Reservoir Performance

Project Number: 1022403

Car Stor_FY14, Task 2

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National Energy Technology Laboratory

U.S. Department of Energy

National Energy Technology Laboratory

Carbon Storage R&D Project Review Meeting

Developing the Technologies and

Infrastructure for CCS

August 12-14, 2014

Presentation Outline

- FY14 Reservoir Performance Project Structure
- Goals, Outcomes, & Accomplishments
- FY15 Reservoir Performance Project Structure

FY14 Reservoir Performance

1. Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals
2. Impact of Microbial Processes on Storage Formations and Seals
3. Impact of CO_2 on Shale Formations as Seals
4. Characterization of Reservoir & Seal Material Performance
5. Understanding of Multiphase Flow for Improved Injectivity and Trapping
6. Geochemical Model Sensitivity at Caprock Interfaces

FY14 Reservoir Performance

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Benefit to the Program

- Geomechanical and flow properties of rock formations that affect the storage capacity, injectivity, and permanence of CO_2 storage are examined. CO_2 injection can introduce significant perturbations to the subsurface environment that can initiate a range of processes.
- Laboratory and numerical studies are being conducted to understand the impacts of CO_2-brine-rock interactions on chemistry and microbial processes, and alteration of geomechanical properties on storage formations and seals.

Project Overview: Goals and Objectives

- The analyses and modeling are being conducted on reservoir and seal samples from RCSP field sites, benefitting both the RCSP and Core Research Program goals for CO_2 storage permanence through improved storage potential assessments and predictions of subsurface behavior.
- **What geologic factors need to be known in order to characterize and select a successful CO_2 storage site?**

Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals

- Perform CO_2-brine exposure tests in static reactor vessels on core samples obtained from the Mount Simon and other available storage/seal formations
- Static Pressure Vessel Capabilities
  - Temperature, 90 °C
  - Pressure, 6000 psi
  - Volume, 1.3 L (600 to 800 mL with Teflon liner)
- Analyze initial samples and samples after exposure to synthetic brine for six months

Mount Simon Sandstone

- SEM analysis provided direct evidence of feldspar dissolution and barite precipitation
- AutoLAB 1500 measurements under pressure revealed an increase in the permeability post-exposure for one sample, and a decrease in permeability in another

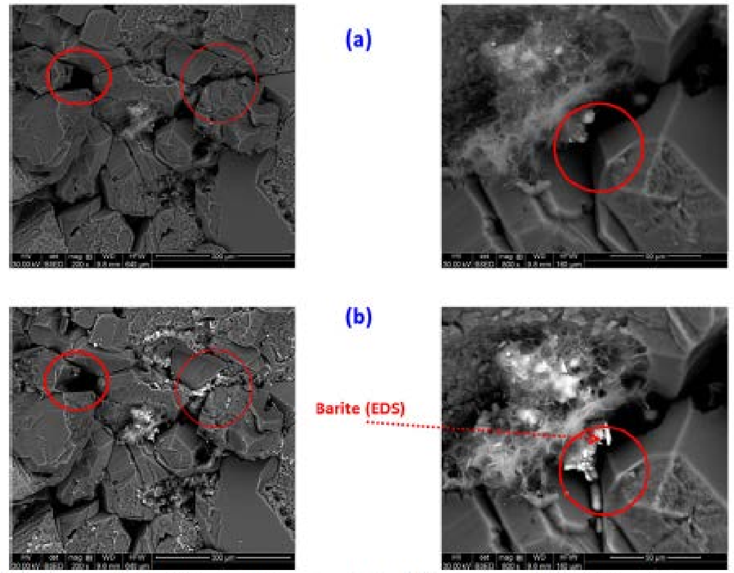

Fig. 5. SEM images of Vermillion sand stone samples fresh (a) vs. exposed to CO_2/brine for six months (b).

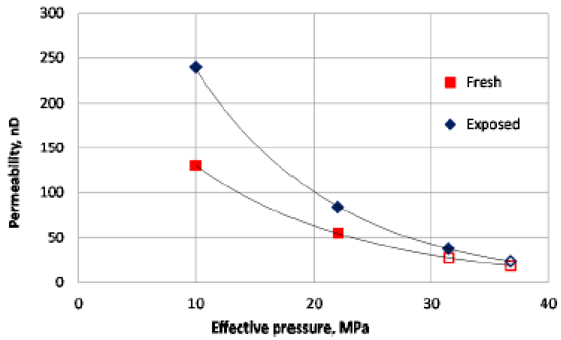

Fig. 6. The measured permeability of Knox sandstone. Note that extrapolated values of permeability are shown in bold. The extrapolated values denoted by hollow markers.

Mount Simon Sandstone

- Computed tomography scans revealed the complex 3D nature of the interactions
- Reduced k likely due to feldspar dissolution and secondary precipitation
- Increased k likely due to preferential dissolution along fracture pathway
- Small scale features coupled with the geochemical interactions critical to understanding behavior.

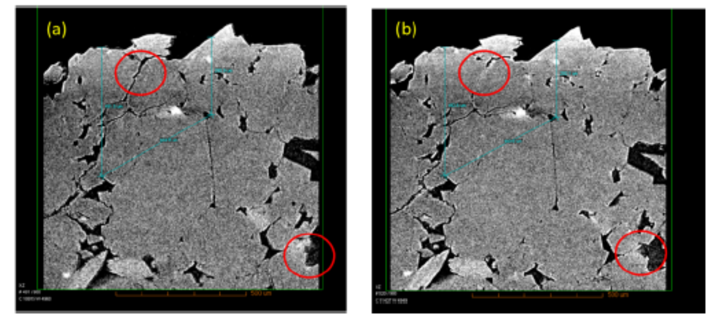

Fig. 4. Reconstructed slice (side view) from Micro-CT analysis of the Vermillion sandstone sample before (a) and after six months exposure to CO_2/brine (b). Top circled areas highlight mineral precipitation. Lower circled areas highlight mineral dissolution. The numbers represent measurements in microns both of features and reference points.

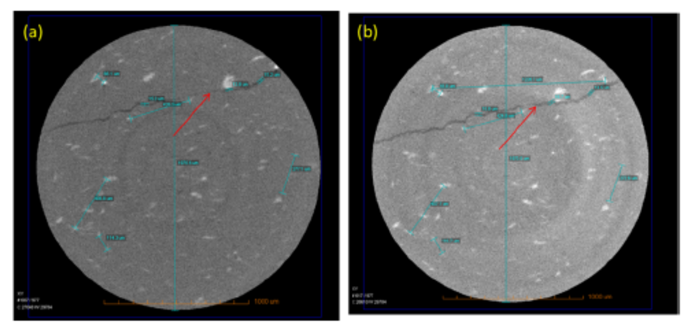

Fig. 7. Reconstructed slice (top view) from Micro-CT analysis of the Knox sandstone sample before (a) and after six months exposure to CO_2/brine (b). Arrows point to an area where some mineral dissolution occurred after exposure to CO_2/brine. The numbers represent measurements in microns both of features and reference points.

Impact of Microbial Processes on Storage Formations and Seals

- A thorough understanding of how microbial communities respond to $scCO_2$ exposure in specific rock systems, the degree to which they may alter formation characteristics, and whether they are able to alter the state of the carbon is essential to the inclusion of appropriate reactions in models.
- This task will characterize the microbes present in CO_2 storage reservoirs, and examine the impact that CO_2 injection could have on altering the microbial community and ultimately how rock permeability and porosity could be impacted

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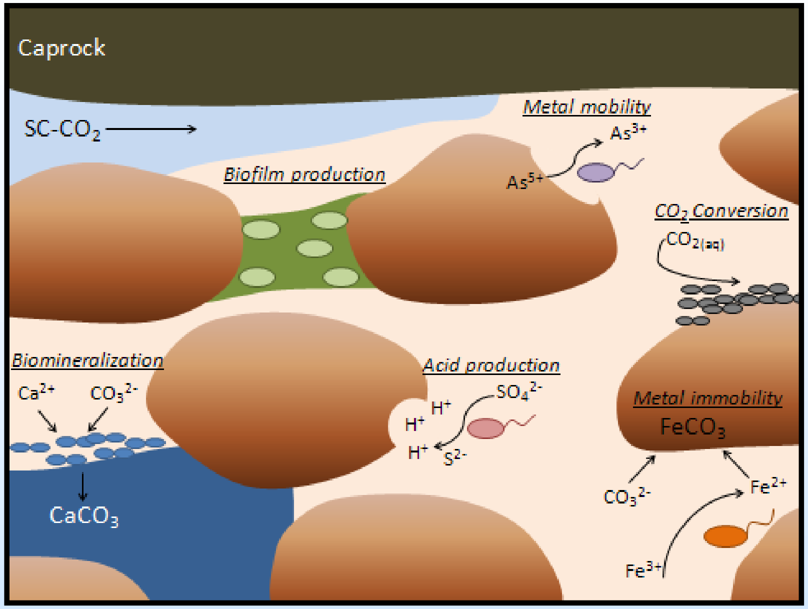


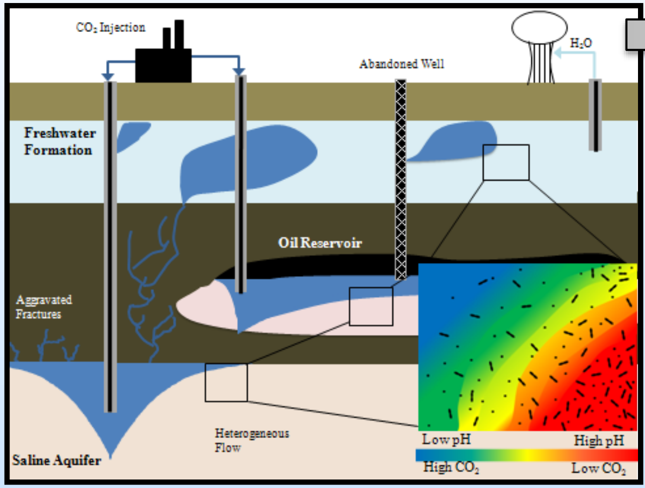
Microbiology may affect geologic CO_2 storage through various biological processes

Biomineralization
Biofilm production
Acid production
Metal mobilization
Metal immobilization
CO_2 conversion

Impact of Microbial Processes on Storage Formations and Seals

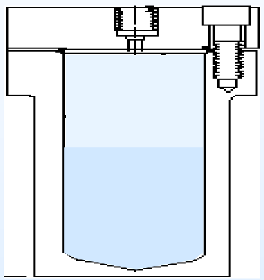
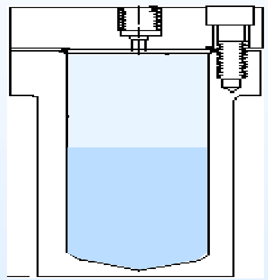
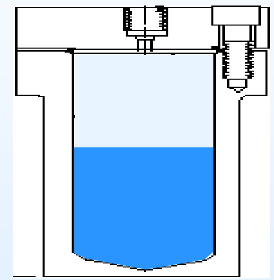
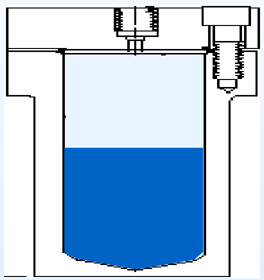
- First, we need to know what the native microbial communities looks like

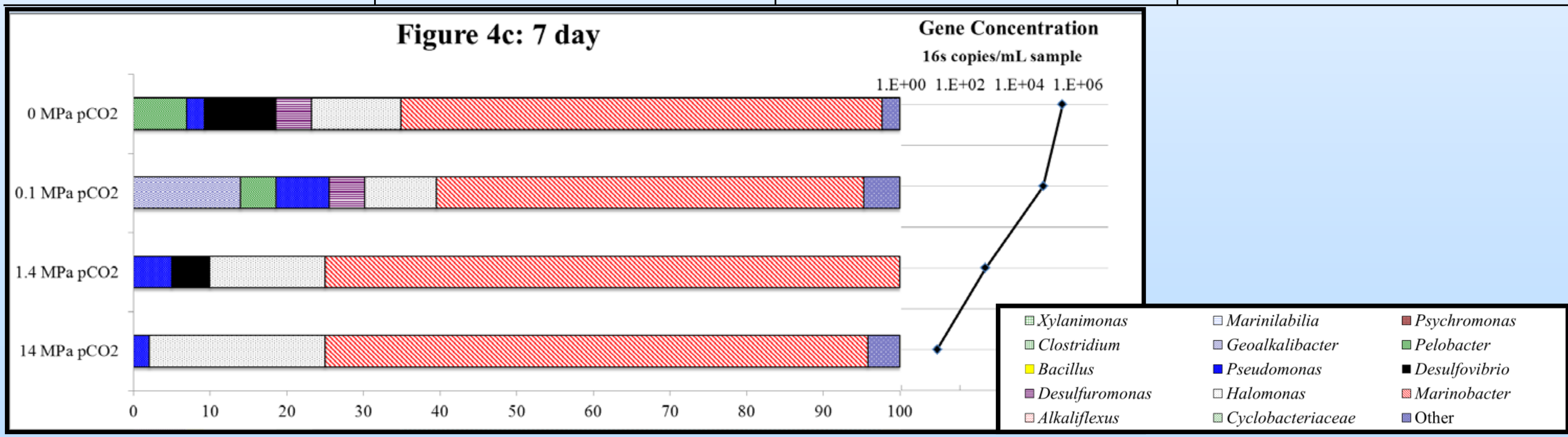
- Then we want to know how they are impacted by changes in the subsurface



Liquid: Arbuckle Saline Aquifer fluid, Mirando Oil Field fluid, East Seminole
Pressure: 15 MPa and 3.5 MPa
Temperature: 40 ˚C
Run time: 1, 7, 56 & 146 days

Impact of Microbial Processes on Storage Formations and Seals

Vessel 1	Vessel 2	Vessel 3	Vessel 4
			
0% CO_2	1% CO_2	10% CO_2	100% CO_2



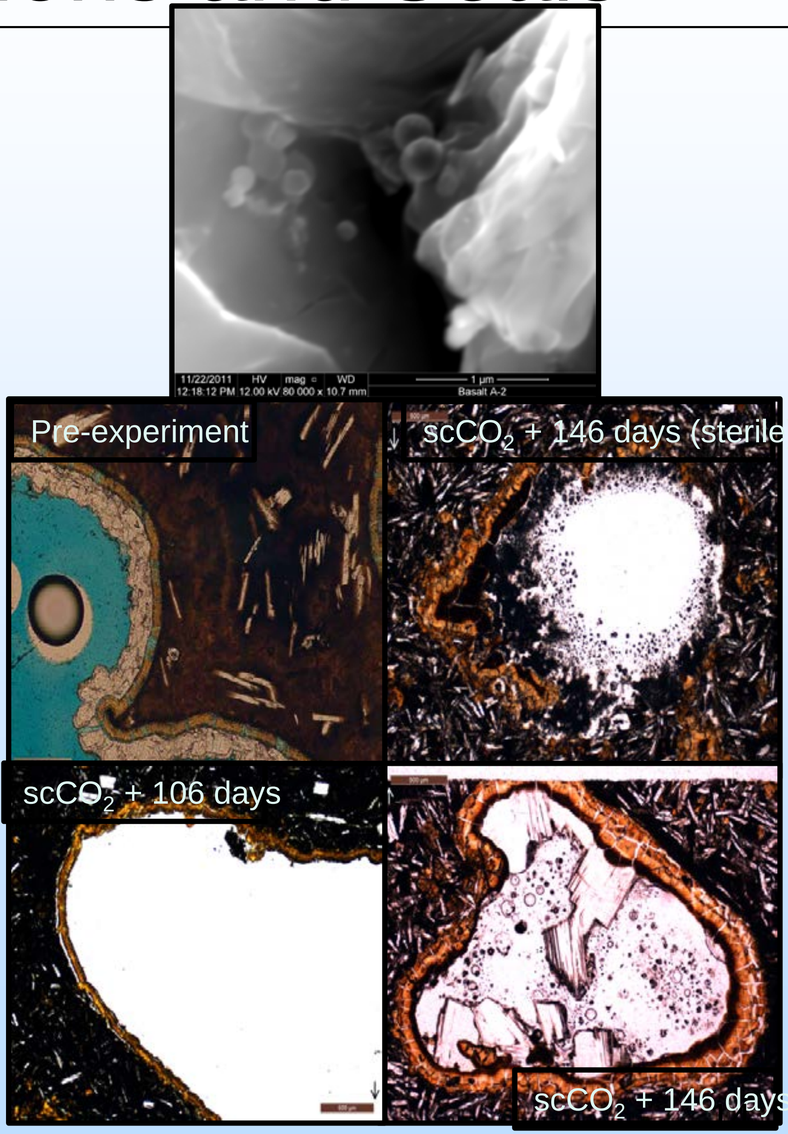
Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals

Observations:

- **Possible microbial features seen by environmental SEM**
- **Thicker** iron carbonate precipitates in basalts incubated with microorganisms versus basalts incubated without microorganisms

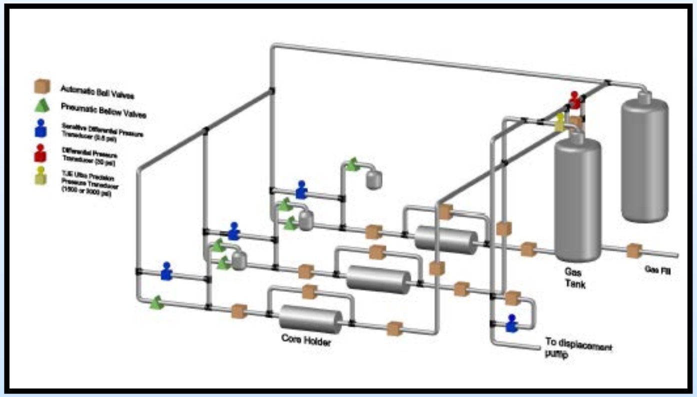
Significance:

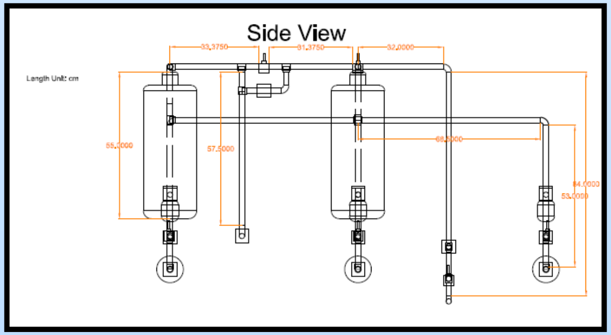
- Native microorganisms survive $scCO_2$ exposure; **may aid in forming carbonates, which could increase permanence of carbon storage**



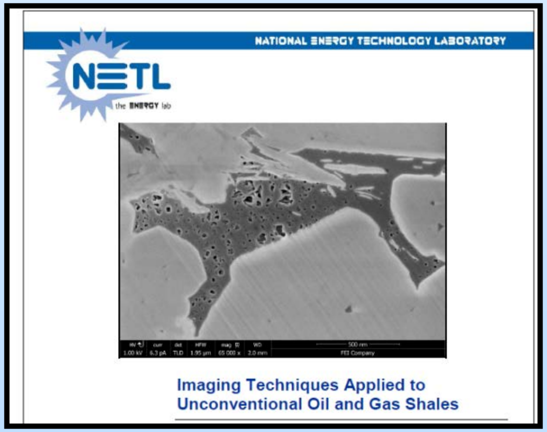
Impact of CO_2 on Shale Formations as Seals

- Two primary goals in FY14
  - Construction of facility to measure the behavior of gas and liquid flow in shales
    - Building delays pushed back apparatus construction, but development is underway



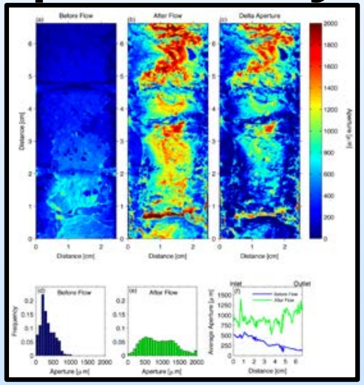


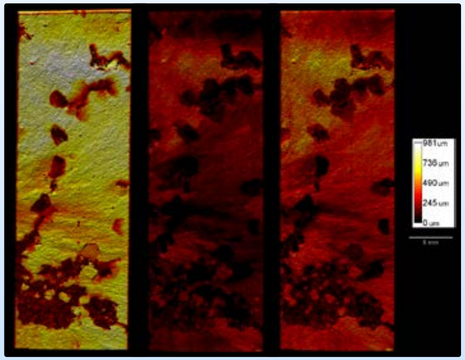
  - Report on the methods visualize and understand the internal pore structure of shales using a variety of techniques
    - Rodriguez, R.; Crandall, D.; Song, X.; Verba, C.; Soeder, D. *Imaging Techniques Applied to Unconventional Oil and Gas Shales*; NETL-TRS-XX-2014; Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2014; p XX.
    - http://www.netl.doe.gov/research/on-site-research/publications/

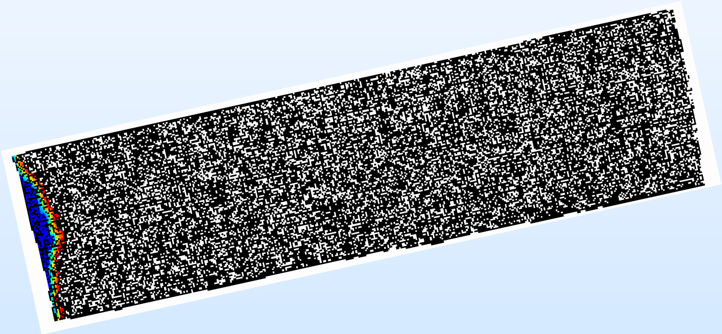


Characterization of Reservoir & Seal Material Performance

- Experimental studies on cores from field projects examining CO_2 interactions, primarily within fractures.



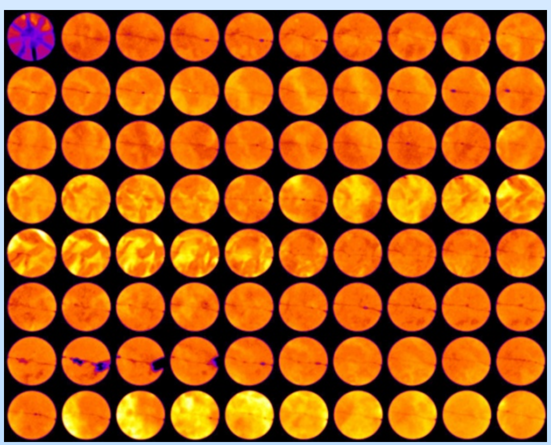


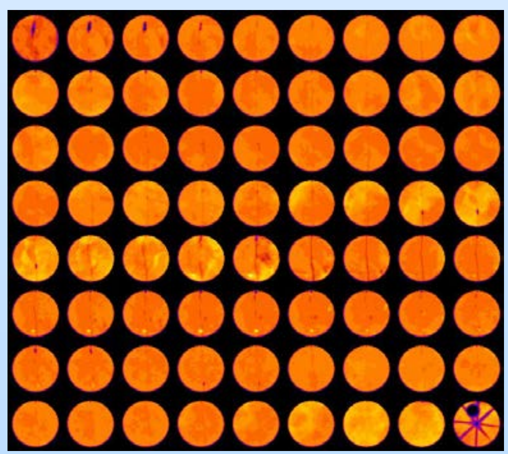


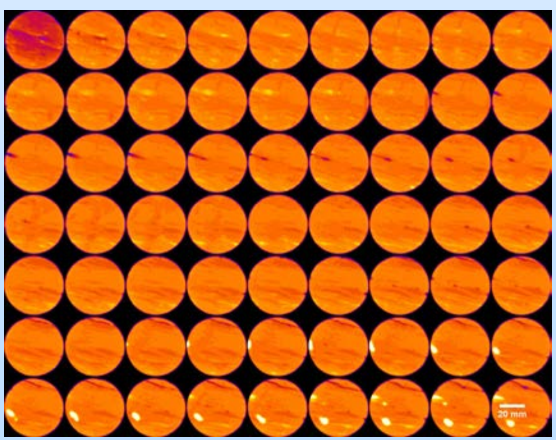
- Laser induced breakdown spectroscopy development for monitoring of CO_2 leakage

Characterization of Reservoir & Seal Material Performance

- Examination of three fractured seal formations within CT scanner, under representative reservoir conditions for 20+ days, with CO_2 saturated brine floods
  - Kirtland Shale, Eau Claire, Tuscaloosa
- Observed minimal change in permeability over experiment lengths; no observed change in geometry

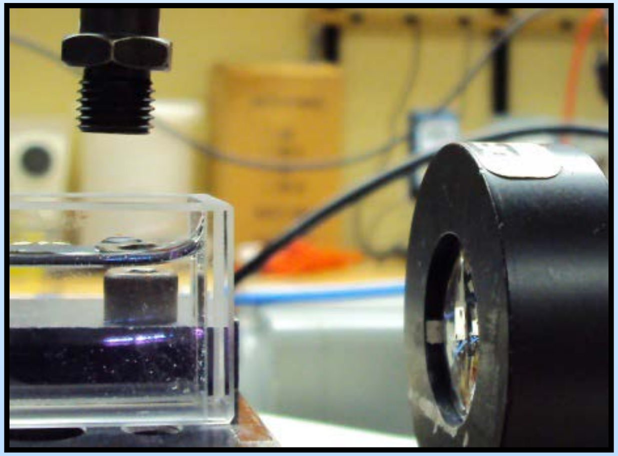


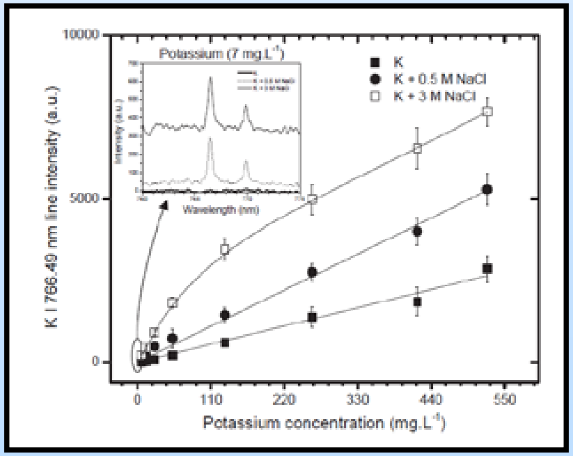




Characterization of Reservoir & Seal Material Performance

- Laser induced breakdown spectroscopy development
  - Proof of concept has been shown to work in lab, and likelihood of field test is high. Probes can be used above ground or down a well.
  - LIBS Patent Issued
    - Woodruff, S.D., McIntyre, D.L., Jain, J.C., "A method and device for remotely monitoring an area using a low peak power optical pump," U.S. Patent 8,786,840, July 22, 2014.



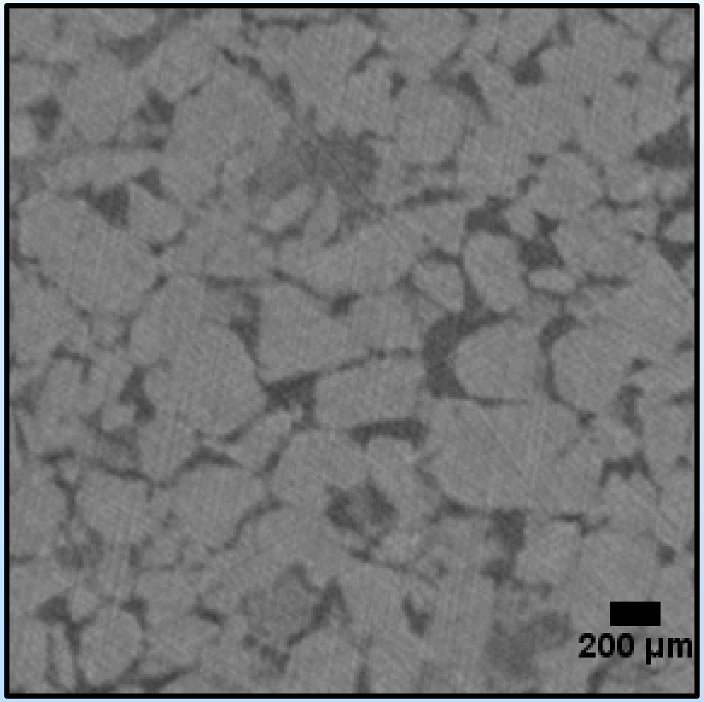


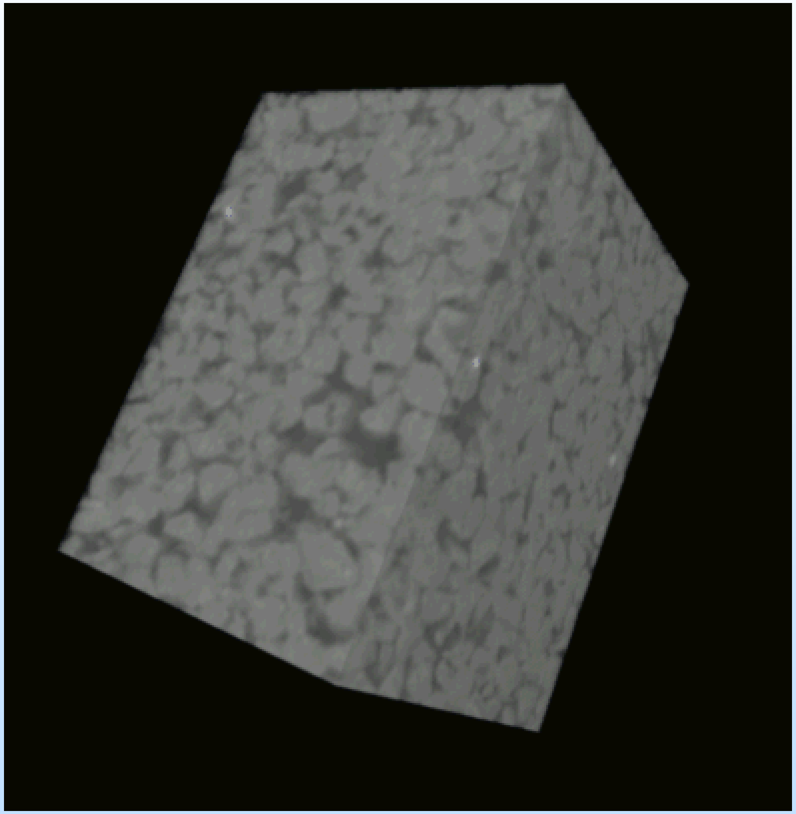
Understanding of Multiphase Flow for Improved Injectivity and Trapping

- This task uses numerical modeling, laboratory measurements and field samples to focus on the key processes that will allow more accurate prediction of capacity, injectivity and storage permanence. The main objectives of this task are to (1) generate usable data on relative permeability and other critical parameters for multiphase flow for CO_2-brine-rock systems as they relate to injectivity and trapping, and (2) develop validated models of multiphase flow on the pore and reservoir scale

Pore Geometry Measurements

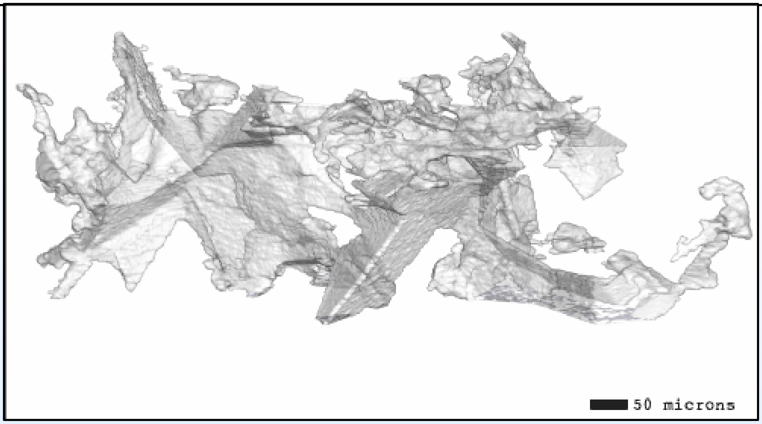
- Characterization of pore space obtained from micro-CT imaging is underway

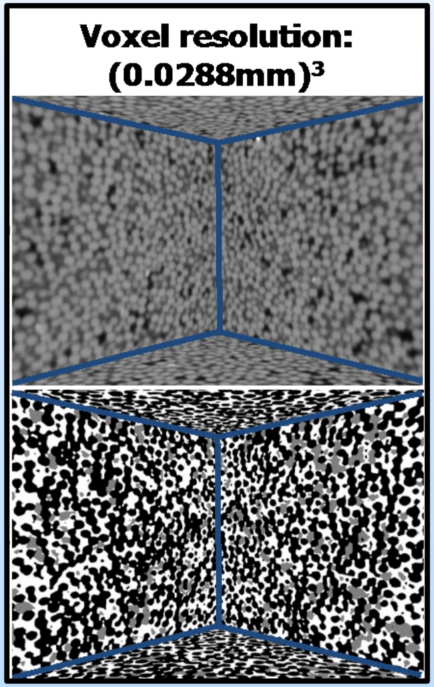


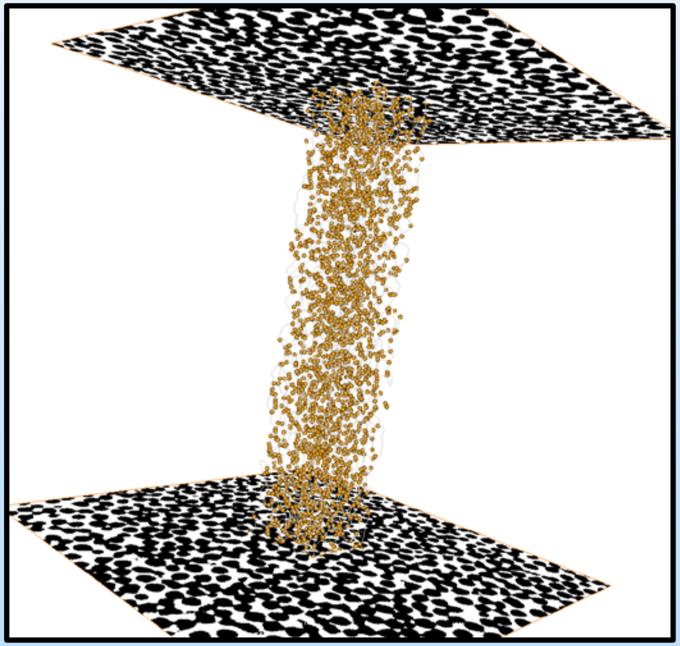


Pore Geometry Measurements

- And pore level modeling of various types, from pore-network models to individual pores, is being performed to understand trapping mechanisms.

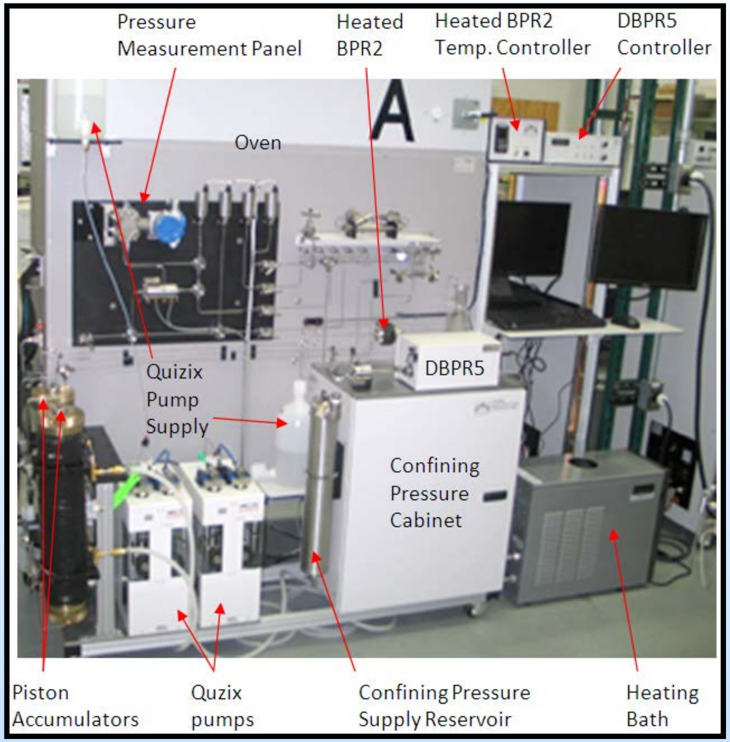




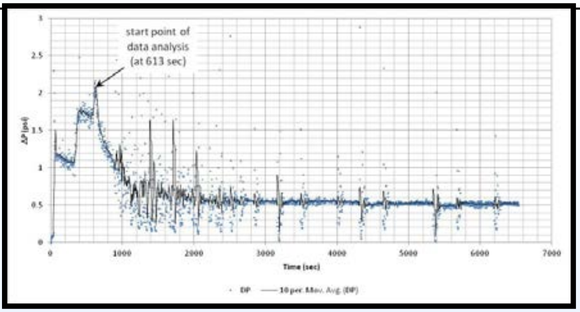


Measurement of $scCO_2$ k_r in the lab

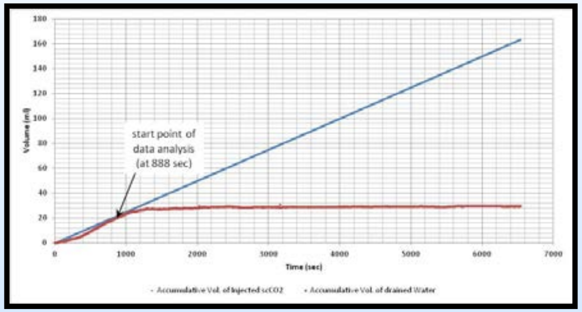
Core Flow Experiment System

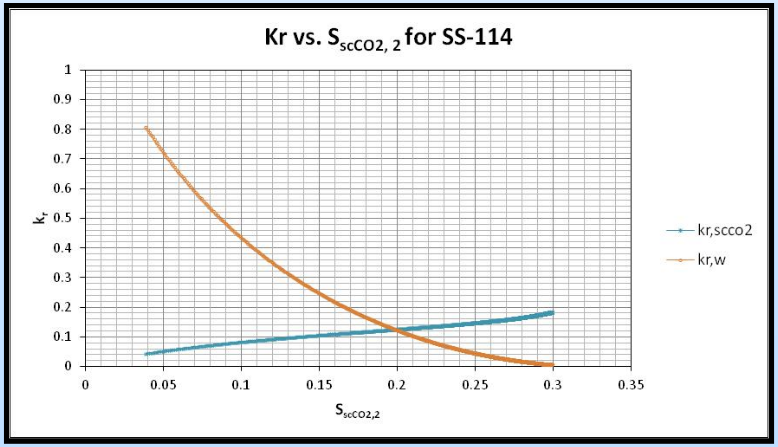


ΔP



Vol. of influent / effluent fluids

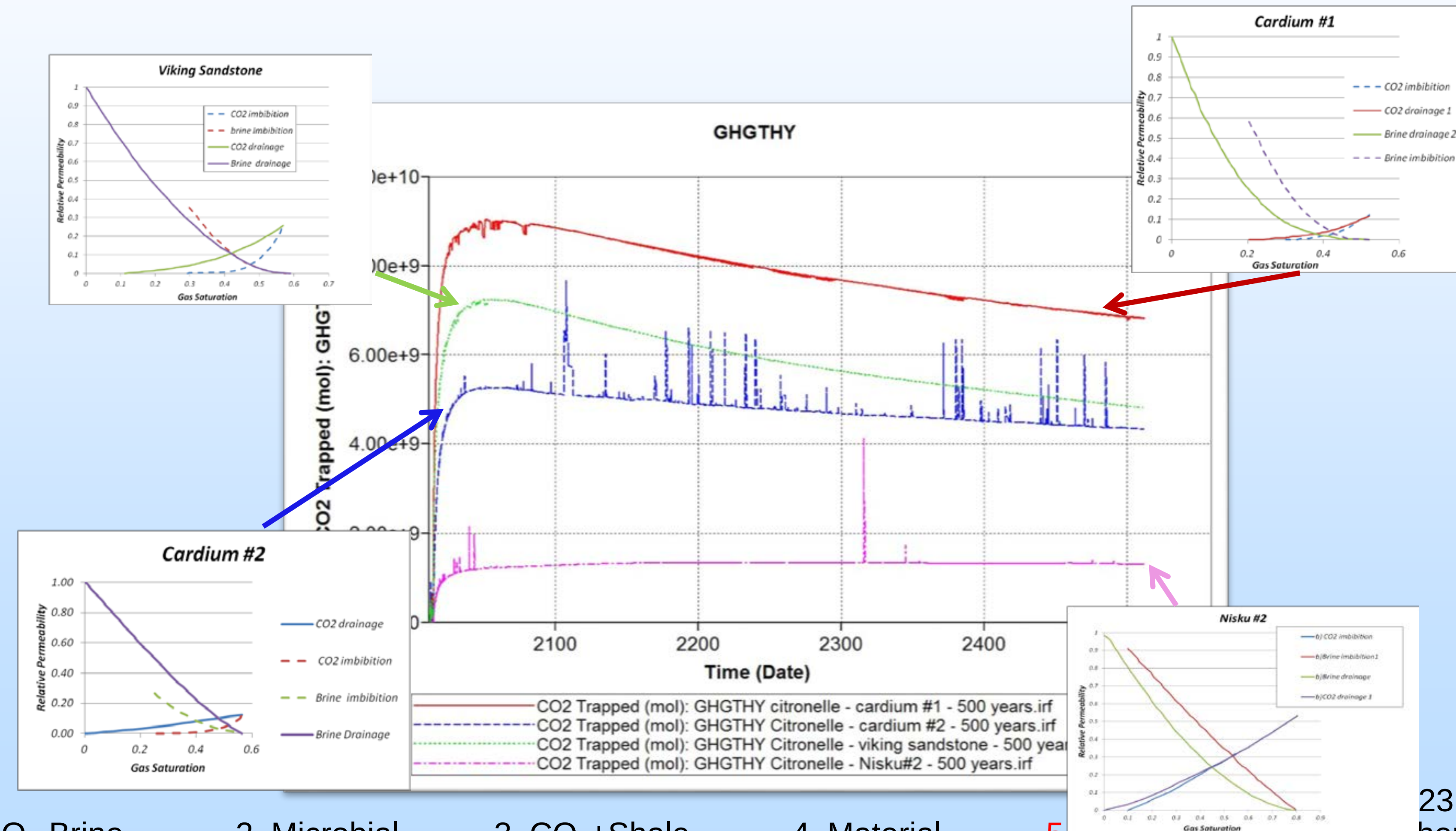




- Method: $scCO_2$ injection to replace water
- P/T condition: P_{pore} = 1500 psi, $P_{confining}$ = 3000 psi; core temp.: 50 ^oC
- K_r curves vs. $scCO_2$ Saturation (right)

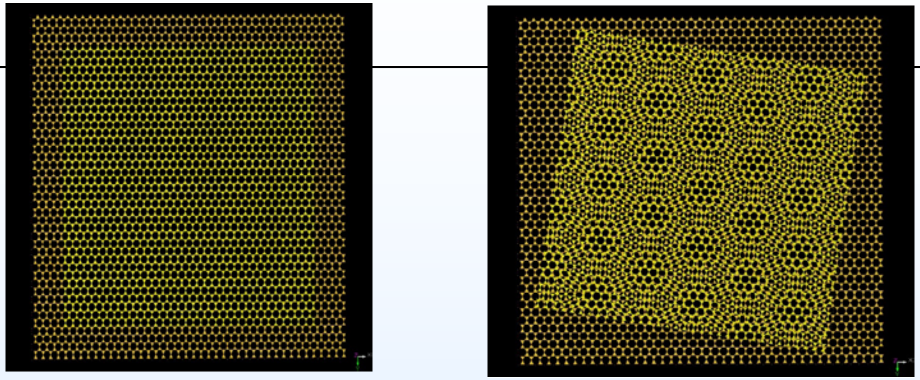
Various $scCO_2$ k_r models in reservoir flow

- Reservoir Scale Impacts of Relative Permeabilities and Residual Saturations on Injectivity and Capillary Trapping

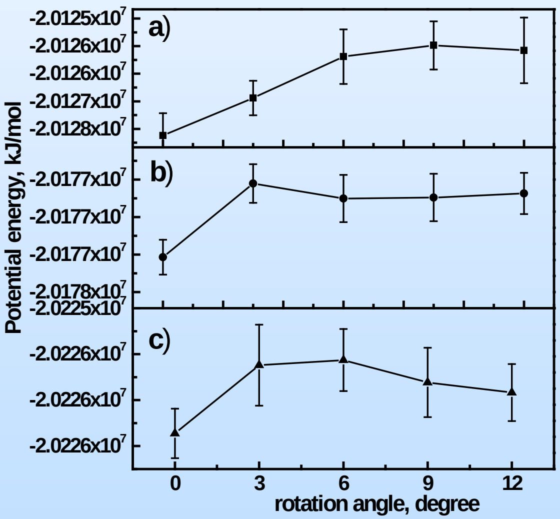


Understanding Clay Interactions with CO_2

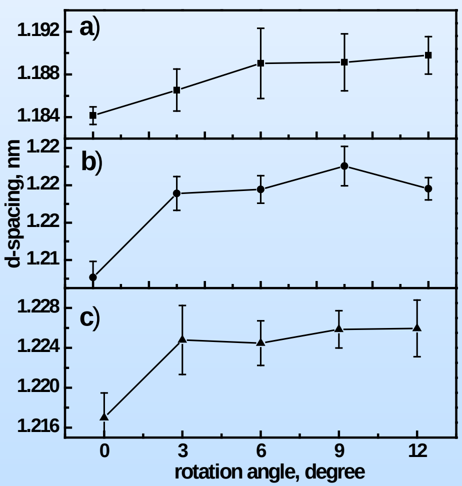
- Predicting clay swelling due to CO_2
- Amount of swelling depends on water present
- Experimental and theoretical



Moiré pattern formed by basal oxygens of two clay layers for (A) 0 degree and (B) 9 degree of the rotational angle



Rotation of hydrated montmorillonite layers is energetically demanding process, which is accompanied by a slight increase of d-spacing. Initial rotation, $0^\circ \rightarrow 3^\circ$ requires a large increase in energy; subsequent rotation proceeds freely.

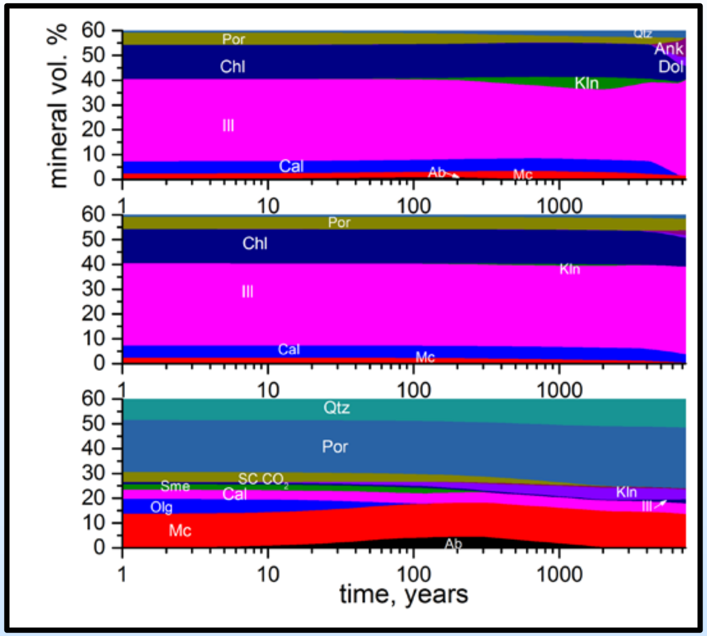


Potential energy (left) and d-spacing (right) as a function of the rotational angle for a) 4-0, b) 6-0, and c) 8-0 water composition in the interlayer space of the 22-14 (18-10) supercell of Na-MMT

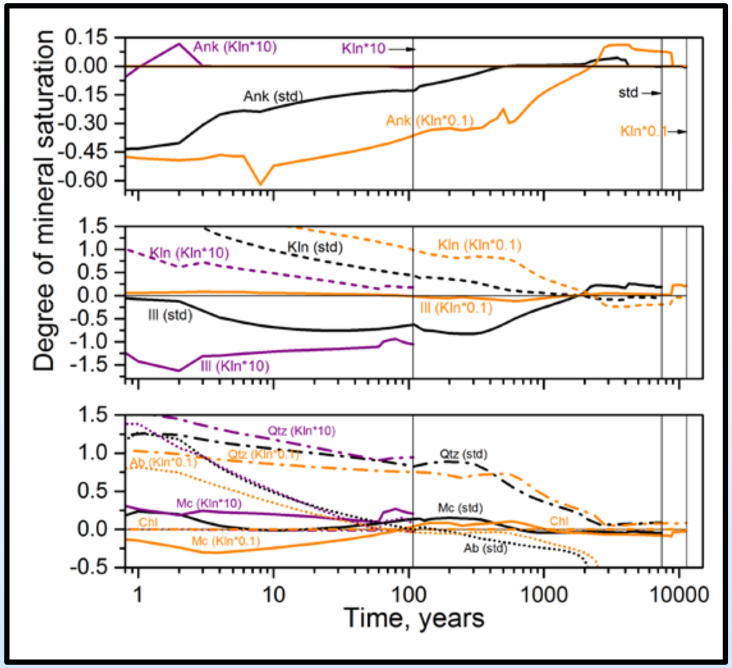
Geochemical Model Sensitivity at Caprock Interfaces

- Reactive diffusion calculations were run to simulate storage of supercritical CO_2 in a hypothetical reservoir at the sandstone/shale (ss/sh) interface at 348.15 K and 30 MPa.
- With standard (published) kinetics, the shale functioned up to 2000 years as a low-permeable barrier (caprock), and the chemical reactions mostly occurred in the sandstone. In the second period (2000 – 4000 years), the CO_2 reactive transport began to initiate the replacement of Mg-Fe chlorite by dolomite, ankerite and illite at the ss/sh interface. In the third period (4000 – 7500 years), this carbonation reaction in the shale led to complete closure of the porosity at the interface, sealing the reservoir and terminating further reaction.
- We also ran sensitivity tests to understand the effect of varying the kinetic constants for the feldspars and clay minerals. The reactive process in ss/sh contact is mostly sensitive to the kinetic constants for kaolinite and illite.
- The increase in the kaolinite kinetic constant by factors of 0.25, 0.5 and 1 logarithmic unit resulted in strong time decreasing for autosealing of the sandstone reservoir at the ss/sh contact by 4300, 650 and 107 years, respectively.

Geochemical Model Sensitivity at Caprock Interfaces



Evolution of the average mineral volume fraction of different minerals in shale at the sandstone / shale interface (top), inside the shale for the entire 0 to 1 m sub-layer above the interface (middle), and in the sandstone for the entire 0 - 2.5 m layer of sandstone (bottom).



Evolution of ankerite saturation is represented in the top figure for a simulation where the kaolinite kinetic constant was set i) 10 times greater than the standard published constant, ii) equal to the standard kinetic constant, and iii) 10 times less than the standard constant. Saturation with respect to calcite and dolomite are indicated by the zero line. The saturation time for kaolinite (dash) and illite (solid) are plotted in the middle figure. The saturation time for quartz (long dash – dot), albite (dot), microcline (solid), and chlorite (dash-dot) are plotted in the bottom figure.

2013-14 Accomplishments (1)

- Balashov, V.N., Brantley, S.L., Guthrie, G.D., Lopano, C.L., and Hakala, J.A., “Impact of Geochemical Kinetics at the Reservoir/Shale Interface on Long Term CO_2 Storage,” abstract submitted for presentation at Goldschmidt2014, Sacramento, CA, June 8–13, 2014. Gold2014:abs:3488, 2014.
- Balashov, V.N., Guthrie, G.D., Lopano, C.L., Hakala, J.A., and Brantley, S.L., “Reaction and Diffusion at the Reservoir/Shale Interface during CO_2 Storage: Impact of Geochemical Kinetics,” manuscript in preparation for submission.
- Brantley, S., “Sensitivity Analysis of Mineral Solution Rates in Reactive Transport,” Carbon Storage Technical Report Series (TRS), under development.
- Colwell, F., “Microbial Studies of Geologic Systems Exposed to Supercritical CO_2,” Carbon Storage Technical Report Series (TRS), under development.
- Goueguel, C., McIntyre, D., Singh, J., Jain, J., and Karamalidis, A.K., “Laser-Induced Breakdown Spectroscopy of High-Pressure CO_2-Water Mixture: Application to Carbon Sequestration,” submitted to *Applied Spectroscopy*, accepted for publication.
- Goueguel, C., Singh, J.P., McIntyre, D.L., Jain, J., and Karamalidis, A.K., “Effect of NaCl Concentration on Elemental Analysis of Brines by Laser-Induced Breakdown Spectroscopy,” *Journal of Applied Spectroscopy*, Volume 68, Number 2, February 2014, p. 213–221.
- Gregory, K., and Lowry, G., “Impact of CO_2 on the Evolution of Microbial Communities Exposed to Carbon Storage Conditions, Enhanced Oil Recovery, and CO_2 Leakage,” Carbon Storage Technical Report Series (TRS), under development.
- Gulliver, D.M., Lowry, G.V., and Gregory, K.B., “CO_2 Concentration and pH Alters Subsurface Microbial Ecology at Reservoir Temperature and Pressure,” *RSC Advances*, in press.
- Lopano, C., Parthasarathy, H., Hakala, A., Scheckel, K., Dzombak, D., and Karamalidis, A.K., “The Dissolution of Arsenic and Iron from Seal Rock Samples of the Lower Tuscaloosa Formation of the Cranfield Field CO_2 Sequestration Site,” in preparation.
- Jain, J.C., McIntyre, D.L., Ayyalasomayajula, K.K., Dikshit, V., Goueguel, C., Yu-Yueh, F., Singh, J.P., “Application of laser-induced breakdown spectroscopy in carbon sequestration research and development,” *PRAMANA Journal of Physics*, Indian Academy of Sciences, XX (2014) DOI:10.1007/s12043-014-0788-4.

2013-14 Accomplishments (2)

- McIntyre, D.L., Jain, J.C., Goueguel, C.L., and Singh, J.P., “Application of Laser-Induced Breakdown Spectroscopy (LIBS) to Carbon Sequestration Research and Development,” *Spectroscopic Techniques for Security, Forensic, and Environmental Applications*, Nova Science Publishers, 2014, ISBN: 978-1-63117-404-9, p. 25–51.
- Myshakin, E.M., Makaremi, M., Romanov, V.N., Jordan, K.D., and Guthrie, G.D., “Molecular Dynamics Simulations of Turbostratic Hydrated Montmorillonite with and without Intercalated Carbon Dioxide,” presented at the 50th Annual Meeting of the Clay Minerals Society, Urbana-Champaign, IL, October 6–10, 2013. http://www.clays.org/annual%20meeting/50th_annual_meeting_website/docs/CMS-2013-Program.pdf.
- Myshakin, E.M., Saidi, W., Romanov, V.N., Cygan, R., Jordan, K.D., and Guthrie, G.D., “Molecular Simulation Models of Carbon Dioxide Intercalation in Hydrated Sodium Montmorillonite,” NETL-TRS-3-2013, Carbon Storage Technical Report Series (TRS), U.S. Department of Energy, National Energy Technology Laboratory, Morgantown, WV, 2013, p. 1–40.
- Rodriguez, R., Crandall, D., Song, X., Verba, C., and Soeder, D., “Imaging Techniques Applied to Unconventional Oil and Gas Shales,” Carbon Storage Technical Report Series (TRS), under development.
- Soong, Y., Howard, B.H., Hedges, S.W., McIntyre, D., Warzinski, R., Irdi, G., Haljasmaa, I., and Crandall, D., “CO_2/Brine/Rock Interactions under CO_2 Sequestration Conditions,” presented at the American Institute of Chemical Engineers (AIChE) meeting, San Francisco, CA, November 3–8, 2013.
- Soong, Y., Zhang, L., Howard, B.H., Hedges, S.W., Warzinski, R., Dilmore, R., Soeder, D.J., McLendon, R.T., Gray, M.L., Haljasmaa, M.L., and Crandall, D., “The Interactions of Rock with CO_2 and Brine under CO_2 Sequestration Conditions,” abstract submitted for presentation at the 7th International Conference on Environmental Science and Technology 2014, Houston, TX, June 6–13, 2014.
- Zhang, L., Soong, Y., and Dilmore, R., “Numerical Simulation of Porosity and Permeability Evolution of Mount Simon Sandstone under Geological Carbon Sequestration Conditions,” manuscript under revision.

Accomplishments Summary

- 30+ publications in various venues
  - 1 book chapter
  - 5 Technical Report Series documents, https://edx.netl.doe.gov/
  - LIBS Patent Issued
    - Woodruff, S.D., McIntyre, D.L., Jain, J.C., “A method and device for remotely monitoring an area using a low peak power optical pump,” U.S. Patent 8,786,840, July 22, 2014.
  - Peer reviewed articles in journals ranging from SPE to AIChE & Royal Society of Chemistry

FY15 Reservoir Performance

1. Impact of CO_2-Brine-Rock on Storage Formations and Seals
2. Impact of Microbial Processes on Storage Formations and Seals
3. Understanding of Multiphase Flow for Improved Injectivity and Trapping

Appendix

– These slides will not be discussed during the presentation, but are mandatory

Organization Chart

- NETL
  - Lopano, Romanov, Sams, Gulliver, Bromhal, McIntyre, Jain, Soeder, Rodriguez, Choi, Soong, Seol, Goodman, Haljasmaa, Myshakin, and many more
- Universities
  - Gregory (CMU), Brantley (PSU), and Colwell (OSU)

Gantt Chart

Carbon Storage
FWP Number Car Stor_FY14
Schedule and Milestones

U.S. DEPARTMENT OF ENERGY

Task No.	Activity Name (Task/Sub-task)	Start	Finish	FY14
1.0	**Project Management**	**10/1/13**	**9/30/14**	
1.1	Project Management	10/1/13	9/30/14	
2.0	**Reservoir and Seal Performance**	**10/1/13**	**9/30/14**	M1.14.2.A
2.1	Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals	10/1/13	9/30/14	
2.2	Impact of Microbial Processes on Storage Formations and Seals	10/1/13	9/30/14	
2.3	Impact of CO_2 on Shale Formations as Seals	10/1/13	9/30/14	
2.4	Characterization of Reservoir and Seal Material Performance	10/1/13	9/30/14	
2.5	Understanding of Multiphase Flow for Improved Injectivity and Trapping	10/1/13	9/30/14	
2.6	Geochemical Model Sensitivity at Caprock Interfaces	10/1/13	9/30/14	
3.0	**Monitoring Groundwater Impacts**	**10/1/13**	**9/30/14**	M1.14.3.A
3.1	Natural Geochemical Signals for Monitoring Groundwater Impacts	10/1/13	9/30/14	
4.0	**Resource Assessments and Geospatial Resource**	**10/1/13**	**9/30/14**	M1.14.4.A
4.1	Resource Assessments	10/1/13	9/30/14	
4.2	Geospatial Data Management	10/1/13	9/30/14	
5.0	**Monitoring CO_2 and Pressure Plume**	**10/1/13**	**9/30/14**	M1.14.5.A
5.1	Development of Technology to Monitor CO_2 and Pressure Plume	10/1/13	9/30/14	
6.0	**Catalytic Conversion of CO_2 to Industrial Chemicals**	**10/1/13**	**9/30/14**	M1.14.6.A
6.1	Catalytic Conversion of CO_2 to Industrial Chemicals	10/1/13	9/30/14	

FY14: Q1 (O N D), Q2 (J F M), Q3 (A M J), Q4 (J A S)

◇ Milestone — Summary

Page 1 of 1

Milestone Identifier	Title	Planned Date	Verification Method
Task 2.0 Reservoir and Seal Performance			
M1.14.2.A	**Complete pre-exposure characterization of Mount Simon and/or Lower Tuscaloosa samples.**	**12/31/13**	**Characterization data**
Task 3.0 Monitoring Groundwater Impacts			
M1.14.3.A	Coordinate experiments at PNNL/EMSL about in-situ, on-line and simultaneous measurements of organics in both sc-CO_2 and brine phases to determine partitioning coefficients.	12/31/13	**Experimental plan**
Task 4.0 Resource Assessments and Geospatial Resources			
M1.14.4.A	Provide draft methodology products for oil and gas formations.	03/30/14	**Draft report**
Task 5.0 Monitoring CO_2 and Pressure Plume			
M1.14.5.A	Paper on evaluation of fracture behavior (elastic vs. inelastic) including failure.	09/30/14	**Draft manuscript**
Task 6.0 Catalytic Conversion of CO_2 to Industrial Chemicals			
M1.14.6.A	**Complete design for first version of electrocatalytic reactor to be used with atomically precise clusters and initiate construction.**	**06/30/14**	**Design document**

1.1	Project Management	10/1/13	9/30/14	
2.0	**Reservoir and Seal Performance**	**10/1/13**	**9/30/14**	M1.14.2.A
2.1	Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals	10/1/13	9/30/14	
2.2	Impact of Microbial Processes on Storage Formations and Seals	10/1/13	9/30/14	
2.3	Impact of CO_2 on Shale Formations as Seals	10/1/13	9/30/14	
2.4	Characterization of Reservoir and Seal Material Performance	10/1/13	9/30/14	
2.5	Understanding of Multiphase Flow for Improved Injectivity and Trapping	10/1/13	9/30/14	
2.6	Geochemical Model Sensitivity at Caprock Interfaces	10/1/13	9/30/14	
3.0	**Monitoring Groundwater Impacts**	**10/1/13**	**9/30/14**	M1.14.3.A

Bibliography

Please see accomplishments slides.

Thank you!