A Coupled Geomechanical, Acoustic, Transport and Sorption Study of Caprock Integrity in Carbon Dioxide (CO2) Sequestration Project Number: DE-FE-0023223 Manika Prasad, Colorado School of Mines

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# **Presentation Outline**

- Objectives and motivation
- Experimental Updates
  - Mineralogy Control on CO2 Accessibility on Micropores of Shales for CCUS Application
  - 2. Acoustic Measurements with CO2 saturation
  - 3. NMR studies of CO2-saturated brine
  - 4. Direct-shear experiments on shale permeability
- Accomplishments to date
- (Near-) Future work

#### Objectives

- Determine the behavior of intact and fractured caprocks when exposed to supercritical CO<sub>2</sub> at elevated pressures
- Quantify adsorption and acoustic properties of shales with sorbed CO<sub>2</sub>
- Provide framework for monitoring, verification and accounting (MVA) efforts of CO<sub>2</sub> sequestration and its effect on caprock

#### (1) CO2 Accessibility in Shale Micropores

- Gas adsorption to characterize nanopores
- Samples Used
- Analysis methods and Results
- Application to CO2 storage

#### Motivation

Storage capacity estimates:

- Economically feasible CO<sub>2</sub> capacity of Utica + Marcellus + Antrim + Devonian Ohio ≈ 50 Gt (Godec et al, 2014)
- Theoretical CO2 capacity of Utica = 10 Gt (Godec et al, 2014)

– 80% storage capacity by sorption (Ambrose et al, 2012)

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#### Pore characterization methods



Kinetic diameters:  $CO_2 (0.33 \text{ nm}) < N_2 (0.36 \text{ nm})$ . We use  $CO_2$  to access smaller micropores than those accessible to  $N_2$ 

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#### Previous studies

- Recommended practice (IUPAC 1985 & IUPAC 2015)
- Adapted N<sub>2</sub> adsorption to characterize shales, also compared to WIP (Kuila, 2013)
- Limited accessibility for  $N_2$  in immature oil window samples due to blockage by bitumen (Saidian, 2015)
- Limited pore accessibility dependent on mineralogy and gas type; preferential  $CO_2$  uptake in OM (Kumar, 2016)
- In presence of water, preferential uptake of CO<sub>2</sub> only in OM not in clay minerals (Kumar, 2016)

•  $N_2$  - and  $CO_2$ - derived PSD on shales with 2-21% TOC

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## Samples Used

- Standard clay samples benchmarking
   Illite, Illite-smectite, Na-rich montmorillonite
- Producing shales in North America
  Bakken (7-21% TOC), Utica (2% TOC) and Niobrara (3-5% TOC)
- Analog to caprock of CO<sub>2</sub> storage site in the Norwegian North Sea
  - Agardhfjellet (12% TOC), Rurikfjellet (2% TOC)
  - CCS candidates

#### Measured adsorption isotherm



- Diffusional limitations of N<sub>2</sub> molecules in narrow pores
  - Underestimate micropores
- Joewondo and Prasad, 2018

to measure full isotherm

•  $P_0 > 1$  atm

#### TOC controls on micropore volume



**Note:** Opposite trend of  $N_2$ - and  $CO_2$ - derived pore structures; Mudrocks with high TOC have higher  $CO_2$  storage potential

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#### Implications for Storage Capacity

Micropore volume measured in this work Utica = 2E-3 cc/gAgardhfjellet = 11E-3 cc/gAssume micropores are filled with  $CO_2$  $CO_2$  density 0.6 g/cc (30 C, 8 Mpa) (van der Meer 2005) Shale density 2.4 g/cc Calculated CO<sub>2</sub> storage capacity in 1  $m^3$  of shales from this work Utica (2% TOC): 2.8 kg<sub>CO2</sub> Agardhfjellet (12 % TOC): 15.8 kg<sub>CO2</sub> Compare with Godec et al. (2014) for the same area: Average thickness of 150 ft or 45.7 m (Refayee et al. 2016) Theoretical CO<sub>2</sub> capacity of Utica formation 19.7  $Gt_{CO2}$  (this work) and 10  $Gt_{CO2}$  (Godec et al. 2014)

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#### Comparing CO2 and N2- accessible volumes



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#### Surface Area and Clay Content



- OM pores are hydrophobic
- OM pore development starts at the onset of oil window
- Presence of bitumen free OM pores

• Cryogenic  $N_2$  blocked by nano-sized pores in organic matter Kumar, 2016 Center for Rock Abuse

### Preferential sorption of fluids

Preferential sorption of fluids depends on polarity of surfaces





Hydrophilic pores Hydrophobic pores

Quantification of hydrophilic and hydrophobic pores of shales

Kumar, 2016

#### Sorption in shales with water



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#### Sorption in shales with water

In presence of water: Illite pores take up water; CO<sub>2</sub> fills OM pores

#### Illite: Water Imbibed





#### Bakken: Water Imbibed





#### Environmental Scanning Electron Spectroscopy (ESEM)



Center for Rock Abuse

Murugesu, 2018

#### Sorption in Zeolite



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### Waveforms and Velocities with CO<sub>2</sub>



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### Frequency and Velocities with CO<sub>2</sub>



#### Ultrasonic Velocities



Carbonate core

#### Seismic Velocities



### Conclusions

- CO<sub>2</sub>-accessible micropore volume depends on TOC
  - Need to complement  $\mathrm{N}_2$  measurements with  $\mathrm{CO}_2$  for  $\mathrm{CO}_2$  storage capacity
  - CO<sub>2</sub> storage capacity increases with TOC
  - CO<sub>2</sub> storage capacity decreases in presence of water (clay effect)
- Frequency content (seismic attenuation) is sensitive to gas content
- Fluid in micropores depends on mineralogy should be accounted for in seismic inversion

# Synergy Opportunities

- Calibrate rock physics models with partial saturation due to mineralogy – dependent pore volumes and preferential fluid sorptions. Relevance: 4D seismic operations
- Investigate well log NMR signals for changes in fluid signatures versus changes in the rock due to rock –fluid interactions. Relevance: CCUS and Oil & Gas operations
- Joint acoustic –permeability changes with CO<sub>2</sub> before and after shearing. Relevance: caprock changes with stress changes
- Imaging CO2 migration student intern with SINTEF