Utilization and Storage of CO_2 in Unconventional Reservoirs

Project Number 58159 Task 2

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Pacific Northwest National Laboratory

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 12-14, 2014

Presentation Outline

- Program Focus Area and DOE Connections
- Goals and Objectives
- Scope of Work
- Technical Discussion
- Accomplishments to Date
- Project Wrap-up
- Appendix (Organization Chart, Gantt Chart, and Bibliography

Benefit to the Program

- Program goals addressed:
  - Technology development to predict CO_2 storage capacity
  - Demonstrate fate of injected CO_2
- Project benefits statement: This research project conducts modeling and laboratory studies to lower cost and to advance understanding of storing pure CO2 and mixed gas emissions produced from post- and oxy-combustion flue gas in unconventional geologic reservoirs.

Project Overview:
Goals and Objectives

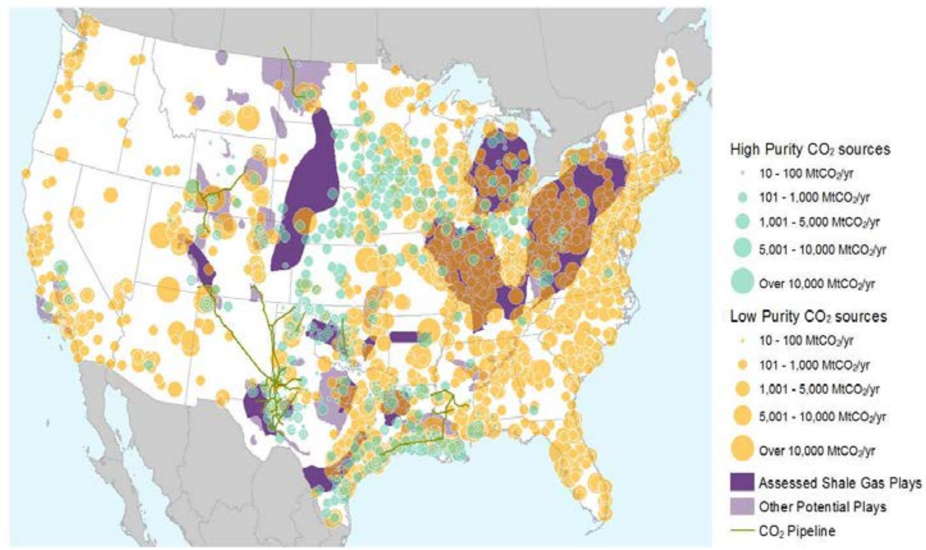
- Goal: Development of geologic storage technology with a near zero cost penalty goal – a grand challenge with enormous economic benefits.
- Objective: Employ a multidisciplinary approach for identifying key sequestration opportunities and for pursuing major research needs in:
  - Identifying R&D needs and pursuing R&D on promising low-cost technologies for utilizing CO_2 and CO_2 containing other constituents in depleted shale gas and shale oil reservoirs.
  - phase behavior and fate and transport of supercritical gas mixtures in fractured geologic formations.
  - casing material studies with water and mixed gas systems
  - development of acoustically responsive contrast agents for enhanced monitoring of injected CO_2.

Project Overview:
Scope of work

- Task 2 – Utilization in Unconventional Reservoirs
  - 2.1 Storage in Depleted Shale Gas Reservoirs
    - Economics of Utilizing CO_2 in Depleted Shale Gas Reservoirs
    - Laboratory Studies
      - Evaluate reaction products, mechanisms, and rate of reactions in the shale reservoirs
      - Distinguish chemical reactivity versus physisorption processes
      - Quantify CH_4/CO_2 adsorption capacities for important shale minerals
      - Quantify effects of solvated water on gas adsorption and desorption processes
    - Molecular Dynamics Modeling
      - Identify possible reactive products and the barriers to such transformations\
      - Compare with experimental measurements to provide mechanistic insight
    - Reservoir Modeling
      - Field scale simulation utilizing CO_2 in a depleted fractured shale reservoir utilizing CO_2
      - Incorporate laboratory findings to optimize methane production
  - 2.2 Casing Materials Studies
    - Evaluating corrosion behavior of stainless steel piping
  - 2.3 Enhanced Monitoring Agents

Costs, Offsetting Revenues, and Deployment Potential of EGR in Gas Shales

- Analysis based upon USGS shale gas resource assessment volumes (OGIP); 27 assessment units in 10 basins
- Total CO_2 storage capacity presented includes:
  - Replacement of initial volume of CH_4 via primary recovery based on USGS estimates of recoverable reserves
  - Displacement of some fraction of CH_4 via CO_2-flood taken from analysis of EGR potential
- ~30 and 50 $GtCO_2$ of storage capacity
- Total incremental recovery ~100-5900 BCM
- Production and storage cost algorithm development

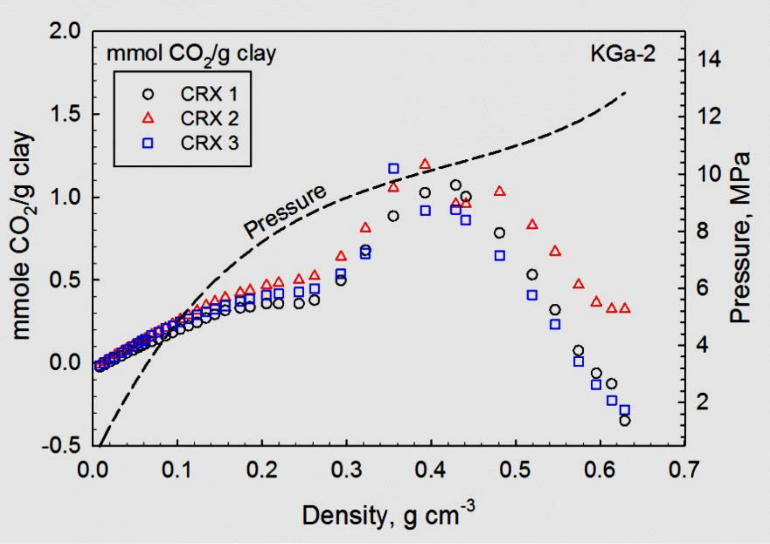


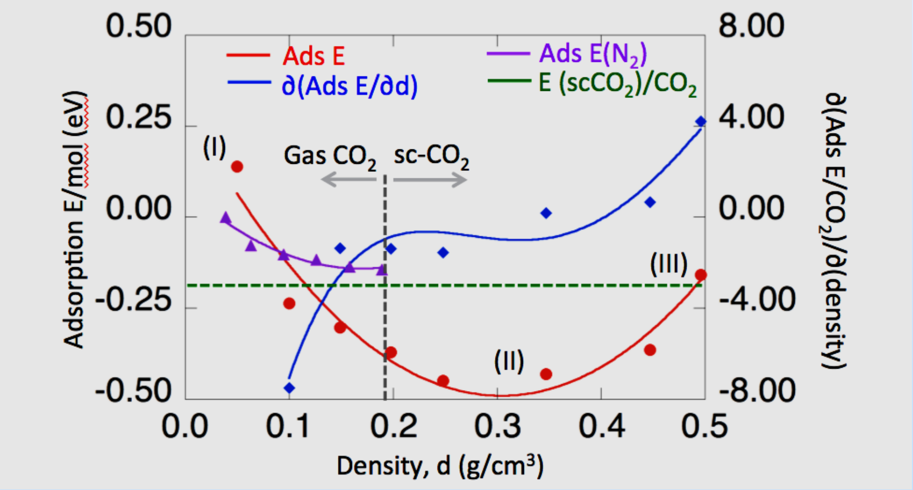
Province	Theoretical CO_2 Storage Resource ($MtCO_2$)		
	Low	Moderate	High
Paradox Basin	932	1,181	1,426
Denver Basin	83	105	127
Permian Basin	2,972	3,766	4,547
Bend Arch-Ft. Worth Basin	2,219	2,812	3,395
Gulf Coast	10,565	13,389	16,166
Anadarko Basin	1,931	2,447	2,954
Arkoma Basin	2,256	2,859	3,452
Michigan Basin	632	801	968
Illinois Basin	321	407	491
Appalachian Basin	10,609	13,445	16,233
TOTAL CAPACITY, GAS SHALES	**32,519**	**41,212**	**49,759**
TOTAL CAPACITY, U.S. EOR PLAYS		**11,943**	
TOTAL CAPACITY, U.S. (NON SHALES)		**3,046,989**	

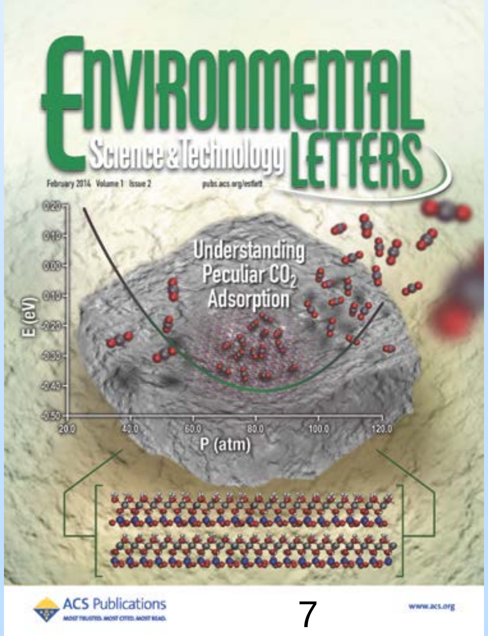
CL Davidson & BP McGrail. 2014. Economic assessment of revenues associated with enhanced recovery and CO_2 storage in gas-bearing shales, IJGGC, submitted.

Fundamental Gas Adsorption Studies

- Gas adsorption isotherms by QCM
  - Use N_2 and He to verify correction factors (i.e. N_2 ~0.2 mmol/g clay)
  - $scCO_2$ adsorption reaches a max (0.9-1.2 mmol CO_2/g clay) near 0.4 g/cm^3 (50°C)
- Molecular Simulations: explaining desorption behavior
- **Implications:** Enhanced reservoir modeling capabilities.



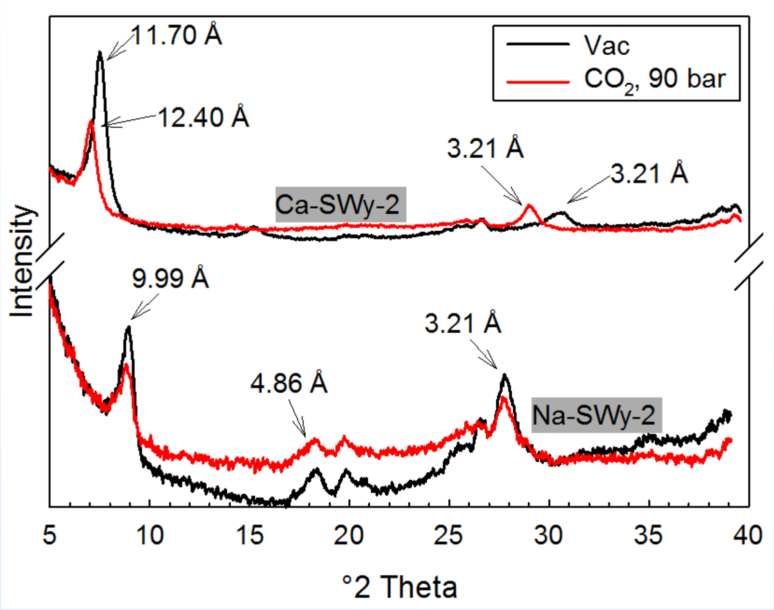


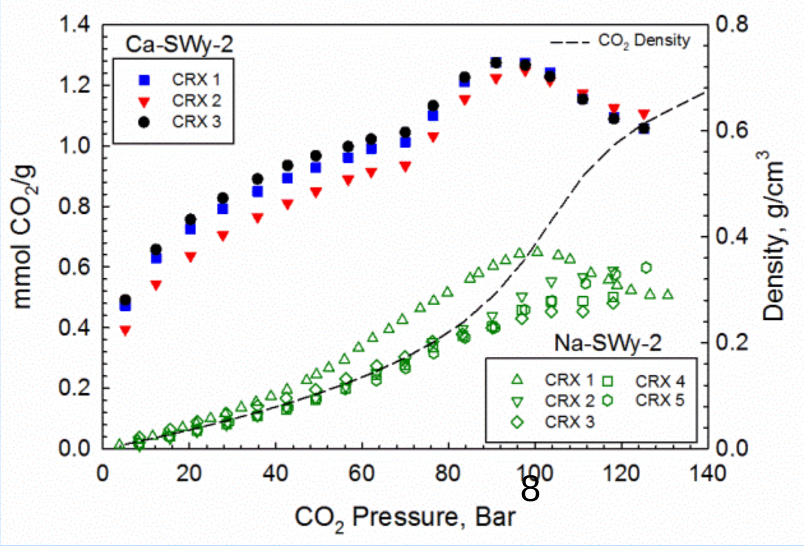


HT Schaef, V-A Glezakou, et al, 2014. “Surface Condensation of CO_2 onto Kaolinite”, ES&T *Letters* ,1(2): 142-145.

Fundamental gas adsorption studies: expanding clays with CO_2

- **Objective**: Measure adsorbed and interlayer concentrations of CO_2 on montmorillonite
- **Pressurized XRD Results:**
  - 0W hydrated Na-SWy-2 is collapsed and does not expand with $scCO_2$
  - 1W hydrated Ca-SWy-2 expands in the presence of pressurized CO_2
- **QCM Results:** CO_2 concentrations on Ca-SWy-2 > Na-SWy-2; the difference can be assigned to the interlayer of Ca-SWy-2.
  - Highest concentration interlayer CO_2 is estimated at ~0.81 mmol/g clay.
- **Implications:** Maximizing CO_2 adsorption and managing reservoir fluid transport properties is possible through designing injection strategies.

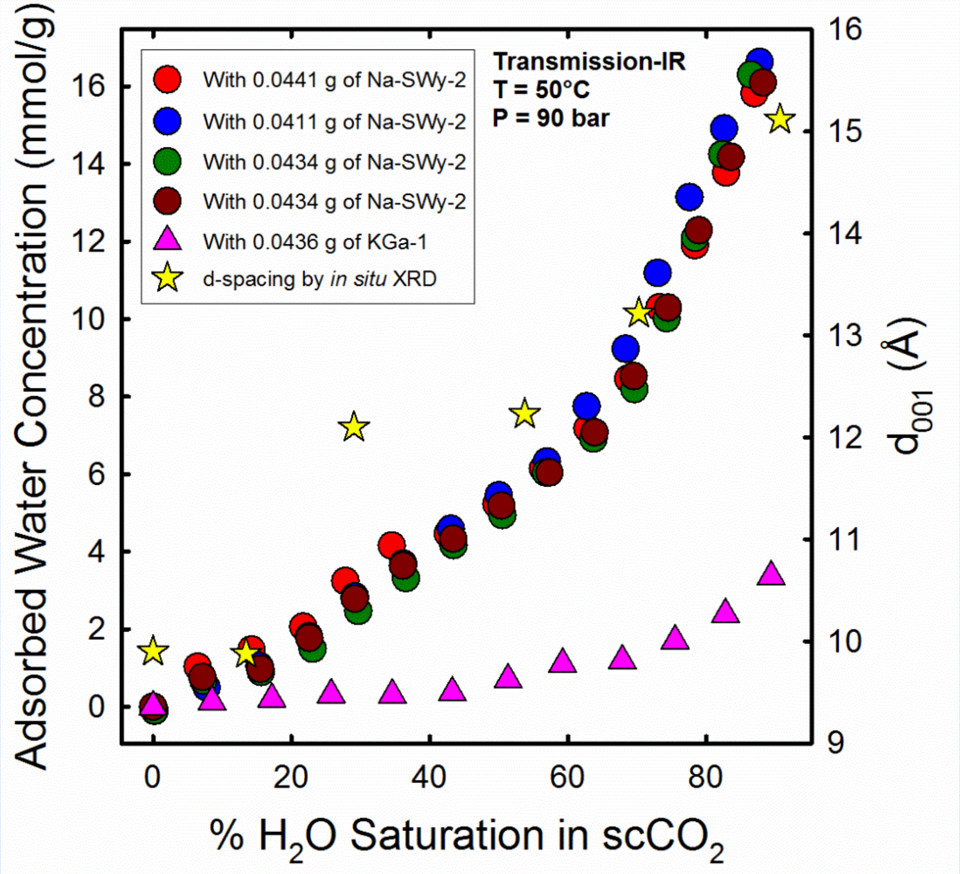




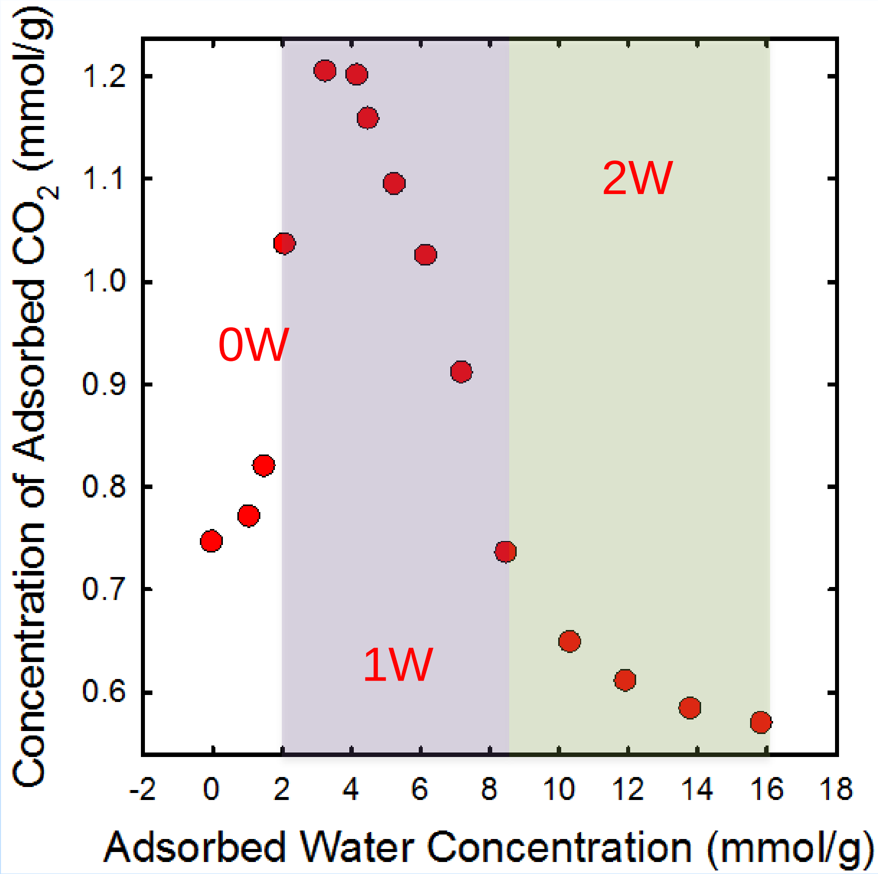
HT Schaef, JS Loring, et al., **2014**. Competitive Sorption of CO_2 and H_2O in 2:1 Layer Phyllosilicates, GCA, **submitted**.

Fundamental gas adsorption studies: H_2O and CO_2 adsorption on Na-SWy-2

Adsorbed H_2O



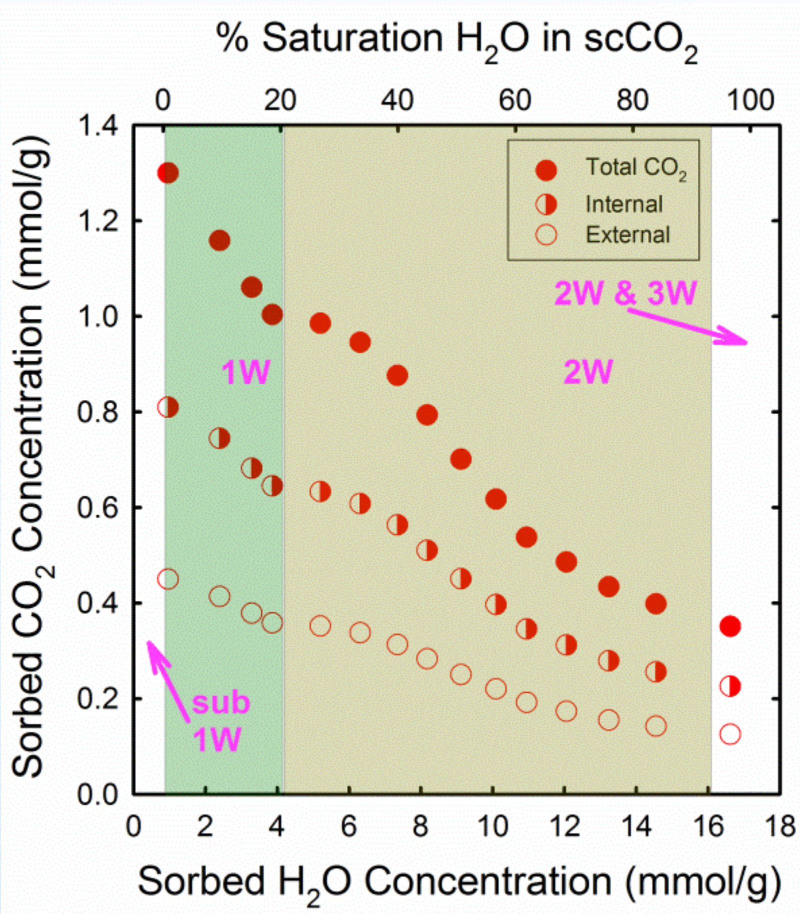
Adsorbed CO_2



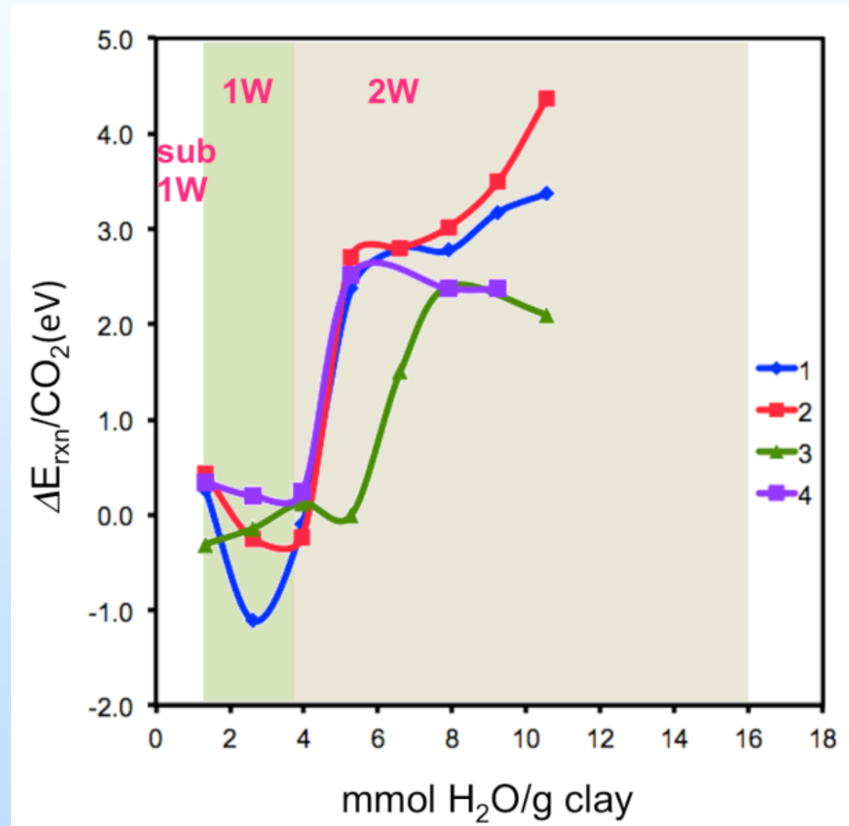
JS Loring, et al., **2014**. *In situ* study of CO_2 and H_2O partitioning between Na-montmorillonite and variably wet supercritical carbon dioxide. *Langmuir*, 30 (21), pp 6120–6128.

Fundamental gas adsorption studies: H_2O and CO_2 adsorption on Ca-SWy-2

Adsorbed H_2O



Adsorbed CO_2



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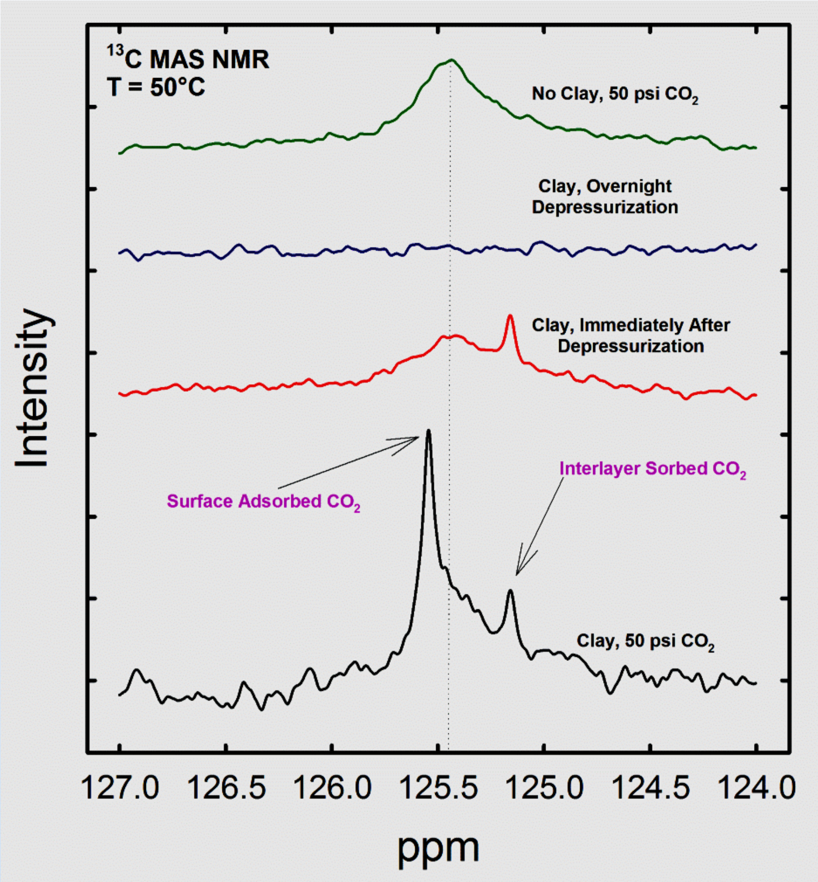
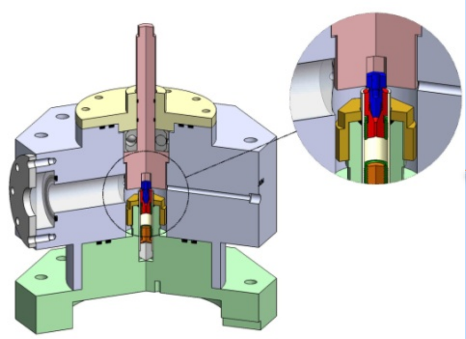
Distinguishing CO_2 Interactions: *In situ* MAS-NMR Studies

- **Experimental Objective**: Exposing montmorillonites to $^{13}CO_2$ to study sorbed CO_2 species
  - Bulk CO_2 (no clay): single resonance at 125.4 ppm
  - Exposure to clay (50 psi): two new resonances are observed, indicating two different types of CO_2
  - Depressurization: a single resonance remains and is attributed to intercalated CO_2
- **Application:** CH_4/CO_2 mixed gas systems



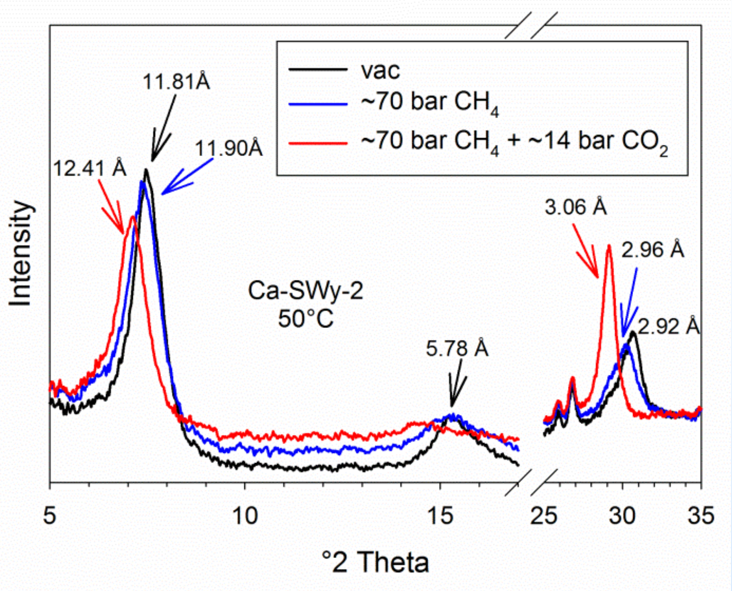
Pressurizable Reaction Vessel with NMR Rotor



Powdered clay sample in side rotor

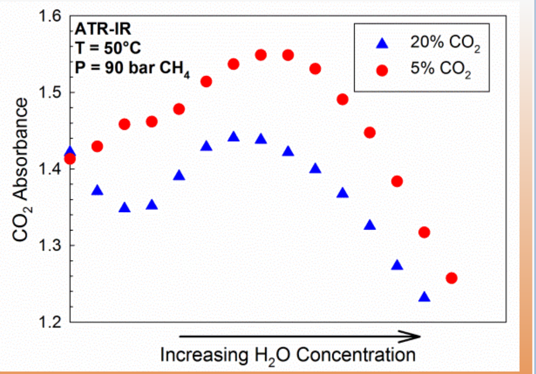
Characterizing Interactions Between Clays and Mixed Gases (CO_2/CH_4)

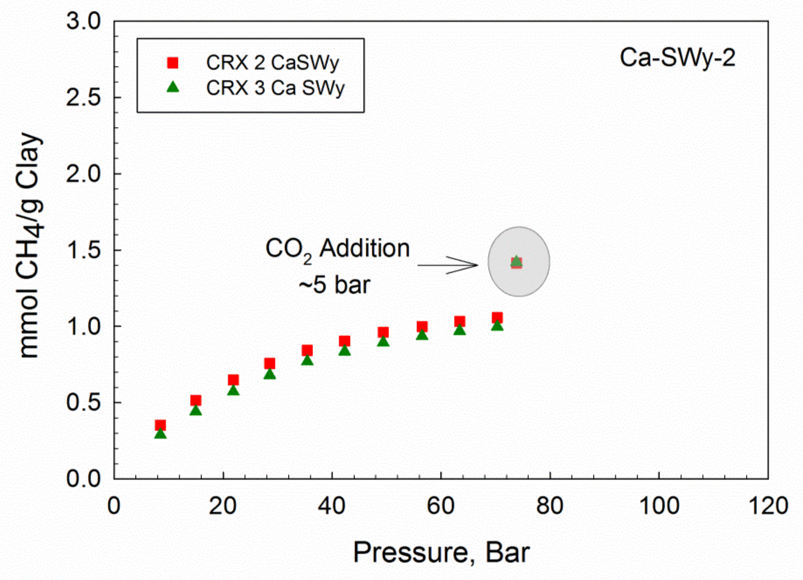
- **Experiment Approach**: Utilize *in situ* techniques to examine clay behavior in mixed gas systems
- **HXRD**
  - Basal spacing constant in pure CH_4 with only minor changes to the basal spacing
  - Low partial pressure of CO_2: expansion of *d*(001) spacing to 12.41Å
- **QCM**
  - Maximum concentrations ~0.9 mmol CH_4/g clay
  - Low partial pressure of CO_2: large mass change



ATR-FTIR Titration Study

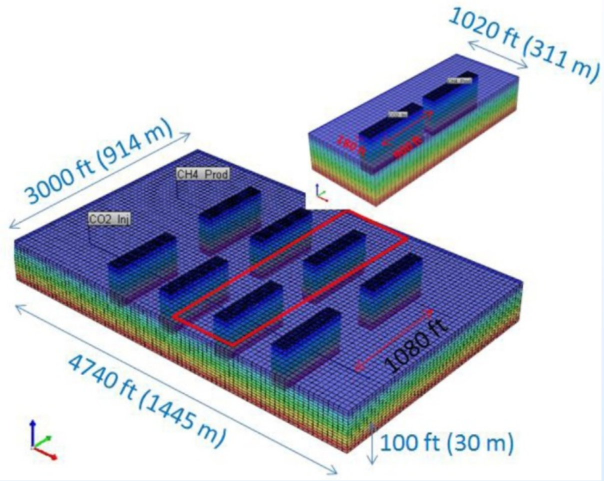
- No direct evidence of CH_4 intercalation
- CO_2 sorption in CH_4/CO_2 system behaves similar to pure CO_2 system



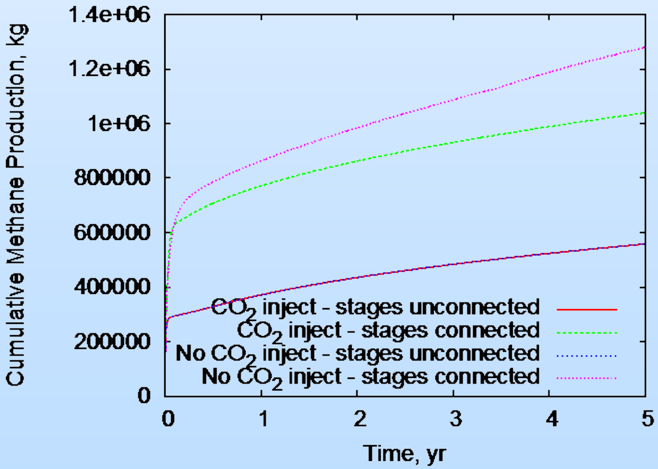


Modeling Enhanced Recovery of Methane with CO_2

- STOMP-EOR simulates multiphase, multicomponent flow and transport of CO_2, methane and oil components coupled with geochemical reactions
- Simulations are being used to investigate relative importance of methane release mechanisms at the field scale
  - advection through hydraulic and natural fractures
  - diffusion and desorption from the shale matrix
- CO_2 is being utilized for its ability to preferentially adsorb to kerogen and clays enhancing the desorption of methane

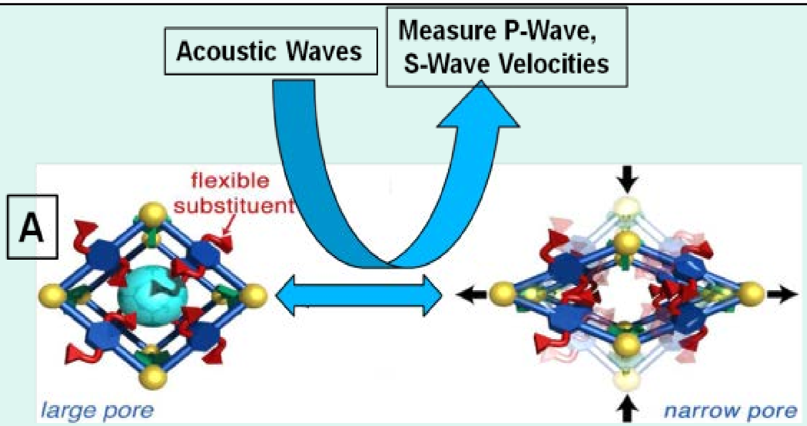


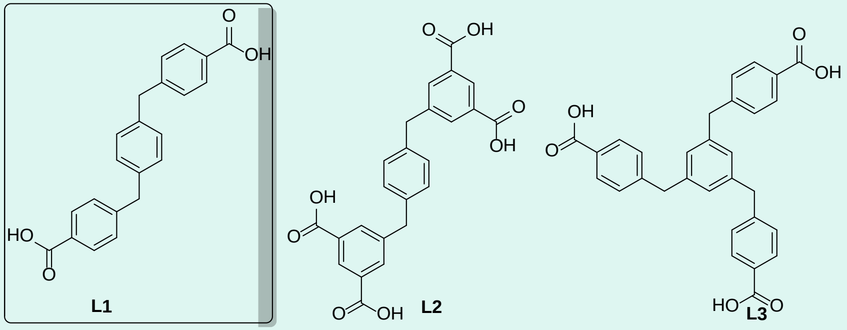
Hydraulic Fracture stages in CO_2 injection and CH_4 production wells (unconnected)



Comparison of methane recovery rates w/wout CO_2 injection and w/wout connected stages between inject/production wells

Acoustically Responsive Contrast Agents for Enhanced Monitoring of Injected CO_2 in Geologic Formations

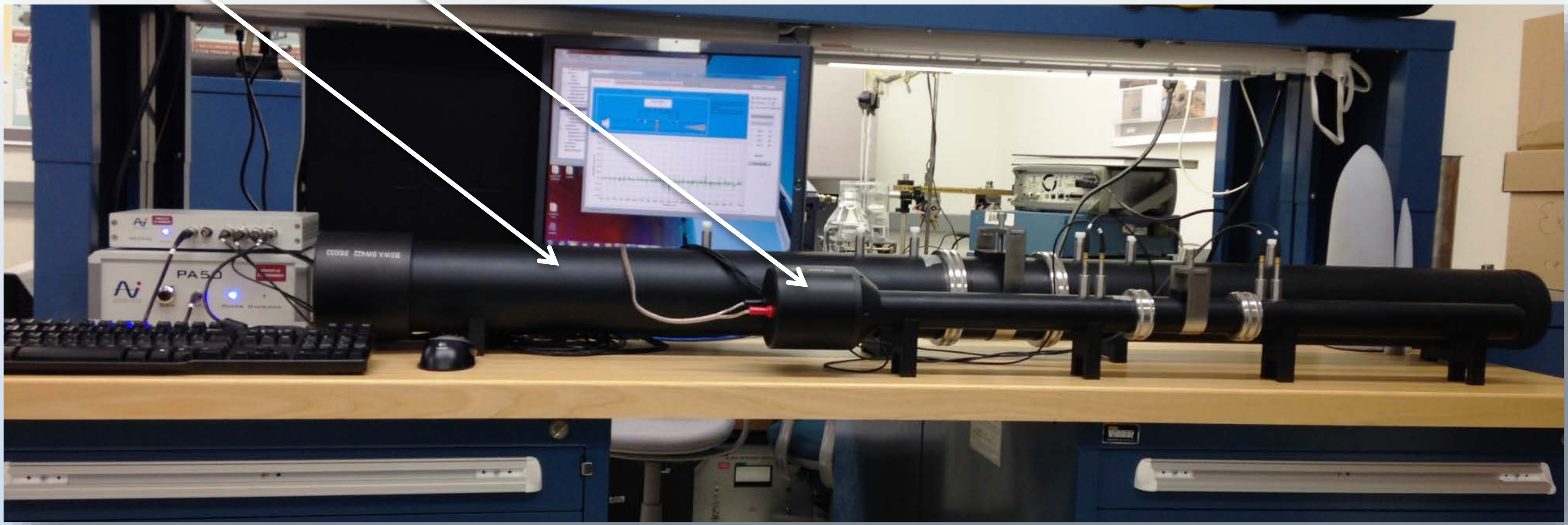




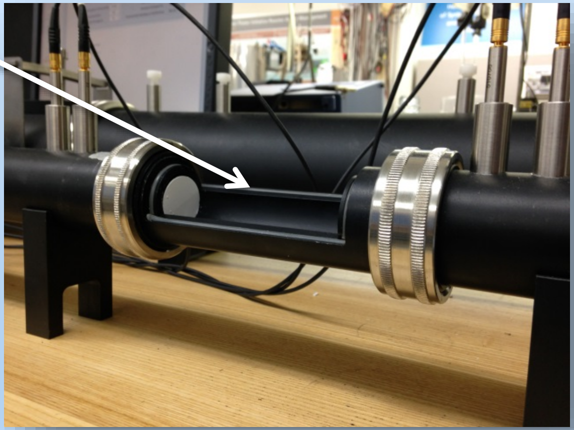
- MOF nanomaterials offer opportunity to expose a very large surface area in limited volume
- Introduction of flexible ligands in MOF structure allows for tuning of librational absorption modes that are detectible through conventional seismic imaging or by new laser Doppler vibrometry methods.
- Dispersion in scCO2 to form a nanofluid provides for injectable acoustic contrast agent

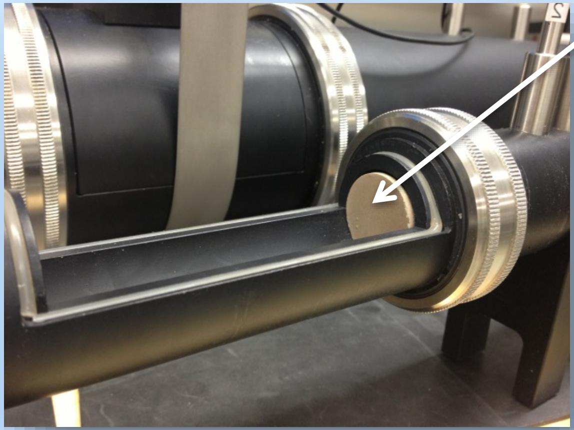
Acoustic Impedance Tube Instrument

100-mm and 30-mm diameter impedance tubes



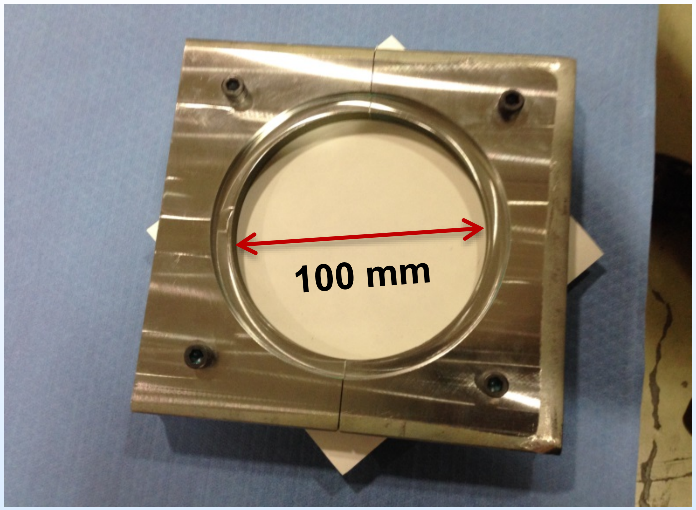
30-mm diameter impedance tube sample holder

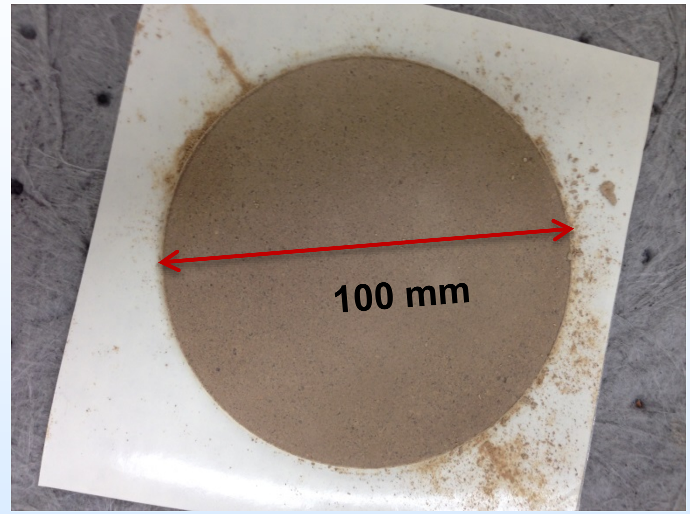


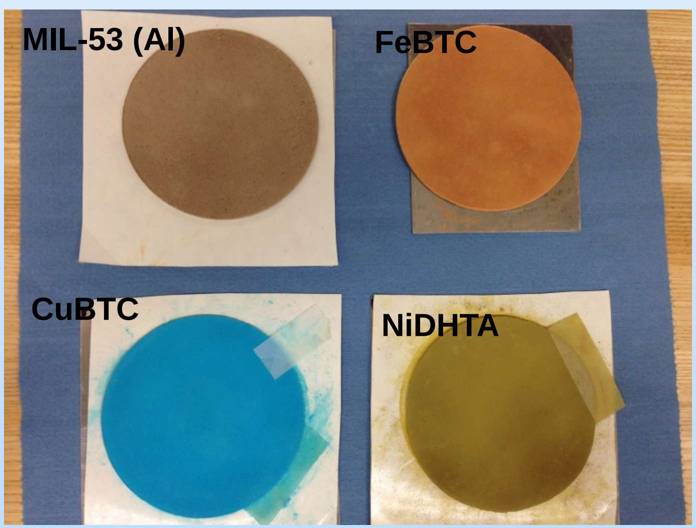


~30-mm diameter MOF pellet in sample holder

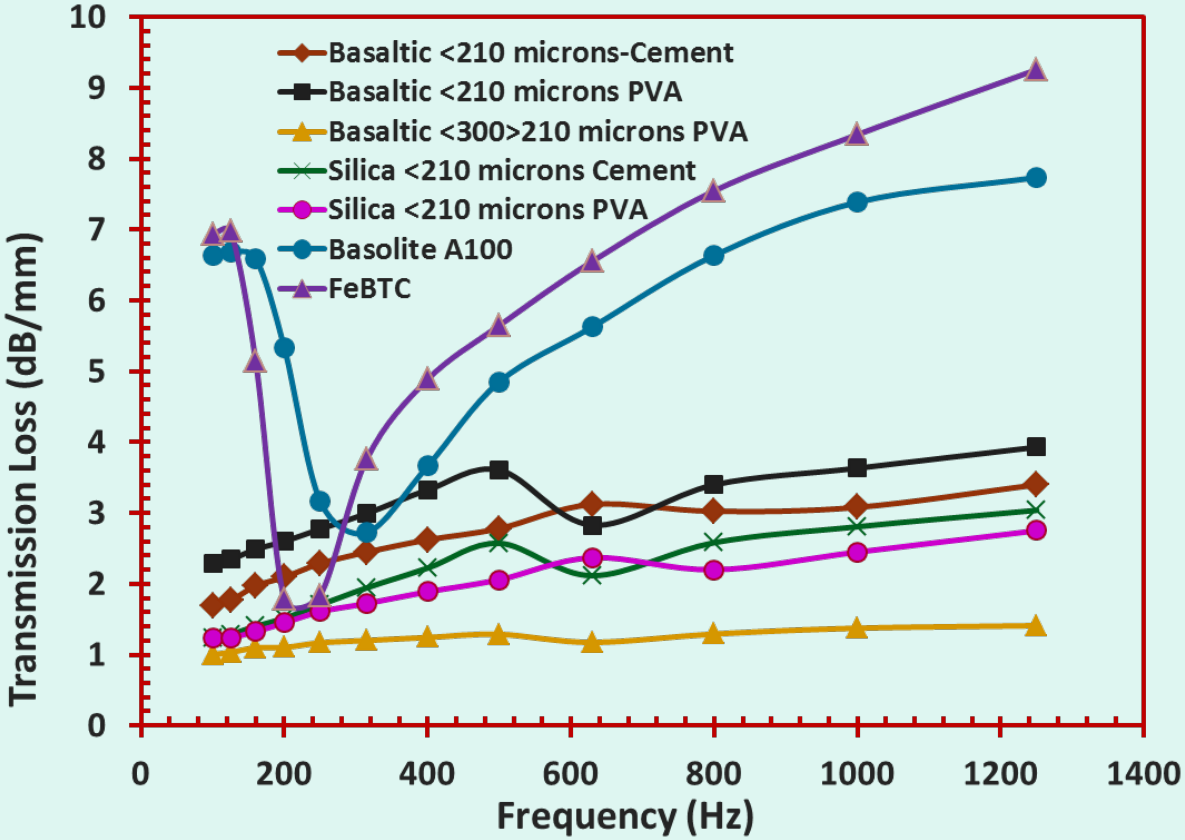
Making 100 mm DIA MOF Pellets







Transmission Loss Comparison Between MOF and Sand Discs



- **MOF exhibited significantly higher transmission loss (dB/mm) compared with sand materials**
- **Transmission loss increases as a function of frequency in the critical region <300 Hz**
- **Tests with new flexible MOFs underway**
- **Nanofluid dispersion trials planned after completion of impedance tube tests identify most promising materials**

Accomplishments to Date

- Significant progress has been made in developing new high pressure adsorption data on key minerals in shales
- Set of new in situ tools enabling separation of adsorption, intercalation, and reaction processes in $scCO_2$
- Influence of water in the system is being elucidated by molecular simulations
- Proof-of-principle demonstrated for novel acoustic contrast agents for CO_2 monitoring and fracture network mapping

Appendix

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

Organization Chart

- Project team has participants that cut across the Energy & Environment and Fundamental Sciences Directorates at PNNL
- Pacific Northwest National Laboratory is Operated by Battelle Memorial Institute for the Department of Energy

Gantt Chart

#	Task Name / Project Management	Start	Finish
1	Manage Project	Jul-08	Sep-14
2	Casing Materials Studies	Jul-08	Sep-14
3	Storage in Depleted Shale Gas Reservoirs	Jul-08	Sep-14
3.1	Economics of Utilizing CO2	Oct-10	Sep-14
3.2	Laboratory Studies and Molecular dynamics	Oct-10	Sep-14
3.3	Reservoir Modeling	Oct-10	Sep-14
3.3	Enhanced Monitoring Agents	Mar-13	Sep-14

#	Milestone Description	Milestone Date
4	Quarterly Reports	
9	Issue Journal article on Raman spectrum of scCO2-O18 and re-evaluation of the Fermi resonance	Mar-12
10	Complete MD simulations and issue journal article on selected pure silicate mineral reactivity in the CO2-H2O-SO2 system	Sep-12
11	Issue journal article on model clay minerals and their reactivity in wet scCO2 containing impurities	Jun-13
12	Complete MD simulations and issue journal article on selected clay minerals in the CO2-H2O-SO2 system	Sep-13
13	Journal article detailing volumetric changes occurring in swelling clays when exposed to wet scCO2	Dec-14
14	Submit journal article of the economics of CO2 storage in shale reservoirs.	Dec-14
15	Submit journal article on gas adsorption on clay minerals.	Mar-15
16	Complete synthesis of acoustic absorber candidate, obtain sound absorption coefficients using impedance tube measurements and issue journal article	Mar-15
16	Submit journal article on filed scale simulations of EGR utilizing CO2 in depleted shale gas or shale oil reservoirs	Sep-15

Project: Advanced sequestration studies — Task

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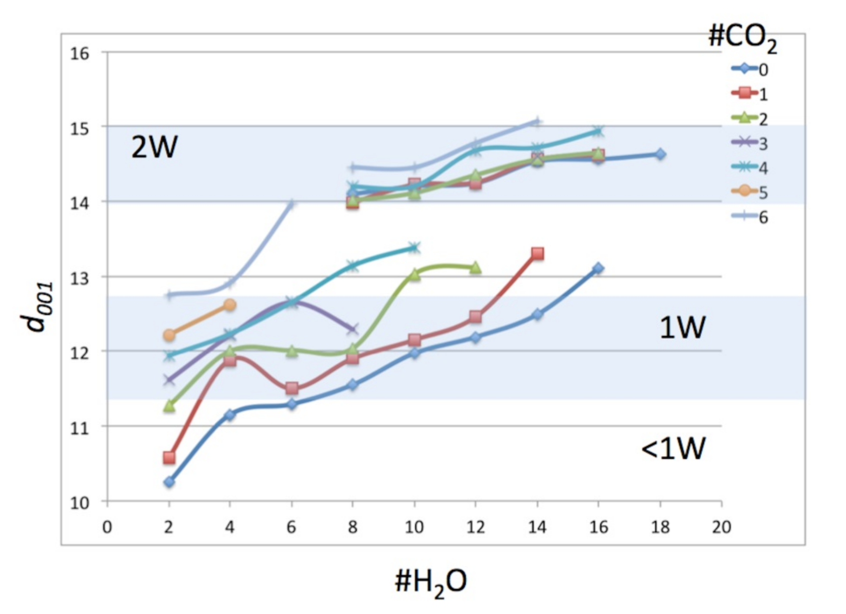
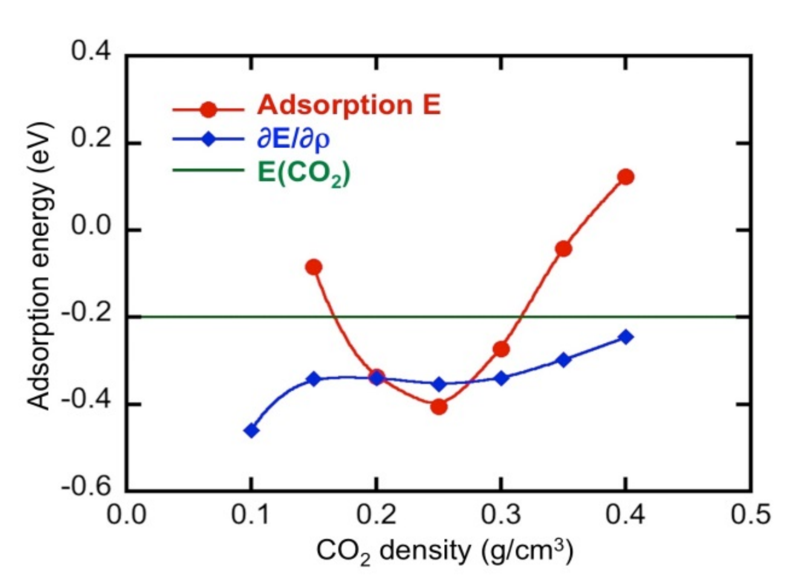
Molecular modeling with Ca-montmorillonite analogs: CO_2 sorption and intercalation

- Ca-montmorillonite analog containing two interlayer cations in unit cell
- Under saturated clays (1-3 H_2O/Ca^{2+}) have significant capacity for CO_2 intercalation (up to 2 CO_2/Ca^{2+}) maintaining ≤ 1W expansions





- Adsorption is driven by a $scCO_2$ film formation on the surface resulting in adsorption energies (red line) more favorable (more negative) than the average CO_2-CO_2 interaction in bulk $scCO_2$ (green)
- Blue line provides an estimate of the chemical potential driving the film formation

HT Schaef, JS Loring, et al., **2014**. Competitive Sorption of CO_2 and H_2O in 2:1 Layer Phyllosilicates, GCA, **submitted**.