Single Particle Model for C_3S Hydration: A Multi-Component Distributed Parameter Continuum Approach

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Abstract:

Tricalcium silicate, the main constituent of many types of cements including Portland cement, white cement, and oil well cement applications, is frequently used as a model material to study hydration. Although theories in the literature over the past 40 years have offered considerable insights into hydration process, reaction mechanisms, and microstructure development, a detailed quantitative representation of kinetics and transport phenomena has not been agreed upon. To help train our intuition and to test various assumptions we have build a progression of single particle models from the simple to more complex. We propose to eventually develop a rigorous multi-component model that can be used to test various hypothesis. Such models are suitable for integration with microstructure simulation tool-kits such as μic and those developed by the VCCTL and are vital inputs to other multi-scale formalisms including Population Balance Models (PBM).

Objective:

To provide a rigorous multi-component kinetic based formalism for the qualitative and quantitative study of reaction and transport mechanisms for C_3S hydration.

Reaction Mechanism:
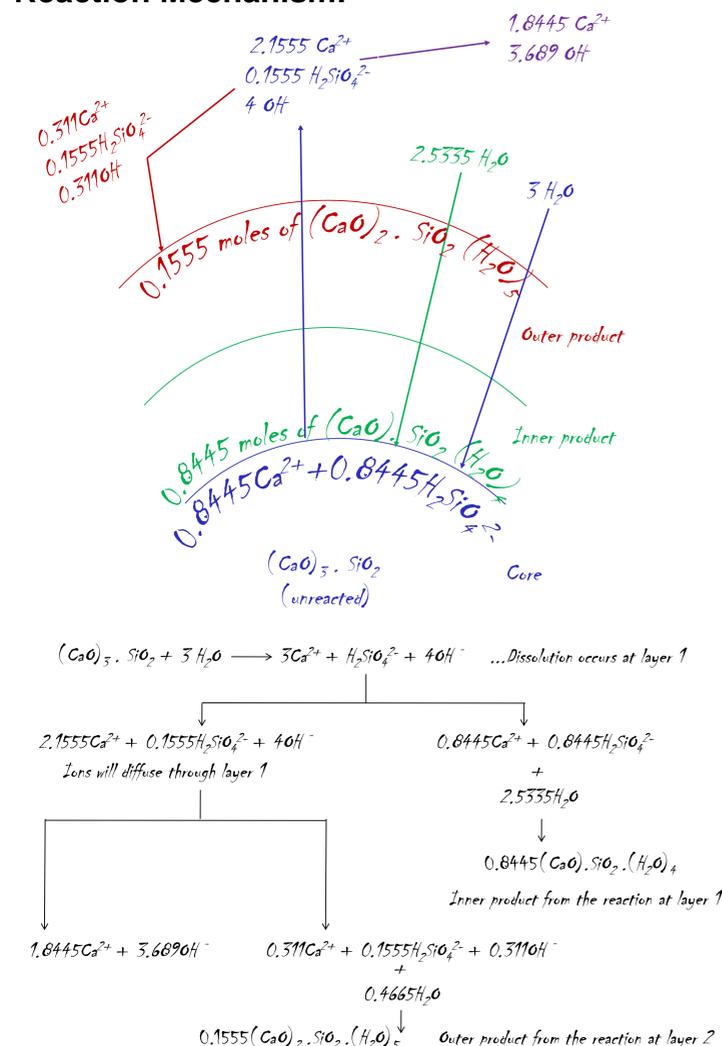
Computational software: COMSOL

COMSOL is a multi-physics finite element computational platform for solving many types of scientific and engineering problems based on partial differential equations (PDEs).

Assumptions:

- The rate of core shrinkage is given by the dissolution rate which is proportional to the concentration of H_2SiO_4 ions.
- The rate of outer product expansion is given by the rate of reaction occurred at outer boundary.
- The diffusion coefficients are assumed to be independent of concentration of ions.
- The activities of ions are assumed to be equal to concentrations since activity coefficient were approximated to be 1 for diluted solutions, e.g. $a_i = \gamma_i c_i / \rho_i$.

Modeling approach:

A 1-D coordinate system is chosen and modified according to spherical geometry. Four diffusion equations are utilized and the moving boundaries are tracked by moving mesh.

Subdomains:
A – Particle/core
B – Inner product
C – Outer product
D – Continuous Phase

Boundaries:
1 – no flux   2 – flux discontinuity
3 – flux continuity   4 – flux discontinuity
5 – no flux
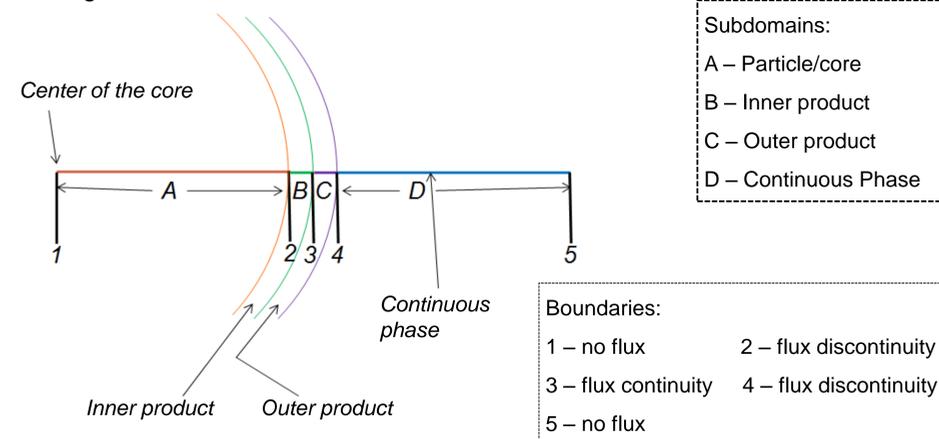
Governing equation and boundary conditions

Diffusion equation is given by:
$$\frac{\partial c_i}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i \right) = 0$$

At boundary 2:

For H_2SiO_4 ions: $N_0 = Ki_{rea}^f a_{C_3S} - Ki_{rea}^b a_{ca} a_{H_2SiO_4} + Ki_{dis}^f a_{C_3S} - Ki_{dis}^b a_{ca}^3 a_{H_2SiO_4} a_{OH}^4$

For OH ions: $N_0 = 4\left(Ki_{rea}^f a_{C_3S} - Ki_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2 \right)$

For Ca ions: $N_0 = Ki_{rea}^f a_{C_3S} - Ki_{rea}^b a_{ca} a_{H_2SiO_4} + 3\left(Ki_{rea}^f a_{C_3S} - Ki_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2 \right)$

For water: $N_0 = 3\left(Ki_{rea}^f a_{C_3S} - Ki_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2 \right)$

At boundary 4:

For H_2SiO_4 ions: $N_0 = Ko_{rea}^f a_{C_3S} - Ko_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2$

For OH ions: $N_0 = 2\left(Ko_{rea}^f a_{C_3S} - Ko_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2 \right)$

For Ca ions: $N_0 = 2\left(Ko_{rea}^f a_{C_3S} - Ko_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2 \right)$

For water: $N_0 = 3\left(Ko_{rea}^f a_{C_3S} - Ko_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2 \right)$

Parameters:

Constant	Value	Units	Description
D_w	3×10^{-9}	m²/sec	Water diffusion coefficient
D_{Ca}	0.72×10^{-9}	m²/sec	Ca ions diffusion coefficient
D_{OH}	5.28×10^{-9}	m²/sec	OH ions diffusion coefficient
$D_{H_2SiO_4}$	0.70×10^{-9}	m²/sec	H_2SiO_4 ions diffusion coefficient
D_{C_3S}	20-Oct	m²/sec	Particle diffusion coefficient
Tf_i	0.01	-----------	Transport factor in inner product
Tf_o	0.75	-----------	Transport factor in outer product
Ki_{dis}^f	1×10^{-5}	mol/m².sec	Forward rate constant for dissolution of C_3S
Ki_{dis}^b	3.3×10^{-4}	mol/m².sec	Backward rate constant for dissolution of C_3S
Ki_{rea}^f	1.6×10^{-7}	mol/m².sec	Forward rate constant for hydration of C_3S at inner layer
Ki_{rea}^b	1.33	mol/m².sec	Backward rate constant for hydration of C_3S at inner layer
Ko_{rea}^f	1.9×10^{-8}	mol/m².sec	Forward rate constant for hydration of C_3S at outer layer
Ko_{rea}^b	1.32×10^4	mol/m².sec	Backward rate constant for hydration of C_3S at outer layer
R	10×10^{-6}	m	Radius of the C_3S particle
V_{C_3S}	71×10^{-6}	m³/mol	Molar volume of C_3S
$V_{C-S-H(1)}$	85×10^{-6}	m³/mol	Molar volume of C-S-H (1)
$V_{C-S-H(2)}$	161×10^{-6}	m³/mol	Molar volume of C-S-H (2)
Rho_w	1000	Kg/m³	Mass density of water
Ci_w	$10^6/18$	mol/m³	Initial concentration of water

Results:

C-S-H growth trajectories for both inner and outer product formation. Trajectories and time constants seem in line with intuition and other models.

Concentration profiles in C-S-H product layers and continuous phase. Appear consistent with thermochemistry and experimentally expected values for Ca, OH and H_2SiO_4 ions.
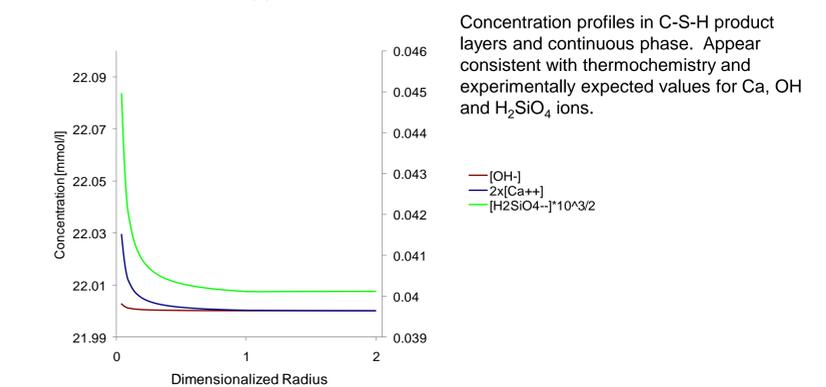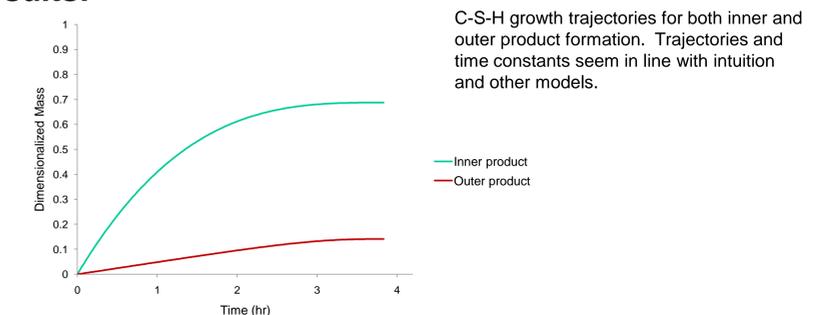
Discussion and Conclusions:

This more elaborate continuum-based model appears to be somewhat consistent with both simpler codes as well as with the original more detailed automaton-based model from which the rate constants and physical properties were taken.

These results encourage the further development of continuum-based models. More rigorous property estimation, thermochemistry and electrochemical surface effects should be considered in turn.

References:

Jeffery W. Bullard, 2008, "A Determination of Hydration Mechanisms for Tricalcium Silicate Using a Kinetic Cellular Automation Model", J. Am. Ceram. Soc., 91[7], pp. 2088-2097.