23rd Australasian Conference on the Mechanics of Structures and Materials

2014

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Publication details

Rupasinghe, M, San Nicolas, R, Mendis, P & Sofi, M 2014, 'Analysing the pozzolanic reactivity of nano-silica in cement paste', in ST Smith (ed.), *23rd Australasian Conference on the Mechanics of Structures and Materials (ACMSM23)*, vol. I, Byron Bay, NSW, 9-12 December, Southern Cross University, Lismore, NSW, pp. 131-136. ISBN: 9780994152008.

ANALYSING THE POZZOLANIC REACTIVITY OF NANO-SILICA IN CEMENT PASTE

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ABSTRACT

Nano-engineering of 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 in order to improve the structure of concrete from the nano-meter scale through to higher dimensions. This paper explores the hydration characteristics of cement paste with nano-silica, focusing on the pozzolanic reactivity. It considers replacing the cement content of the cement paste by small amounts of nano-silica (at percentage replacement levels of 4, 8 and 12 by weight of cement) and compares the hydration characteristics of these mixes against the plain cement paste. Colloidal nano-silica is used in this research. Thermal Gravimetric Analysis (TGA) has been carried out on the cement pastes at different ages to analyse the Calcium Hydroxide (CH) content of the nano- modified pastes. It is shown that the CH content of the mixes including nano-silica is lower than that of the plain cement paste, indicating that nano-silica reacts with the cement paste through a pozzolanic reaction. Increased pozzolanic activity results in higher amounts of Calcium Silicate Hydrate in the paste, which in turn results in higher compressive strength for nano-silica modified cement pastes.

KEYWORDS

Cement paste, nano-silica, CH content, hydration, pozzolanic activity.

INTRODUCTION

With the increasing research focus on nano-materials and nano-technology within the past couple of decades, the effects of nano-particles on construction materials has been of great research interest. Concrete is the most widely used man made material in the world. Most of the current research on nano-engineering concrete has been focused on including nano- materials into concrete with the aim of increasing its performance. These include increasing strength characteristics, reduction of porosity and increasing durability. Nano-materials that have been included in concrete include Carbon Nano-Tubes(Konsta-Gdoutos et al., 2010), nano-silica (Belkowitz and Armentrout, 2010, Li et al., 2004, Qing et al., 2007, Senff et al., 2010, Sobolev et al., 2009), nano-TiO_2 (Nochaiya and Chaipanich, 2010) nano-Fe_2O_3, nano-Al_2O_3 (Nazari et al., 2010b, Nazari et al., 2010a) and nano-clay (Tregger et al., 2010). Nano-materials facilitates cement hydration through providing more nucleation sites for the cement particles to hydrate and acts as a filler material within the paste (Sobolev et al., 2009). This paper focuses the effects of nano-SiO_2 on cement paste and it mainly concentrates on the pozzolanic reactivity of the nano-material.

Nano-silica is available in both powder form and colloidal dispersion. Research have been carried out on including both these forms in concrete (Jo et al., 2007, Sobolev et al., 2009, Said et al., 2012, Shih et al., 2006) . The colloidal form, when compared with the powder form, has the advantage of better dispersion within the cement paste, thus reducing the probability of forming agglomerates (Said et al., 2012). In contrast to many of the nano-materials previously studied, nano-silica not only provides 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 (Li et al., 2004, Sobolev et al., 2009). Ordinary cement hydration produces Calcium Silica Hydrate (CSH) and CH (Mehta and Monteiro, 1986, Neville, 1995). 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 (Mehta and Monteiro, 1986). Nano-silica reacts with the CH and produces more CSH into the paste, thereby increasing the overall strength characteristics of the cement paste (Sobolev et al., 2009).

However, despite these previous studies, there is still a lack of in-depth understanding of the mechanism of incorporation of nano-silica on the hydration of a cement binder, and its role in microstructural evolution and gel chemistry. This is crucial in understanding the long-term mechanical and durability performance of concrete. Therefore, this study reports the microstructural changes taking place in nano-silica/cement binders up to the age of 28 days, as a function of the time of curing and the nano-silica content in the range 0-12%, using thermogravimetry.

MATERIALS AND METHODS

Materials

General purpose cement confirming to the AS 3972-2010 (Australian Standard for General purpose and blended cements) was used for this study. It has a density of 3.12 g/ml and specific area of 352 m^2/kg. An amorphous colloidal nano-silica suspension, Cembinder 8, was used which was produced by Akzo Nobel, Germany(Akzo Nobel, 2014). Table 1 and Table 2 below provide the chemical composition of cement specifications of nano- silica, respectively.

Table 1. Chemical composition of cement

Compound	Chemical composition (%)
Silica (SiO_2)	20.38
Alumina (Al_2O_3)	7.89
Iron oxide (Fe_2O_3)	0.75
Calcium oxide (CaO)	65.02
Magnesium oxide (MgO)	0.98
Sulphur trioxide (SO_3)	2.21

Table 2. Specifications of nano-silica

Property	
Density (g/cm^3, 20^0C)	1.4
pH	9.5
Viscosity (mPas)	<15
Solid content (% w/w)	50

Introduction to Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is a widely used method for the quantification of the pozzolanic reaction extent. In this method, the sample is gradually heated from room temperature to a defined maximum temperature, and the weight of the sample and the temperature is monitored and recorded. As the temperature is increased, the mass of the sample reduces at particular temperature ranges due to decomposition of its chemical components. Through obtaining the reduction of the mass at the corresponding temperature range and following the necessary calculation steps, the amount of the chemical component that was decomposed at that temperature range can be quantified. This method was used to quantify the amount of CH in the samples, and is described further in the section below.

Sample Preparation

For the preparation of the cement paste samples, constant water to binder ratio of 0.4 was used for all cement pastes. The water content of the nano-silica suspension was taken into consideration, and the externally added water content was altered to maintain a constant w/b ratio. Table 3 provides the description of the samples. Isothermal calorimetry was carried out just after mixing the samples, and rest of the paste was poured into moulds to harden.

Isothermal calorimetric experiments were conducted using a TAM Air isothermal calorimeter, at a base temperature of 25 ± 0.02 ℃. Fresh paste was mixed externally, weighed into an ampoule, and immediately placed in the calorimeter, and the heat flow was recorded for the first 140 h of reaction. All values of heat release rate were normalised by total weight of paste.

For TG analysis, the cement paste samples were de-moulded after 1 day, and were cured at a constant temperature of 20 ℃. Crushed samples were obtained from the hardened cement pastes at different ages 1, 3, 7 and 28 days. Acetone was used to stop the proceeding of the hydration reaction, and the prepared samples were tested for TGA using a Perkin Elmer Diamond instrument. In the TGA procedure, the sample was first held at 30 ℃ for 20 minutes, and then heated from 30 ℃ to 1000 ℃ at 10.00 ℃/min. After holding the sample at 1000 ℃ for 5 minutes it was cooled back to 30 ℃ at a rate of 40 ℃/min (Neithalath et al., 2009).

Table 3. Sample descriptions

Sample ID	% Nano-silica (by weight)	Cement (g)	Cembinder (g)	Water(g)	w/b
CO	0	100	0	40	0.4
NS4	4	96	8	36	0.4
NS8	8	92	16	32	0.4
NS12	12	88	24	28	0.4

Calculation of the CH Content

The pozzolanic reactivity of nano-silica is calculated based on the CH content of the cement paste samples at different ages. Details of the evaluation of CH content based on TG data can be found in (Marsh and Day, 1988) .

The CH content of the hydrated paste samples is calculated as at time t, CH1(t)

$$CH1(t) = \frac{74.09}{18.01} \cdot \frac{m_{420}(t) - m_{540}(t)}{m_s} \qquad (1)$$

where $m_{420}(t)$ and $m_{540}(t)$ are the mass of the sample recorded at 420 ℃ and 540 ℃ 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, the CH produced within the mix can react to produce $CaCO_3$ as in the following reaction.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

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

$$CO(t) = \frac{100.09}{44.01} \cdot \frac{m_{600}(t) - m_{800}(t)}{m_s} \quad (2)$$

where $m_{600}(t)$ and $m_{800}(t)$ are the mass of the sample recorded at 600 ℃ and 800 ℃ during the TGA. (100.09/44.01) is the molar mass ration between $CaCO_3$ andCO_2. The CH content from equation 1 was adjusted according to the stoichiometry of the carbonation equation, and the final CH content was obtained as,

$$CH(t) = CH1(t) + \frac{74.09}{100.09} . CO(t) \quad (3)$$

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

RESULTS AND DISCUSSIONS

Figure 1 shows the results of isothermal calorimetric analysis. It can be seen that nano-silica accelerates the initial hydration process. As the percentage of nano-silica increases in the paste, the quicker the peak occurs. It can also be noted that peak heat flow is also increased as nano-silica content increases within the paste. When comparing the curves for 8% and 12% nano-silica levels, it can be seen that they almost overlap on each other, indicating that after 8% replacement, the effect of increase in the reaction rate is not significant. This gives an indication 8% replacement level is a threshold limit for the acceleration of the initial reactivity of the cement paste. Beyond 8% replacement, there is limited possibility of nano-silica accelerating the hydration reaction. It should be noted that this behaviour was only observed for initial heat of hydration curves. When analysing the pozzolanic reactivity of nano-silica, as described below, no such threshold level (up to 12% cement replacement with nano-silica) was observed.

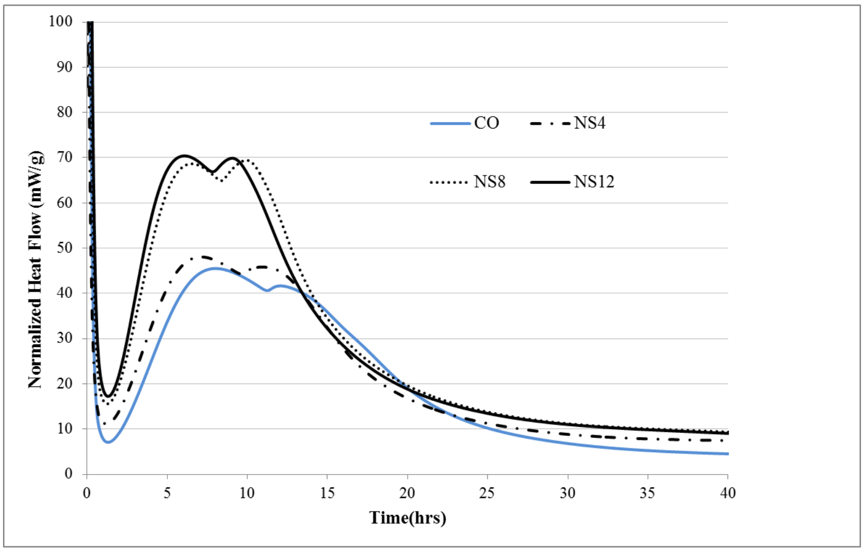

Figure 1. The heat release curves of the samples

Figure 2 illustrates a curve obtained from TGA, along with a plot of the first derivative of the TG curve (DTG). Three main peaks can be seen on the DTG curve, and among them, the peaks occurring around 420 ℃-540 ℃ and 600 ℃-800 ℃ are the peaks corresponding to the decomposition of CH and $CaCO_3$, respectively (Marsh and Day, 1988).

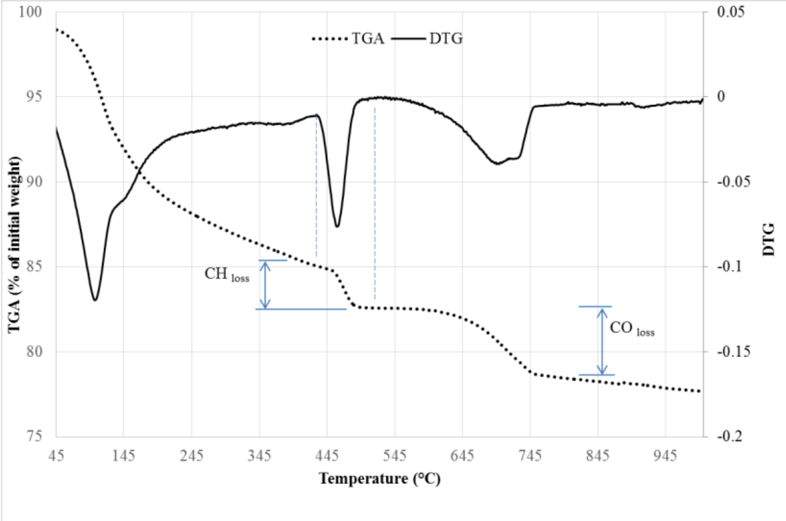

Figure 2. The TG curve and the DTG curve for one sample

The calculated CH content for different samples at 1 day, 3 day, 7 day and 28 day are shown in Figure 3. The CH content of any particular paste increases over time, due to more cement being hydrated as time proceeds. When considering nano-modified cement pastes at any time, it can be seen that the CH content is less than that of the control sample (i.e. the sample without nano-silica). It is also observed that with the increase in the amount of nano-silica present within the paste, the CH content decreases. This is because when more nano-silica is introduced in the mix, the more the pozzolanic reaction occurs, and as a result CH content in the paste is reduced. Pozzolanic activity can result in higher amounts of strength carrying CSH into the paste, which ultimately makes the nano-modified paste to have higher compressive strength (Sobolev et al., 2009, Qing et al., 2007).

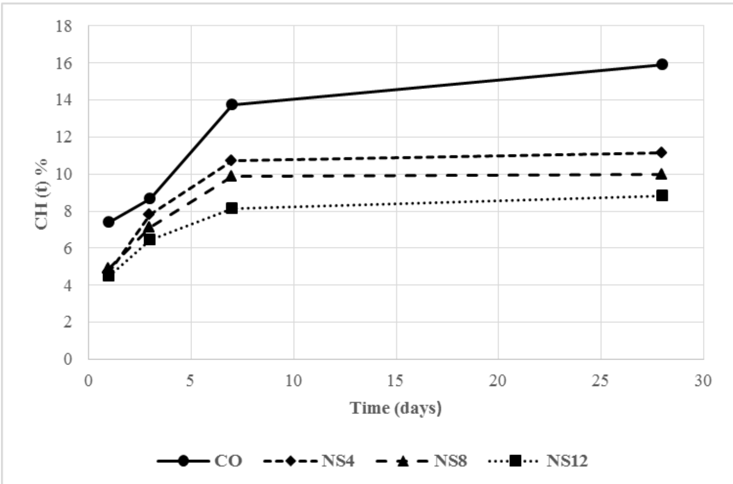

Figure 3. The CH content of the paste samples over time

CONCLUSIONS

Following the hydration reactions and investigating the microstructure of the nano-silica substituted matrices brings a new understanding of the microstructural evolution and sustainability of this system. From the results, it can be concluded that nano-silica actively reacts with the CH from the hydration of the cement paste through the pozzolanic reaction. The above characterisation of samples over the time of curing has enhanced our understanding of the behaviour of binders with nano-silica when replacing cement. Such a micro-scale understanding is essential for predicting the macro-scale mechanical and durability performance of nano-silica/cement based construction materials.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the commitment and support provided by Laura Jukes for the experimental component of this research.

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