Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi

Afyon Kocatepe University Journal of Science and Engineering

AKÜ FEMÜBİD **20** (2020) 065601 (1051-1067) AKU J. Sci. Eng. **20** (2020) 065601 (1051-1067)

DOI: 10.35414/akufemubid.825862

Araştırma Makalesi / Research Article

Combined Effects of Nano-Sized Calcite and Fly Ash on Hydration and Microstructural Properties of Mortars

Serhat DEMİRHAN[1*]

[1] *Batman Üniversitesi, Mühendislik-Mimarlık Fakültesi, İnşaat Mühendisliği Bölümü, Batman.*

[*] *Sorumlu yazar; e-posta: drserhatdemirhan@gmail.com* *ORCID ID: https://orcid.org/0000-0001-5448-9495*

Geliş Tarihi: 14.11.2020 Kabul Tarihi: 23.12.2020

Abstract

Even though a reduction in pollution and CO_2 emission can be achieved by the utilization of fly ash in cement-based materials, using a high volume of fly ash results in a reduction at the early age strength development and also setting time delays. In order to assess hydration mechanism and microstructural characteristics of high-volume fly ash blended cement mortars, nano-sized calcite was introduced into the mortars to evaluate the combined effect of fly ash (FA) and nano-sized calcite (NC). For this purpose, twelve mixtures in which fly ash to Portland cement ratios and NC (used as minor addition up to 5%) percentages were varied as 0.0, 0.25, 0.54, 1.0 and 0.0%, 2.5%, 5%, respectively, were designed. Consistency, setting times, compressive strength, ultrasonic pulsive velocity and SEM analysis were conducted at varied curing ages (which depends on the testing method) in terms of fresh and hardened properties and micro-structural characteristics. Experimental test results confirmed that fresh and hardened properties of standard mortars were significantly improved with the combination of both FA and NC especially at early ages. Even though decrease in early age compressive strength values was obtained as FA amount was increased, (comparing to control mixture which was 43.2 MPa at 90 days) higher compressive strength result (45.9 MPa) was obtained at 90-day curing age of mixture including 50% of FA content being utilized by NC of 2.5%.

Keywords
Fresh and Hardened Properties; Nano-Sized Calcite; Fly Ash; SEM

Nano Boyutlu Kalsit ve Uçucu Külün, Harçların Hidratasyonu ve Mikroyapısal Özellikleri Üzerindeki Kombine Etkileri

Öz

Çimento esaslı malzemelerde uçucu külün kullanılmasıyla kirlilik ve CO_2 emisyonunda bir azalma sağlansa da, yüksek hacimde uçucu kül kullanılması, erken yaş mukavemet gelişiminde bir azalma ile neticelenmekte ve ayrıca priz alma süresinde gecikmelere neden olur. Yüksek hacimli uçucu kül katkılı çimento harçlarının hidratasyon mekanizması ve mikroyapısal özelliklerini değerlendirmek amacıyla, uçucu kül (UK) ve nano kalsitin (NK) birleşik etkisini incelemek için harçlara nano boyutlu kalsit eklenmiştir. Bu amaçla, uçucu kül/Portland çimentosu oranı ve NK ikame oranı (% 5'e kadar minör ilave bileşen olarak kullanıldı) sırasıyla 0.0, 0.25, 0.54, 1.0 ve %0, %2.5, %5 olarak yer değiştirilmiş on iki karışım tasarlanmış. Kıvam, priz süreleri, basınç dayanımı, ultrasonik ses hızı (UPV) ve SEM analizi test yöntemine bağlı olarak farklı kür yaşlarında gerçekleştirilmiştir. Deneysel test sonuçları, standart harçların taze ve sertleşmiş özelliklerinin hem UK hem de NK kombinasyonu ile özellikle erken yaşlarda önemli ölçüde iyileştiğini göstermiştir. UK kullanım oranı artışıyla birlikte erken yaş basınç dayanımında azalma gözlemlenmiş olmasına rağmen, kontrol karışımına kıyasen (ki 90 günlük basınç dayanımı 43.2 MPa olarak elde edildi), %50 UK ve %2.5 NK ikame oranlı karışımın 90 günlük basınç dayanımı daha yüksek (45.9 MPa olarak) elde edilmiştir.

Anahtar kelimeler
Taze ve Sertleşmiş Özellikler; Nano Kalsit; Uçucu Kül; SEM

1. Introduction

Ordinary Portland Cement is one of the most consumed construction materials whose production results in high CO_2 emission, therefore, it is a CO_2 intensive process (He et al. 2019). These are major disadvantages associated with cement production, such as greenhouse gas emissions and high energy consumption. Fly ash being widely employed as a partial-substitute of cement has a positive effect on the environment which will result in maintaining landfill area, preserving natural resources, decreasing CO_2 emission and energy saving. Therefore, Fly ash as a by-product could be further converted to a value-added construction material by enhancing high volume fly ash-based greener types of cement (Shwekat and Wu 2018; Sandanayake et al. 2018; Jamora et al. 2020). Unfortunately, due to its poor pozzolanic reaction, delayed hydration process and low early age strength development are some of the most important drawbacks of fly ash in the case of higher volume usages (Zou et al. 2020; Xiao et al. 2017). Therefore, in order to overcome reduced early age strength development and delay setting time in the case of higher replacement amount of cement with fly ash, nano materials are introduced in high volume fly ash blended cement systems to induce early age strength and hydration properties (Liu et al. 2019; Tosti et al. 2020).

Top-down and bottom-up synthesis approaches are two methods being followed in the production of nanomaterials. The choice of “top-down” and “bottom-up” production approaches depends on the suitability and cost of nano material (Sanchez and Sobolev 2010). In general, particle size of nano materials in top-down approach are not uniform and they are cheaper comparing to bottom-up approach (Sobolev and Gutiérrez 2015). C-S-H formation is promoted in the presence of Nano $CaCO_3$ (NCC) particles which accelerate hydration mechanism due to nucleation/seeding effect (Wang et al. 2018; Wu et al. 2018; Zaitri et al. 2014; Supit and Shaikh 2014; Sato and Beaudoin 2011). In addition, NCC reacts with C_3S and produces CSH gels, CH, and calcium carbosilicate hydrates (Pera et al. 1999; Kakali et al. 2000). NCC also reacts with aluminate phase which is known as chemical effect and hemi carboaluminates and monocarboaluminates are produced where CH is depleted by hemicarboaluminates (Bonavetti et al. 2001; Voglis et al. 2005). Since aluminate phase in the normal Portland cement is limited meaning that relatively lower, contribution of NCC (in terms of additional hydration products formed as a result of this chemical effect) is also limited (Thongsanitgarn et al. 2014; Yeşilmen et al. 2015). With the additional higher source of aluminate phase, namely any supplementary cementitious material as fly ash, additional hydration products are formed and more contribution has been obtained in the presence of combined conditions (ordinary portland cement+nano $CaCO_3$+aluminate phase) (De Weerdt et al. 2011; Cao et al. 2019; Damidot et al. 2011; Arora et al. 2016; Ipavec et al. 2011; Vance et al. 2013). The significant contribution of NCC in the presence of high-volume fly ash cement-based material is known as higher and remarkable early-age performance properties (Sato and Beaudoin 2011; De Weerdt et al. 2011). Chemical effect of NCC on the hydration mechanism depends on both particle size and synergic influence with supplementary cementitious material, namely alumina content. Surface energy and physical property (morphology) are significantly altered as particle size decreases and thus resulted in an enhanced chemical reactivity of NCC (Thongsanitgarn et al. 2014; Vance et al. 2013; Shaikh and Supit 2014; Uysal 2012; Kenai et al. 2004; Bosiljkov 2003; Lertwattanaruk et al. 2018; Sumanta et al. 2014).

As previously mentioned, the effect of NCC with and without high volume fly ash content on blended cement have been investigated however these experimental studies are still limited and NCC produced in the bottom up approach is mainly used in most of them. NCC or nano calcite produced in top down approach is still limited. Also, previously mentioned studies have mainly focused on compressive strength of the cement-based materials with or without high volume fly as content. This experimental study focused on hydration properties, compressive strength, ultrasonic pulsive velocity and microstructural characteristics by SEM. In addition to this, all mixture proportions are chosen in the limit of EN 197-1 and therefore results in this research is more affirmative to applications.

This experimental research preliminarily aims to evaluate efficacy and effectiveness of comparingly cheaper (comparing to nano $CaCO_3$ produced by bottom up approach) nano-sized calcite (in the range of minor addition replacement level up to 5%) and high-volume fly ash (up to 50%) on the improvement and enhancement of fresh and hardened properties of standardly produced cement mortars. Both NC and FA were employed as a substitution of cement. Consistency, setting times, compressive strength, ultrasonic pulsive velocity and scanning electron microscopy (SEM) characteristics of standard mortars were measured and analysed.

2. Materials and Method

2.1 Materials

All standard mortars were produced with Normal Portland Cement (PC) CEM I 42.5 (which was produced at the laboratory by grinding the clinker and 5% gypsum up to enough fineness) satisfying minimum requirements of EN 197-1, Class-F Fly Ash (FA), CEN Reference Sand with a maximum grain size of 2 mm satisfying requirements of EN 196-1 and drinkable water. Nano-sized calcite (NC) obtained from Nigtaş Mikronize in Turkey was also used. Particle size distributions of cementitious materials and NC are illustrated in Figure 2.1. Both chemical compositions and physical properties of PC, FA and NC are presented in Table 2.1. SEM images (of PC, FA and NC) and TGA/DTA&XRD results of NC are given in Figure 2.2 and Figure 2.3, respectively. In TGA/DTA analysis, the typical expected major peak of $CaCO_3$ was observed at about 800 °C [37,38]. Also, in XRD diagram, the calcite peaks obtained in the XRD diagram has been observed at smaller peaks and therefore this result in the diagram supports the literature that the material is a pure calcite (Yeşilmen et al. 2015; Bentz et al. 2015).

2.2 Mixture Proportions, Method and Specimen Preparation

As a result of high inter-particle attraction of nano-sized materials (i.e. Van Der Walls forces), they tend to show a behaviour of agglomeration. For this reason, uniformly distribution of mineral additions (nano-calcite) in the matrix was of primary importance. In order to reduce this problem and provide an efficient dispersion in the matrix, (i) ultrasonication that creates a vibration effect, (ii) the use of surfactant that provides chemical repulsion between the particles and also (iii) mechanical grinding method are the most effective and widely used methods. Since mechanical grinding is more suitable for application, this method was preferred in the current experimental study. Therefore, before casting mortars, preparation of cementing materials was separated into two steps. In the former step, clinker was intergrinded with gypsum (5% of clinker, by weight) up to 25 minutes. In the latter one, depending on the mixture, CEM I (previously produced in the former step), Fly Ash and Nano-calcite were grinded together up to an additional 10 min. In order to elucidate the combined effects of FA and NC twelve different mixtures were tailored in accordance with EN 197-1 and then all of the mixtures were cast and tested/analysed with a method meeting requirement of EN 196-1 (for the compressive strength), EN 196-3 (for consistency, initial and final setting) and ASTM C597 (for Ultrasonic pulsive velocity) standards. In the tailored twelve mixtures FA/PC ratio and NC replacement levels were chosen as 0.0, 0.25, 0.54, 1.0 and 0.0%, 2.5% and 5.0%, respectively. Proportions of all mixtures are given in Table 2.2. Each mixture has been abbreviated and is shown by a combination of letters and numbers. An example of abbreviated label of mixtures is illustrated in Figure 2.4.

Standard mortars incorporating different amount of cementitious materials and nano-sized particles were investigated in terms of consistency, intial and final setting times, compressive strength, SEM analysis and ultrasonic pulsive velocity (UPV) analysis. Standard consistency and setting times were determined by Vicat test and performed according to EN 196-3. Compressive strength test was conducted in accordance with EN 196-1 by using a compression machine of 2000 kN capacity. Standard prisms of 4 cm × 4 cm × 16 cm in dimension were produced from the standard cement mortars. The water-cement ratio was kept constant as 0.50. The specimens were cured at standard curing conditions until the testing ages of 1, 3, 7, 28 and 90 days. Five selected mixtures whose test results were better in term of compressive strength were evaluated by using a scanning electron microscopy (SEM). No additional samples were prepared for UPV test. UPV test was applied to prisms produced for compressive strength just before they were tested under compressive strength for curing ages of 1, 3, 7, 28 and 90 days.

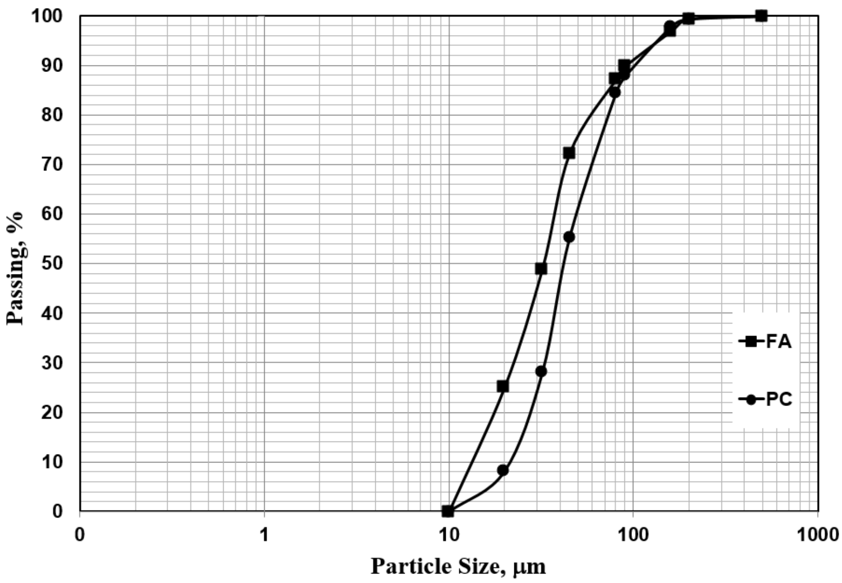
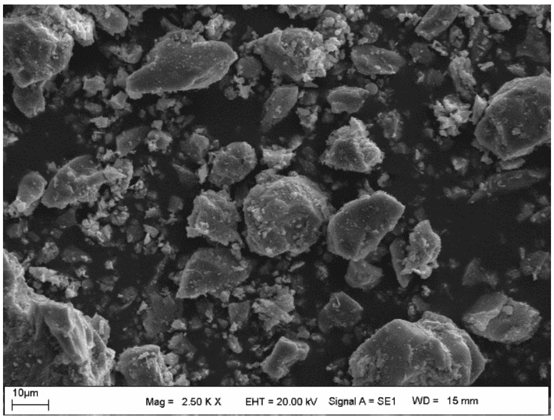
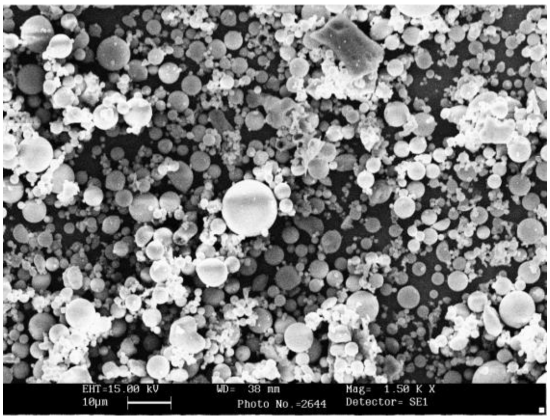


Figure 2.1. Particle size distributions of binders

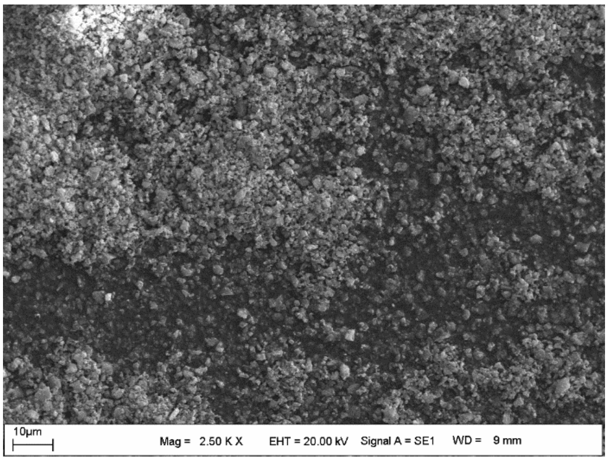
Table 2.1. Chemical composition and physical properties of mortar ingredients

Chemical Composition, %	**PC**	**FA**	**NC**
SiO_2	20.41	61.07	0.24
Al_2O_3	5.34	19.99	0.21
Fe_2O_3	3.10	8.94	0.04
MgO	3.48	1.48	0.55
CaO	61.36	1.95	56.14
SO_3	2.57	0.43	0.06
Na_2O	0.37	0.91	-
K_2O	0.94	2.15	-
Loss on ignition	2.15	2.08	42.76
Physical Properties			
Specific gravity, gr/cm^3	3.24	2.38	2.69
Blaine, cm^2/gr	3092	3560	-
BET surface area, m^2/kg	-	-	7.4



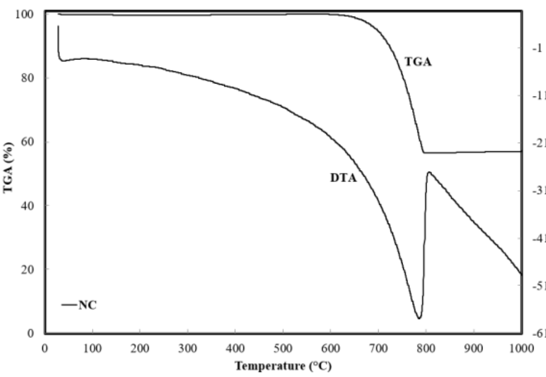


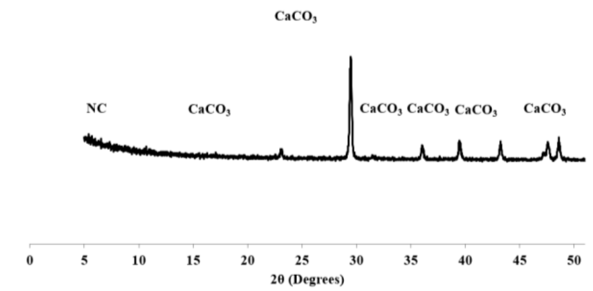
PC FA



NC

Figure 2.2. SEM images of PC, FA and NC





TGA/DTA XRD

Figure 2.3. TGA/TDA curves and XRD diagram of crystal structure of NC

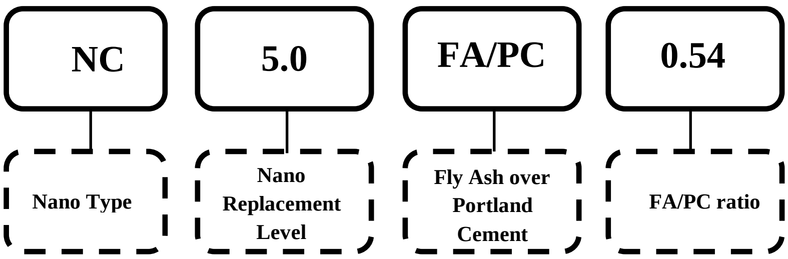


Figure 2.4. Representative labelling of the mixtures

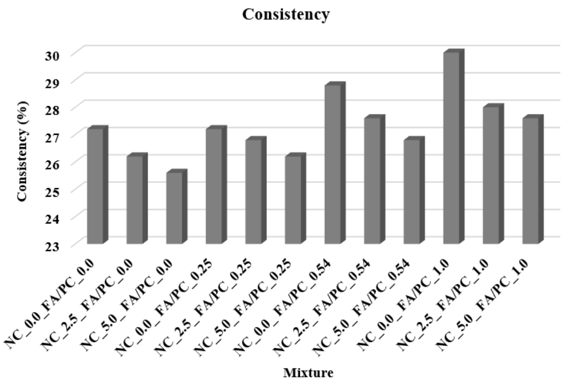
Table 2.2. Mixture proportions of standard mortars

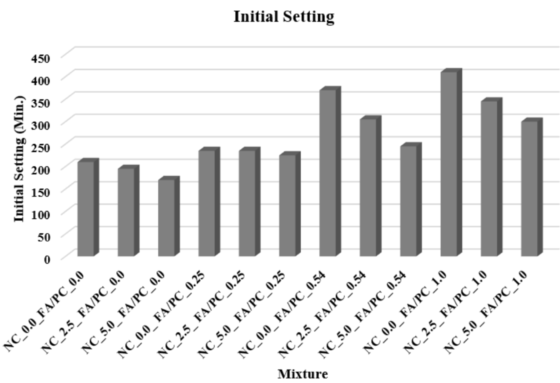
Mix #	Mix ID	Cement Type	PC	FA/PC	Water/Binder	Sand	NC/Binder, %	Blaine, cm^2/gr	Specific Gravity, gr/cm^3
1	NC_0.0_FA/PC_0.0	CEM I	1	0	0.5	3	0	3092	3.24
2	NC_2.5_FA/PC_0.0	CEM I	1	0	0.5	3	2,5	3821	3,22
3	NC_5.0_FA/PC_0.0	CEM I	1	0	0.5	3	5,0	4283	3,18
4	NC_0.0_FA/PC_0.25	CEM II-A/V	1	0.25	0.5	3	0	3567	3,08
5	NC_2.5_FA/PC_0.25	CEM II-A/V	1	0.25	0.5	3	2,5	3958	3,06
6	NC_5.0_FA/PC_0.25	CEM II-A/V	1	0.25	0.5	3	5,0	4786	3,07
7	NC_0.0_FA/PC_0.54	CEM II-B/V	1	0.54	0.5	3	0	3960	2,95
8	NC_2.5_FA/PC_0.54	CEM II-B/V	1	0.54	0.5	3	2,5	4396	2,92
9	NC_5.0_FA/PC_0.54	CEM II-B/V	1	0.54	0.5	3	5,0	4982	2,91
10	NC_0.0_FA/PC_1.0	CEM IV-B	1	1.0	0.5	3	0	4217	2,88
11	NC_2.5_FA/PC_1.0	CEM IV-B	1	1.0	0.5	3	2,5	4720	2,84
12	NC_5.0_FA/PC_1.0	CEM IV-B	1	1.0	0.5	3	5,0	5069	2,83

3. Results and Discussion

3.1 Setting Times

One of the goals of the current experimental research is to evaluate the hydration mechanism of blended types of cementitious materials including varying replacement levels of fly ash (FA) by using Nano-sized calcite (NC), which is produced by the top-down method and is much cheaper than some other nanomaterials such as Nano $CaCO_3$, Nano SiO_2 and Nano $Al2O_3$. Average results found via Vicat Test Method are given in Figure 3.1. As seen in the Figure, test results showed that although nanomaterials are expected to increase the water requirement due to their high specific surface area, as the usage rate of NC increases, the water requirement needed for standard consistency has decreased due to the hydrophobic structure of NC (Lu and Wang 2010; Turgut 2018; Turgut 2019; Demirhan et al. 2019). Fly ash which is finer than cement has increased the water demand required for standard consistency as fly ash replacement level increased. Combined effects of the nucleation effect (reaction of NC with C_3S) and the chemical effect (reaction of NC with the aluminate phase in the binder, namely fly ash and cement) resulted in more hydration products which promoted setting times, therefore, relatively shorter initial and final setting times. In general, the reduction in setting times was more clearly observed in mixtures including both NC and fly ash. Comparing to CEM I, as the replacement level of fly ash increased, an increase was observed in initial and final setting times due to delayed pozzolanic reactions.





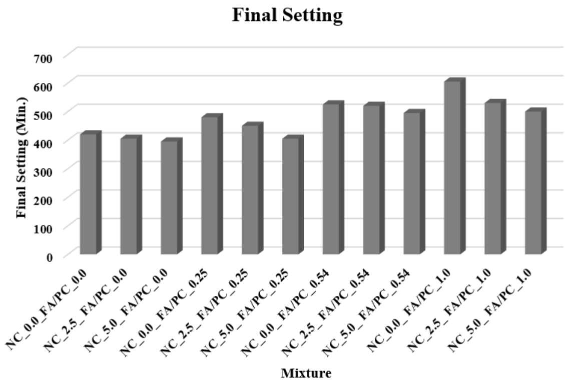


Figure 3.1. Consistency, Initial and Final Setting Times

3.2 Compressive Strength

Compressive strength values as mechanical property was obtained for all of the mixtures at the curing ages of 1, 3, 7, 28 and 90 days in order to monitor strength development and evolution. The average results of compressive strength and strength development are presented in Figure 3.2 and Figure 3.3, respectively. From the Figures, it was revealed that a pronounced enhancement in the compressive strength development of the mortars with/without fly ash was observed at all of the curing ages especially at the early age due to the increase in the hydration products formed in both chemical effect (reaction with the aluminate phase in binder) and nucleation/seeding effect (accelerated reaction with C_3S in cement) of Nano-calcite (NC).

It is seen from the Figures that in the first three mixtures including only normal Portland cement, a clear strength development was observed especially at the early ages in the presence of NC particles and the increment was almost the same or a slight decrease was observed when the replacement level of cement with NC was exceeded 2.5%. In the case of 2.5% replacement level of NC, 17.4% and 1.41% of strength development was obtained for the curing ages of 3 and 28 days, respectively while 15.42% and 1.64% development in strength was obtained for 5.0% of NC for the curing ages of 3 and 28 days, respectively. This shows that 2.5% or may be less than 2.5% is adequate for the NC since 1% replacement level of nano $CaCO_3$ is advised by Supit et al. (2014). Even though NC has no potential of pozzolanic activity its presence in cementing environment has an influence on the hydration kinetics of C_3S accelerating cement hydration, promoting C-S-H precipitation, obtaining less porous and homogeneously refined microstructure resulting in an early strength development (Wu et al. 2018; Wu et al. 2016; Camiletti et al. 2013). Therefore, strength-gain-accelerating efficacy is attributed to presence of NC particles acting as a nuclei and seed in order to promote hydration of cement and to densify microstructure of matrix at the early ages (Sanchez and Sobolev 2010; Duval 2002). In the case of normal Portland cement, the presence of NC mainly promotes the hydration mechanism for C_3S and also has a little hydration accelerating effect with aluminate phase of cement resulting in a slight increase in 90-day strength development since aluminate phase is limited in the cement. Though early strength development of cement-based mortars obtained in the presence of NC (Vance et al. 2013; Kenai et al. 2004; Bosiljkov 2003; Lertwattanaruk et al. 2018), high replacement level of NC decreases dosage of cement and therefore results in lower strength improvement in the long-term curing ages (Liu et al. 2012; Ge et al. 2014; Hosan and Shaikh 2020). Thus, slight decreases observed in the %5 of NC may be attributed to this mechanism (namely dilution effect). The dilution effect directly depends on the replacement level of NC in the matrix. In cementitious systems with low alumina content (such as mixtures including only normal Portland cement), only a small proportion of NC is involved in the reactions (except reactions with C_3S). Therefore, the addition of a larger NC fraction as a supplementary to the cement reduces the content of cement clinker and hence hydration products. In addition to this, with the same water/binder ratio, since NC particles do not have binder property or pozzolanic reactivity, replacement with cement increases the free water to react with the cement particles, known as dilution effect.

As seen in the Figures, regardless of curing age, increase in the fly ash content in the presence of NC resulted in higher enhancement rates as a result of the addition of higher aluminate content introduced to the system with the replacement of cement by fly ash amplifies chemical effect of NC which results in more hydration products at both early and late ages (De Weerdt et al. 2010; Aashay et al. 2016). Pozzolanic reactivity of fly ash has been accelerated by NC at both early and late ages (Meng et al. 2017) and synergy between NC and FA improves the formation of the additional hydration products where increment of cement replacement level resulted in higher carbonate consumption thus more hydration products. The synergy with the pozzolanic material varies depending on the replacement level of NC use and the ratio of the pozzolanic material and/or the aluminate phase in the pozzolanic material. Depending on all these two parameters, the alumina phase reacts with NC in order to form the additional hydration products, namely hemi-carbonate and mono-carbonate (which is a substance with special framework with strong hydrogen bonds between oxygen atoms and interlayer waters in carbonate groups) (Moon et al. 2012; De Weerdt et al. 2011).

The development of compressive strength in blended cement mortars including higher volume of fly ash in the presence of NC and predominantly as a result of the chemical effect, a contribution to the strength development has been obtained. Compressive strength values of NC_0.0_FA/PC_0.0 and NC_2.5_FA/PC_1.0 at the curing age of 90-day were 43.2 MPa and 45.9 MPa, respectively. Therefore, these types of blended cements including higher amount of fly ash can significantly reduce the carbon footprint of cement-based materials as they contain lower volumes of cement and also show higher compressive strength values (Nath et al. 2018; Tosti et al. 2018).

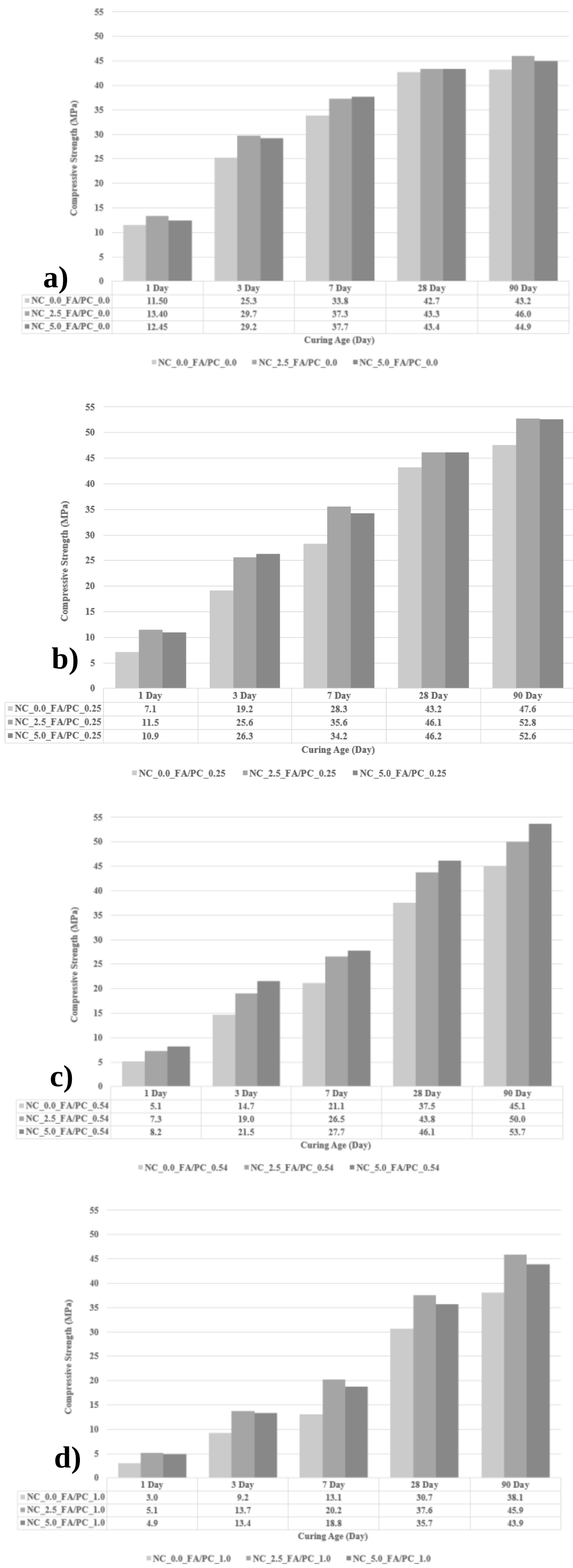


Figure 3.2. Average Compressive Strength (MPa) Values of 1, 3, 7, 28 and 90-day Mortars

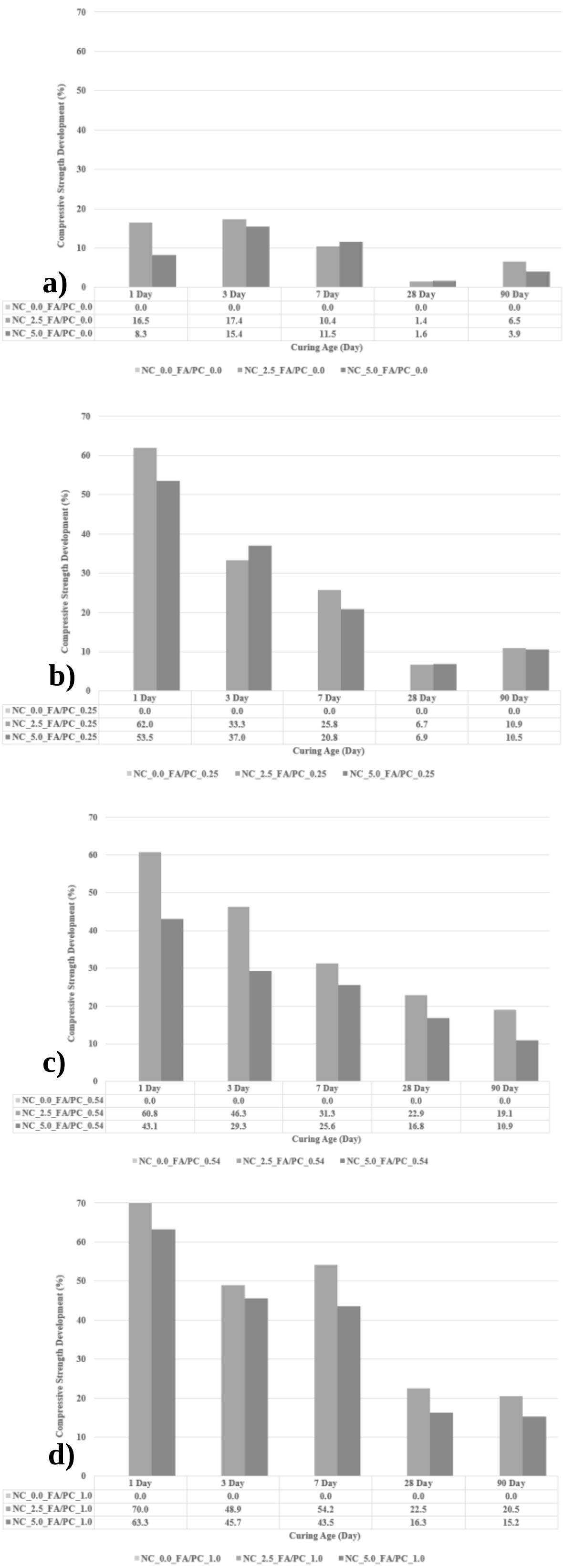


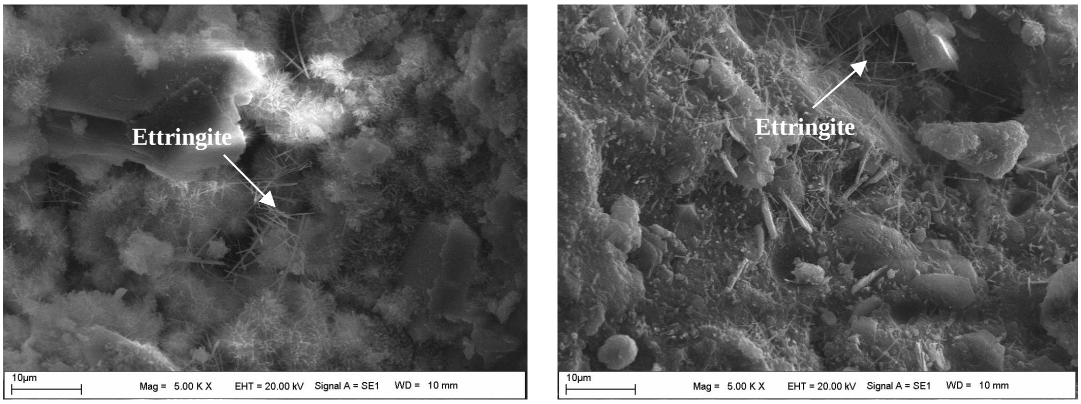
Figure 3.3. Strength Development (%) values of 1, 3, 7, 28 and 90-day Mortars

3.3 SEM Analysis

In order to elucidate the influence of NC particles on the hydration mechanism for curing age of 180 days on cement-based mortars with/without fly ash, scanning electron microscope (SEM) analysis has been conducted. For this purpose, mortar specimens including only normal Portland cement without NC and also specimens with only a 2.5% of NC, regardless of fly ash content, were subjected to SEM analysis.

As seen in the Figure 3.4, more ettringite formation was monitored in NC_2.5_FA/PC_0.0 (where a 2.5% of NC used) than NC_0.0_FA/PC_0.0 (only Normal Portland Cement). It is known that ettringite has been formed as a result of the reactions conducted between gypsum (source of calcium sulphate) and aluminate phases of cement, namely C_3A and C_4AF. On the depletion of gypsum, the rest of aluminate phase (C_3A and C_4AF) is reacted with the ettringite and thus monosulphate or hydroxy-AFm solid solution forms. In the presence of NC (as a source of $CaCO_3$), NC is reacted with aluminate phase of cement and/or pozzolanic materials in order to generate mono- or hemi-carboaluminates and consequently prevent the decomposition of ettringite formation. Therefore, in the presence of NC, the formed ettringite (AFt) is indirectly stabilized not to be transformed to monosulfate (AFm) (De Weerdt et al. 2011) and the ettringite has remained in the cement-based matrix. In term of ettringite formation/decomposition, the results of SEM (in Figure 3.4) are in line with the literature as mentioned.

In addition, SEM images in Figure 3.5 showed that there were unreacted/agglomerated NC particles and calcium hydroxide (CH) in the mixtures of NC_2.5_FA/PC_1.0 (Figure 3.5-a) where the highest volume of fly ash was used and of NC_0.0_FA/PC_0.0 (Figure 3.5-b), respectively. These unreacted NC particles may be an evidence that (i) 2.5% is still too high for replacement level of NC (this finding was also confirmed by the results of compressive strength results where 2.5% of NC is adequate for current mixture proportions and there was no or a slight increase when the replacement level of cement with NC was exceeded 2.5%.) since some researchers (Yang et al. 2018) has also found that a 1-2 % of NC is adequate or (ii) may be attributed to nonuniform dispersion due to agglomeration of NC particles being exposed to high Wan der Wall forces. In addition to these, in the SEM images of mortars after 180 days, it is seen that there was also unhydrated fly ash particles (Figure 3.5-c) deposited in the cement-based matrix. Even though both unreacted NC and fly ash particles exists in the matrix they are still behaves as a filler to heal/enhance cement microstructure being led to a more densified and compacted morphology. Weerdt et al. (2011) has found that NC affects both calcium hydroxide and carboaluminate content where calcium hydroxide (CH) as a hydration product has been consumed by the formation of calcium hemicarboaluminate hydrate (Hc) which is a hydration product of reaction conducted between aluminate phase and NC. In addition, they were also noted that after 7 days and longer a larger peak for Hc is observed, which gradually decreased later on as monocarbonate (Mc) has been formed instead (Ipavec et al. 2011). These findings are in line with the result of the current experimental study in which fly ash as a supplementary cementitious material could not be able to consume CH since CH has been consumed by calcium hemicarboaluminate hydrate after 7 days and longer (De Weerdt et al. 2011) and thus resulting in unhydrated fly ash particles. In addition to this, it was also found in the SEM image of Figure 3.5-d that only the additional hydration product of Mc has been identified after 180 days and no calcium hemicarboaluminate hydrate has been detected which proves the results mentioned previously.



a) NC_0.0_FA/PC_0.0

b) NC_2.5_FA/PC_0.0

Figure 3.4. Ettringite formation a) without NC and b) with NC

3.4 Ultrasonic Pulsive Velocity (UPV)

Ultrasonic pulsive velocity (UPV) which is a non-destructive testing method is used in order to evaluate microstructural characteristics of cement-based materials, such as compactness, quality, homogeneity, uniformity, density, internal cracks and also porosity (Sumesh et al. 2017; Karagol et al. 2013). UPV test results for curing ages of 1-, 3-, 7-, 28- and 90-Day are represented in Figure 3.6. As seen in the Figure 3.6-a, b and c, it is easily seen that using higher volume of FA as a partial replacement to cement decreases the UPV values of mixtures. This is attributed to lower pozzolanic reaction of FA at the early age (Mohammed et al. 2018) which leads to decrease in density of microstructure, thus resulting in more discontinuities, less improvement in strength and consequently lower UPV values (Rao et al. 2016). It was also revealed that regardless of FA and NC replacement levels, the difference between UPV values at early ages are very high while this difference decreased in the later curing ages. Higher UPV values obtained (where the higher transmission speed of wave means more compactness and therefore higher compressive strength) at the later ages as a result of increased hydration reactions and products (Demirhan et al. 2019). This might be because of the decrease in the pore structure being filled by NC particles and also due to the formation of C-S-H gels and the additional hydration products as a result of pozzolanic reactions and seeding and/or chemical effects (Zareei et al. 2019). In the mixtures without FA (Figure 3.6-d), a decrease in microstructural density was found as a result of dilution effect as NC replacement level increased. Thus, a slight decrease in UPV values was observed. In addition, there was a slight decrease in UPV values with the increase in NC replacement level (Figure 3.6.-d) and thus better UPV results were observed in mixtures including a 2.5% of NC.

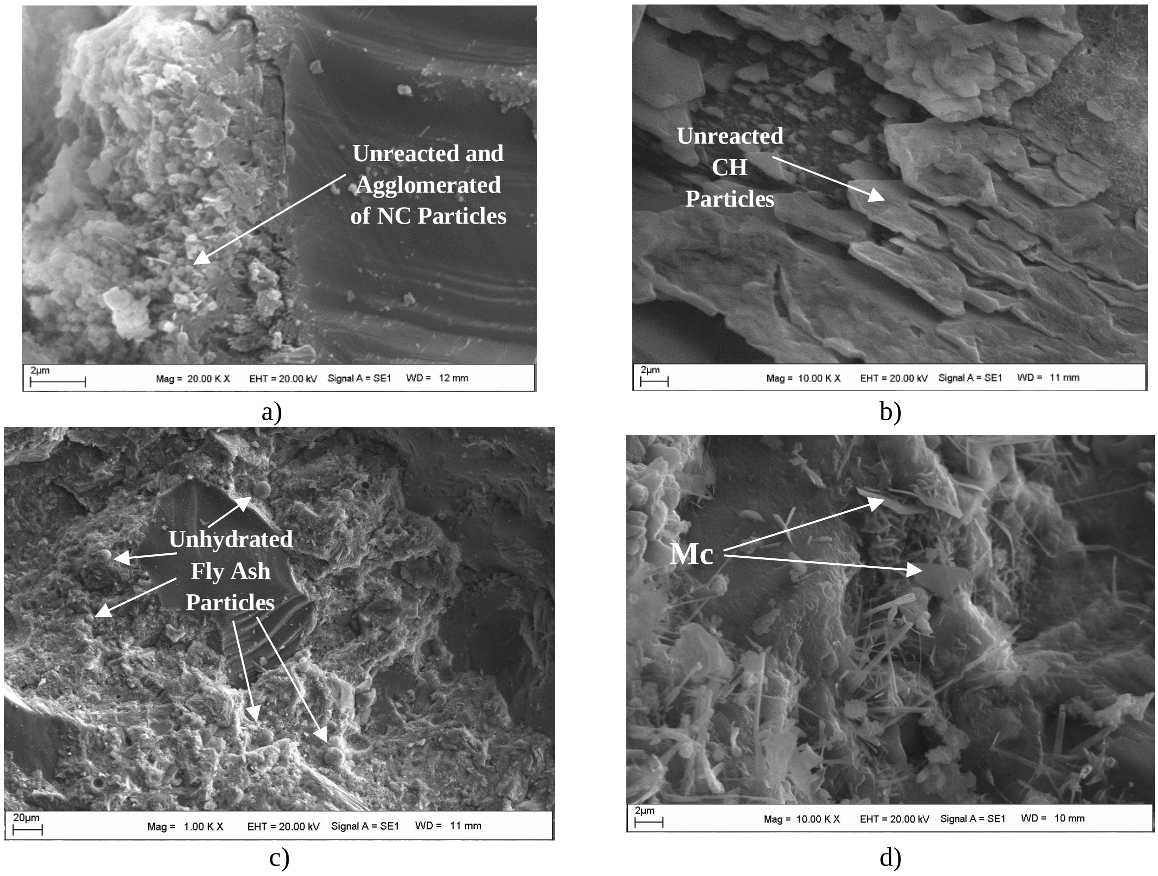
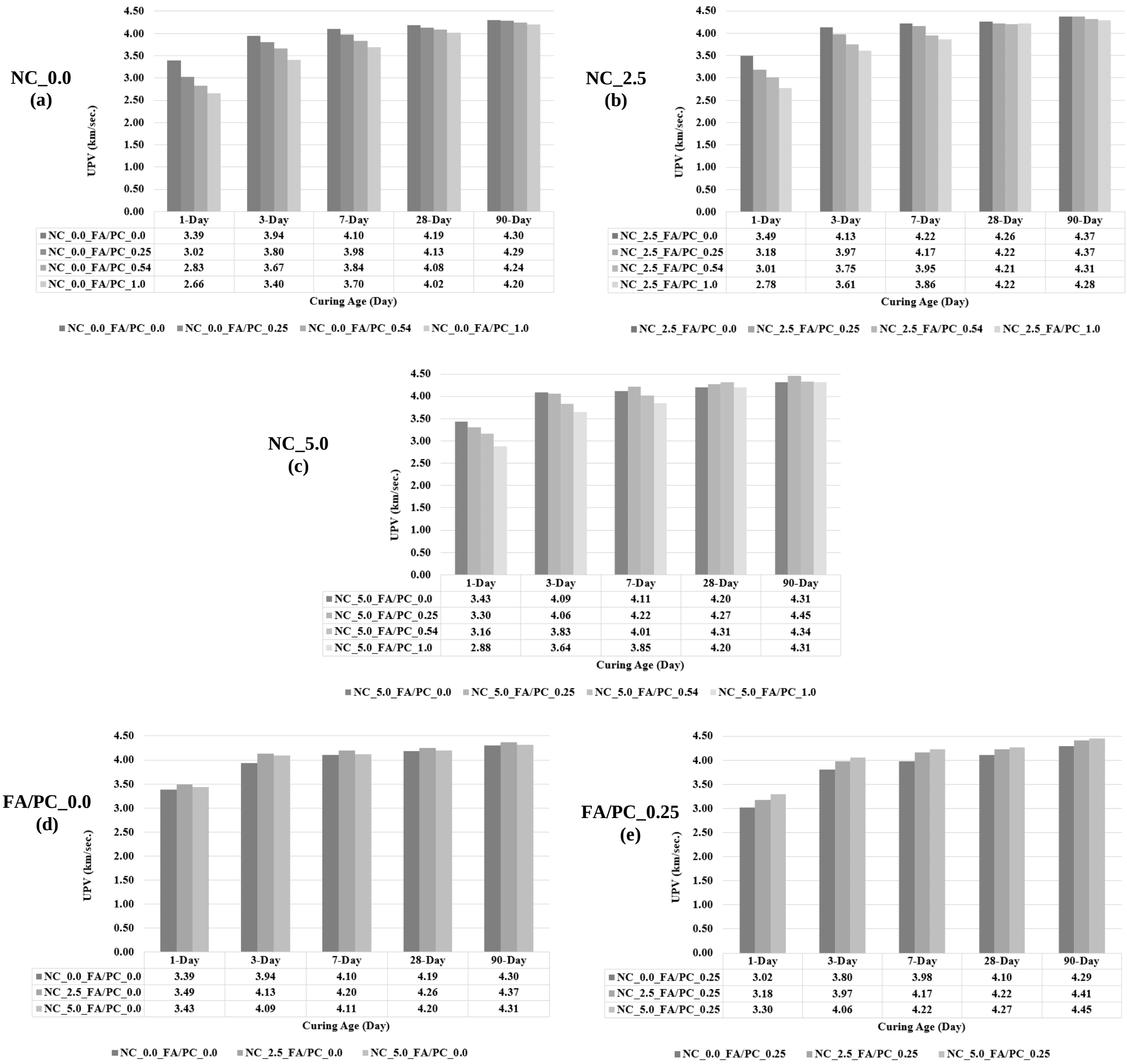


Figure 3.5. SEM images of a) unreacted and/or agglomerated NC particles, b) unreacted CH particles, c) unreacted Fly Ash particles and d) Mc products detected in mixtures including both of NC and Fly Ash

In all mixtures given in the Figure 3.6. d-g, especially at the 3-day curing age, an increase in hydration products was observed as a result of combined effects of the nucleation effect (promoted reactions of C_3S in the presence of NC) and the chemical effect (reactions occurring between total aluminate phases and NC). Therefore, due to the increase in microstructural density, an increase in UPV value was obtained. In addition to this, it is also seen that (Figure 3.6. e-g) as the FA replacement level increased due to including higher aluminate phase (comparing to ordinary normal Portland cement) (See Table 1), the UPV values increased as a result of both nucleation and chemical effects. The highest contribution to the microstructure was observed in mixtures coded as FA/PC=0.25 while a slight decrease was also obtained with the increase in FA replacement level. Even though decrease in early age UPV values was obtained as FA amount was increased, (comparing to 0.0 coded mixtures of without FA) almost the same UPV results were obtained at later curing ages of mixtures including the highest FA content (50% of FA) (Figure 3.6. e-g).

Combined effect of nucleation and chemical effects resulted in almost the same microstructural property in NC_2.5_FA/PC_1.0 (50% Cement+50% FA) comparing to NC_0.0_FA/PC_0.0 (100% Cement). Microstructural quality of cement-based material could be classified as excellent, good, doubtful, poor and very poor for UPV values more than 4.5 km/sec., 3.5-4.5 km/sec., 3.0-3.5 km/sec., 2.0-3.0 km/sec. and less than 2.0 km/sec., respectively (Belaribi et al. 2016). Regardless of the FA utilization rate, the UPV value of all mixtures was observed over 4 km/sec. at the curing age of 28-day in the presence of NC. Malhotra (1976) suggested that cement-based material has a good durability when its UPV value is in the interval of 3.66–4.58 km/sec. In the current experimental research, since the UPV values were higher than 4 km/sec. all mixtures could be classified as a durable mortar (Mohseni et al. 2015), namely, they could be considered as “good”.



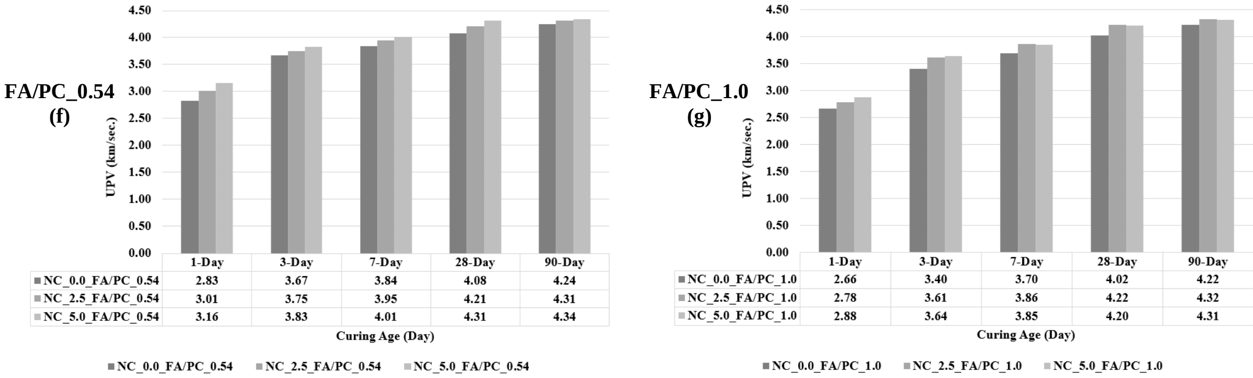


Figure 3.6. 1-, 3, 7-, 28- and 90-Day UPV results

4. Conclusion

Influence of nano-sized calcite produced by top-down approach and high-volume fly ash (up to 50%) on the fresh and hardened properties of standardly produced cement mortars and also microstructural characteristics were investigated in this research. Based on the findings and discussions given before, the following conclusions can be drawn:

- ✓ Different mechanisms [nucleation (seeding) effect, dilution effect and chemical effect] were observed in the presence of nano-sized calcite with and/or without fly ash.
- ✓ Even though surface area to volume ratio is very high in nano-sized materials which results in higher water requirement, increase in NC replacement level resulted in lower degree of wetness since NC shows a hydrophobic property. In addition, the higher volume of fly ash the higher standard consistency value.
- ✓ Regardless of fly ash content, as a result of both seeding and chemical effects, hydration was promoted and thus shorter setting times were observed. Higher volume of fly ash lead to more delayed setting times because of slow pozzolanic reactivity. Moreover, reduction in setting times was clearer in the mixtures where NC and FA used together.
- ✓ Increase in fly ash content showed a lower strength development due to delayed pozzolanic reactivity. Regardless of fly ash, enhancement was monitored at both early and later curing ages of mixtures and this strength-gain-accelerating efficacy was attributed to presence of NC particles which was acted as a nuclei in order to promote hydration of cement and to densify microstructure of matrix at the early ages
- ✓ For the mixtures including only normal Portland cement increase in NC amount showed a dilution effect, namely, the same or a slight decrease in compressive strength.
- ✓ Compressive strength values of NC_0.0_FA/PC_0.0 (including 100% cement) and NC_2.5_FA/PC_1.0 (including 50% cement) at curing age of 90 days were 43.2 MPa and 45.9 MPa, respectively, where a significant reduction in the carbon footprint of cement is obtained.
- ✓ In general, a 2.5% replacement level of NC showed better results in terms of contribution and economy.
- ✓ Tailored blended cements composed of higher fly ash content (up to 50% replacement level) can significantly reduce the carbon footprint of cement-based materials.
- ✓ In SEM images, more ettringite formation was observed in the mixtures including NC and ettringite was indirectly stabilized not to be transformed to monosulfate since the aluminate phase has been consumed by NC.
- ✓ Since CH has been consumed by calcium hemicarboaluminate hydrate (Hc) unhydrated fly ash particles (which were not

able to take place in pozzolanic reaction) were detected in some mixtures.

- ✓ UPV values were decreased in higher fly ash contents while UPV values were increased with the increase in the curing age.
- ✓ UPV results of NC_0.0_FA/PC_0.0 (including 100% cement) and NC_2.5_FA/PC_1.0 (including 50% cement) had almost the same value in common.

5. References

Arora, A., Sant, G., & Neithalath, N. (2016). Ternary blends containing slag and interground/blended limestone: Hydration, strength, and pore structure. *Construction and Building Materials*, **102**, 113-124.

Bentz, D. P., Ardani, A., Barrett, T., Jones, S. Z., Lootens, D., Peltz, M. A., ... & Weiss, W. J., (2015). Multi-scale investigation of the performance of limestone in concrete. *Construction and Building Materials*, **75**, 1-10.

Bonavetti, V. L., Rahhal, V. F., & Irassar, E. F., 2001. Studies on the carboaluminate formation in limestone filler-blended cements. *Cement and Concrete Research*, 31(**6**), 853-859.

Bosiljkov, V.B., 2003. SCC mixes with poorly graded aggregate and high volume of limestone filler. *Cement and Concrete Research*, **33**, 1279–1286.

Camiletti, J., Soliman, A. M., & Nehdi, M. L., 2013. Effect of nano-calcium carbonate on early-age properties of ultra-high-performance concrete. *Magazine of Concrete Research*, 65(**5**), 297-307.

Cao, M., Ming, X., He, K., Li, L., & Shen, S., 2019. Effect of macro-, micro-and nano-calcium carbonate on properties of cementitious composites—A review. *Materials*, 12(**5**), 781.

Damidot, D., Lothenbach, B., Herfort, D., & Glasser, F. P., 2011. Thermodynamics and cement science. *Cement and Concrete Research*, 41(**7**), 679-695.

Das, S., Aguayo, M., Dey, V., Kachala, R., Mobasher, B., Sant, G., & Neithalath, N., 2014. The fracture response of blended formulations containing limestone powder: Evaluations using two-parameter fracture model and digital image correlation. *Cement and Concrete Composites*, **53**, 316-326.

De Weerdt, K., Justnes, H., Kjellsen, K. O., & Sellevold, E., 2010. Fly ash-limestone ternary composite cements: synergetic effect at 28 days. *Nordic Concrete Research*, 42(**2**), 51-70.

De Weerdt, K., Haha, M. B., Le Saout, G., Kjellsen, K. O., Justnes, H., & Lothenbach, B., 2011. Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash. *Cement and Concrete Research*, 41(**3**), 279-291.

De Weerdt, K., Kjellsen, K. O., Sellevold, E., & Justnes, H., 2011. Synergy between fly ash and limestone powder in ternary cements. *Cement and concrete composites*, 33(**1**), 30-38.

Demirhan, S., Turk, K., & Ulugerger, K., 2019. Fresh and hardened properties of self-consolidating Portland limestone cement mortars: Effect of high-volume limestone powder replaced by cement. *Construction and Building Materials*, **196**, 115-125.

Duval, R., 2002. Effect of ultrafine particles on heat of hydration of cement mortars. *Materials Journal*, 99(**2**), 138-142.

Ge, Z., Wang, K., Sun, R., Huang, D., & Hu, Y., 2014. Properties of self-consolidating concrete containing nano-CaCO3. *Journal of Sustainable Cement-Based Materials*, 3(**3-4**), 191-200.

Hassiba, B., Mekki, M., & Fraid, R., 2018. The relationship between the compressive strength and ultrasonic pulse velocity concrete with fibers exposed to high temperatures. *International Journal of Energetica*, **3**, 31-6.

He, Z., Zhu, X., Wang, J., Mu, M., & Wang, Y., 2019. Comparison of CO2 emissions from OPC and recycled cement production. *Construction and Building Materials*, **211**, 965-973.

Hosan, A., & Shaikh, F. U. A., 2020. Influence of nano-CaCO3 addition on the compressive strength and microstructure of high-volume slag and high-volume slag-fly ash blended pastes. *Journal of Building Engineering*, **27**, 100929.

Ipavec, A., Gabrovšek, R., Vuk, T., Kaučič, V., Maček, J., & Meden, A., 2011. Carboaluminate Phases Formation During the Hydration of Calcite-Containing Portland Cement. *Journal of the American Ceramic Society*, 94(**4**), 1238-1242.

Jamora, J. B., Gudia, S. E. L., Go, A. W., Giduquio, M. B., & Loretero, M. E., 2020. Potential CO2 reduction and cost evaluation in use and transport of coal ash as cement replacement: A case in the Philippines. *Waste Management*, **103**, 137-145.

Kakali, G., Tsivilis, S., Aggeli, E., & Bati, M., 2000. Hydration products of C3A, C3S and Portland cement in the presence of CaCO3. *Cement and concrete Research*, 30(**7**), 1073-1077.

Karagöl, F., Demirboğa, R., Kaygusuz, M. A., Yadollahi, M. M., & Polat, R., 2013. The influence of calcium nitrate as antifreeze admixture on the compressive strength of concrete exposed to low temperatures. *Cold Regions Science and Technology*, **89**, 30-35.

Kenai, S.; Soboyejo,W.; Soboyejo, A., 2004. Some engineering properties of limestone concrete. *Materials and manufacturing processes*, **5**, 949–961.

Lertwattanaruk, P.; Sua-iam, G.; Makul, N., 2018. Effects of calcium carbonate powder on the fresh and hardened properties of self-consolidating concrete incorporating untreated rice husk ash. *Journal of Cleaner Production*, **172**, 3265–3278.

Liu, X.; Chen, L.; Liu, A.; Wang, X., 2012. Effect of Nano-CaCO3 on properties of cement paste. *Energy Procedia*, **16**, 991–996.

Liu, M., Tan, H., & He, X., 2019. Effects of nano-SiO2 on early strength and microstructure of steam-cured high volume fly ash cement system. *Construction and Building Materials*, **194**, 350-359.

Lu, G., & Wang, K., 2010. Investigation into yield behavior of fresh cement paste: model and experiment. *ACI Materials Journal*, 107(**1**), 12.

Malhotra, V. M., 1976. Testing hardened concrete: Non-destructive methods, ISBN: 13: 978-1-4200-4005-0, ACI Monograph No. 9, ACI. Iowa State University Press, Ames, Iowa, USA, 8-14.

Meng, T., Yu, Y., & Wang, Z., 2017. Effect of nano-CaCO3 slurry on the mechanical properties and micro-structure of concrete with and without fly ash. *Composites Part B: Engineering*, **117**, 124-129.

Mohammed, B. S., Adamu, M., & Liew, M. S., 2018. Evaluating the effect of crumb rubber and nano silica on the properties of high volume fly ash roller compacted concrete pavement using non-destructive techniques. *Case studies in construction materials*, **8**, 380-391.

Mohseni, E., Ranjbar, M. M., & Tsavdaridis, K. D., 2015. Durability properties of high-performance concrete incorporating nano-TiO2 and fly ash. American *Journal of Engineering and Applied Sciences*, 8(**4**), 519-526.

Moon, J., Oh, J. E., Balonis, M., Glasser, F. P., Clark, S. M., & Monteiro, P. J., 2012. High pressure study of low compressibility tetracalcium aluminum carbonate hydrates 3CaO· Al2O3· CaCO3· 11H2O. *Cement and Concrete Research*, 42(**1**), 105-110.

Nath, P., Sarker, P. K., & Biswas, W. K., 2018. Effect of fly ash on the service life, carbon footprint and embodied energy of high strength concrete in the marine environment. *Energy and Buildings*, **158**, 1694-1702.

Pera, J., Husson, S., & Guilhot, B., 1999. Influence of finely ground limestone on cement hydration. *Cement and Concrete Composites*, 21(**2**), 99-105.

Rao, S. K., Sravana, P., & Rao, T. C., 2016. Experimental studies in Ultrasonic Pulse Velocity of roller compacted concrete pavement containing fly ash and M-sand. *International Journal of Pavement Research and Technology*, 9(**4**), 289-301.

Sanchez, F., & Sobolev, K., 2010. Nanotechnology in concrete–a review. *Construction and building materials*, 24(**11**), 2060-2071.

Sandanayake, M., Gunasekara, C., Law, D., Zhang, G., & Setunge, S., 2018. Greenhouse gas emissions of different fly ash based geopolymer concretes in building construction. *Journal of cleaner production*, **204**, 399-408.

Sato, T., & Beaudoin, J. J., 2011. Effect of nano-CaCO3 on hydration of cement containing supplementary cementitious materials. *Advances in Cement Research*, 23(**1**), 33-43.

Shaikh, F. U., & Supit, S. W., 2014. Mechanical and durability properties of high-volume fly ash (HVFA) concrete containing calcium carbonate (CaCO3) nanoparticles. *Construction and building materials*, **70**, 309-321.

Shwekat, K., & Wu, H. C., 2018. Benefit-cost analysis model of using class F fly ash-based green cement in masonry units. *Journal of Cleaner Production*, **198**, 443-451.

Sobolev, K., & Gutiérrez, M. F., 2005. How nanotechnology can change the concrete world. *American Ceramic Society Bulletin*, 84(**10**), 14.

Sumesh, M., Alengaram, U. J., Jumaat, M. Z., Mo, K. H., & Alnahhal, M. F., 2017. Incorporation of nano-materials in cement composite and geopolymer based paste and mortar–A review. *Construction and Building Materials*, **148**, 62-84.

Supit, S. W., & Shaikh, F. U., 2014. Effect of nano-CaCO3 on compressive strength development of high-volume fly ash mortars and concretes. *Journal of Advanced Concrete Technology*, 12(**6**), 178-186.

Thongsanitgarn, P., Wongkeo, W., & Chaipanich, A., 2014. Hydration and compressive strength of blended cement containing fly ash and limestone as cement replacement. *Journal of Materials in Civil Engineering*, 26(**12**), 04014088.

Tosti, L., van Zomeren, A., Pels, J. R., & Comans, R. N., 2018. Technical and environmental performance of lower carbon footprint cement mortars containing biomass fly ash as a secondary cementitious material. *Resources, Conservation and Recycling*, **134**, 25-33.

Tosti, L., van Zomeren, A., Pels, J. R., Damgaard, A., & Comans, R. N., 2020. Life cycle assessment of the reuse of fly ash from biomass combustion as secondary cementitious material in cement products. *Journal of cleaner production*, **245**, 118937.

Turgut, P., 2018. Production of block by using fly ash, lime and glass powder. *Pamukkale Unıversıty Journal Of Engineering Sciences-Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi*, 24(**3**), 413-418.

Turgut, P., & Ogretmen, A., 2019. Optimum limestone powder amount in mortars with over silica fume. *Epitoanyag-Journal of Silicate Based & Composite Materials*, 71(**2**).

Uysal, M., 2012. Self-compacting concrete incorporating filler additives: Performance at high temperatures. *Construction and Building Materials*, **26**, 701–706

Vance, K., Aguayo, M., Oey, T., Sant, G., & Neithalath, N., 2013. Hydration and strength development in ternary portland cement blends containing limestone and fly ash or metakaolin. *Cement and Concrete Composites*, **39**, 93-103.

Voglis, N., Kakali, G., Chaniotakis, E., & Tsivilis, S., 2005. Portland-limestone cements. Their properties and hydration compared to those of other composite cements. *Cement and Concrete Composites*, 27(**2**), 191-196.

Wang, D., Shi, C., Farzadnia, N., Shi, Z., Jia, H., & Ou, Z., 2018. A review on use of limestone powder in cement-based materials: Mechanism, hydration and microstructures. *Construction and Building Materials*, **181**, 659-672.

Wu, Z., Shi, C., & Khayat, K. H., 2018. Multi-scale investigation of microstructure, fiber pullout behavior, and mechanical properties of ultra-high-performance concrete with nano-CaCO3 particles. *Cement and Concrete Composites*, **86**, 255-265.

Wu, Z., Shi, C., Khayat, K. H., & Wan, S., 2016. Effects of different nanomaterials on hardening and performance of ultra-high strength concrete (UHSC). *Cement and Concrete Composites*, **70**, 24-34.

Xiao, H., Wang, W., & Goh, S. H., 2017. Effectiveness study for fly ash cement improved marine clay. *Construction and Building Materials*, **157**, 1053-1064.

Yang, H., Che, Y., & Leng, F., 2018. High volume fly ash mortar containing nano-calcium carbonate as a sustainable cementitious material: microstructure and strength development. *Scientific reports*, 8(**1**), 16439.

Yeşilmen, S., Al-Najjar, Y., Balav, M. H., Şahmaran, M., Yıldırım, G., & Lachemi, M., 2015. Nano-modification to improve the ductility of cementitious composites. *Cement and Concrete Research*, **76**, 170-179.

Zaitri, R., Bederina, M., Bouziani, T., Makhloufi, Z., & Hadjoudja, M., 2014. Development of high performances concrete based on the addition of grinded dune sand and limestone rock using the mixture design modelling approach. *Construction and Building Materials*, **60**, 8-16.

Zareei, S. A., Ameri, F., Bahrami, N., Shoaei, P., Moosaei, H. R., & Salemi, N., 2019. Performance of sustainable high strength concrete with basic oxygen steel-making (BOS) slag and nano-silica. *Journal of Building Engineering*, **25**, 100791.

Zou, F., Hu, C., Wang, F., Ruan, Y., & Hu, S., 2020. Enhancement of early-age strength of the high content fly ash blended cement paste by sodium sulfate and C–S–H seeds towards a greener binder. *Journal of Cleaner Production*, **244**, 118566.