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Mixing-induced calcite precipitation and dissolution kinetics in micromodel experiments

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OVERVIEW

Objectives

Imaging results from micromodel experiments were used to

- evaluate the mechanisms of calcite precipitation and dissolution (morphology and growth rate) and its impact on permeability change (Zhang et al., 2010)
- determine if pore-scale numerical modeling can be utilized to accurately account for experimental micromodel results.

Methods

◆ **Micromodel Experiments**

- 2D representation of porous media etched into Si wafer
- Grain diameter (300μm), pore body/throat (180/35 μm), and porosity (~0.39) in a homogeneous micromodel

◆ **Pore Scale Modeling**

- 2D Lattice-Boltzmann (LB) method for water flow
- Finite volume method for reactive transport

Micromodel Experimental Setup

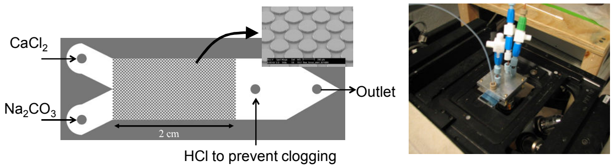
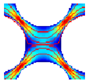


Figure. Schematic of the micromodel including inlet and outlet ports (left) and the back of the micromodel manifold mounted on an fluorescent microscope (right).

Pore Scale Modeling



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

Finite Volume Method: Reactive transport at pore scale

Δt

$$(u\cdot\nabla)C_H-\nabla\cdot(D_H\nabla C_H)=0\quad H=\{H\}_{total}$$

$$(u\cdot\nabla)C_A-\nabla\cdot(D_A\nabla C_A)=0\quad A=\{Ca\}_{total}$$

$$(u\cdot\nabla)C_B-\nabla\cdot(D_B\nabla C_B)=0\quad B=\{CO_3\}_{total}$$

⇄ Chemical equilibrium in bulk fluid (e.g., H^+, HCO_3^-, …)

$$D\nabla C_{total}\cdot n=K_C\left(\frac{a_{Ca^{2+}}a_{CO_3^{2-}}}{K_{sp}}-1\right)$$

Heterogeneous reaction at mineral surfaces is treated as a boundary condition

Calcite Precipitation and Growth

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

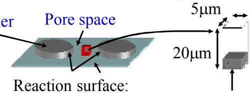
Calcite volume fraction (V_m) is updated explicitly over time

u = velocity, C = total concentration of primary species, a = activity, D = molecular diffusion coefficient, K_c = local reaction-rate constant, K_{sp} = solubility product, V_m = volumetric mineral content, $\overline{V_m}$ = molar volume of calcite, and a_m=specific surface area; activity coefficients from the extended D-H eqn.

Key Model Components

◆ Effective diffusion coeff. (D_{eff}): D_m * tortuosity (τ) where $\tau(\theta)=(1-\theta)^n$

◆ Reactive surface area (quasi 3D grid cell)

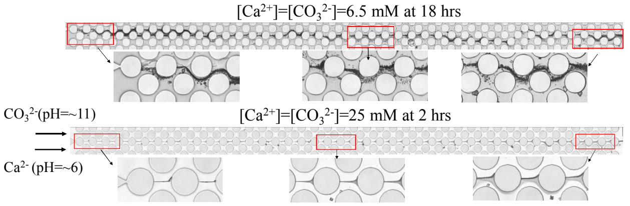


- Specific surface area (a_m) = Surface area of calcite precipitate/ Volume of a grid cell
- a_m ~ f(space, time)

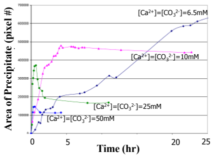
Reaction surface: bottom of micromodel & cylinder surface

Calcite precipitate (Assumption: calcite grows from bottom and cylinder surface)

Precipitate Morphology and Growth Rate



◆ Precipitate is more uniform and narrow transverse to flow at higher concentrations



◆ Precipitation rates are greater at higher concentration, but less precipitate forms

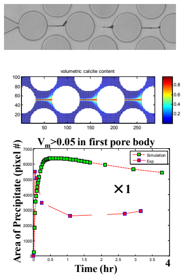
◆ Overshoot of precipitate attributed to decrease in diffusion rate through precipitate over time and pore blocking by calcite precipitate

Figure. Micromodel images during calcite precipitation (top) and calcite growth (# of pixel area of precipitate) over four influent concentrations (bottom).

Pore Scale Modeling Results

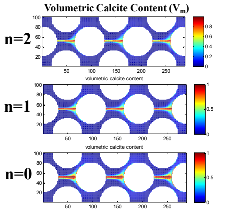
25 mM Case

95 min



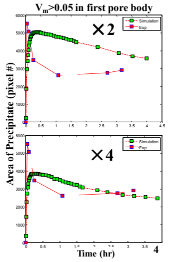
Eff. Diffusion Coeff.

$D_{eff}=D_m$ × tortuosity (τ)
$\tau(\theta)=(1-\theta)^n$ where θ = porosity



Reaction Rate Constant

$$K_C=k_1a_{H^+}+k_2a_{H_2CO_3}+k_3$$

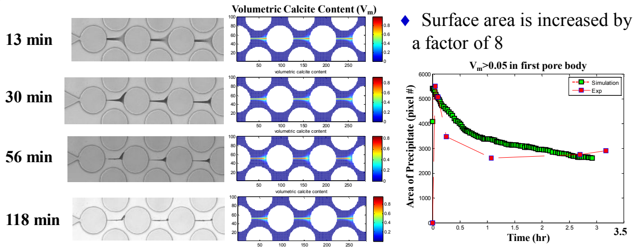


Colorbar (scale=0~1) = volumetric calcite content; **Area of precipitate** is counted in the first pore body; Reaction rate constant is obtained from the literature (Chou et al., 1989)

Summary

- 25 mM Case: Initial precipitation is modeled well, but modeling was not able to capture the dissolution process after ~5 min
- D_{eff} : As n decreases, calcite precipitates more (n=0 case is constant D)
- D_{eff} : n=2 will be a good choice to prevent too much diffusion
- K_C : As reaction rate constant increases, less precipitate forms due to fast pore blocking.
- Experimental images show that
  - Calcite dissolution can be pH-dependent
  - At high influent solution case, precipitate remains very thin (< 10 μm), which requires a fine grid size for pore-scale modeling

Effect of Surface Area (25 mM)



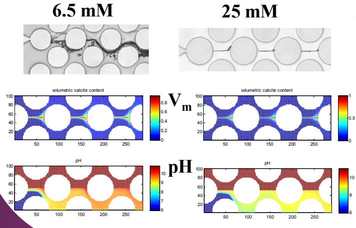
◆ Surface area is increased by a factor of 8

◆ Experimental results can be predicted better by adjusting the surface area in dissolution-dominant area after pore-blocking

◆ At 25 mM, fine precipitate particles (vaterite) are observed to form (Zhang et al., 2010), which may account for much higher reactive surface area

◆ Effect of surface area on reaction rate needs to be further investigated

Low (6.5 mM) vs. High (25 mM) Influent Conc.



◆ At 6.5 mM, pore blocking is not completed, allowing both solutions to flow through the center line -> area of precipitate continuously increases over time

◆ After pore blocking at 25 mM, pH below the centerline becomes slightly lower than before pore blocking due to dissolution

SUMMARY & FUTURE WORK

- Pore-scale modeling captures governing physics (precipitate morphology and growth pattern) in transverse-mixing induced calcite formation.
- The effects of geochemical reactions and flow field change due to calcite precipitation are coupled properly.
- There is a need to incorporate different rules for updating reactive surface areas during precipitation and dissolution.
- 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.

Reference: Changyong Zhang, Karl Dehoff, Nancy Hess, Mart Oostrom, Thomas W. Wietsma, Albert J. Valocchi, Bruce W. Fouke, and Charles J. Werth. Pore-Scale Study of Transverse Mixing Induced CaCO3 Precipitation and Permeability Reduction in a Model Subsurface Sedimentary System. Environ. Sci. Technol., 2010, 44 (20), pp 7833–7838.

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