(How) Can C-S-H Growth Behavior Be Predicted?

Questions from a Modeling Perspective

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Objectives of Modeling

Primary purposes of modeling are to:

**Gain Insight:** Distill real system into one with simpler physics/chemistry that you think are relevant. Analyze behavior of model to better understand qualitative behavior of the real system. Represents a research tool.

**Predict:** Use basic mathematical equations, perhaps with some physical basis, having fitting parameters that can be calibrated to experiment. Use to interpolate predictions on similar systems... an empirical approach.

**Both:** Build as much realistic physics/chemistry back into the research tool to gain better quantitative predictions. Represents a design tool.
A Sampling of Cement Hydration Models

**HYMOSTRUC (TU Delft):**
- multi-parameter semi-empirical equation for kinetics, based on PSD, w/c ratio, and clinker composition
- C-S-H assumed as a continuous layer around spherical particles

**µIC (EPFL):**
- modeling platform for representing microstructure
- user-defined kinetic equations (Avrami-type, multi-parameter semi-empirical, etc.)
- user specifies growth rules for C-S-H and CH

**CEMHYD3D (NIST):**
- discretized, heterogeneous particles
- probabilistic rules for dissolution, nucleation, growth
- rules calibrated to simulate OPC hydration
Materials Science Microstructure Models

**Cellular Automaton Models:**
- Used to simulate dendrite growth and morphology during solidification, recrystallization, grain growth, etc.
- Crystallographic orientation dependence

**Phase Field Models:**
- Based on localized reduction in free energy using TDGL
- Captures phase separation, solidification, coarsening, sintering
- Parameters directly linked to local composition and phase volume fraction
Localized Kinetic Description

Let \( \varphi \) be a material parameter that can be distributed heterogeneously in a system (like a microstructure representation).

In any volume element **small enough** that \( \varphi \) and all other parameters are approximately homogeneously distributed, then

\[
\dot{\varphi} = (\text{Kinetic factor}) \times (\text{Thermodynamic driving force})
\]

**Examples:**

\[
\dot{c} = \frac{Dc}{kT} \nabla^2 \mu
\]

Single component diffusion

\[
[C] = k_+ \{A\} \{B\} \left(1 - \frac{K}{K_{eq}}\right)
\]

Rate of elementary reaction \( A + B \rightarrow C \)
Why is a Localized Description Important?

1. Cement paste has heterogeneous phase distribution and composition
2. Dissolution, nucleation, and growth are mediated by pore solution.
3. Driving force, e.g. saturation index, for each phase is generally different from point to point
4. Location and morphology of precipitated phases is inherently localized
5. The parameters describing the process are actual physical/chemical properties of the materials comprising the system, instead of model-dependent empirical parameters
6. Any change to the system that affects local driving force or kinetics can be accommodated naturally — w/c, particle size distribution, temperature, chemical additives.
**Why is a Localized Description Important?**

Morphology of C-S-H varies significantly over small distances.

Therefore, morphology appears to be governed by some differences in local growth conditions:

(solution chemistry, confinement ... ?)
What are the Effects of Length Scale?

If C-S-H is built from 5-nm “bricks”, then

1. What determines how the bricks assemble together at greater length scales?

2. How can bricks collectively “know” whether to grow as foils, fibers, etc., and what determines the fiber width and length?
What are the Effects of Solution Chemistry?

Several studies have indicated a composition range for C-S-H gel

- C-S-H(I) has Ca/Si ~ 1.2 and forms in solutions with low Ca/Si ratios. Reported to form a dense layer on C₃S surfaces
- C-S-H(II) has Ca/Si ~ 2 and forms in solutions with high Ca/Si ratios. Reported to be less dense, less protective on C₃S

Pore solution chemistry also influences the kinetics of hydration dramatically

Nonat and coworkers also argue that solution chemistry affects the growth anisotropy of C-S-H nuclei on C₃S surfaces

Each lattice site has a set of **occupation numbers**, \( \{N\} \) of cells of each type of substance. \( \langle N \rangle = \zeta C \)

Cells at a given node can, with defined probability

- Diffuse, with specific mobility, to a neighboring node
- React with other cells at that node according to values of \( \{N\} \) and a given rate constant for the reaction
C₃S Hydration Simulation

Real-shape particles obtained by FIB (R. Flatt and L. Holzer)

w/c = 1.4
\[ \lambda = 1.0 \ \mu m/site, \ with \ C-S-H(m) \]
\[ \log K_{sp}(C_3S) = 0.48 \]
\[ \log K_{sp}(C-S-H(m)) = -17.1 \]

Open points are experimental data from Garrault and Nonat.

Example: Influence of Calcium Salts

Ca(OH)$_2$ is predicted to delay hydration of C$_3$S, extending the induction period and reducing hydration rates everywhere.

CaCl$_2$ is predicted to have no effect on the induction period, but to accelerate hydration through more rapid growth of hydration products.
Ongoing Questions

1. These simulations assume that reaction order is equal to the molecularity. Can we obtain experimental measurements of reaction order, i.e. rate law, for growth of C-S-H and other complex minerals like ettringite?

2. These simulations assume that C-S-H nucleates heterogeneously on C₃S surfaces, but there are reports that C-S-H may rapidly fill capillary pore space at very early ages and then “densify” with time. What mechanism could explain this rapid growth?

3. How do other solution components, especially aluminates and other anions (Cl⁻, SO₄²⁻) affect C-S-H in terms of its growth rate constant, its composition, its morphology, and its density?

4. Can we characterize C₃S surfaces to better understand how its dissolution rate varies with time (see talk by Patrick Julliand)?

5. HydratiCA simulations indicate that induction period can be modeled well by assuming either (a) low-solubility C₃S surface or (b) high-solubility C3S surface protected by a metastable layer of a calcium silicate hydrate (Stein & Stevels). Can experiments be devised to distinguish between these two mechanisms?
Many questions persist about the nature of C-S-H growth kinetics and morphology

A model framework that uses a localized description of microstructure evolution can provide much-needed links between solution chemistry, temperature, and material properties that are not provided by other kinds of cement hydration models. HydratiCA is one example.

This modeling approach requires knowledge about fundamental properties or materials and their interactions with water: $K_{eq}$, growth and dissolution rate constants, density, activation energies, adsorption isotherms for impurities, nucleation barriers.

Also requires more research into the link between nanoscale C-S-H structure and the emergence of various C-S-H morphologies. We can build this detail into the model if we understand the mechanism.

As more fundamental information becomes available, it can be incorporated into this modeling approach and make the model increasingly powerful.

This will require a sustained collaboration between experimentalists and modelers.