



# Hydration for the Alite mineral: Morphology evolution, reaction mechanism and the compositional influences



Zhang Lina<sup>a</sup>, Cheng Xin<sup>a</sup>, Hou Dongshuai<sup>b,\*</sup>, Guo Siyao<sup>b</sup>

<sup>a</sup> University of Jinan, No. 336 Nanxinhuang West Road, Shandong 250022, China

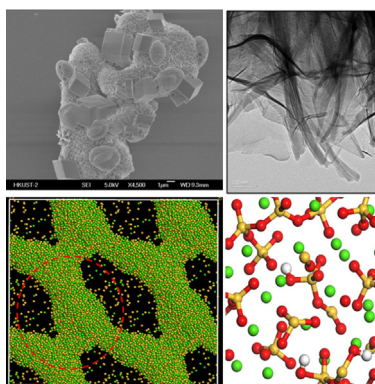
<sup>b</sup> Qingdao University of Technology, Qingdao, Shandong 266033, China

## HIGHLIGHTS

- C-S-H gel showed morphology of foil-like wrinkled clusters.
- The C<sub>3</sub>S hydration product possessed poor crystalline feature.
- Ca<sup>2+</sup> ions restrict the silicate polymerization during hydration.
- Mean silicate chain length decreases with increasing Ca/Si ratio.
- The C-S-H gel varies from branch structure to ellipsoid cluster.

## GRAPHICAL ABSTRACT

Morphology of the calcium silicate hydrate from micro-meter to nano-meter.



## ARTICLE INFO

### Article history:

Received 30 May 2016

Received in revised form 9 July 2017

Accepted 16 August 2017

Available online 23 September 2017

### Keywords:

Hydration

Polymerization

Molecular dynamics

Branched cluster

## ABSTRACT

Hydration of minerals, playing fundamental role in many technological applications, involves multi-stage chemical reactions, morphology changes and compositional variations. For the first time, the hydration mechanism for the tricalcium silicate was investigated by the combination of C<sub>3</sub>S hydration experimentally and polymerization of silicate monomers via molecular dynamics simulation. Tricalcium silicate was self-synthesized and utilized to hydrate with water at the water/solid ratio of 50. Samples hydrated from one day to one year were obtained and characterized by XRD, IR, SEM, NMR and TEM techniques. Based on SEM observation, the morphology of hydrated C<sub>3</sub>S transformed from small localized to foil-like wrinkled clusters with fibrillar-like wrinkles distributed randomly. Wrinkled product of C-S-H possessed poor-crystalline or amorphous feature based on XRD and TEM analysis. Such was also evidenced by the fact that no layered crystal phase was observed in simulated calcium silicate gel clusters. Besides, the simulated pair distribution function of C-S-H gel demonstrating the structure feature of short range order and long range disorder, also confirmed glassy structural nature for the C-S-H gel. Furthermore, based on NMR and SEM results C/S ratio changed to 1.2 and the mean silicate chain length in C-S-H was obtained at around 4 after hydration for one year with Q1 and Q2 species representing linear silicate chain structure present dominantly. The molecular dynamics helped illuminate the hydration mechanism that the morphology of C-S-H gel was closely related with C/S ratio. At C/S ratio of 1, solid branched 3-dimensional cluster was segregated from the solution while ellipsoid colloid particle with the size of 4 nm × 4 nm × 8 nm was formed at C/S ratio of 1.75. It was also found that calcium ions prevented the

\* Corresponding author.

E-mail address: [dshou@outlook.com](mailto:dshou@outlook.com) (D. Hou).

polymerization reaction of silicate monomers and silicate chains were shortened significantly at high Ca/Si ratio, amplifying the predominate percentage of Q1 species in the C-S-H gel.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Hydration reactions of minerals have been intensively investigated in many natural and industrial processes. The formation of hydration productions, modifying the local chemical and physical environment, for example, can improve the colonization by microbial communities in the soil sediment formation [1], stabilize the detrimental ions in radioactive waste repositories [2], play catalyzing role in water-oxidation reactions [3], enhance the microstructure and durability of the marine concrete structures [4] and so forth. One important example is the dissolution of Alite mineral to recombine and form in cement paste that is ubiquitously utilized as the construction materials. Meanwhile, considering 5% emission of global green housing gases due to the manufacture of cement production, investigation on the Alite mineral, involving the hydration mechanism and processing improvement, is of crucial importance to the environmental sustainability development.

The reaction of Alite mineral produces Calcium silicate hydrate (C-S-H), which makes dominant contribution to mechanical properties of cement-based materials with its great significance emphasized. However, after decades of research and study, the insights of  $C_3S$  hydration were continuously developing [5] and there were still some fundamental questions about C-S-H to be explicated [6]. Such was due to the complex components of cement as well as the intrinsic complicated structure and properties of C-S-H as gel product. Large amount of studies have been conducted based on cement hydration [7–10]. But such was not that easy to grasp the nature of calcium silicate hydrate in a multi-complex reacting system. Consequently, the hydration studies based on  $C_3S$  and  $C_2S$  were carried out by many researchers [11–13]. As was widely accepted, the reactivity of  $C_3S$  was higher than that of  $C_2S$  [14]. Hence, it was more effective and reasonable to study C-S-H from the hydration of  $C_3S$ .

Up till now, some valuable results have been acquired for the hydration evolution of  $C_3S$  and C-S-H produced. Considering the hydration mechanism of  $C_3S$  at early period of hydration, some theoretical studies have been released. Juilland and co-authors proposed the dissolution theory of  $C_3S$ . They emphasized the role of saturation state of the solution and proposed the dominate dissolution control transited from etch pits formation initially to step retreats of such etch pits later. And this was the onset of induction period mechanism as well [15]. Fernandez conducted particle size effect of  $C_3S$  to the hydration kinetics and formation of C-S-H microstructure [16]. Based on her study, the hydration kinetics was closely affected by the size of  $C_3S$  particles. The smaller ones resulted in higher dissolution peak, more heat release as well as earlier nucleation and growing process. On the contrary, there did not exhibit much difference on the microstructure formed, amplifying the independency between particle size and microstructure. Research on middle stage of  $C_3S$  hydration was also carried out. Kjellsen and Lagerblad compared hydration product of cement with  $C_3S$ , in which Hadley grain phenomenon could be observed. [17] In terms of structure characterization, various experiments were carried out by XRD, NMR, Raman, SEM, XPS, thermal analysis and so forth [18–21]. Moreover, there were also quite amount of studies carried out on the influence of  $C_3S$  hydration with other components or elements incorporated [22–24].

In addition to experimental efforts, computational methods, such as molecular dynamic, played supplement role in understand-

ing experimental findings and provided molecular insights on the hydration of minerals. The C-S-H gel investigation has made great progress with the assistance of such computational method. The simulation of silicate sol-gel reaction has been developed by Feuston and Garofalini [25] for more than 20 years. They first simulated the oligomerization in silica sols by modified BMH potential and RSL2 potential. The basic methodology was that randomly distributed silicic monomers and water molecules were heated to 2500 K, thus the reaction rate could be accelerated. Although the silicate sol-gel simulation has been developed for quite a long time, the introduction of sol-gel reaction to C-S-H gel is recent-year's effort. Dolado first simulated the silicate sol-gel reaction with the existence of calcium ions [26]. Polymerization of silicic acid ( $Si(OH)_4$ ) in calcium-riched region was taken as the process of cementitious hydration. Their study demonstrated that the addition of calcium ions slowed down the polymerization process of silica. Additionally, by counting Si–OH and Ca–OH bonds, C-S-H gel was showed similarity with tobermorite and jennite at different Ca/Si(C/S) ratio. Furthermore, based on the model constructed, they simulated the hydration process with the existence of aluminum atoms which indicated aluminum elongated the silicate chain and contributed to the 3-dimensional silicate-aluminum structures. Currently,  $3 \times 3 \times 6$  nm calcium silicate segmental branches have been discovered when the simulation system was enlarged to nearly 9 nm in one dimension after running for 2.3 ns [27].

However, most of the studies by experiment and computation up to date were mainly focused on the early stage of the hydration and the water to solid ratios (w/s) mainly equaled to smaller values from 0.2 to 1. There were quite a few studies designed for high w/s ratio in long-term hydration. HAGA conducted quite high w/s ratio from 10 to 2000 for the hydration understanding of Ordinary Portland Cement [28]. The aim of designing higher w/s ratio was to help promote full hydration of  $C_3S$  as well as induce the separation of calcium hydroxide and C-S-H which both incorporated with each other and could not be easily distinguished to some extent [29]. To understand the hydration process of  $C_3S$  and acquire C-S-H as single phase as possible to answer some basic questions of C-S-H, including composition, crystal phase, structure and so forth, higher w/s ratio was utilized for the hydration of  $C_3S$ .

In this paper, the hydration of  $C_3S$  at high w/s ratio of 50 was conducted from one day to one year to follow the structure evolution of  $C_3S$  and C-S-H produced. Synthesized  $C_3S$  was utilized as the reactant. Hydrated product was characterized by various techniques to trace the hydration process of  $C_3S$  as well as the properties of C-S-H. Furthermore, to better understand the hydration mechanism, under the environment of high water concentration, the silicic polymerization with different amounts of calcium ions introduced was simulated by performing molecular dynamics method. The silicate morphology, the influence of C/S ratio and the reaction mechanism has been analyzed in accordance with the atomic trajectory.

## 2. Methodology

### 2.1. Experimental section

#### 2.1.1. Material

$C_3S$  was self-synthesized by traditional method.  $CaCO_3$  (A.R., Alfa Aesar) and  $SiO_2$  (4N, Sinopharm Chemical Reagent Co. Ltd)

Download English Version:

<https://daneshyari.com/en/article/4918089>

Download Persian Version:

<https://daneshyari.com/article/4918089>

[Daneshyari.com](https://daneshyari.com)