

Morphology of cementitious material during early hydration

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ABSTRACT

Morphology of hydration products, mainly calcium-silicate-hydrate (C-S-H), has a strong influence on the mechanical and transport properties of hardened cementitious materials. This paper examines the effect of curing conditions and drying methods during specimen preparation on C-S-H morphology. It shows that an appropriate drying method, either supercritical drying (SCD) or isopropanol (IPA) replacement, is able to preserve the delicate microstructure on both macro and micro scales. On the surface of the specimen, the structure is fibrillar for specimens cured in high relative humidity (RH) chamber or reticular for specimens cured in pore solution/limewater. A thin layer with cluster-like structure was found for specimens cured in high RH. By observing the fracture surface, it is found that the interior morphology is complex and varies with depth and curing methods. Consequently, one must take into account the effect of ion transport during the curing and drying when preparing specimens for microstructure analysis. We proposed that the basic units of C-S-H are fine fibers and thin sheets.

1. Introduction

When water is added to cementitious materials, a series of hydration and precipitation reactions eventually leads to hardened porous products. The reaction is initially relatively rapid, and the early development of strength and stiffness is essential for constructability with concrete. The reactions may continue for years, and the evolving microstructure determines the long-term mechanical and transport properties that control the durability of the material. In this study, we exploit supercritical drying [1] to prepare hydrated cement samples at early ages (≤ 24 h) that are free of artifacts created by capillary pressure during conventional drying processes. The goal is to reveal the microstructure of the calcium-silicate-hydrate (C-S-H) phase², which is the binder in concrete, to guide efforts to develop theoretical models of the hydration process [2,3] for prediction of long-term properties.

2. Review of morphologies of hydration products

Hydrated cementitious materials are composed of C-S-H, calcium hydroxide (CH), residual unhydrated cement constituents, and minor hydrated components including ettringite, and calcium monosulfoaluminate. C-S-H is the dominant component for pastes with a reasonable degree of hydration, so that we will primarily focus on the

morphology of C-S-H in this study.

Hydration products can be divided into two broad groups. Different terminologies have been used for them, such as inner product (IP) and outer product (OP) [4], phenograins and groundmass [5], and high density and low density C-S-H [6,7]. Taplin [4] concluded that OP forms in the originally water-filled spaces and IP within the boundaries of the original clinker particles. Although there is not necessarily an exact correspondence between the positions of the outer boundaries of IP and the original grains [8], the scheme is straightforward and has been widely adopted [9,10]. In terms of morphology, inner products are nearly devoid of morphological characteristics. Only extremely fine pore structure can be seen. The morphology we can see by microscopy is mainly from the outer products.

2.1. Types of C-S-H morphologies

It is generally believed that there are numerous types of C-S-H morphologies. To the best of our knowledge, the morphology of cement hydration was first documented in the 1950s [11,12]. The change in morphology from “foils” to “fibers” was described by Grudemo in the results of the transmission electron microscopy (TEM) studies on calcium silicate hydrates [12,13]. He also argued that this morphological change is due to Ca/Si ratio going from low to high. In the following

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² The cement chemistry notation: C= CaO, S= SiO₂, H= H₂O, A= Al₂O₃, F= Fe₂O₃ and \bar{S} = SO₃.

decades, a number of studies using the SEM/TEM were reported (e.g. [3,14–25]).

Using TEM (powder mounts), Grudemo [14] concluded that fibrous or acicular C-S-H morphologies were observed in the hydrated Portland cement pastes, and C-S-H seems ultimately to have a lamellar structure [26]. By using a single stage carbon replica technique to prepare hardened tricalcium silicate (C_3S) pastes for electron microscopy analysis, Copeland and Kanro [27] reported that the bundles of fibrous C-S-H resemble the “sheaf of wheat” morphology. Williamson [26] explained these observations as “the result of multiple layers of a thin crystalline material overgrowing itself”. Diamond [15] documented two types of microstructure for C-S-H: a “branching or dendritic mode which generates spherulitic or globular clusters in favorable circumstances”, and a “reticular network or ‘spongy’ structure”. Changes in C-S-H morphology on hydrating C_3S pastes at different hydration times were studied with TEM by Collepardi and Marchese [28]. They found that the initial product was foil-like (at 4 h of hydration) and was transforming into fibrils with increasing hydration time (1 day and 100 days of hydration). The similar tendency was also observed in SEM images recently reported by Bazzoni [25] who showed tiny blades (at 3 h) changing to short fibers (at 6 h). In contrast, Ciach et al. [16] and Ciach & Swenson [17,18] reported that the morphology of the C-S-H gel in Portland cement paste changes from foils and fibrous particles to platy form (7 days) and then eventually to a massive tabular structure (6 months). They believed that these transformations are created by a process of “filling in” with hydration products, such as CH and C-S-H. Berger and McGregor [20] analyzed the C-S-H morphology in hydrated C_3S pastes including various different admixtures. They classified the resulting morphologies in two types: fibrillar and foil-like, which are denoted by Type I and Type II C-S-H, respectively. Their results showed Type I morphology for samples without admixture (just water), and Type II C-S-H for samples with $CaCl_2$. This classification was further extended in 1976 by Diamond [21] to include Types III and IV, the latter being inner product. By using high resolution SEM, Menetrier et al. [22] studied the morphological development during hydration from several minutes to hours by examining the surface of pressed pellets of C_3S . They observed the change from “corroded” surface at 15 min to “honeycomb” after 3 h (Type 2 morphology, similar to Fig. 6a). They also found that the typical pore in this structure is about 200 nm.

A morphological classification for C-S-H formed in hydrating C_3S pastes was introduced by Jennings et al. [23] based on observations of ion-thinned sections in a TEM. It consists of Type E (or early) and Type O (or “middle”) product, formed in the middle hydration period (Stages III & IV, see Fig. 1). Depending on the available space, Type O changes into Type 1 - slightly tapered needles radiating perpendicularly from C_3S grains with an aspect ratio of about 10 (in open areas $> 1 \mu m$) - or Type 3 (crumpled foils where inter-particle spacing is $< 1 \mu m$). Type 4 is a dense gelatinous inner product that forms in the later hydration stages. Note that Arabic and Roman numerals and letters used here follow the C-S-H classification in the literature (mainly in [21] and [23]). Jennings et al. did not find the Type 2 C-S-H in their studies as reported by Menetrier et al. [22], and they argued that Type 2 morphology might form readily on the free surface of specimens. Groves et al. [24], also using TEM of ion-thinned C_3S pastes, found it difficult to make a sharp distinction between Jennings et al.’s Types 1 and 3 morphologies, and preferred instead to characterize all outer product C-S-H in hardened C_3S or Portland cement as “fibrillar”. This simplification is reasonable as we will show later in this paper that one of the basic units for all morphologies is the fine fiber.

The classification of C-S-H morphologies reported in the literature is summarized in Table 1. The observed morphologies do not necessarily correspond to the period listed in the table, as we will show in this paper. It is generally agreed that the morphology of C-S-H changes with hydration time and the space for C-S-H growth. In a short hydration, only flake-like structure can be seen on the surface of a cement

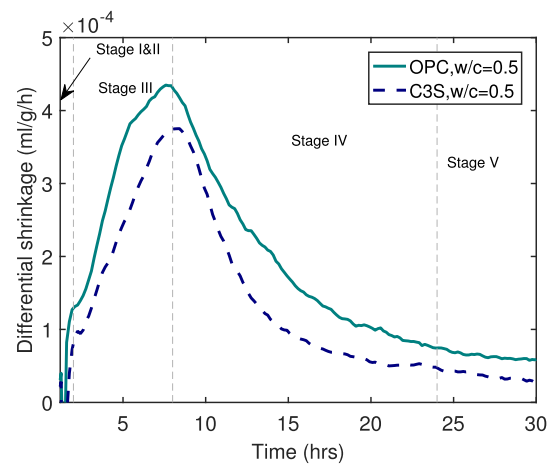


Fig. 1. Chemical shrinkage curves of OPC and C_3S with water-to-solid ratio = 0.5. The main measurement procedure follows [69] and [70], but a multiple de-airing procedure was used to remove air bubbles in the measurement system. It needs about 1 h for sample preparation and system stabilization, so measured data at short times are not reliable; time is measured from first contact with water.

grain [23,29]. In the later stages, if sufficient space is available for growth, C-S-H becomes fiber/needle-like [30], while if the space is constrained, a “honeycomb” [31] or foil-like [20,23] microstructure can develop. This may occur when fibers/needles from two or more cement grains impinge in the constrained space. Richardson [9] pointed out that this morphological transition is more obvious with higher slag loading. Slag particles are finer than cement grains [32] so that they can fill the gaps between cement grains and then create constrained space for C-S-H growth. The microstructural development of a cement grain, summarized by Scrivener [33], showed that the presence of AFt had an influence on the transition of C-S-H from flake-like to fiber-like structures. Since the 1990s, fewer studies have been focused on the classification of C-S-H morphologies, and most morphologies reported in the literature can be included in the classification in Table 1 (e.g. [25,34–36]). Researchers shifted their attention to model the microstructure of C-S-H (e.g. [6,7,37,38]), understand the hydration mechanism (e.g. [39]) and develop hydration models (e.g. [2,40–43]).

The morphologies of other phases, mostly crystalline, are much simpler than C-S-H. Calcium hydroxide appears as thin hexagonal plates or flakes giving well defined scanning electron diffraction patterns. Ettringite (calcium trisulphoaluminate hydrate) appears as long coarse rods or splines; the monosulfate form appears as thin plates (e.g. [14]).

2.2. Factors affecting morphology

The morphology of C-S-H changes in response to different conditions of formation. Main factors that can affect the morphology of hydration products are summarized as follows.

2.2.1. Curing temperature

The hydration of cement is sensitive to temperature for many reasons. High temperature is able to significantly increase the rates of hydration and precipitation of hydration products during the first hours and days. Thomas et al. [44] reported that the saturation levels of ettringite decrease with increasing temperature which reduces precipitation of ettringite at the higher temperature, while monosulfate becomes the favored phase due to its smaller enthalpy of reaction. Lothenbach et al. [45] showed that the fast hydration in the initial stage leads to a more heterogeneous distribution of the hydration products [46] and precipitation of a denser inner product of C-S-H [47]. In contrast, low temperature results in a less dense C-S-H and more uniform distribution of hydration products [48,49]. Gallucci et al. [50]

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