

Review and study of effect of nano-CaCO₃ on compressive strength development of high volume fly ash mortar and concrete

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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% (by 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.

Index Terms: Introduction, Nano-CaCO₃, Result, Conclusion

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).

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 nano particles 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 nano particles 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.

2. WHAT IS NANO-CaCO₃? AND ITS APPLICATION.

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 replaced 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 material. 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 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 (Ramezani pour 2010). Elsewhere, Sato and Beaudoin (2011) carried out an investigation on the incorporation of micro- and nano CaCO₃ 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-CaCO₃ by weight of the binders. It was found that the replacement of cement 179 with nano-CaCO₃ accelerated the early hydration of cement and enhanced the early development of modulus of elasticity as the amount of nano-CaCO₃ was increased.

The presence of nano-CaCO₃ particles has been suggested to have a significant effect on the hydration kinetics of C3A and C3S which may cause acceleration of setting and early strength development. On another study, Sato and Diallo (2010) reported the seeding effect of nano-CaCO₃ where the rapid growth of CSH is obtained on the surface of the C3S 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 nano particles. It was shown that the 5% nano-CaCO₃ 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-CaCO₃ on the hydration, setting, microstructure and compressive strength of fly ash pastes, there has been limited progress on the effect of nano-CaCO₃ in HVFA

mortars and concretes. Therefore, the objectives of the present work are to study the effects of nano-CaCO₃ 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 analysis to support the findings.

3. RESULTS AND DISCUSSION

3.1 Effect of nano-CaCO₃ on workability of mortars and concrete.

The effect of nano on workability of control cement and HVFA mortars is evaluated using CaCO₃ flow table test according to ASTM C1437 (2012). It can be seen from Fig. 2 that the mortars containing nanoCaCO₃ exhibited slightly lower workability than the control cement mortar and the flow values decrease 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.

On Y-axis flow diameter (mm)

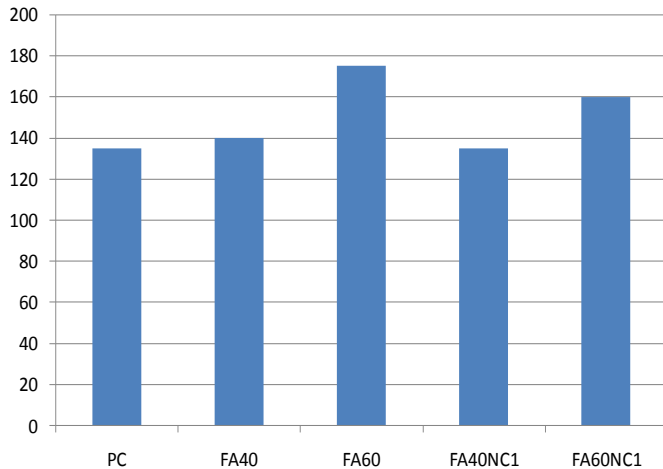


Fig.1 Type of Mixes

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 FA59.NC1 mortar is increased from 12 to 24MPa at 7 days and from 16 to 33 MPa at 28 days, which are about 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. 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.

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).

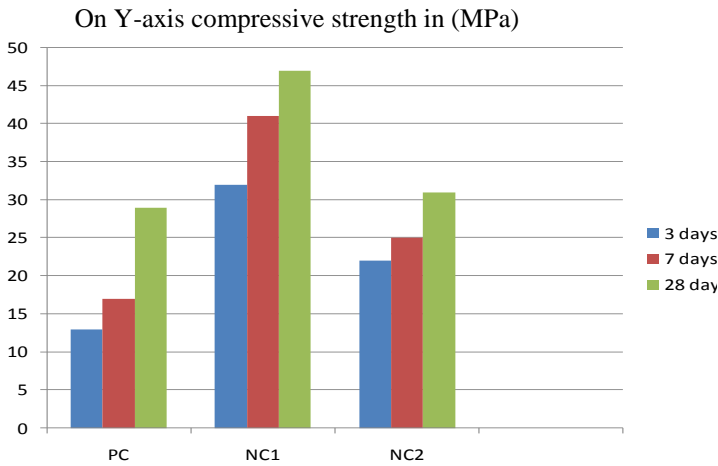


Fig.2 Type of Mixes

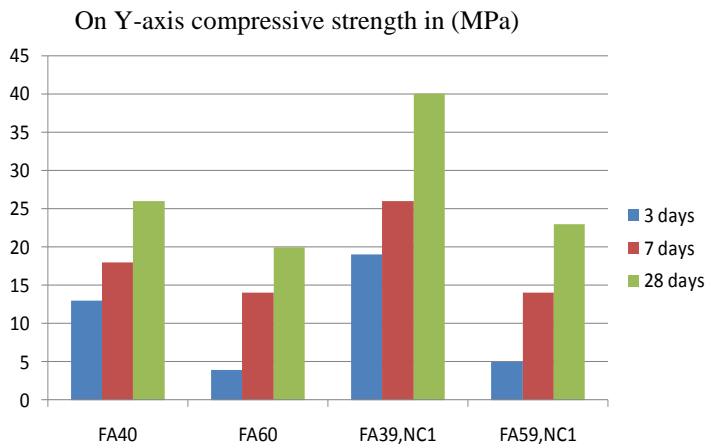


Fig.3 Type of Mixes

4. CONCLUSIONS

Analysis of cement paste and that containing 1% nano-CaCO₃ (NC) cured at 28 days. Based on workability, 3,

7 and 28 days compressive strength, 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.
- (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 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.

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