IS THERE A POTENTIAL OF EMISSION OF SEQUESTERED CO₂ FROM ILLINOIS BITUMINOUS COAL UNDER SHOCKWAVES?

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Abbreviation List: FTIR, Fourier transform infrared; MPa, mega Pascal; GPa, gega
Pascal; M, moment magnitude; cm⁻¹, wavenumber, MCT, mercury cadmium telluride

ABSTRACT

The mitigation of potential global warming due to the emission of greenhouse gases, especially CO₂, would require large-scale geological sequestration. Though current emphasis has been on identifying and characterizing the potential geological sequestration reservoirs, there is also an urgent need to ensure that the sequestered CO₂ will remain in place under reasonable perturbations, e.g., under seismic activity. One of the potential geological reservoirs identified is unmineable coal seams due to the advantage of recovering fuel gas like CH₄ while sequestering CO₂. Therefore, a closed experimental setup was constructed where Illinois bituminous coal cores could be subjected to compressive shockwaves while simultaneously monitoring the emission of gases from CO₂ pressurized coal cores. The results from the pressurized coal cores were compared with the behavior manifested by un-pressurized coal cores as well as porous pumice stone cores, which were also subjected to shockwaves. As expected, the un-pressurized cores showed no significant emission of CO₂ when subjected to shock; however, this was not the case for the cores which were pressurized with CO₂. The results indicate that massive amounts of CO₂ would be emitted if the cores were exposed to atmospheric pressure simulating a situation where caprock has been compromised during primary seismic activity. Irrespective of the belief that coal interacts strongly with CO₂, both chemically and physically, compressive (0.374 MPa) shockwaves forced almost all the CO₂ to be ejected from the coal cores. Surprisingly, most, if not all, the sequestered CO₂ would be emitted in less than 1 hour if the cores were subjected to reasonably moderate shocks. In actual seismic activity conditions, one expects conditions to be even more severe than in the experimental setup used in

46 this study because of the presence of compressive and transverse stresses and shears.
47 If such is the case, CO₂ may be emitted even faster. It is reasonable to argue that
48 Illinois bituminous coals may not be suitable hosts for sequestering CO₂ because the
49 region is prone to seismic activity.

50

1. Introduction

The environmental concerns associated with carbon dioxide (CO₂) production when fossil fuels are combusted are coming to the fore because of potential global warming. The ensuing warming could affect the food production of the world as well as may intensify deleterious weather events. Because of these reasons, a considerable research effort is being undertaken in the USA, as well as in Europe, towards economically separating CO₂ from flue gas, capturing it, and then developing strategies for long-term storage of the captured gas. Though at present separating and capturing CO₂ from the flue gas is expensive and needs further research, the long-term storage of the greenhouse gas, which the public perceives to be safe, must also be evaluated. The United States Department of Energy has developed a roadmap for potentially storing CO₂ in various mediums [1,2]. It is generally agreed that sequestering CO₂ in geological formations holds the most promise for the large-scale storage of the greenhouse gas.

A number of geological reservoirs have been identified [1-3], such as deep sandstone formations, shale reservoirs, and unmineable coal seams, for sequestering captured CO₂ produced by fossil fuel burning power plants. Though there is a considerable body of data available, which deals with injecting supercritical CO₂ in various reservoirs including adsorption and absorption characteristics, very little is known at present about how the sequestered CO₂ would behave under external perturbations [1-5]. Among the geological storage reservoirs, long-term immobilization of CO₂ in unmineable coal seams presents an added advantage of coal bed methane recovery while simultaneously sequestering CO₂. However, successful sequestration

74 projects will only be feasible if the public perceives it to be safe and environmentally
75 friendly.

76 Recently researchers [6-9] have cautioned about large scale CO₂ sequestration
77 in geological reservoirs because of the potential of induced seismicity. The amount of
78 CO₂ to be sequestered is gigantic. Zoback and Gorelick [7] point out that the United
79 States produces about 2.1 billion metric tons per year of CO₂ from coal burning, while
80 China generated almost 6.3 billion metric tons of CO₂ from coal combustion in 2011
81 alone. These authors argued "that there is a high probability that earthquakes will be
82 triggered by injection of large volume of CO₂ into the brittle rocks commonly found in
83 continental interiors". Zoback and Gorelick point out that high pressure fluid injection
84 results in increased pore pressure which in turn reduces frictional resistance to fault
85 slippage, potentially triggering earthquakes. However, the problem could be further
86 compounded if there are unmapped faults near the vicinity of the injection wells.
87 Mazzoldi et al. [8] raise concerns that the induced seismicity "may provide preferential
88 pathways for CO₂ leakage out of the reservoirs".

89 It is also known that earthquakes have long range effects, e.g., after the 26th
90 December 2004 earthquake in Sumatra, the Rayleigh waves swept across Alaska
91 approximately 11,000 km (~ 6831 miles) distance and initiated "an 11-minute swarm of
92 14 local earthquakes" [10]. West et al. [10] pointed out that surface waves from the
93 Sumatra earthquake (moment magnitude, M = 9) created vertical trough-to-peak ground
94 displacement of 1.5 cm in Alaska. West et al. also argued that shear and normal
95 stresses work in tandem to promote faulting. Because, "Shear stresses alter the forces
96 acting along fault planes, whereas normal stresses alter the confining pressure and

friction across the fault” [10], the possibility of transient, though short-lived extreme local temperatures, cannot be discounted. The potential temperature rise along with rapidly varying pressure can have a serious consequence for both absorbed and adsorbed CO₂ in organic rocks like coal.

Our recent research efforts [11,12] have been directed towards evaluating the potential risks which may be associated with sequestering CO₂ in Midwestern coal seams and shale formations. The flexural strength and flexural modulus measurements on Illinois bituminous coal [11] suggested that there is a considerable strength and modulus heterogeneity in the coal samples which were free of visible defects. The strength of strips derived from a single chunk of coal showed strength variations from 2.8 MPa to 11.2 MPa, while modulus variations were 0.7 GPa to 3.4 GPa. These heterogeneities may be the source of defects and faults generation during even mild induced seismic activity. The other concern that was dealt with was whether Illinois bituminous coal showed glass transition. If Illinois coals do manifest glass transition close to the reservoir temperature, then there is a potential of reservoir instability during injection of high pressure CO₂, as it is known that CO₂ acts as a plasticizer and lowers the glass transition temperature. However, thermal, thermo-mechanical, and vibrational measurements indicated no glass transition for the Illinois bituminous coal at $30^{\circ}\text{C} \leq T \leq 300^{\circ}\text{C}$. Furthermore, because the Illinois basin is prone to high magnitude ($5.5 \leq M \leq 7.5$) earthquakes, it is important to understand how shockwaves affect the CO₂ stored in organic rocks like coal. The seismic activity may come from manmade or natural geological events. As pointed out earlier, there is a considerable body of data available on the adsorption and controlled desorption of CO₂ from coal [2], but practically nothing

is known about how CO₂ pressurized coals behave when subjected to shockwaves. This paper reports how CO₂, which was sequestered in Illinois bituminous coal, behaved when the samples were exposed to shockwaves.

2. Materials and Methods

2.1 Illinois Bituminous Coal Core: For the present study, Herrin bituminous coal from the Cottage Grove mine was chosen and was procured from east of Harrisburg (just inside Gallatin County), Illinois, USA. The proximate and ultimate analyses of Cottage Grove mine coal have been reported in the literature [13]. The coal samples were first obtained in large chunks. These coal chunks were cut into thick sheets with the help of a diamond band saw. From these sheets, 4 cm circular coal cores were drilled out, using a drill press with diamond coring bit chucks. The drilled coal cores were vacuum dried at 25.4 cm of Hg at 50°C in a heated vacuum desiccator for 24 hours. After mildly vacuum drying, the bituminous coal cores were stored under atmospheric conditions prior to subjecting them to high pressure CO₂ injection. For comparison purposes, porous pumice stone was also obtained and 4 cm circular stone cores were machined in a manner similar to coal cores. A belt sander was used to make the samples relatively flat on both ends of the cylindrical cores, if needed, so that the maximum surface contact would occur with the plunger during shockwave experiments.

2.2 Shockwave Setup: As pointed out earlier, no experimental studies are available in the literature where researchers have explored how seismic activity may affect the behavior of adsorption/desorption of sequestered CO₂ in geological formations. To answer some of the questions related to how seismic activity may affect

the reemission characteristics of sequestered CO₂, a closed, high pressure cell system was designed and built. In the cell system, cylindrical coal cores could be subjected to shockwaves while simultaneously studying the emission behavior of sequestered gases and/or vapors from the coal cores. Figures 1 and 2 show the block diagram and photographs of the overall system, respectively. The main features of the shockwave system are:

- Application of the Shockwaves: A number of cylindrical iron rods of various lengths were machined from a 1.3 m iron bar stock rod. These rods were calibrated for weight and were used to apply shockwave to coal cores by dropping the rods from well-defined heights. To ensure the iron rods would strike the center of the piston, the iron rods were dropped from the top of rigid, transparent Plexiglas tubes. Heights of the tubes were varied as needed, with heights of 0.31 m, 0.61 m, 1.22 m, and 2.44 m possible for the weight drop experiments. Holes were drilled into the tubes at the lower end. This was done to allow air to flow easily out of the tubes and minimize the drag on the falling weight, as well as to hold a safety catch to prevent a premature impact. Prior to the drop, the iron rods were held at the top of the Plexiglas tube by an electromagnet. The impulse on the piston was determined by calculating the final velocity of the iron rod. The approximate time of contact between the iron rod and the piston was determined with the help of a high speed camera. This allowed us to calculate the impact force on the piston, thus, the applied shock pressure to the sample cores.

- High Pressure Die: The coal cores were housed in a 4 cm diameter modified high-pressure die (see Fig. 2) with a piston, made from hardened stainless steel, which could compress or transfer shock to the samples when impacted. The die had O-rings both at the bottom and at the top to ensure that no gases escaped from the die during the shockwave experiments. The design of the die is such that during compression or shockwave experiments, the emitted gases were driven to the high-pressure fittings at the bottom of the die.
- Monitoring of Emitted CO₂: The high pressure die is coupled to an optical high pressure gas cell, shown in Fig. 3, mounted inside a fast scanning Fourier transform infrared (FTIR) spectrometer (Nicolet 6800). The gas cell was fitted with well-polished KBr windows. The infrared beam is passed through the cell. The beam then strikes the fast response, liquid nitrogen cooled MCT detector of the spectrometer. As the hardened stainless steel piston applied a transient pressure to the coal cores in the die, the emitted gases were driven to the gas cell by injecting N₂ gas to the high pressure line just as the gases were being ejected from the high pressure die. Because N₂ gas has no vibrational modes in the frequency range 4000 – 400 cm⁻¹, only the CO₂ bands will be observed in the arrangement. It is possible to observe other emitted vapors, such as water vapor and/or organic gases, in the arrangement. Water vapor bands do not interfere with the measurements of the CO₂ vibrational modes. If a CO₂ pressurized coal core degasses with or without the impact of sudden shockwaves, then CO₂ vibrational bands in our FTIR system would be observed. Carbon dioxide produces strong stretching oscillators at ~ 2345 cm⁻¹ and bending vibrational

modes at $\sim 667\text{ cm}^{-1}$. It is difficult to control the amount of CO_2 emitted from the coal cores, especially CO_2 pressurized cores, when subjected to shockwaves. The amount of emitted CO_2 gas in the optical cell may saturate the MTC detectors even though the emitted gas is continuously being diluted by the injection of N_2 . The intensity of the observed vibrational modes may not scale with the amount of gas in the cell, especially when the Beer-Lambert law is not being strictly obeyed. Therefore, the observed vibrational modes' intensity behavior should be visualized as a trend rather than the absolute amount of CO_2 emitted.

2.3 CO_2 Pressurized Coal Cores: The coal cores were transferred to aluminum containers, and the containers were placed in a high pressure vessel (Parr Instruments Co.), which could be pressurized ($\text{ambient} \leq P \leq 27\text{ MPa}$) with CO_2 . A SFT-10 supercritical fluid CO_2 pump (Supercritical Fluid Technologies, Inc.) was used to pressurize the vessel. Typically, Illinois unmineable coal seams are not very deep ($\sim 340\text{ m}$), therefore, the CO_2 injection pressure was limited to 6.9 MPa . The high pressure vessel was maintained at the desired CO_2 pressure for 72 hours. After 72 hours of adsorption and/or absorption of CO_2 , the high pressure pump was shut off, and the pressure vessel was slowly bled so that the samples could be removed from the vessel. In general, it took one hour to bleed the gas from the vessel before the coal cores could be extracted. Special attention was paid to whether it was feasible to collect any fluids which may have come out from the coal samples when they were pressurized with CO_2 in the high pressure vessel. However, no fluids were observed being extracted from the coal samples when they were pressurized with CO_2 . In sample

preparation, the coals had been dried at low pressure at 50°C. As such, it was felt that maybe all the fluids had been removed during the vacuum drying. Cottage Grove coal chunks, which were not machined or vacuum dried, were subjected to high pressure CO₂ at 10.35 MPa. Again, no fluids were observed when the samples were extracted during the pressurization experiments. After recovering CO₂ pressurized coal cores from the high pressure vessel, the cores were immediately transferred to the high pressure die system for shockwave experiments. Table 1 summarizes the experimental parameters used to ascertain the fate of adsorbed/absorbed CO₂ in bituminous coal cores, which were pressurized with CO₂.

3. Results and Discussion

The main focus of this research is on how shockwaves may affect the fate of sequestered CO₂ in coal seams. The assumption is that during seismic activity, whether manmade or natural, leakage pathways through the caprock are established. Arguments have been presented that the large-scale injection of CO₂ may induce seismicity, resulting in a compromise of the caprock seal integrity [7,9]. However, some researchers believe that the seal integrity will be maintained during induced seismicity [9]. At present, no conclusive evidence is available to support one view point or the other. Moreover, these arguments do not take into account any potential natural seismic activity, which may originate from unknown faults. The natural seismic activity could be much more severe than the CO₂ induced activity. It is known that CO₂ interacts with coal both chemically and physically [2,14,15], thus, it may be resistant to emission from coal under external perturbations. Therefore, these results may provide

information about whether during seismic activity CO₂ would stay sequestered in coal seams.

3.1 Effects of Shockwaves on Non-Pressurized Samples:

In the first set of experiments, an attempt was made to establish a baseline behavior for coal (CGC-CS) cores and pumice stone (PPS) in which the non-pressurized cores were subjected to shockwaves. Figures 4 and 5 show the FTIR spectra of emitted CO₂ from Cottage Grove coal and pumice stone cores when they were subjected to shockwave experiments, respectively. For the CGC-CS core, the samples were allowed to degas for 10 minutes in the shockwave setup prior to subjecting them to shockwaves. It should be noticed that no CO₂ bands were observed prior to 10 minutes, indicating no gas emission. However, once the shockwaves were applied to the CGC-CS core, very weak vibrational bands were observed in the frequency range of 2400 to 2100 cm⁻¹, indicating that some CO₂ was emitted from the coal. Because this coal core was not pressurized with CO₂, the potential sources of the observed CO₂ vibrational bands most likely are due to gas adsorbed in the coal cores either in the seam or when the samples were being machined for experiments. The intensity of the emitted CO₂ bands as a function of time is graphed in Fig. 6.

It can be seen from Figs. 5 and 7 that when a highly porous medium like PPS core is subjected to shockwaves no discernible vibrational bands of CO₂ gas were observed, suggesting no CO₂ emission. The fact that no CO₂ gas was emitted from the PPS core further supports the argument that the CO₂ bands observed from non-pressurized Cottage Grove are due to most likely inherent CO₂ in the coal.

3.2 Effects of Shockwaves on CO₂ Pressurized samples:

To understand how CO₂ pressurized coal would behave if the caprock was compromised either via fracture or seepage pathways developing, a 6.9 MPa pressurized coal core (hereafter labeled CGC-S1) was allowed to degas at atmospheric pressure in the closed cell system for approximately 50 minutes. This degassing was in addition to ~ 1 hour of degassing required for extracting the coal core from the high pressure (6.9 MPa) CO₂ vessel and transferring it to the closed cell system. Figure 8, which shows the intensity of the vibrational bands of emitted CO₂, indicates how much and how fast CO₂ was emitted from the Illinois bituminous coal as a function of time. In the system, nitrogen was used as a purge gas to continuously drive gases out of the FTIR optical gas cell (see Figs. 1 and 2) to the exhaust system. Therefore, the high pressure cell system monitors the gases being emitted from the coal cores as a function of time. As the exposure time to atmospheric pressure increased, the intensity of the vibrational bands steadily decreased, which can be clearly seen in Fig. 8. The results suggest that when CO₂ pressurized coal cores were exposed to atmospheric conditions, massive amounts of CO₂ were emitted from the Illinois bituminous coal during the first 50 minutes. Figure 9 shows a comparative behavior of the intensity as a function of time of the observed vibrational CO₂ bands for pressurized and non-pressurized Cottage Grove coal cores. From the figure, it can be seen that while the intensity of the non-pressurized core remained unchanged, the intensity of the emitted CO₂ for the pressurized core exponentially decreased as a function of time. Thus, it is reasonable to conclude that if leakage pathways develop through the caprock, the emission of the sequestered CO₂ from Illinois bituminous coal would be very rapid, i.e., on a timescale

of less than an hour. Moreover, it appears that the major fraction of the sequestered gas would be emitted during the first few minutes. As the difference in the pressure is expected to be significant between the unmineable coal seam and the surface, it would not be surprising if rapid and significant amounts of sequestered CO₂ are ejected. The results presented in Figs. 8 and 9, however, do not answer whether coal, which is known to react with CO₂ physically and chemically, still continues to hold significant amounts of CO₂ even if leakage pathways have been established.

After allowing the CO₂ pressurized CGC-S1 core to emit gas under atmospheric conditions for 50 minutes, the core was subjected to a 0.374 MPa (54 psi) shockwave at the 51 minute mark. As can be seen from Fig. 10, on the application of the shockwave, additional CO₂ was ejected from the coal core. The intensity of the emitted CO₂ jumped in the gas cell on the application of the shockwave at the 51 minute, and the intensity of the emitted gas further increased at the 52 minute. Thereafter, the intensity of the CO₂ rapidly decreased as the purging gas swept out the gases which were emitted on the application of the shockwave. Results presented in Fig. 11 suggest that almost all of the CO₂, which was either adsorbed or absorbed in the sample, was emitted when the shockwaves were applied to the coal core.

In a second experiment, the Cottage Grove coal core (hereafter listed as CGC-S2), which was pressurized with CO₂ at 6.9 MPa, was allowed to emit CO₂ for 5 minutes in the closed cell system at atmospheric pressure before a 0.374 MPa shockwave was applied to the sample. Again, the 5 minutes degassing was in addition to the degassing which occurred in removing the core from the high pressure vessel and transferring it to the closed cell system as described for CGC-S1. For this

experiment, the emphasis was placed on evaluating the fate of sequestered CO₂ if the aftershocks were more closely spaced in time. Again, the assumption was that during primary seismic activity the caprock had been compromised. As the pressurized sample was exposed to the atmospheric pressure in the closed system, massive amounts of emitted CO₂ were observed from the core (see Figs. 11, 12, and 13). However, this is to be expected because of the pressure differences involved, i.e., pressure difference between the die and the optical cell. It is worth pointing out that because the cylindrical core is confined in a tightly-fitted hardened stainless steel die, the compressive waves generated on the application of the shock would be complex as the core would experience a primary compressive wave followed by reflections at the boundaries. However, these reflective waves are also expected in nature as the primary wave encounters different medium interfaces.

On the application of the shockwave at the 5 minute mark, observations showed a massive ejection of CO₂ from the core as can be seen from Figs. 11 and 12. The intensity of the emitted gas decreased rapidly and exponentially during the next 20 minutes. At that stage, a second shockwave of 0.374 MPa was applied. Only a very minor increase in the intensity of the emitted gas was observed as can be seen in Figs. 11 and 13. During the next 10 minutes, almost all the sequestered gas in the coal core was emitted. Figure 14 shows a photograph of the core (CGC-S2) after the core had been subjected to shockwave experiments. Clearly, the core showed brittle failures during the shockwave experiments. A number of fractures were also initiated in the coal core. These fractures, along with the brittle failure, may have facilitated the emission of the CO₂ from the coal core during shockwave experiments. However, there was no

evidence that CO₂ molecules remained trapped in the coal pores after the application of the shockwaves.

4. Summary and Conclusions

At present, there is a lack of consensus on whether seismic activity could compromise the caprock in the areas where potential geological CO₂ sequestration could occur. Nevertheless, the public acceptance of the large-scale geological CO₂ sequestration would require evidence that it is safe. One potential source for CO₂ sequestration is unmineable coal seams. Therefore, experiments were undertaken to identify the fate of CO₂ pressurized Cottage Grove Illinois bituminous coal cores under conditions which may be prevalent during seismic activity, whether manmade or natural. A closed experimental system was developed in which pressurized coal cores could be subjected to compressive shockwaves, while the emission of CO₂ from the coal cores could be simultaneously monitored. The following is concluded from the experiments:

- (i) Non-CO₂ pressurized coal and porous pumice stone cores showed no significant emission of CO₂ when they were subjected to 0.374 MPa shockwaves.
- (ii) A massive loss of CO₂ occurred rapidly and exponentially from the coal cores, which were pressurized with 6.9 MPa of CO₂, when they were exposed to atmospheric pressure in the system. Thereafter, the rate of emission of CO₂ decreased though CO₂ continued to be ejected from the coal. However, this is to be expected as the pressure difference between the coal cores and atmosphere decreased.
- (iii) The Illinois bituminous coal did adsorb and/or absorb CO₂, and this CO₂ was not emitted by simply exposing the CO₂ pressurized coal to atmospheric pressure conditions in the closed system. However, all the adsorbed/absorbed CO₂ was ejected when the Illinois bituminous coal cores were

subjected to compressive shocks as moderate as 0.374 MPa. (iv) The results suggest that almost all the CO₂ would be emitted in less than 60 minutes if the caprock had been compromised during the primary seismic activity and the coal cores experienced shockwaves during any subsequent shocks. Therefore, the conclusion that massive, if not total, emission of the sequestered CO₂ in Illinois bituminous coal during seismic activity cannot be discounted.

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REFERENCES

- [1] National Energy Technology Laboratory (USA). Carbon sequestration technology Roadmap and Program Plan 2007.
- http://www.netl.doe.gov/technologies/carbon_seq/refshelf/project%20portfolio/2007/2007roadmap.pdf (accessed 10.31.2010).

- 371 [2] White C.M., Smith D.H., Jones K.L., Goodman A.L., Jikich S.A., LaCount R.B.,
372 DuBose S.B., Ozdemir E., Morsi B.I., Schroeder K.T. Sequestration of Carbon
373 Dioxide in Coal with Enhanced Coalbed Methane Recovery - A Review. Energy
374 & Fuels 2005, 19:659-724 [and references therein].
- 375 [3] National Energy Technology Laboratory (USA). Monitoring, Verification, and
376 Accounting of CO₂ Stored in Deep Geological Formations. Report DOE/NETL-
377 311/081508, www.netl.doe.gov, 2009.
- 378 [4] Haszeldine, R. S. Carbon Capture and Storage: How Green Can Black be?
379 Science 2009, 325:1647-1652.
- 380 [5] Orr, Jr., F. M. Onshore Geologic Storage of CO₂. Science 2009, 325:1656-1658.
- 381 [6] Person, M., Banerjee, A., Rupp, J., Medina, C., Lichtner P., Gable, C., Pawar, R.,
382 Celia, M., McIntosh, J., Bense, V. Assessment of basin-scale hydrologic impacts
383 of CO₂ sequestration, Illinois basin. International Journal of Greenhouse Gas
384 Control 2010, 4:840-854.
- 385 [7] Zoback, M. D., Gorelick, S. M. Earthquake triggering and large-scale geological
386 storage of carbon dioxide. PNAS 2012, 109:10164-10168; Reply to Juanes et al.:
387 Evidence that earthquake triggering could render long-term carbon storage
388 unsuccessful in many regions. PNAS 2012, 109:E3624.
- 389 [8] Mazzoldi, A., Rinaldi, A. P., Borgia, A., Rutqvist J. Induced seismicity within
390 geological carbon sequestration projects: Maximum earthquake magnitude and
391 leakage potential from undetected faults. International Journal of Greenhouse
392 Gas Control 2012, 10:434-442.

- 393 [9] Kramer, D. Scientists poke holes in carbon dioxide sequestration. *Physics Today*
394 August 2012 (8), 65:22.
- 395 [10] West, M., Sanchez, J. J., McNutt, S. R. Periodically triggered seismicity at Mount
396 Wrangell, Alaska, after the Sumatra earthquake. *Science* 2005, 308:1144-1146.
- 397 [11] West, R. D., Markevicius, G., Malhotra, V. M., Hofer, S. Variations in the
398 mechanical behavior of Illinois bituminous coals. *Fuel* 2012, 98:213-217.
- 399 [12] Markevicius, G., West, R. D., Malhotra, V. M., Hofer, S. Does Illinois bituminous
400 coal manifest glass transition: DMA, DSC, and FTIR results. *Fuel* 2012, 103:220-
401 226 [and references therein].
- 402 [13] Tillman, D., Duong, D. N. D., Harding, N. S. *SOLID FUEL BLENDING Principles,*
403 *Practices, and Problems,* (Waltham USA), Butterworth-Heinemann, 2012.
- 404 [14] Romanov, R. Coal Chemistry for Mechanical Engineering: From Macromolecular
405 Thermodynamics to Reservoir Simulation. *Energy & Fuels* 2007, 21:1646-1654.
- 406 [15] Romanov, V. N., Ackman, T. E., Soong, Y., Kleinman, R. L. CO₂ Storage in
407 Shallow Underground and Surface Coal Mines: Challenges and Opportunities.
408

Figure Captions

- Figure 1. The schematic of the high-pressure cell system for imparting shockwaves to cylindrical cores of diameter 2.54 cm and 4 cm.*
- Figure 2. Photographs of the high pressure cell system for subjecting the coal cores to shockwaves. A: Electromagnetic trigger, B: FTIR spectrometer, C: Plexiglas guide tube, D: High-pressure die, E: 4 cm piston, F: High-pressure fittings.*
- Figure 3. The high pressure optical cell mounted in FTIR spectrometer to track emitted gases from the coal cores during shockwave experiments. A: KBr windows, B: High-pressure line, C: Exhaust line.*
- Figure 4. Effects of the shockwaves on the emission of CO₂ from an un-pressurized Cottage Grove coal core (CGC-CS). Shockwaves were applied at 10 minutes. The spectra have been displaced along the y-axis (absorbance) for easy comparison.*
- Figure 5. Effects on the emission of CO₂ from an un-pressurized porous pumice stone (PPS) core. The shockwaves were applied at 10 minutes. The spectra have been displaced along the y-axis (absorbance) for easy comparison.*
- Figure 6. Effects of shockwaves on the integrated intensity (arbitrary units) of the stretching mode of the emitted CO₂ from an un-pressurized Cottage Grove coal (CGC-CS) core.*
- Figure 7. Changes in integrated intensity (in arbitrary units) of the vibrational bands of CO₂ as a function of exposure time for an un-pressurized pumice stone (PPS) core. The shockwaves to the core were applied at 10 minutes.*

Figure 8. The FTIR spectrum of the gases emitted from the pressurized coal (CGC-S1) core under atmospheric pressure conditions. The spectra have been displaced along the y-axis (absorbance) for easy comparison.

Figure 9. Changes in the integrated intensity (in arbitrary units) of the vibrational bands of CO₂ as a function of exposure time for (a) the control (CGC-CS) core (non-pressurized) and (b) the pressurized (CGC-S1) core.

Figure 10. Effects of the shockwave on the emission of CO₂ from pressurized coal (CGC-S1) core. A: Spectrum after 50 minutes of degassing at atmospheric pressure, prior to the applied shockwave. B: Spectrum at 51 minutes when the shockwave was applied. C: Spectrum from 1 minute after shockwave application. D: Spectrum from 8 minutes after shockwave application. The y-scale represents absorbance.

Figure 11. Changes in the integrated intensity (in arbitrary units) of the vibrational bands of the emitted CO₂ as a function of exposure time for cores pressurized to 6.9 MPa of CO₂. Pressurized coal (CGC-S1) core was allowed to emit CO₂ for 50 minutes at atmospheric pressure prior to the application of shockwave at the minute 51 (point C). Pressurized coal (CGC-S2) was allowed to emit CO₂ at atmospheric pressure for 4 minutes before first shockwave was applied (point A). A second shockwave (point B) was applied after 20 minutes of the first shockwave.

Figure 12. Effects of the shockwave on the emission of CO₂ from coal (CGC-S2) core. A: Spectrum after 1 minute of degassing at atmospheric pressure. B: Spectrum at minute 5 when the shockwave was applied. C: Spectrum from 2

minutes after shockwave application. D: Spectrum from 7 minutes after shockwave application. E: Spectrum from 17 minutes after shockwave application. F: Spectrum from 19 minutes after shockwave application. The y-scale represents absorbance.

Figure 13. Effects of the shockwave on the emission of CO₂ from coal (CGC-S2) core.

A: Spectrum from 17 minutes after shockwave application. B: Spectrum from 20 minutes after a second shockwave was applied. C: Spectrum from 1 minute after the second shockwave application. D: Spectrum from 3 minutes after the second shockwave application. E: Spectrum after 10 minutes of the second shockwave application. The y-scale represents absorbance.

Figure 14. The photograph of the Cottage Grove bituminous coal (CGC-S2) core after it underwent shockwave experiments.

Table 1

Parameters used for shockwave experiments on CO₂ pressurized Cottage Grove Illinois bituminous coal cores. The cores were subjected to a compressive shock of 0.374 MPa under atmospheric pressure in a high pressure die.

Sample ID	Pressurized with CO ₂	CO ₂ Pressure (MPa)	Time under CO ₂ Pressure (hours)	Shockwave application after degassing at atmospheric pressure in high pressure die (minutes)
Cottage Grove coal control sample (CGC-CS)	No	-	-	10
Porous pumice stone (PPS)	No	-	-	10
Cottage Grove coal sample 1 (GCC-S1)	Yes	6.9	72	51
Cottage Grove coal sample 2 (GCC-S2)	Yes	6.9	72	4 (first shock) 25 (second shock)

Figure

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14