Flow and reactive transport at pore to continuum scales: Application to a natural analogue for leakage

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We expect pore-scale geochemical processes to be important in many of the proposed US storage sites for carbon dioxide.

We combine laboratory micro-scale experimental and modeling efforts to examine:

What are the relevant physics of dissolved CO_2 transport in a reactive environment?

- How do precipitation and dissolution alter 3D pore structure?
- How do the 3D structural changes affect the flow?
- How do the changing flow conditions impact later stage precipitation and dissolution?

1) Experimental and Numerical Pore Scale Reactive Transport

- Well-controlled transverse mixing induced calcium carbonate ($CaCO_3$) precipitation followed by dissolution in micromodel laboratory experiments

2D Analysis of Micromodel Laboratory Experiments

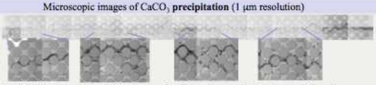
Micromodel Schematic

Experiment Conditions

Phase	Inlet A	Inlet B	Duration
1: Precipitation	Na_2CO_3, pH=11	$CaCl_2$, pH = 6	75 hours
2: Dissolution	H_2O, pH=4	H_2O, pH=4	130 hours

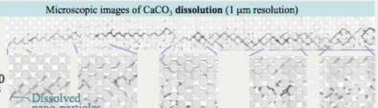
- Solutes are injected with a syringe pump set at a steady rate of 50 µL/hour

Microscopic images of $CaCO_3$ **precipitation** (1 µm resolution)



- Precipitation occurs within 2 pore bodies of central reactive mixing line
- Pattern depends on location and time

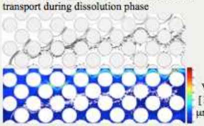
Microscopic images of $CaCO_3$ **dissolution** (1 µm resolution)



- Dissolution spreads precipitates from 2 to 10 pore bodies

Flow Simulation

Observed precipitates and dissolved CaCO3 transport during dissolution phase



Flow velocity from Lattice Boltzmann

- Simulations capture precipitation and dissolution patterns observed in the micromodel
- Spreading of dissolved $CaCO_3$ component (i.e., nano-particles) correlates well with flow streamlines
- Precipitation and dissolution impact and are affected by the evolving flow field demonstrating feedback

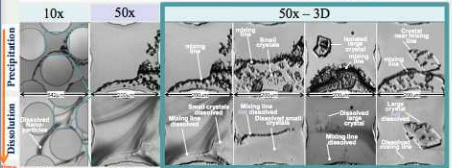
2) Characterizing structural evolution in pores

3D Analysis of Micromodel Laboratory Experiments

3D images of $CaCO_3$ in individual pores using laser scanning confocal microscope

2D images at multiple depths capture 3D distributions

Microscopic images of CaCO3 precipitation and dissolution in same pore

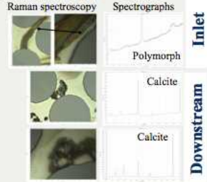


- Single pore bodies contain a range of crystal sizes and distributions
- with non-uniform geometries over depth
- Small crystals formed near inlet were extensively dissolved along with some isolated larger crystals downstream
- Dissolution processes preferentially remove small or isolated crystals

$CaCO_3$ Polymorphs with Raman Spectroscopy

Microscopic images of regions analyzed with Raman spectroscopy

Raman Spectrographs



- After dissolution, Raman spectra indicate small crystals are unstable $CaCO_3$ polymorphs, lacking the peaks that indicate the stable polymorph of calcite
- Unstable polymorphs that formed near the inlet were extensively dissolved while calcite crystals formed at various downstream positions experienced minor dissolution effects

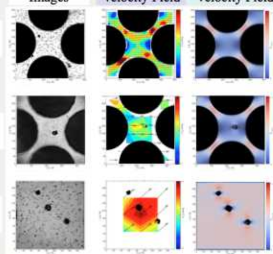
3) Summary

- Dissolution and precipitation induce 3D structural changes within pores
- $CaCO_3$ pattern depends on space and time suggesting tools relying on bulk spatial and temporal averages (i.e. velocity distribution, reaction rate) may not capture the observed behavior

4) Characterizing 3D flow effects in pores

Simulated flow in individual pores

Observations and Simulations



5) SUMMARY

- Simple precipitation patterns significantly alter laboratory and simulated flow fields from the case without precipitation suggesting the flow field is sensitive to small changes in the structural configuration

6) Summary, Implications, and Future Work

- Evolving pore configurations in a micromodel due to calcium carbonate ($CaCO_3$) precipitation and dissolution induce 3D flow effects that influence later precipitation and dissolution
- 3D heterogeneous structures and flow fields may significantly impact bulk reaction rates (i.e., reactive surface area and concentration gradient)
- Future work will include validation of 3D velocity fields, estimates of reactive surface area, experiments at reservoir pressure/temperature conditions and with multiphase flow, continuum-scale reaction models for precipitation/dissolution

Natural Analogue for Carbonate Sealing of CO_2 Leakage Pathways

- Reaction rate models for precipitation and dissolution will be developed as a function of system parameters using the pore scale model and micromodel experiments based on field observations at the Crystal Geyser natural analogue

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