RISK ASSESSMENT AND MONITORING OF STORED CO_2 IN ORGANIC ROCKS UNDER NON-EQUILIBRIUM CONDITIONS

DOE (NETL) Award Number: DE-FE0002423

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DOE supported undergraduate student participants:

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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 21-23, 2012

Benefit to the Carbon Storage Program

- **Program goals being addressed:**
  - To attempt to answer whether CO_2 sequestered in unmineable coal seams would retain 99% of injected CO_2 gas under external and internal perturbations

- **Project benefits statement:**
  - How the interactions between coals and CO_2 affect the strength and stability of coals, especially under high CO_2 pressure ($<$ 27.6 MPa or 4000 psi)
  - Whether CO_2-saturated coals indicate any significant leakage of CO_2
  - How shock pressure waves may affect the interactions between adsorbed and/or absorbed CO_2 in coals

Presentation:

- Mechanical properties: Do we need to be concerned about only fractures, cleats, defects, etc. ➔ coal is very inhomogenous ➔ what about coal's chemical structure controlling the mechanical behavior?

- Are there any glass-transition(s) in coal and can they be a source of reservoir instability?

- How pressurization with CO_2 affects coal's properties ➔ are there any potential concerns?

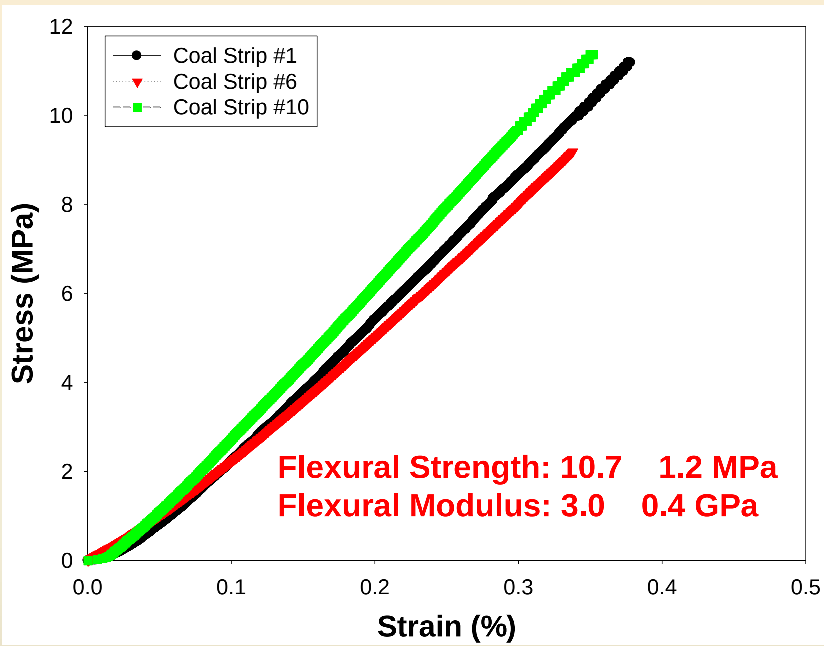
- Coal grabs CO_2, diffuses, swells, etc. ➔ How fast CO_2 is re-emitted?

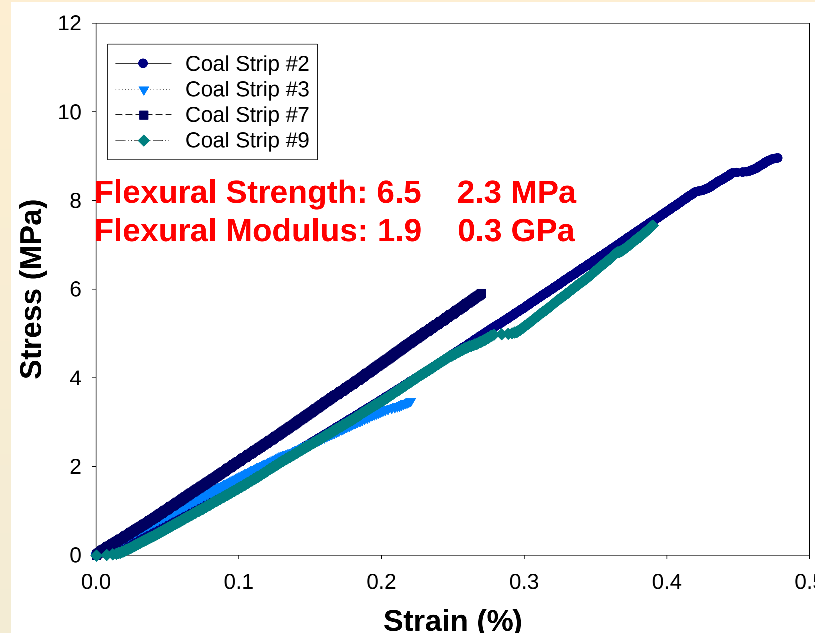
Mechanical Properties (Illinois coal): Flexural Mode

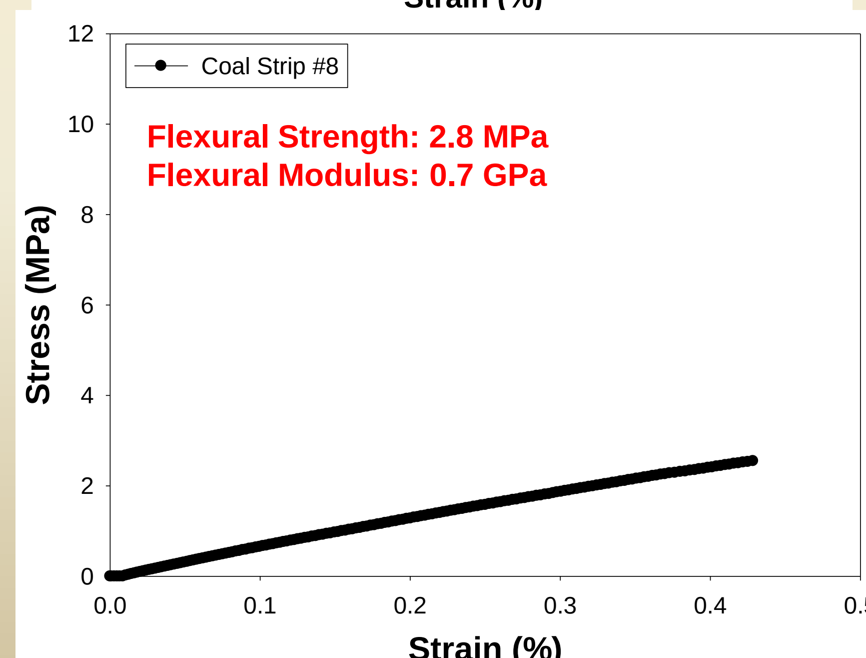
Coal strips cut with a high precision diamond rotatory saw ➔ strips generated from a single core

Strips examined under optical microscope ➔ if visible cleats and fracture(s) observed ➔ samples rejected ➔ only visible defect -free samples subjected to mechanical properties analyses

Mechanical Behavior of Murphysboro seam coal under N_2 (T = 25°C)

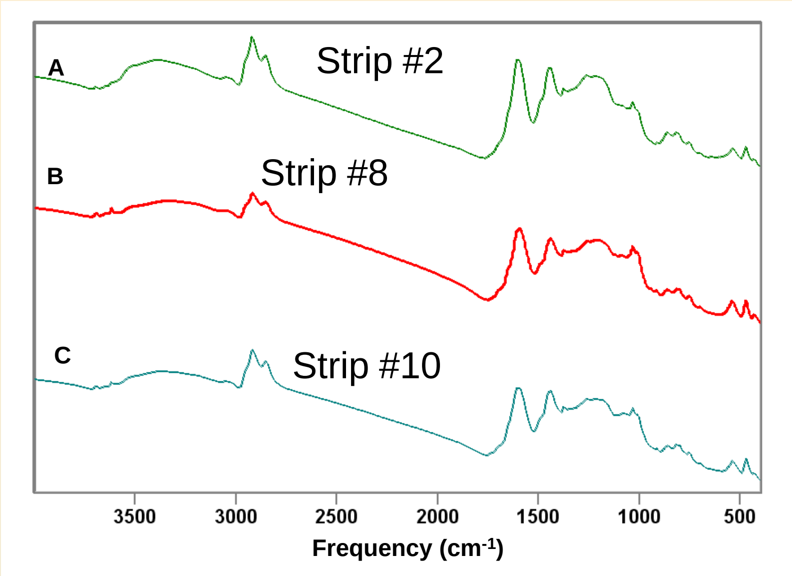


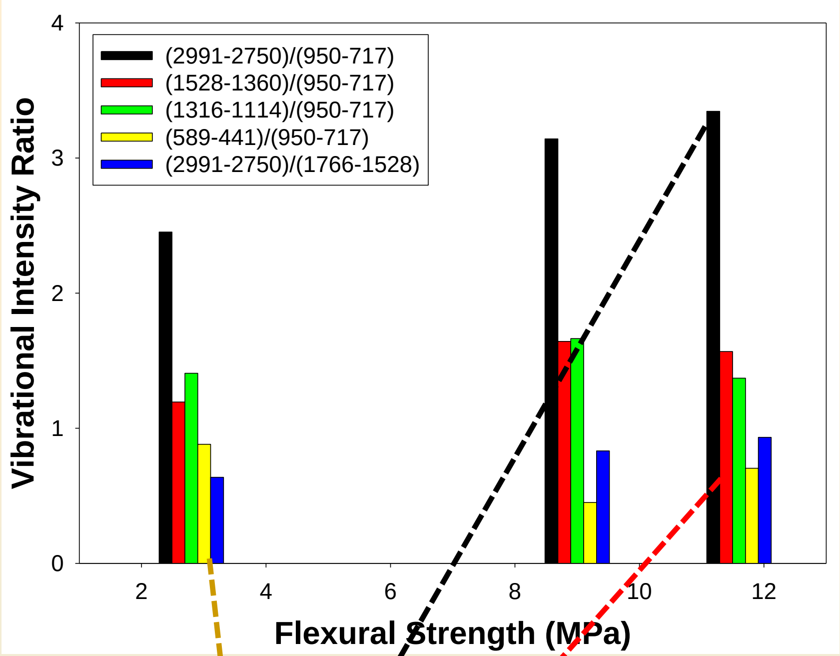




*West, Markevicius, Malhotra, Hofer: Fuel **98**, 213 – 217 (2012)*

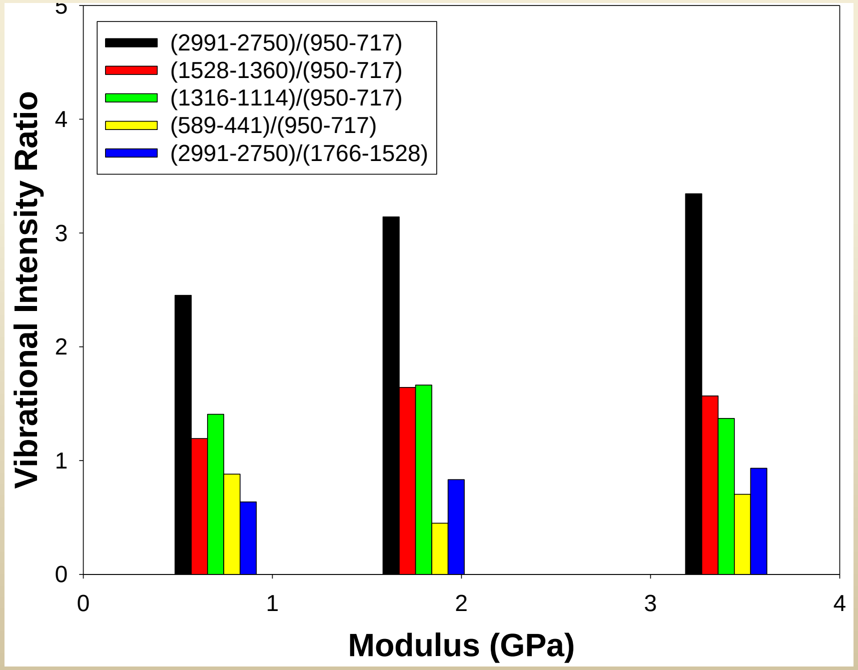
FTIR results on the coal strips which underwent mechanical testing





clays and silicates

mostly –CH3 and –CH2-aromatic



Mechanical Behavior of Murphysboro seam coal

*West, Markevicius, Malhotra, Hofer: Fuel **98**, 213 – 217 (2012)*

Glass Transition Issue

Larsen (2004) suggested coal undergoes glass-to-rubber transition ➔ most of the experimental evidence presented is based on differential scanning calorimetry measurements (DSC) ➔ not particularly a sensitive technique for ascertaining glass transitions because the involved discontinuities in the specific heat capacity (C_p) are not large

Hall and his group (1996, 2006) from DSC experiments:

(i) argued that North Dakota, Wyodak, Illinois #6, and Pittsburgh #8 coals undergo glass transition at $100^oC < T < 130^oC$ (under N_2 environment) ➔ these coals were not pressurized with CO_2

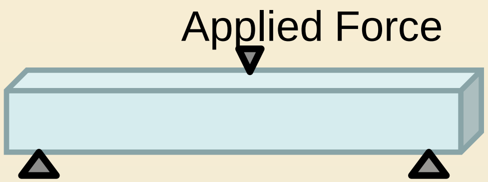
(ii) presented data that showed when Wyodak coal was pressurized with 3 MPa (435 psi) CO_2 ➔ glass transition shifted from 121^{o}C to 81^{o}C

Pakom Opaprakasit and Paul Painter (2003) of Penn State reported that they failed to reproduce the glass transition near 100^{o}C in coal as suggested by Hall (sample not pressurized with CO_2)

Could glass-transition in coal {as suggested by previous researchers} pose reservoir stability issues?

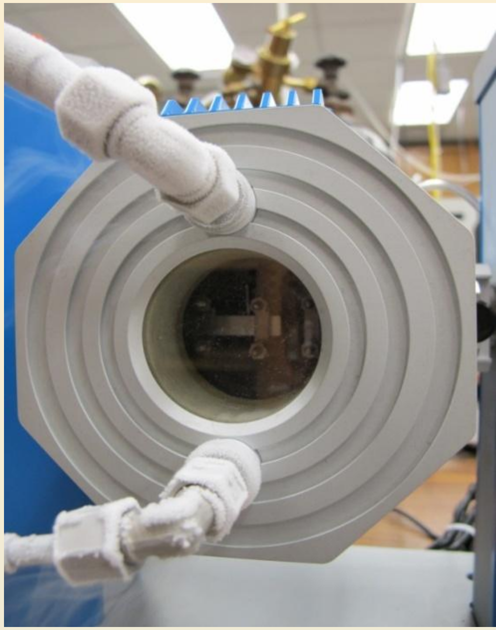
Our question: do bituminous coals even have a transition?

DYNAMIC MECHANICAL ANALYZER (DMA)



Dynamic mechanical analysis (DMA) involves the measurement of the response of a material to a sinusoidally oscillating stress.

DMA 7



DMA 8000

$$\sigma = \sigma_0 \exp[i(\omega t + \delta)]$$

$$\varepsilon = \varepsilon_0 \exp[i\omega t]$$

$$E^* = \frac{\sigma_0}{\varepsilon_0}(\cos\delta + i\sin\delta) = E' + iE''$$

$$\tan\delta = \frac{Loss\ Modulus\,(E'')}{Storage\ Modulus\,(E')}$$

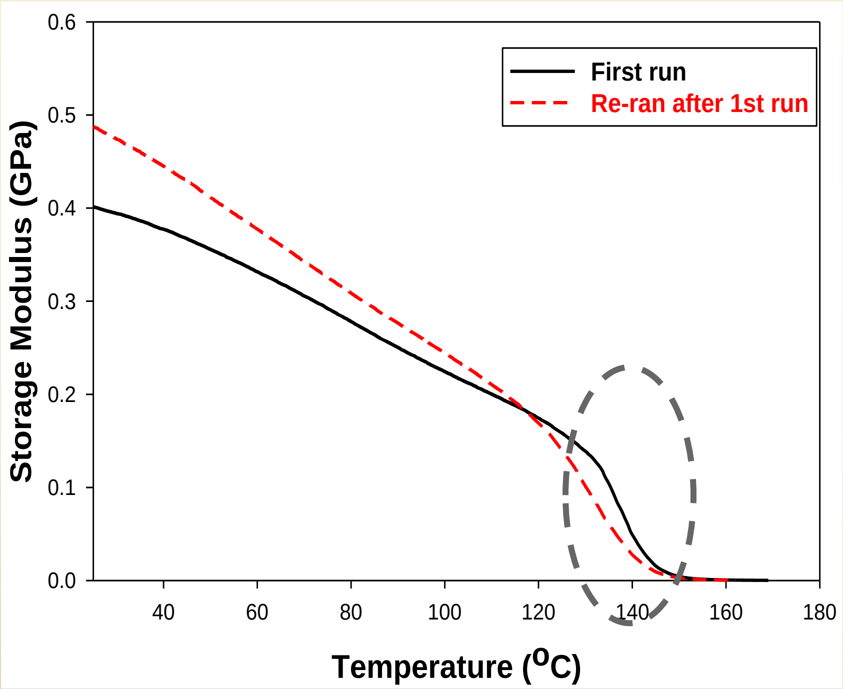
DMA 100 times more sensitive technique than DSC for glass transitions

DMA OUTCOMES

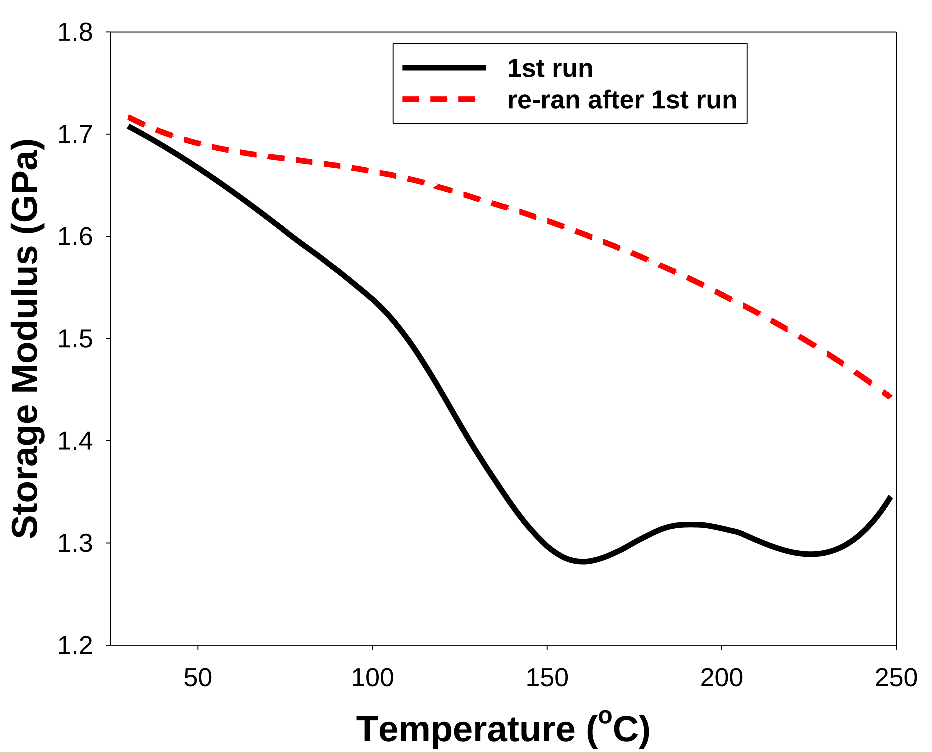
Do Illinois bituminous coals have a glass-transition?

Let us compare standard polymer with Illinois Murphysboro bituminous coal

Standard PMMA polymer

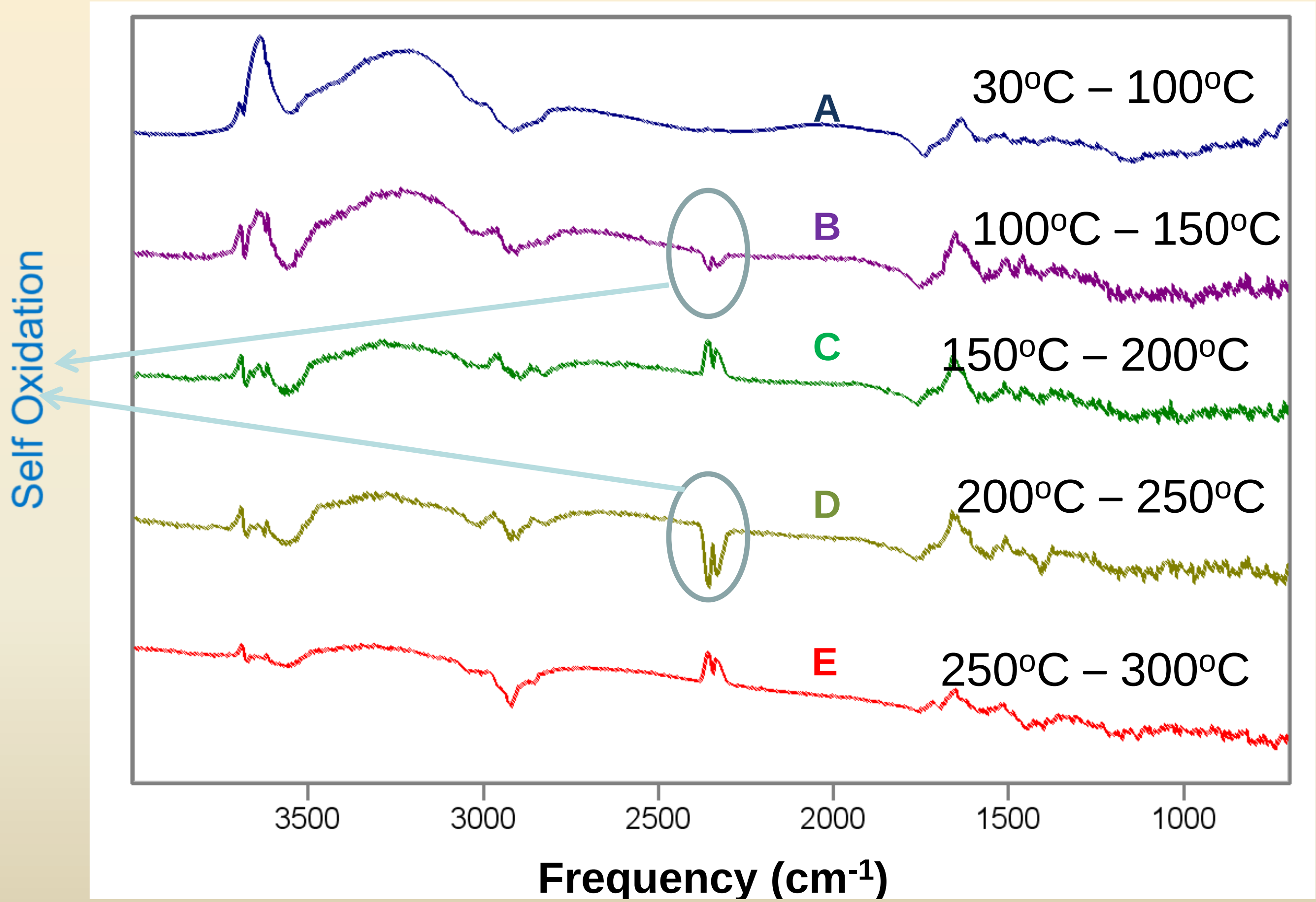


Illinois bituminous coal



Markevicius, West, Malhotra, Hofer:
Fuel ***98****, (accepted to appear in 2012)*

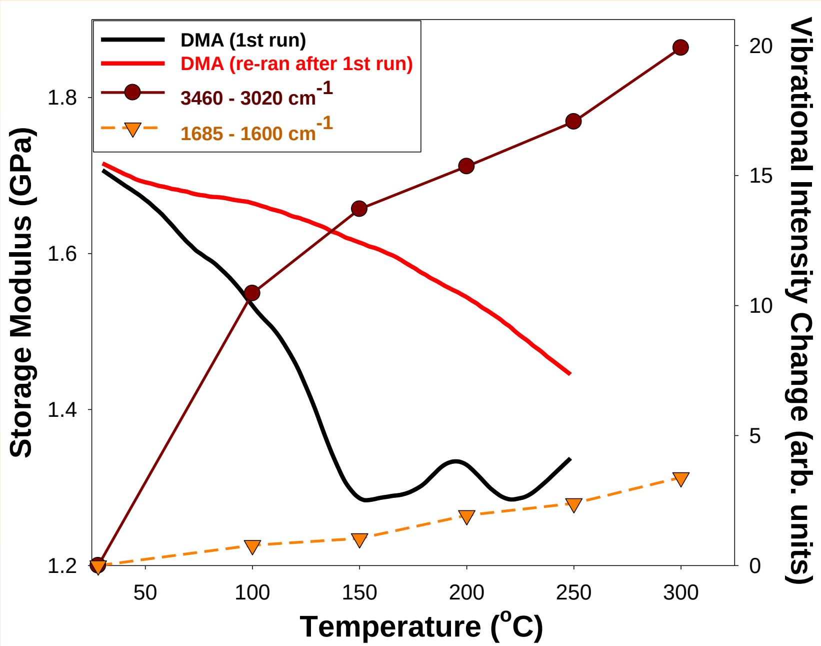
In-Situ Temperature Dependent Diffuse Reflectance-FTIR Measurements: Murphysboro Seam Coal (N_2 purge)



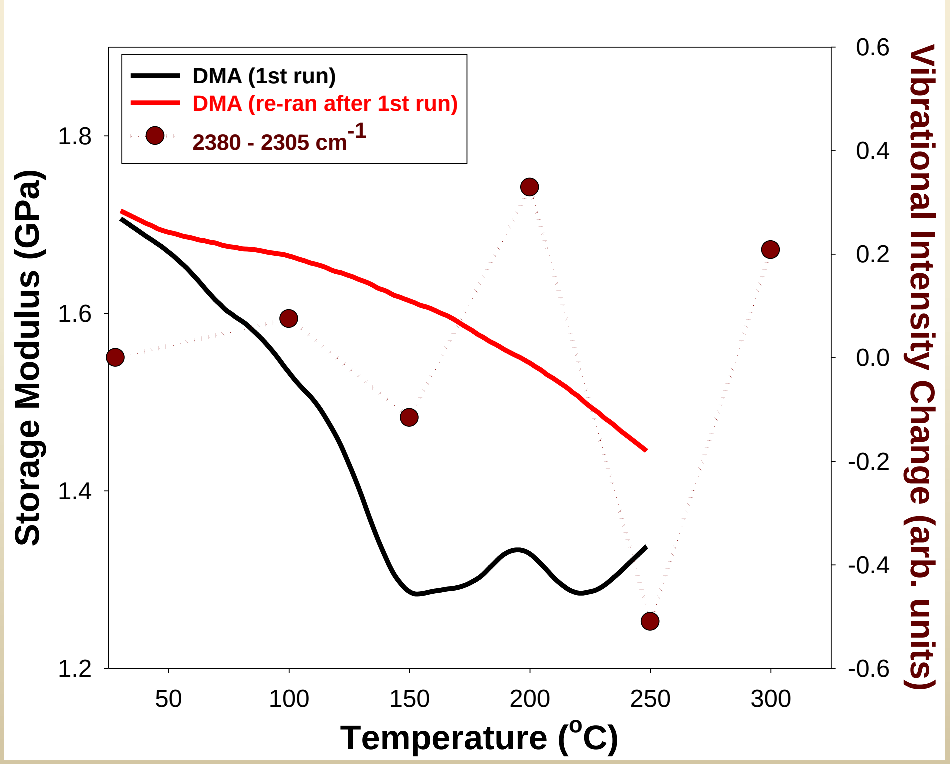
Markevicius, West, Malhotra, Hofer:
Fuel ***98****, (accepted to appear in 2012)*

Malhotra: Southern Illinois University-Carbondale

Murphysboro Seam Coal



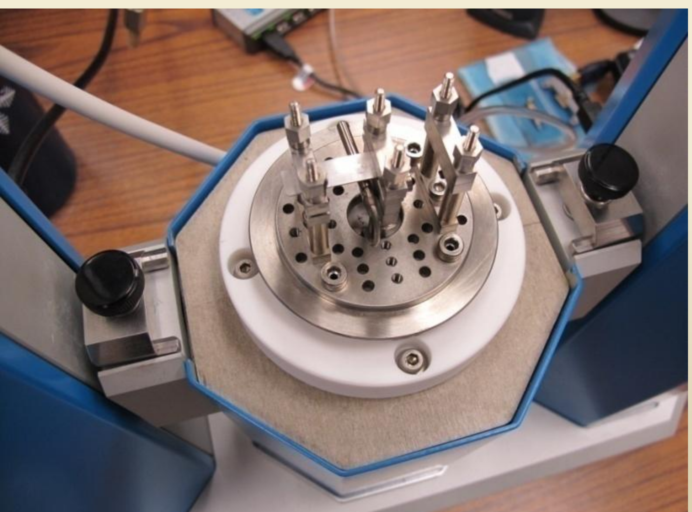
Murphysboro Seam Coal



Markevicius, West, Malhotra, Hofer: Fuel ***98****, (accepted to appear in 2012)*

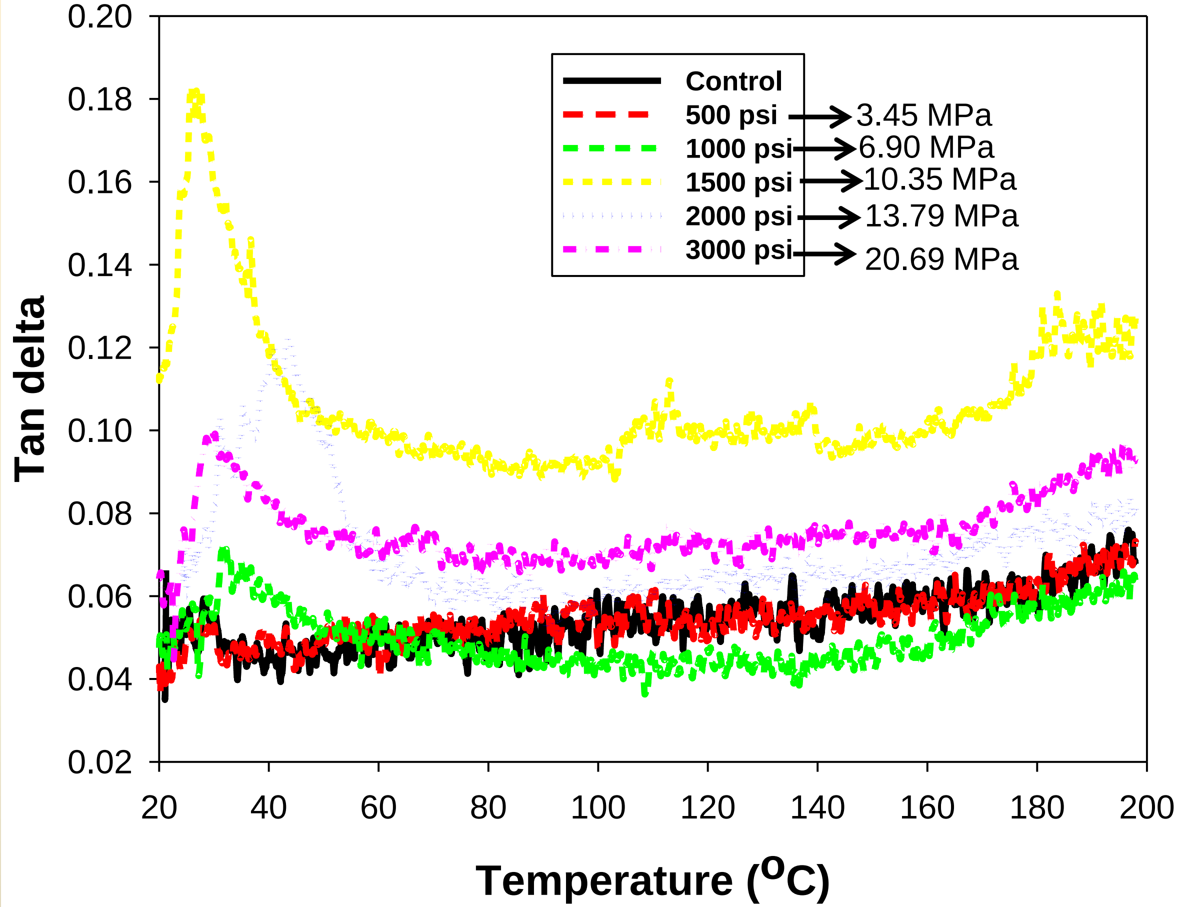
Effects of high pressure CO_2 on Illinois bituminous coal

High Pressure Cell



DMA 8000

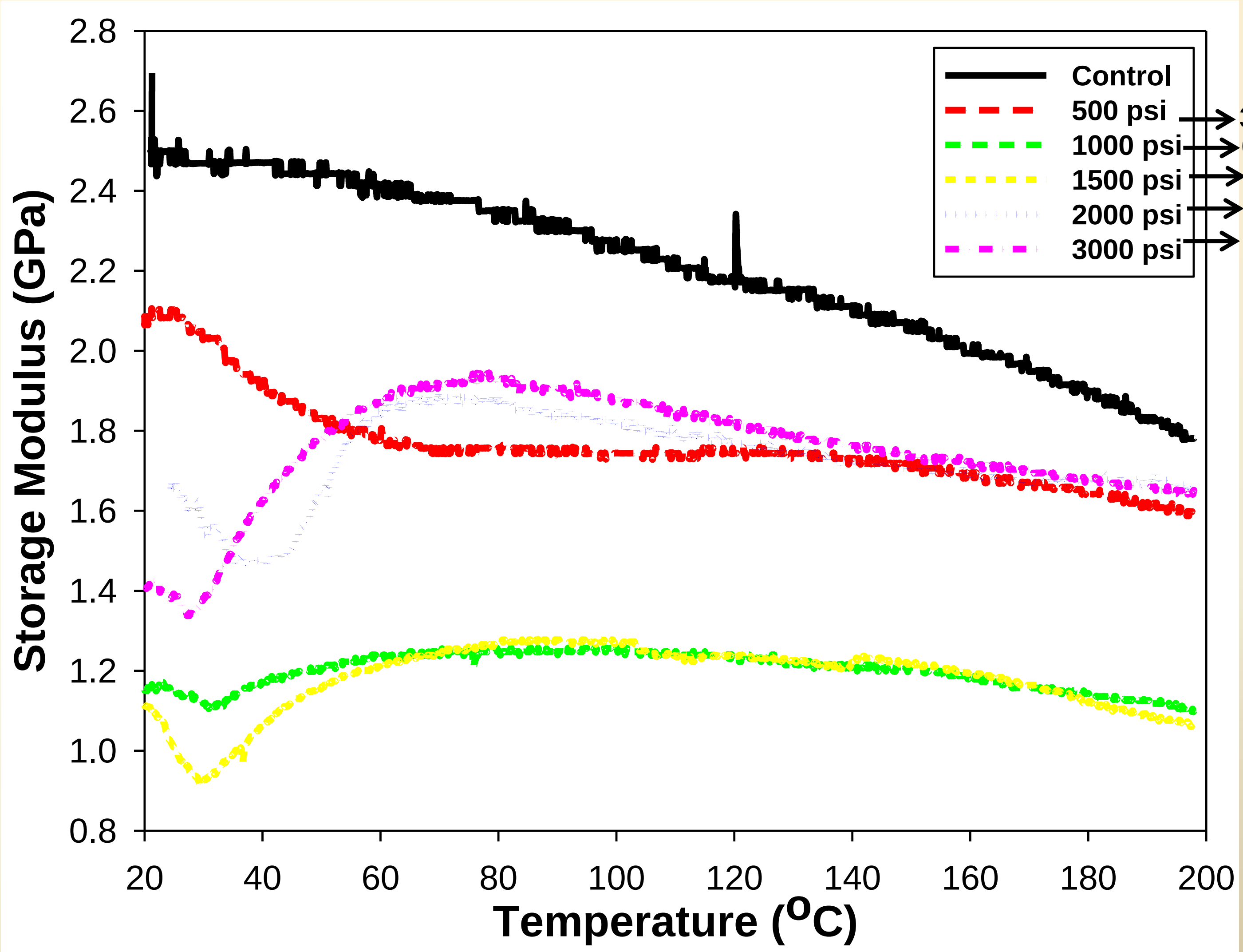
Houchin Creek Coal



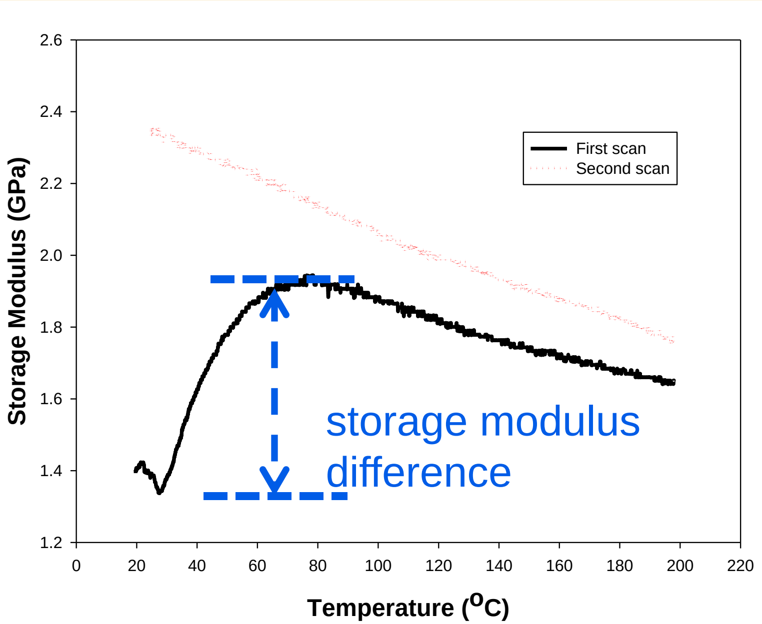
This figure shows how high pressure CO_2 affected the tan δ curves of Houchin Creek coal. The peak in the graph indicates the presence of a thermal event.

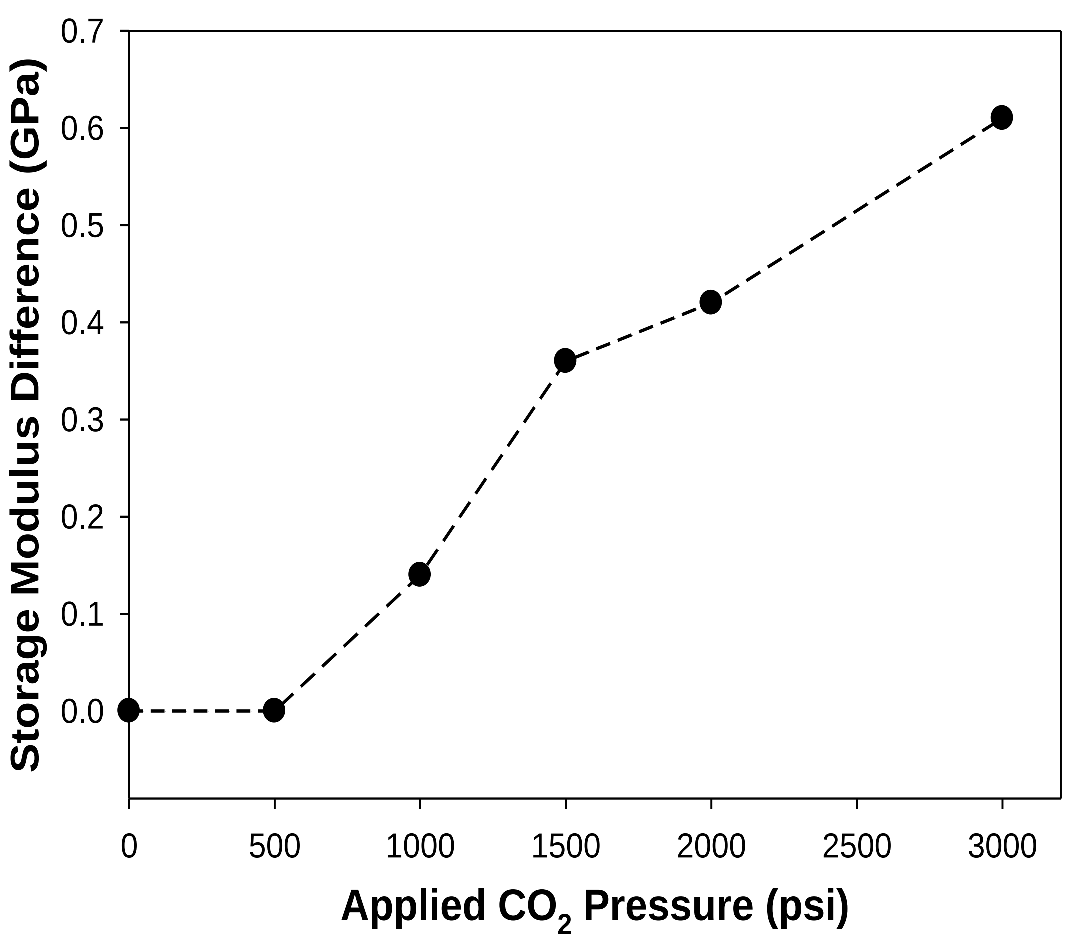
Houchin Creek Coal

This figure shows how high pressure CO_2 affected the storage modulus of Houchin Creek coal.



Houchin Creek Coal





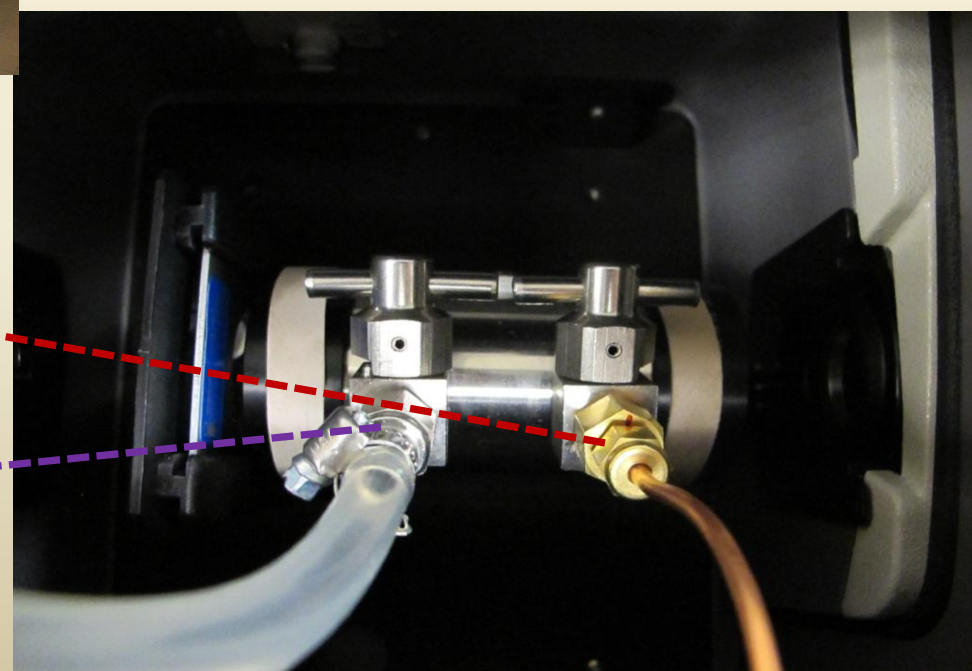
The observed storage modulus difference (SMD), i.e., the maximum storage modulus observed minus the corresponding minimum storage modulus observed of samples pressurized with different CO_2 pressures.

Coupled high pressure cell system with optical gas cell of FTIR spectrometer fitted with fast response MTC detector.

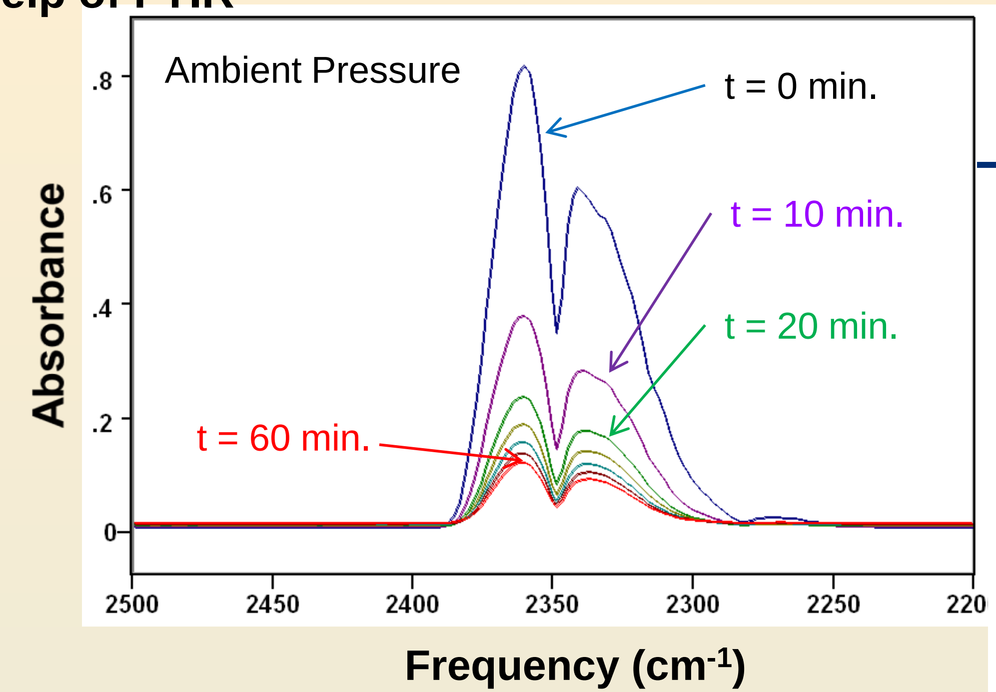
Optical gas cell to monitor CO_2 re-emission

Gas inlet from variable high pressure cell

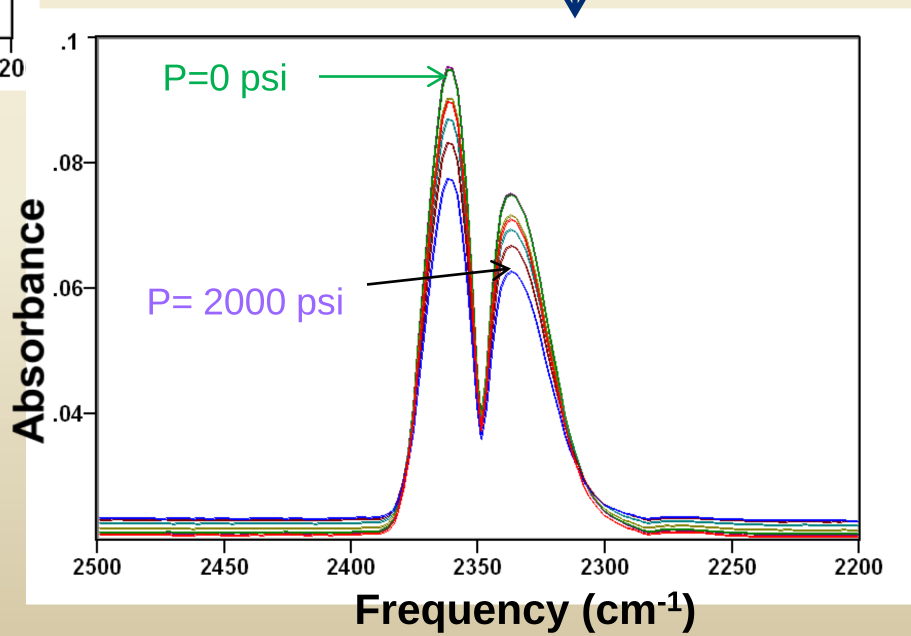
Gas vented to fume hood



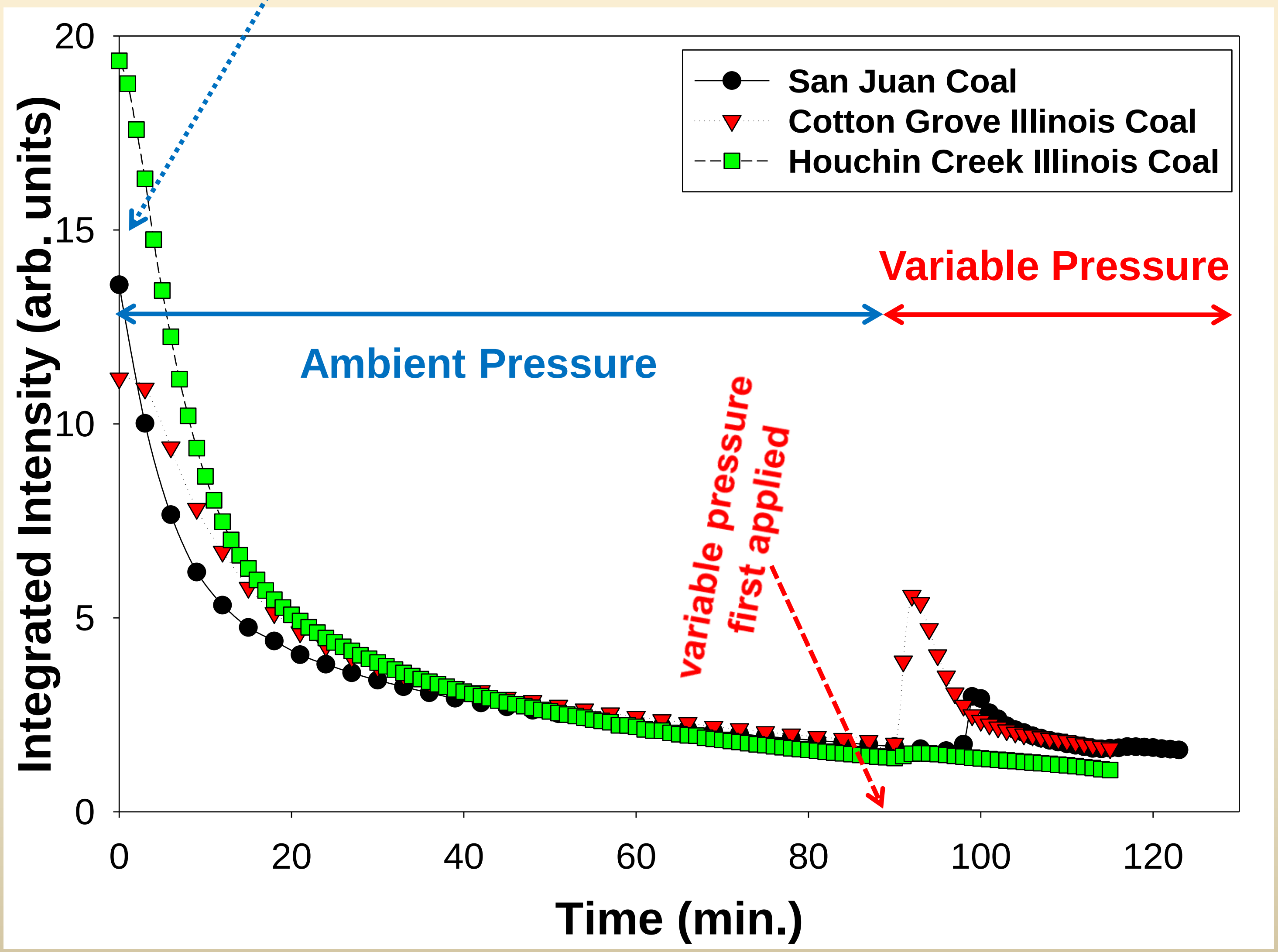
Houchin Creek coal pressurized with 1500 psi CO_2 ➔ Suddenly exposed to atmospheric pressure ➔ CO_2 re-emission monitored as a function of time for 90 minutes with the help of FTIR



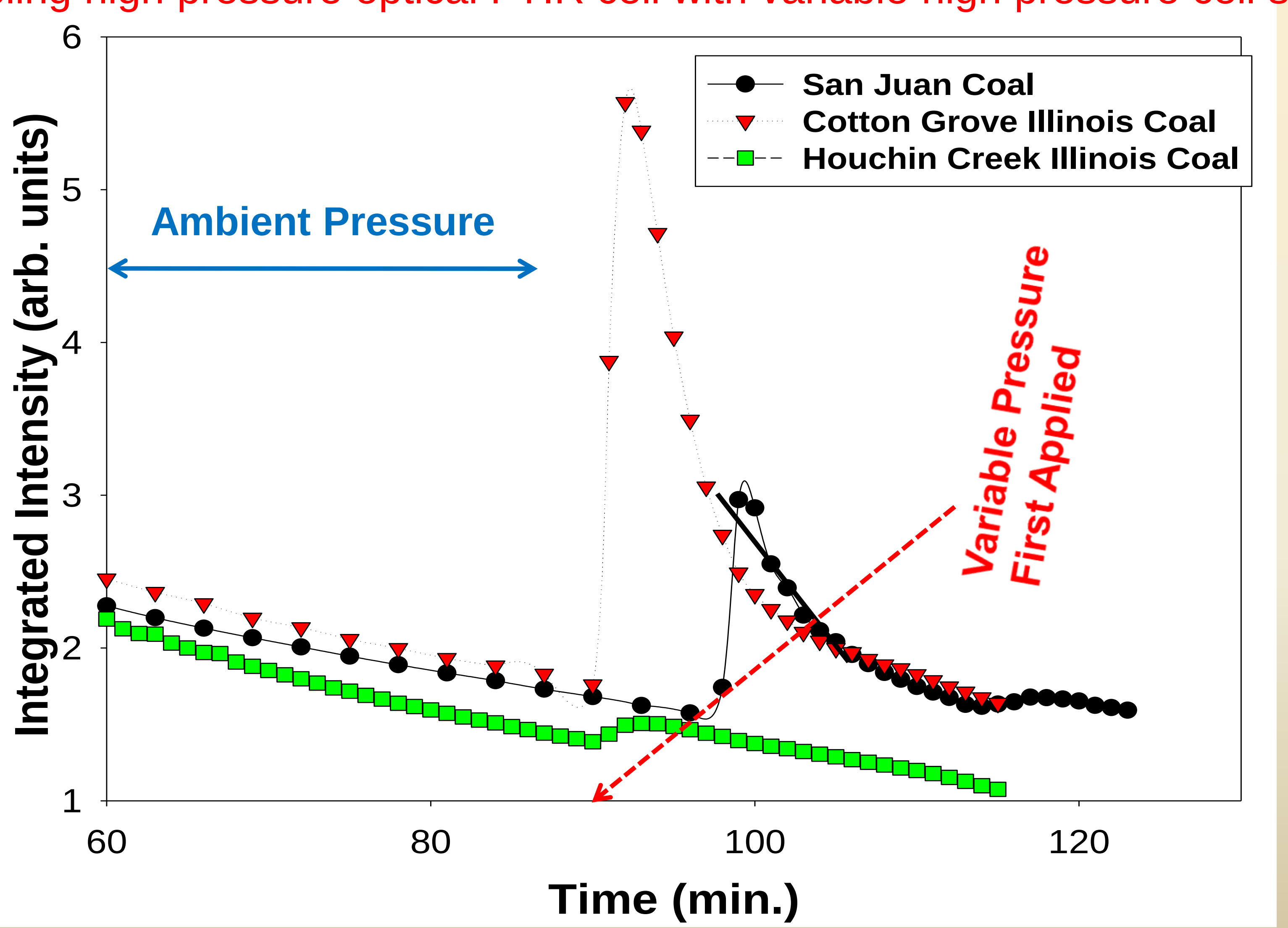
After 90 mins. at ambient pressure ➔ Variable pressure applied to the coal disk



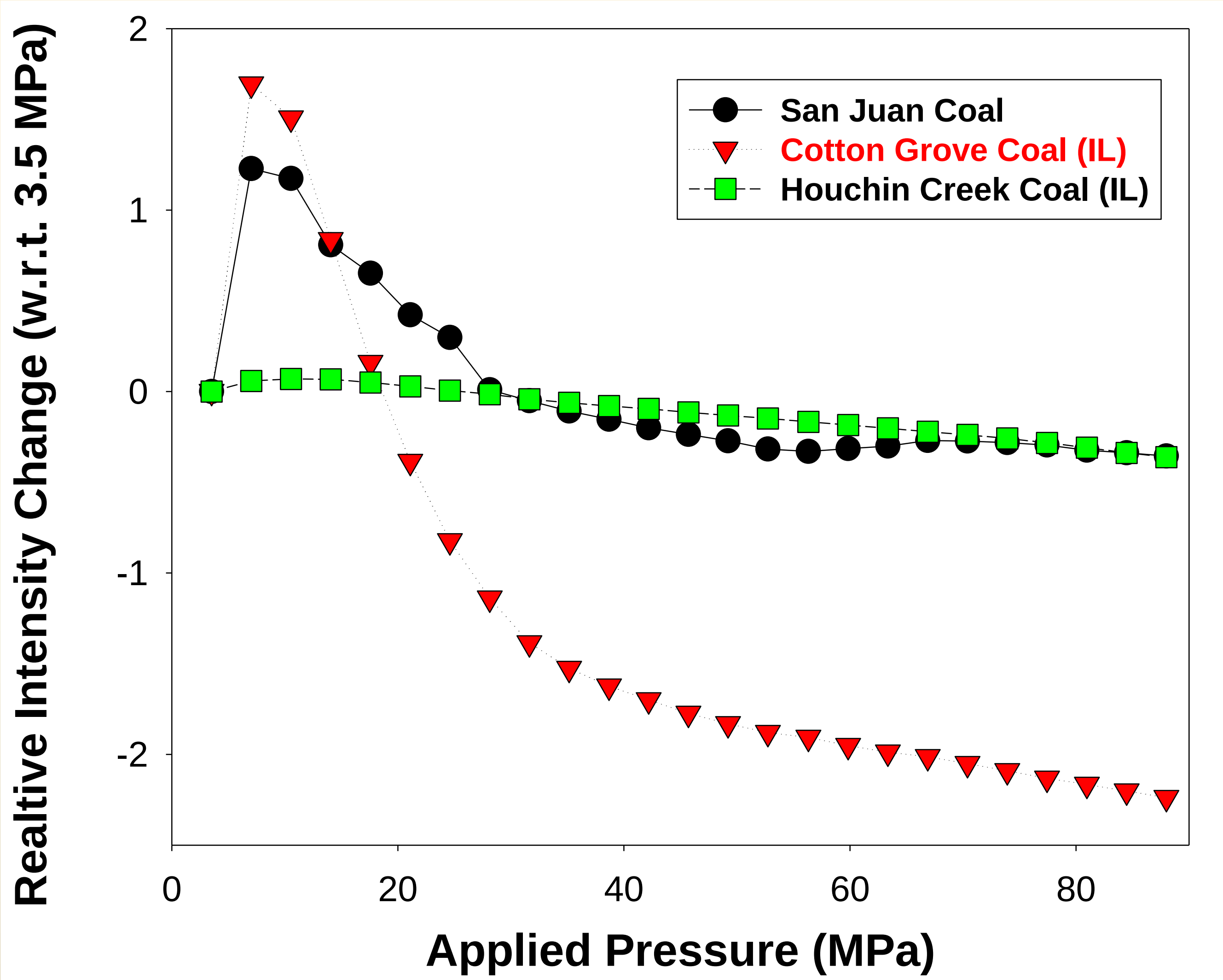
Coal cylindrical disks pressurized with CO_2 at 10.35 MPa (1500 psi) for 72 hrs ➔ coal exposed to ambient pressure ➔ potential re-emission monitored by coupling high pressure optical FTIR cell with variable high pressure cell system



Coal cylindrical disks pressurized with CO_2 at 10.35 MPa (1500 psi) for 72 hrs ➔ coal exposed to ambient pressure ➔ potential re-emission monitored by coupling high pressure optical FTIR cell with variable high pressure cell system



Coal cylindrical disks pressurized with CO_2 at 10.35 MPa (1500 psi) for 72 hrs ➔ coal exposed to ambient pressure ➔ potential of re-emission monitored by coupling high pressure optical FTIR cell with high pressure cell system



Summary and Highlights

- ❑ Are there variabilities (macro and micro) in the mechanical strength of Illinois coal which may pose a problem with CO_2 sequestration ➔ we did observe large variations independent of defects ➔ needs to be taken into account
- ❑Under ambient conditions, i.e., when coal samples were not pressurized with CO_2, we did not observe any glass transition in any of the coals (Houchin Creek, Illinois #2, Wyodak, or San Juan) ➔ contrary to the DSC results of Mirzaeian and Hall (2006)
- ❑We also did not observe any glass transition when coals were pressurized with low pressure (< 3.45 or 500 psi) CO_2 ➔ Mirzaeian & Hall reported a different outcome
- ❑The viscoelastic properties of coal are dramatically altered when coal is pressurized with CO_2. Our results suggest that coal starts to flow under high pressure CO_2, which results in cleat and pore closure
- ❑Developed an experimental lab system to monitor non-equilibrium conditions on sequestered CO_2 in organic rocks
- ❑The potential of catastrophic loss of CO_2 can not be discounted from Illinois coals if cap rock is fractured

Appendix

Organization Chart

Southern Illinois University-Carbondale

Investigator: Vik Malhotra

Undergraduate Student Team Members:
Ryan Belscamper, Stephen Hofer, Kyle Flannery, Jacob Huffstutler, Bradley Wilson, Jamie Pfister, Jeffrey Pieper, Joshua T. Thompson, Collier Scalzitti-Sanders, and Shaun Wolfe

Gantt Chart

Quarters after Project Initiation

TASKS	0 1 2 3 4 5 6 7 8 9 10 11 12
Task 1: Collect coal samples	X-----------a---------------------------X
Task 2: Mechanical properties	X----------------b-----------------------------X
Task 3: Design High pressure cell	X--c---------------------------X
Task 4: CO_2 pressure on coal:	X------d----------------------------—X
Task 5: Pressure variation effects:	X--e-------------------
Task 6: Leachable chemicals:	X----------------------

Milestones
a. Collect coal cores and shale cores: completed
b. How adsorbed gases affect the mechanical properties of organic rocks: completed
c. Build high pressure cell system for non-equilibrium measurements on coal cores: completed
d. Initiate studies on how pressure waves affect the adsorbed/absorbed CO_2 in organic rocks: currently undergoing
e. Initiate studies on how hydrostatic pressure variations induced by shock pressure waves affects the adsorbed/absorbed CO_2 in organic rocks: currently undergoing

In the summer of 2010, there was a chemical fire in a laboratory adjacent to the investigator's laboratory. The university authorities closed the whole wing of Neckers building (where the investigator's lab is located) for 4 months to undertake professional clean up. Additional 6 months were taken to clean individual optical equipment in the investigator's lab. A no-cost, 10 month extension request was submitted this summer.

Bibliography

Markevicius, G., West, R. D. and Malhotra, V. M., 2011, The Effects of CO_2 Adsorption on the Mechanical Behavior of Illinois Bituminous Coal, Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. V. 56(1), p. 284-285.

Huffstutler, J. D., Pfister, J., West, R. D. and Malhotra, V. M., 2012, Is there a potential of sequestering CO_2 in Montmorillonite Clay?, Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. V. 57(1), p. 345-347.

West, R. D., Markevicius, G., Malhotra, V. M., and Hofer, S., 2012, Variations in the mechanical behavior of Illinois bituminous coals: Fuel, V. 98, p 213-217.

Markevicius, G., West, R. D., Malhotra, V. M., and Hofer, S., 2012, Does Illinois bituminous coal manifest glass transition: DMA, DSC, and FTIR results, Fuel (accepted, to appear in 2012).

Malhotra, V. M. and Markevicius, G., 2012, Effects of high pressure CO_2 ($P \leq 3000$ psi) on Houchin Creek Illinois bituminous coal cores (depth = 1000 ft), Fuel (being submitted 2012).

Malhotra V. M., 2012, Effects of pressure variations on bituminous coals pressurized with CO_2, Environmental Science and Technology (being submitted 2012).

Huffstutler, J. D., Pfister, J., West, R. D. and Malhotra, V. M., Are expandable clays suitable host for sequestering CO_2?, Energy & Fuels (being submitted 2012)