



# Studies on early stage hydration of tricalcium silicate incorporating silica nanoparticles: Part I



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## HIGHLIGHTS

- Dissolution of  $C_3S$  is accelerated in presence of nanosilica.
- XRD results revealed the presence of additional C–S–H at early stages of hydration in nanosilica incorporated  $C_3S$ .
- Nanosilica causes supersaturation of calcium hydroxide 30 min later.
- 50% addition C–S–H formed in the presence of nanosilica.
- More polymerized C–S–H is formed using nanosilica.

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## ABSTRACT

Hydration of tricalcium silicate ( $C_3S$ ) in presence of nano silica at early stage has been investigated and formation of additional calcium silicate hydrate (C–S–H) has been quantitatively estimated. Prepared  $C_3S$  was hydrated in the presence of powder nanosilica (30–70 nm) using w/b ratio 0.4 for paste study and 5.0 for aqueous phase study. Results of ICP and XRD showed that the stage of supersaturation of  $Ca^{2+}$  is delayed by 30 min and formation of secondary/additional C–S–H starts at the early stages of  $C_3S$  hydration in the presence of nano silica. This additional C–S–H is responsible for higher dissolution of  $C_3S$  as observed by FTIR. SEM/EDX results show the formation of denser C–S–H with low C/S ratio in the presence of nano silica, whereas TG analysis revealed the formation of additional C–S–H (~50%) in nano silica incorporated  $C_3S$  system which is accountable for the higher specific surface area as obtained by  $N_2$ -adsorption.

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## 1. Introduction

Hydration of cement is a complex process due to the presence of various kinetic steps and rapidly changing mineralogy and morphology, especially at early stages. Presently, efforts are being made to improve the performance of cementitious system by incorporating nanomaterials and understanding the physical and chemical attributes from nano to mesoscale. A few theories, viz., Protective membrane, Semi-permeable membrane, Double layer theory, Crystallographic defects, Nucleation of calcium hydroxide (CH) and calcium silicate hydrate (C–S–H), etc. have been proposed to explain the phenomena occurring during hydration. In 1997, Taylor [1] reviewed these hypotheses and concluded that a different phase of C–S–H is formed on the surface of cement grains within a few seconds of hydration, which prevents its continued

dissolution. In 1962 and 1964, Kantro et al. and Stevels et al. [2,3] have reported that at first the hydrates are formed within a few seconds of hydration, which then are converted into another hydrate that is less closely fitted to the anhydrous surface and more permeable to water. In 1989, Gartner and Gaidis [4] also indicated the existence of an impermeable hydrate at the cement grains. Thermodynamic studies consider that this impermeable metastable C–S–H, formed during the initial stage of hydration, has greater solubility than C–S–H and lesser solubility than tricalcium silicate ( $C_3S$ ) and remains stable only in the induction period. In 2010, Bellmann et al. [5] have emphasized that the hydration of  $C_3S$  proceeds in two consecutive steps. In the first reaction, an intermediate phase containing hydrated silicate monomer is formed, which is subsequently transformed into C–S–H as the final hydration product in the second step (Fig. 1).

In 1986 and 2004, Jennings et al. [6,7] has reported the existence of more than one type of metastable C–S–H formed during hydration of  $C_3S$  having a unique structure and composition.

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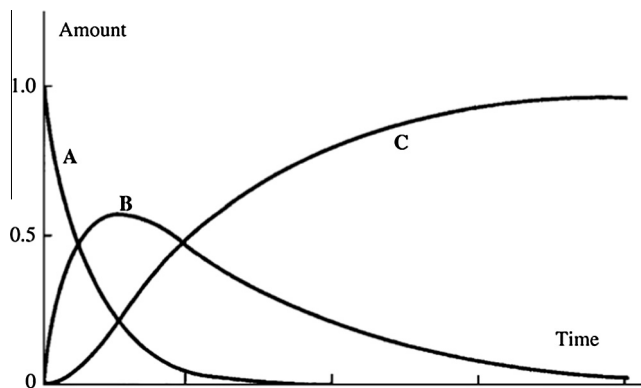


Fig. 1. Schematic representation of a process consisting of two consecutive reactions, (A =  $\text{Ca}_3\text{SiO}_5$ , B = the intermediate phase and C = C–S–H) [5].

Further, in Jennings et al., 2000 [8] proposed a ‘J–T model’ and accordingly, hydration process is completed in early, middle and late periods. During hydration, two types of C–S–H are formed: low density (LD) and high density (HD) C–S–H (Fig. 2). First stage is a period of possibly diffusion-controlled slow reaction, called the “early period,” that ends at the time of initial set. Secondly, there is a nucleation and growth stage enduring until 12–14 h or may be up to 24 h, called the “middle period.” Finally, there is the “late period” or diffusion-controlled stages, for the remaining period of the reaction. They reported that under normal conditions generally LD C–S–H is formed during the middle period, whereas during the later stage, formation of HD C–S–H is predominant.

In contrast, Scrivener et al., 2011 [10] has reported that the slowdown in the initial reaction of  $\text{C}_3\text{S}$  is caused by the changes in ion concentration in the solution, not by the presence of inhibiting layers formed on the surface of  $\text{C}_3\text{S}$  grains. Further, Scrivener et al., 2012 [11] have reported that hydration of alite is well simulated by two mechanisms: Solution Controlled Dissolution (SCD) up to the end of the induction period and Nucleation with Densifying Growth (NDG) to capture the main heat evolution peak. They proposed a scheme for early stage hydration and according to this, as  $\text{C}_3\text{S}$  grains come to the contact of water, some primary hydrates are precipitated on the surface of  $\text{C}_3\text{S}$  grains, but they do not form a continuous layer [12]. Change in dissolution rate of alite is mainly responsible for the onset of the acceleration period (Fig. 3).

Other theories postulate that the length of the induction period is governed by the nucleation and growth of hydrates, i.e. C–S–H or

(CH) [13,14]. According to nucleation theory of CH, the nucleation of CH is rate determining parameter and induction period occurs because CH is not precipitated, even after the saturation of the solution due to the poisoning of the nuclei by silicate ions. The induction period ends when the level of super-saturation is sufficient to overcome this effect [15–17]. In nucleation theory of C–S–H, the rate of reaction during the induction period is controlled by nucleation and growth of the initially formed C–S–H and the induction period ends when growth of C–S–H begins [19].

An important unresolved issue in the cement hydration is to understand the hydration chemistry during the dormant period with additives. Several additives are being used to improve the performance of cementitious system, but understanding their chemistry during hydration is a challenging task for cement and concrete technologists. Applications of nano materials in construction have brought a new revolution by improving the properties of traditional building materials [20–23]. Aim of the nano materials in cementitious system is to improve the characteristics of materials. Shah et al., 2010–2013 [24–29] have studied various engineering properties of cementitious systems using different kinds of nanomaterials such as colloidal nano silica, nanolime, carbon nanotubes, etc. Nano silica addition significantly alters the proportion of low and high stiffness C–S–H [30]. Several studies show that the application of nano silica in cementitious system improves the compressive strength at early age of hydration [31–33]. Land and Stephan, 2011 [34] have reported that the acceleration occurs during hydration of  $\text{C}_3\text{S}$ , due to the formation of C–S–H seed on the surface of nano silica. Singh et al., 2012 [35] have reported that addition of nano silica into the cement paste refined the microstructure of the paste and calcium leaching is significantly reduced as nano silica reacts with CH and forms additional C–S–H gel. The chemistry of hydration in the presence of nano silica is an important issue from the point of research, especially during the induction period. In the present studies, influence of nano silica on hydration during pre-induction and induction period of  $\text{C}_3\text{S}$  was examined using ICP, XRD, TGA, FTIR and SEM/EDX techniques.

## 2. Material and methods

### 2.1. Preparation and characterization of tricalcium silicate ( $\text{C}_3\text{S}$ )

$\text{C}_3\text{S}$  was prepared by high-temperature solid-state reaction between calcium carbonate and silicic acid. Starting materials were mixed in the stoichiometric ratio (3:1) and then heated up to 1000 °C with a rate of 10 °C/min and a curing of 5 h at this temperature. The mixture was further heated to 1500 °C with a rate of 5 °C/min and a curing of 12 h at the final temperature. The prolong heating at 1500 °C is

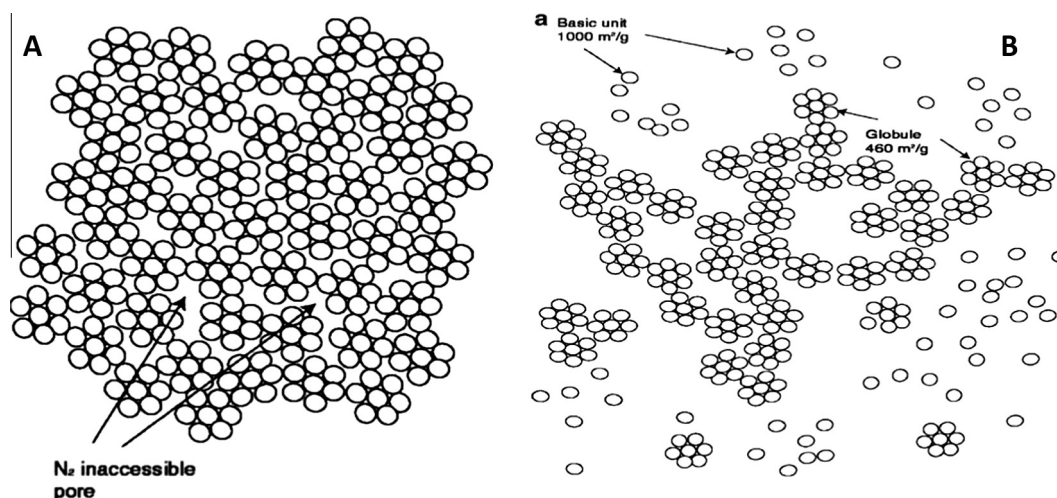


Fig. 2. 2-D schematic representation of HD C–S–H (A) and semidispersed LD C–S–H (B), respectively.

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