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Pore-scale Simulation of Mixing-induced Calcium Carbonate Precipitation and Dissolution in a Microfluidic Pore Network

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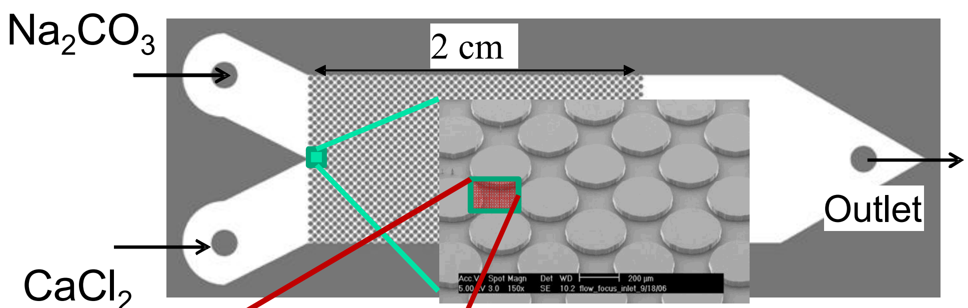
Motivations

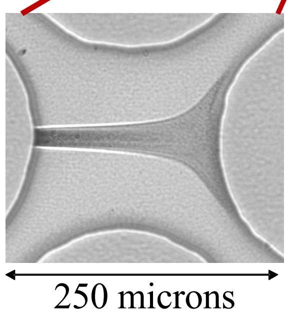
- Formation of Calcium Carbonate ($CaCO_3$) plays an important role in many natural and engineered systems
  - Geological CO_2 storage
  - Growth of calcite concretions in fractured and porous media
  - Biomineralization of products from microorganisms
  - Formation of scale in boilers and cooling towers
- Pore scale mixing and reaction can affect CO_2 injection efficiency and storage capacity
  - Reactions in the field (e.g., flowing conditions) can be limited by rates of transverse mixing
  - Recent development of in-situ measurement techniques for (sub) pore-scale reactive transport experiments provides a unique opportunity to test and validate pore-scale modeling approaches

Methods

Experimental setup



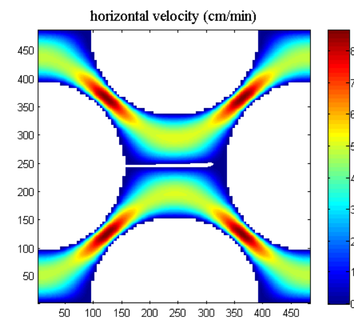
Zhang et al. (2010)



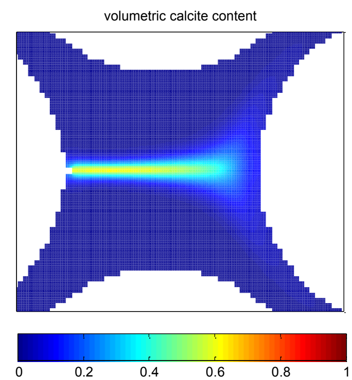
Microscopic image of calcium carbonate ($CaCO_3$) precipitates

- Two solutions are mixing along the centerline and $CaCO_3$ precipitates
- Microscopic images are taken over time

Pore scale modeling



Water flow velocity in pore space (resolution: 1 micron)



Simulation result of calcium carbonate ($CaCO_3$) precipitates

- Lattice Boltzmann Method for water flow
- Direct numerical simulation of $CaCO_3$ precipitation and dissolution

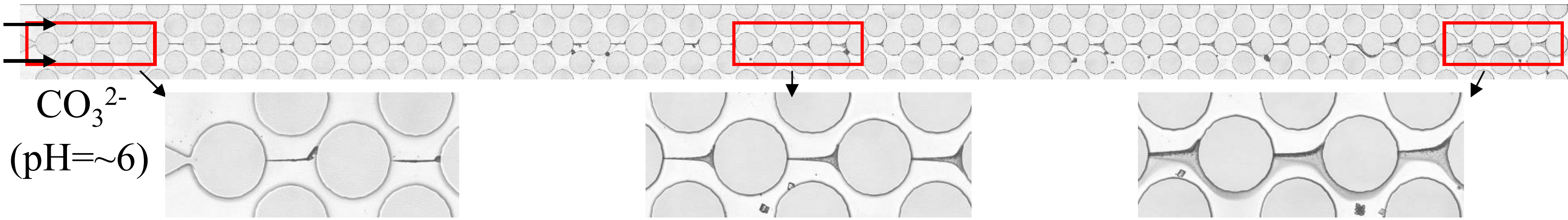
Precipitate morphology and growth rate

$[Ca^{2+}]_T=[CO_3^{2-}]_T=25$ mM at 2 hrs

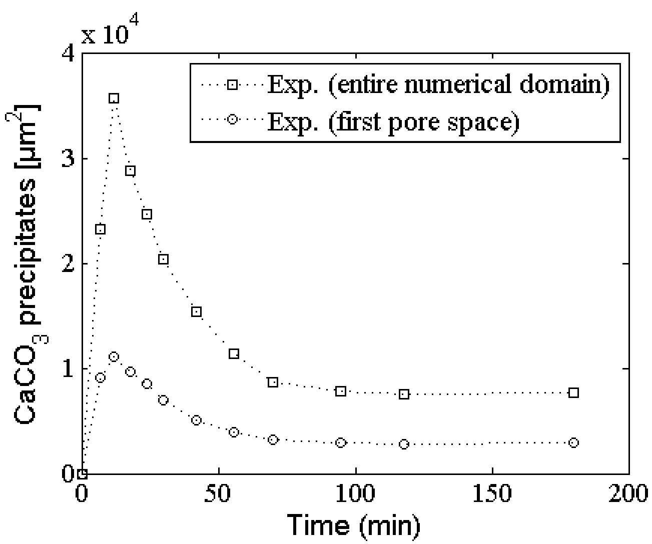
Zhang et al., ES&T (2010)

Ca^{2-} (pH=~11)

CO_3^{2-} (pH=~6)



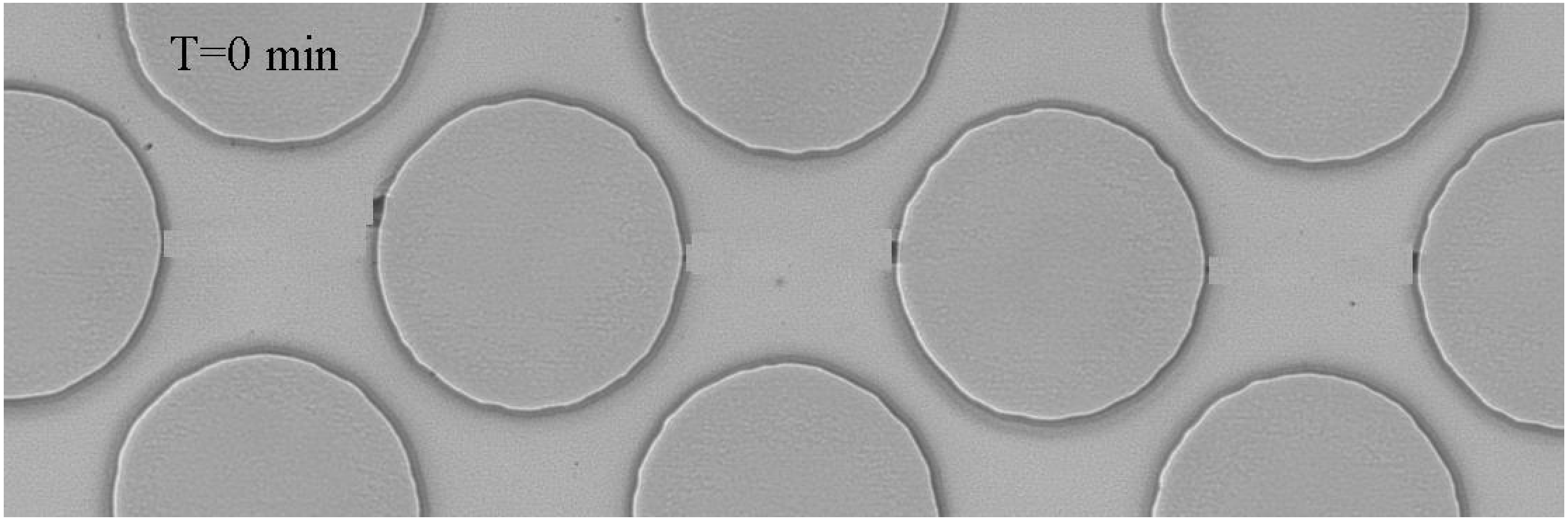
- Precipitation ~ along the centerline within one pore space transverse to the primary flow direction, with some large crystals off the centerline
- Width of the precipitate line ~ increase with distance from the inlet



Yoon et al., WRR (2011)

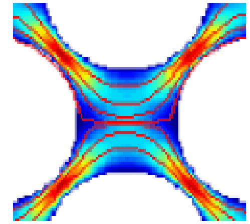
- Precipitate area increases rapidly due to fast precipitation
- and then decreases due to fast dissolution within 13 min
- until a relatively constant but lower plateau is reached over 3-4 hours

Experimental Results



$CaCO_3$ Precipitation and Dissolution

Lattice Boltzmann Method: Velocity field (*u*) at pore scale



Finite Volume Method: Reactive transport at pore scale

$\nabla \cdot (\mathbf{u}\Psi_j - D\nabla\Psi_j) = 0$ in liquid phase (Ψ_j: total concentration of primary species j)

$D\frac{\partial \Psi_j}{\partial \mathbf{n}} = -I_m$ on reactive surface

$\Psi_j = C_j + \sum_{i=1}^{N_{eq}} \upsilon_{ji} C_i$ Chemical equilibrium in bulk fluid (e.g., H^+, HCO_3^-, …) Extend Debye-Hückel Equation for activity coefficients

$I_m = -k_{cc}(1-\Omega) = -(k_1 a_{H^+} + k_2 a_{H_2CO_3} + k_3)\left(1 - \frac{Q_{cc}}{K_{sp}}\right)$ Heterogeneous reaction at mineral surfaces Ω= supersaturation index; Q_{cc}= ion activity product; K_{sp}= solubility product

Δt

Calcite Precipitation and Dissoluion

$$\frac{\partial V_m}{\partial t} = \overline{V_m} a_m K_C \left(\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}} - 1 \right)$$

Calcite volume fraction (V_m) is updated explicitly over time

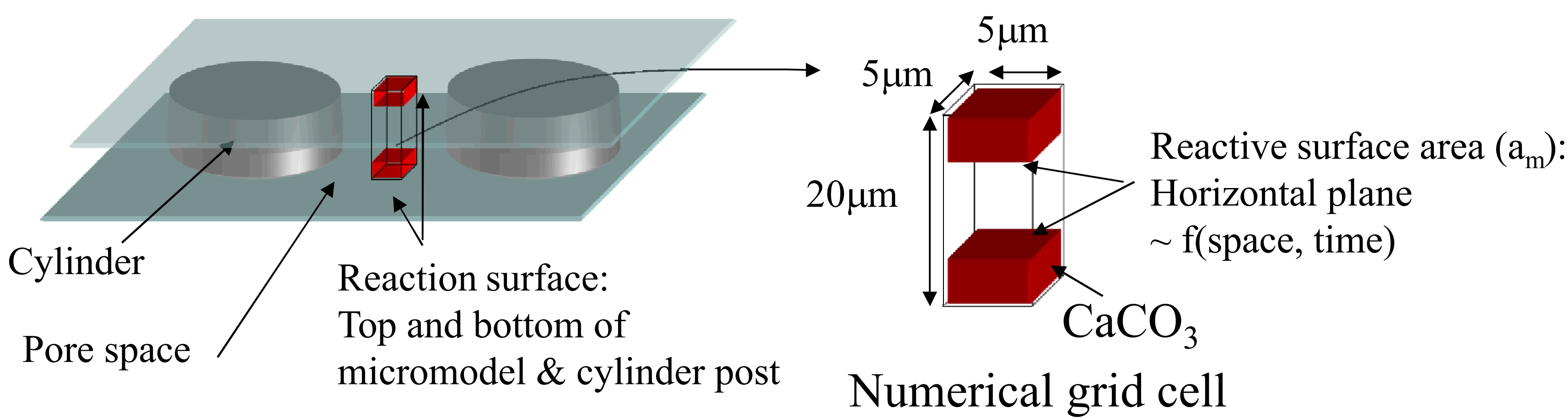
$\overline{V_m}$ is the molar volume of calcite

Key features of modeling

1. Flow field (solved by Lattice Boltzmann method)
   - $CaCO_3$ volume fraction (θ) of a grid cell (5μm x 5μm x 20μm) is greater than a threshold value (e.g.,0.6), then no flow is allowed through the grid cell
   - Diffusion is still allowed until the grid cell is fully occupied by calcite

2. Effective diffusion coefficient = D_m * tortuosity (τ)
   - $\tau(\theta) = (1-\theta)^n$ where n ~ 0 to 3

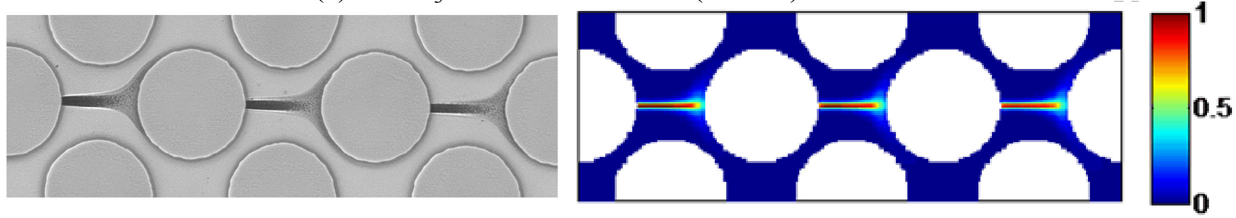
3. Quasi 3D grid cell for reactive surface



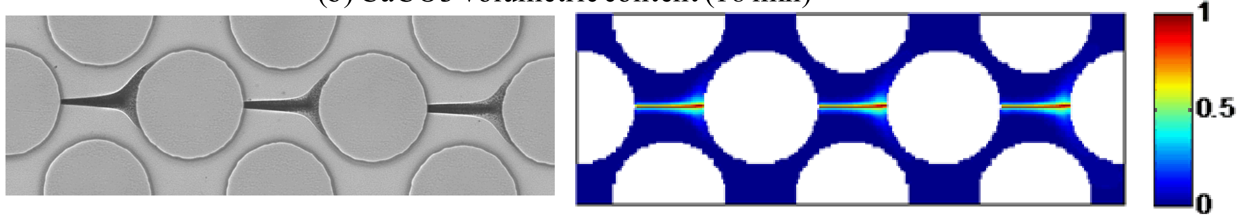
4. Effects of n, k_{cc}, and dissolution factor on precipitation and dissolution rate

Model results: Reference case (25 mM)

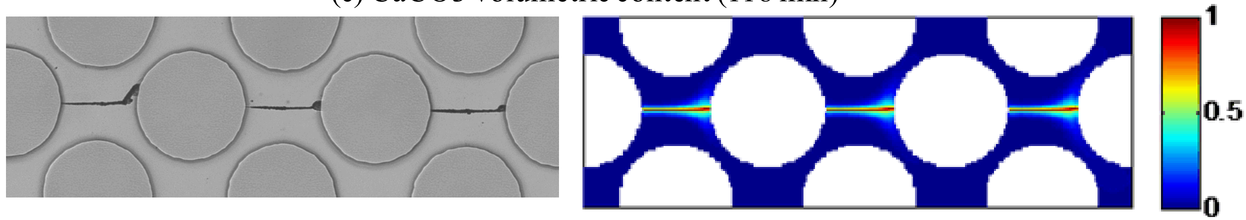
(a) $CaCO_3$ volumetric content (13 min)



(b) CaCO3 volumetric content (18 min)



(c) CaCO3 volumetric content (118 min)



Reference case with literature values (n=2, kcc from Chou et al. (1989):

- Initial precipitation is modeled well
- Simulation was not able to capture the dissolution process after ~13 min
- Experimental results show $CaCO_3$ dissolution may be pH-dependent

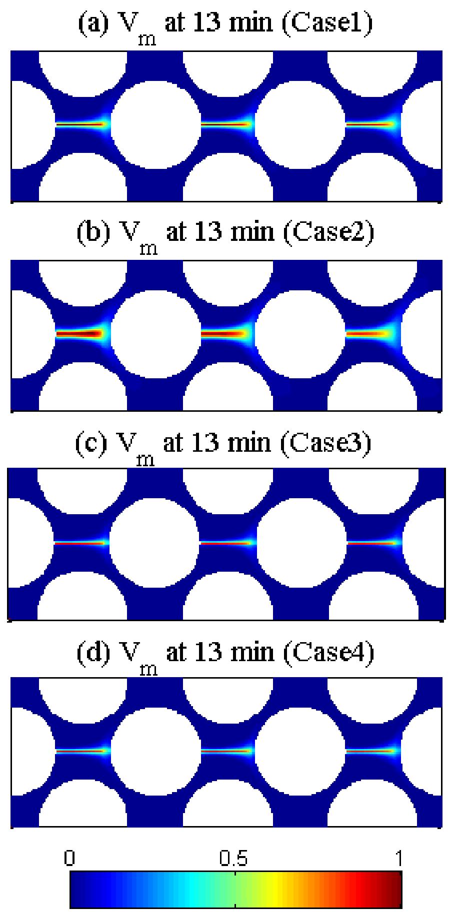
Sensitivity: D_{eff} & k_{cc}

(n=2)

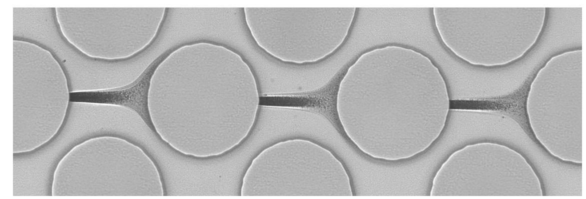
(n=0)

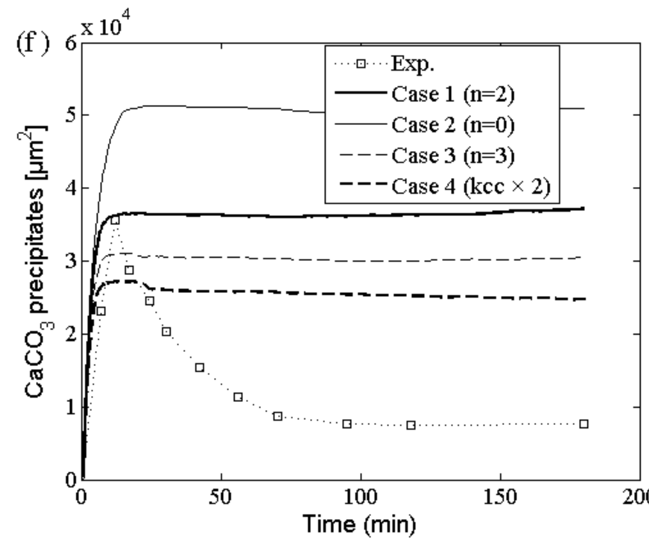
(n=3)

(n=2 & k_{cc} x 2)



(e) Image of precipitates at 13 min

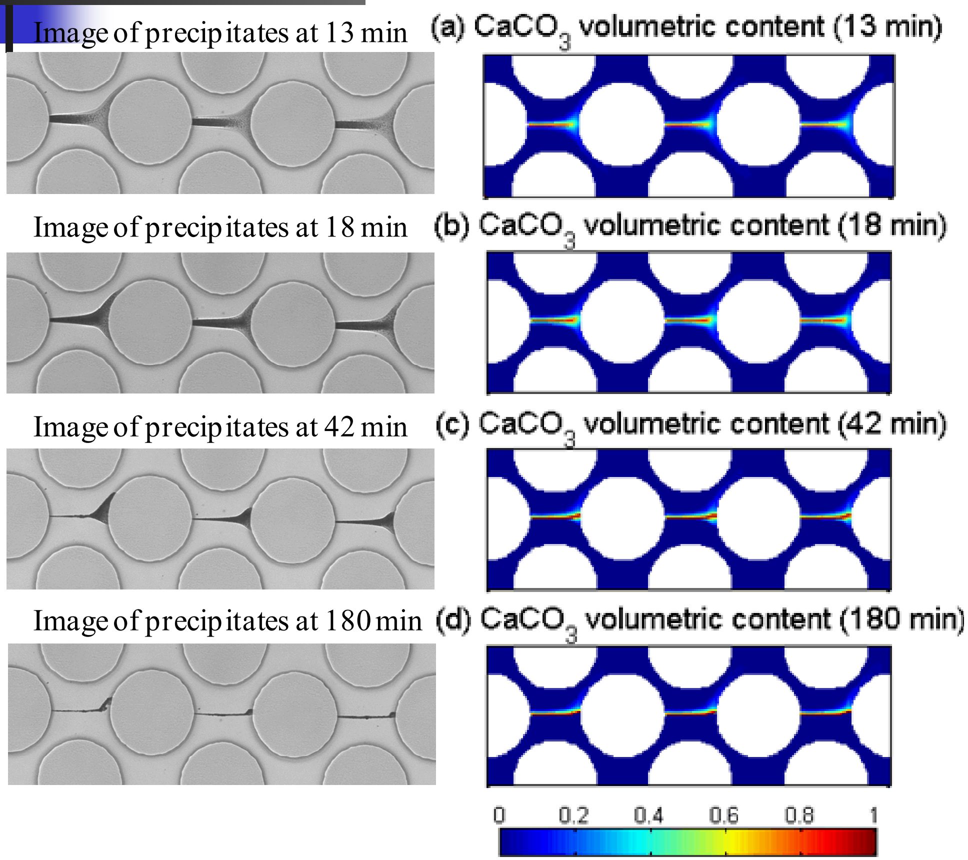


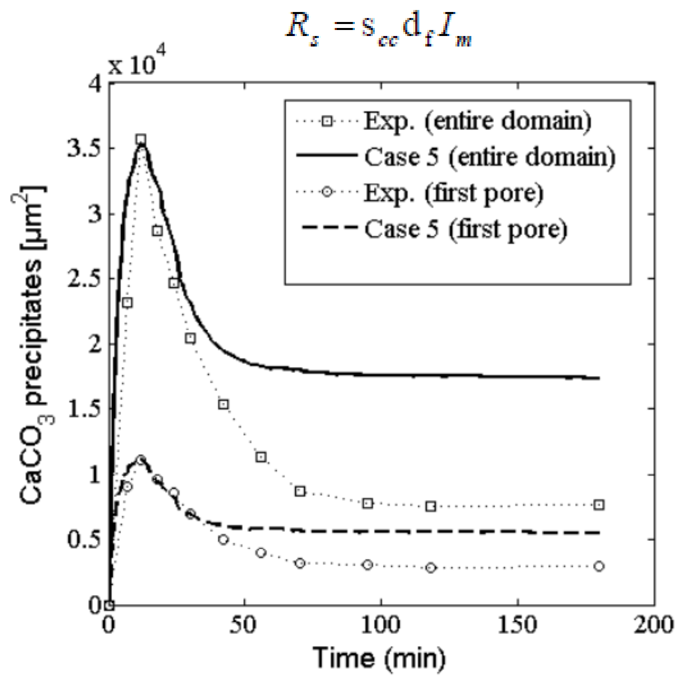


$$D_{eff} = D_m * (1-\theta)^n$$

- As the n value decreases (increases), D_{eff} decreases less (more) as V_m increases, resulting in more (less) precipitation compared to the experimental results
- As k_{cc} increases, precipitation occurs faster, particularly along the centerline, resulting in a reduction of diffusion (i.e., mixing) -> decreasing the maximum precipitate area

Dissolution factor (factor=300)



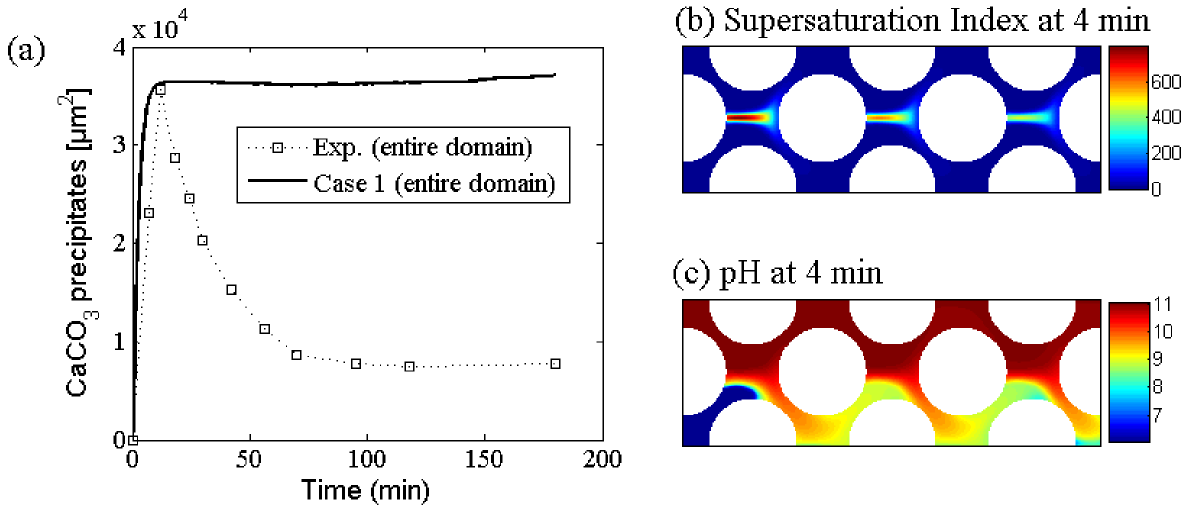


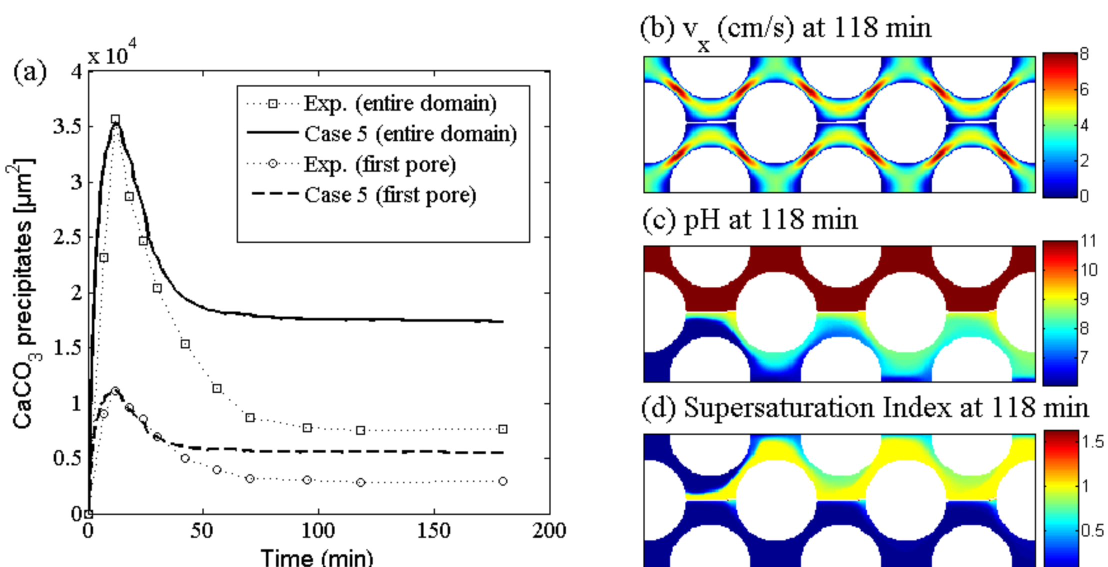
- Thickness and area of precipitate along the centerline after 13 min decreases more quickly, and the precipitate area matches the experimental data until 30 minutes
- Model predicts dissolution below the centerline well, but not above the centerline
- The need to include a higher dissolution factor may be attributed to an increase in the precipitate surface area and the recrystallization process during dissolution

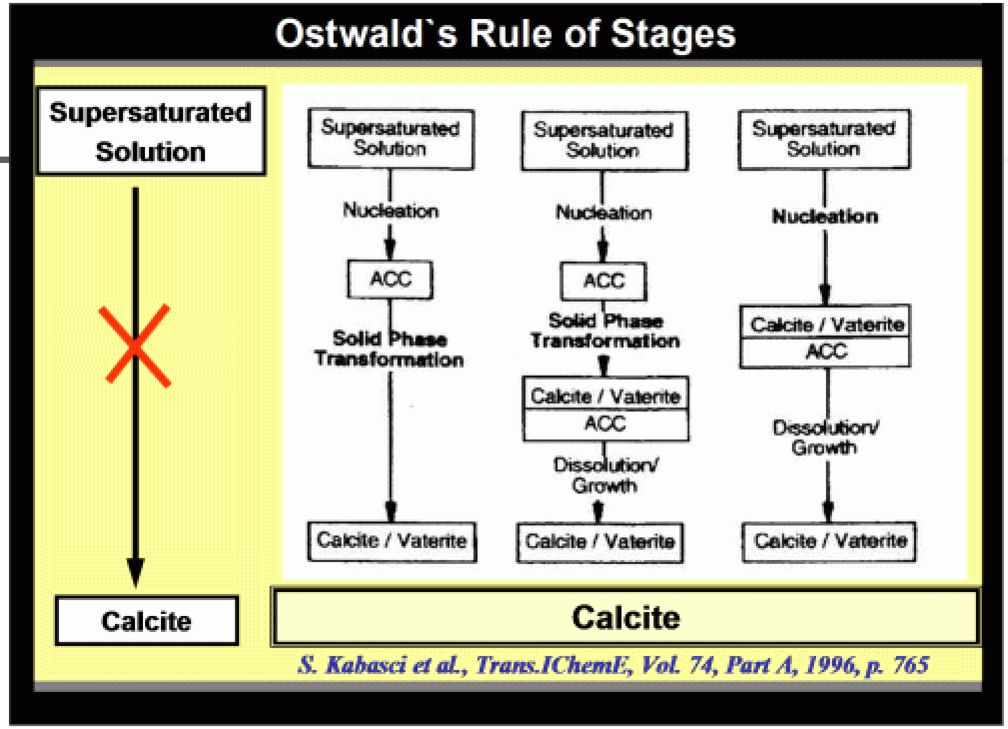
Summary and Challenges

- Pore Scale LB-FVM qualitatively captures governing physics in transverse-mixing induced $CaCO_3$ formation
  - $CaCO_3$ formation and precipitate patterns
  - Pore blocking due to precipitation
- The effects of geochemical reactions and flow field change are coupled properly
- There is a need to account for the enhanced dissolution, possibly linking to reactive surface area at sub-micro scale and recrystallization processes
- Pore-scale modeling and experimental results will be used to test the validity of various upscaling (pore to continuum) and multi-scale (hybrid) methods, and to develop a new method of obtaining effective dispersion coefficient values and reactive surface area

Questions?


(a)
x 10^4
CaCO3 precipitates [μm^2]
Time (min)
Exp. (entire domain)
Case 1 (entire domain)
(b) Supersaturation Index at 4 min
600
400
200
0
(c) pH at 4 min
11
10
9
8
7


(a)
x 10^4
CaCO3 precipitates [μm^2]
Time (min)
Exp. (entire domain)
Case 5 (entire domain)
Exp. (first pore)
Case 5 (first pore)
(b) vx (cm/s) at 118 min
8
6
4
2
0
(c) pH at 118 min
11
10
9
8
7
(d) Supersaturation Index at 118 min
1.5
1
0.5
0



Modifications of Calcium Carbonate

CALCITE	ρ = 2.8 g/cm	crystalline	thermod. stable
ARAGONITE	ρ = 3.0 g/cm^3	crystalline	metastable
VATERITE	ρ = 2.7 g/cm^3	crystalline	metastable
MONOHYDRATE	ρ = n. a.	crystalline	metastable
HEXAHYDRATE	ρ = 1.8 g/cm^3	crystalline	metastable
COLLOIDAL	ρ = n. a.	amorphous	metastable

Bolze et al., Langmuir(2002)