



# Single Particle Model for C<sub>3</sub>S Hydration: A Multi-Component Distributed Parameter Continuum Approach

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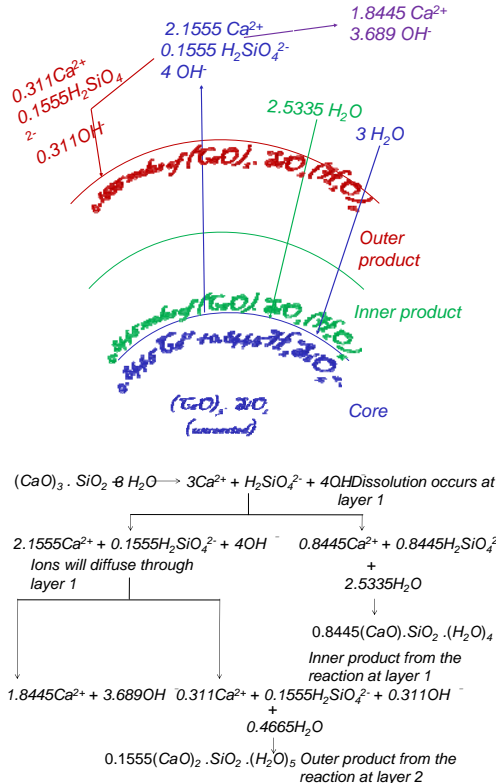
## Abstract:

Tricalcium silicate, the main constituent of many types of cements including portland cement, white cement, and oil and well cement applications, is frequently used as a model material to study the hydration. Although theories in the literature over the past 40 years have offered considerable insights into the 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  $\mu\text{ic}$  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<sub>3</sub>S hydration.

## Reaction Mechanism:



## Computational software: COMSOL

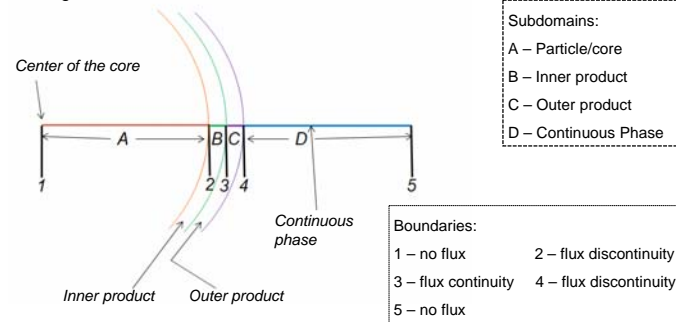
COMSOL is a multi-physics finite element computational platform for solving many types of scientific and engineering problems based on partial differential equations (PDEs).

## Assumptions:

- The rate of core shrinkage is given by the dissolution rate which is proportional to the concentration of H<sub>2</sub>SiO<sub>4</sub> 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.



## Governing equation and boundary conditions

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

At boundary 2:

$$\text{For H}_2\text{SiO}_4 \text{ ions: } N_0 = Ki_{rea}^f a_{C_3S} - Ki_{rea}^b a_{ca} a_{H_2SiO_4} + Ki_{dis}^f a_{C_3S} - Ki_{dis}^b a_{ca}^3 a_{H_2SiO_4} a_{OH}^4$$

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

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

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

At boundary 4:

$$\text{For H}_2\text{SiO}_4 \text{ ions: } N_0 = Ko_{rea}^f a_{C_3S} - Ko_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2$$

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

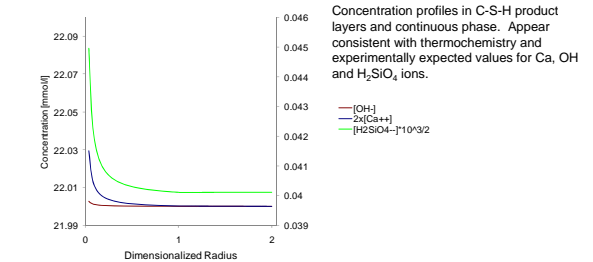
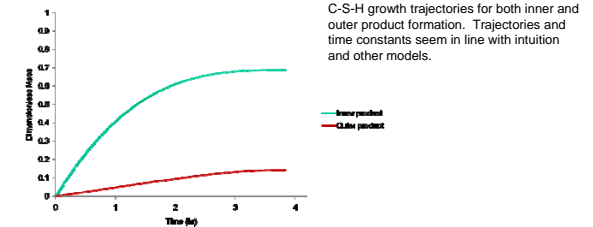
$$\text{For Ca ions: } N_0 = 2(Ko_{rea}^f a_{C_3S} - Ko_{rea}^b a_{ca}^2 a_{H_2SiO_4} a_{OH}^2)$$

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

## Parameters:

Constant	Value	Units	Description
D <sub>w</sub>	3 × 10 <sup>-9</sup>	m <sup>2</sup> /sec	Water diffusion coefficient
D <sub>ca</sub>	0.72 × 10 <sup>-9</sup>	m <sup>2</sup> /sec	Ca ions diffusion coefficient
D <sub>oh</sub>	5.28 × 10 <sup>-9</sup>	m <sup>2</sup> /sec	OH ions diffusion coefficient
D <sub>H<sub>2</sub>SiO<sub>4</sub></sub>	0.70 × 10 <sup>-9</sup>	m <sup>2</sup> /sec	H <sub>2</sub> SiO <sub>4</sub> ions diffusion coefficient
D <sub>C<sub>3</sub>S</sub>	20-Oct	m <sup>2</sup> /sec	Particle diffusion coefficient
T <sub>f</sub>	0.01	-----	Transport factor in inner product
T <sub>f</sub>	0.75	-----	Transport factor in outer product
K <sub>f</sub> <sup>f</sup>	1 × 10 <sup>-5</sup>	mol/m <sup>2</sup> .sec	Forward rate constant for dissolution of C <sub>3</sub> S
K <sub>f</sub> <sup>b</sup>	3.3 × 10 <sup>-4</sup>	mol/m <sup>2</sup> .sec	Backward rate constant for dissolution of C <sub>3</sub> S
K <sub>i</sub> <sup>f</sup>	1.6 × 10 <sup>-7</sup>	mol/m <sup>2</sup> .sec	Forward rate constant for hydration of C <sub>3</sub> S at inner layer
K <sub>i</sub> <sup>b</sup>	1.33	mol/m <sup>2</sup> .sec	Backward rate constant for hydration of C <sub>3</sub> S at inner layer
K <sub>o</sub> <sup>f</sup>	1.9 × 10 <sup>-8</sup>	mol/m <sup>2</sup> .sec	Forward rate constant for hydration of C <sub>3</sub> S at outer layer
K <sub>o</sub> <sup>b</sup>	1.32 × 10 <sup>4</sup>	mol/m <sup>2</sup> .sec	Backward rate constant for hydration of C <sub>3</sub> S at outer layer
R	10 × 10 <sup>-6</sup>	m	Radius of the C <sub>3</sub> S particle
V <sub>C<sub>3</sub>S</sub>	71 × 10 <sup>-6</sup>	m <sup>3</sup> /mol	Molar volume of C <sub>3</sub> S
V <sub>C-S-H (1)</sub>	85 × 10 <sup>-6</sup>	m <sup>3</sup> /mol	Molar volume of C-S-H (1)
V <sub>C-S-H (2)</sub>	161 × 10 <sup>-6</sup>	m <sup>3</sup> /mol	Molar volume of C-S-H (2)
Rho <sub>w</sub>	1000	Kg/m <sup>3</sup>	Mass density of water
C <sub>iw</sub>	10 <sup>3</sup> /18	mol/m <sup>3</sup>	Initial concentration of water

## Results:



## 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.