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Novel understanding of calcium silicate hydrate from dilute hydration

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ABSTRACT

The perspective of calcium silicate hydrate (C-S-H) is still confronting various debates due to its intrinsic complicated structure and properties after decades of studies. In this study, hydration at dilute suspension of w/s equaling to 10 was conducted for tricalcium silicate (C_3S) to interpret long-term hydration process and investigate the formation, structure and properties of C-S-H. Based on results from XRD, IR, SEM, NMR and so forth, loose and dense clusters of C-S-H with analogous C/S ratio were obtained along with the corresponding chemical formulae proposed as $Ca_5Si_4O_{13} \cdot 6.2H_2O$. Crystalline structure inside C-S-H was observed by TEM, which was allocated at the foil-like proportion as well as the edge of wrinkles of the product. The long-term hydration process of C_3S in dilute suspension could be sketchily described as migration of calcium hydroxide and in-situ growth of C-S-H with equilibrium silicon in aqueous solution relatively constant and calcium varied.

1. Introduction

Calcium silicate hydrate (C-S-H) is the most essential and significant hydrates produced in cementitious material, constituting 70% of the quantity in cement paste and responsible for the cohesion in cement and concrete [1]. It is mainly generated from the reaction of tricalcium silicate (C_3S) or dicalcium silicate (C_2S) with water molecules through dissolution-precipitation process, with two precipitated product C-S-H and calcium hydroxide (CH) attained [2]. However, due to the complexity and uncertainty in structure, composition, crystallinity and other properties, C-S-H is still confronting lively debate [3]. Up to date, investigations have been widely conducted for structure establishment of C-S-H from the perspectives of hydration process, dissolution mechanism, model establishment and so forth [4–9] with various techniques covered for its characterization [10–17]. Valuable results have been achieved for understanding the nature of such gel compound. Juilland and co-authors proposed the theory of C_3S hydration mechanism at the early stage by dissolution theory [18]. They emphasized the role of saturation state of the solution and proposed the dominate dissolution control transited from initially etch pits formation to step retreats of those etch pits later, which was the onset of induction period mechanism as well. Kjellsen and Lagerblad compared the hydration product of cement with that of C_3S, in which Hadley grain phenomenon was observed in both cement and C_3S at the very early stage but disappeared in C_3S after 24 h [19]. Allen and co-workers utilized SANS/SAXS techniques to measure the composition and density of C-S-H in cement with Ca/Si (C/S) ratio of 1.7 and density of $2.6\ g{\cdot}cm^{-3}$attained [15]. At the mean time, there were still some contradictories on contemporary understandings. For example, in terms of C-S-H structure the majority of current models established were founded on tobermorite/jennite [5], which however, lacked obvious evidence under hydration of C_3S or alite validating its close relationships with C-S-H [20]. Although the widely accepted C/S ranged from 1.2 to 2.3 with the mean value of 1.7 to 1.8 [8], taking the mean C/S into account, large amount of Q0 silicate sites were theoretically to be acquired on the basis of structure built-up requirements of silicate ions fully bonded with calcium cations (For instance, nesosilicate, sorosilicate and inosilicate (single chain) were mixed in a proportion of 1:3:2 to constituent C/S of 1.67, with the corresponding Qn fractions of Q0 = 11%, Q1 = 67%, Q2 = 22%) which experimentally on the contrary maintained at very small amount by NMR [21] and required further investigations to interpret the nature of C-S-H. If large quantities of calcium hydroxyl groups were then supposed to be incorporated, the data obtained by Chen proposed the intermixure of C-S-H with CH at such mean ratio [22], which required more investigations to interpret. Besides, while colloidal model for C-S-H structure were proposed by some researchers [23] others supported fibrillar, wrinkled, inner product/outer product of C-S-H with various structure [13] and there did not come to good agreement on its morphologies as well. Moreover, some small crystals in nanoscale were observed in hydration product

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[24] which was whether originated from C-S-H and in what kind of manner such crystalline structure distributed was ambiguous without clear interpretation stated yet [7].

Aiming at grasping the properties of C-S-H, investigations from the hydration of single phase C_3S or alite and C_2S or belite compounds were more preferable considering the complicate feature of cementitious system. In general term, C_3S was admitted to have higher reactivity than C_2S [2], interpretation of C-S-H from C_3S hydration was more effective and reasonable, which had been conducted and discussed widely as mentioned above. For practical application of cementitious material, w/s ratio basically covered was lower than 1 for the acquisition of structure and strength development. To better interpret the nature properties of C-S-H, dilute suspension of C_3S with large w/s ratio was focused on [25–28]. HAGA utilized high w/s ratio ranging from 10 to 2000 for the hydration of ordinary Portland cement [14]. Nonat and co-workers conducted extensive studies on dilute hydration of C_3S as well as reaction of lime and silica in which calcium ion concentration was controlled to interpret the dissolution kinetics and solubility of C-S-H [29–30]. Founded on the solution equilibrium with solid phase, they have proposed three C-S-H phases with varied ranges of C/S ratio of 0.7–1, 1–1.5, and greater than 1.5 respectively. Currently, the early stage of hydration for C_3S have been widely discussed and overviewed with the initial hydration, induction, acceleration, steady stage and deceleration summarized within hydration of 1 day [31]. However, there is a paucity of knowledge on the mechanisms controlling hydration kinetics beyond one day [7]. Systematical characterization on structure and morphology evolution and crystalline properties for long-term hydration was far from reported.

In this study, self-synthesized C_3S was hydrated covered from one day to one year at w/s of 10 with diverse characterizations conducted tracing the hydration process and hydrates evolution. With high w/s conducted, full hydration of C_3S were to be promoted for C-S-H precipitated as single component or pure compound to the most probability to clarify C-S-H properties, including morphology, composition, crystalline structure and so forth. In combination with the silicate structure evolution, the long-term hydration of C_3S under dilute suspension was deduced, in the hope of facilitating the nature of C-S-H worked out and providing valuable data for the establishment of long-term hydration in future.

2. Experimental section

2.1. Materials

C_3S was self-synthesized via traditional method [32] by solid state sintering reaction of calcium carbonate (A.R., Alfa Aesar) and silicon dioxide (4N, Sinopharm Chemical Reagent Co. Ltd.) and characterized with satisfied quality obtained (Appendix). Ultrapure water (UP water, ultrapure Millipore water with resistivity greater than 18.2 MΩ·cm at 25 °C (Milli-Q, Millipore)) was used to prepare all solutions.

2.2. Experimental procedure

Self-synthesized C_3S were evenly mixed with UP water at w/s of 10, kept and sealed in PVC bottle (UP water washed and dried) for 1 day (d), 3 d, 7 d, 14 d, 28 d, 180 d and 365 d respectively in constant 20 °C dry cabinet (DRY-70, WEIFO). Vacuum filtration was then carried out in a fast speed to separate solid with liquid, followed by drying (less than 20 min) of the solid product in vacuum oven at 80 °C and sealed in desiccators. The liquid solution was collected in clean PVC bottles and put into dry cabinet.

2.3. Characterizations techniques

X-ray diffraction data were collected on Philips diffractometer using Ni filtered CuK$_\alpha$ radiation at 40 kV and 40 mA. The measurements were performed with a step size of 0.02° and a scan rate of 2°/min in the scan range of 5°–80° 2 theta (2θ). FT-IR spectroscopic measurements were conducted using Fourier transform infrared spectrometer (Bruker Vertex 70) covering mid-IR range (frequency: 4000–400 cm^{-1}). For the measurements, the samples were diluted by KBr with a sample/KBr weight ratio of around 1/100, compressed to give self-supporting pellets and measured relatively to the KBr as a reference. The morphology of the samples was controlled on JEOL6300, 6700 scanning electron microscope at an accelerating voltage of 5–20 kV, depending on the sample state at varied magnifications. To minimize electric charging during measurement, the samples were sputtered with a fine layer of gold. Energy dispersive spectroscopy analysis (X-Max 80 mm^2, Oxford instruments) was equipped for chemical composition determination. For the basic bulk quantifications approximately 50 results were acquired for each result. The equipment was calibrated with Ca and Si. Transmission electron microscopy images were taken using JEOL2010F operating at 200 kV with sample held on copper grid. For one specific sample, diffraction was firstly conducted, followed by image capture and finally energy dispersive spectroscopy (X-Max 50 mm^2, Oxford instruments) when necessary, aiming at keeping crystalline information, the morphology as well as the composition consistently. All NMR experiments were performed at room temperature on a Bruker Avance III 900WB spectrometer, operating at frequencies of 178.8 MHz Larmor frequency for ^{29}Si with a 3.2 mm CP-MAS probe. Single-pulse ^{29}Si spectra were attained at a MAS frequency of 10 kHz with a ^{29}Si 90 degree pulse length of 3.25 μs used. 640 scans were accumulated for each sample and a long recycle delay of 120 s were conducted necessary to yield quantitative spectra. Chemical shifts were referenced using tetramethylsilane as the external reference. Thermogravimetric analysis was conducted with Perkin Elmer Thermogravimeric Analyzer. The ramping rate was 20 K·min^{-1} and 10 K·min^{-1} below and above 100 °C respectively under a nitrogen flow of 100 cm^3·min^{-1}. The analyzed mass was around 0.05 g. pH measurements were performed with an Xplorer GLX Instruments (PS-2002, Pasco) and a glassy electrode. Standardization was conducted with buffer solution at pH of 6.86 and 9.18. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was taken with IRIS Intrepid II XSP instrument (ThermoFisher) which had been standardized by Ca and Si. All the samples were filtered on a 0.22 μm filter (MILLEX-GP, Millipore) before the tests were conducted.

3. Results and discussion

3.1. XRD

Phase analysis of the hydrates was described in Fig. 1. Characteristic peaks of C_3S (32°–33°, 51°–52° and 41°–42° 2θ) were gradually weakened during one year's reaction, indicating continuous increment

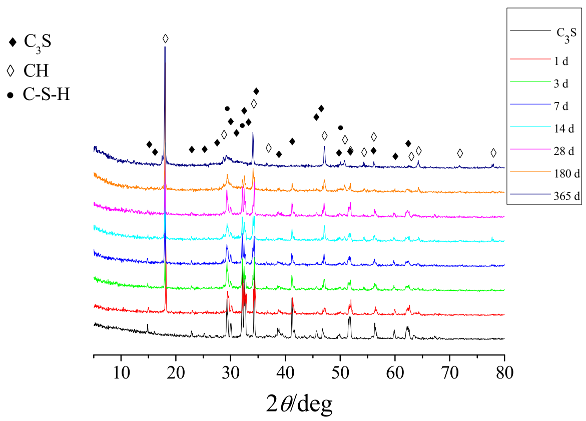

Fig. 1. XRD spectra of hydrated C_3S from 1 d to 365 d.