

Mechanical and Morphological Investigation of Cement Paste Containing Nano Silica

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Abstract

Cement paste matrix is a porous material composed primarily of calcium hydroxide (portlandite), aluminates and anhydrate cement (clinker) embedded into an amorphous structured hydration product called calcium silicate hydrate gel. The enhancement in calcium silicate hydrate product leads to enhancing the cement paste properties and thus improves the entire concrete composites properties. NS replacement of cement paste (at 3%, 6% and 9% of binder) was investigated and compared to a control cement paste. Fresh and mechanical properties were investigated according to the appropriate standards. XRD and TGA analyses were used to determine the physical properties of the components and SEM was used to identify morphological changes for comparison. Flowability was found to increase from 20 cm in the control mixture to 24 cm in with 9% NS replacement. The 3% replacement specimen provided 50% and 29% higher compressive and flexural strength at early ages, compared to the control, respectively. The 6% NS replacement provided the highest compressive and flexural strengths at 28 days, but the 9% replacement performed worse than all other specimens for all mechanical tests. XRD results indicate that, the cement powder contained three main elements C₂S, C₃S, and CaCO₃, there were shortages of Al, and Fe compared with what was expected. The TGA indicated 3% NS replacement increased CSH content and a decrease in enthalpy of Ca(OH)₂ and had the smallest decrease in weight at 1000°C. SEM images show a denser microstructure with fewer voids when comparing the 3% NS replacement to the control and free NS randomly distributed in structure indicating NS has the ability to improve the hydration process by providing numerous hydration sites.

KEYWORDS

Cement Paste, Nano Silica, Mechanical Properties, Physical Properties, Hydration Process

INTRODUCTION:

Although Portland cement has been one of the most utilized commodities in the world for decades, it is improving continuously. Investigating the complex structure of cement-based materials at the micro and the nano levels may facilitate the discovery of a new type of concrete, which is stronger and more durable than currently available with more optimal stress-strain behavior and, potentially, an entire range of new mechanical and physical properties. Cement paste is a composite material with multi-scale internal structures. The cement paste matrix is a porous material composed of calcium hydroxide (portlandite), aluminates and anhydrate cement (clinker) embedded into a nano-structured hydration product called the C-S-H gel. This gel is the most important hydration product of the cement paste, not only because it is the most abundant component (50–70% by volume), but also because it carries exceptional mechanical properties (Gaitero, et al. 2008).

Recently, with the rapid advancement and availability of nano-materials, several research programs have investigated their effects on durability and strength of nano-enhanced cement paste. Sobolev et al. (2006) investigated the mechanical properties of mortars with NS synthesized by the sol-gel method. Their experimental results demonstrated an increase in the compressive strength of mortars with developed nanoparticles at early stages of hardening followed by strength reduction at a later age. Addition of a superplasticizer was proposed to

overcome this obstacle. Superplasticized mortars with selected NS demonstrated a 15-20% increase in the compressive strength up to 144.8 MPa at the 90-day age. Mechano-chemical activation was found to be an effective method to improve the strength of cement-based materials. It was proposed that this process is governed by the solid-state interaction between the organic modifiers and cement. During this process, the surface of the cement particles attach the functional groups introduced from the modifiers to form the mineral nano-layers or nano-grids on the surface of cement. High-performance cements demonstrate the 28-day compressive strength at the range of 93 - 115 MPa, which is higher than the 72 - 89 MPa strength of reference cements.

Jo et al. (2007) added nano-SiO₂ particles to achieve high-performance of concrete. They found that the compressive strengths of mortars with nano-SiO₂ particles were higher than those of mortars incorporating silica fume at 7 and 28 days. It has been confirmed that the NS are more valuable in enhancing strength than silica fume. Scanning electron micrograph (SEM) was utilized to monitor the hydration process. The findings indicated that NS behaves not only as a filler to improve the microstructure, but also as an activator, which promotes the pozzolanic reaction.

Zaki et al. (2010) investigated the technical feasibility of modifying the water permeability of high performance concrete by NS. Four different percentages of NS: 0%, 0.5%, 0.7% and 1% by cementitious weight concrete mixtures were studied in water permeability tests after 28 days. The morphology of nano particles was determined using transmission electron microscopy (TEM), and the minerals were identified using X-ray diffraction (XRD). High Performance Concrete (HPC) containing 0 and 1% NS by cement weight were both identified using scanning electron microscopy (SEM). The results indicate that the addition of NS leads to a significant decrease in water permeability for concrete.

Nazari and Riahi (2011) studied the heat of hydration up to 70 h of cement pastes modified with NS. Cement was partially replaced with NS at levels of 0%, 0.5%, 1%, 1.5% and 2%, by weight. A fixed w/b ratio of 0.4 was used, and either water or saturated limewater was used for mixing. The results showed that decreasing the NS content in the pastes retarded peak times and raised the heat release rate values. Additionally, the specimens containing saturated limewater showed a reduction in the peak time and heat release rate values, with respect to the corresponding specimens containing water.

Stefanidou and Papayianni (2012) added NS at levels of 0%, 0.5%, 1%, 2% and 5% by weight in cement pastes; various w/b ratios were used. The results showed that the addition of 0.5% NS provided the highest compressive strength followed by 2% and 1%, respectively. The addition of 5% NS resulted in a comparable compressive strength to the control at early ages, but had a lower compressive strength than the control at the age of 28 days. They also studied the effect of fixed dosage of superplasticizer on compressive strength. The results showed that the addition of 1% NS gave the highest compressive strength, while the addition of 5% NS gave the lowest compressive strength.

In order to be sustainable, the physical and mechanical properties of cement paste must be improved and the use of nano-particles holds considerable promise, based on the literature.

The main aim of this research work is to generally improve and amplify our knowledge of NS and its properties in cement paste. Need to generate more calcium-silicate-hydrate (C-S-H) gel by making use of all calcium hydroxide Ca(OH)₂, to obtain high durability for cement past. The effects of main factors (nano material content percent) that would impact the cement paste behavior are intensively investigated. Based on the experimental results, more information about several aspects of cement paste incorporating NS is gained.

EXPERIMENTAL PROGRAM

The experimental program was divided into two main phases. The first phase was designed to intensively investigate mechanical properties. In the second phase, to study physical properties and micro structure characteristics of mixtures with various compositions. Cement paste properties were classified based upon two factors: NS content and age of curing.

All materials involved in the current experimental work were selected from local sources in Egypt with the exception of the Nanoparticles of Silica (NS), which were obtained from an international commercial supplier. The physical properties of the NS are listed in **Table 1**, and clearly illustrated in **Figure 1**. A commercially available Portland cement (CEM I 42.5 N) of surface area 3500 cm²/g and specific gravity 3.15 g/cm³ was used. The chemical properties of the cement are shown in **Table 2**. Potable water was used as the mixing water in the production of all tested cement paste mixtures. A non-retarding high range water reducer was used for both concrete and mortar mixes. A 2%, by weight of the binder, dosage of high range water reducer was used to produce the 20 cm ASTM.C1437 flowability desired for the control sample. **Table 3** indicates some of the physical and chemical properties of the polycarboxylate admixture used in the experiments.

Table 1: Physical Properties of Silica Nanoparticles

Diameter (nm)	Surface area (m ² /g)	Density (g/cm ³)	Purity (%)
20-60	400-600	<0.15	99.9



Figure 1: NS particles

Table 2: Chemical Composition of Portland cement

Chemical Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	NaO	K ₂ O	Loss on Ignition
%	20.39	5.6	3.43	63.07	2.91	0.7	0.38	0.35	2.06

Table 3: Physical and Chemical Properties of the Used Polycarboxylate Admixture

Appearance	Solid residue	pH	Specific gravity	Rotational Viscosity (MPa)	C %	Na ⁺ PPM	K ⁺ PPM
Yellow-Brown Liquid	36%	6.6	1.10	79.30	52.25	9150	158

Cementitious composite mixtures were produced using a rotating pan mixer with a 3 liter capacity. For each mixture, an identical mixture was disposed of immediately before mixing the true batch, a process often called “buttering” of the mixer. This operation limited

the effect of the mixer dryness/wetness condition on the first intended mixture, and eliminated the possibility of a damp drum mixer affecting the results of the first intended mixture. Cement paste was prepared at a water–binder (cement + NS) ratio “W/B=0.35”. The amount of superplasticizer (SP) was 2% of the weight of the binder. The cement paste was produced with the components listed in **Table 4** with 0%, 3%, 6% and 9% NS in weight replacing cement. The mixing process depends on the presentation of the nanoparticles as a colloidal dispersion (CS). Where the dispersion was mixed with the superplasticizer, water and stirred for 5 min at a high speed 120 rpm before adding the solution to the cement. The solution was then gradually added to the cement, and mixed at a medium speed of 80 rpm.

Table 4: Cement Paste Formulations

No	NS%	Mixture Components			
		Cement (g)	NS (g)	Superplasticizer (g)	Water (ml)
MS0	0	5606.53	0.00	112.13	2242.61
MS3	3	5438.34	168.20		
MS6	6	5270.14	336.39		
MS9	9	5101.94	504.59		

Samples were cast into a (50x50x50 mm) cube for compression and (40×40×160 mm) prisms were utilized for flexure using steel molds. The molds were oiled first, and placed horizontally on the floor. After mixing, cement paste was released from the mixer, and fresh mix properties were measured. Casting was then conducted in two layers, and compacted on an electrical vibration table, where each layer was vibrated for 10 sec. The samples were placed for 24 hours in a control room at 20 °C with 99% relative humidity. After that time, samples were demolded, and placed into a saturated lime solution, with a concentration of 4 grams of lime to 4 litres of water to prevent any premature loss of calcium during the remaining 27 days of curing. The water solution was stirred daily. At the end of this period, the samples were moved into a 105°C furnace for drying until their weight became constant and then the samples were then tested.

Test Program

The testing process was comprised two main types of testing: mechanical properties testing and physical properties testing after confirming the consistency of fresh samples.

The flow table test was performed after mixing following the **ASTM C 1437-07, (2007)**. This test is widely used to evaluate the workability of cement paste and mortar, because it is easy to conduct, and allows some parameters such as viscosity to be inferred. Compressive, flexure strength, modulus of elasticity (MOE) and toughness factor testing were carried out according to the **Egyptian.Code, (2007)** test method at 3, 7 and 28 days using cube specimens. The MOE and toughness factor were calculated using a compressometer apparatus in the elastic range. All specimens were continuously water-cured prior to oven drying just before testing. At each testing age, three specimens representing each paste mixture were tested using a Universal Testing Machine under load control, and its average value was reported. The rate of loading was 0.24 MPa/sec. The XRD test was carried out on the various raw materials according to **ASTM E1361-02, (2007)** in order to identify the atomic and molecular structure of the crystals. A differential scanning calorimeter (DSC) is a fundamental tool in thermal analysis and combined with the XRD used to understand the amorphous and crystalline behavior. DSC was used to ascertain thermo-grams of the hardened paste. Scanning electron microscopy (SEM) (FEI- Inspect S) was used to examine

the microstructure of the different mixes, and to observe the surface of the specimens.. The SEM examination was done according to **ASTM.C1723, (2010)**.

RESULTS AND DISCUSSIONS

Fresh Properties

Additional details about the mix proportions are provided as fresh properties identified through the flow table test. The workability of the cement paste with different percentages of NS and the flow diameters were increased by increasing the NS content in the mixture. The plot in **Figure 2** shows that the higher the percentage of NS, the greater the flowability of the CP to reach the table diameter; this also indicates and confirms the hydrophobicity of NS, and its foamy consistency.

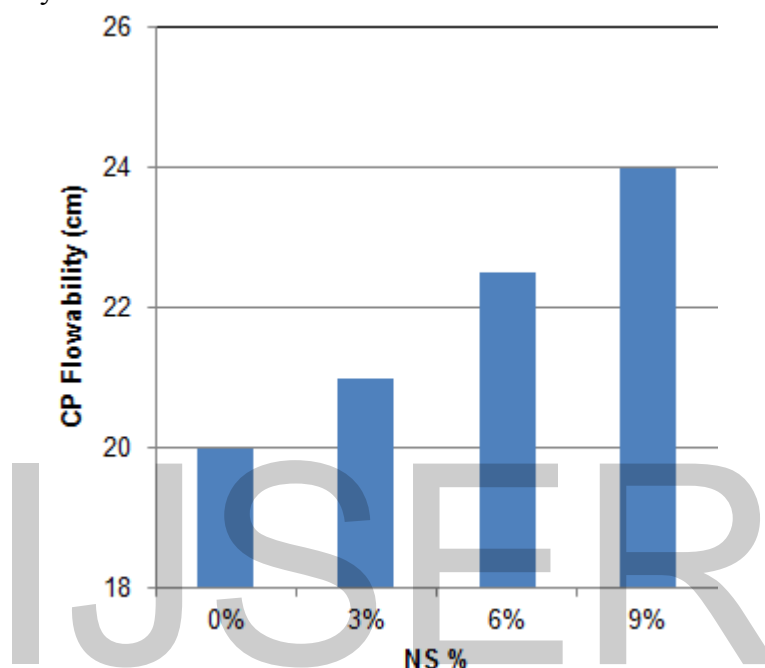


Figure 2: Results of flow table test based on NS percent in Cement Paste

Mechanical Properties

The average compressive strengths of cement paste were measured at 3, 7 and 28 days of curing to assess the development of the hydration process and strength gain. **Figure 3** indicates the average compressive strength of whole samples at ages 3, 7 and 28 days is graphed in **Figure 3**. The 3% percentage of NS improves the compressive strength by 50.15 % and 20.02% over the control sample at 3 days and 7 days, respectively. These results suggests that such an admixture at the 3% dosage could be utilized to obtain an early high strength, but the effect on final strength is unclear. The 6% replacement did not have the same effect on the early strength, but provided the highest 28 day strength, exhibiting a compressive strength 42.44% higher than the control specimen. Interestingly, the 9% replacement provided the lowest strengths at all times, even lower than the control mixture. This may be attributed to the free silica that is not hydrated and consequently not contributing to load carrying capacity of the specimen samples tested.

These results are comparable to those from **Qing et al., (2006)** where partially replaced cement with 3% NS by weight, in pastes showed that the compressive strength and flexural strength increased with the addition of NS. In the Qing et al. (2006) study, the enhancement in the compressive strength was 29.41% and 72.4% at ages of 7 and 28 days, respectively, whilst the enhancement in the flexural strength was 26.92% and 27.59% at the same ages, respectively. This result is also match with **Arefi et al., (2011)**, when studied the compressive

strength, flexural strength, and tensile strength, at early age of 7 days, of mortars modified with NS. Cement was partially replaced with NS at levels of 0%, 3% and 5%, by weight. The results showed an increase in all strengths with the addition of NS and the content of 3% NS gave the optimum strengths followed by 5% NS.

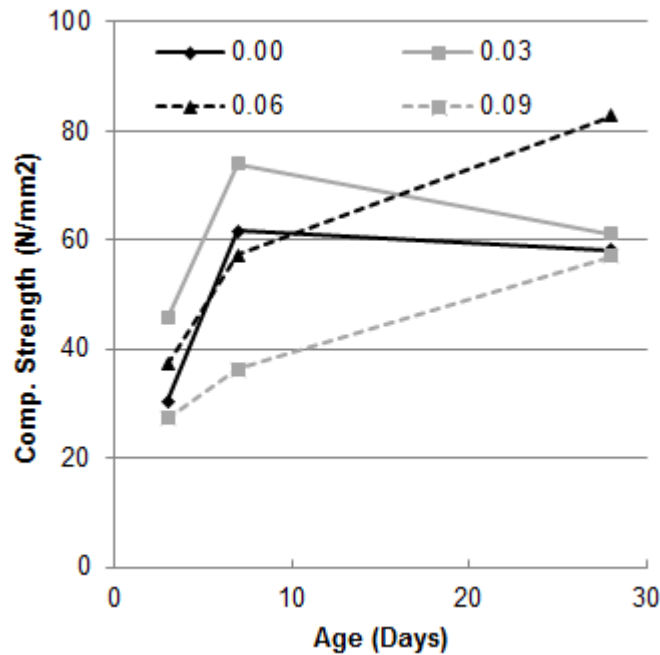


Figure 3: Assessment of compressive strength of cement paste with NS

Figure 4 depicts the average flexure strength of whole specimens at ages 3, 7 and 28 days of curing. With the exception of the specimen with 3% NS replacement, all the percentages of replacement at 3 days of curing had a lower flexure strength than the control sample. Previous research has indicated polycarboxylate superplasticizers can generate a detrimental amount of CH crystals in the composite (Soleymani Farzad 2011), possibly reducing the flexural strength. However, at age 7 days, the specimen with 3% NS replacement demonstrated improved flexure strength of 29.21% over the control sample, while the average flexure strength at 28 days of curing of the specimen with 6% NS replacement improved by 50.51% over the control sample. These levels of NS replacement can be used to get increased flexure strength at later ages. The 3% NS replacement seems to provide a higher flexural strength at 7 days and at later ages provides similar strengths to the 6% replacement, which provided the highest 28 day flexural and compressive strength.

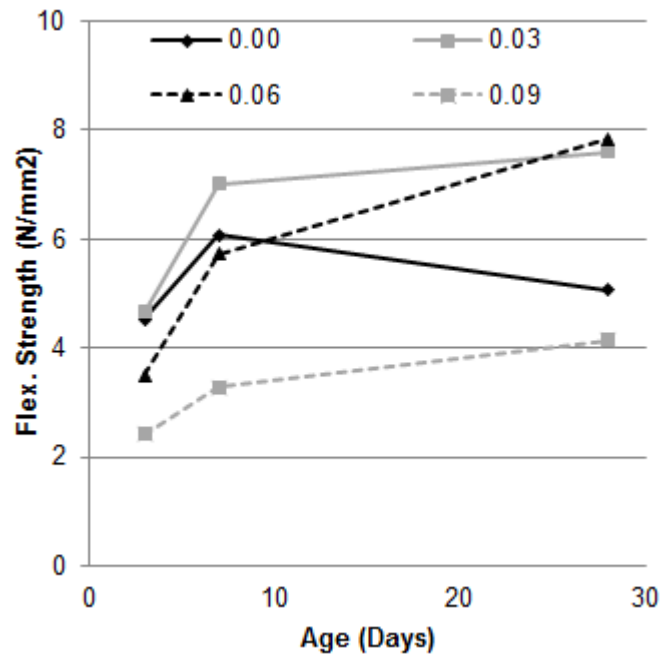


Figure 4: Assessment of flexure strength of cement paste with NS

The static MOE values of the best percent of cement paste incorporating NS at ages of 3, 7 and 28 days is presented in **Figure 5**. It is well known that the MOE depends on compressive strength and the same trend was observed for cement paste mixtures with NS replacement. **Figure 5** depicts the average elastic modules and toughness factor of best percentage of NS specimens (3%) comparison with control specimens at ages 3, 7 and 28 days of curing. It can be noted that, 3% of NS improves the elastic modulus by 23.72%, 30.60% and 87.00% over the control sample at 3, 7, and 28 days respectively. While the toughness factor enhanced by 38.82%, 26.56%, and 29.62% than the control samples at 3, 7, and 28 days respectively.

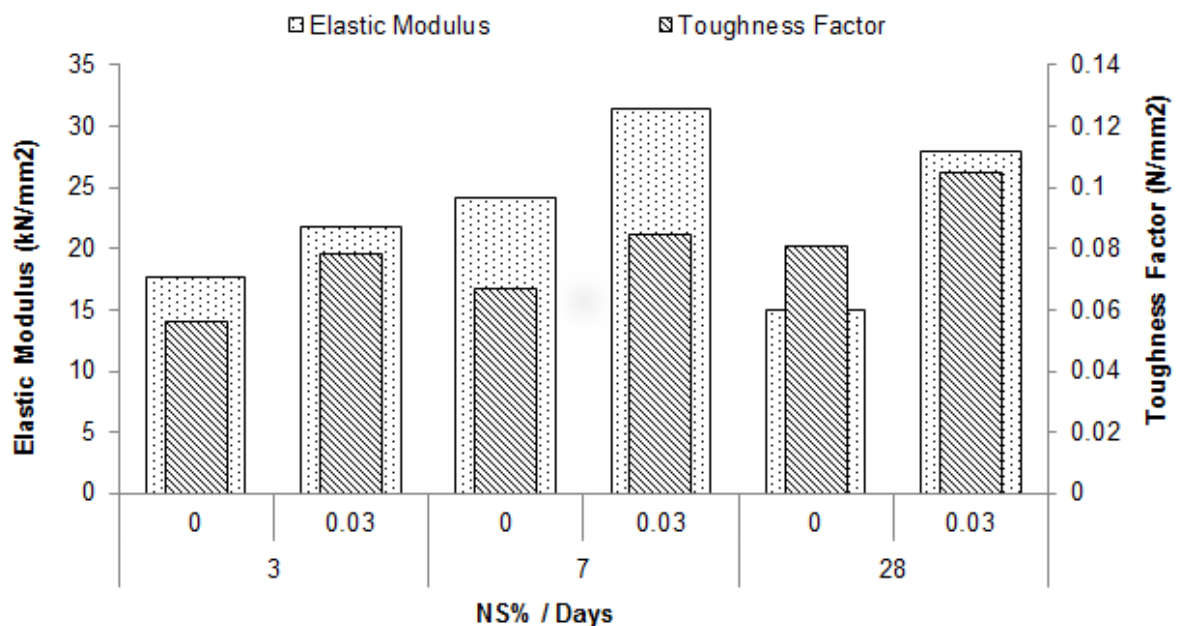


Figure 5: Elastic Modulus and Toughness Factor of NS / Cement Paste

Physical Properties

The addition of NS to cement paste leads to the formation of very fine hydration products, which, in turn, lead to a refinement of pores. As those disperse in ordinary Portland cement (OPC), they generate a large number of nucleation sites for the precipitation of the hydration products resulting in better distribution of fine pores; this produces a homogeneous and dense microstructure (**Riahi Shadi and Nazari Ali 2011**). In general, the pozzolanic effect depends not only on the pozzolanic reaction, but also on the physical or filler effect of the smaller particles in the mixture.

The XRD test was utilized to identify the size of raw materials. The thermal characteristics, and particularly thermal resistance, were indicated through DSC equipment. Finally, a SEM was employed to clarify the form of bonding.

a. X- Ray Diffraction Test Result

Results of the XRD pattern of the cement powder used are illustrated in **Figure 6**. The chemical composition, type of crystal structure, unit cell parameters and fractional atomic parameters can all be compared. **Figure 6** illustrates the peaks related to different compounds. These compounds can be categorized based upon three main elements as summarized in **Table 5**. Note that there seems to be a shortage of Al and Fe compared with the expected cement composition, which may affect the sample properties such as loss grade and hydration efficiency. Sample data were compared to the database to identify the phases as C2S (larnite), C3S (hatrurite) and CaCO₃ (calcite). There was no attempt to determine the cement crystal size due to its rapid changes, even in simple environmental conditions.

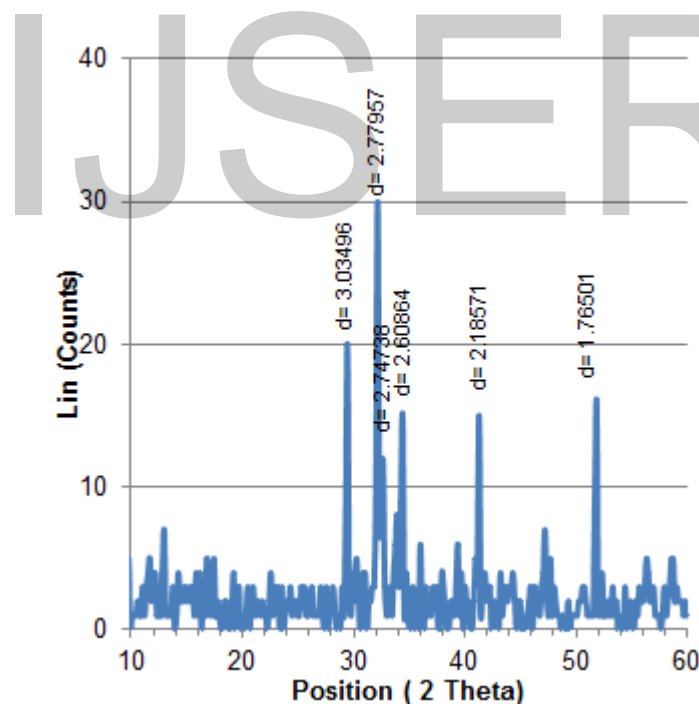


Figure 6: XRD of cement powder

Table 5: Summary of Distinguishing features of various components present in cement powder

Phase	Chemical Composition	Polymorphs	PDF card	Percentage Content %	Distinct features of diffractograms
Belite	Ca ₂ (SiO ₄) Larnite	β-C2S	83-0461	45.6	Strong peaks between (33-34)° and at 34.2°

"C2S"		γ -C2S			Strong peaks at 41.5°
Alite "C3S"	Ca ₃ (SiO ₄) Harttrurite	Monoclinic M3	85-1378	43.3	Strong peak with a shoulder at 32.5°
		Triclinic T			Triplet at 34.5°
		Rhombohedral, R			Strong singlet at 41.5°
lime	Ca(CO ₃) Calcite	3.03496	88-1808	11.1	Strong peak with a shoulder at 29.4°

The XRD pattern of the NS sample is shown in **Figure 7**. There is a peak centred on the 2 θ position of 20-25° which demonstrates the characteristics of amorphous silica that is completely free of sodium nitrate **Senff et al., (2012)**. Therefore, the state of NS was amorphous; activated NS has a pozzolanic activity, which able to enhance the structure of cement paste used in construction.

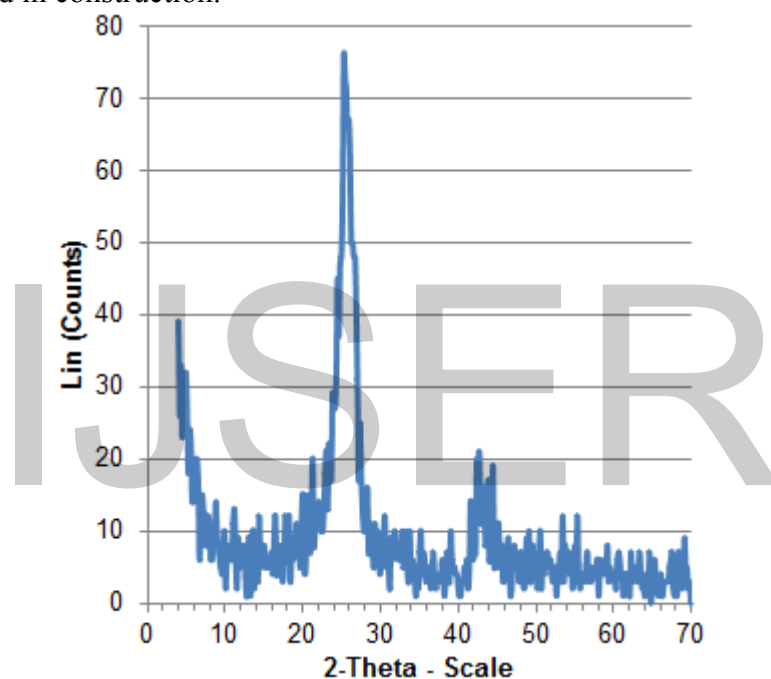


Figure 7: XRD of Nano-Silica (SiO₂)

b. Thermogravimetric Analysis

A TGA was performed at the ages of 3, 7 and 28 days of cement hydration. The thermogravimetric test demonstrates the specimen's weight loss and characterizes the composite's solidarity which affected by NS content. The portlandite phase Ca(OH)₂ decreased with increasing NS content. Ca(OH)₂ released during cement hydration was consumed as a result of the interaction with active amorphous silica to form the C-S-H phase which could contribute to the increase in the mechanical properties. Increased CaCO₃ is attributed to an increase in NS content. The specimens were evaluated according to total weight lost by temperature (1000 °C). The thermal analysis will be further explained in later sections.

In general, the thermogram output in the TGA Test illustrate the existence of an endothermic peak located at about 50°C, due to decomposition of C-S-H. The second endothermic peak was observed at about 470°C representing the decomposition of calcium hydroxide Ca(OH)₂. The third endothermic peak located at about 740°C represents the

thermal decomposition of calcium carbonate CaCO_3 **Nuruddeen Musa, (2014)**. Over the total weight of the sample, the greatest loss was at close to 1000 °C as shown in **Figure 8**.

Cement hydrate after 3 days

The control sample lost approximately 20.25% of weight at 1000°C. Loss of weight was 19.89%, 21.79% and 24.80% for 3%, 6% and 9% cement replacement by NS, respectively. The 3% NS specimen displayed the optimum characteristics, because it had the smallest weight decrease. The curves show increases in C-S-H content and a decrease in the enthalpy of Ca(OH)_2 consumption. These findings agree with the mechanical strength results where the C-S-H increase contributes to the strength at day three. The existence of the CaCO_3 crystal, which lacks decomposition elements, explains the weight retention of the sample in the high temperature. The observed strength changes of 6% and 9% NS replacements, which exhibited compression and flexural strength weakness at 3 days, may be due to free silica which not incorporate with the hydration process and therefore cannot bear mechanical stresses. This is also corroborated by **Figure 8** in that there seems to be more CaCO_3 in the control and NS3 samples.

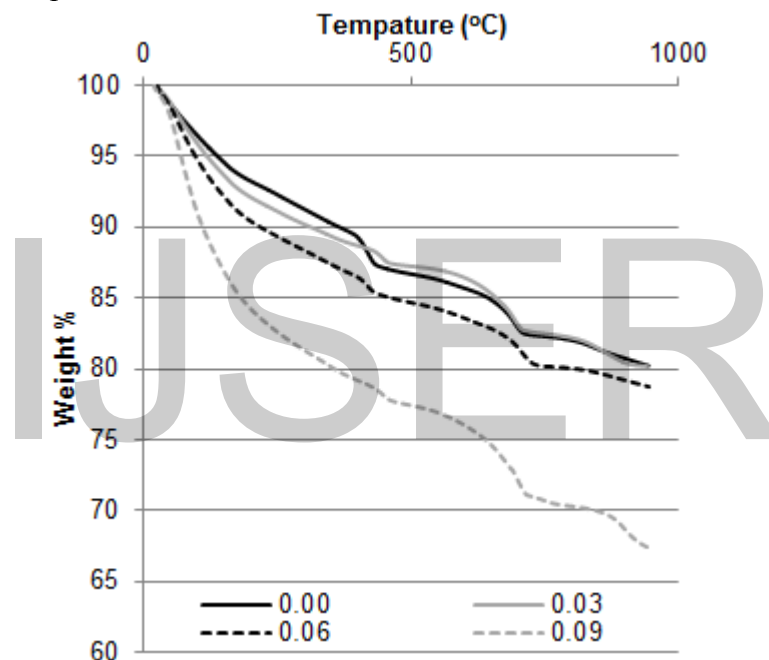


Figure 8: Temperature-Weight chart comparing cement paste of different percentages of NS at 3 days

Cement hydrate after 7 days

Figure 9 contains the TGA of samples after 7 days of curing. With age, the enthalpy of Ca(OH)_2 decreases during the pozzolanic reaction progress **Stefanidou M, Papayianni I, (2012)**. Some similarities in behaviour among all specimens were seen at the start of decomposition of C-S-H. The plain cement paste had a decreased enthalpy of Ca(OH)_2 , CaCO_3 and a loss in weight of 17.81%. Losses of weight were by 19.39%, 20.44%, and 21.84% for 3%, 6% and 9% of cement replacement by NS, respectively. These numbers indicate that with more free NS, more weight will be lost, further indicating 3% NS replacement is most efficient. All of these specimens have improved more physically through enhance the structure by increase the content of C-S-H and decrease of Ca(OH)_2 contents, as compared to the control specimen. This is most likely due to the hydration process that is not yet stabilized. This means fluctuating increases in C-S-H content, and decreases in enthalpy of Ca(OH)_2 consumption. These findings are in agreement with the mechanical strength results where an increase in C-S-H contributes to the strength. This investigation found that

the 6% and 9% NS replacements in the cementitious material do not contribute and are actually detrimental when compared to the control mechanical strength at this age.

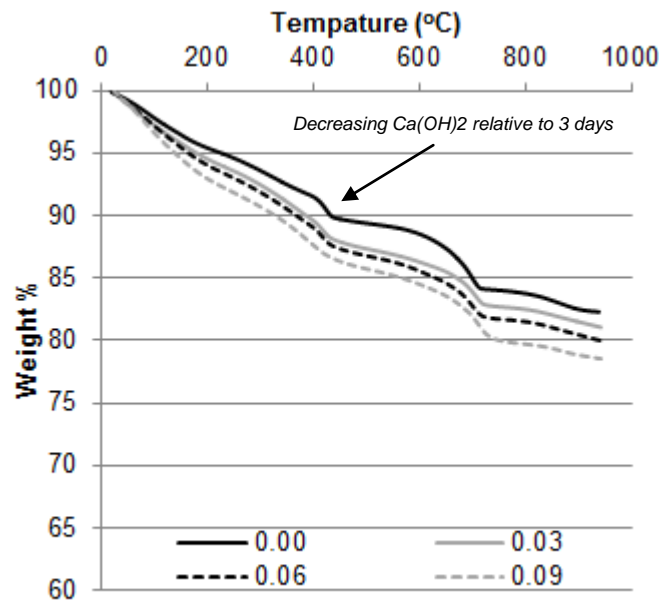


Figure 9: Temperature-weight chart for specimens with different percentages of NS at 7 days

Cement hydrate after 28 days

Figure 10 illustrates the TGA results for each sample at 28d. The control specimens indicate increment in enthalpy of Ca(OH)_2 through shifts the curve over the others, which implies improvement in crystallization consistency with only 19.73% its destroyed at close to 1000C. Total weight loss was 18.22%, 19.19% and 22.95% for 3%, 6% and 9% NS replacement, respectively. The 3% NS replacement specimen showed the smallest percent of Ca(OH)_2 . The C-S-H enthalpy increase improved crystallization, and bonding between hydration products. The Ca(OH)_2 in the 6% NS replacement specimen had an expected increase in enthalpy due to quickly are formed during hydration of Portland cement, specifically at early ages, as a result of high reactivity of NS (**Ali Nazari and Shadi Riahi 2010**). This led to the improved mechanical properties. For the 9% replacement by NS specimen, it was found that the enthalpy of Ca(OH)_2 lowered, which was corroborated by the mechanical testing because free NS content will weaken the composite.

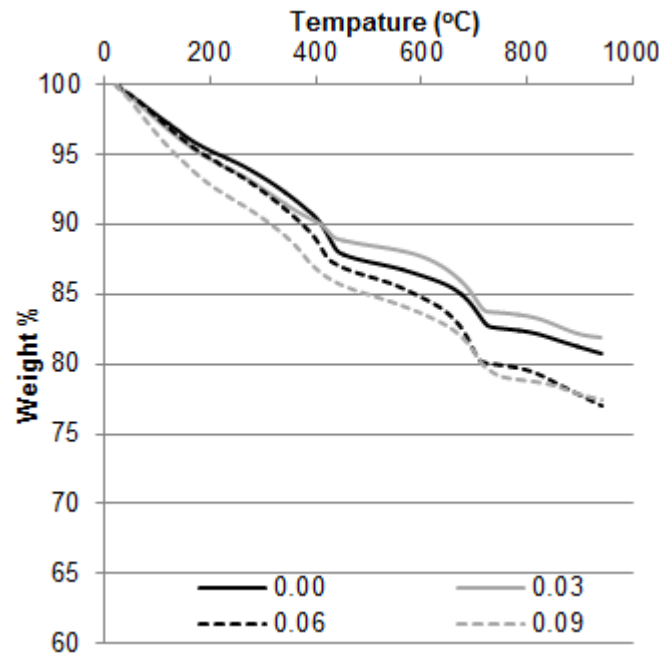


Figure 10: Temperature-Weight Chart of Cement Paste with Different Percentages of NS at 28 days

Summary of Thermogravimetric Analysis

Based upon these findings, it can be concluded that the 3% replacement of cement by NS sample demonstrated the optimal characteristics through enhancing the chemical composition at the various ages. The 6% NS specimen behaved similarly to the 3% NS replacement specimen at 28d only as shown in **Table 6**. This is consistent with the mechanical strength results (see **Figure 4** and **Figure 5**).

Table 6: Summary of Total Specimens Weight Losses

Specimens	Age	Weight Losses (%)	Age	Weight Losses (%)	Age	Weight Losses (%)
NS0	3 days	20.25	7 days	17.81	28 days	19.73
NS3		19.89		19.39		18.22
NS6		21.79		20.44		19.19
NS9		24.8		21.84		22.95

c. Scanning Electron Microscopy Test Analysis

Cement powder, amorphous NS powder and the various cement pastes, were studied via scanning electron microscope (SEM) to elucidate their physical states. SEM was also used to identify changes in the microstructure of the formed and/or decomposed phases in the cement paste.

Findings from scanning the cement and NS specimens are shown in **Figures 11a and 11b**, respectively. In the cement scan, hexagonal crystals are easily identifiable, which indicates the presence of tricalcium silicate (C3S) and the dicalcium silicate (C2S) shows as spherical morphology. The agglomeration of NS, shown in **Figure 11b**, is nearly spherical,

and regular in shape. The amorphous NS also had high purity compared to other reactivity materials and a rich silicon content without any visible of impurities.

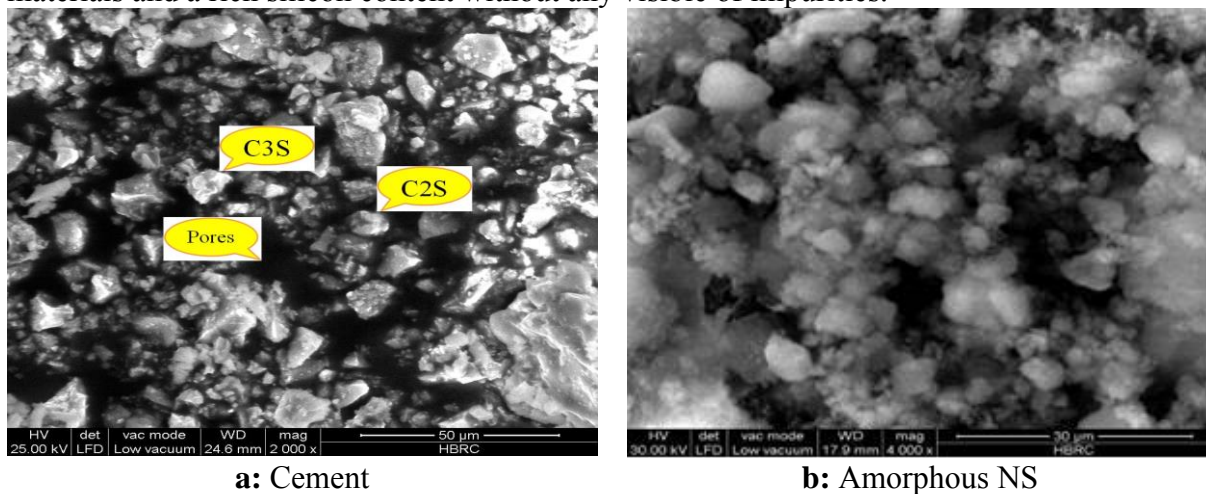


Figure 11: SEM of (a) Cement powder and (b) Amorphous NS Powder

SEM analysis was performed on the control and the 3% NS replacement samples. Findings from the micrographs, organized into three stages by age, are described below.

a. Cement hydrate after 3 days

The fracture surface of the 0% NS cement paste is shown in **Figure 12.a**. It consists of a combination of smooth and rough areas typical of the fracture features of cementitious material.

The 3% NS fracture surface in **Figure 12.d** shows a dense microstructure with lesser voids than the 0% NS sample at the same time (note the 2x magnification difference). This indicates that the 3% NS has considerably improved the packing density of the mixture. Although the NS have randomly distributed in different parts of the image one can see a meandering line at Figure 12(d, e and f), where the NS has the ability to improve the hydration process by providing numerous hydration sites for the chemical reaction.

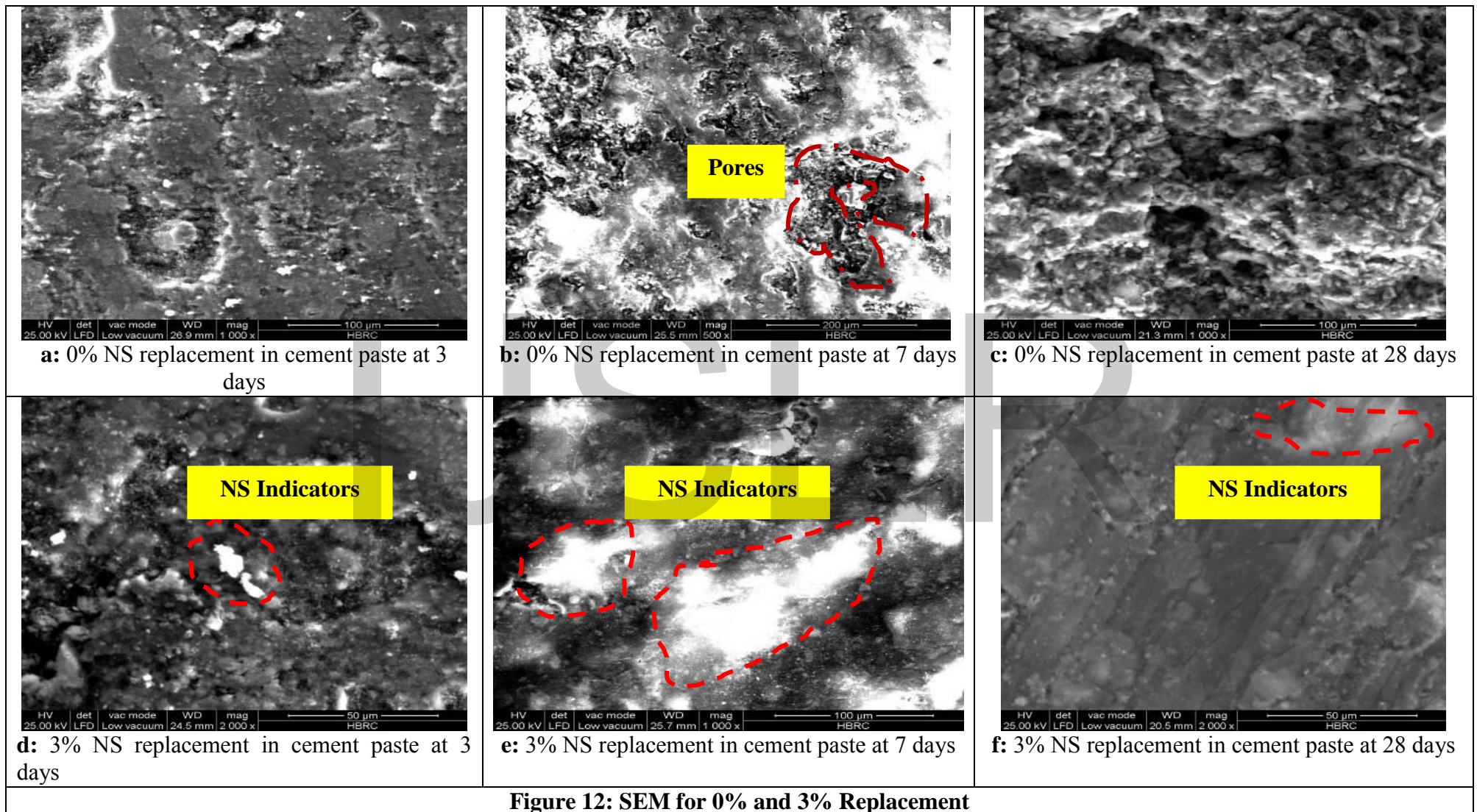
Stefanidou M, Papayianni I, (2012)

b. Cement hydrate after 7 days

The plain cement paste at 7d, is shown in **Figure 12.b**. Gaps presenting as a meandering line appear in the images image, but it has begun to stabilize in shape and size as characterized by the uneven surface. The 3% NS fracture surface (see **Figure 12.e**) shows a smooth and dense surface by comparison. This indicates that the NS has mixed well with the hydration products and is aiding microstructure development. The scan shows decreases in the void and gap sizes which will have positive effects on the mechanical properties.

c. Cement hydrate after 28 days

The plain cement paste after 28 days of reaction is shown in **Figure 12.c**. The observable wrinkles and pores characterize the image and is considerably coarser than the 3% NS sample in **Figure 12.f**.



CONCLUSIONS

In the above paper, NS replacement of cement paste was investigated and compared to a control cement paste. NS was provided as a cement replacement at 3%, 6% and 9% of the binder. Fresh and mechanical properties were investigated according to the appropriate standards. XRD and TGA analyses were used to determine the physical properties of the components and SEM was used to identify morphological changes for comparison. Based on the results of the analyses the following conclusions can be made:

1. Flowability was found to increase from 20 cm in the control to as much as 24 cm with 9% NS replacement.
2. The 3% replacement was found to provide highest early and compressive and flexural strengths (50% and 29% higher, respectively, compared to the control)
3. The 6% NS replacement was found to provide the highest long 28 day compressive and flexural strengths (42% and 51% higher, respectively, compared to the control)
4. The 9% replacement was found to be detrimental for compression and flexural strength when compared to the control because of free silica.
5. XRD results indicate that, the cement powder contained three main elements C₂S, C₃S, and CaCO₃, there were shortages of Al and Fe compared with what was expected for the cement type.
6. The TGA indicated the 3% NS replacement paste specimen displayed the optimum characteristics with an increase in CSH content and decrease in enthalpy of Ca(OH)₂ consumption and had the smallest overall weight decrease.
7. The plain cement pastes observed wrinkles, coarse pores and paste structures in the SEM images compared to the 3% NS sample, which shows a dense microstructure with lesser voids by comparison.
8. SEM image show free NS randomly distributed in different parts of the image for the 3% NS replacement specimen indicating NS has the ability to improve the hydration process by providing numerous hydration sites for the chemical reaction.
9. Although increase in CSH content was observed with increasing NS up to 9%, (demonstrated by the TGA results) this increase represents free silica, which is weaker by comparison to CSH, causing a decrease in mechanical properties. To a lesser extent, this may have also occurred in the 6% sample at early ages upon observing the lower mechanical properties when compared to the 3% NS replacement specimens.

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