

# Numerical Model for Growth and Porosity of C-S-H Structures in Cement Hydration

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## ABSTRACT

In this paper, we propose a model based on surface reactions and ion transport to capture the development of C-S-H not only at early age but also at later age of hydration. With the assumption of the mass balance between dissolution and precipitation processes, we derive an equation for the C-S-H precipitation rate. The model takes both the coverage of C-S-H on C<sub>3</sub>S surfaces and the ion diffusion through a semi-permeable layer of C-S-H into account. The C-S-H growth model is implemented and investigated in ‘sheet growth’ geometrical platform (Etzold, et al., 2015) with kinetic Monte Carlo method. Furthermore, we introduce a geostatistical method to quantify pore volumes and phase fractions in the simulation, which are shown to be consistent with those obtained from experimental data (X-ray diffraction and 1H NMR).

**KEYWORDS:** *C-S-H calcium-silicate-hydrate, micro-structure, numerical simulation, pore size distribution*

## 1. Introduction

Calcium silicate hydrate (C-S-H) determine the performance of cementitious materials. Understanding the microstructure and the formation process of these phases is a key for improving material properties and minimizing the impact on the CO<sub>2</sub> footprint. Most studies concerning nucleation and growth of C-S-H phases in experiments as well as in modelling focus on the development of C-S-H at early ages (Thomas, et al., 2011; Bullard, et al., 2015; Ouzia & Scrivener, 2019; Nguyen-Tuan, et al., 2020). This early reaction rate is observed indirectly via heat flow measured by means of calorimetry. However, 80 % of the strength of cement paste develops at later ages i.e. from 24 hours to 28 days (Marchese, 1983), when C-S-H fibres mostly fill the capillary pore and interlock with each other. Many authors (Nguyen-Tuan, et al., 2020; Scherer & Bellmann, 2018; Bellmann, et al., 2019) have proposed growth models assuming that the coverage of C-S-H on C<sub>3</sub>S surface determines the decelerating rate of C-S-H formation. The simulation results showed a qualitative agreement with the reaction rate measured by calorimetry within 48 hours. However, for long-term hydration, when the C<sub>3</sub>S surface is fully covered, these models no longer fit experimental data, where it is observed that the growth of C-S-H still continues (Muller, et al., 2013).

Here we introduce a model, which associates ion transport with the sheet growth geometrical model (Etzold, et al., 2015; Nguyen-Tuan, et al., 2020) to capture the growth as well as the transient structures of C-S-H during hydration process. The growth model is based on the physical and chemical laws on surface reaction and transport. The mass balance between dissolution and precipitation processes is used with the assumption that the ion transport is at steady state. The model takes thereby both the coverage of C-S-H on C<sub>3</sub>S surfaces (Bellmann, et al., 2019) and the ion diffusion through a semi-permeable layer of C-S-H (Hou, et al., 2015; Gartner, et al., 2002) into account, which allows simulating a slow growth of C-S-H at the later age.

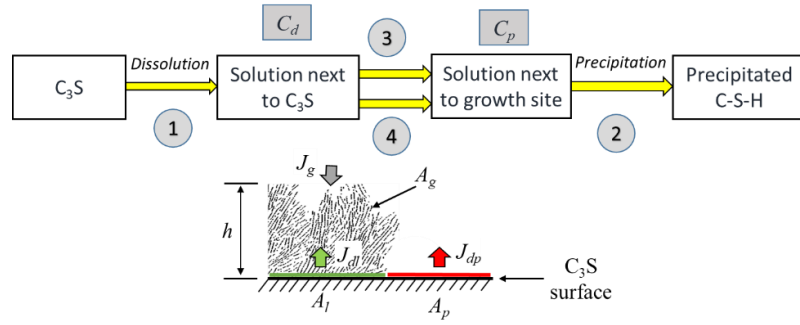


Figure 1: Scheme describing dissolution-precipitation processes: ① Reaction at C<sub>3</sub>S surface, ② Reaction at C-S-H surface, ③ Diffusive transport through C-S-H layer, ④ Diffusive transport through pore fluid. The lower figure visualizes the parameters contributing to the process;  $J_{dl}$  and  $J_{dp}$  are the diffusion through C-S-H layer and pore, respectively;  $J_g$  is the precipitation rate.

## 2. Modelling

### 2.1 Growth model

It is denoted that  $D_{CSH}$  and  $D_d$  are the diffusions coefficients of the C-S-H layer and the pore water;  $h$  is the thickness of the C-S-H layer;  $A$  is the total surface of C<sub>3</sub>S grain;  $A_p$  and  $A_l$  are the free and covered surfaces of C<sub>3</sub>S grain respectively (Fig.1);  $A_g$  is the available C-S-H surface where other C-S-H elements can grow;  $c_d$  and  $c_p$  are the ion concentrations for dissolution and precipitation at the respective surfaces;  $C_{deq}$  and  $C_{peq}$  are the equilibrium concentrations at dissolution and precipitation surfaces;  $k_d$  and  $k_g$  are the reaction rates at surfaces of C<sub>3</sub>S and C-S-H, respectively.

The model is based on the mass balance concept, assuming that ion transports takes place in steady state (Nicoleau, et al., 2013), i.e. the mass transport of dissolution is equal to the mass transport in precipitation. The flowchart presenting the mass transport processes is shown in Fig.1, the lower figure describes the quantities and parameters. A series of processes is presented here. In the first step, the ions dissolve from the unhydrated surface to the pore fluid next to the surface. This process is controlled by the reaction rate, according to the first-order reaction. The next process is the ion transport from the surface to the fluid next to the growth site, assuming that the transport length is the C-S-H layer thickness as Fig.1. This transport occurs in two parallel processes: The transport through pore fluid and the transport through C-S-H layer, both are described by Fick's law (Fick, 1855). The transport through the pore fluid dominates at initial state, whereas, the transport through the C-S-H layer dominates at the final state, when C-S-H covers all the unhydrated surface. Finally, the reaction process describes the precipitation of ions to C-S-H at its surface. The processes from 1 to 4 are described in Eq. 1 to 4, respectively.

- Reaction at the C<sub>3</sub>S surface as the dissolution is calculated via net rate of dissolution of C<sub>3</sub>S

$$J_d = -A k_d (C_d - C_{deq}) \quad (1)$$

- Reaction at the C-S-H surface as precipitation is calculated via net rate of product of C-S-H

$$J_g = A_g k_g (C_p - C_{peq}) \quad (2)$$

- Diffusive transport through the pore fluid defined by Fick's law:

$$J_{dp} = -A_p D_p \frac{C_p - C_d}{h} \quad (3)$$

- Diffusive transport through C-S-H layer defined by Fick's law:

$$J_{dl} = -A_l D_{CSH} \frac{(C_p - C_d)}{h} \quad (4)$$

where the total C<sub>3</sub>S surface is the sum of two surfaces

$$A = A_p + A_l \quad (5)$$

The total area  $A$  is normalized as area fractions and is equal to 1,  $A_l = \phi$  the fraction of the surface covered by C-S-H phases. Finally, the mass balance conditions at steady state lead to

$$\begin{aligned} J_d &= J_g, \\ J_{dl} + J_{dp} &= J_d, \end{aligned} \quad (6)$$

substituting Eq. 6 to Eqs. 1 to 4.

$$J_g = \frac{A_g k_g k_d (C_{deq} - C_{peq}) [D_{\{CSH\}(1-\phi)} + D_p \phi]}{D_{CSH} (k_d + A_g k_g) (1-\phi) + D_p k_d \phi + A_g k_g (h k_d + D_p \phi)} \quad (\text{mol/h}) \quad (7)$$

Assuming that the density of a C-S element does not change during the hydration. At steady state, the precipitation rate is proportional to the volumetric growth or  $\kappa = \lambda J_g$ , where  $\kappa$  (h<sup>-1</sup>) is volumetric growth rate,  $\lambda$  (mol<sup>-1</sup>) ratio converting from molar mass to number of a C-S backbone element. The rate  $R$  using in kinetic Monte Carlo approach can be computed as

$$R = \kappa S, \quad (8)$$

Where  $S$  is the number of available surface for the element growth.

## 2.2 Parameters

The geometrical parameters (i.e.  $A_l$ ,  $\phi$ ,  $A_g$  and  $h$ ) are determined directly from model geometry. The thickness of C-S-H layers  $h$  is the difference between highest C-S-H solid elements and the substrate. The C-S-H interface ( $A_g$ ) is calculated by the number of available surfaces  $S$  (Nguyen-Tuan, et al., 2020). The covered surface  $A_l$  is computed each time step via geometry of C-S-H phases,  $A_l$  is the projected area of all C-S-H elements, which place at the height smaller than 10 nm from the bottom side of the domain. The pre-determined parameters (i.e.  $D_{CSH}$ ,  $D_p$ ,  $C_{deq}$ ,  $C_{peq}$ ) are from literature, the growth parameters ( $k_g$  and  $k_d$ ) are assumed.

## 3. Model evaluation

The growth model allows to simulate the acceleration and deceleration of C-S-H growth at early age (up to 24 h). Furthermore, the model can capture the slow growth at later age (i.e. 10 days), which has been determined by means of <sup>1</sup>H NMR spectroscopy (Muller, et al., 2013). Results in Fig. 2 show how the variation of model parameters affects the hydration kinetics. It is obvious, that the variation in ion diffusion coefficient of C-S-H insignificantly affects the growth rate at the early age, however, it affects the cumulative C-S-H growth at the later ages (Fig. 2, a and c). The change in ion diffusion coefficient of the pore water affects significantly the growth rate and cumulative C-S-H at both early and later ages (Fig. 2, b and d).

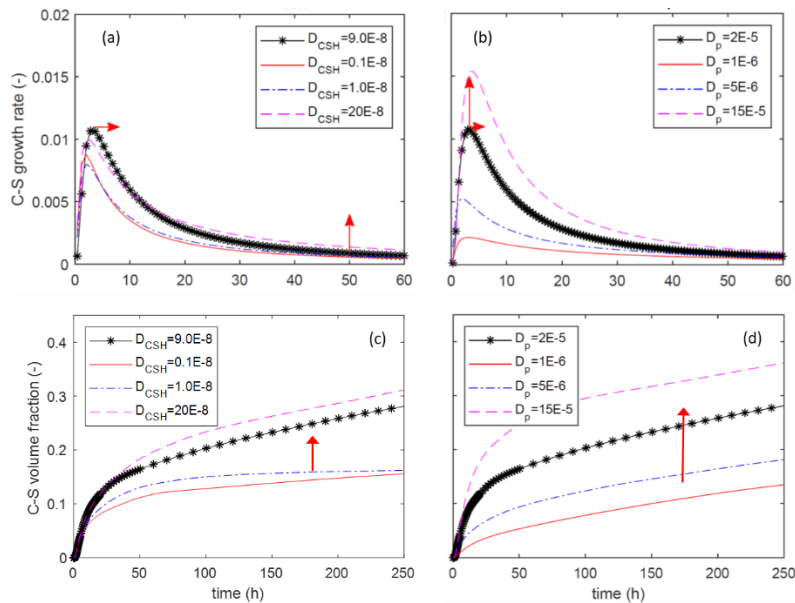


Figure 2: Model evaluation using one-at-a-time sensitivity analysis for diffusion parameters ( $D_{CSH}$  and  $D_p$ ): (a,b) Growth rate; (c,d) Cumulative growth.

With combination with the ‘sheet growth’ geometrical model, the model can capture the rate of C<sub>3</sub>S surface coverage, the development of C-S-H, and the development of pores in C-S-H. However, due to limitation of the paper length, these aspects of the model will be only shown in the presentation.

#### 4. Conclusions

It is generally believed that C-S-H phases surrounding C<sub>3</sub>S grains are semi-permeable and the diffusion through this layer attributes to a slow C-S-H formation at the later ages. Based on this idea, we propose a physico-chemical model for the C-S-H growth, which considers surface reactions and ion transports as factors controlling the growth rate. Therefore, the new model allows simulating not only the acceleration and deceleration of C-S-H growth at the early age but also the slowing growth of C-S-H at the later hydration age.

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