Enhanced early hydration properties of Nano Silica incorporated cement paste

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Abstract

In the direction of evaluate the influence of nano silica particles (NS) on calcium silicate hydrate (CSH) formed at early-stage, hydration of tricalcium silicate (C_3S), hydration rate and Ca $(OH)_2$ content of hydration products were measured. An experimental study was carried out on five mixes of cement paste with water/cement ratio of 0.28 by weight. The studied dosages of NS are 0.5%, 1%, 1.5% and 2% by weight of cement as an addition. The degree of hydration was measured by Thermo-Gravimetric Analysis test (TGA) after 1 day. TGA allows determination of the amount of water bound in portlandite, and the total amount of chemically bound water. TGA was used to calculate all Differential Thermal Analysis (DTG) curves, TG curves, mass losses and temperature peaks by using apparatus software. It was concluded that adding of NS to cement paste up to 2%, NS improves the microstructural characteristics in comparison with the neat cement paste. The test results shows that NS be good not only as filler to improve the microstructure, but also as an activator to enhance the pozzolanic reaction, which promote the formation of hydrated products. Furthermore, the CSH gel of cement paste increases with the increase of NS content, which finally leads to the more compact and dense structure of hardened paste.

Keywords: Nano Silica, hydration products, Thermo-gravimetric analysis, degree of hydration.

1 Introduction

Application of nanotechnology in concrete is a research area gaining significant interest at present. It involves engineering of concrete at the nano-meter scale by inclusion of nano materials to improve the structure of concrete from the nano-meter scale through to higher dimensions, which can change the concrete world. Nano materials improve the most concrete properties [1, 2]. The effect of the Nano materials can be summarized as follows: (i) NS not only act as fillers to improve the microstructure, but also as an activator to promote pozzolanic reactions [3], (ii) work as a nucleation site for CSH seeds which then accelerate the cement hydration [4], (iii) NS accelerated the consumption of C_3S and the formation of portlandite (small sized CH) crystals and homogeneous clusters of CSH composition [4], and (iv) NS improve the microstructure of the interfacial transition zone (ITZ) between aggregates and cement pastes [5]. NS improves the mechanical properties of cement, mortars, and concrete [6, 7]. Many of the nano materials previously studied, nano silica particles not only provide nucleation sites for cement hydration, but also participates in the hydration process by reacting with the Calcium Hydroxide (CH) produced during cement hydration, which is known as the pozzolanic reaction [2, 6, 8]. Ordinary cement hydration produces CSH and CH [9, 10]. CSH is the main strength carrying material in the cement paste, and CH is considered to have a detrimental effect on strength characteristics of concrete [10]. Nano silica reacts with the CH and produces more CSH into the paste, thereby increasing the overall strength characteristics of the cement paste [6, 8]. Thermo-Gravimetric analysis (TGA) has been widely accepted as an accurate method for the determination of crystalline CH content [11]. The methods of interpretation of thermograms, however, have varied among researchers [11-13]. A weight loss vs temperature curve for hardened cement paste between the temperatures of 105 and 1000 °C can generally be separated into: (a) an abrupt weight loss near 450 °C, associated with the dehydration of CH; (b) another fairly sudden, but less distinct weight loss between 700 and 800 °C, associated with decomposition of calcium carbonate (this may not be present if care has been taken to prevent carbonation), and (c) a continuous weight loss over the whole range from 105 to 1000 °C but most pronounced before 500 °C; this loss is due to the dehydration of CSH, calcium aluminate hydrates and other minor hydrates. It should be noted that it is possible to isolate particular hydrates from a rigorous interpretation of the thermogram, or by using special techniques [5, 14]. In the present work, hydration properties of cement paste with different dosage of NS at the early age, including hydration rate, CH content and quantification of CSH, have been investigated by using TGA test. All these results aim to provide a comprehensive explanation for the modification effects of NS on C_3S.

2 Materials and experimental work

2.1 Materials

The materials used in this experimental work were Ordinary Portland Cement (OPC) and nano silica particles (NS). The OPC used throughout this investigation was obtained from MISR BENI-SUEF CEMENT COMPANY, it’s trade name CIM I 52.5N which conforming to BS EN 197-1/2011 [15] and Egyptian Standards Specification ESS 4756-1/2013 [16] and had a 28-day mortar compressive strength of 57.5 MPa. The initial and final setting times were 150 min and 230 min respectively. NS was supplied by Housing & Building National Research Centre (HBRC), Cairo, Egypt. The morphology and XRD analysis of NS are shown in Figures 1 and 2, which indicate the amorphous nature of NS particles. The Dynamic Light Scattering test (DLS) was used to detect the particle size distribution of NS as shown in Figure 3. From this figure it is observed that the NS particle sizes ranged from 45 nm to 85 nm. The chemical composition and physical properties of OPC and NS are presented in Table 1 and Table 2.

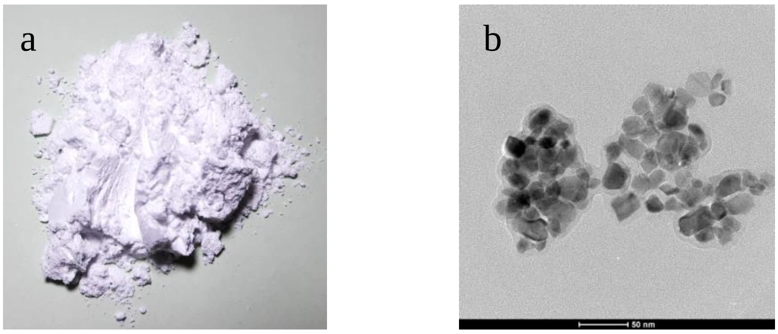

Figure 1: *Morphology of NS; (a) NS powder, (b) TEM image of NS.*

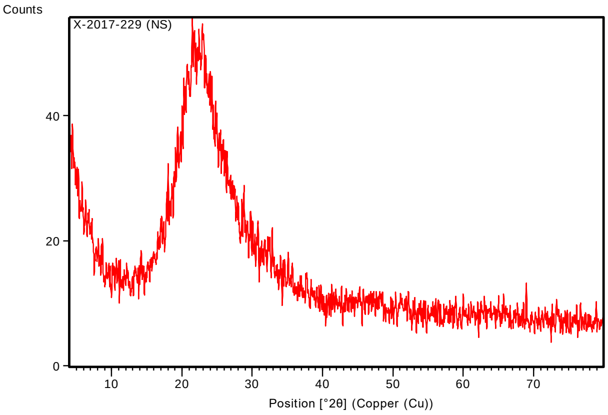

Figure 2: *XRD analysis of NS.*

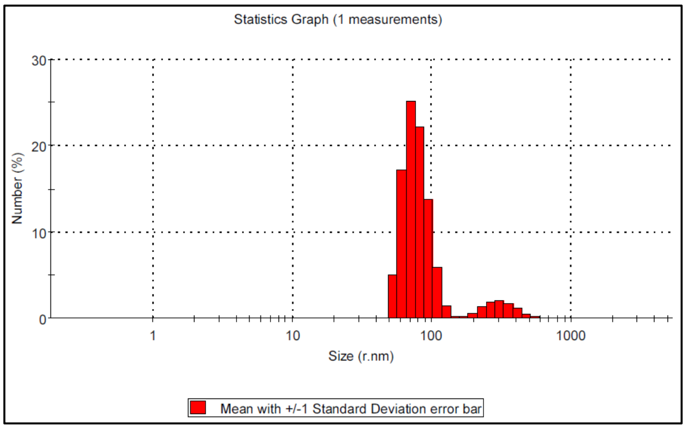

Figure 3: *Particle size distribution of NS by DLS test.*

Table 1: *Chemical compositions of raw materials.*

OXIDE %	OPC	NS
SiO_2	20.8	98.98
Al_2O_3	4.6	0.033
Fe_2O_3	2.8	0.015
CaO	65.4	0.130

MgO	1.9	< 0.01
SO_3	2.2	< 0.01
Na_2O	0.31	0.180
K_2O	0.44	< 0.01
TiO_2	-	0.025
Cl	-	0.270

Table 2: *Physical properties of raw materials.*

PROPERTY	OPC	NS
Specific Gravity	3.15	2.3
Average Particle Size	1-10 µm	65 nm
Specific Surface Area (m^2/g)	0.35	135.5
Density	-	-

2.2 Experimental techniques

2.2.1 Preparation of cement paste

Cement paste was designed using ordinary Portland cement as a binder material. The water to cement ratio (W/C) was kept constant at 0.28 by weight. The flow table standard tests for all samples were between 105% to 115%. The NS particles was added in amounts equaling 0.0% (control), 0.5%, 1.0%, 1.5% and 2.0% of cement weight. All of cement paste specimens were cured using potable water.

2.2.2 Mixing procedure

To ensure good distribution and good mixing NS with cement paste, special mixing procedure should be carried out, using the mechanical method. Laboratory drum mixer was used, and the mixing procedures were performed according to the following steps: firstly; nano particles solution was prepared through mixing NS thoroughly with a mixing water using a high-speed stirring machine for 2 min. Then, the solution was placed in sonication device (Figure 4) for 15 min at temperature of 60 °C to disperse the nanomaterial in the solution. Finally, the previous solution was added to cement and were mixed together for 3 min.

Figure 4: *Sonication for mixing nano particles.*

2.2.3 Test Specimens Preparation

The TGA specimens used in this investigation are Cylinders with height of 100 mm and a diameter of 100 mm. All specimens are cast using cement paste with w/c = 0.28 in a plastic molds. TGA procedure is conducted after 24 hours, fine powders were first obtained by drilling a hole to a depth of 10 mm from the surface of the specimen using electrically driven powder driller with high speed.

2.2.4 Curing conditions

The cement paste was casted in molds as required to scheduled tests. An electric vibrator was used to ensure good compaction after pouring the mixes into oiled molds. The specimens were then surface smoothed and covered with plastic sheet. All specimens were demolded after 1 day of casting, thereafter; they were cured in standard water tank. The cement paste samples were removed from curing tank at the specified testing age and any deposits on the test faces were removed before testing.

3 Results and discussion

3.1 Thermogravimetric analysis

The degree of hydration was measured by TGA after 1-day according to ASTM C1131-14 [17]. TGA allows determination of the amount of water bound in portlandite, and the total amount of chemically bound water. TGA consists of the recording of the loss of weight of a sample being progressively heated up to a constant weight. In the case of cementitious hydrated materials, weight loss is due mainly to mineral decomposition and evaporation of the total chemically bound water (considered from 105 °C to 925 °C). The test was conducted on 30 mg cement paste samples. These samples were heated in an inert N2 atmosphere from 25 to 925 °C with a heating rate of 20 °C/min by using THASS simultaneous analyser, model TGA i1000 to calculate all differential thermal (DTG) curves, TGA curves, mass losses and temperature peaks by using apparatus software. The amount of water bound in portlandite is determined by the step between 425 °C and 550 °C measured from the loss of weight-temperature curves. The slope and the intercept of the tangent at 550 °C are computed by linear regression, and the water bound in portlandite is obtained by the difference of weight loss between 425 °C, read on the curve, and the ordinate of the tangent for 425 °C. The degree of hydration can be calculated from TGA curves using the following equation [11, 13, 17, 18]:

$$h_\alpha = \frac{W_{n(t)}}{M_c \times W_{n(\infty)}} \qquad \text{Eq. (1)}$$

Where:

$W_{n(t)}$ is defined as mass loss recorded between 145 °C and 925 °C.

$W_{n(\infty)}$ is the non-evaporable water corresponding to full hydration, this value was 0.23

M_c for typical Portland cement, it’s the initial anhydrous cement mass of sample in gram.

TGA results of cement pastes specimens with different dosages of NS after 1 day are shown in Figure 5. Also, Figures 6,7,8,9 and 10 show the TGA and Differential Thermal Analysis (DTG) curves of cement pastes specimens with different dosages of NS after 1 day.

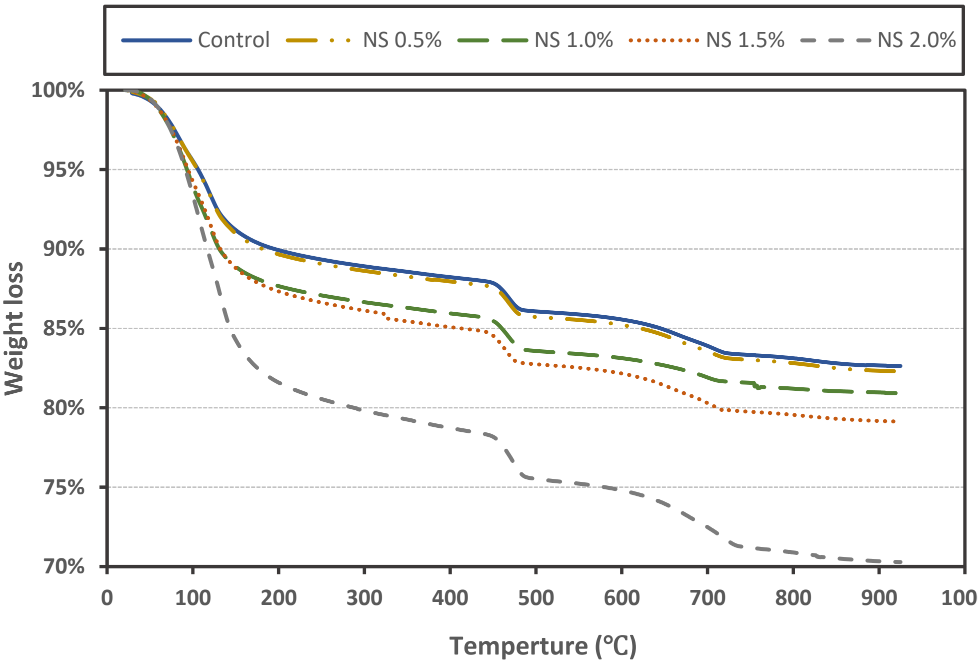

Figure 5: *TGA curves of cement paste with different content of NS after 1 day.*

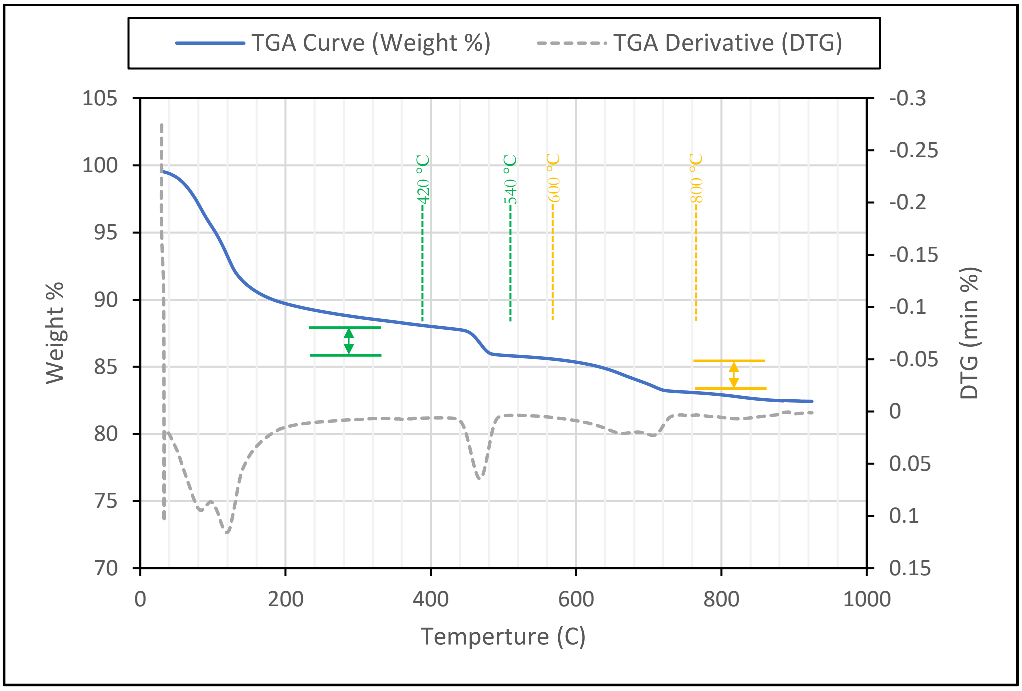

Figure 6: *TGA analysis of the cement paste without NS after 1 day.*

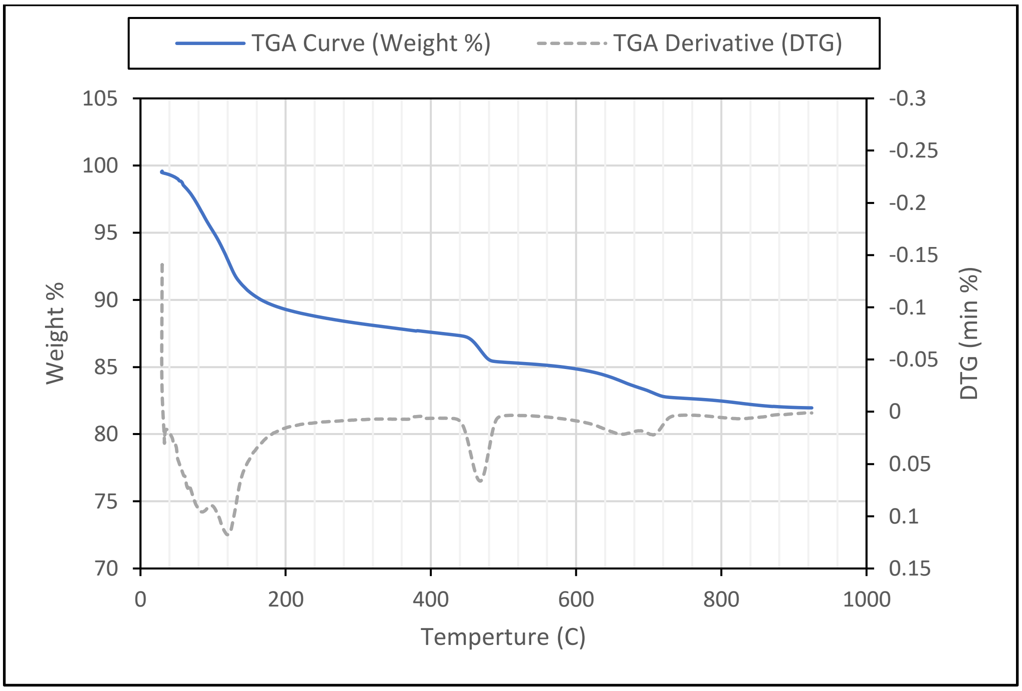

Figure 7: *TGA analysis of the cement paste incorporating with 0.5% NS after 1 day.*

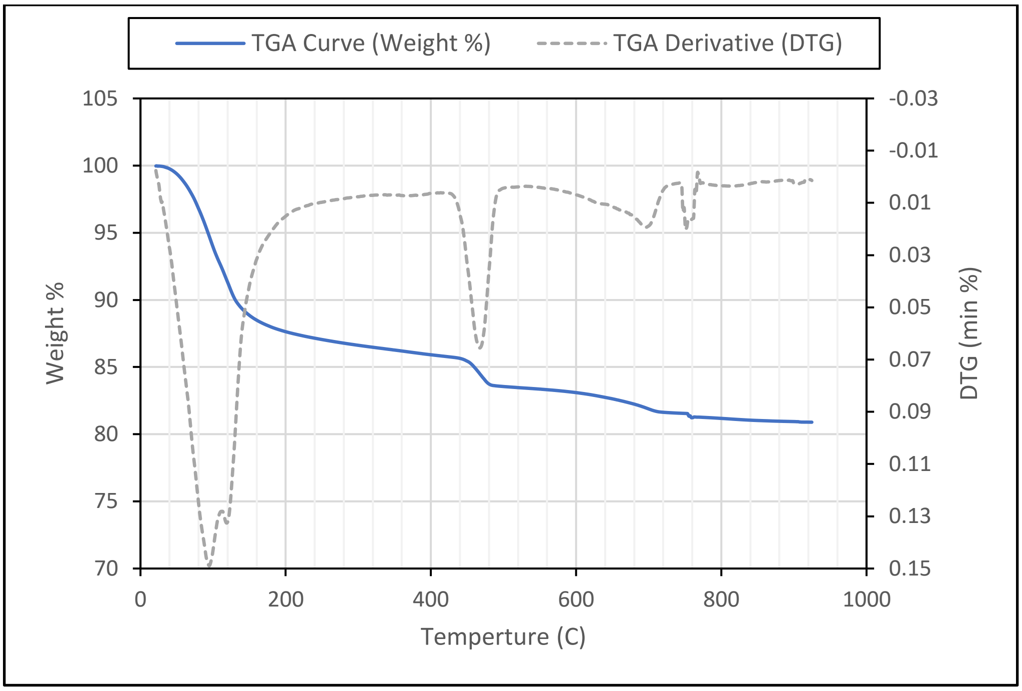

Figure 8: *TGA analysis of the cement paste incorporating with 1.0% NS after 1 day.*

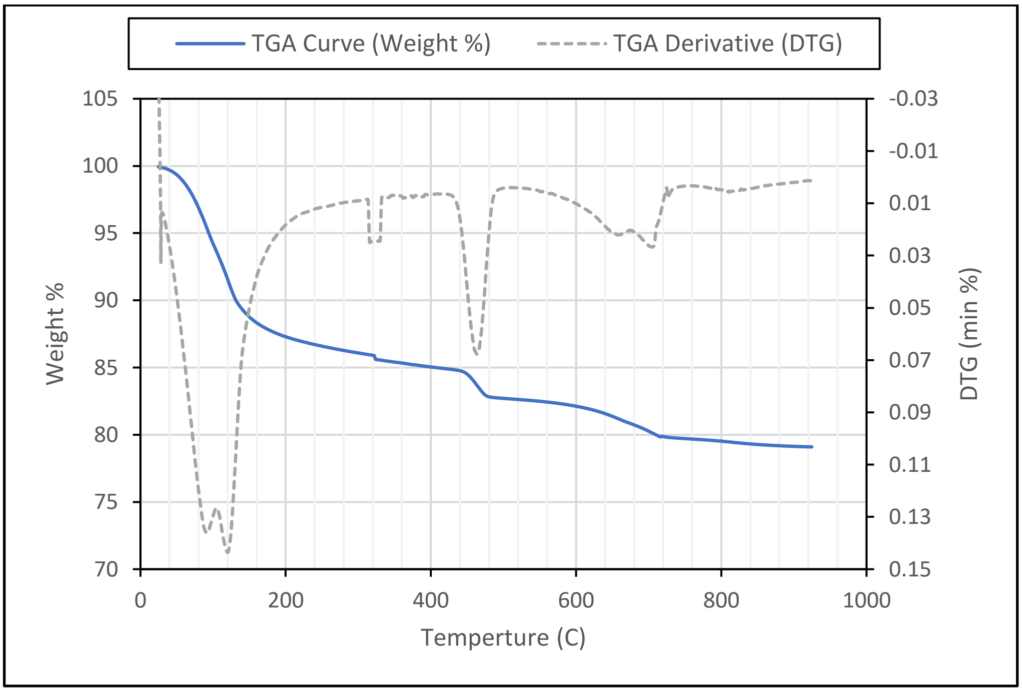

Figure 9: *TGA analysis of the cement paste incorporating with 1.5% NS after 1 day.*

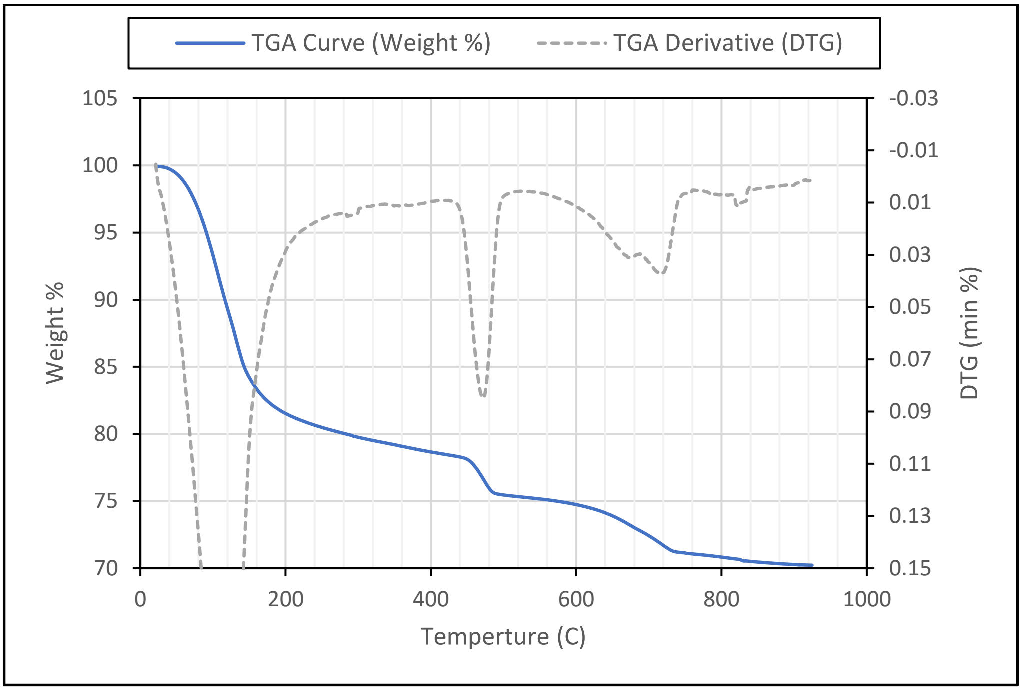

Figure 10: *TGA analysis of the cement paste incorporating with 2.0% NS after 1 day*.

There are some notes and differences can be observed between the DTG curves of the specimens. First, there is a peak above 90 °C - 120 °C. This peak is due to loss of free water. Secondly, there is a remarkable difference between the curves at temperature of 400 to 500 °C. The differences indicate that there is a decrease in amount of portlandite with the increase of the NS dosage. Adding of NS to cement paste seems to increase the degree of hydration at 1 day comparing with the control specimen. In addition, there is dissimilarity between 600 °C and 800 °C due to the decomposition of the $CaCO_3$. The test results clearly show that using different dosages of NS have a positive effect on enhancing the hydration process compared with that of control mix. This will be further explained later when calculating the degree of hydration of all samples.

TGA test results can be used to evaluate the hydration characteristics in terms of CH content and degree of hydration. CH content can be used also to evaluate the pozzolanic reactivity of used NS [19]. The CH content of the hydrated cement pastes specimens is calculated as at time t:

$$\mathrm{CH(t)} = \frac{74.09}{18.01} \times \frac{\mathrm{m_{420}(t) - m_{540}(t)}}{\mathrm{m_s}} \qquad \text{Eq. (2)}$$

Where:

$m_{420}(t)$ and $m_{540}(t)$ are the mass of the sample recorded at 420 °C and 540 °C during the TGA test, and m_s is the anhydrous mass of the sample. (74.09/18.01) is the molar mass ratio between CH and H_2O.

Due to the carbonation reaction, amount of CH can be transformed to $CaCO_3$ as given in the following reaction:

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O} \qquad \text{Eq. (3)}$$

The $CaCO_3$ content of the cement paste at time t, CO(t), is calculated as:

$$\mathrm{CO(t)} = \frac{100.09}{44.01} \cdot \frac{\mathrm{m_{600}(t) - m_{800}(t)}}{\mathrm{m_s}} \qquad \text{Eq. (4)}$$

Where:

$m_{600}(t)$ and $m_{800}(t)$ are the mass of the sample recorded at 600 °C and 800 °C during the TGA and (100.09/44.01) is the molar mass ration between $CaCO_3$ and CO_2. So, the amount of CH that transformed to $CaCO_3$ should be calculated to determine the total content o CH ($\mathrm{CH_{Total}(t)}$).

The $CH_{\textit{due to carbonation reaction}}$ (t) can be calculated as following:

$$\mathrm{CH_{due\ to\ carbonation\ reaction}(t)} = \frac{74.09}{100.09} \times \mathrm{CO(t)} \qquad \text{Eq. (5)}$$

Where:

The ratio (74.09/100.09) is the molar mass ratio between CH and $CaCO_3$.

From Eq. 4 and Eq. 5

$$\mathrm{CH_{due\ to\ carbonation\ reaction}(t)} = \frac{74.09}{100.09} \times \frac{100.09}{44.01} \times \frac{\mathrm{m_{600}(t) - m_{800}(t)}}{\mathrm{m_s}} \qquad \text{Eq. (6)}$$

$$\mathrm{CH_{due\ to\ carbonation\ reaction}(t)} = \frac{74.09}{44.01} \times \frac{\mathrm{m_{600}(t) - m_{800}(t)}}{\mathrm{m_s}} \qquad \text{Eq. (7)}$$

The total CH content can be estimated by the summation of CH (t) (from Eq. 2 and $CH_{\textit{due to carbonation reaction}}$ (t) from Eq. 7 as following:

$$\mathrm{CH_{Total}(t)} = \mathrm{CH(t)} + \mathrm{CH_{due\ to\ carbonation\ reaction}(t)} \qquad \text{Eq. (8)}$$

$$\mathrm{CH_{Total}(t)} = \mathrm{CH(t)} + \frac{74.09}{44.01} \times \frac{\mathrm{m_{600}(t) - m_{800}(t)}}{\mathrm{m_s}} \qquad \text{Eq. (9)}$$

The degree of hydration of cement (α) is determined by TGA test. It can be estimated using the following equation [18]:

$$\alpha(\%) = \frac{\mathrm{M_b\ (t)}}{\mathrm{M_c} \cdot \mathrm{M_b}\ (\infty)} \qquad \text{Eq. (10)}$$

Where:

M_b (t) is the non-evaporable water mass at time (t), is defined here as the mass loss recorded between 145 °C and 925 °C minus the mass loss due to CO_2 releases produced by the calcite decomposition between 600 and 800 °C.

M_c is the initial anhydrous cement mass of the sample (g).

M_b (∞) is the non-evaporable water mass (g/g of cement) at time (∞) corresponding to full hydration of 1 g of cement which is estimated from the mineralogical composition of cement (Pane's formulae and Hansen's [20] results): $M_b(\infty) = 0.256$ g.

Figure 11 shows the calculated CH contents for different cement pastes specimens after 1 day. Form this figure, all different specimens that modified with different dosages of NS yield lower CH contents compared with control specimens (i.e. the specimens without NS). It is also observed that CH contents decrease with the increase of amount of NS. For example, for cement pastes specimens modified with NS, the reduction in CH contents that measured after 1 day is 3.1%, 11.1%, 19.5% and 24.4% for concrete mixes modified with 0.5%, 1.0%, 1.5% and 2.0% of NS, respectively, compared with that of control specimens (0.0% NS). This attributed to the pozzolanic reactivity of nano materials, and as a result CH content in the paste is reduced. The results are in a good agreement with what were obtained by Z. Wu et al. [21], M. Rupasinghe et al. [22] and P. Hou et al. [23].

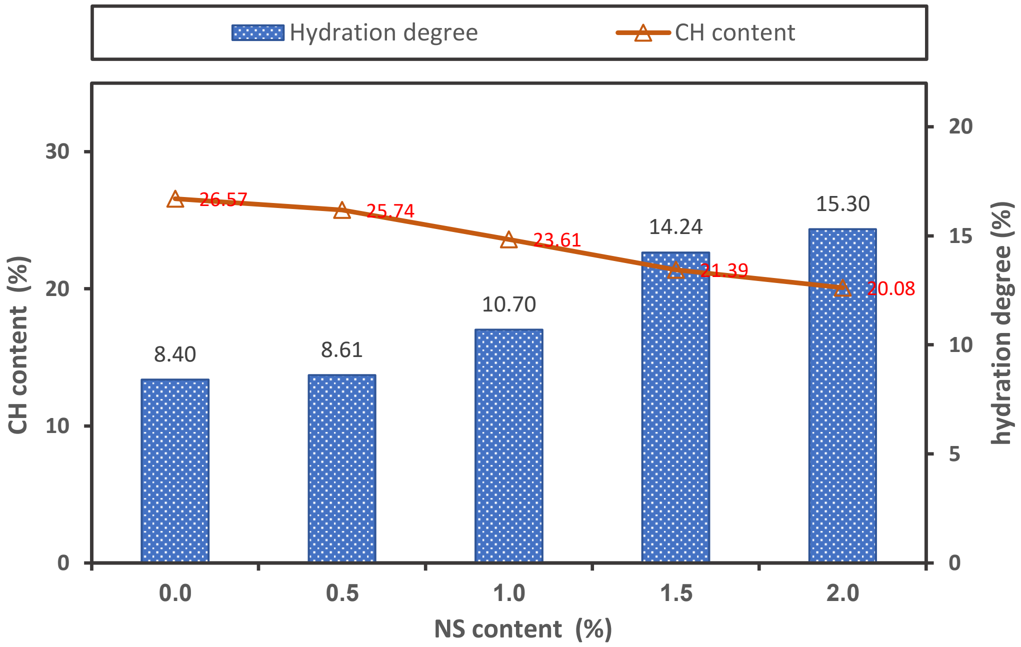

Figure 11: *Effect of NS dosages on CH content and hydration degree of cement paste after 1 day.*

The hydration degree of different cement pastes after 1 day is computed. As shown in Figure 11, with increasing amount of added NS, the cement hydration degree linearly increases. As observed here, the cement hydration degree of the reference cement paste after 1 day is about 8.40% and increases to about 15.30% when a 2% addition of NS is included.

4 Conclusion

1. The high surface area and active particulate nature is responsible for high reactivity of nano materials.
2. The accelerated pozzolanic reaction between cement and NS results in conversion of $Ca(OH)_2$ to additional calcium silica hydrate material, filling the voids in the concrete and interfacial transition zone thus effectively reducing the permeability of concrete which in turn enhance many of the durability issues.
3. Thermal gravimetric analysis results indicated that the addition of NS leads to a significant consumption of portlandite (CH) in the pozzolanic reaction. However, increasing the dosage of NS from 1.5% to 2.0% does not significantly increase in the consumption of CH.
4. The incorporation of NS results in changes in the content of hydration products generated during the hydration process, etc. For example, silicate content decreases, and hydrated calcium silicate gel increases, etc. The changes of these hydration products content optimizes the microstructure of concrete and make the concrete more compact. The changes of these surround layers lead to changes in macroscopical performance.
5. The addition of NS accelerates the hydration rate at an early age (within 24 h of hydration) and helps to promote the formation of high-density C-S-H.
6. The results clearly show that NS not only accelerates the hydration rate but also improved the packing density of CSH particles.

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