Characterizing Shales as Seals for CO_2 Containment and Shales as Reservoirs for Geologic Storage of CO_2

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US DOE NETL, Research and Innovation Center

U.S. Department of Energy

National Energy Technology Laboratory

Mastering the Subsurface Through Technology Innovation, Partnerships and Collaboration:
Carbon Storage and Oil and Natural Gas Technologies Review Meeting

August 13-16, 2018

Tuesday, August 14th 2:30 PM

Presentation Outline

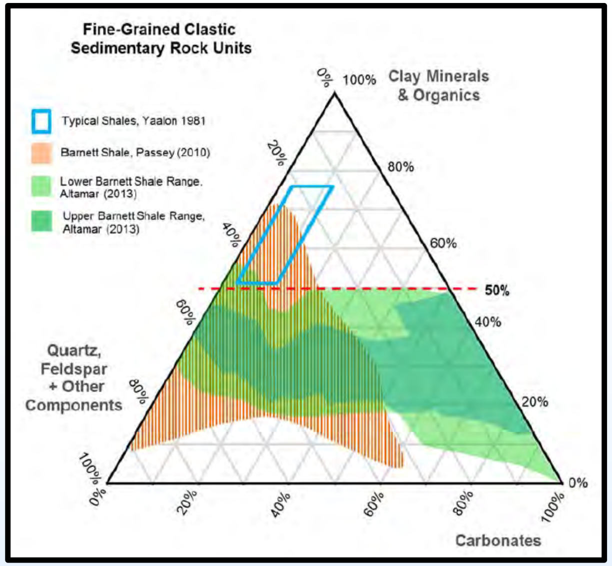
Research Theme: Shales, Characterizing Interactions of CO_2 with Shale for Potential Storage Needs and Seal Integrity

- **Task 17.0 CO_2-Shale Interactions- Macroscopic**
- *Team Members: Johnathan Moore, Sarah Brown, Ernest Lindner, Michael Hannon, Yael Tucker, Leebyn Chong, Eugene Myshakin, Guanyi Lu, Andrew Bunger, Dustin Crandall*
- **Task 18.0 CO_2-Shale Interactions- Microscopic**
- *Team Members: Angela Goodman, Sean Sanguinito, Barbara Kutchko, Jeff Culp, Mary Tkach, Sittichai Natesakhawat, Dustin Crandall, Patricia Madden*

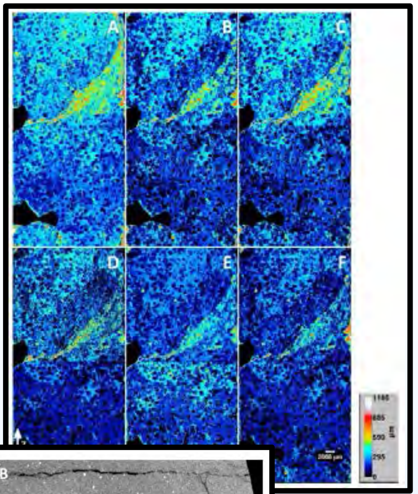
Task 17.0 CO_2-Shale Interactions- Macroscopic

Shale Response to CO_2 Literature Review

- Over 350 pages of detailed reviews and over 300 references
  - Lindner, E. N. **Review of the Effects of CO_2 on Very-Fine-Grained Sedimentary Rock/Shale – Part III: Shale Response to CO_2**; NETL-TRS-11-2017; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017; p 228.
  - Lindner, E. N. **Review of the Effects of CO_2 on Very-Fine-Grained Sedimentary Rock/Shale – Part II: Clay Mineral & Shale Response to Hydration**; NETL-TRS-10-2016; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2016; p 68.
  - Lindner, E. N. **Review of the Effects of CO_2 on Very-Fine-Grained Sedimentary Rock/Shale – Part I: Problem Definition**; NETL-TRS-1-2016; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2016; p 68.



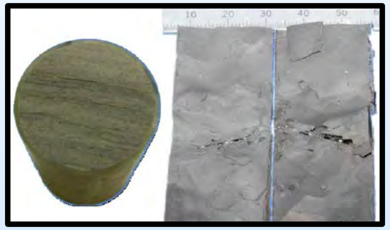
Task 17.0 CO_2-Shale Interactions- Macroscopic

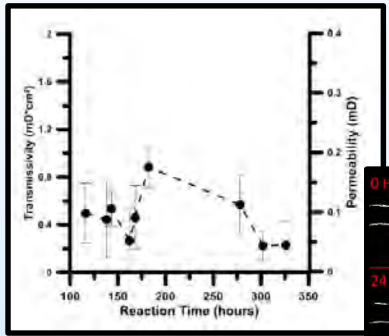


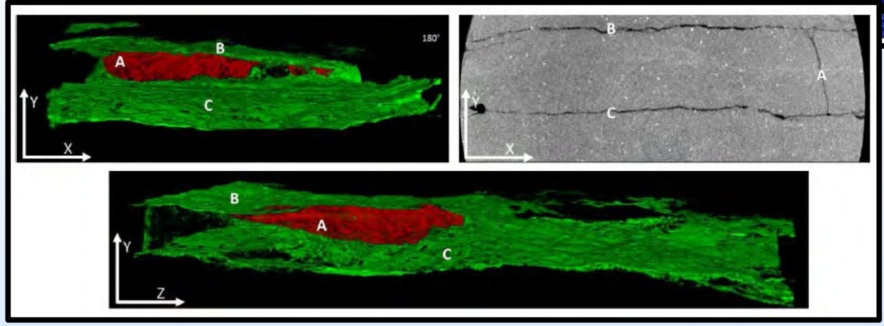
Shale swelling due to CO_2

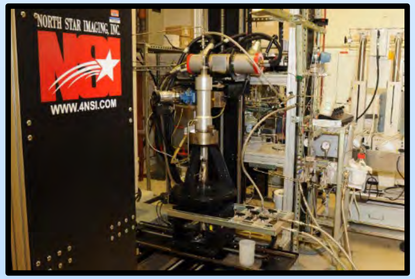
– Inconclusive experiments have led to MD simulations

Bakken Shale

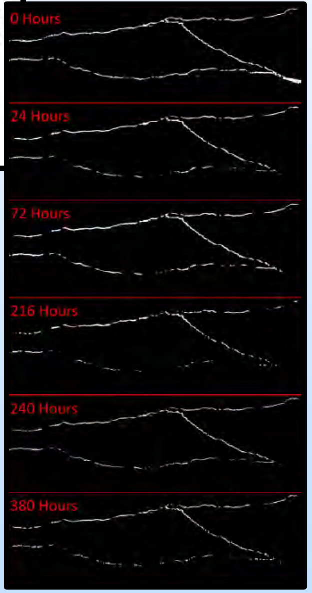


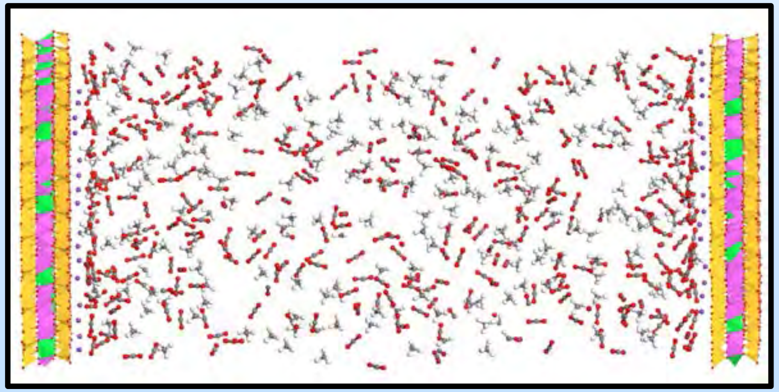


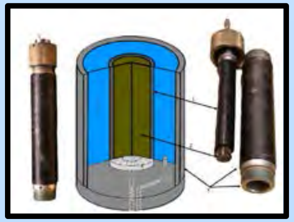




Hour	b_{Videal} (mm)	b_H (mm)
0	102.01	15.63
24	75.15	13.71
72	81.83	
120		12.94
216	62.94	12.91
240	72.49	11.86
264		10.51
290		8.45
384	57.34	8.50







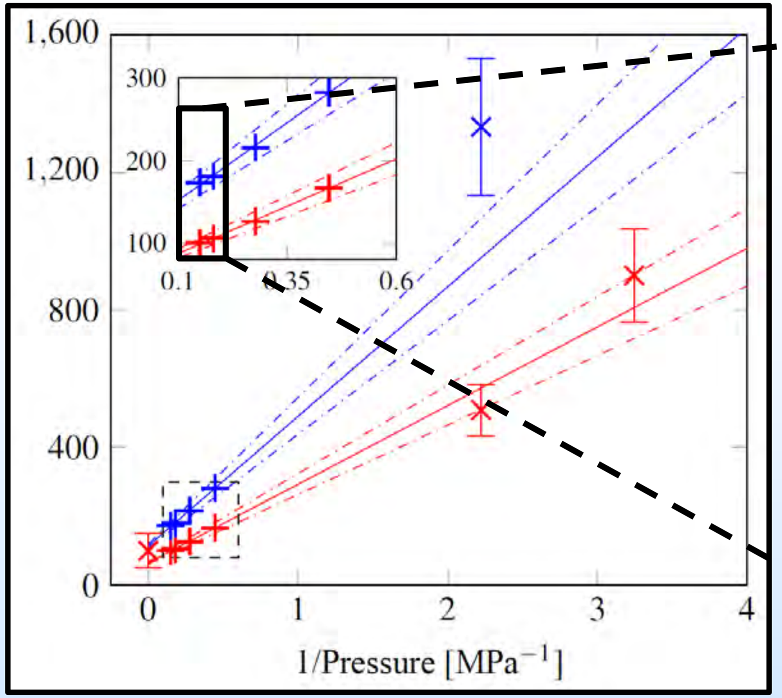
Representation of the clay/CH_4/CO_2 system. The color coding of atoms is purple, red, white, gray, yellow, pink, and green for K, O, H, C, Si, Al, and Mg, respectively.

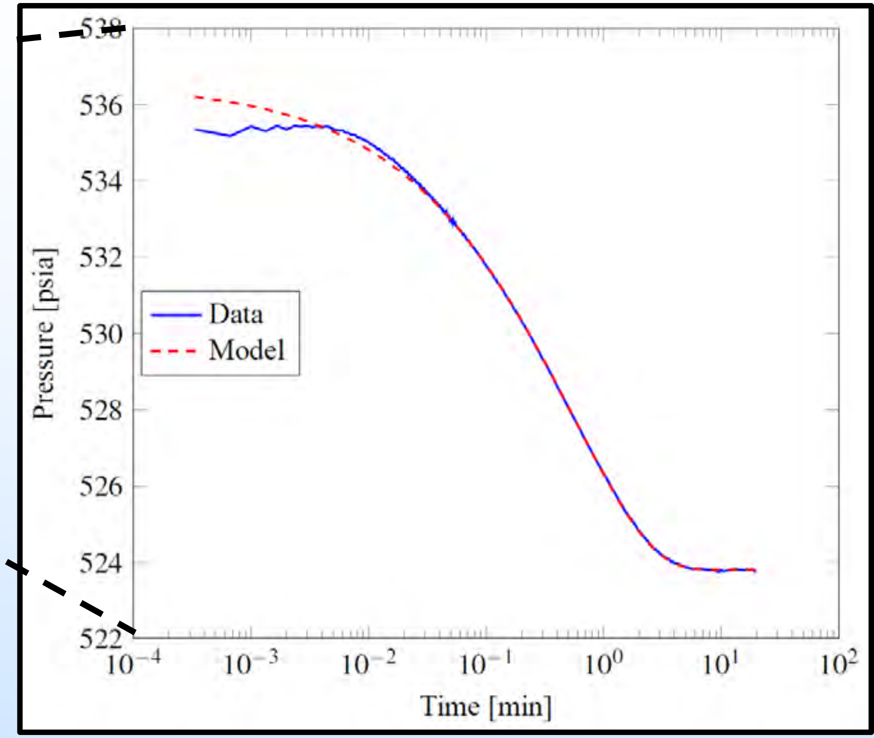
Chong, L., Myshakin, E.M. (2018) Molecular simulations of competitive adsorption of carbon dioxide – methane mixture on illitic clay surfaces, Fluid Phase Equilibria, Vol 472, 2018

Task 17.0 CO_2-Shale Interactions- Macroscopic

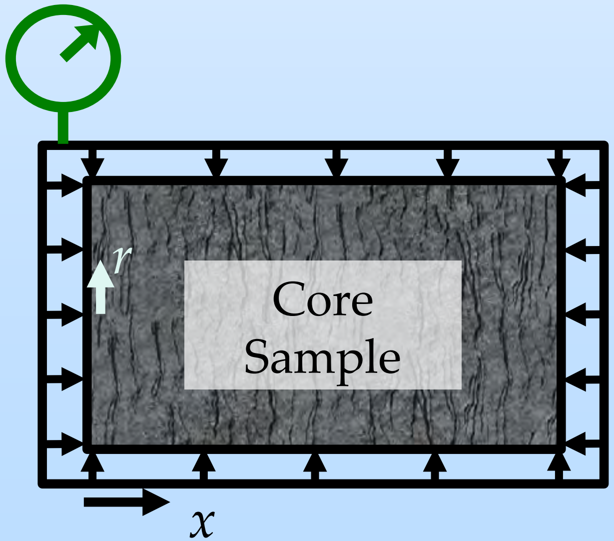
Full Immersion Pressure Pulse Decay

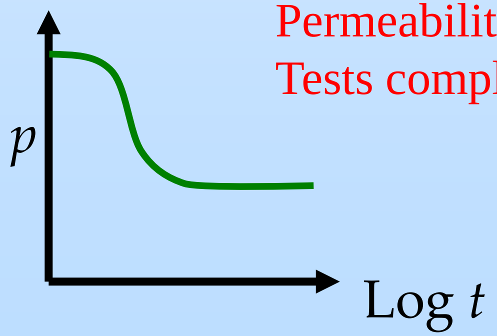
- Apply pressure disturbance to entire outer surface area.
- Assume uniform but distinct permeabilities in radial and axial directions.
- Numerical simulation to predict pressure response
- Experimental tests have shown excellent agreement with traditional measurements.
- Simultaneously determine both permeabilities from a single test!





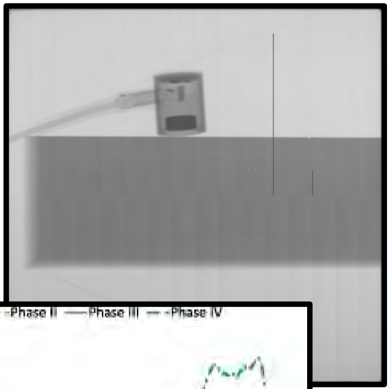
$\widehat{p_0}$ = 491.6 psia, $\widetilde{p_p}$ = 536.5 psia, $\tilde{\phi}$= 8.5%, $\widetilde{k_r}$ = 215.8 nd, $\widetilde{k_x}$ = 126.6 nd





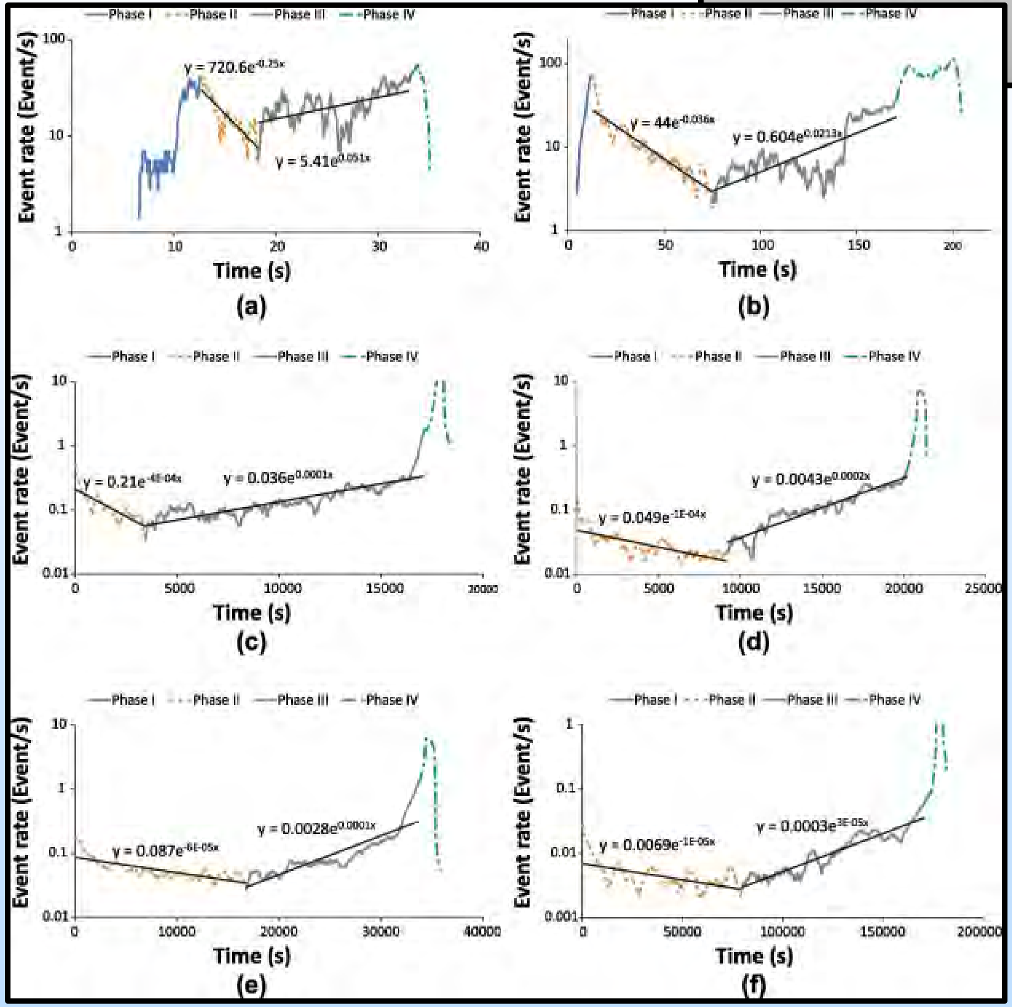
Permeabilities ~ 100s of nD
Tests complete in 5-20 minutes!

Task 17.0 CO_2-Shale Interactions- Macroscopic



Stress Corrosion in Shales

- The goal of the proposed research is to observe and quantify the impact of stress corrosion on shale permeability.
  - Stress corrosion is the time dependent failure due to stresses that are insufficient to instantaneously break the rock.
- Development of a coupled numerical model to account for this behavior, benchmarked on experimental observations, will enable greater seal characterization for long term stress behavior of shale sealing formations.
- Just started experiments in July.



From Winner, R.A,, Lu, G., Prioul, R., Aidagulov, G., Bunger, A.P. (2018) Acoustic emission and kinetic fracture theory for time-dependent breakage of granite, Engineering Fracture Mechanics, v 199, doi.org/10.1016/j.engfracmech.2018.05.004.

Task 18 - CO_2-Shale Interactions- Microscopic

Task Technical Approach and Project Relevancy

- Objective: Quantify CO_2 interactions with shale at the nano- and micro-scale and provide quantitative inputs at the macro-scale to understand flow properties and inputs for reservoir simulations of large-scale storage activities in shale.

- Question: How does CO_2 interact with fracturing fluid and shale for storage, as an alternative fracturing agent, and as an EOR agent?

J.A. Chermak, M.E. Schreiber
International Journal of Coal Geology 126 (2014) 32–44

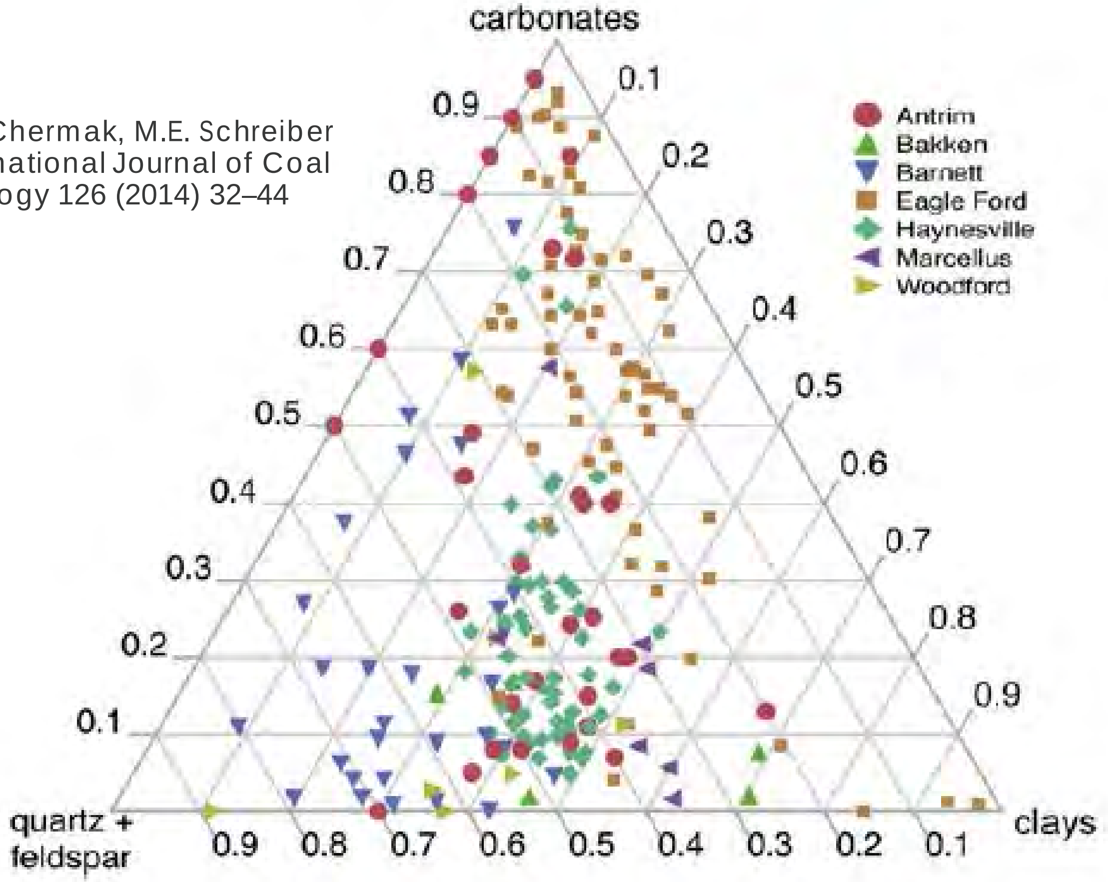


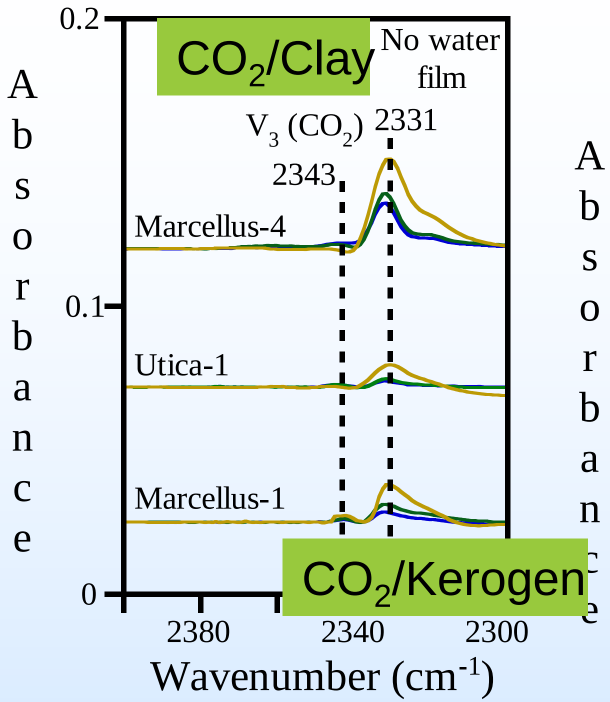
Fig. 2. —A comparison of quartz and feldspar, carbonate content, and clay conte
References for data are provided in Table 2.

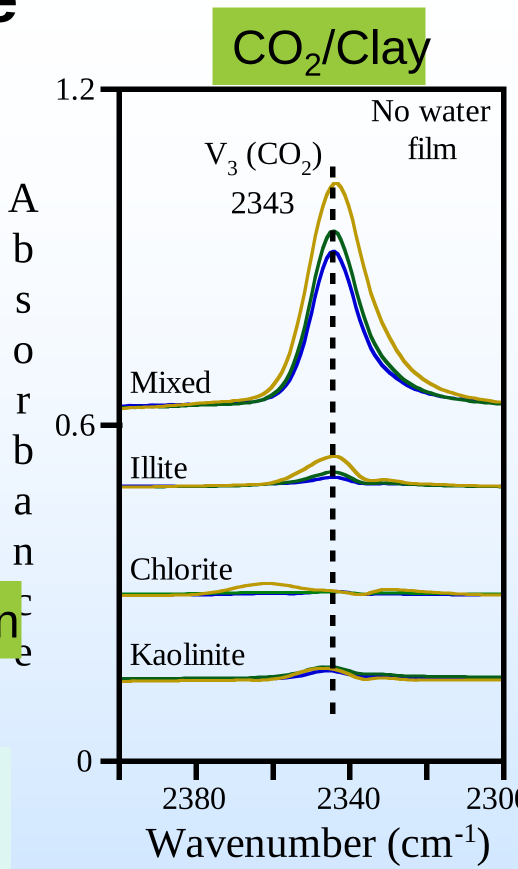
- Method: Examining petrophysical characteristics including reaction mechanism, precipitation, dissolution, surface area, porosity, permeability, and mineralogy of the host formation

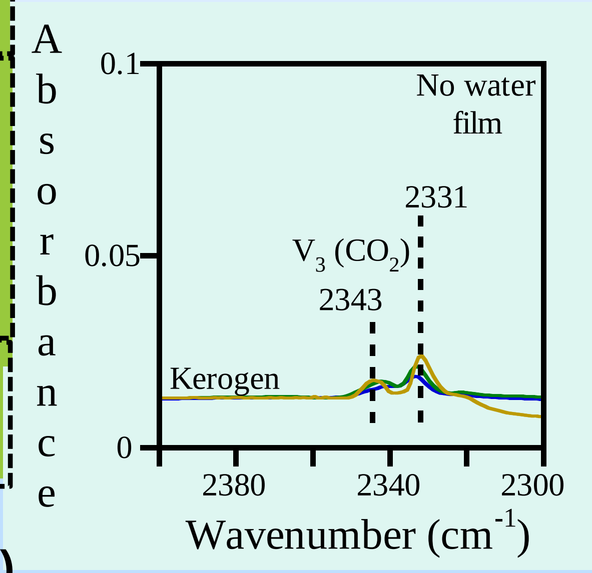
Results: Infrared Spectroscopy of the CO_2-Shale Interface

- Infrared frequencies consistent with weak electrostatic interactions between CO_2 and Shale, Kerogen or Clays interface
- ***CO$_2$ sorption in micro-porosity of organic fraction and internal layers and surfaces of clay minerals***

Sample	Infrared Frequency (cm^{-1}) Dry	Spectral Assignment	
Marcellus Shale: Oatka Creek Member	2343, 2331	Organic and Inorganic	CO_2 Kerogen Clay
Marcellus Shale: Union Springs Member	2343, 2331	Organic and Inorganic	
Utica Shale: Flat Creek Member	2343, 2331	Organic and Inorganic	
Illite-Smectite	2343	Inorganic	CO_2 Clay
Illite	2343	Inorganic	
Kaolinite	2343	Inorganic	
Chlorite	2343	Inorganic	
Extracted kerogen from the New Albany Shale	2331	Organic	CO_2 Kerogen







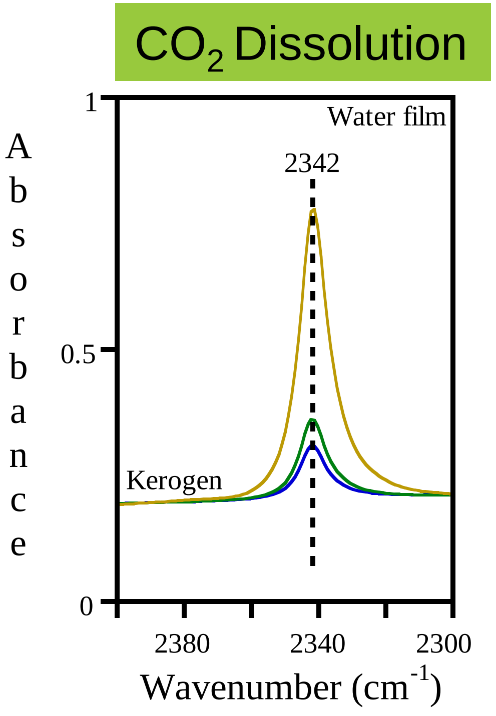
Utica Shale (US-1)

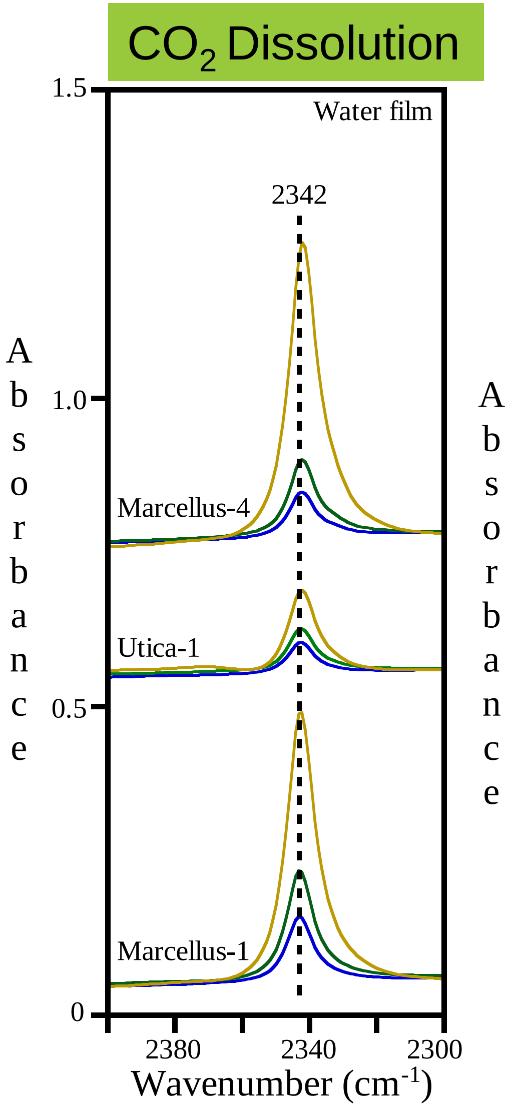
Results: Infrared Spectroscopy of the CO_2-Fluid-Shale Interface

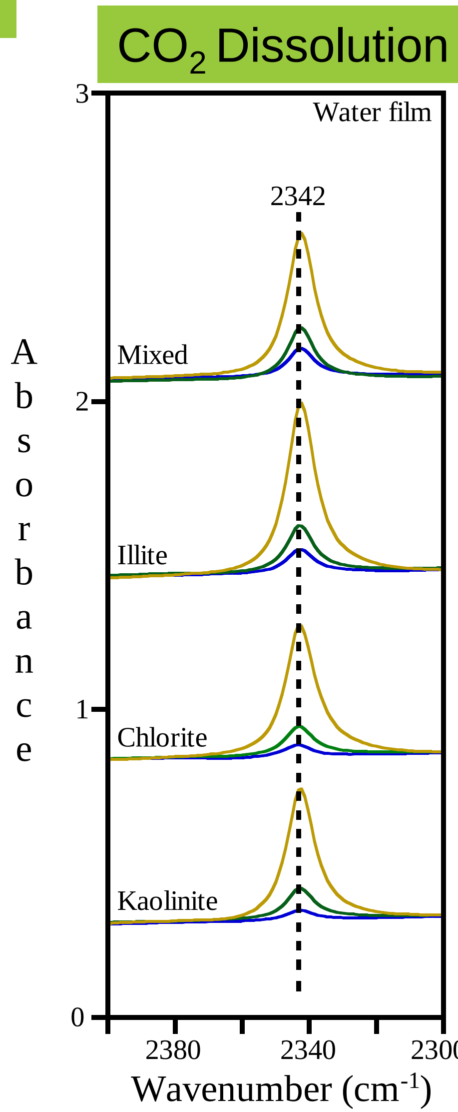
- Infrared frequencies consistent with CO_2 dissolution in water in high pressure geological storage conditions
- ***CO_2 not interacting with Shale, Kerogen or Clays***

Sample	Infrared Frequency (cm^{-1}) Wet	Spectral Assignment
Marcellus Shale: Oatka Creek Member	2342	CO_2 dissolution
Marcellus Shale: Union Springs Member	2342	CO_2 dissolution
Utica Shale: Flat Creek Member	2342	CO_2 dissolution
Illite-Smectite	2342	CO_2 dissolution
Illite	2342	CO_2 dissolution
Kaolinite	2342	CO_2 dissolution
Chlorite	2342	CO_2 dissolution
Extracted kerogen from the New Albany Shale	2342	CO_2 dissolution

CO_2 Dissolution

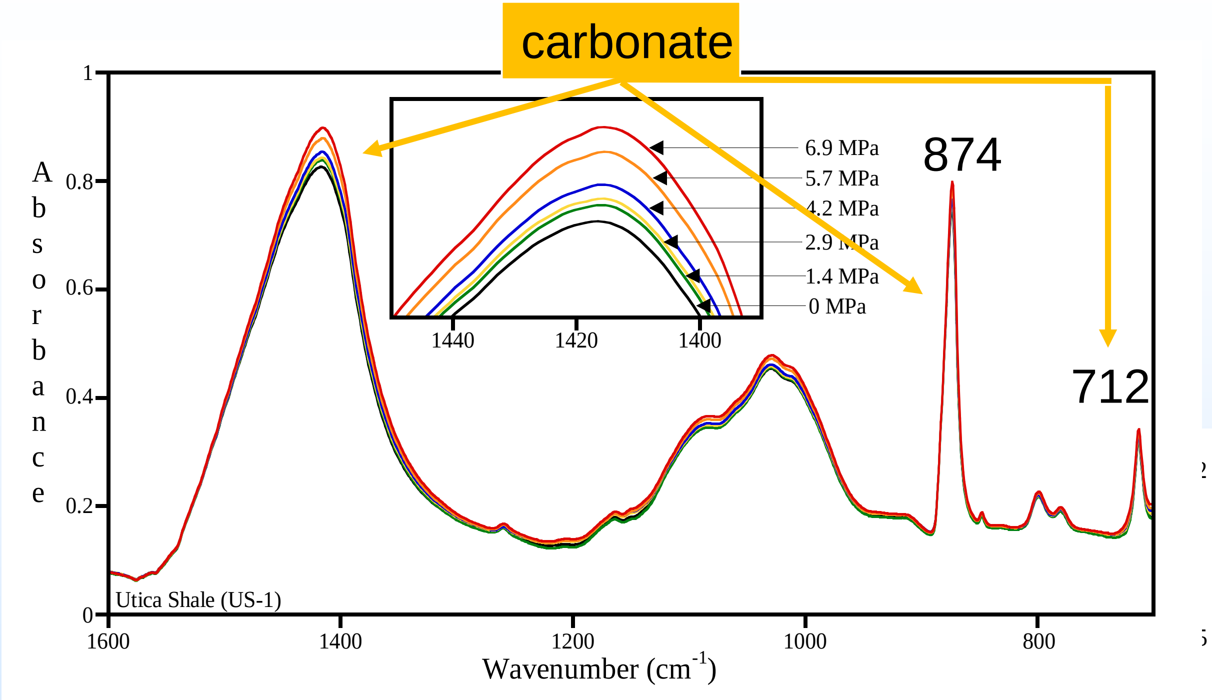






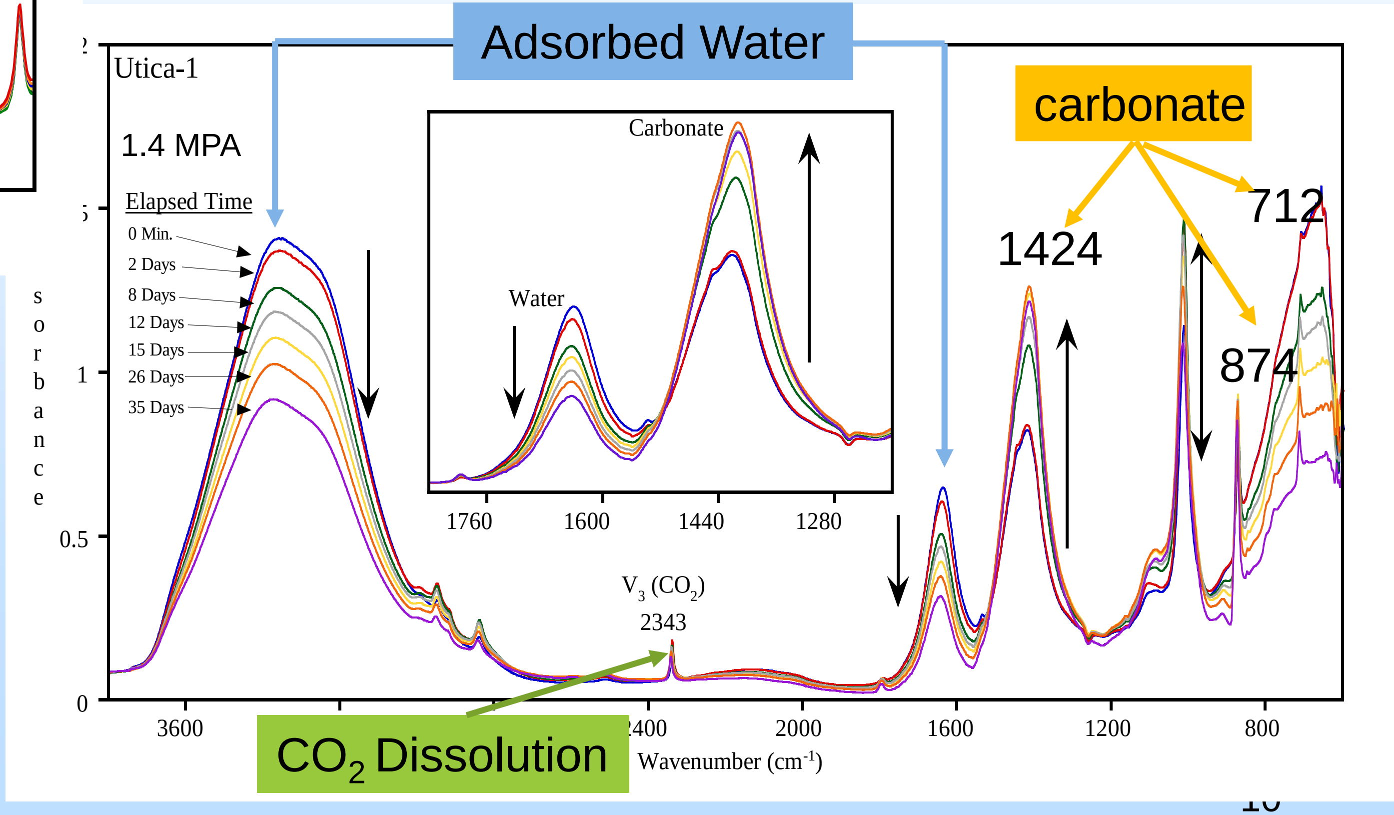
Utica Shale (US-1)

Results: Infrared Spectroscopy of Changes in Carbonate Chemistry



CO_2-Shale

- Overall - intensity of the carbonate bands increased with pressure
- Buffering observed



CO_2-Fluid-Shale

- Indicate carbonate formation and dissolution and mineral dissolution
- Buffering occurring

Results: Scanning Electron Microscopy of Utica Shale

- *Long-term effects of carbon dioxide and fluid remaining in the subsurface*
- *Changes in porosity are observed after reaction with CO_2 and fluid*

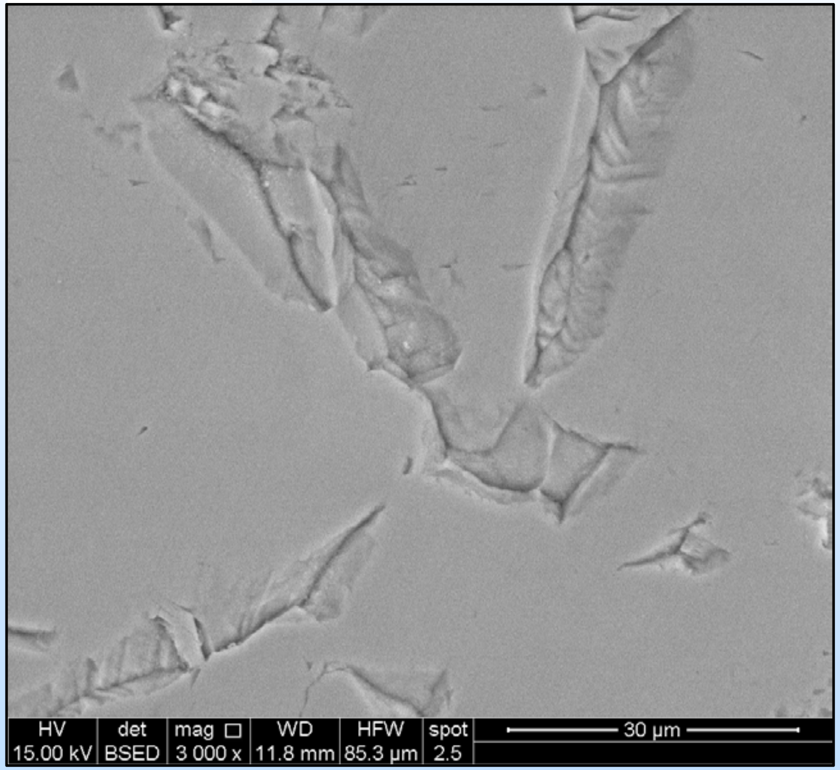

Fuel

Full Length Article

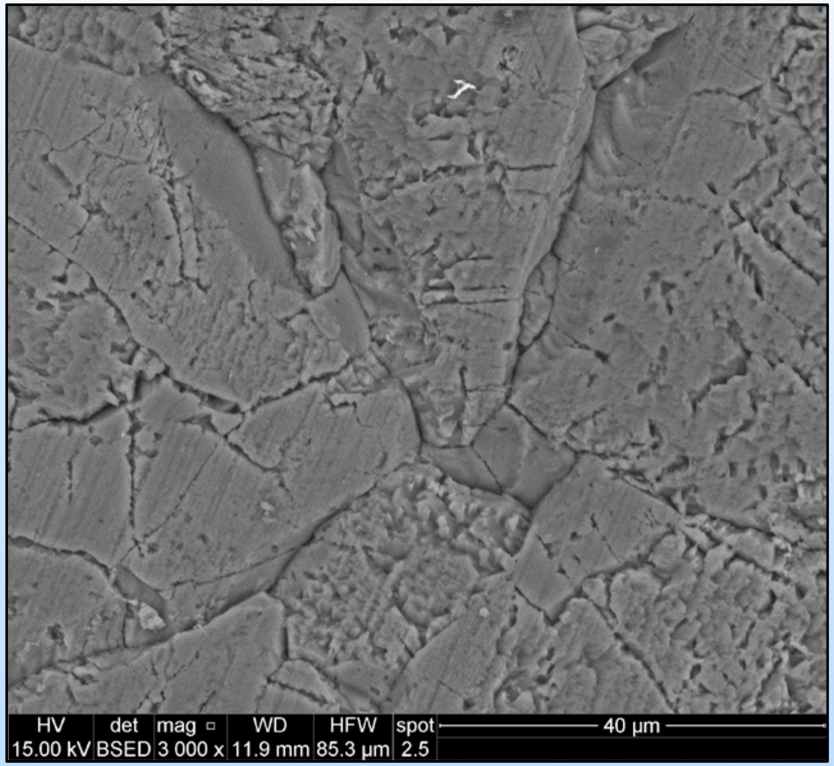
Quantifying dry supercritical CO_2-induced changes of the Utica Shale

Sean Sanguinito, Angela Goodman, Mary Tkach, Barbara Kutchko, Jeffrey Culp, Sittichai Natesakhawat, Jim Fazio, Isis Fukai, Dustin Crandall

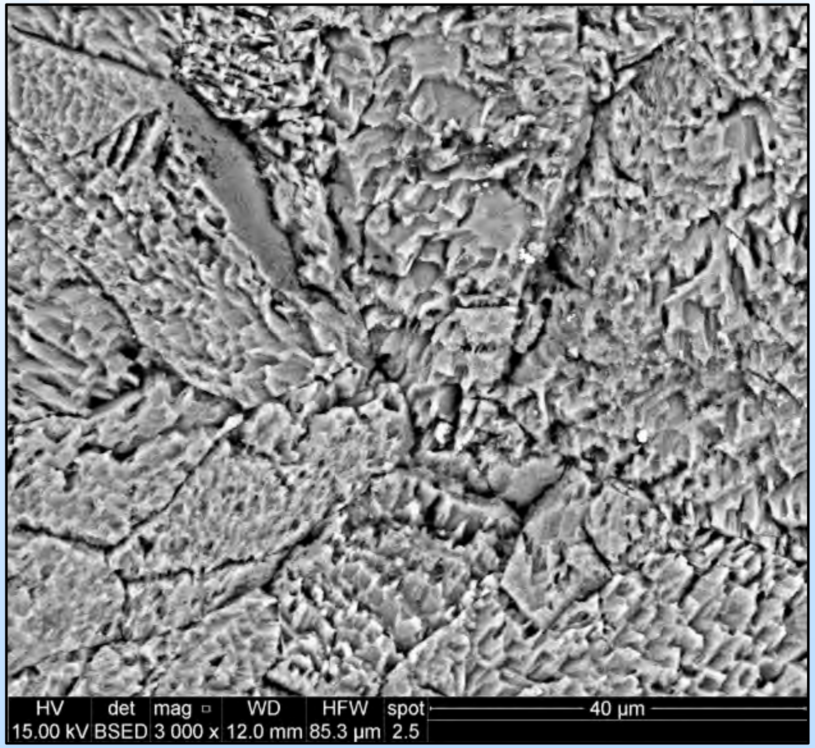
BEFORE



AFTER with CO_2



AFTER with CO_2 and Fluid



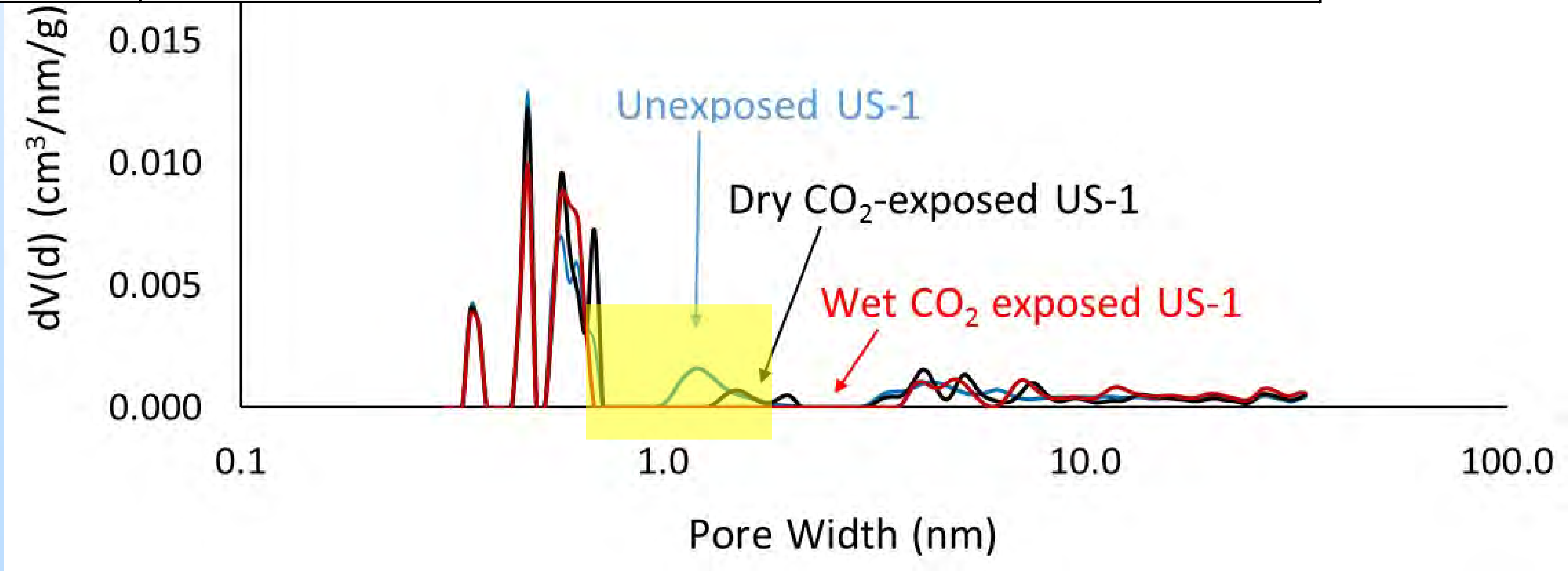
Mineral dissolution and etching was observed

Potential to alter flow pathways and impact hydrocarbon production

Results: BET surface area and pore size analysis of Utica Shale

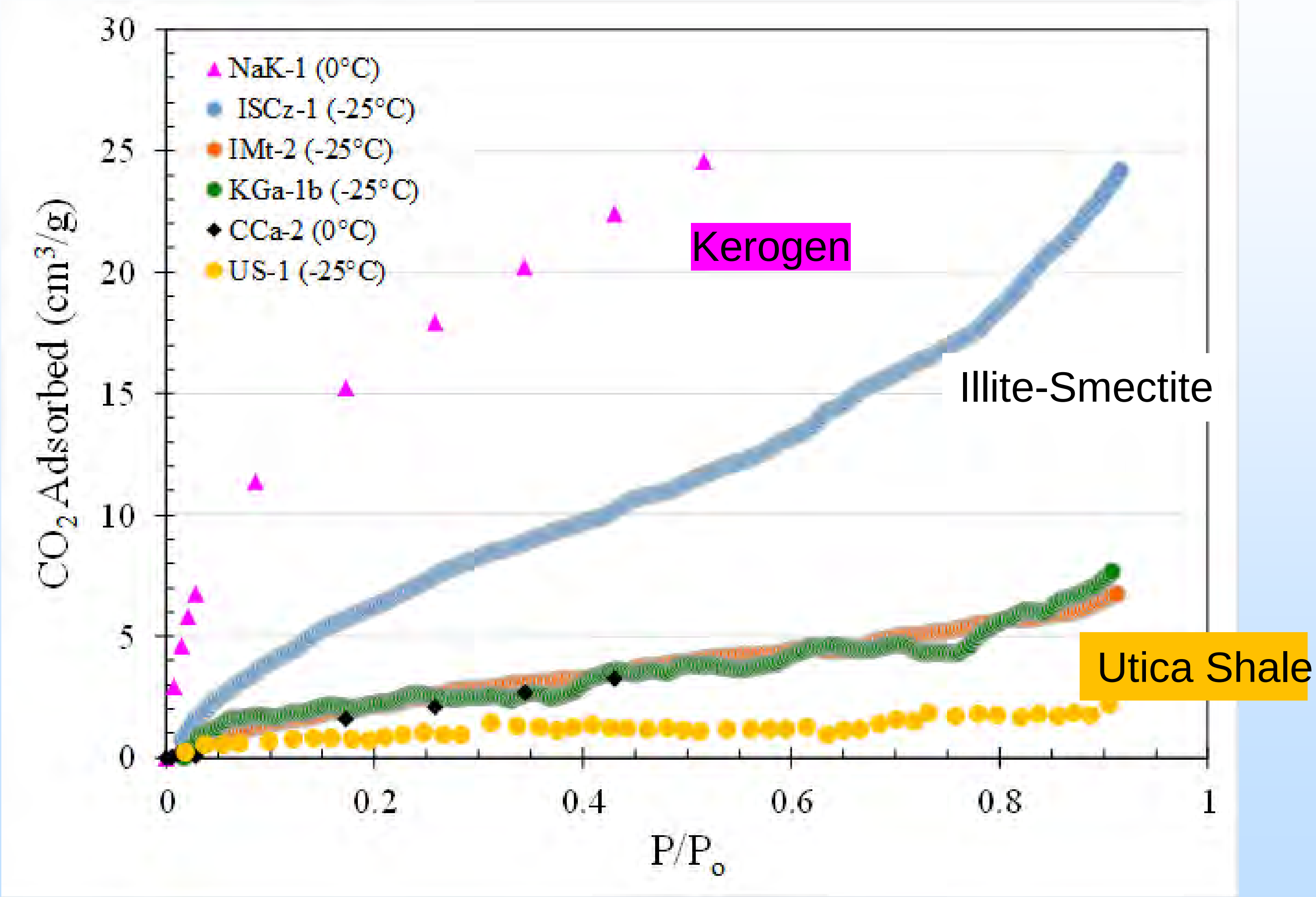
	Unexposed	CO2-exposed	Wet CO2-exposed
Sample amount (g)	0.3030	0.3042	0.3091
BET surface area (m^2/g)	6.8	6.3	5.7
Micropore surface area (m^2/g)	1.4	0.4	0.0
Micropore volume from N2-77K (cm^3/g)	0.00071	0.00030	0.00000
Ultramicropore volume from CO2-273K (cm^3/g)	0.00127	0.00141	0.00127
Total micropore volume (cm^3/g)	0.00197	0.00171	0.00127
Mesopore volume (cm^3/g)	0.01177	0.01239	0.01539
Fitting error for N2-77K (%)	0.570	0.978	1.553
Fitting error for CO2-273K (%)	0.179	0.257	0.255

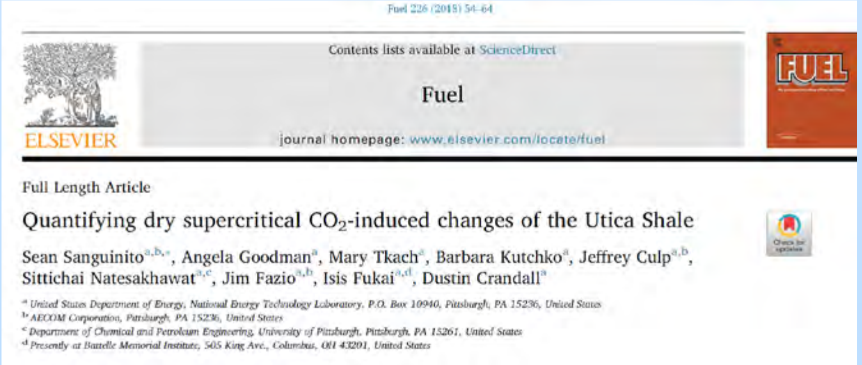
- Micropore surface area and volume decreased significantly after CO_2 exposure, possibly altering overall permeability and fracture networks



Results: Quantitative CO_2 Adsorption isotherms for Utica Shale

- Isotherms are similar to the BET isotherms
- Filling of micro-pores at low pressure followed by meso-pores
  - Sharp initial uptake of ~ 1 cm³/g CO_2 in the lower P/P_0 range of the isotherm followed by a shallow positive slope over the remainder of the isotherm.
- Individual components show greater uptake than shale
  - Constituents inaccessible even when finely ground?
- Significant uptake of CO_2 by kerogen
  - Higher fraction of micropores favorable for CO_2 interaction




Fuel 226 (2018) 54–64

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Quantifying dry supercritical CO_2-induced changes of the Utica Shale

Sean Sanguinito[a,b,*], Angela Goodman[a], Mary Tkach[a], Barbara Kutchko[a], Jeffrey Culp[a,b], Sittichai Natesakhawat[a,c], Jim Fazio[a,b], Isis Fukai[a,d], Dustin Crandall[a]

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[b] AECOM Corporation, Pittsburgh, PA 15236, United States
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[d] Presently at Battelle Memorial Institute, 505 King Ave., Columbus, OH 43201, United States

Accomplishments to Date

– Task 17.0 CO_2-Shale Interactions- Macroscopic

- Publication of detailed literature review of CO_2/shale interactions to guide future research.
- Fundamental understanding of swelling behavior examined from MD simulations and laboratory experiments.
- Development of faster techniques to measure permeability of low permeability shales.
- Examine and upscale pressure corrosion relationships relevant to shales as CO_2 seals.

– Task 18.0 CO_2-Shale Interactions- Microscopic

- Quantified interactions between CO_2, and fluid with Utica and Marcellus Shale.
  (Sanguinito et al, *Quantifying dry supercritical CO_2-induced changes of the Utica Shale, **Fuel**, 2018, 54-64)*
- Beginning measurements to understand changes in dynamic conditions.

Lessons Learned

– Some take away points from the literature review –

1 – Mineralogy of shale/mudstone is critical to understanding interactions with CO_2. Clay content, clay type and organic content should be measured when testing.

2 – Chemical interactions vary with time and occur over long-durations. We're not doing a good job on long term testing in the laboratory.

3 – Water content influences sorption and swell. Laboratory content and *in-situ* content should be understood to provide context to presented results.

4 – Micro-fabric of shale influences and controls CO_2 reactions. Laboratory testing will always incur some disturbance; understanding and minimizing this is important.

5 – Lab-scale swell tests with CO_2 indicate minor deformation (a couple of percent), but clay mineral layer spacing swell is shown up to 60%. More work linking these scales is required over longer exposure periods.

6 – CO_2 sorption in shales does not follow typical Langmuir or BET isotherms at higher pressures (>5 MPa). Increased sorption up to pressures ~ 7 MPa, but decreases substantially after ~10 MPa.

7 – Fracture dynamics with CO_2 complex and poorly understood. Channeling, dissolution, and the impact of surface alteration affect flow properties. Flow velocity and exposure duration play an important role in this response.

8 – Near-well vs. far-field environments drastically different. Dry out may occur near to injection point and induce shrinkage. Carbonic acid far-field will dominate reactions. Chemical interactions need field studies to identify these boundaries.

Synergy Opportunities

We are very happy to utilize the skills and resources at NETL RIC to further the mission(s) of FE across portfolios. The number of ongoing collaborative studies is numerous, and if you identify places where we can help with your studies, please let us know.

Figure 1. Toshiba Aquilion™ RXL medical CT

Figure 4. North Star Imaging M-5000 industrial CT scanner.

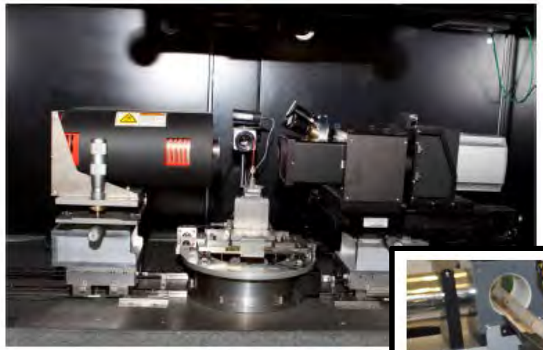


Figure 7. ZEISS Xradia Micro-CT s

Figure 9. Multi-sensor core logging unit.

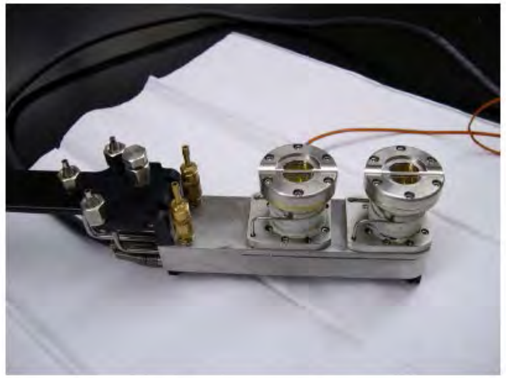


Figure 12. High-temperature/high-pressure in situ diffuse reflectance accessory.

Task 18.0 CO_2-Shale Interactions- Microscopic

Pursuing SANS/USANS measurements with NIST to further probe pore changes at the micro and nano scale

Project Summary

Task 17.0 CO_2-Shale Interactions- Macroscopic

- Comprehensive literature review of CO_2/shale interactions published.
- MD determined excess adsorption isotherms for single-component carbon dioxide and methane show that carbon dioxide demonstrates greater affinity to the illite surface.

Task 18.0 CO_2-Shale Interactions- Microscopic

- Changes in pores are occurring on the micron (opening) and nano (closing) scale after reaction with CO_2 and fluid
- Further investigate pore changes to understand possible alteration of overall permeability and fracture networks

Appendix

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

Benefit to the Program

Task 17.0 CO_2-Shale Interactions- Macroscopic

- **Carbon Storage Program Major Goals**
  - Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness.
  - Support industry's ability to predict CO_2 storage capacity in geologic formations to within ±30 percent.
- **Project Benefits Statement:**
  - Publication of detailed literature review of CO_2/shale interactions to guide future research.
  - Fundamental understanding of swelling behavior examined from MD simulations and laboratory experiments.
  - Development of faster techniques to measure permeability of low k shales.
  - Examine and upscale pressure corrosion relationships relevant to shales as CO_2 seals.

Task 18: CO_2-Shale Interactions – Microscopic

- **Carbon Storage Program Major Goals**
  - Develop and validate technologies to ensure for 99 percent storage permanence.
  - Develop technologies to improve reservoir storage efficiency while ensuring containment effectiveness.
  - Support industry's ability to predict CO_2 storage capacity in geologic formations to within ±30 percent.
- **Project Benefits Statement:**
  - Determine how CO_2 and fluid induced alterations of Marcellus, Utica, Mancos, Eagleford, and Barnett shale affect flow pathways in terms of precipitation, dissolution, and pore space alteration.
  - Identify key properties of shale formations (carbonate rich vs silicate rich) at the nano- and micro-scale needed for quantifying CO_2 storage and seal activities.

Project Overview

Goals and Objectives

Task 17: CO_2-Shale Interactions – Macroscopic

- **Objective:** The product of this work is to deliver a literature review of CO2/shale interactions and a novel full immersion pulse decay device that measures shale properties under stressed conditions. The objective of this task is to develop an understanding of the interaction of CO2 with shale. Direct measurements of shale properties under stressed conditions and analysis of interactions of fractured shale with CO2 are the primary thrusts of this project.

- **Benefit:** Shale formations are widespread throughout the United States and understanding how they could be properly used in a national storage strategy is important. Development of techniques to rapidly measure shale properties, identification of shale mineralogy that will interact poorly with CO2 and understanding of how shale could fracture under low consistent stresses will all directly benefit geologic CO2 storage efforts.

- **Challenges:** Several R&D challenges exist for the development of CO2/shale interactions. As identified in a comprehensive literature review of CO2/shale interactions (Lindner 2017) there is wide variability in the reported behavior of shale and CO2. In part, a poorly defined understanding of what constitutes a shale is at fault; mineralogical content as opposed to organic content in the context of gas plays. Focusing efforts on fundamental mineralogical descriptions of shale instead of shale play names should alleviate this challenge. A second challenge is replication of subsurface conditions: (1) shale acquired from depth has been altered by the removal of stresses and fluids and (2) shale acquired from outcrops has undergone long term changes due to its uplift and exposure. By combining in situ conditions for laboratory testing and simulating subsurface environments best practices will be used to overcome these challenges.

- **Approach:** Coupled experimental and numerical modeling of phenomena.

Project Overview

Goals and Objectives

Task 18: CO_2-Shale Interactions – Microscopic

- Task Technical Approach and Project Relevancy (PI: Angela Goodman)

- Objective: Quantify CO_2 interactions with shale at the nano- and micro-scale and provide quantitative inputs at the macro-scale to understand flow properties and inputs for reservoir simulations of large-scale storage activities in shale.
- Benefit: Reaction of CO_2 with in situ fluids, fracturing fluids, and reactive shale interfaces may generate new reactive surfaces or intermediates that may alter the properties of the formation. A fundamental understanding of the reactivity of CO_2 with shale and fluid interfaces will help in identifying how storage in shale formations plays a role in CCS activities.
- Challenges:
  - Fundamental research examining the geochemical interactions of CO_2 and fluids with shale is limited.
  - Limited understanding of how reaction of CO_2 with in situ fluids, fracturing fluids, and reactive shale interfaces may generate new reactive surfaces or intermediates that may alter the properties of the formation.
- Approach:
  - Complete experimental analysis of CO_2, fluid, and shale interactions at the nano- and micro-scale for a suite of shales suitable for potential CO_2 storage activities.
  - Relate shale attributes to CO_2 storage potential.
  - Scale results observed at the nano- and micro-scale to the macro-scale to understand flow properties and inputs for reservoir simulations of large-scale storage activities in shale.

Organization Chart

Research Theme: Shales: Characterizing Interactions of CO_2 with Shale for Potential Storage Needs and Seal Integrity

- **Task 17.0 CO_2-Shale Interactions- Macroscopic**

Team Members: Johnathan Moore, Sarah Brown, Ernest Lindner, Michael Hannon, Yael Tucker, Leebyn Chong, Eugene Myshakin, Guanyi Lu, Andrew Bunger, Dustin Crandall

- **Task 18.0 CO_2-Shale Interactions- Microscopic**

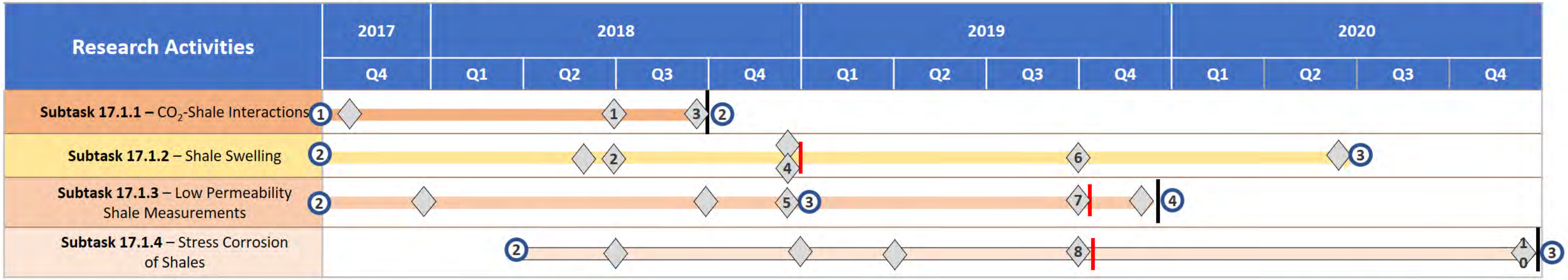
Team Members: Angela Goodman, Sean Sanguinito, Barbara Kutchko, Jeff Culp, Mary Tkach, Sittichai Natesakhawat, Dustin Crandall, Patricia Madden

Gantt Chart

Timeline Overview – Task 17

CO_2-Shale Interactions - Macroscopic

NATIONAL ENERGY TECHNOLOGY LABORATORY



Milestones

Numbered milestones in above image are listed in detail in the following subtask level Gantt charts.

Go / No-Go

Please see subtask Gantt charts for details.

Impact

Key Accomplishments/Deliverables	Value Delivered
• a novel permeability measurement technique (patent pending) developed, • simulations of CH_4/CO_2 interactions with clays performed to understand sorption, • CO_2 has been observed to reduce fractured shale permeability under in situ conditions, • a comprehensive, literature review of CO_2/H_2O/shale interactions has been published describing uncertainties in the current basic understanding of shale.	• Direct measurements of shale properties under stressed conditions and analysis of interactions of fractured shale with CO_2 provide stakeholders with an improved understanding of how shale will react under conditions expected in storage applications.

U.S. DEPARTMENT OF ENERGY

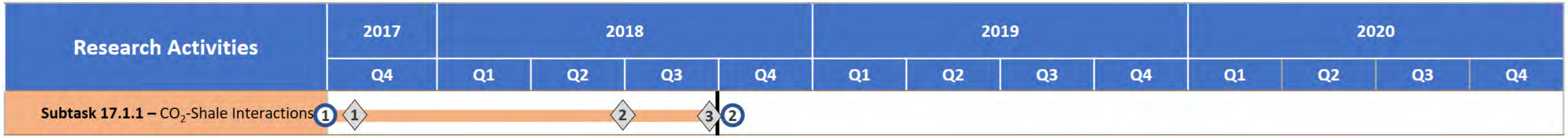
Chart Key
TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Gantt Chart

Timeline Overview – Sub-Task 17.1.1

NATIONAL ENERGY TECHNOLOGY LABORATORY

CO_2-Shale Interactions



Milestones

1. Publication of detailed literature review of CO_2 and H_2O interactions with shale. (Completed - November 2017)
2. Presentation of literature review at a scientific conference. (June 2018)
3. Submission of peer-reviewed publication describing unknowns of CO_2 and H_2O interactions with shale. (September 2018)

Go / No-Go

Not applicable, project ending in 2018.

Impact

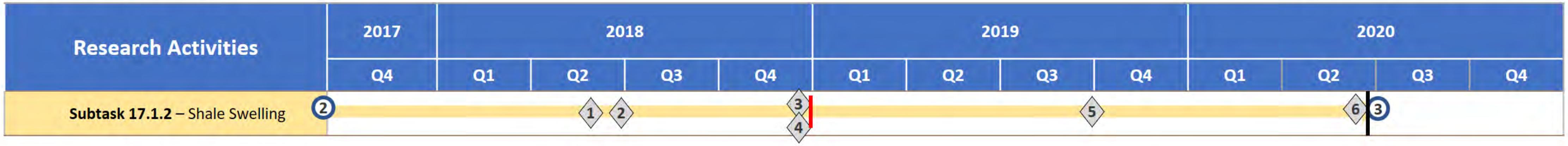
Key Accomplishments/Deliverables	Value Delivered
2016-2017: Literature review of CO_2 and water interactions with shale • Lindner, E. *Review of the Effects of CO_2 on Very-Fine-Grained Sedimentary Rock/Shale – Part III: Shale Response to CO_2; NETL-TRS-11-2017; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017; p 228.* • Lindner, E. *Review of the Effects of CO_2 on Very-Fine-Grained Sedimentary Rock/Shale – Part II: Clay Mineral & Shale Response to Hydration; NETL-TRS-10-2016; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017; p 68.* • Lindner, E. *Review of the Effects of CO_2 on Very-Fine-Grained Sedimentary Rock/Shale – Part I: Problem Definition; NETL-TRS-1-2016; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017; p 68.*	• There has been decades of research in multiple disciplines that examine the interactions of CO_2, H_2O and shale; even with this research there are some knowledge gaps in how CO_2 and shale will interact during geologic carbon storage. By performing a detailed literature review across disciplines, we are illuminating the most relevant research problems that remain. • To date, a three part literature report of over 350 pages was completed, but this needs to condensed to reach a broader audience. Delivering this report in a consumable fashion will enable the value of these reports to be utilized.

Gantt Chart

Timeline Overview – Sub-Task 17.1.2

NATIONAL ENERGY TECHNOLOGY LABORATORY

Shale Swelling



Milestones

1. EERC Collaborative tests complete. (June 2018)
2. Molecular simulations of CH4/CO2 and clay under different water saturations complete. (July 2018)
3. Molecular simulations of CH4/CO2 retention in kerogen under dry conditions and with residual water complete. (December 2018)
4. Paper with a tentative title: "Molecular modeling of ternary CO2-CH4-H2O mixture adsorption on illitic clay surfaces in shales" submitted to a peer-reviewed international journal. (December 2018)
5. Three fracture flow experiments complete. (September 2019)
6. Six fracture flow experiments complete and relationship between shale content and fracture permeability developed. Submission of results to peer reviewed journal. (June 2020)

Go / No-Go

December 2018 – Are there cases tested with molecular dynamics simulations at representative GCS conditions where the amount of swelling would indicate that fracture closure likely?

Impact

Key Accomplishments/Deliverables	Value Delivered
<u>2017</u>: Through collaborative studies with the EERC, CO_2 permeability tests in fractured and unfractured Bakken shale have been performed. The results are mixed. Fractured shale permeability has been shown to decrease, but no consistent trend or observable deformation of structure has been observed. Unfractured shale exposure to CO_2 differs from behavior observed at EERC.	• The interaction of CO_2 and shale can be complex, and a basic understanding of how various shale formations will interact as seals or potential reservoir formations must be described in order to provide reliable long term estimates of storage potential

Chart Key

\# TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

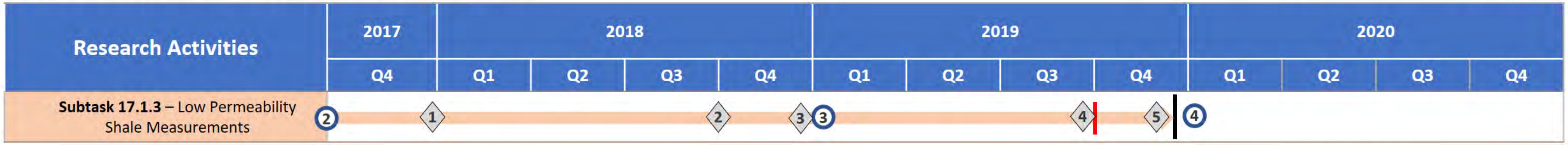
U.S. DEPARTMENT OF ENERGY

Gantt Chart

Timeline Overview – Sub-Task 17.1.3

NATIONAL ENERGY TECHNOLOGY LABORATORY

Low Permeability Shale Measurements



Milestones

1. Compare and contrast traditional pulse decay with high resolution steady state gas permeability measurements. (Completed - December 2017)
2. Peer reviewed manuscript of modification to high-resolution steady-state permeability measurements with low downstream pressure submitted to journal. (September 2018)
3. Assemble a bench scale full immersion pulse decay device and shakedown apparatus. Compare/contrast measurements to traditional pulse decay. (December 2018)
4. Develop a full immersion pulse decay permeability technique for fractured shales. Examine this technique numerically to confirm measurements can be obtained, and perform shakedown on experimental prototypes. (June 2019)
5. Commercialization of full immersion pulse decay technique with external partner. (December 2019)

Go / No-Go

September 2019 - Test full immersion pulse decay permeability technique for fractured shales experimentally and show match numerical expectations. If successful continue towards commercialization with partners.

Impact

Key Accomplishments/Deliverables	Value Delivered
<u>2017</u>: Numerical simulations and preliminary experimental measurements have shown that the full immersion pulse decay technique (patent pending) is able to measure shale permeability faster than any other reliable method on the market. Discussions with industry and applications for technology commercialization funds are underway.	• Shale permeability measurements that are accurate, can be obtained efficiently, and with a process that is openly described will provide greater confidence in measurements for stakeholders and regulators that need to quantify carbon storage seal integrity.

Chart Key

TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Gantt Chart

Timeline Overview – Task 17.1.4

NATIONAL ENERGY TECHNOLOGY LABORATORY

Stress Corrosion of Shales

Research Activities	2017	2018				2019				2020			
	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Subtask 17.1.4 – Stress Corrosion of Shales													

Milestones

1. Modifications to existing CT and flow systems approved for stress corrosion testing. (June 2018)
2. Successful test of shale microstructure cracking observed in laboratory due to stress corrosion. (December 2018)
3. Complete parametric study demonstrating acoustic emission and specimen failure rate at various levels of stress, fluid pressure, and with various fluid/rock combinations. (December 2018)
4. Observe microstructural changes during stress corrosion cracking and complete core-scale experiments. (September 2019)
5. Implement geomechanically-coupled numerical simulations and benchmark to core-scale experiments. (December 2020)

Go / No-Go

September 2019 – Successful observation of microstructural changes due to stress corrosion cracking with laboratory experiments.

Impact

Key Accomplishments/Deliverables	Value Delivered
2017: New start in 2018. Prior work in mechanical deformation of rocks in the Carbon Storage, NRAP, and Onshore Unconventional FWPs, using the computed tomography scanner facility at NETL and stress corrosion measurements in shale by personnel at the University of Pittsburgh will be leveraged to accomplish this task.	• The goal of the proposed research is to observe and quantify the impact of stress corrosion on shale permeability. Stress corrosion is the time dependent failure due to stresses that are insufficient to instantaneously break the rock. • Development of a coupled numerical model to account for this behavior, benchmarked on experimental observations, will enable greater seal characterization for long term stress behavior of shale sealing formations.

U.S. DEPARTMENT OF ENERGY

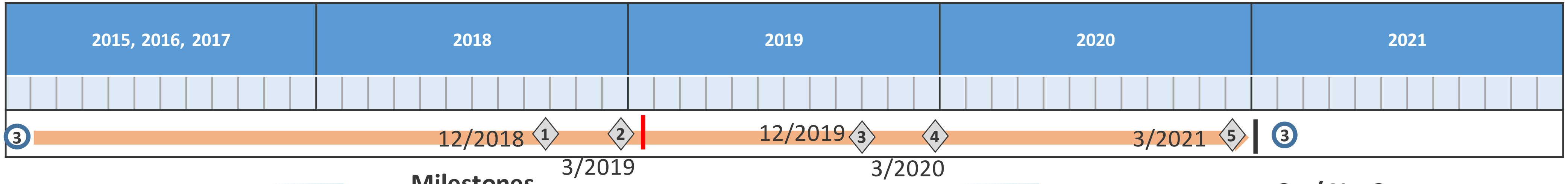
Chart Key

TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Gantt Chart

Task 18: Project Timeline Overview

CO_2-Shale Interactions- Microscopic (PI: Angela Goodman)



Milestones

1. M.8.1 – Quantify the geochemical impact of CO_2 and fluid interactions on Utica and Marcellus shale at the nano- and micro-scale.
2. Quantify the potential changes in flow properties of Utica Shale that has been modified with CO_2 and fluid.
3. Quantify the geochemical impact of CO_2 and fluid interactions on Barnett, Eagleford, and Mancos Shale at the nano- and micro-scale.
4. Quantify the potential changes in flow properties of Barnett, Eagleford, and Mancos Shale that has been modified with CO_2 and fluid.
5. Initial database of shale properties at the nano-, micro-, and macro-scale needed for quantifying CO_2 storage potential.

Go / No-Go

Dependent upon quantitative results with the Utica and Marcellus samples

Impact

Key Accomplishments/Deliverables	Value Delivered
2015: Quantified CO_2 interaction with Na+ exchanged montmorillonite **2016**: Effects of short and long term geochemical reactions of fracturing fluid with Marcellus Shale and Huntersville Chert **2017:** Quantified interactions of CO_2 with Utica Shale	• Determine how CO_2 and fluid induced alterations of Marcellus, Utica, Mancos, Eagleford, and Barnett shale affect flow pathways in terms of precipitation, dissolution, and pore space alteration. • Identify key properties of shale formations (carbonate rich vs silicate rich) at the nano- and micro-scale needed for quantifying CO_2 storage and seal activities

Chart Key

TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

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Task 18.0 **CO_2-Shale Interactions- Microscopic**

Estimating the Prospective CO_2 Storage Resource and Quantifying CO_2 Induced Changes of Shales

In-situ Surface Chemistry, Surface Topography, Surface Area, and Porosity

2013 Feature relocation microscopy of Coal **Fuel** *(cited >24 times) (Recognized by Renewable Energy Global Innovations Series) (Impact Factor of 4.6)* [2]

2014 Initial Methodology for Assessment of Shale Systems **Energy Procedia** *(cited >12 times) (Impact Factor of 1.1)* [3]

2015 CO_2 interaction with Na+ exchanged montmorillonite **Applied Clay Science** *(cited >17 times) (Impact Factor of 2.8)* [5]

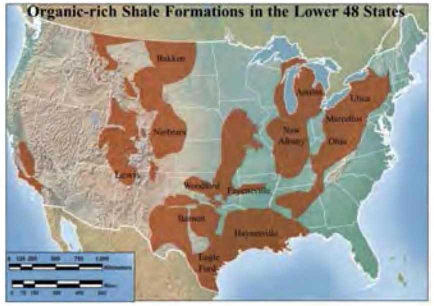
2016 Methodology for Assessment of Shale Systems **Int. J. Greenhouse Gas Control** *(cited >17 times) (Impact Factor of 3.7)* [7]

2018 CO_2 Interactions with Utica **Fuel** *(Impact Factor of 4.6)* [9]

2018 Development of Shale Storage Efficiency Factors , **Int. J. Greenhouse Gas Control** *(Impact Factor of 3.7)* [10]

2019 Investigate pore changes with SANS

2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019



2015 Experimental Characterization of Marcellus Shale **NETL-TRS-1-2015** [4]

2016 Investigation of factors affecting the interaction of CO_2 and CH_4 Appalachian Basin **J. Uncon. Oil and Gas Res.** *(cited >5 times) (Impact Factor of 2.4)* [6]

2016 Characterization of Marcellus Shale and Huntersville Chert **Fuel** *(cited >12 times) (Impact Factor of 4.6)* [8]

2018 Role of water on CO2 interactions with Utica *in progress*

2018 Role of water on CO2 interactions with Marcellus *in progress*

2019 Role of water on CO2 interactions with Eagleford, Mancos, and Barnett *in progress*

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