SAND2011-6108C

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

Hongkyu Yoon

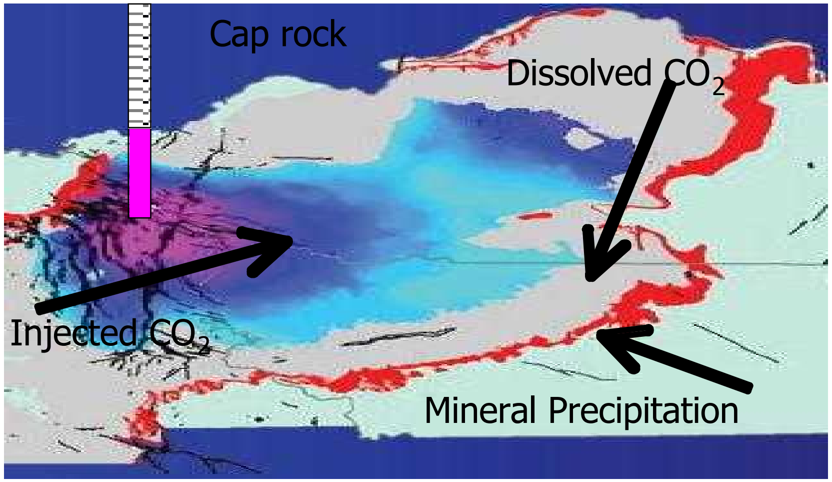
Sandia National Laboratories

ACS 2011 National Meeting

Collaborators: Profs. Albert Valocchi and Charlie Werth (UIUC)
Dr. Thomas Dewers (SNL)

This material is based upon work supported as part of the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001114.

Motivations



S.E. Greenberg (2007), Midwest Geological Sequestration Consortium

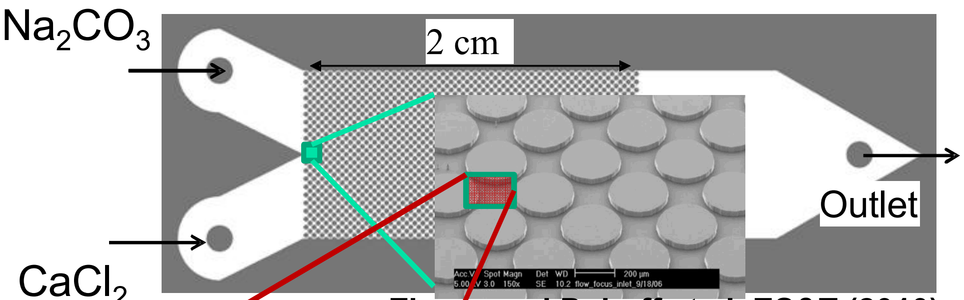
Reactions in the field can be limited by rates of transverse mixing

Pore scale mixing and reaction can affect CO2 injection efficiency and storage capacity

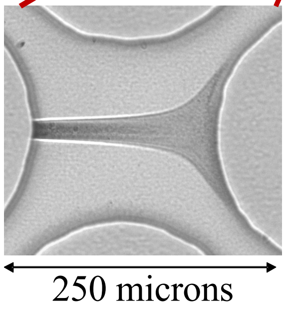
- Recent development of in-situ measurement techniques for (sub) pore-scale reactive transport experiments provides a unique opportunity to test and validate pore-scale modeling approaches

Methods

Experimental setup

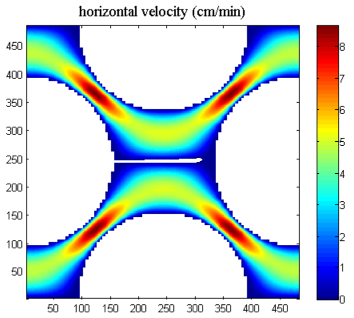


Zhang and Dehoff et al. ES&T (2010)

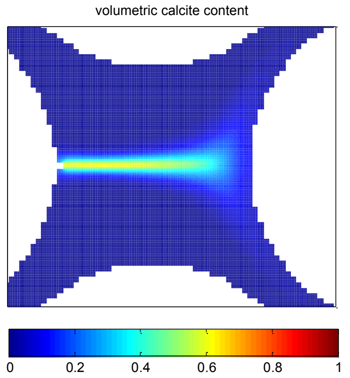


Microscopic image of calcium carbonate ($CaCO_3$) precipitates

Pore scale modeling



Water flow velocity in pore space (resolution: 1-5 micron)



Simulation result of calcium carbonate ($CaCO_3$) precipitates

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

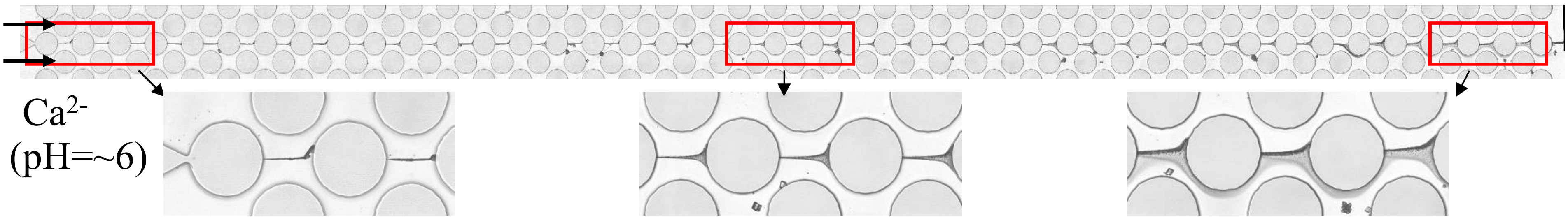
- Lattice Boltzmann Method for water flow
- Direct numerical simulation of reactive transport

Precipitate morphology and growth rate

CO_3^{2-}(pH=~11)

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

Zhang et al., ES&T (2010)



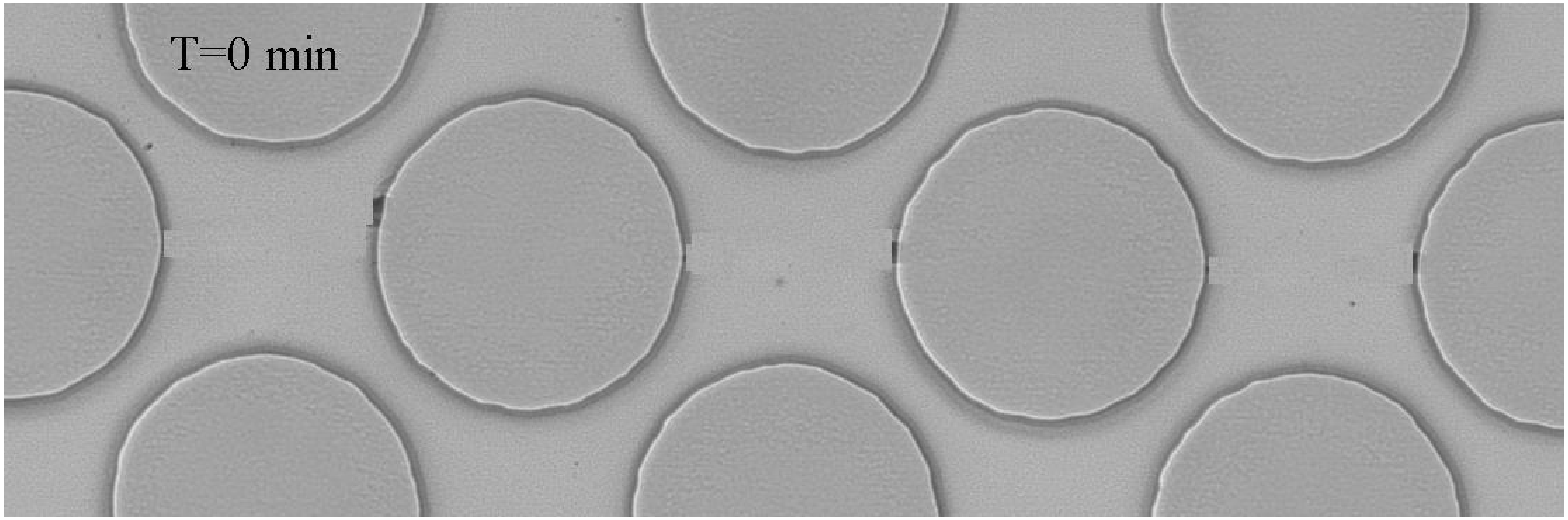
Ca^{2-} (pH=~6)

- Precipitation ~ along the centerline within one pore space in the transverse direction
- Width of the precipitate line ~ increase with distance from the inlet

The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.

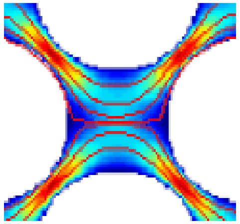
Yoon et al., submitted to WRR (2011)

Experimental results



Model Framework

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



Δt

Finite Volume Method: Reactive transport at pore scale

$\nabla\cdot\left(\mathbf{u}\Psi_j - D\nabla\Psi_j\right)=0$ 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^-, …)
Extended Debye-Hückel Equation for activity coefficients

$I_m = -k_{cc}\left(1-\Omega\right) = -\left(k_1 a_{H^+} + k_2 a_{H_2CO_3} + k_3\right)\left(1-\frac{Q_{cc}}{K_{sp}}\right)$

Heterogeneous reaction at mineral surfaces
Ω= Supersaturation index; Q_{cc}= Ion activity product; K_{sp}= Solubility product

Update of $CaCO_3$ volumetric content

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

$CaCO_3$ volume fraction (V_m) is updated explicitly over time

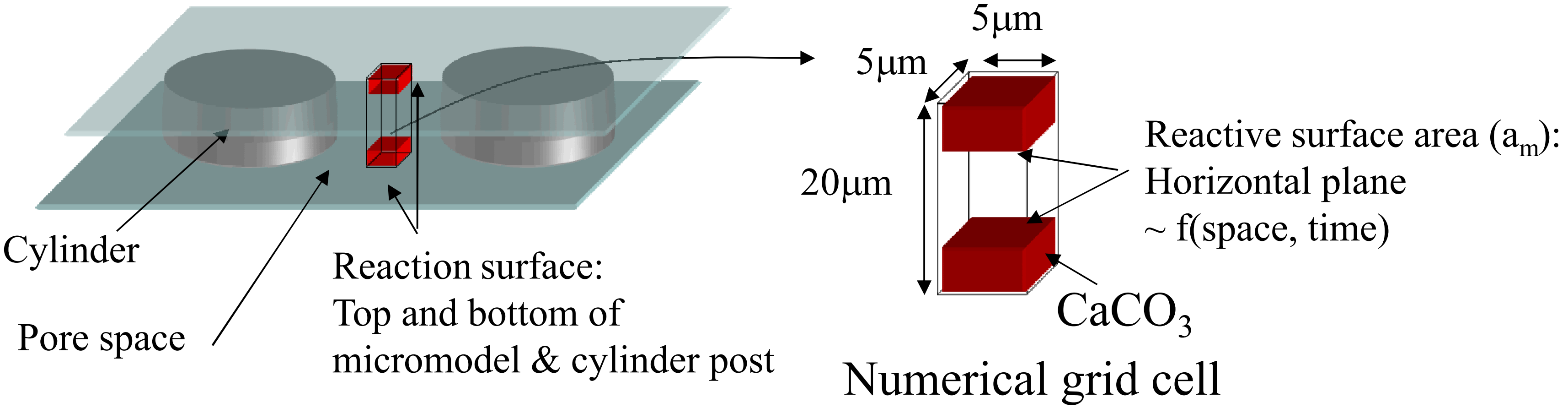
$\overline{V}_m$ is the molar volume of calcite

Key features of model

1. Flow field
   - $CaCO_3$ volumetric fraction (V_m) of a grid cell (5µm x 5µm x 20µm) > a threshold value (e.g.,0.6) → no flow is allowed
   - Diffusion is allowed until the grid cell is fully occupied by $CaCO_3$

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

3. Quasi 3D grid cell for reactive surface

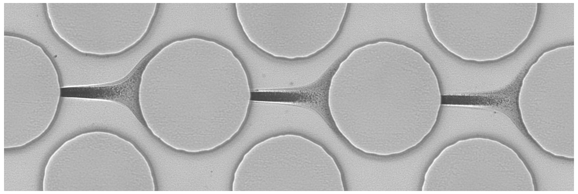


- Simulation results:
  Effects of n, k_{cc}, and dissolution factor on $CaCO_3$ precipitation and dissolution rate

Sensitivity: D_{eff} & k_{cc}

(n=2)

(e) Image of precipitates at 13 min



(n=0)

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

(n=3)

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

- 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)

Image of precipitates at 13 min

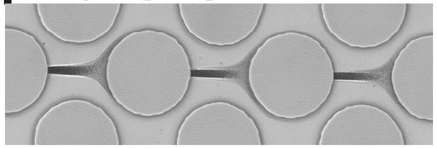


Image of precipitates at 18 min

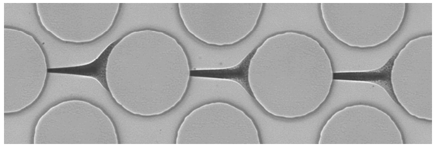


Image of precipitates at 42 min

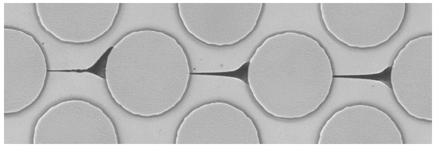
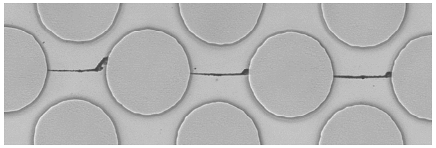
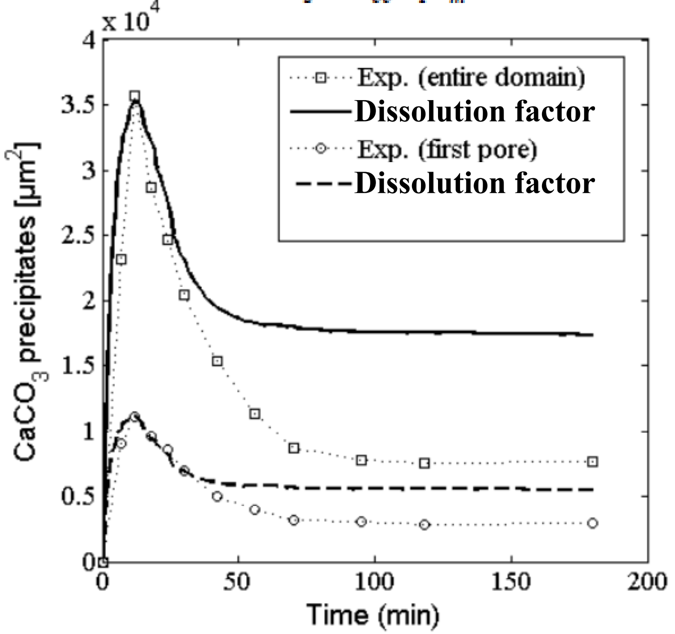


Image of precipitates at 180 min



$$R_s = s_{cc} d_f I_m$$



- 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

Reference case vs. dissolution factor

Questions?

The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.

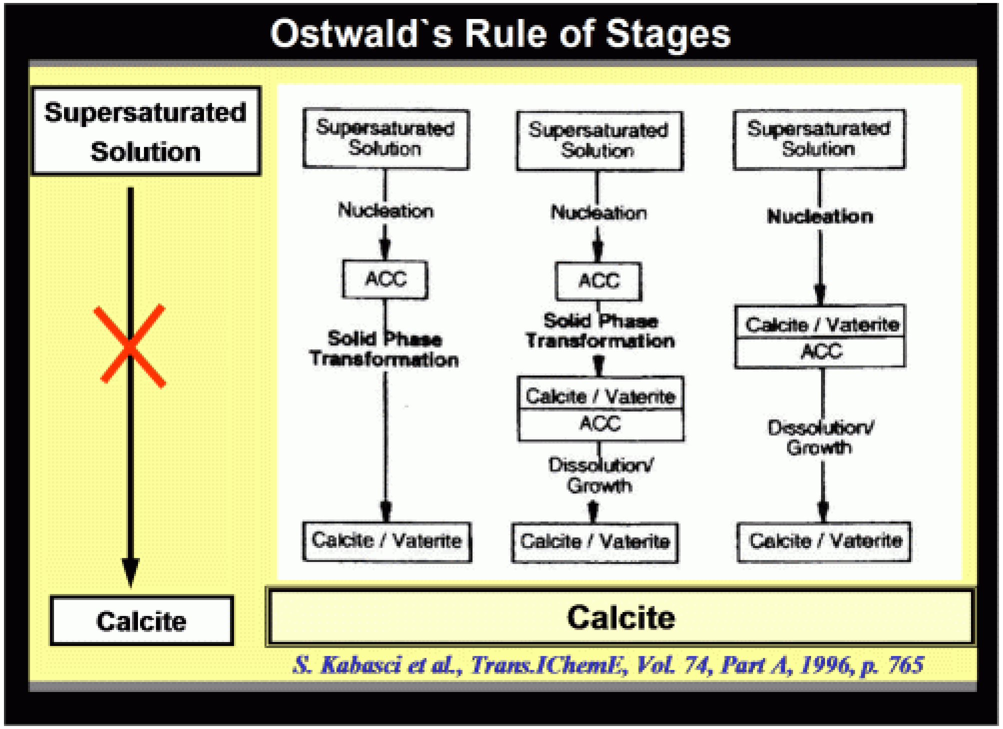
Summary and Challenges

- Pore-scale model captures governing physics in transverse-mixing induced $CaCO_3$ precipitation and dissolution
  - $CaCO_3$ formation and precipitate patterns
  - Pore blocking due to precipitation
- The effects of geochemical reactions and flow field change due to precipitation 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 under different chemical and physical conditions can 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 diffusion (or dispersion) coefficients and reactive surface area

CFSES

Questions?



S. Kabasci et al., Trans.IChemE, Vol. 74, Part A, 1996, p. 765