Characterizing Shales as Seals for CO<sub>2</sub> Containment and Shales as Reservoirs for Geologic Storage of CO<sub>2</sub>

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# **Presentation Outline**

Shales as Seals and Unconventional Reservoirs: Product of this work is to quantify shales as sealing units for large scale  $CO_2$  storage operations. Shales is investigated in the following terms:

- (1) quantifying the chemical reactivity of shales with CO<sub>2</sub> in natural fractures and matrix pores
- (2) quantifying flow properties of shale sealing units in both the matrix and natural fractures in terms of CO<sub>2</sub> containment
- (3) explaining shale fracture behavior when stressed and exposed to scCO2 and fluids

#### **Task 18.0** CO<sub>2</sub>-Shale Interactions

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## **Task Technical Approach and Project Relevancy**

#### Characterizing Shales as Seals for CO<sub>2</sub> Containment

Objective:

Quantify shales as sealing units for large scale CO<sub>2</sub> storage operations.

Challenges:

•

- Very few studies are considering the reactivity of CO<sub>2</sub> and fluids with shales.
- Reactions between  $CO_2$ , fluids, and shale may alter:
  - Petrophysical **properties** such as porosity and permeability
  - **Integrity** of the shale as a sealing unit
  - Potential as a storage reservoir
  - Flow pathways potentially impacting carbon storage seals, carbon storage reservoirs, and hydrocarbon extraction

Approach:

- Quantify the Chemical Reactivity of Shales with CO<sub>2</sub> in Natural Fractures and Matrix Pores
- Investigate How Sub-Critical Stresses Break Shale when Under Elevated Pressures Due to CO<sub>2</sub> Injection
- Quantify Flow Properties of Shale Sealing Units in Both the Matrix and Natural Fractures in Terms of CO<sub>2</sub> Containment



## **Shale Properties**





Matrix Interparticle Pores (<2000 nm) between mineral particles are more likely to be connected and hydrophilic. Examples include crystals, grains, clay platelets, and rigid grains



Natural Fractures (<4000 nm) can be sealed with calcite or bitumen and have a significant effect on hydrocarbon production.



Hydraulic Fractures (>10,000 nm) are induced after hydraulic fracturing and have a significant effect on hydrocarbon production.



Matrix Organic–Matter Pores (~5-750 nm) intra-pores within the organic matter are more likely to be connected and hydrophobic.



Matrix Intraparticle Pores (<2000 nm) within mineral particles are less likely to be connected and hydrophilic. Examples include clay aggregates, pyrite, pellets, and moldic pores.

## **Shale Properties**





NETL has the capability to measure these pore types

# **Research Questions**

#### How does CO<sub>2</sub> interact with shale and fluids?

- How is  $CO_2$  stored in shales?
- How does CO<sub>2</sub> alter seals?
- How do we classify shales?
- Can CO<sub>2</sub> enhance hydrocarbon recovery?
- Can  $CO_2$  be used as a fracturing agent?





### **Research Capabilities**



Feature Relocation SEM/EDS



High-Resolution Industrial Computed Tomography



Static batch reactors for longterm experimentation



In-situ Fourier Transform Infrared Spectroscopy



BET Pore Size Analysis



Autolab 1500



X-Ray Diffraction



Rapid Medical Computed Tomography with Controlled Flow

# **Key Findings**

Chemical composition of shale has a major effect on CO<sub>2</sub>-shale reactivity

- <u>Carbonate-rich shale samples</u>
  - CO<sub>2</sub> and water cause significant alterations in pore sizes by increasing porosity at the micro-scale while decreasing porosity at the nano-scale.
- <u>Carbonate-poor shale samples</u>
  - CO<sub>2</sub> and water DO NOT alter pore sizes
  - Moderate increases in fracture sizes were observed.
- Shale fluid saturation and structure influence geomechanical properties
  - Dry shales exhibit more localized breakage under stress than water saturated shale
  - Shear fracturing along bedding planes common in low stress experiments.

# **Mineralogy Characterization**



# **Mineralogy Characterization**



![](_page_10_Figure_1.jpeg)

![](_page_11_Figure_1.jpeg)

#### Carbonate-Rich Shale

![](_page_12_Figure_2.jpeg)

![](_page_13_Figure_1.jpeg)

Porosity = 5.6%

Porosity = 3.6%

Porosity = 13.5%

#### **Organic-Rich Shale**

![](_page_14_Figure_2.jpeg)

тс

S

0.62

BDL

### CO<sub>2</sub>-Shale Interactions- Geomechanics

### Low pressure cracking of shales

The goals of the proposed research was to observe and quantify breakage in shales due to low stresses using acoustic emissions (AE) and CT.

![](_page_15_Figure_3.jpeg)

![](_page_15_Figure_4.jpeg)

![](_page_15_Picture_5.jpeg)

- Time dependent failure of shale due to stresses that are insufficient to instantaneously break the rock may still create flow pathways.
- Successfully used AE to identify low stress crack formation and type
- Successfully used CT to confirm the location of these cracks and structural influence of the shale on fracture modes
- Unsuccessful at merging these two measurements simultaneously and missed a Go/No-Go milestone associated with this work.
- Work halted and manuscript submitted covering observations completed.

![](_page_15_Figure_11.jpeg)

Lu, G., Crandall, D., and Bunger, A. (*submitted*) Observations of breakage for transversely isotropic shale using Acoustic Emission and X-Ray Computed Tomography: Effect of bedding orientation, preexisting weaknesses, and pore water, International Journal of Rock Mechanics and Mining Sciences

# **Next Steps: Flow Pathways**

- Quantify if pore alterations impact flow pathways
  - Core flow tests in progress to evaluate whether pore changes impact flow pathways in the shale matrix
- Investigate other shale properties:
  - Thermal maturity
  - Ductility
  - Mineralogy other than carbonate
  - Clay Content
  - Organic Content (kerogen)

#### Carbonate-Rich Shale

![](_page_16_Picture_10.jpeg)

# Summary

- Chemical composition of shale has a major effect on CO<sub>2</sub>-shale interactions
  - Carbonate-Rich vs Carbonate-Poor shales affect CO<sub>2</sub>-fluid interactions
- Carbonate-rich: changes in pore sizes, etching/pitting
  - Micro-scale porosity increases with  $CO_2$  and  $CO_2/H_2O$
  - Nano-scale porosity decreases with  $CO_2$  and  $CO_2/H_2O$
- Carbonate-poor: Increase in micro fracture abundance and size
- Shale fluid saturation and structure influence geomechanical properties
  - Dry shales exhibit more localized breakage under stress than water saturated shale
  - Shear fracturing along bedding planes common in low stress experiments.

![](_page_17_Figure_10.jpeg)

# Appendix

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

# Benefit to the Program

#### **Problem Statement**

• Shale formations are expected to be impermeable sealing layers for CO2 storage reservoirs due to their low permeability. Although a large body of work has been conducted on shales, fundamental research is needed to understand shale properties in terms of sealing layers for CO2 storage reservoirs. The injected CO2 will interact with reservoir fluids and shale components such as clays and organic matter. The injection process will affect shale properties through chemical alteration, matrix swelling/shrinkage, and geomechanical stress effects from either chemical reactivity or changes in reservoir pressure. These changes in shale properties could alter the flow pathways of the shale sealing unit. As potential changes in shale sealing properties will impact anthropogenic CO2 storage, it is imperative to quantify CO2-shale and stress related interactions with shale sealing units. This work directly addresses the administration goals relevant to the Program: *Reduce risk and ensure certainty in safe, permanent storage and cost-effective integrated storage facilities*.

#### **Justification and Benefits**

Shale formations are widespread throughout the United States. Quantifying fundamental shale properties in terms of a sealing layer for CO2 storage reservoirs is needed to develop a national strategy for CS. Fundamental research examining the geochemical and stress-induced interactions of CO2 and fluids with shale is limited from the perspective of understanding shale as an effective natural seal. Reaction of CO2 with native fluids and reactive shale interfaces may generate new reactive surfaces or intermediates that may alter the properties of the formation. It is known that geochemical reactions influence storage mechanisms and that reaction kinetic rates vary significantly from occurring immediately after injection to hundreds of years later. When shale interacts with CO2 and fluids the geomechanical properties of the shale may change. Geochemical and stress-induced alterations have a direct impact on flow pathways, porosity and permeability changes, and integrity of the formation seal. A fundamental understanding of the reactivity of CO2 with shale and how shale fracture properties alter under stresses will help in identifying and reducing risk associated with shale sealing units in CCS activities.

#### **Task 18: Project Timeline Overview**

• CO<sub>2</sub>-Shale Interactions (PI: Angela Goodman/Dustin Crandall)

![](_page_20_Figure_2.jpeg)

#### Milestones

<ul> <li>18.A Present the results of the CO<sub>2</sub>/shale interactions literature review. Completed</li> <li>18.B Continue testing the Bakken shale/CO<sub>2</sub> interactions with core flow apparatus and EERC. Completed</li> <li>18.C Submit a peer reviewed publication on the assembled literature review. 3 TRS - Completed</li> <li>18.D Perform MD simulations of hydrated and dry shale with mixtures of CH<sub>4</sub>/CO<sub>2</sub> to determine preferential sorption potential under varying realistic conditions. Completed</li> <li>18.E Assemble a bench scale full immersion pulse decay device and shakedown apparatus. Compare/contrast measurements to traditional pulse decay. NO-GO</li> <li>18.F Quantify the geochemical impact of CO<sub>2</sub> and fluid interactions on Utica and Marcellus Shale at the nano- and micro-scale. Completed</li> <li>18.G Quantify the potential changes in flow properties of Utica Shale that has been modified with CO<sub>2</sub> and fluid. Completed</li> </ul>	<ul> <li>18.I Observe microstructural changes during stress corrosion cracking and complete corescale experiments. Completed</li> <li>18.J Quantify the geochemical impact of CO<sub>2</sub> and fluid interactions on shale as a seal. Completed</li> <li>18.K Quantify the potential changes in flow properties of shale as a seal that has been modified with CO<sub>2</sub> and fluid. On-going</li> <li>18.L Complete experiments of two shale fractures showing alteration of fracture geometry and flow when exposed to (1) water and (2) water and CO<sub>2</sub>.</li> <li>18.M Quantify the geochemical impact of CO<sub>2</sub> and fluid interactions on shale as a seal and potentially relate shales as seals and shales as storage reservoirs.</li> <li>18.N Submission of manuscript describing observed changes in fracture closure, with recommendations about what constituents in the shale matrix can have the largest impact on the fracture closure behavior.</li> </ul>
Key Accomplishments/Deliverables	Value Delivered
Quantified interactions of CO <sub>2</sub> with Utica, Marcellus Shale, Eagle Ford, Barnett, Eau Claire Published comprehensive literature review of CO <sub>2</sub> /H <sub>2</sub> O/shale interactions Observed CO <sub>2</sub> can reduce fractured shale permeability under in situ conditions <b>Go / No-Go</b>	<ul> <li>How geochemical CO<sub>2</sub> alterations and subcritical stress of shale may affect flow pathways and sealing properties</li> <li>Database of shale sealing properties when influenced by CO<sub>2</sub> reactivity and subcritical stress</li> <li>Chart Key 21</li> <li>TRL Score Go / No-Go Timeframe Project Completion Milestone</li> </ul>

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