

# Pore Scale Modeling of Calcium Carbonate Reactive Transport

---

**Hongkyu Yoon**  
**Sandia National Laboratories**

EFRC Blue Team Monthly Teleconference  
October 25, 2012

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.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science



**Sandia**  
National  
Laboratories



# Pore Scale Modeling of Calcium Carbonate Reactive Transport

## Scientific Achievement

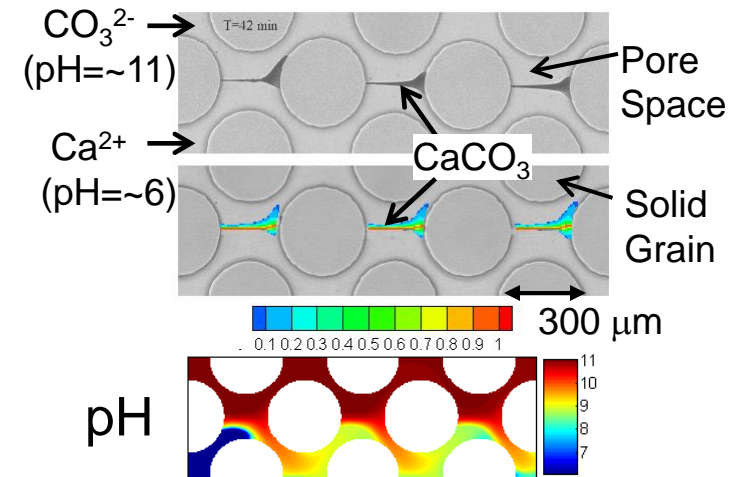
Developed a novel pore scale reactive transport model of coupled fluid flow, reactive transport, and calcium carbonate ( $\text{CaCO}_3$ ) precipitation and dissolution

## Significance and Impact

Improved understanding of the fundamental physico-chemical processes of  $\text{CaCO}_3$  precipitation and dissolution at micro (pore) scale for coupled reactive transport systems perturbed by geological  $\text{CO}_2$  injection

## Research Details

- A newly developed pore-scale model is used to simulate transient experimental results of  $\text{CaCO}_3$  precipitation and dissolution in a microfluidic pore network (shown in Figure)
- Pore scale model was able to capture the precipitate morphology and precipitation rate
- Proper estimation of the effective diffusion coefficient and the reactive surface area is necessary to adequately simulate precipitation and dissolution rates
- The model developed in this study allows us to simulate and mechanistically evaluate precipitation and dissolution of  $\text{CaCO}_3$  observed at pore scale



**Experimental image of  $\text{CaCO}_3$  precipitates (top), simulated  $\text{CaCO}_3$  volumetric content (middle), and simulated pH distribution at 42 min.** In the microfluidic pore network, precipitation is induced by transverse mixing along the centerline in pore bodies.

H. Yoon, A. J. Valocchi, C. J. Werth, and T. Dewers, Water Resources Research, 48, W02524 (2012)



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science



TEXAS

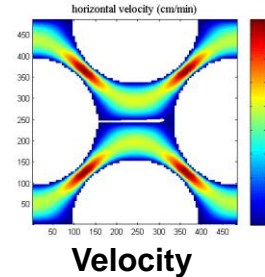


Sandia  
National  
Laboratories



# Pore Scale Model Framework

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



Finite Volume Method: Reactive transport at pore scale

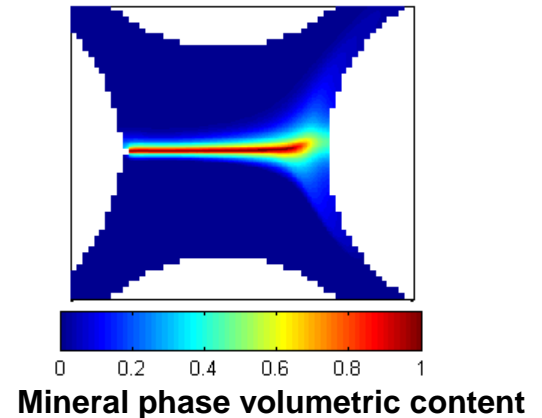
$\Psi_j = C_j + \sum_{i=1}^{N_{eq}} \nu_{ji} C_i$  Chemical equilibrium in bulk fluid (e.g.,  $H^+$ ,  $HCO_3^-$ , ...)  
Extended Debye-Hückel Equation for activity coefficients

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

$$I_m = k_{cc} \left( [\Omega]^n - 1 \right)^m \quad \Omega = \frac{Q_{cc}}{K_{sp}} \text{ or } \ln \left( \frac{Q_{cc}}{K_{sp}} \right)$$

Update of  $CaCO_3$  volumetric content ( $V_m$ )

$$\frac{\partial V_m}{\partial t} = \bar{V}_m s_m k_{cc} \left( \left[ \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}} \right]^n - 1 \right)^m$$



$\Delta t$



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science

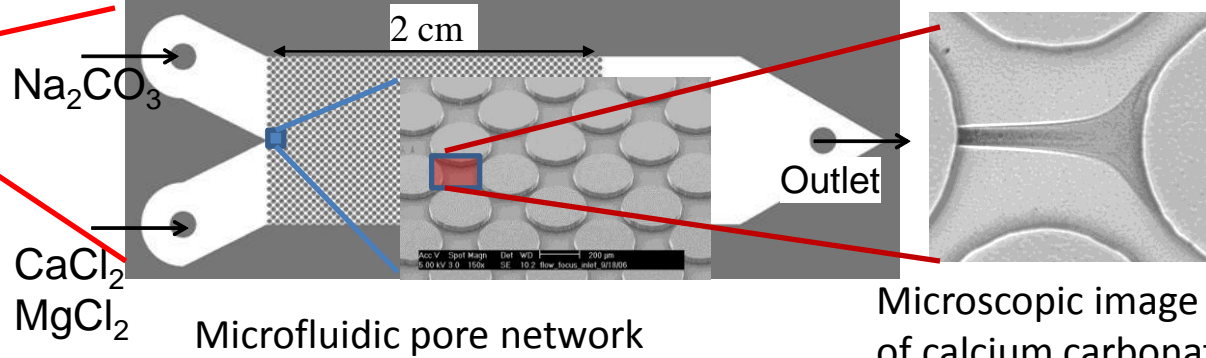


# Microfluidic Experiment

## Experiment Setup



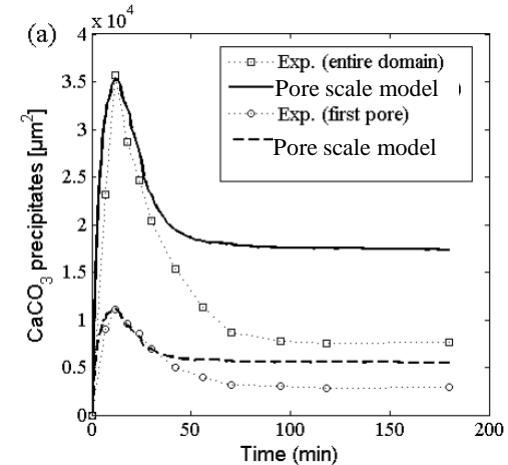
3D Laser scanning confocal microscope



Microfluidic pore network

Microscopic image of calcium carbonate (CaCO<sub>2</sub>) precipitates

- Microfluidic pore network (micromodel)
  - 2D representation of porous media etched into Si wafer with any pore geometries at  $\sim 0.1 \mu\text{m}$
- Two solutions are mixing along the centerline and reactive product (e.g., CaCO<sub>3</sub>) forms
- Flexible with a range of concentrations and solution chemistry
- 2D and 3D in-situ observations with optical or confocal microscope



Comparison of CaCO<sub>3</sub> precipitation area over time. Model captures precipitation and dissolution rates well up to 30 minute, and then under-predicted dissolution rate

H. Yoon, A. J. Valocchi, C. J. Werth, and T. Dewers, Water Resources Research, 48, W02524 (2012)