra of PC, FA and NC used in this study are shown in Fig. 1. The chemical analysis and physical properties of PC, FA and NC are listed in Table 1.

2.2 Mixture proportions

The experimental work is divided into two parts - mortars and concretes. The mixture proportions are shown in Tables 2 and 3, respectively. In first part, the effects of different nano- CaCO_3 contents on compressive strength development of cement mortar and HVFA mortars are evaluated. Four series of mixes are considered in the first part. The first series is the control cement mortar, while the second series investigated the effects of different nano- CaCO_3 contents (e.g. 1%, 2%, 3%, and 4% (by wt.)) as partial replacement of cement on compressive strength of mortars. The effects of high fly ash contents e.g. 40 and 60% (by wt.) as partial replacement of cement on compressive strength of mortars are evaluated in the third series. The nano- CaCO_3 content that exhibited the highest compressive strength in the second series is used in the fourth series to study its effect on

Table 2 Mix proportions of mortars.

Series	Mix designation	Cement (kg/m ³)	Class F Fly Ash (kg/m ³)	Nano CaCO ₃ (kg/m ³)	Sand (kg/m ³)	Water (kg/m ³)
1	PC	400	-	-	1100	160
2	FA40	240	160	-	1100	160
	FA50	200	200	-	1100	160
	FA60	160	240	-	1100	160
3	NC1	396	-	4	1100	160
	NC2	392	-	8	1100	160
	NC3	388	-	12	1100	160
	NC4	384	-	16	1100	160
4	FA39.NC1	240	156	4	1100	160
	FA59.NC1	160	236	4	1100	160

Table 3 Mixture proportions of concretes.

Series	Mix designation	Cement (kg/m ³)	Class F Fly Ash (kg/m ³)	Nano CaCO ₃ (kg/m ³)	Sand (kg/m ³)	Coarse Aggregate (kg/m ³)	Water (kg/m ³)
1	PC	400	-	-	684	1184	163
2	FA40	240	160	-	684	1184	163
	FA60	160	240	-	684	1184	163
3	NC1	396	-	4	684	1184	163
	NC2	384	-	8	684	1184	163
4	FA39.NC1	240	156	4	684	1184	163
	FA59.NC1	160	236	4	684	1184	163

the compressive strength of mortars containing 40% and 60% class F fly ash (by wt.) as partial replacement of cement. The above study is also extended to HVFA concretes containing 40% and 60% fly ash in second part of this study.

2.3 Mixing methods

2.3.1 Mortar

All mortars are mixed in a Hobart mixer at an ambient temperature of approximately 25°C using water/ binder ratio of 0.4 and sand/binder ratio of 2.75. Dry sand, cement, fly ash and nano-CaCO₃ powder are mixed in high speed Hobart mixer for approximately 2-3 minutes. The dry mixing of nano-CaCO₃ powder with cement powder is also used by other researchers (e.g. Sato and Beaudoin 2011 and Sato and Diallo 2010). Water is added thereafter and mixed for another 2-3 minutes. The flow values of mortars are determined according to ASTM C 1437 (2005). The 50 mm mortar cubes are cast and demoulded after 24h. The mortar specimens are cured in water at room temperature for 7 and 28 days. Compressive strength of mortar specimens are tested according to ASTM C109 (2012) using a loading rate of 0.7 MPa/s.

2.3.2 Concrete

The concrete mixes are prepared in a pan mixer with the same water/binder ratio used for mortars. Similar to the mortar mixing, dry mixing time of cement, fly ash, nano-CaCO₃ and aggregates are extended to 4-5 minutes due to higher volume of mix and presence of coarse aggregates. Standard cylinders having diameter of 100

mm and height of 200 mm are cast and cured in water at room temperature. The compressive strengths of concretes are determined at 3, 7 and 28 days according to ASTM C873 standard (2010).

2.3.3 Paste

The mix proportions of pastes were similar to those of mortars except the exclusion of sand. The water/binder ratio of paste was same as that of mortar. The 50 mm cube samples were also cast for pastes and followed similar curing to those of mortars. Small portions were cut from the cubes to perform scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis of pastes containing NC, FA and combined FA and NC.

2.4 XRD analysis

Small fragment of paste samples were grinded manually to prepare the powder sample for XRD analysis. XRD patterns were acquired on a Siemens D500 Bragg-Brentano Diffractometer (Munich, Germany). Operating conditions were set a 40 kV and 30 mA using a CuK α X-ray source. During data collection 2 θ step was 0.02°, the counting time per step was 3s and the 2 θ range was 7° to 70°.

2.5 Scanning electron microscope (SEM) analysis

The microstructures of different paste samples were examined on a Zeiss EVO-40 (Carl-Zeiss, Germany) using backscattered electron (BSE) detector. The small cut paste samples were polished using silicon carbide paper and coated with carbon before imaging in the

SEM.

3. Results and discussion

3.1 Effect of nano-CaCO₃ on workability of mortars and concretes

The effect of nano-CaCO₃ on workability of control cement mortar and HVFA mortars is evaluated using flow table test according to ASTM C1437 (2012). It can be seen from Fig. 2 that the mortars containing nano-CaCO₃ exhibited slightly lower workability than the control cement mortar and the flow values decreases with increase in nano-CaCO₃ contents as partial replacement of cement. The effect of 1% (by wt.) nano-CaCO₃ on workability of HVFA mortars can also be seen in the same figure. Similar to the control mortar, the use of 1% nano-CaCO₃ also reduced the workability of HVFA mortars. For instance, the FA40 mortar yielded a flow diameter of 140 mm while this flow is reduced to 135 when 1% nano-CaCO₃ is used as partial replacement of fly ash (e.g. FA39.NC1 mortar). Similar behaviour is also observed in FA59.NC1 mortar. This can be explained due to high specific surface area of nano-CaCO₃.

The workability of concretes containing HVFA and combined HVFA and nano-CaCO₃ are also measured to evaluate the effect of nano-CaCO₃ on the workability. It can be seen in Fig. 3 that the addition of 1% nano-CaCO₃ in HVFA concretes exhibited very similar behaviour to that observed in the mortars. The high surface area of nano-CaCO₃ can be attributed to the reduced workability of mortar and concrete and their HVFA counterparts.

3.2 Effect of nano-CaCO₃ on compressive strength of cement mortar and HVFA mortar

The effects of nano-CaCO₃ on the compressive strengths of control cement mortar and HVFA mortars are shown in Fig. 4. It can be seen that 1% nano-CaCO₃ exhibited the highest compressive strength at both 7 and 28 days among all four nano-CaCO₃ contents and the compressive strength is decreased gradually with increase in nano-CaCO₃ contents. The NC1 mortar exhibited about 22% and 18% higher compressive strengths at 7 and 28 days, respectively than control mortar (PC). The lower compressive strength of mortars containing high nano-CaCO₃ contents can be attributed to the agglomeration of nano-CaCO₃ in wet mix due to its higher van der Waal's forces than cement.

The 1% nano-CaCO₃, which exhibited the highest 7 and 28 days compressive strength in control cement mortar, is used in the HVFA mortars containing 40% and 60% fly ash. It can be seen from Fig. 4 that the 7-day compressive strength of mortar containing 40% fly ash is increased by about 21% due to addition of 1% nano-CaCO₃ and at 28 days this improvement is ceased, indicating the effectiveness of nano-CaCO₃ in compensating the low compressive strength at early age of

HVFA system. A similar increase (approximately 21%) in 7-days compressive strength of paste containing 30% fly ash and 5% nano-CaCO₃ is also reported by Kawashima *et al.* (2013). By comparing the 7 day compressive strength of FA39NC1 with that of control cement mortar in the same figure, it can be seen that addition of 1% nano-CaCO₃ significantly reduce the gap in 7 days compressive strength between the HVFA mortar and the control mortar. The results also show significant improvement of both 7 and 28 days compressive strengths of mortar containing 59% of fly ash mortar and 1% nano-CaCO₃. For example, the compressive strength of

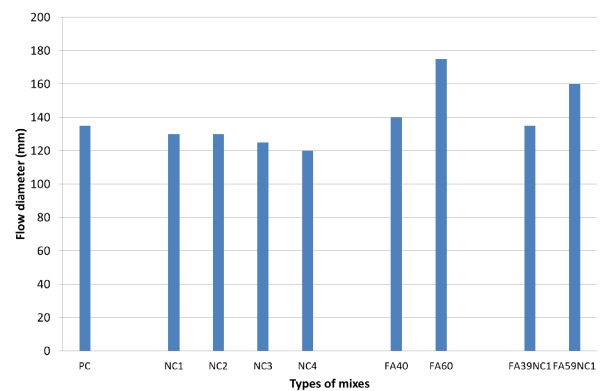


Fig. 2 Workability of mortars and HVFA mortars containing nano-CaCO₃.

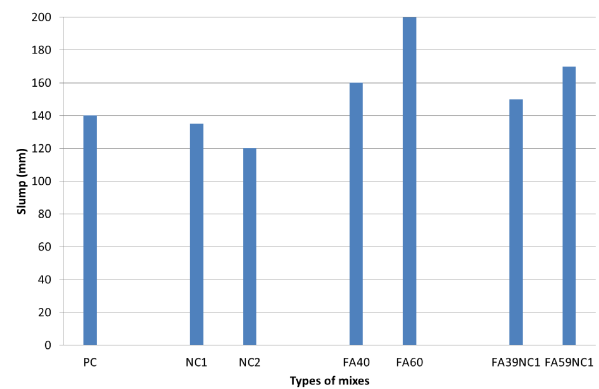


Fig. 3 Effect of nano-CaCO₃ on workability of concrete and high volume fly ash concretes.

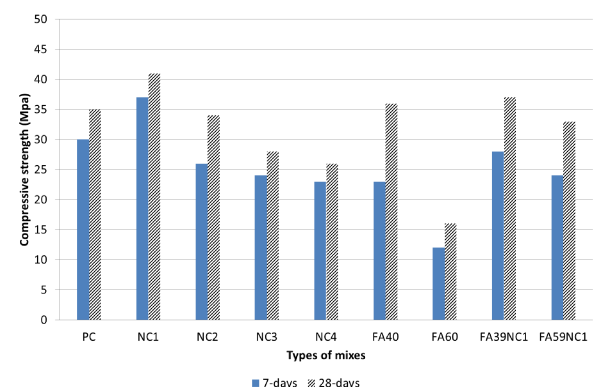


Fig. 4 Effect of nano-CaCO₃ on compressive strength of mortar and high volume fly ash mortars.

FA59.NC1 mortar is increased from 12 to 24MPa at 7 days and from 16 to 33 MPa at 28 days, which are about 100% and 111% improvement at 7 and 28 days, respectively. From the results obtained in this study, it is apparent that the blending of nano-CaCO₃ with fly ash is effective in compensating the low early age compressive strength of HVFA mortars at 40% and 60% of cement replacement levels. However, more study need to be done to evaluate the efficiency of improving the early age compressive strength of HVFA mortar/concrete beyond this fly ash level.

3.3 Effect of nano-CaCO₃ on compressive strength of HVFA concretes

The effect of nano-CaCO₃ on the compressive strength development of HVFA mortar is also extended to HVFA concretes in this study. **Fig. 5** shows the effect of 1% and 2% nano-CaCO₃ on 3, 7 and 28 days compressive strength of ordinary concrete. It can be seen in **Fig. 5a** that the concretes containing 1% and 2% nano-CaCO₃ exhibited higher compressive strength at all ages than the ordinary concrete. And among both nano-CaCO₃ contents, the 1% nano-CaCO₃ exhibited the highest compressive strength at all ages. Therefore, the 1% nano-CaCO₃ is used in HVFA concretes to evaluate its synergistic effect with fly ash on the compressive strength development. It can be seen in **Fig. 5b** that the 1% nano-CaCO₃ significantly improved the 3 and 7 days compressive strength of HVFA concrete containing 39% fly ash, where about 47% and 44% improvement is observed, respectively. At 28 the improvement is even higher (about 87%) for the concrete containing 39% fly ash. If this result is compared with that of mortars, it can be seen that the addition of 1% nano-CaCO₃ performed better in improving the 3 and 7 days compressive strength of HVFA concrete containing 39% fly ash than its mortar counterpart. However, an opposite trend is observed in HVFA concrete containing 60% fly ash, where the improvement in early age compressive

strength of HVFA mortar containing 60% fly ash is more than its concrete counterpart. Although due to limited published results on early age compressive strengths of HVFA concretes containing nano-CaCO₃ the above results cannot be compared, the above trend, however, is very similar to that of HVFA concretes containing fine limestone powder reported by Tanesi *et al.* (2013). In that study, the addition of fine limestone powder showed about 15% to 28% improvement of early age (3 and 7 days) compressive strength of both 40% and 60% fly ash concretes and the improvement at 28 days is about 42% and 23% in concrete containing 40% and 60% fly ash, respectively. The relatively small improvement in early age compressive strengths of HVFA concretes in their study can be attributed to the relatively coarser particle size of limestone powder than that of nano-CaCO₃ used in this study. Due to high specific surface area of nano-CaCO₃, its reactivity during early hydration reaction is much higher than micro-limestone powder (Camiletti *et al.* 2013).

3.4 Microstructural analysis of cement and HVFA cement pastes containing nano-CaCO₃

The backscatter scanning electron microscope (SEM) observations on a series of HVFA paste samples with nano-CaCO₃ addition have also been carried out to observe the microstructure changes. The specimens for SEM analysis were taken from paste samples that had been fractured after 28 days of water curing. The specimens were then cut to expose a new surface, mounted in epoxy, polished and coated with Platinum. SEM images of paste samples are shown in **Figs. 6-7**. The constituents' phases in the images can be identified through their brightness. The un-hydrated cement particles appear brightest, followed by CH, CSH and finally the black spots as pores or cracks (Zhao and Darwin 1992 and Scrivener, 2004). In **Fig. 6b**, it is clearly seen that the NC1 sample has very few white and black areas (represents un-hydrated cement particles and voids, re-

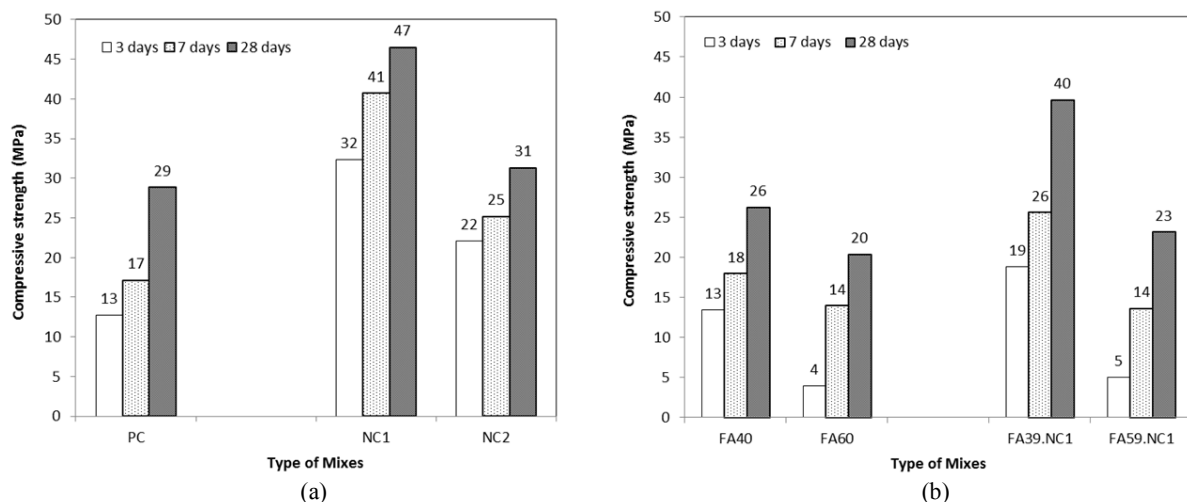
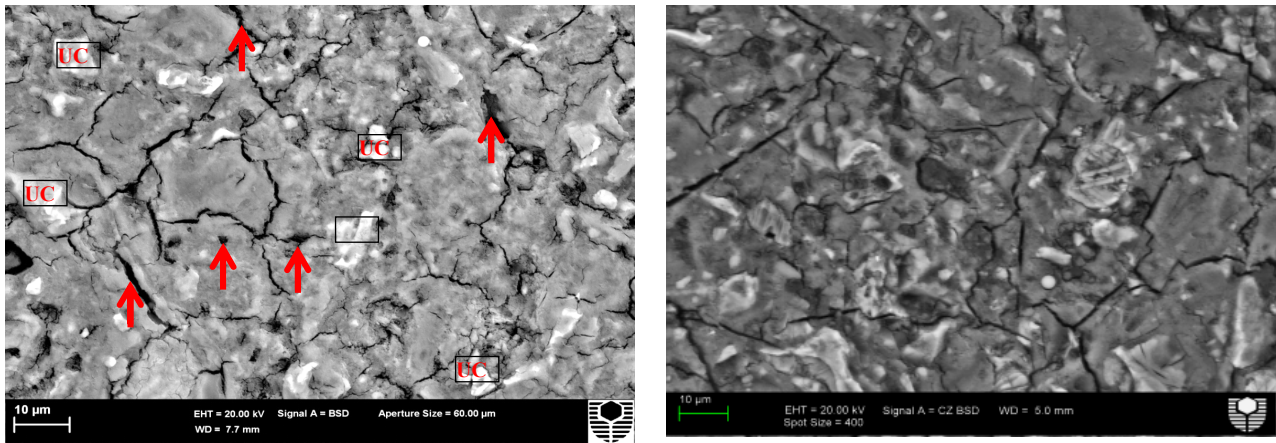


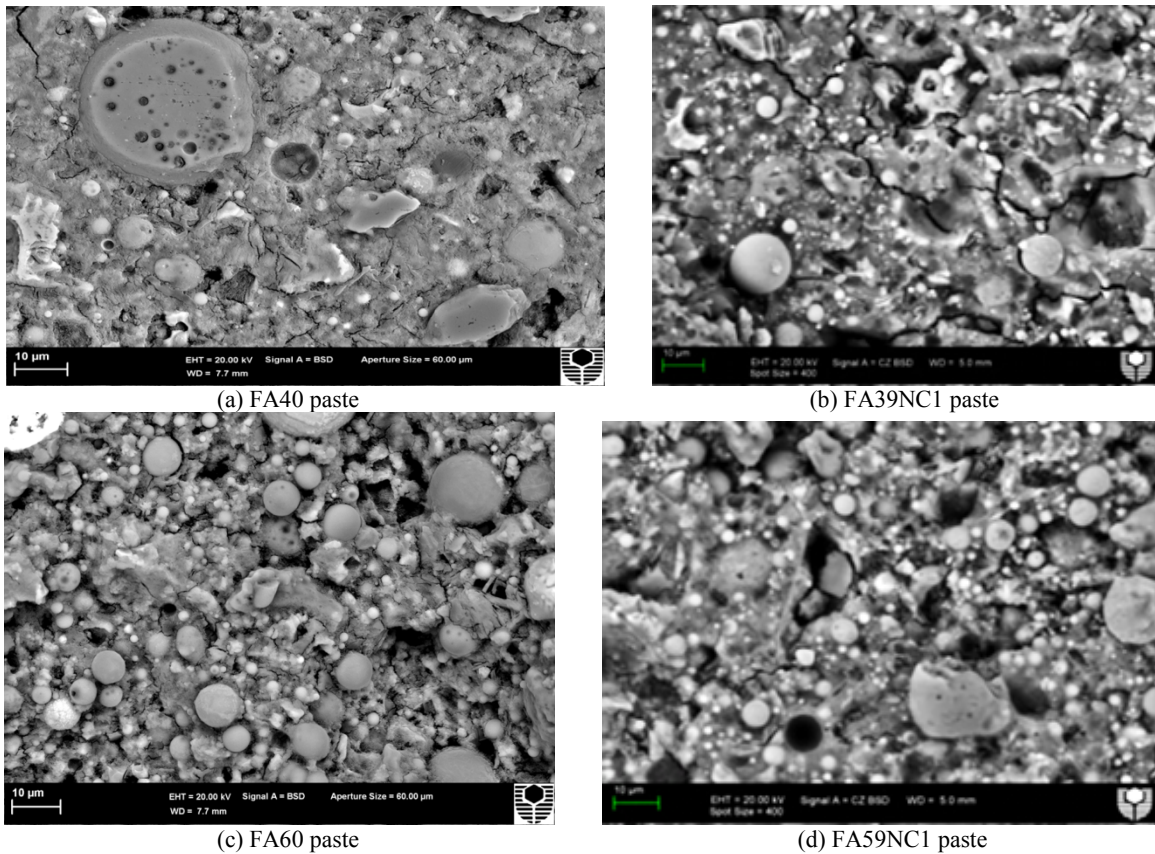
Fig. 5 Compressive strength development of (a) concretes containing nano-CaCO₃ and (b) HVFA concretes containing nano-CaCO₃.



(a) Cement paste (UC represents as unhydrated cement particle, Black spots are represented by arrows as voids)

(b) Cement paste containing 1% NC

Fig. 6 Backscattered electron images of (a) Cement and (b) NC1 pastes cured at 28 days.



(a) FA40 paste

(b) FA39NC1 paste

(c) FA60 paste

(d) FA59NC1 paste

Fig. 7 Backscattered electron images of (a) FA40 paste, (b) FA39NC1paste, (c) FA60 paste and (d) FA59NC1 pastes cured at 28 days.

spectively) and more grey to dark grey areas than control cement paste sample (see Fig.6a), which indicates that the microstructure of NC1 paste is more uniform and dense than that of the cement paste. Similar dense microstructure can also be seen in HVFA paste samples containing 1% nano-CaCO₃ in Figs. 7(b) and (d) for FA39NC1 and FA59NC1 samples, respectively.

3.5 X-ray diffraction analysis of cement and HVFA pastes with and without nano-CaCO₃

In order to identify different phases of each mixture XRD analysis is also performed. Figs.8-10 show the XRD patterns of cement pastes containing HVFA, nano-CaCO₃ and combined HVFA and nano-CaCO₃. The X-ray diffractograms of paste samples were obtained with a D8 Advance Diffractometer (Bruker-AXS), using

CuK α radiation. Samples were scanned from 7⁰ to 70⁰ (2 θ) at a speed of 0.5⁰/min. The horizontal scale (diffraction angle) of a typical XRD pattern gives the crystal lattice spacing, measured in degrees, and the vertical scale (peak height) gives the intensity of the diffracted ray, measured in pulses/second. The diffraction spectra of cement paste and that containing 1% nano-CaCO₃ shown in Fig. 8 do not show any significant difference in different peaks.

The addition of 1% nano-CaCO₃ in HVFA pastes shows reduction in CH peak intensity compared to that of HVFA pastes (see Figs.9-10). In the 7 days cured

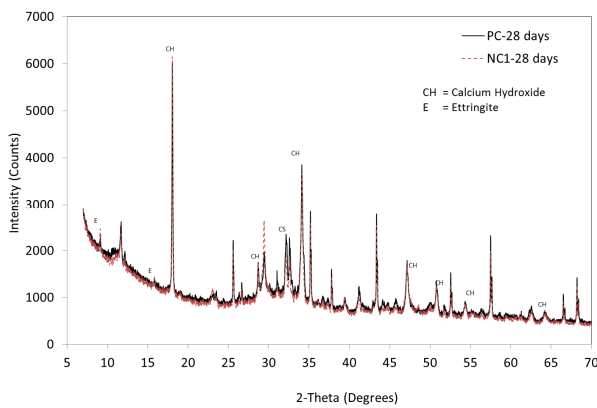


Fig. 8 XRD analysis of cement paste and that containing 1% nano-CaCO₃ (NC) cured at 28 days.

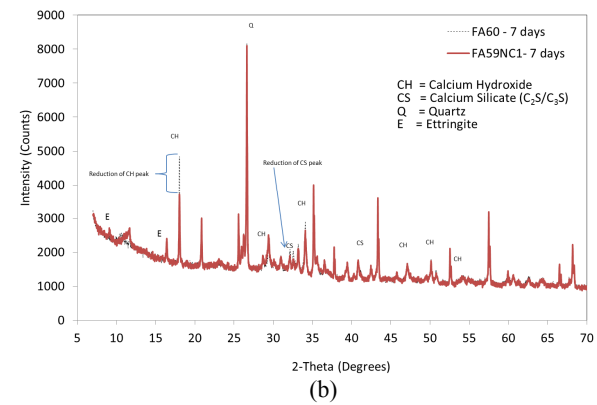
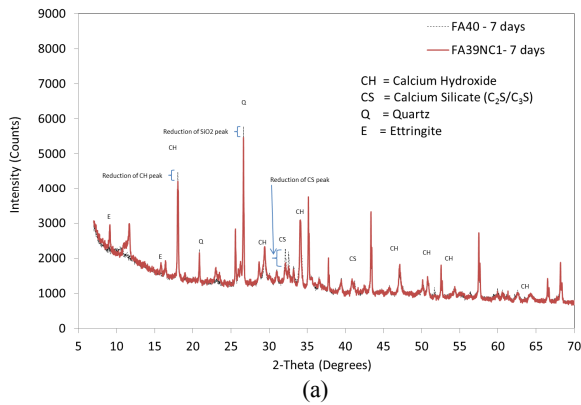


Fig. 9 XRD analysis of HVFA pastes with and without nano-CaCO₃ at 7 days.

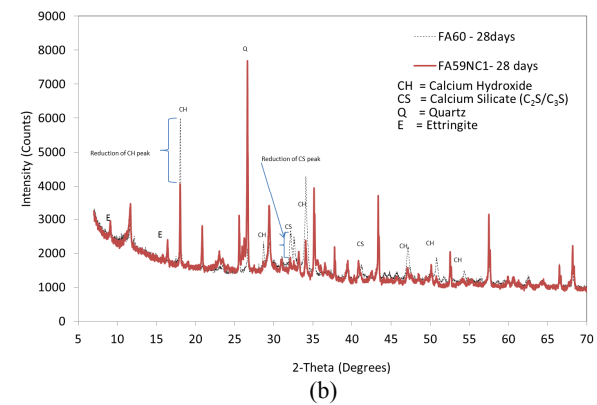
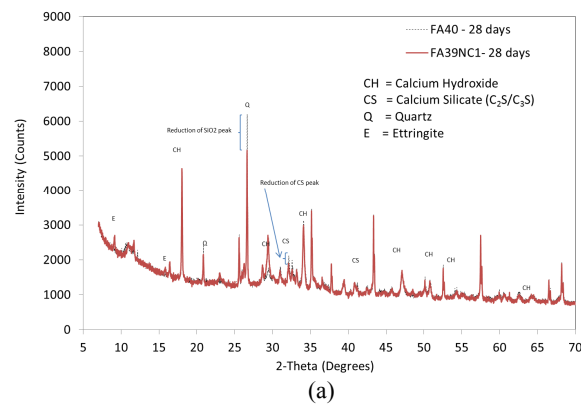


Fig. 10 XRD analysis of HVFA pastes with and without nano-CaCO₃ at 28 days.

paste sample containing 39% fly ash and 1% nano-CaCO₃ the intensity peak of CH decreased from 4481 to 4218 (Fig. 9a) at 2 θ =18.05 $^{\circ}$, while no significant reduction of CH peak is noticed in 28 days cured sample (Fig. 10a). The same trend was also observed in paste containing 59% fly ash and 1% nano-CaCO₃, where the intensity of CH peak at 2 θ =18.05 $^{\circ}$ decreased from 4840 to 3698 (Fig. 9b) and from 5485 to 4057 (Fig. 10b) at 7 and 28 days, respectively. The XRD results in Figs. 8-9 also show reduction of calcium silicate (CS) peaks for both HVFA pastes at both curing ages due to addition of 1% nano-CaCO₃. The reduction of CS is a clear indication of formation of hydration products in the system. Moreover, new ettringite peaks are also noticed in the XRD results of both HVFA pastes due to addition of 1% nano-CaCO₃. In addition, due to high silica and alumina contents in fly ash, the presence of nano-CaCO₃ maximizes the additional aluminate in the system by decreasing the SO₃/Al₂O₃ ratio, which influences the short-term strength of the pastes (De Weerd 2010).

4. Conclusions

Based on workability, 3, 7 and 28 days compressive strength, SEM and XRD results on the effect of nano-CaCO₃ in high volume fly ash mortars and concretes, the following conclusions can be drawn:

- (1) Nano-CaCO₃ slightly reduced the workability of

both ordinary and HVFA mortars/concretes.

- (2) Concrete containing 1% nano-CaCO₃ as partial replacement of cement exhibited about 140% improvement of early age compressive strength (e.g. at 3 and 7 days) as compared to control concrete. At 28 days, the improvement was 62%. In the case of mortars, the improvement at 7 and 28 days compressive strength is only 22% and 18%, respectively. The findings show that the nano-CaCO₃ has a more pronounced effect on early age compressive strength than 28 days compressive strength due to its very high surface area, which increases the rate of hydration reaction of C₃A and C₃S (Pera *et al.* 1999 and De Weerd *et al.* 2011).
- (3) The addition of 1% nano-CaCO₃ increased the compressive strength at early ages (e.g. at 3 and 7 days) of HVFA concrete containing 39% fly ash by about 44-46%. At 28 days, the improvement was about 53%. In the case of HVFA mortar, the addition of 1% nano-CaCO₃ increased the 7 and 28 days compressive strength of HVFA mortar containing 59% fly ash by about 100% and 111%, respectively. However, the improvements were about 22% and 3% at 7 and 28 days, respectively in HVFA mortar containing 39% fly ash.
- (4) According to backscattered image analysis, the incorporation of 1% nano-CaCO₃, as partial cement replacement of cement densified the microstructure of cement and HVFA pastes which is believed to be the reason for the improvement of compressive strength.
- (5) The XRD analysis results showed that the nano-CaCO₃ replacement of cement is effective in reducing the CH and CS in HVFA pastes and hence the formation of additional CSH gels. New peaks of Ettringite are also noticed in HVFA pastes due to addition of 1% nano-CaCO₃.
- (6) The compressive strengths of FA39NC1 concrete at all ages exceeded the ordinary Portland cement concrete. This shows that sustainable concrete with 40% less cement can be produced by adding 1% nano-CaCO₃.

Acknowledgements

Authors acknowledge fly ash Australia for donating class F fly ash and ultrafine fly ash in this study.

References

- ASTM C109, (2012). "Standard test method for compressive strength of hydraulic cement mortars (Using 50-mm cube specimens)."
- ASTM C873, (2010). "Standard test method for compressive strength of concrete cylinders cast in place in cylindrical moulds." Annual book of ASTM standard.
- ASTM C1437, (2012). "Standard test method for flow of hydraulic cement mortar."
- Bendapudi, S. C. K., (2011). "Contribution of fly ash to

the properties of mortar and concrete." *International Journal of earth Sciences and Engineering*, 4(6), 1017-1023.

- Camiletti, J., Soliman, A. M. and Nehdi, M. L., (2013). "Effects of nano- and micro-limestone addition on early-age properties of ultra-high-performance concrete." *Materials and Structures*, 46, 881-898.
- Chalee, W., Jaturapitakkul, C. and Chindaprasirt., (2009). "Predicting the chloride penetration of fly ash concrete in seawater." *Marine structures*, 22, 341-353.
- Crouch, L. K., Hewitt, R. and Byard, B., (2007). "High volume fly ash concrete." *2007 World of Coal Ash (WOCA)*, May 7-10, 2007, Northern Kentucky, USA.
- De Weerd, K., Ben Haha, M., Le Saout, G., Kjellsen, K. O., Justnes, H. and Lothenbach, B., (2011). "Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash." *Cement and Concrete Research*, 41, 279-291.
- De Weerd, K., Kjellsen, K. O., Sellevold, E. J. and Justnes, H., (2011). "Synergy between fly ash and lime stone powder in ternary cements." *Cement and concrete composites*, 33, 30-38.
- Dhir, R. K. and Jones, M. R., (1999). "Development of chloride-resisting concrete using fly ash." *Fuel*, 78, 137-142.
- Georgescu, M. and Saca, N., (2009). "Properties of blended cement with limestone filler and fly ash content." *Scientific Bulletin*, 71, ISSN 1454-2331.
- Guo-qiang, X. and Juan-hong, L., (2010). "Experimental study on carbonation and steel corrosion of high volume fly ash concrete." *Power and Energy Engineering Conference (APPEEC)*, 2010 Asia-Pacific, ID: 10.1109/APPEEC.2010.5448649.
- Kawashima, S., Hou, P., Corr, D. J. and Shah, S. P. (2013). "Modification of cement-based materials with nanoparticles." *Cement and Concrete Composites*, 36, 8-15.
- Li, G., (2004). "Properties of high volume fly ash concrete incorporating nano-silica." *Cement and concrete research*, 34, 1043-1049.
- Malvar, L. J. and Lenke, L. R., (2006). "Efficiency of fly ash in mitigating alkali silica reaction based on chemical composition." *ACI Material Journal*, 103(5), 319-326.
- Mann, S., (2006). "Nanotechnology and construction, Nano forum report. "www.nanoforum.org, May 30, 2008.
- Medvescek, S., Gabrovsek, R., Kaucic, V. and Meden, A., (2006). "Hydration products in water suspension of Portland cement containing carbonates of various solubility." *Acta Chim. Slov.*, 53, 172-179.
- Murali, G., Vasanth, R., Balasubramaniam, A. M. and Karikalan, E., (2012). "Experimental study on compressive strength of high volume fly-ash concrete." *International Journal of Engineering and Development*, 4(2), ISSN 2249-6149.
- Pera, J., Husson, S. and Guilhot, B., (1999). "Influence of finely ground limestone on cement hydration."

- Cement and Concrete Composites*, 21,99-105.
- Ramezaniapour, A. A., Ghiasvand, E., Nickseresht, I., Moodi, F. and kamel, M. E., (2010). "Engineering properties and durability of concretes containing limestone cements." *Second International Conference on Sustainable Construction Material and Technologies*, ISBN 978-1-4507-1488-4.
- Sanchez, F. and Sobolev, K., (2010). "Nanotechnology in concrete – A review." *Construction and Building Materials*. 24, 2060-2071.
- Saraswathy, V. and Song, Ha-Won., (2006). "Corrosion performance of fly ash blended cement concrete: a state-of-art review." *Corrosion Reviews*, 24(1), 87-122.
- Sato, T. and Diallo, F., (2010). "Seeding effect of nano- CaCO_3 on the hydration of tricalcium silicate." *Journal of transportation research board*, 2141, 61-67.
- Sato, T. and Beaudoin, J. J., (2011). "Effect of nano- CaCO_3 on hydration of cement containing supplementary cementitious materials." *Advances in Cement Research*, 23, 33-43.
- Scrivener, K. L., (2004). "Backscattered electron imaging of cementitious microstructures: understanding and quantification." *Cement and concrete composites*. 26, 935-945.
- Tahir, M. A., and Sabir, M., (2005). "A study on durability of fly ash-cement mortars." *30th Conference of Our World in Concrete and Structures*, 23-24 August, 2005.
- Tangpagasit, J., Cheerarot, R., Jaturapitakkul, C. and Kiattikomol, K., (2005). "Packing effect and pozzolanic reaction of fly ash in mortar." *Cement and Concrete Research*, 35, 1145-1151.
- Zhao, H. and Darwin, D., (1992). "Quantitative backscattered electron analysis of cement paste." *Cement and concrete research*, 22, 695-706.