Lawrence Livermore National Laboratory

Enhanced porosity and permeability in carbonate CO_2 storage reservoirs: An experimental and modeling study

Project Number: FWP-FEW0174 – Task 5

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage
August 20-22, 2013

Presenter: Megan Smith
PI: Susan Carroll
Yue Hao

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

Presentation Outline

- Benefit to Program
- Project Overview
- Technical Status
- Accomplishments
- Summary
- Appendix

Benefit to the Program

- This research project quantifies relationships between fluid flow, heterogeneity, and reaction rates specific to carbon storage in carbonate reservoirs by integrating characterization, solution chemistry, and simulation data.

- This project meets the Carbon Storage Program goals to develop technologies that will support industries' ability to predict CO_2 storage capacity in geologic formations to within ±30 percent.

Project Overview

Goals and Objectives

- The goal of this project is to calibrate key parameters in reactive transport models that will be used to predict final storage of CO_2 in carbonate EOR fields.
- This project will advance science-based forecasting for the transition of CO_2 – EOR operations to storage sites.
- Success is tied to the ability to scale reactive-flow and transport parameters over a range of carbonate rock types and permeability.

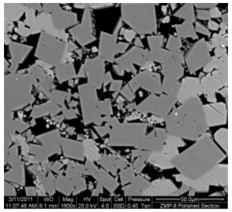
Technical Status

The research scope consists of three major tasks:

- Model calibration against existing experimental database of carbonate rocks from Midale-Weyburn Carbon Storage Project
    - Smith M, Sholokhova Y, Hao Y, and Carroll S, 2012, Evaporite caprock integrity: An experimental study of reactive mineralogy and pore-scale heterogeneity during brine–CO_2 exposure. *Env Sci & Technol,* doi:es3012723.
    - Carroll S, Hao Y, Smith M, Sholokhova Y, 2013, Development of scaling parameters to describe CO_2-carbonate-rock interactions for the Marly Dolostone and Vuggy Limestone, *Int J Greenhouse Gas Control*, doi:10.1016/j.ijggc.2012.12.026
    - Smith M, Sholokhova Y, Hao Y, and Carroll S. (2013) CO_2-Induced Dissolution of Low Permeability Carbonates Part I: Characterization and Experiments, *Adv Water Res*, revised.
    - Hao Y, Smith M, Sholokhova Y, and Carroll S. (2013) CO_2-Induced Dissolution of Low Permeability Carbonates Part 2: Numerical Modeling of Experiments, *Adv Water Res*, revised.
- **Study of a wider permeability range using cores from the Wellington, KS, CO_2 demonstration site (focus of presentation)**
- Refined model and parameter scaling towards predicting changes in reservoir porosity and permeability

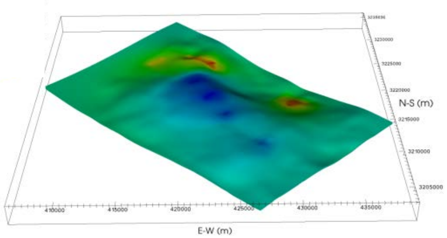
Motivation behind choices of characterization techniques and experimental scales

- Geochemical mineral-fluid interactions induced by CO_2 injection have a major effect on rock porosity and permeability evolution, which may potentially alter the behavior or performance of CO_2 geological storage and EOR operations;
- The mineral dissolution/precipitation and associated flow and reactive transport processes in porous media are described at different scales;



Pore (microscopic) scale ~ µm

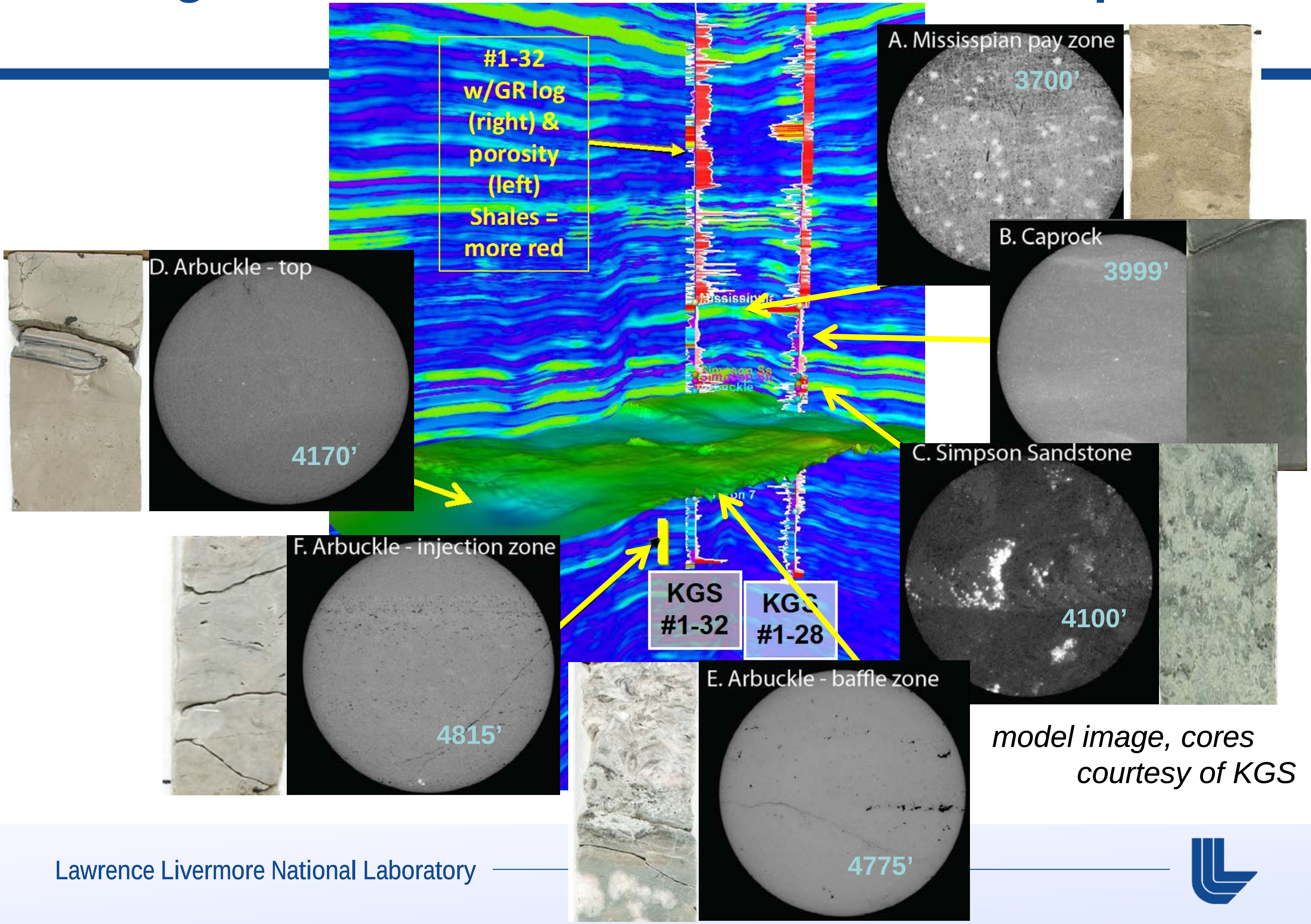
Core (laboratory) scale ~ cm



Large (reservoir/field) scale ~ km

- Reactive transport modeling represents a critical component in assessment of geochemical impact of CO_2 water-rock interactions;
- **However, a lack of proper calibration or upscaling of the effective macroscopic parameters over large field-scales hinders accurate reactive-transport modeling of CO_2 fate and transport.**

Wellington, Kansas, flow unit model & samples



#1-32 w/GR log (right) & porosity (left)
Shales = more red

A. Mississisppian pay zone

B. Caprock

C. Simpson Sandstone

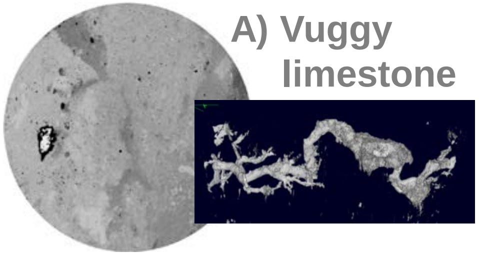
D. Arbuckle - top

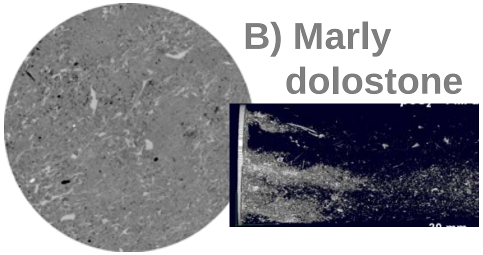
E. Arbuckle - baffle zone

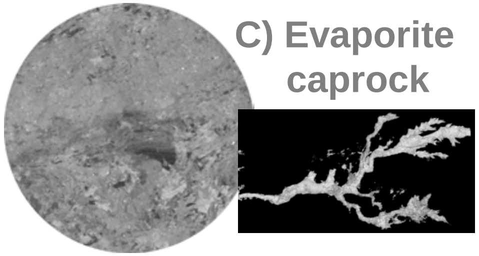
F. Arbuckle - injection zone

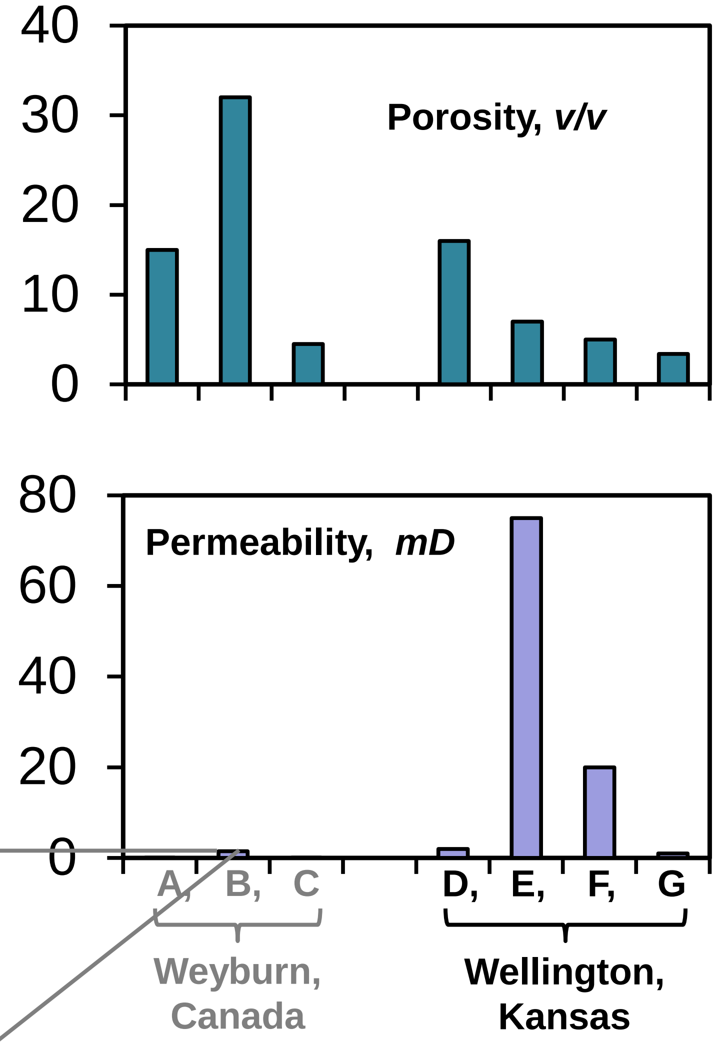
model image, cores courtesy of KGS

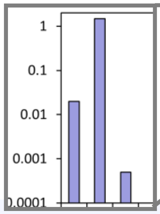
Wellington, KS, samples extend permeability range


A) Vuggy limestone

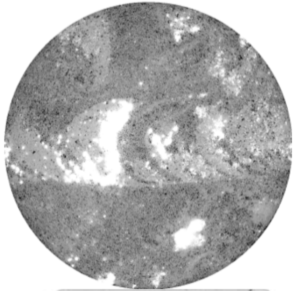

B) Marly dolostone


C) Evaporite caprock

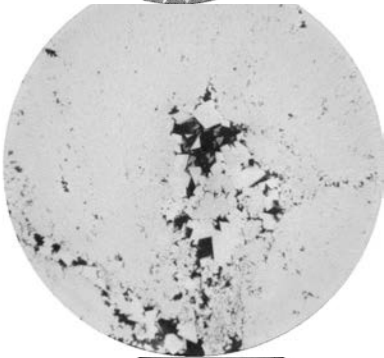




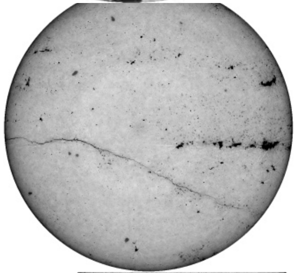
D) Simpson sandstone & carbonate cement



E) Arbuckle injection zone (large)

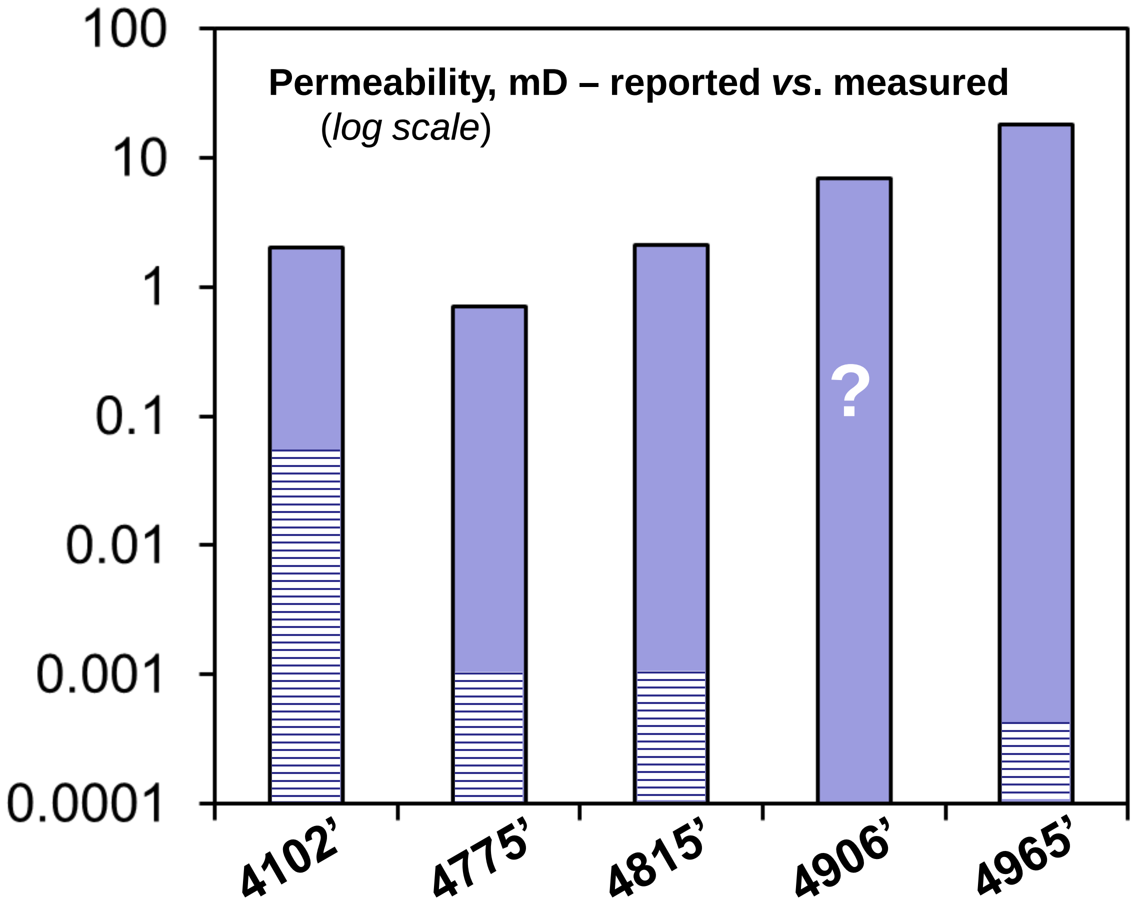


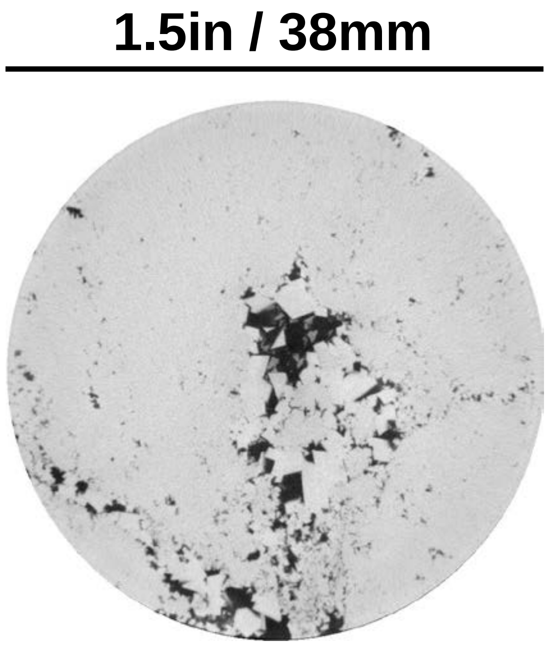
F) Arbuckle injection zone, 2



G) Arbuckle baffle zone

Subcores exhibit lower permeability compared to well log data – larger samples are better

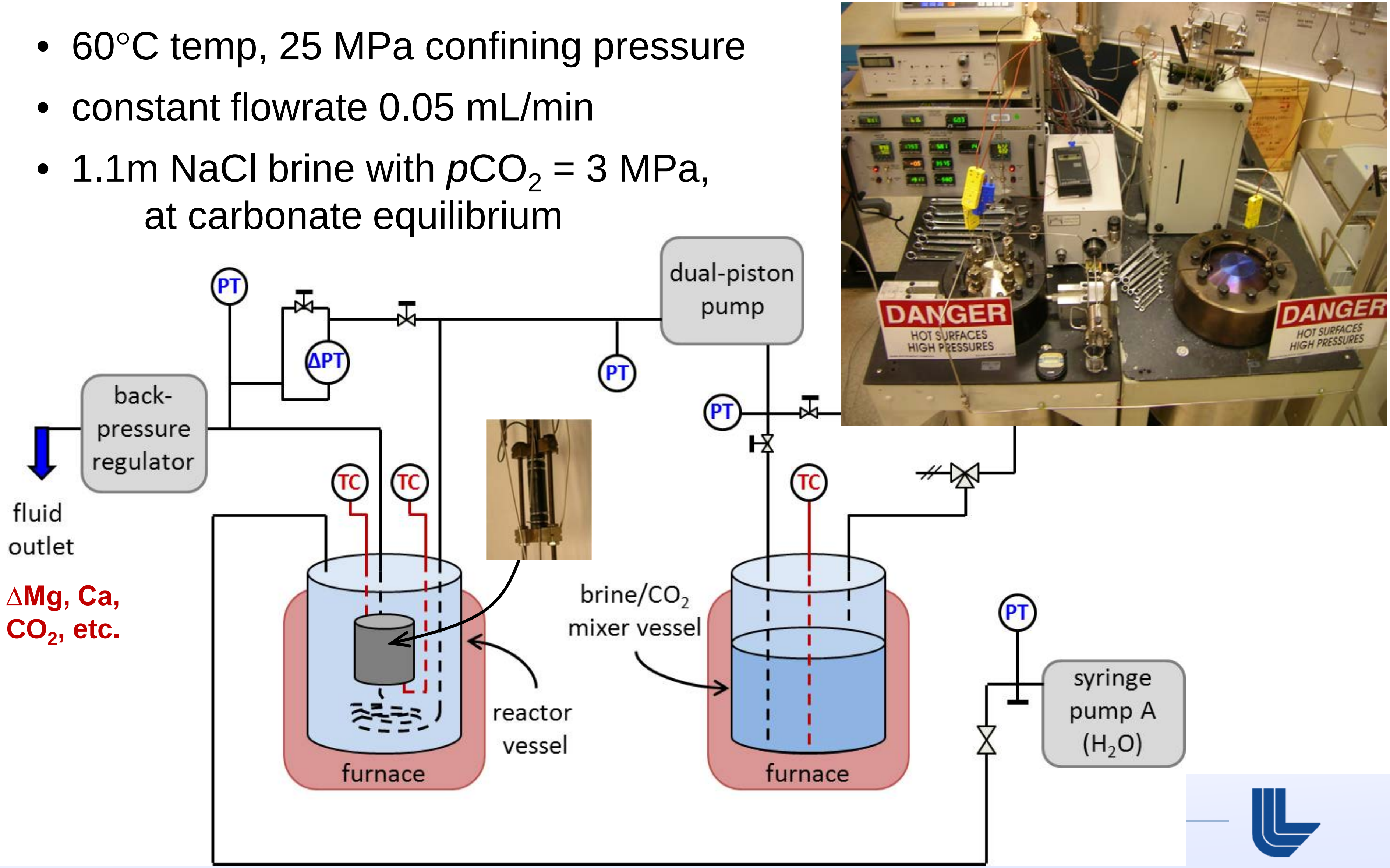




2.5x increase in diameter for "second-generation" Injection zone samples

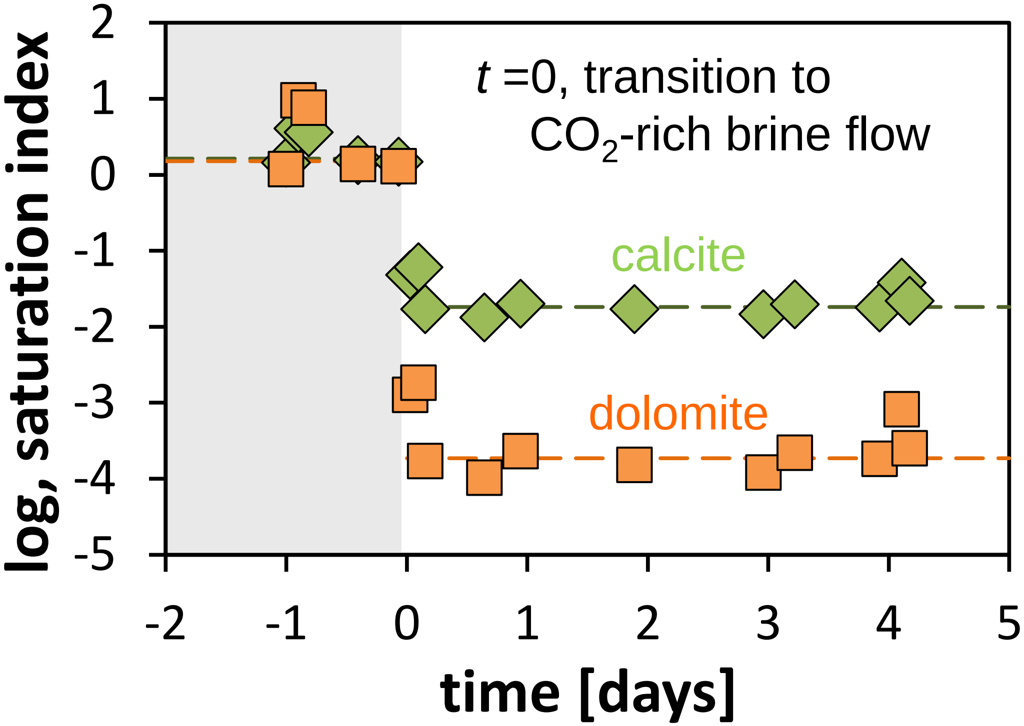
Core-flood set-up adapted for new KS samples

- 60°C temp, 25 MPa confining pressure
- constant flowrate 0.05 mL/min
- 1.1m NaCl brine with $p\mathrm{CO}_2$ = 3 MPa, at carbonate equilibrium

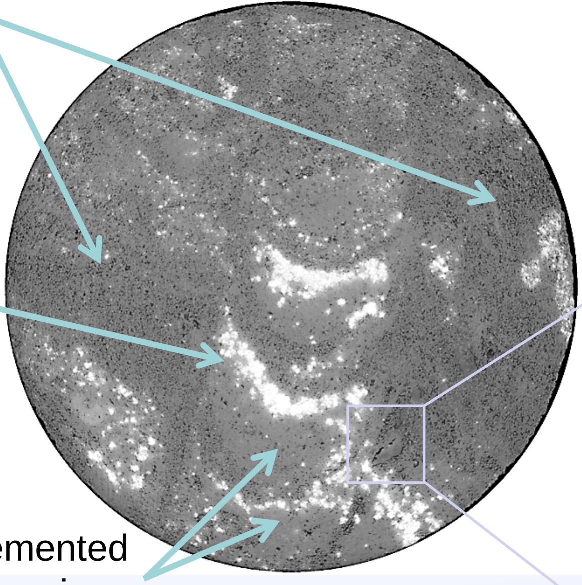


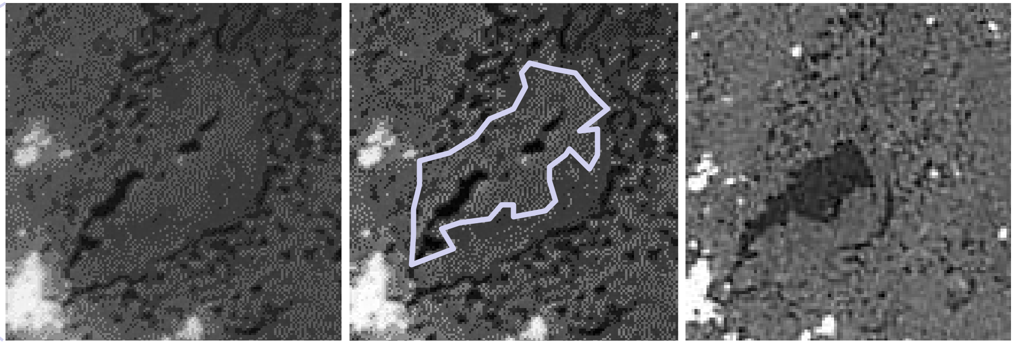
ΔMg, Ca, CO_2, etc.

Brine-CO_2 exposure caused little change to properties of Simpson sandstone sample

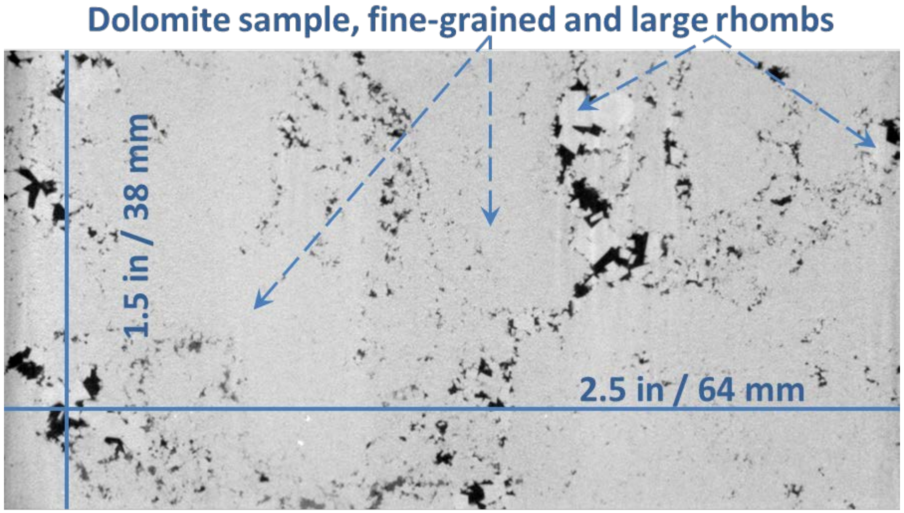


Unreacted Simpson cross-section, (smaller) 15-mm diameter gray-scale tomography image, located ~17mm from inlet

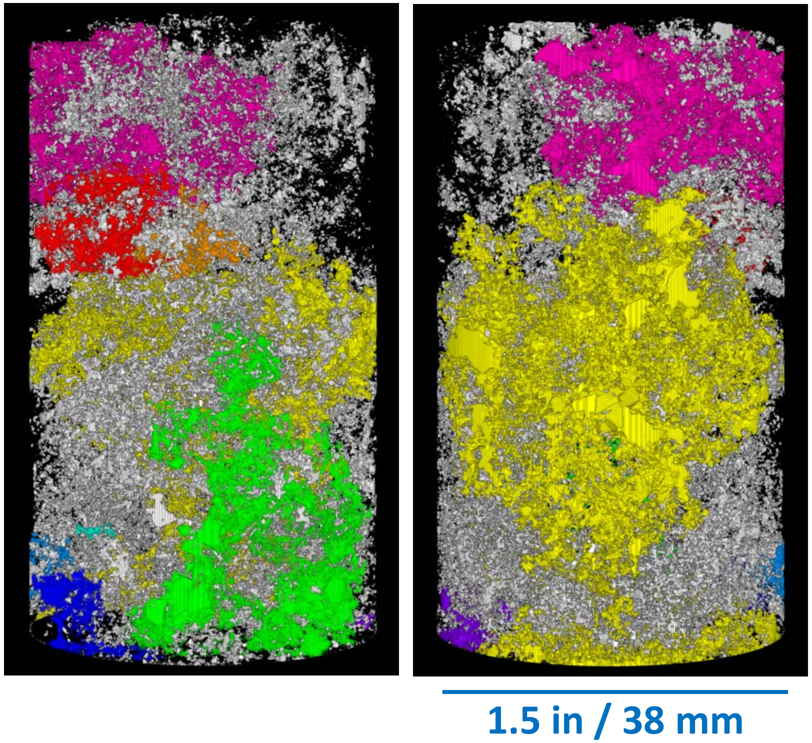




Within larger samples, (macro)pore clusters isolated by finer-grained matrix material



Connected macro-pores, large deep injection zone sample

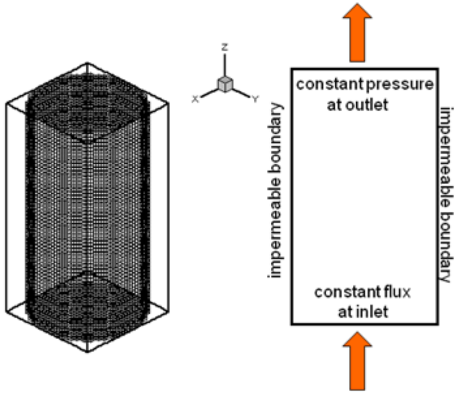


Reactive transport model adaptations for CO_2 core flooding experiments

- 3-D continuum-scale reactive transport model (NUFT)
- CO_2-equilibrated brine with pCO_2 = 3 MPa injected into core sample at a constant 0.05 mL/min rate.
  - Handles either core size (15, 38-mm diameter).
- Model lateral boundaries kept impermeable; constant pressure and flux conditions imposed at top and bottom boundaries.
- Dolomite reaction kinetics

$$\frac{dm}{dt} = -S\left[k_{acid}^{298.15K} e^{-\frac{E_{acid}}{R}\left(\frac{1}{T}-\frac{1}{298.15K}\right)} a_{H^+}^{n} + k_{neutral}^{298.15K} e^{-\frac{E_{neutral}}{R}\left(\frac{1}{T}-\frac{1}{298.15K}\right)}\right]\left(1-\frac{Q}{K}\right)$$

- Utilizes nonlinear porosity–permeability correlation and surface area–porosity relationship



grid size = 0.5 mm

model domain

Reactions
Dolomite + $2H^+$ = Ca^{2+} + Mg^{2+} + 2 HCO_3^-
CO_2(aq) + H_2O = H^+ + HCO_3^-
$MgHCO_3^+$ = Mg^{2+} + HCO_3^-
$CaCO_3$(aq) + H^+ = Ca^{2+} + HCO_3^-
$CaHCO_3^+$ = Ca^{2+} + HCO_3^-

Important lessons from previous Weyburn results carried forward in new simulations

- **Chemical Model** – Experiments allow combined reactivity to be calibrated

$$\frac{dm}{dt} = -S\left[k_{acid}^{298.15K}\, e^{-\frac{E_{acid}}{R}\left(\frac{1}{T}-\frac{1}{298.15K}\right)} a_{H^+}^{n} + k_{neutral}^{298.15K}\, e^{-\frac{E_{neutral}}{R}\left(\frac{1}{T}-\frac{1}{298.15K}\right)}\right]\left(1-\frac{Q}{K}\right)$$

  - Rate equations are tied to equilibrium
  - Literature equilibrium constants provide starting points
  - Calibrations combine rate constants and surface areas
  - Pressure changes are not sensitive to reaction rate

- **Porosity – Permeability – Surface Area Relationships**
  - Change surface area in proportion to decreasing spherical grains
  - "*n*" and permeability contrast terms allow for coupled porosity, permeability evolution

$$S_t = S_0\left(\frac{\theta_t}{\theta_0}\right)^{2/3}\left(\frac{\phi_t}{\phi_0}\right)^{2/3}$$

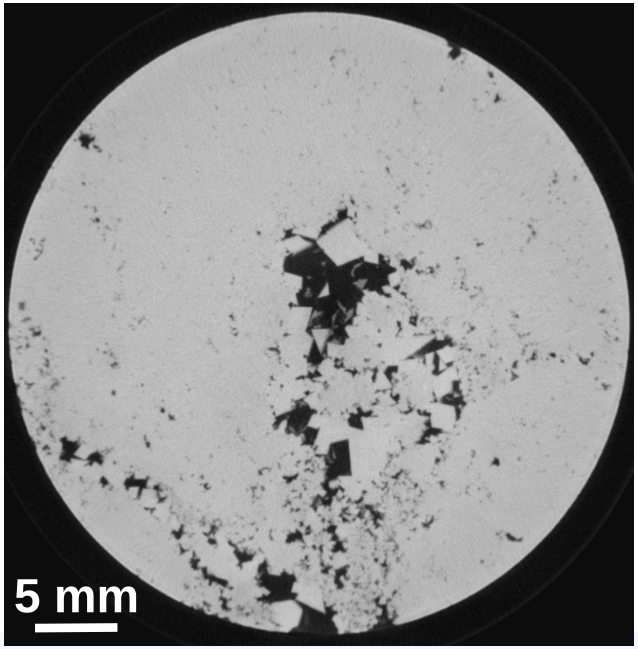
$$K_t = K_0\left(\frac{\phi_t}{\phi_0}\right)^{n}$$

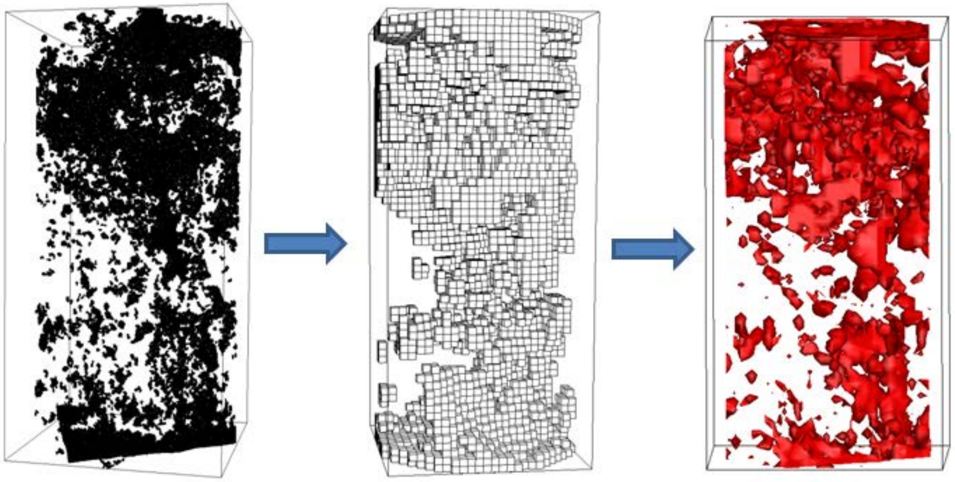
Imaging-based characterization data scaled into larger model grids

- Effective porosity and mineral phase volume fraction were calculated by a volumetric averaging approach.

$$\phi = \sum_{i}^{N} \phi_i \Big/ N \qquad \theta_m = \sum_{i}^{N} \theta_{m,i} \Big/ N$$

- Permeability distributions were estimated by assessing macro-pore distribution and connectivity. Two porous regions were assumed within the rock sample: one representing interconnected ***macro-pore regions***, and the other the ***less porous matrix***.





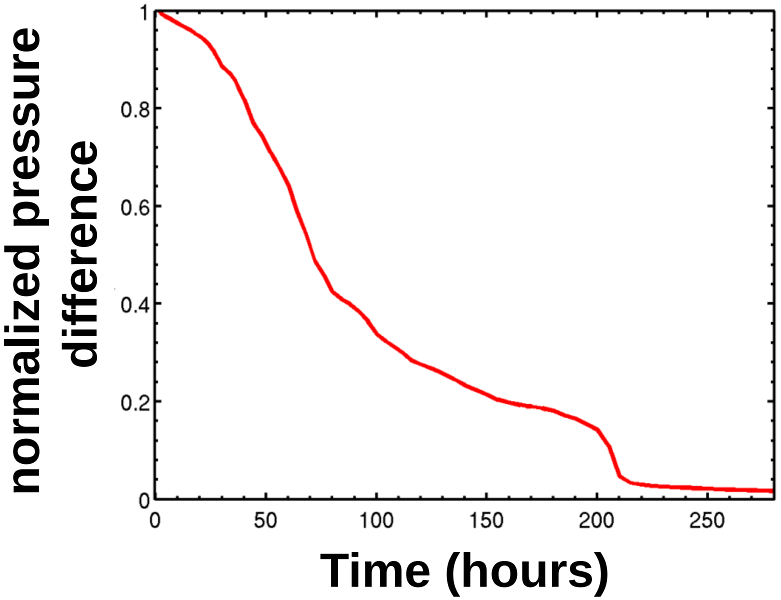
macro-pore connectivity

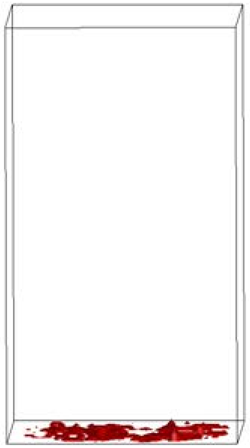
continuum grid representation

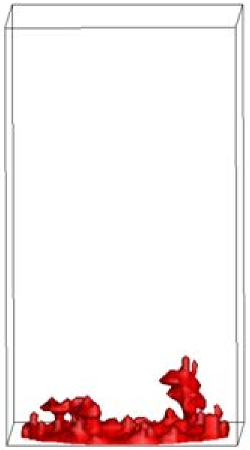
initial model porosity

Pre-experiment modeling results — Base Case

- flow rate = **0.05 mL/min**,
  porosity-permeability relation ***n* = *6***,
  permeability contrast **K_1/K_2 = *100***,
  $k_{acid}^{298.15K}$ = ***$10^{-3.2}$*** mol/m^2/s,
  $k_{neutral}^{298.15K}$ = ***$10^{-7.5}$*** mol/m^2/s.

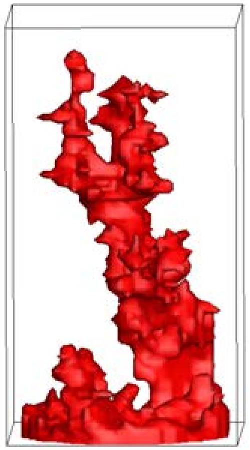


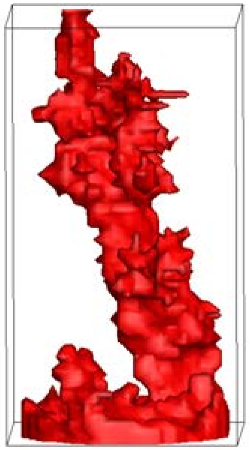

10 hours


30 hours


60 hours


120 hours

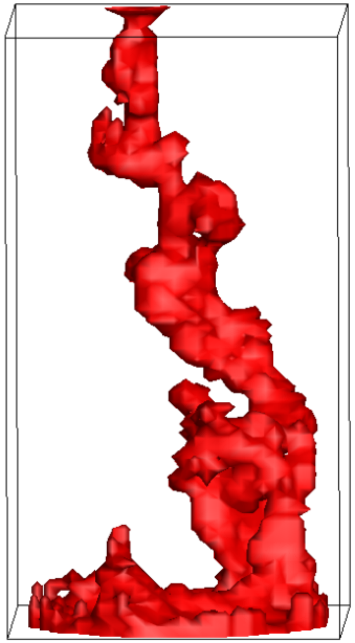

170 hours


240 hours

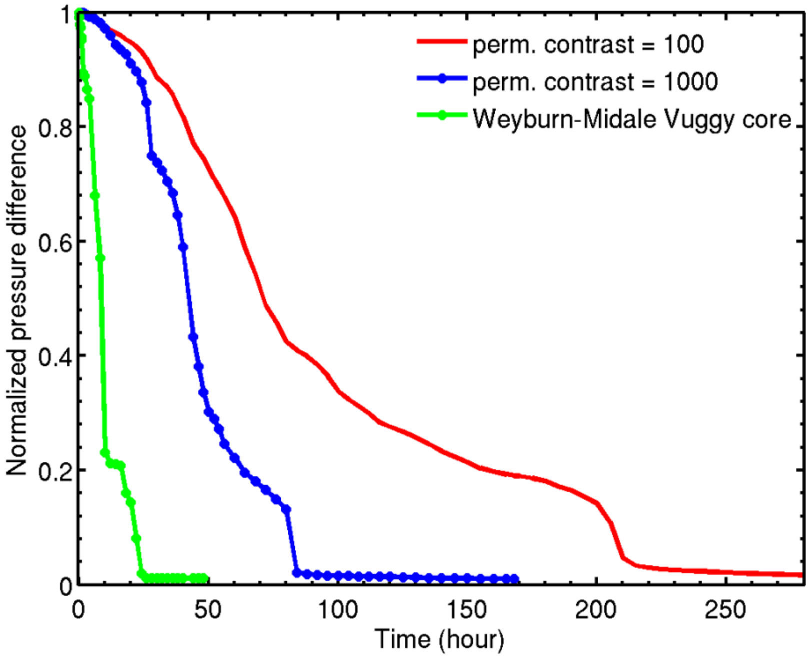
Sensitivity studies — increasing permeability contrast by 10x

Porosity distributions after CO_2 flooding of **120 hours** (5 days)

low permeability contrast
(base case)

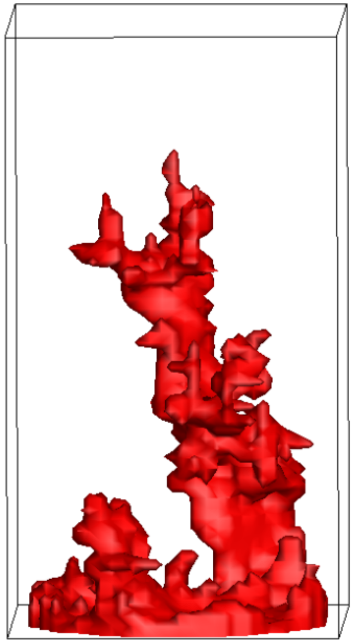


higher
permeability contrast



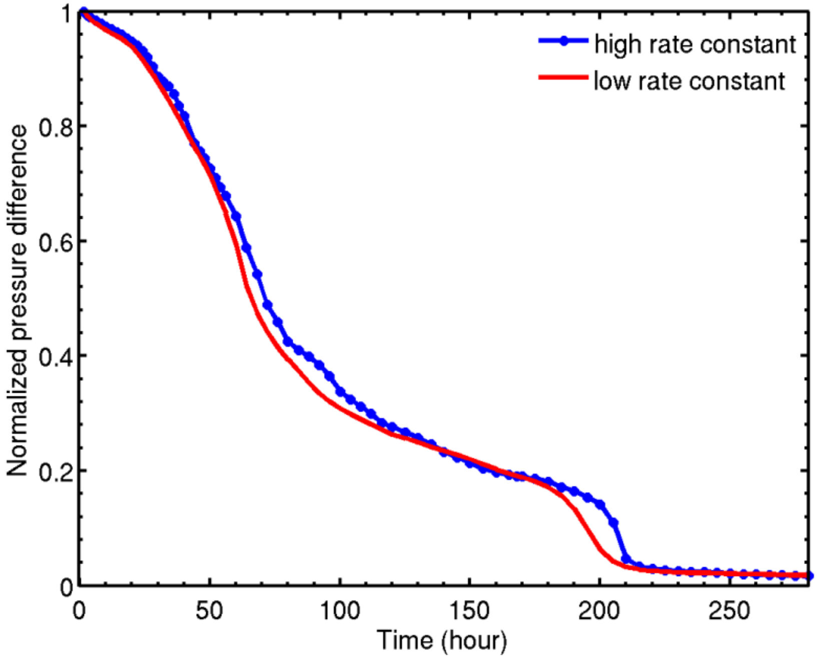
Sensitivity studies — decreasing kinetic constants by 100x (acid) and 10x (neutral mechanism)

Porosity distributions after CO_2 flooding of **120 hours** (5 days)



high reactivity
(base case)

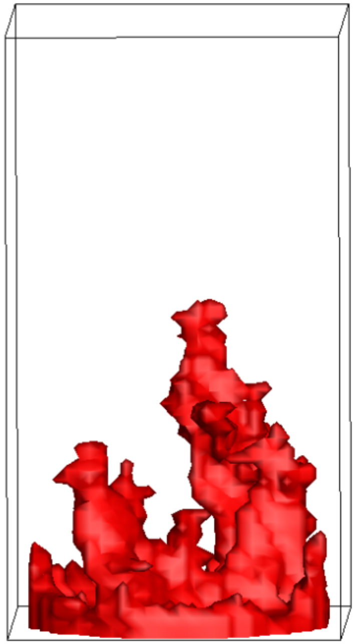
lowered
reactivity



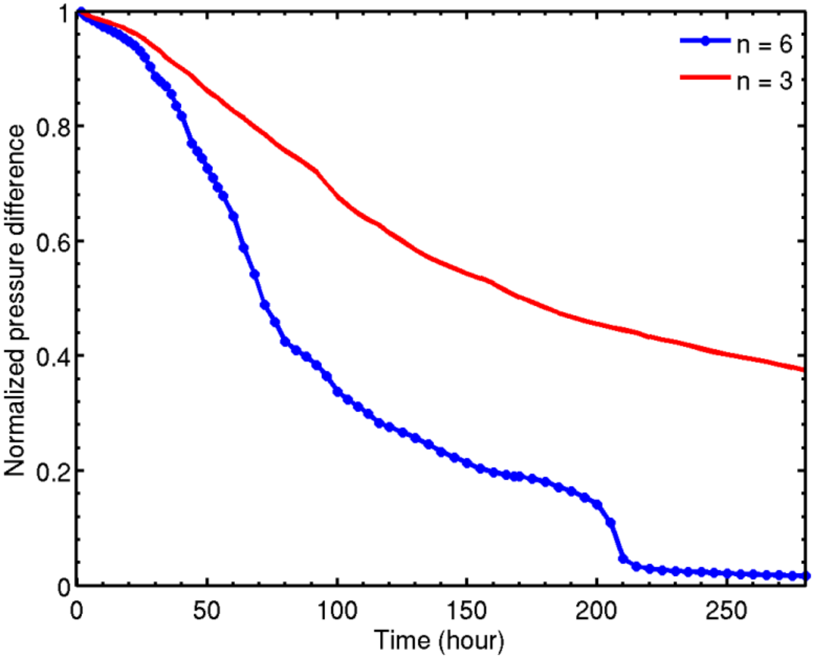
Sensitivity studies — decreasing porosity-permeability relation (*n*) from 6 to 3

Porosity distributions after CO_2 flooding of **120 hours** (5 days)

n = 6
(base case)



***n* = 3**



Accomplishments to Date

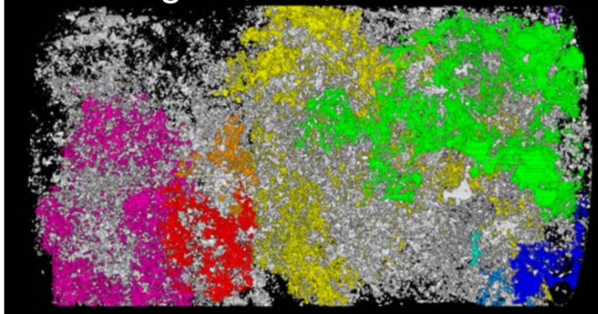
- **Publication of results of low permeability caprock response to CO_2 exposure**
  (*Smith et al., 2012, ES&T*)
- **Weyburn-specific model and scaling results published in special issue**
  (*Carroll et al., 2013, IJGGC*)
- **Development of model methodology to incorporate varying scales of characterization data to be published** (*Hao et al., in final revision, AWR*)
- **Additional samples from Arbuckle reservoir (Wellington, KS, KGS) acquired, imaged via CT, and characterized**
- **One full-length Simpson (Wellington, KS) experiment completed; Results of eight Weyburn experiments to be published** (*Smith et al., in final revision, AWR*)
- **Equipment modified to accept larger core samples**
  (*first larger-scale core to be tested September 2013*)
- **Pre-experimental modeling completed to inform upcoming experiments**

Project Summary
Implications for reservoir scale CCUS simulations

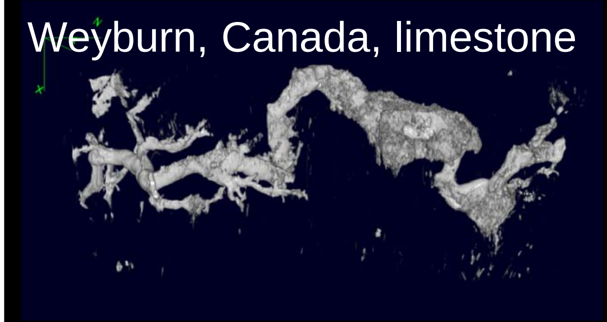
- ❑ **Key Findings**
  - ➢ Anisotropic permeability and mineral dissolution play dominant roles in porosity and permeability changes that will occur during CCUS operations
  - ➢ Calibrated several reactive transport parameters that scale from microns to centimeters
  - ➢ Porosity – Permeability relationships are dependent on sample heterogeneity
    - ➢ pore regions are not well connected at previous core scales

- ❑ **Future Plans:** Refining the reactive-transport model, calibrating NMR well logs with experiments from the Wellington, KS, CO_2 demonstration site

Wellington, KS, dolomite



Weyburn, Canada, limestone

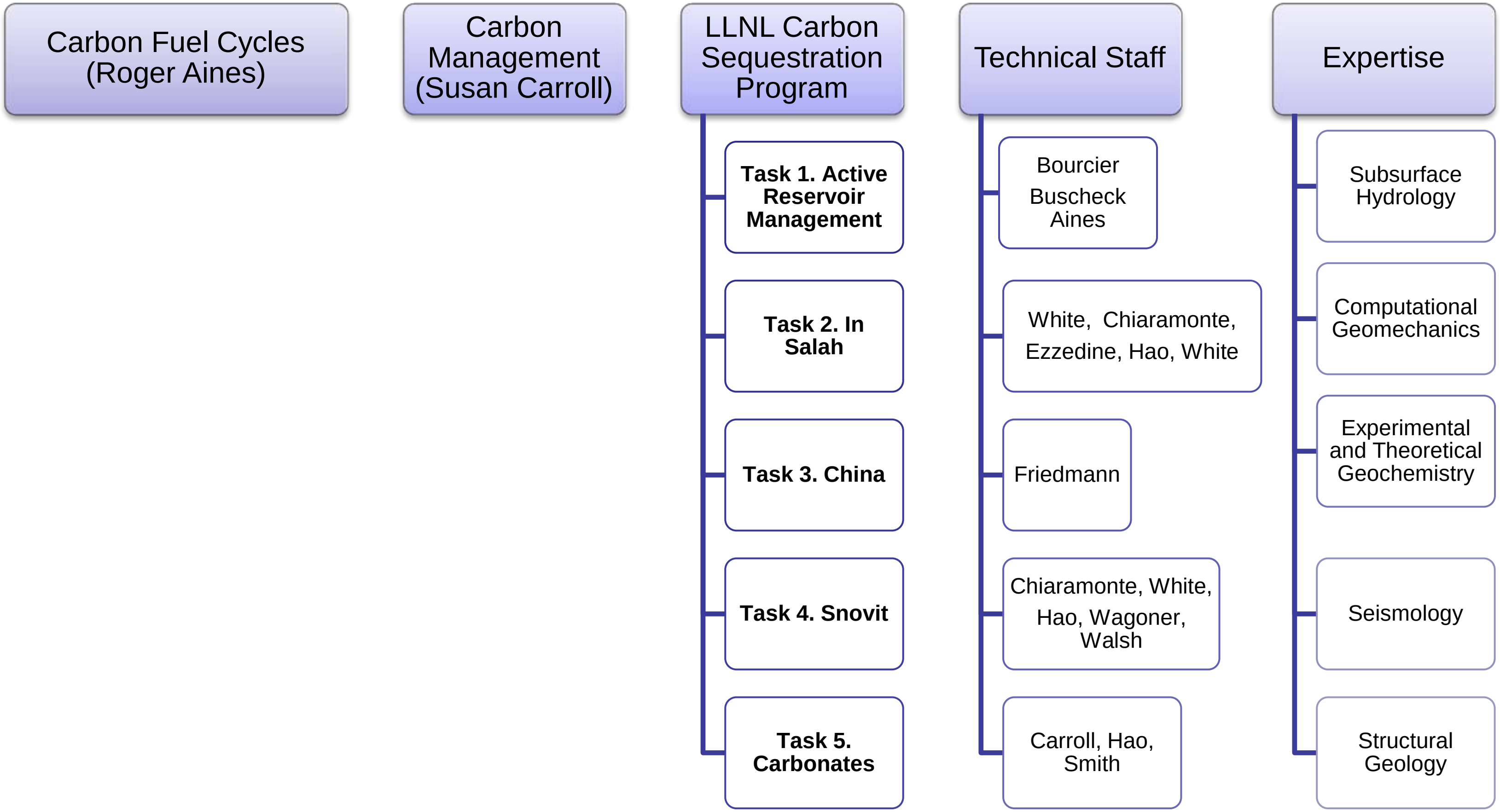


Weyburn, Canada, dolostone

Appendix

- Organizational Chart
- Gantt Chart
- Bibliography

Organization Chart



- Carbon Fuel Cycles (Roger Aines)
- Carbon Management (Susan Carroll)
- LLNL Carbon Sequestration Program
  - **Task 1. Active Reservoir Management**
  - **Task 2. In Salah**
  - **Task 3. China**
  - **Task 4. Snovit**
  - **Task 5. Carbonates**
- Technical Staff
  - Bourcier Buscheck Aines
  - White, Chiaramonte, Ezzedine, Hao, White
  - Friedmann
  - Chiaramonte, White, Hao, Wagoner, Walsh
  - Carroll, Hao, Smith
- Expertise
  - Subsurface Hydrology
  - Computational Geomechanics
  - Experimental and Theoretical Geochemistry
  - Seismology
  - Structural Geology

Gantt Chart: Task 5 Carbonates

		Fiscal Year 2012				Fiscal Year 2013				Fiscal Year 2014			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
5.1.1	Finish model calibration with Weyburn data	🟨	🟨	🟨	🟨	🟨							
5.1.2	Finish premodel simulations for new experiments		🟨	🟨	🟨	🟨	🟨						
5.1.3	Refine model using new data						🟨	🟨	🟨	🟨	🟨	🟨	🟨
5.1.1	Experimental Design	🟨	🟨										
5.2.2	Conduct experiments			🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	
5.2.3	Interpret experimental results						🟨	🟨	🟨	🟨	🟨	🟨	

Bibliography

- Smith, M., Sholokhova, Y., Hao Y., and Carroll, S., 2013, Evaporite caprock integrity: An experimental study of reactive mineralogy and pore – scale heterogeneity during brine – CO_2 exposure. Environmental Science and Technology, http://dx.doi.org/es3012723.

- Carroll, S. Hao, Y., Smith, M., Sholokhova, Y. (2013), Development of scaling parameters to describe CO_2-carbonate-rock interactions for the Marly Dolostone and Vuggy Limestone, *I J Greenhouse Gas Control*, http://dx.doi.org/10.1016/j.ijggc.2012.12.026

- Smith, M. Sholokhova, Y., Hao, Y., and Carroll, S. (2013) CO_2-Induced Dissolution of Low Permeability Carbonates Part I: Characterization and Experiments, Advances in Water Resources, revised.

- Hao, Y., Smith, M., Sholokhova, Y., and Carroll, S. (2013) CO_2-Induced Dissolution of Low Permeability Carbonates Part 2: Numerical Modeling of Experiments, Advances in Water Resources, revised.