A New Model for Predicting Hydration Kinetics and Microstructure Development in Cement Paste

Jeff Bullard
NIST

ACBM Technical Review, March 2006

Modeling Challenges: Chemistry

Tricalcium Silicate (idealized)

Dissolution

$Ca_3SiO_5 + 3\ H_2O \rightarrow 3\ Ca^{2+} + H_2SiO_4^{2-} + 4\ OH^-$

Growth of C-S-H

$x\ Ca^{2+} + H_2SiO_4^{2-} + 2(x-1)\ OH^- \rightarrow CaO_x–SiO_2–H_2O$

Growth of Portlandite

$Ca^{2+} + 2\ OH^- \rightarrow Ca(OH)_2$

Value of x depends on local pore solution chemistry

Modeling Challenges: Chemistry

Tricalcium Aluminate (idealized)

Net Reactions Without Gypsum or CH

$2\ C_3A + 27\ H \rightarrow C_2AH_8 + C_4AH_{19} \rightarrow C_3AH_6$

$C_3A + 6\ H \rightarrow C_3AH_6$ (> 30 °C)

Net Reactions With CH

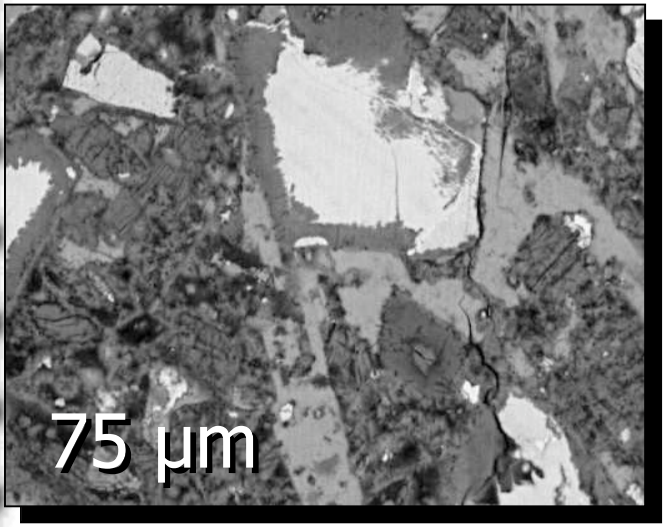
$C_3A + CH + 12\ H \rightarrow C_4AH_{13}$

Net Reactions With Gypsum (> 2-3%)

$C_3A + 3\ C\underline{S}H_2 + 26\ H \rightarrow C_6A\underline{S}_3H_{32}$ (initial)

Modeling Challenges: Structure

Micro-scale



Kinetic Implications

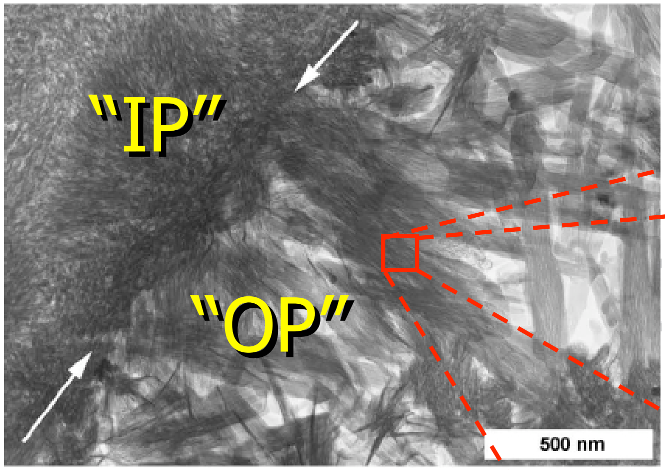
- Nucleation sites
- C-S-H growth = diffusion barrier
- Water availability

Property Implications

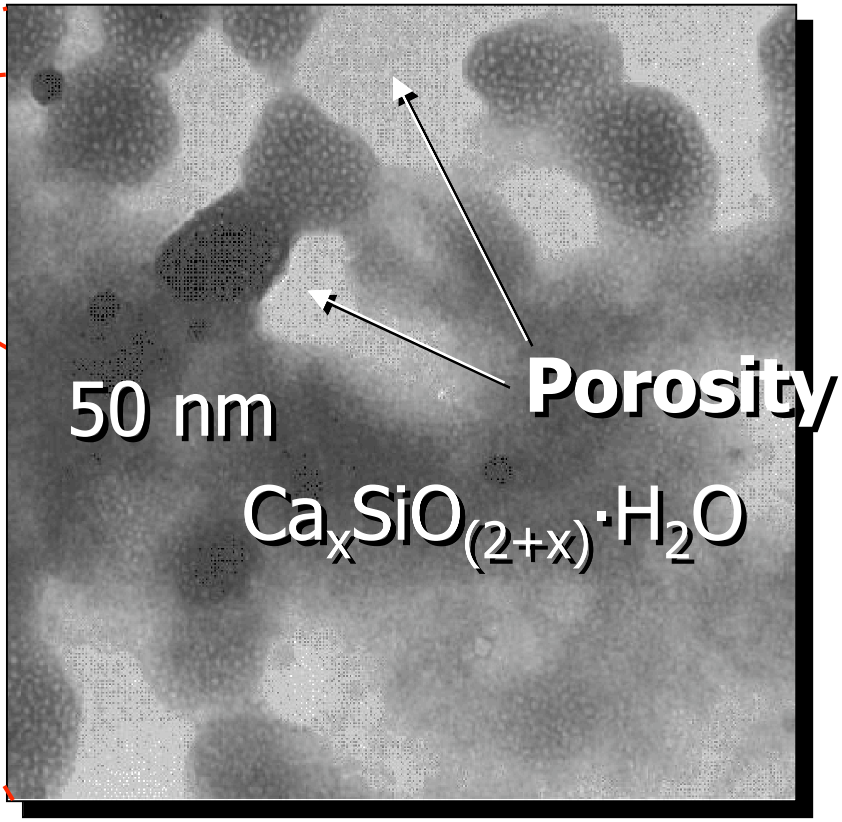
- Porosity forms 3-D percolating network
- Solids may begin as percolating (or not) “soft” clusters; later form stiff percolating network

Modeling Challenges: Structure

Nano-scale

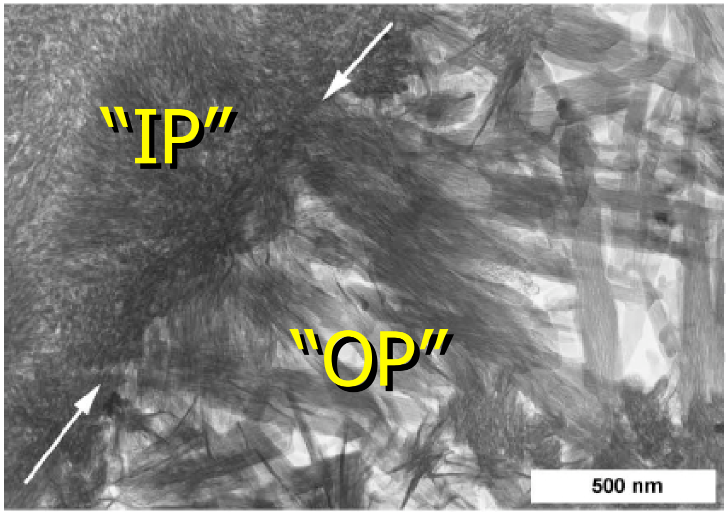


Micrograph courtesy of I.G. Richardson, University of Leeds



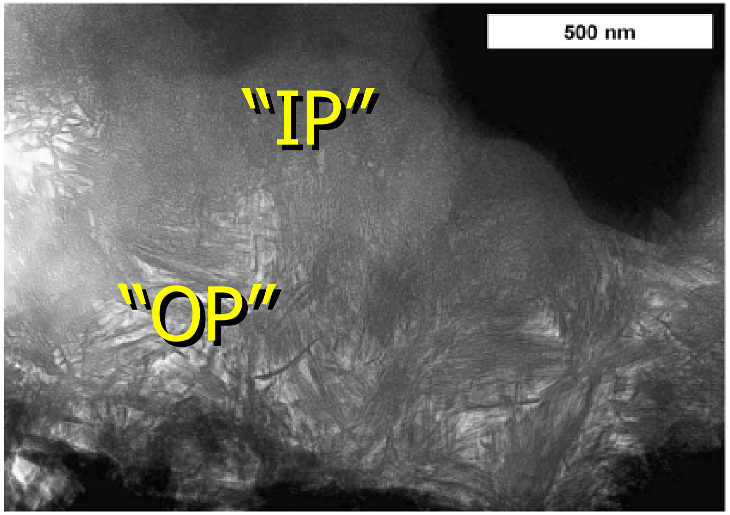
Modeling Challenges: Structure

Nano-scale



C_3S Paste, 20°C, 8 yr

Micrographs courtesy of I.G. Richardson, University of Leeds



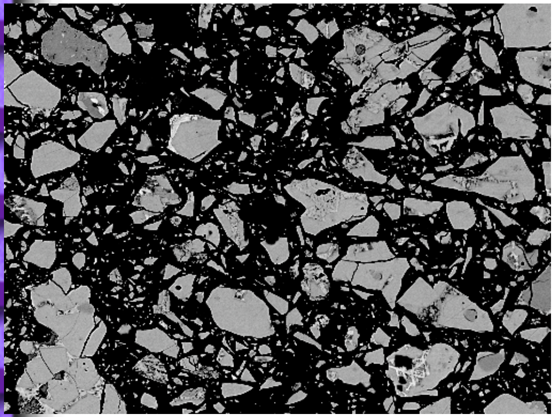
C_3S Paste, 80°C, 8 d

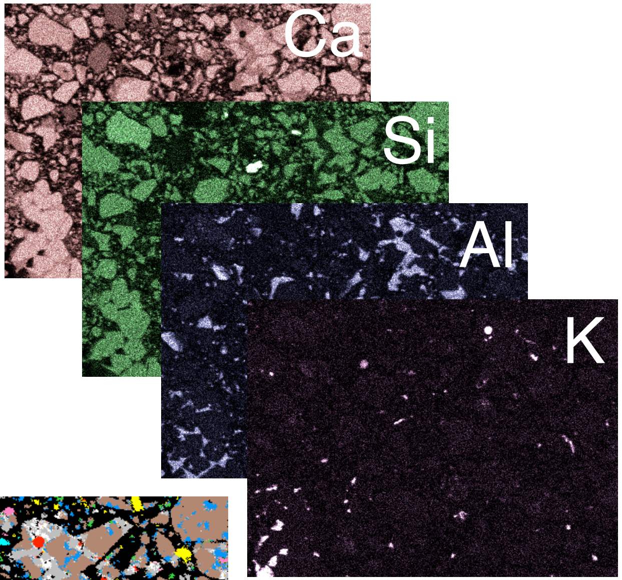
Some Available Models

CEMHYD3D (NIST)

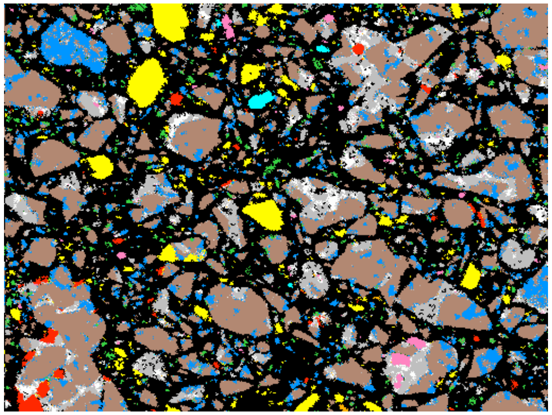
- Digital image basis

SEM/BSE Image...

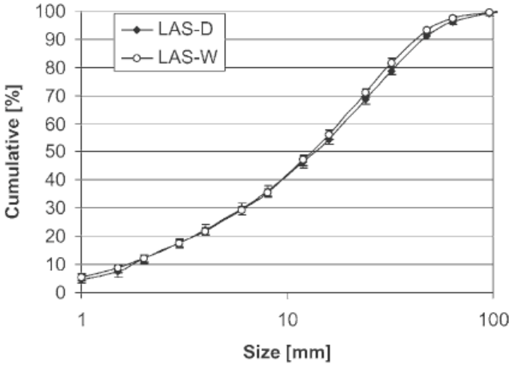




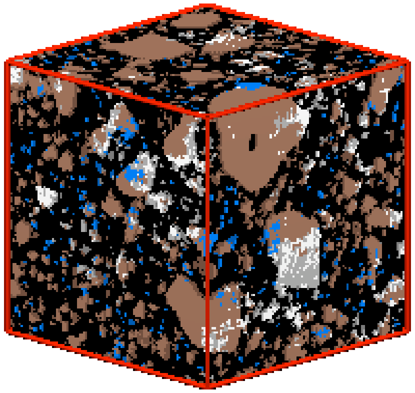
... X-ray element maps ...



... segment image into **phases** ...



... Particle Size Distribution ...



Measure autocorrelation fns on majority phases

Contributors: D. Bentz and P. Stutzman

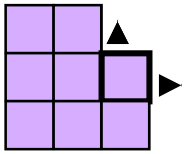
Some Available Models

CEMHYD3D (NIST)

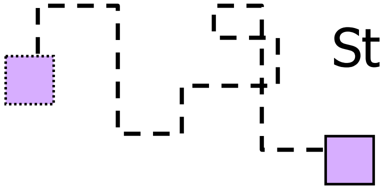
- Digital image basis
- Accurate microstructure representation
- Rule-based to mimic reaction and diffusion

CEMHYD3D

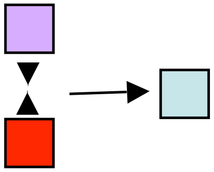
- Cellular automaton approach
  - Each volume element is an independent agent that can
    - **Dissolve**
    - **Diffuse**
    - **React**



Pore solution



Stepwise random walk on lattice



Collisions between agents, governed by reaction “rules”

Some Available Models

CEMHYD3D (NIST)

- Digital image basis
- Accurate microstructure representation
- Rule-based to mimic reaction and diffusion
- Little or no kinetic information
- Magic resolution of 1 µm
- Primarily interpolative

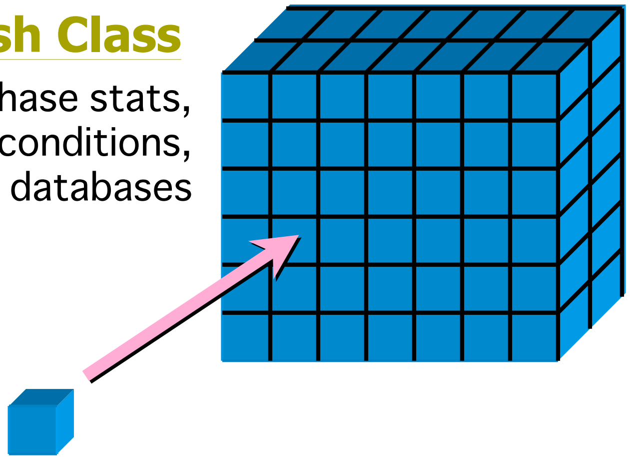
Some Available Models

HYMOSTRUC (TU Delft); IPK (EPFL)

- Continuum basis
- Chemically homogenized particles
- Hydration modeled as growth of interparticle contacts
- Phenomenological kinetic equations (e.g. Johnson-Avrami-Mehl)
- Not easily extensible

New Model: HydratiCA

- Discretize on regular grid
- Retain power of CEMHYD3D microstructure representation
- Stochastic methods for diffusion and reaction
- Algorithms are mechanistically based, and converge to standard PDE rate equations
- Scalable and extensible
- Applies to general aqueous mineral systems

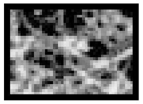


Mesh Class

Dimensions, resolution, clock, phase stats,
thermal condition, moisture conditions,
databases

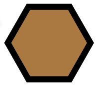
Node Class

neighbors, volume, materials,
methods for transport and rx

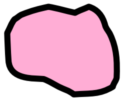


Derived Material Classes

(Liquid, Solid, Gel, Crystal, Solute)



Methods for material-specific behavior
encoded here



Base Material Class

ID, composition, ρ, Ω, C_p, porosity,
mobility, virtual methods for material-specific behavior

Ion Database Class

ID, mol wt, radius, intrinsic diffusivity, charge
(immutable)

Material Database Class

Reaction Database Class

ID, reactants, products, molar
stoichiometric coefficients,
reaction enthalpy, activation
enthalpy, equilibrium constant
baseline rate constant

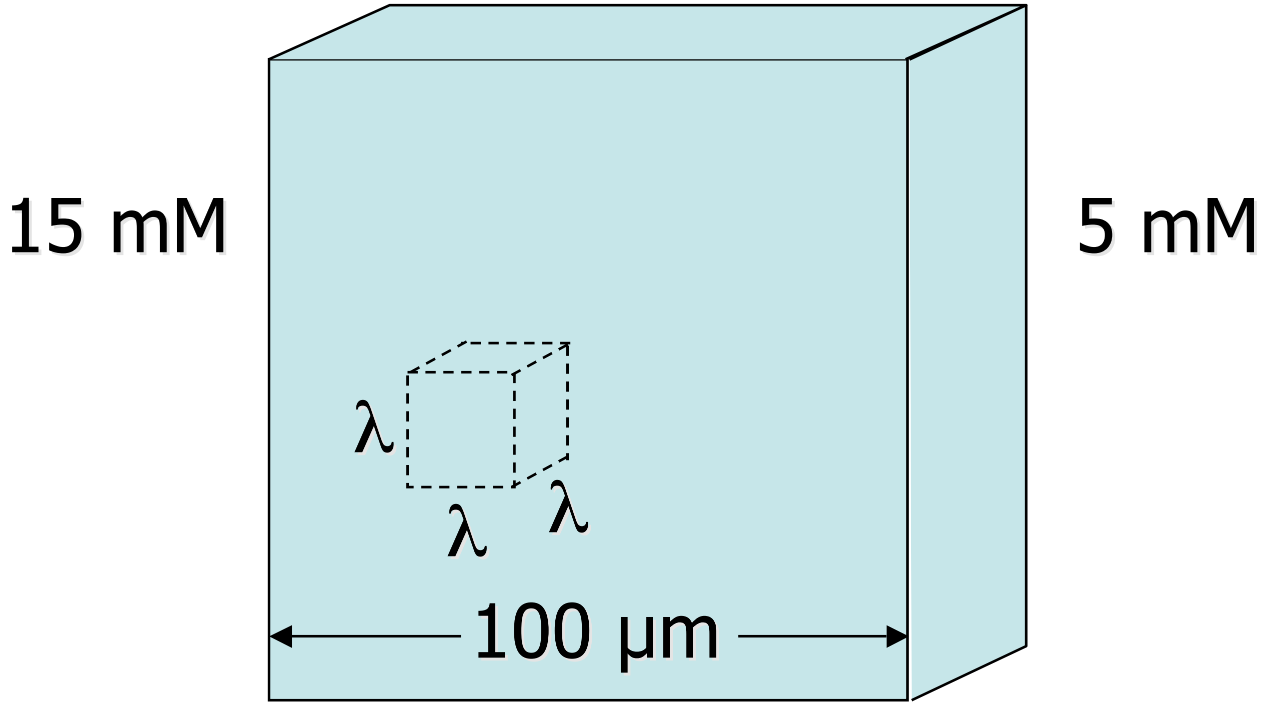
HydratiCA: Modeling Aqueous Diffusion

HydratiCA: Modeling Aqueous Diffusion

- Based on a random walker algorithm
- Each computational node contains a number of "cells" of solute and water
- In any time step, each cell can execute a single step in a random direction
- Probability of stepping is proportional to the solute mobility and the time increment

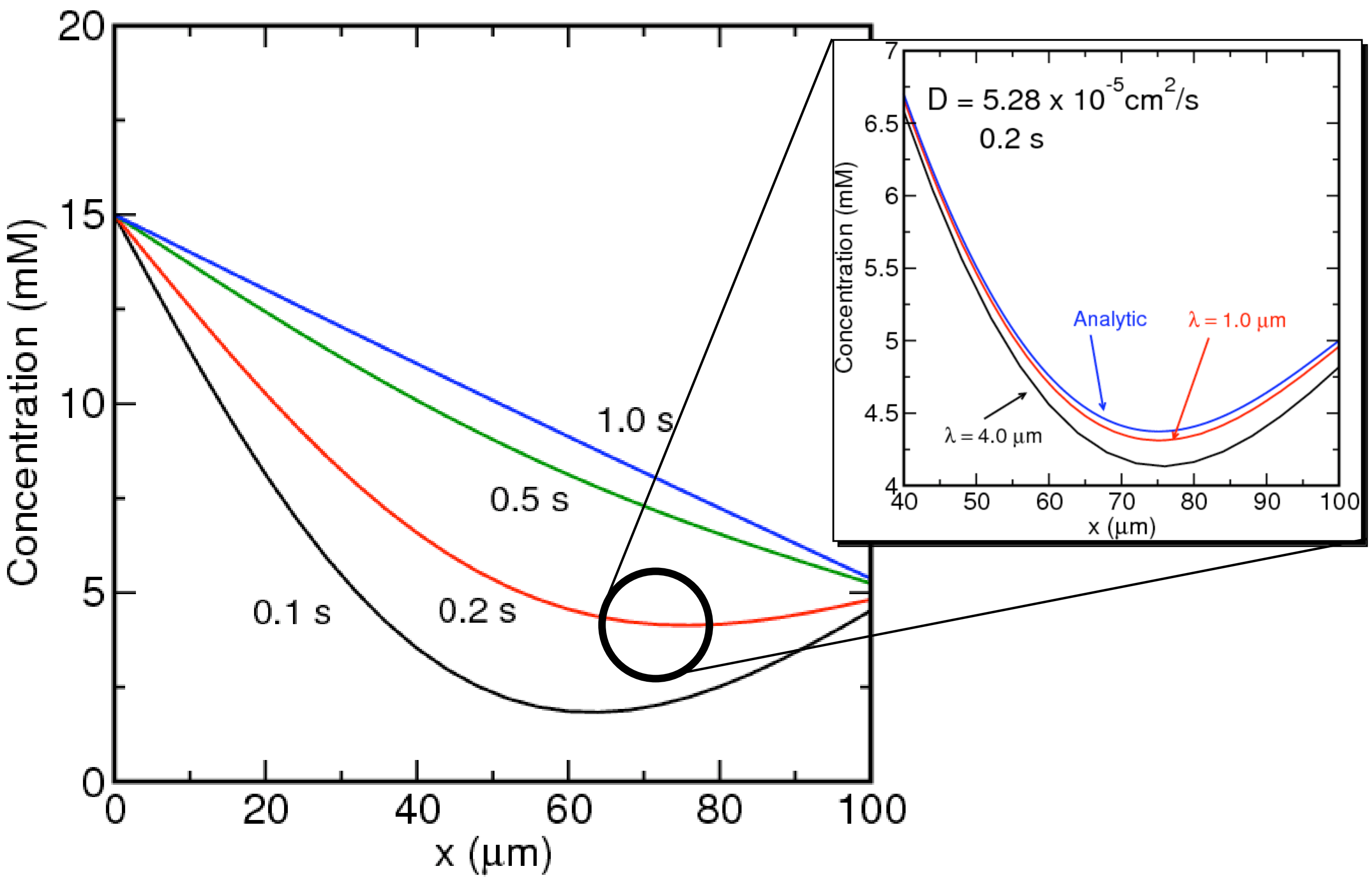
$$p = D\,\Delta t/\lambda^2$$

Non-steady state diffusion of neutral solute



- $C(x,y,z,0) = 0$
- $C(0,y,z,t) = 15$ mM
- $C(100,y,z,t) = 5$ mM

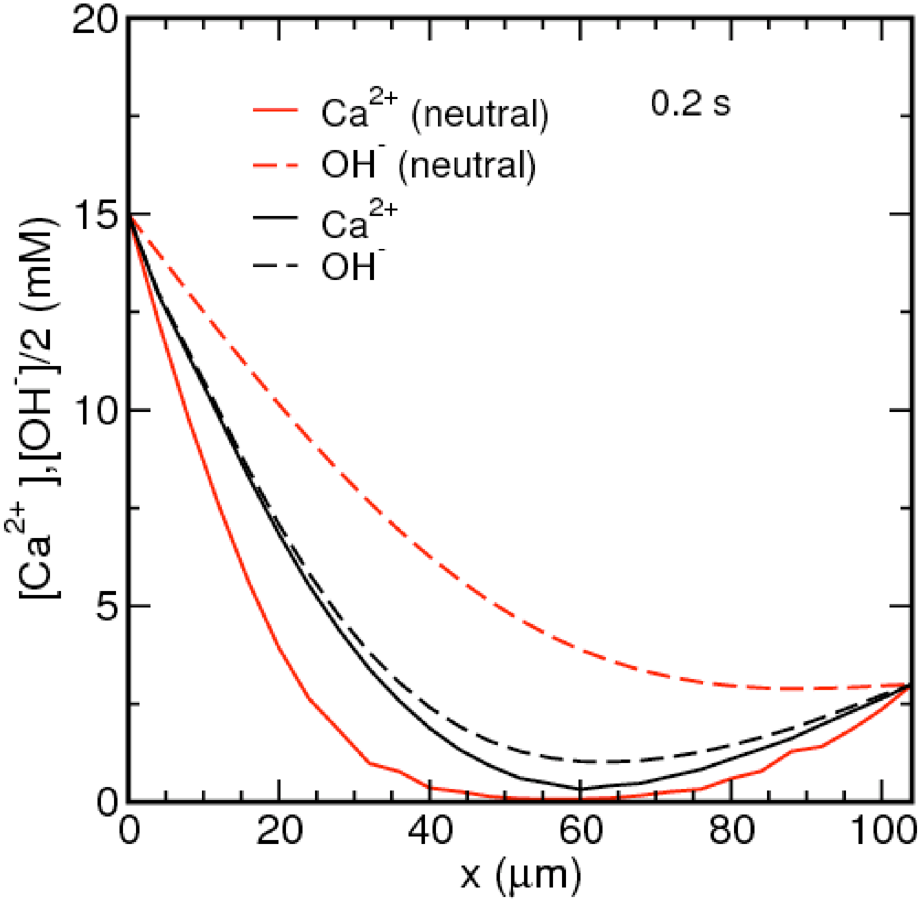
Non-steady state diffusion of neutral solute



HydratiCA: Ionic Diffusion

- Effective mobility of a charged species is influenced by long-range Coulombic interactions with other charged species
- Local charge neutrality is required, even though different ions have different intrinsic diffusion coefficients
- HydratiCA can estimate the electrostatic potential at each time step, and include it in the electrochemical potential
- Results in **biased** random walk

Coupled diffusion of ions



$D_{Ca} = 0.7 \times 10^{-5}\ cm^2/s$

$D_{OH} = 5.3 \times 10^{-5}\ cm^2/s$

HydratiCA: Modeling Chemical Reactions

HydratiCA: Modeling Chemical Reactions

$$a\,A + b\,B \xrightarrow{k} c\,C$$

- Reaction events are localized within a node
- List of available reactants is generated and compared against reaction database
- List of possible reactions is built
- Reaction randomly selected from list
- Unit reaction is executed (n cells of A and m cells of B are removed, p cells of C are added) on a probabilistic basis
- Probability proportional to rate constant k

HydratiCA: Modeling Equilibrium

$$a\,A + b\,B \xrightarrow{k_f} c\,C$$

$$c\,C \xrightarrow{k_r} a\,A + b\,B$$

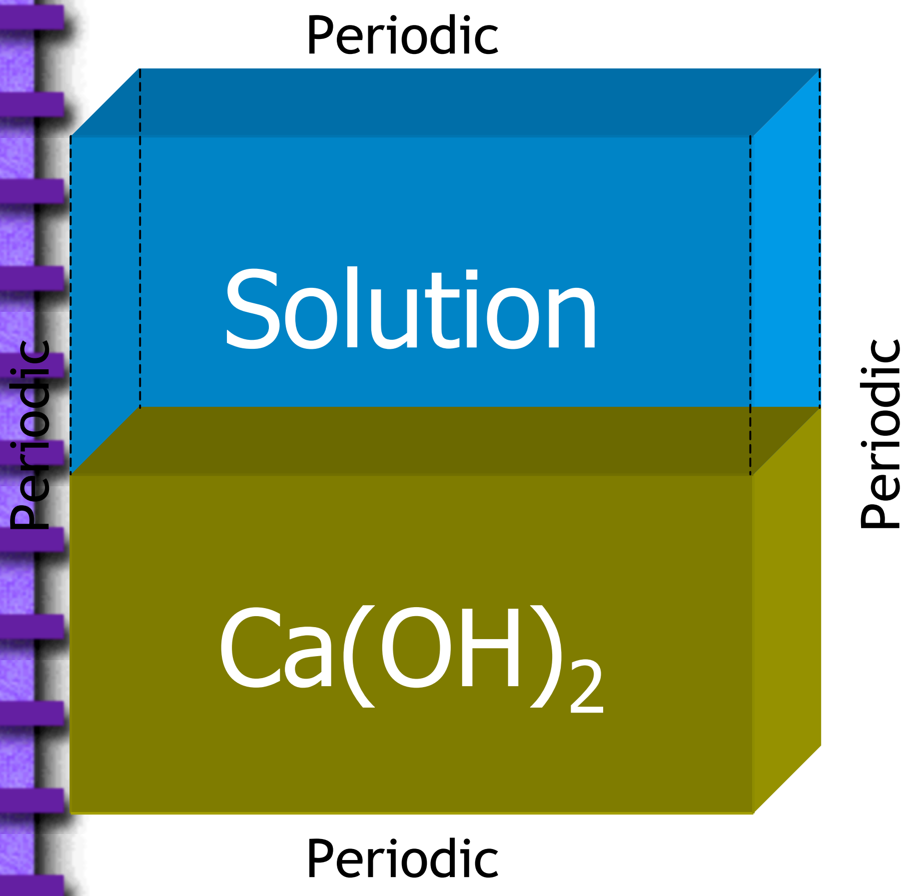
$$\frac{d\{C\}}{dt} = k_f\{A\}^a\{B\}^b$$

$$\frac{d\{C\}}{dt} = -k_r\{C\}^c$$

At equilibrium: $k_r\{C\}^c = k_f\{A\}^a\{B\}^b$

$$\frac{k_f}{k_r} = \frac{\{C\}^c}{\{A\}^a\{B\}^b} = K_{eq}$$

HydratiCA: Modeling Reactions

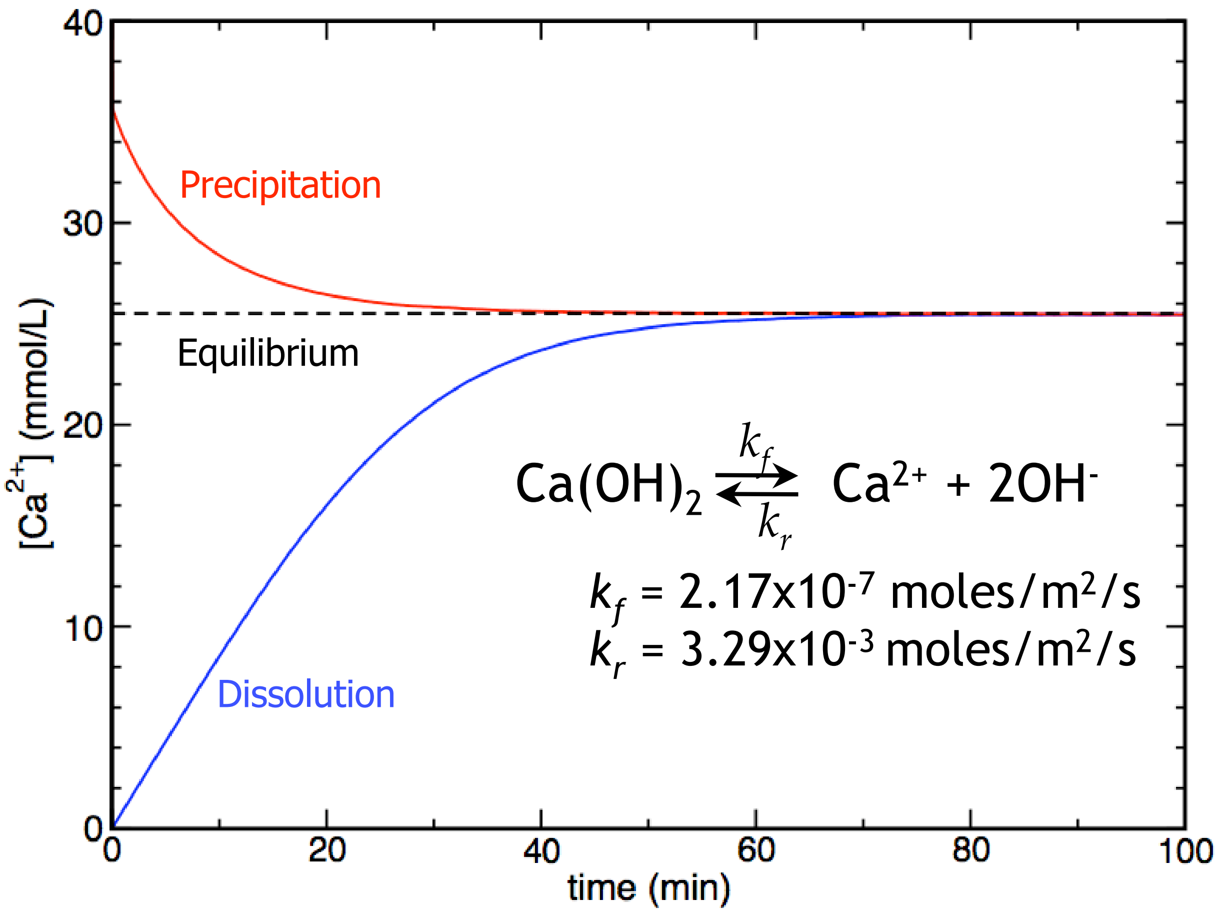


- 10 x 10 x 10 nodes
- Node spacing λ= 3 μm
- T = 298 K

$$Ca(OH)_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ca^{2+} + 2OH^-$$

k_f = 2.17x10^{-7} moles/m^2/s
k_r = 3.29x10^{-3} moles/m^2/s

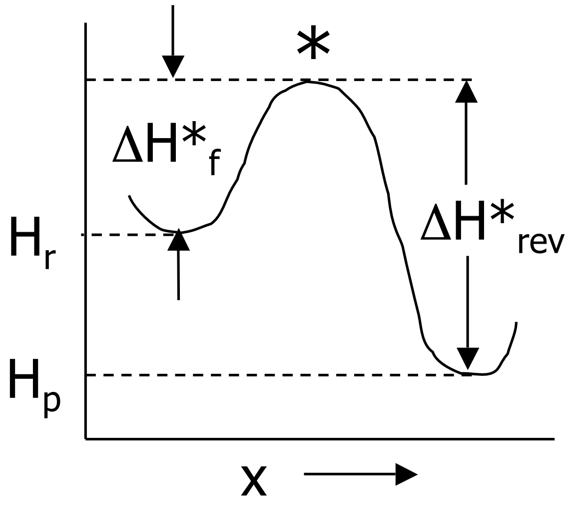
HydratiCA: Chemical Equilibrium



$$Ca(OH)_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ca^{2+} + 2OH^-$$

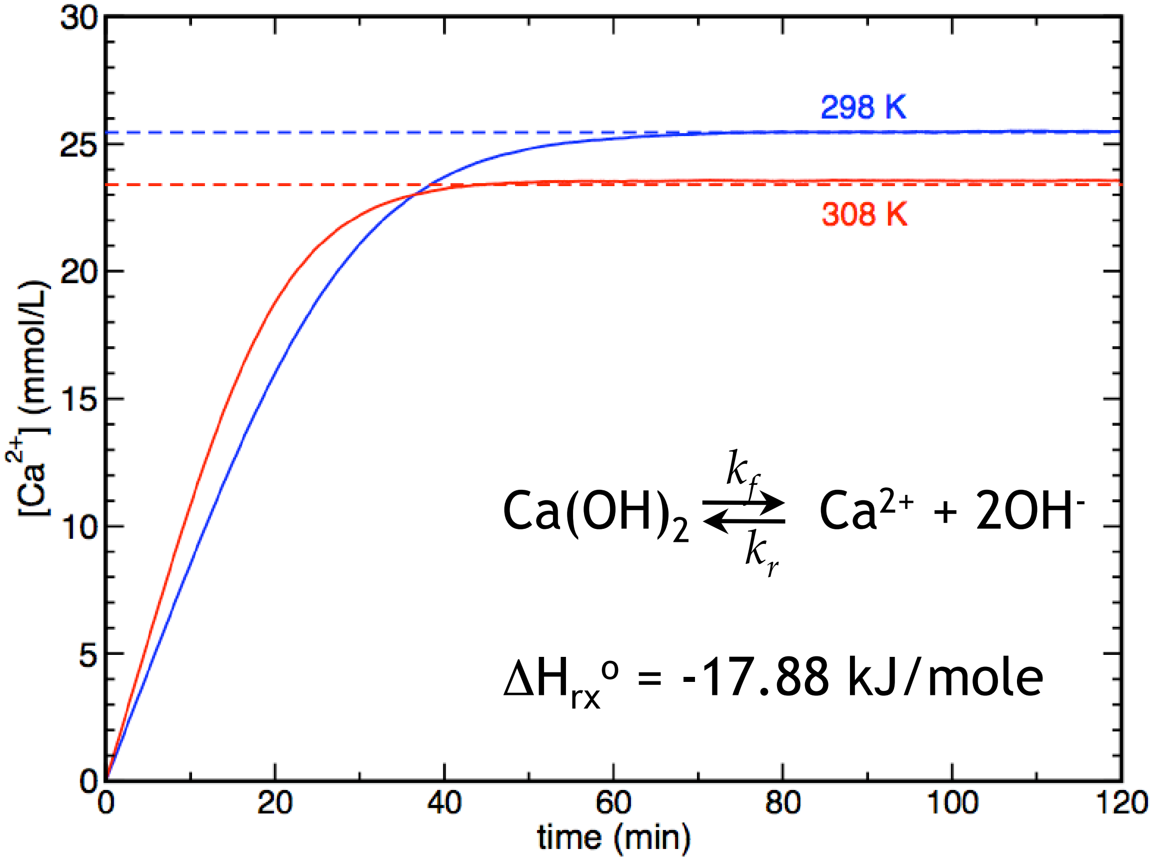
k_f = 2.17x10^{-7} moles/m^2/s
k_r = 3.29x10^{-3} moles/m^2/s

HydratiCA: Temperature Effects



$$\left.\begin{aligned} k_f(T) &= k_f(298)\exp\left[\frac{-Q_f^*}{RT}\right] \\ k_r(T) &= k_r(298)\exp\left[\frac{-Q_r^*}{RT}\right] \end{aligned}\right\} \quad \frac{\partial(\ln K_{eq})}{\partial T} = \frac{\Delta H_{rx}^\circ}{RT^2}$$

HydratiCA: Temperature Effects



$$Ca(OH)_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ca^{2+} + 2OH^-$$

$$\Delta H_{rx}^o = -17.88 \text{ kJ/mole}$$

$$\ln K_{eq}(T) = \ln K_{eq}(298) + \frac{\Delta H_r^\circ}{R}\left[\frac{1}{298} - \frac{1}{T}\right]$$

HydratiCA: Nucleation

- Similar to nucleation of solid from a supercooled melt
- Literature review: D. Kaschiev and G.M. van Rosmalen, Cryst. Res. Technol. 38 [7-8] 555-574 (2003).

$$I(x,t) = AS \exp\left[\frac{-W^*}{kT}\right]$$

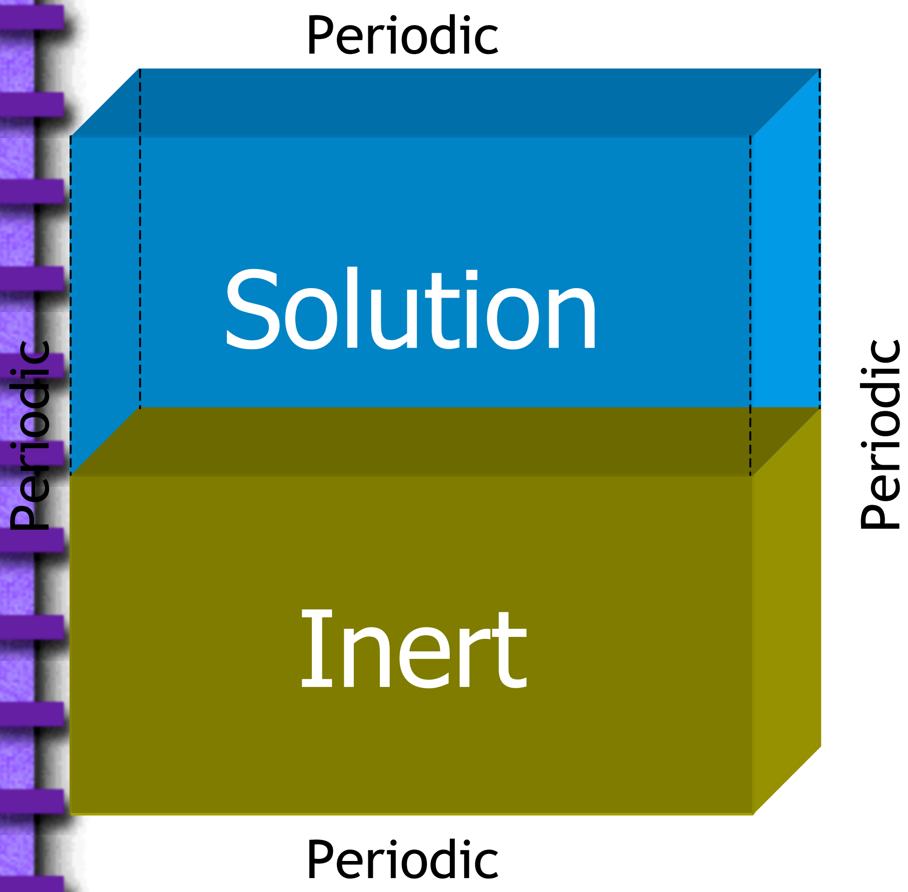
where

$$\left.\begin{aligned} A &= \left(\frac{4\pi}{3\nu_0}\right)^{1/3}\left(\frac{\sigma}{kT}\right)^{1/2} D \prod_{\beta}^{n} a_{\beta}^{\nu_{\beta}^{i}-\nu_{\beta}^{f}} \\ W^* &= \frac{16\pi\nu_0^2\sigma^3}{3(kT\ln S)^2} \end{aligned}\right\} \textbf{For spherical nuclei}$$

$S =$ saturation index $\quad \sigma =$ surface energy

$D =$ diffusion coefficient $\quad \nu_0 =$ molecular volume of solid

HydratiCA: Modeling Nucleation

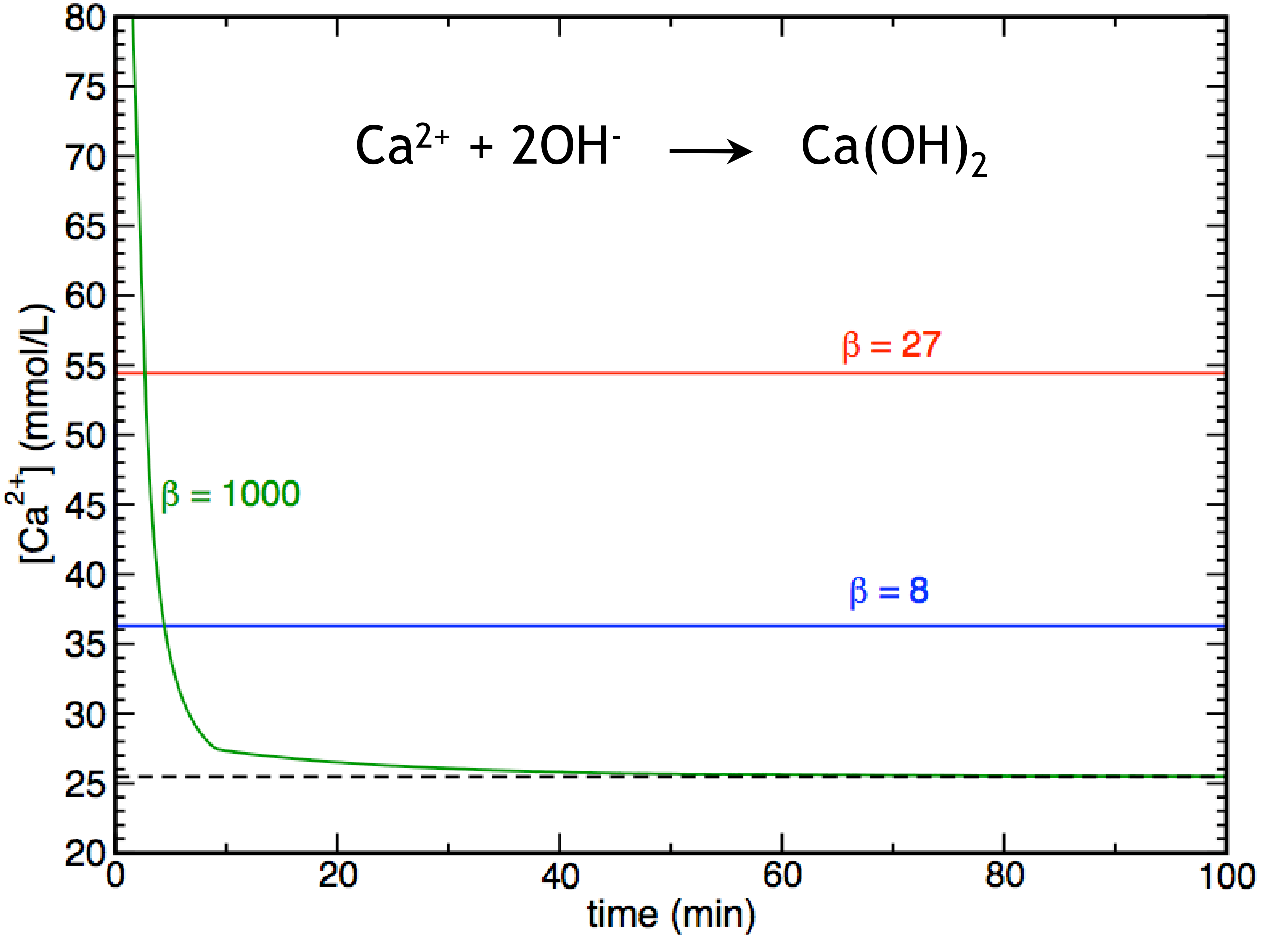


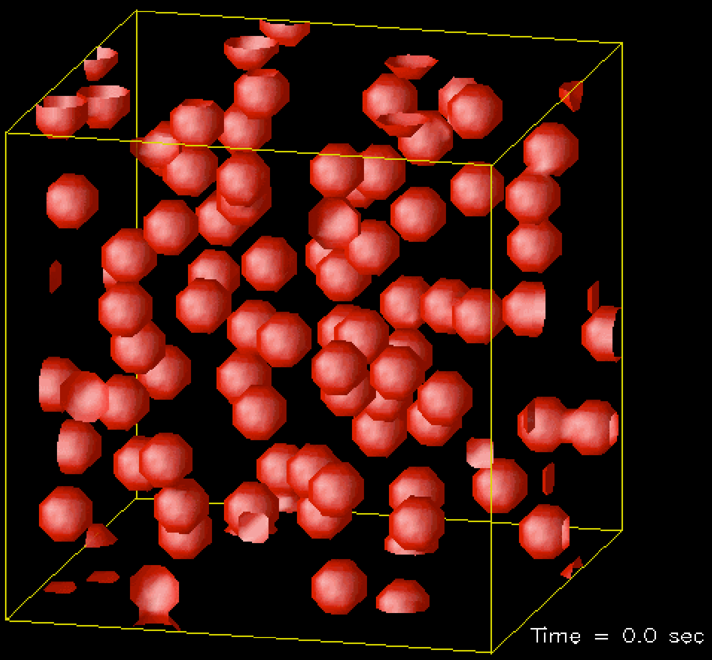
- **10 x 10 x 10 nodes**
- **Node spacing λ= 3 μm**
- **T = 298 K**

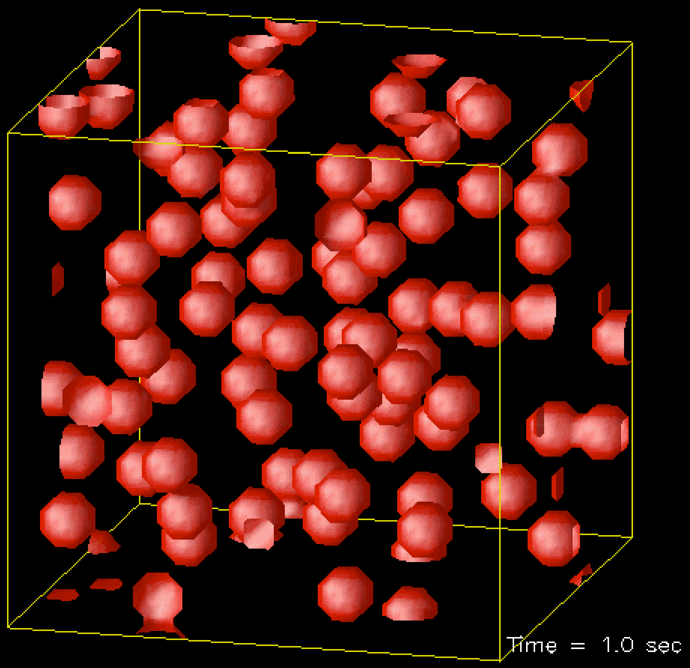
$$Ca(OH)_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ca^{2+} + 2OH^-$$

k_f = 2.17x10^{-7} moles/m^2/s
k_r = 3.29x10^{-3} moles/m^2/s

HydratiCA: Nucleation




Dirt Speck in Water


Surface Nucleation

Nucleation sites distinguished by nucleation work

HydratiCA: Modeling Hydration of C_3S

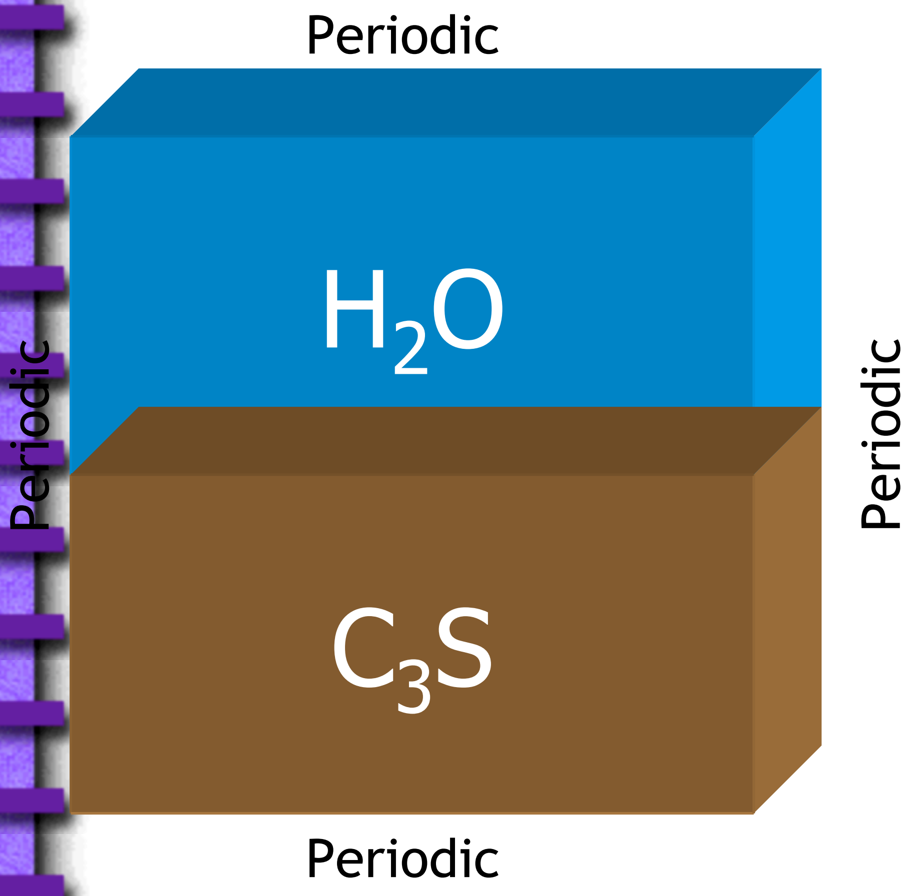
HydratiCA: Hydration of C_3S

- Requires assumptions about chemical reactions and mechanisms
- Alternative theories can, in principle, be tested by HydratiCA
- First theory tested: Garrault and Nonat, *Langmuir* 17, 8131–8138 (2001).
  - Coupled reactions:

$$\begin{aligned} \mathrm{Ca_3SiO_5} + 3\mathrm{H_2O} &\longrightarrow 3\mathrm{Ca}^{2+} + 4\mathrm{OH}^- + \mathrm{H_2SiO_4^{2-}} \\ \mathrm{C/S}\ \mathrm{Ca}^{2+} + 2\,(\mathrm{C/S} - 1)\,\mathrm{OH}^- + \mathrm{H_2O} &\longrightarrow \mathrm{CaO_{C/S}{-}SiO_2{-}H_2O} \\ \mathrm{Ca}^{2+} + 2\mathrm{OH}^- &\longrightarrow \mathrm{Ca(OH)_2} \end{aligned}$$

  - Nucleation of C-S-H occurs on surface of C_3S
  - Growth of C-S-H is "autocatalytic" due to increased area of C-S-H surfaces for growth.

HydratiCA: Hydration of C_3S

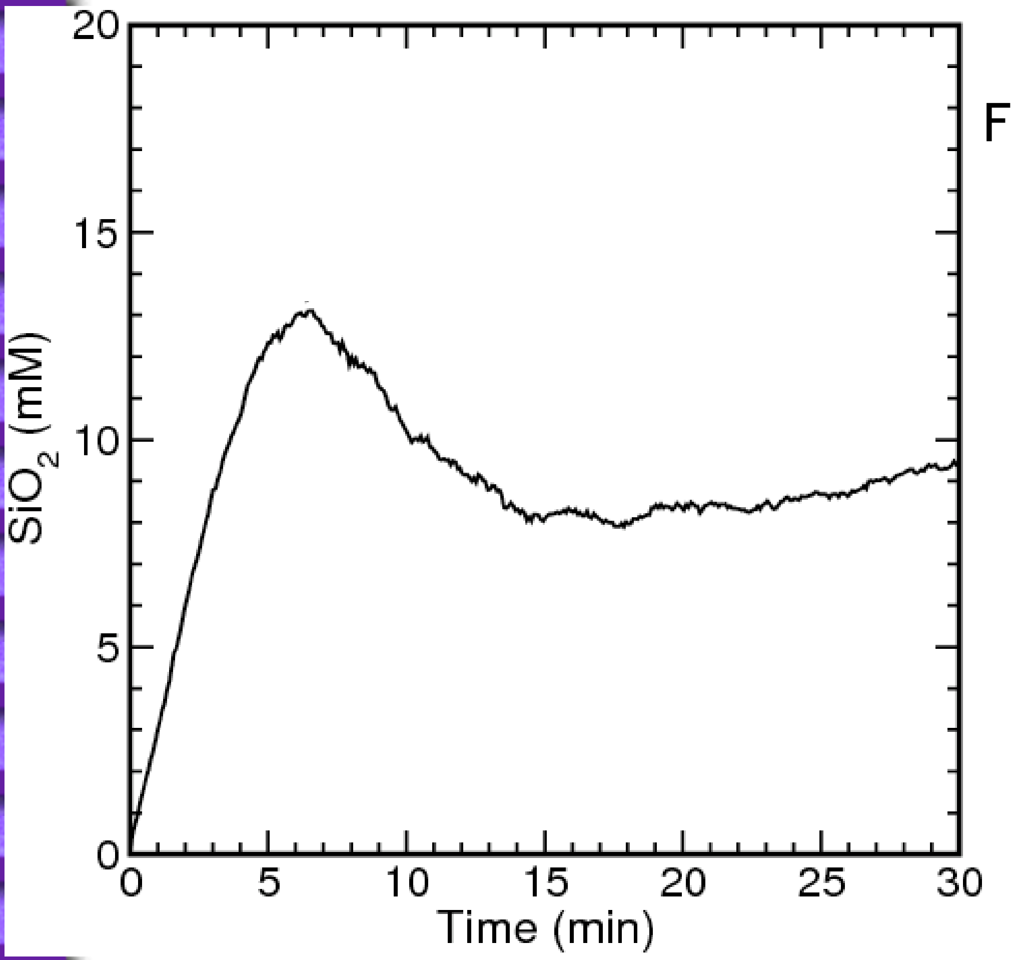


- 25 x 25 x 25 nodes
- Node spacing λ= 4 μm
- T = 298 K

w/c = 0.3125

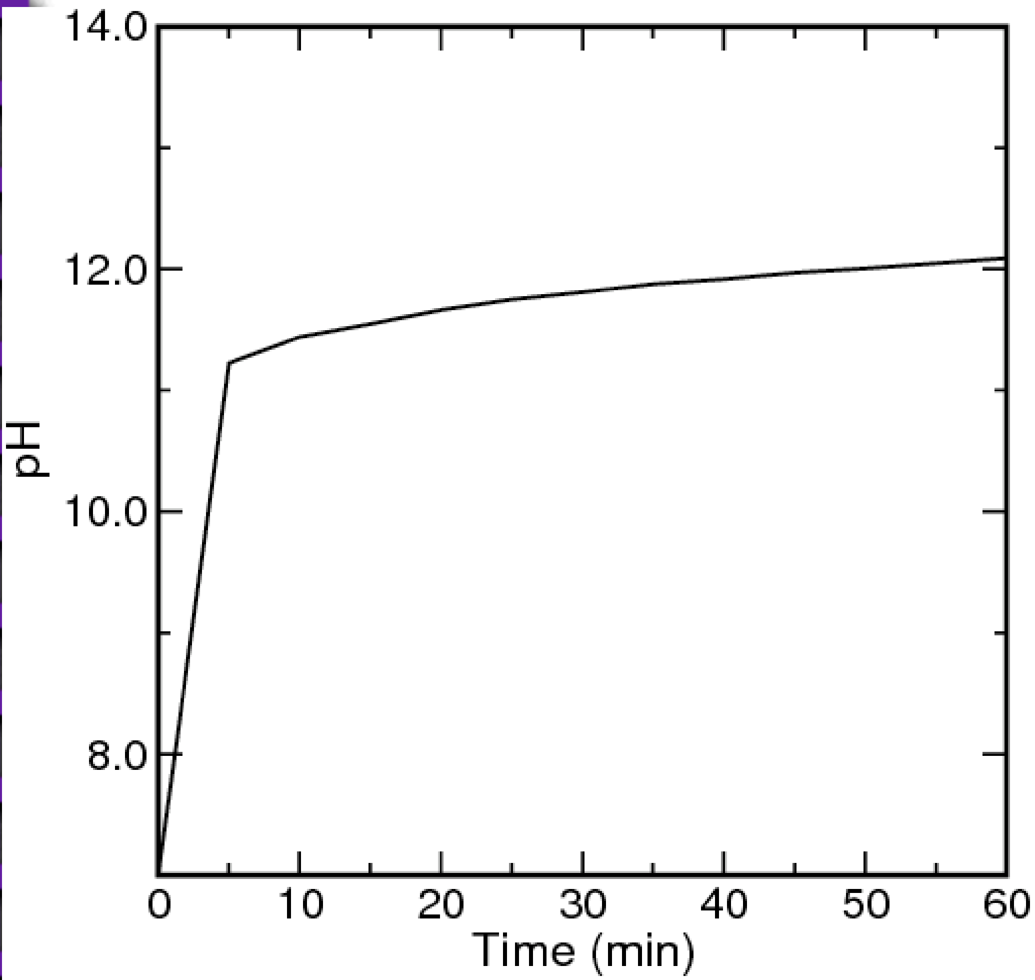
4 m^2/kg

HydratiCA: Hydration of C_3S



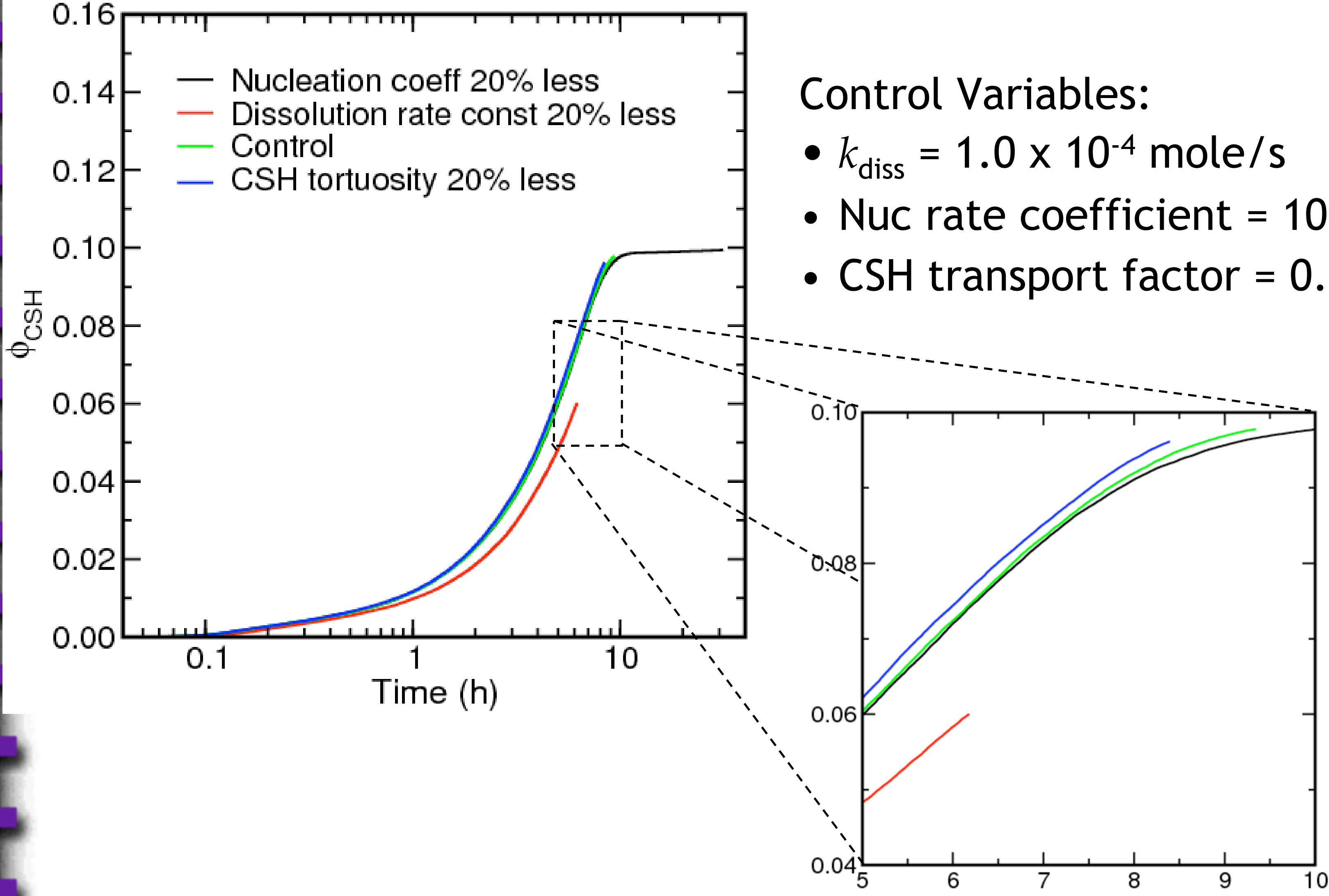
For this **original choice** of parameters, the silicate concentration reaches a local maximum at about 6 minutes.

HydratiCA: Hydration of C_3S



pH increases rapidly over first few minutes, then more slowly with increasing time as the rates of consumption and production of OH^- are comparable.

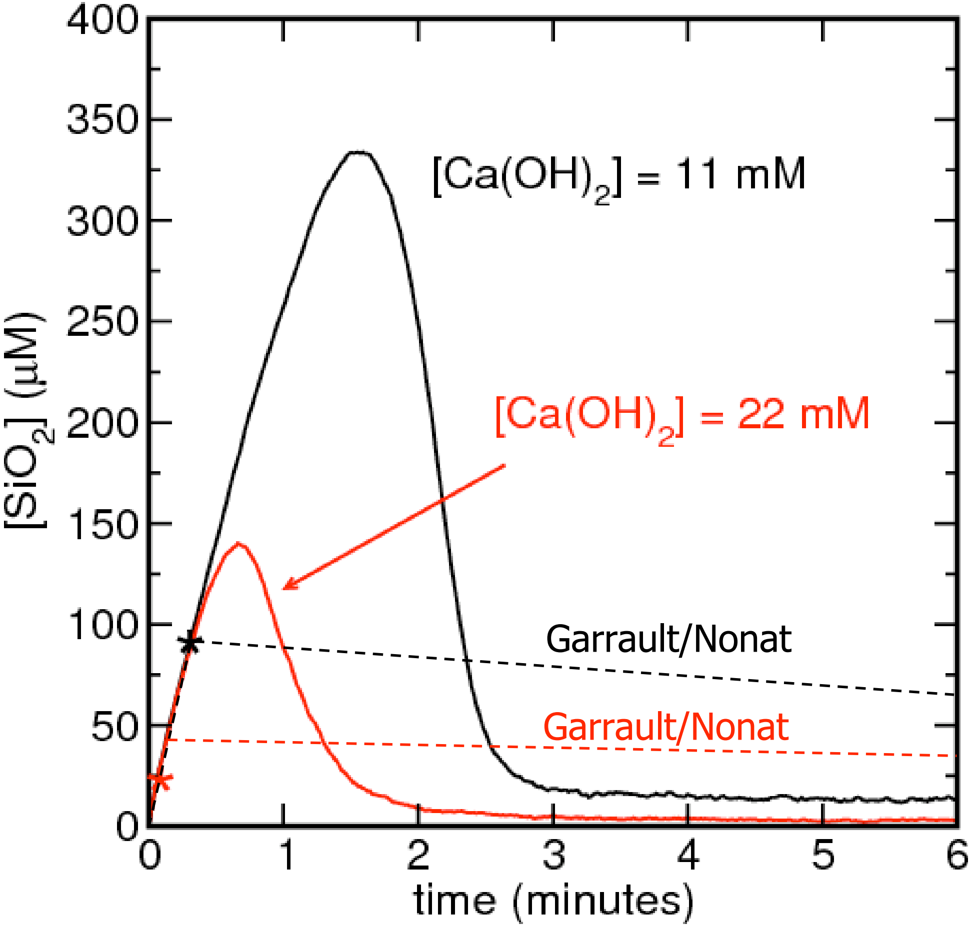
HydratiCA: Hydration of C_3S



Control Variables:

- k_{diss} = 1.0 x 10^{-4} mole/s
- Nuc rate coefficient = 10^9 s^{-1}
- CSH transport factor = 0.3 P

HydratiCA: Hydration of C_3S



The kinetic behavior depends on three main parameters:

1. C_3S dissolution rate const.
2. C-S-H nucleation work
    a) Homogeneous
    b) Heterogeneous
3. C-S-H growth rate constant