



# Is there a potential of emission of sequestered CO<sub>2</sub> from Illinois bituminous coal under shockwaves?



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## HIGHLIGHTS

- Probed how shockwaves may affect the sequestered CO<sub>2</sub> in bituminous coal.
- Fabricated a system to apply shockwaves to cores while monitoring emitted gases.
- Shockwaves did not induce gas emission from non-pressurized coal cores.
- Massive amounts of CO<sub>2</sub> emitted from coal cores under compressive shock.
- Shocks ejected almost all the CO<sub>2</sub> from pressurized coal in less than 1 h.

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## ABSTRACT

The mitigation of potential global warming due to the emission of greenhouse gases, especially CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CH<sub>4</sub> while sequestering CO<sub>2</sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> when subjected to shock; however, this was not the case for the cores which were pressurized with CO<sub>2</sub>. The results indicate that massive amounts of CO<sub>2</sub> 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 CO<sub>2</sub>, both chemically and physically, compressive (0.374 MPa) shockwaves forced almost all the CO<sub>2</sub> to be ejected from the coal cores. Surprisingly, most, if not all, the sequestered CO<sub>2</sub> would be emitted in less than 1 h 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 this study because of the presence of compressive and transverse stresses and shears. If such is the case, CO<sub>2</sub> may be emitted even faster. It is reasonable to argue that Illinois bituminous coals may not be suitable hosts for sequestering CO<sub>2</sub> because the region is prone to seismic activity.

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## 1. Introduction

The environmental concerns associated with carbon dioxide (CO<sub>2</sub>) 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

Abbreviations: FTIR, Fourier transform infrared; MPa, mega Pascal; GPa, giga Pascal; M, moment magnitude; cm<sup>-1</sup>, wavenumber; MCT, mercury cadmium telluride.

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as in Europe, toward economically separating CO<sub>2</sub> from flue gas, capturing it, and then developing strategies for long-term storage of the captured gas. Though at present separating and capturing CO<sub>2</sub> 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 CO<sub>2</sub> in various mediums [1,2]. It is generally agreed that sequestering CO<sub>2</sub> 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 CO<sub>2</sub> produced by fossil fuel burning power plants. Though there is a considerable body of data available, which deals with injecting supercritical CO<sub>2</sub> in various reservoirs including adsorption and absorption characteristics, very little is known at present about how the sequestered CO<sub>2</sub> would behave under external perturbations [1–5]. Among the geological storage reservoirs, long-term immobilization of CO<sub>2</sub> in unmineable coal seams presents an added advantage of coal bed methane recovery while simultaneously sequestering CO<sub>2</sub>. However, successful sequestration projects will only be feasible if the public perceives it to be safe and environmentally friendly.

Recently researchers [6–9] have cautioned about large scale CO<sub>2</sub> sequestration in geological reservoirs because of the potential of induced seismicity. The amount of CO<sub>2</sub> to be sequestered is gigantic. Zoback and Gorelick [7] point out that the United States produces about 2.1 billion metric tons per year of CO<sub>2</sub> from coal burning, while China generated almost 6.3 billion metric tons of CO<sub>2</sub> from coal combustion in 2011 alone. These authors argued “that there is a high probability that earthquakes will be triggered by injection of large volume of CO<sub>2</sub> into the brittle rocks commonly found in continental interiors”. Zoback and Gorelick point out that high pressure fluid injection results in increased pore pressure which in turn reduces frictional resistance to fault slippage, potentially triggering earthquakes. However, the problem could be further compounded if there are unmapped faults near the vicinity of the injection wells. Mazzoldi et al. [8] raise concerns that the induced seismicity “may provide preferential pathways for CO<sub>2</sub> leakage out of the reservoirs”.

It is also known that earthquakes have long range effects, e.g., after the 26th December 2004 earthquake in Sumatra, the Rayleigh waves swept across Alaska approximately 11,000 km (~6831 miles) distance and initiated “an 11-min swarm of 14 local earthquakes” [10]. West et al. [10] pointed out that surface waves from the Sumatra earthquake (moment magnitude,  $M = 9$ ) created vertical trough-to-peak ground displacement of 1.5 cm in Alaska. West et al. also argued that shear and normal stresses work in tandem to promote faulting. Because, “Shear stresses alter the forces 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 CO<sub>2</sub> in organic rocks like coal.

Our recent research efforts [11,12] have been directed toward evaluating the potential risks which may be associated with sequestering CO<sub>2</sub> 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 CO<sub>2</sub>, as it is known that CO<sub>2</sub> 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  $30\text{ °C} \leq T \leq 300\text{ °C}$ . 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 CO<sub>2</sub> 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 CO<sub>2</sub> from coal [2], but practically nothing is known about how CO<sub>2</sub> pressurized coals behave when subjected to shockwaves. This paper reports how CO<sub>2</sub>, 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 h. After mildly vacuum drying, the bituminous coal cores were stored under atmospheric conditions prior to subjecting them to high pressure CO<sub>2</sub> 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 CO<sub>2</sub> in geological formations. To answer some of the questions related to how seismic activity may affect the reemission characteristics of sequestered CO<sub>2</sub>, 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. Figs. 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

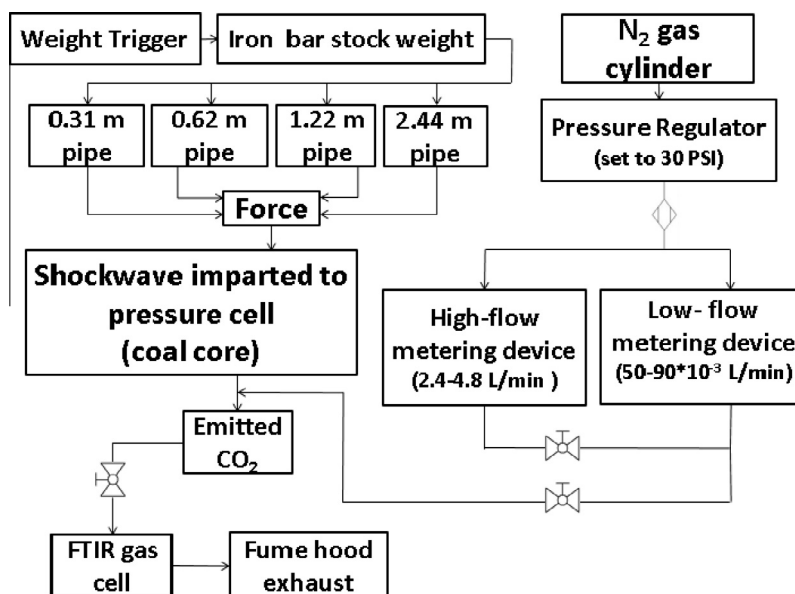


Fig. 1. The schematic of the high-pressure cell system for imparting shockwaves to cylindrical cores of diameter 2.54 cm and 4 cm.

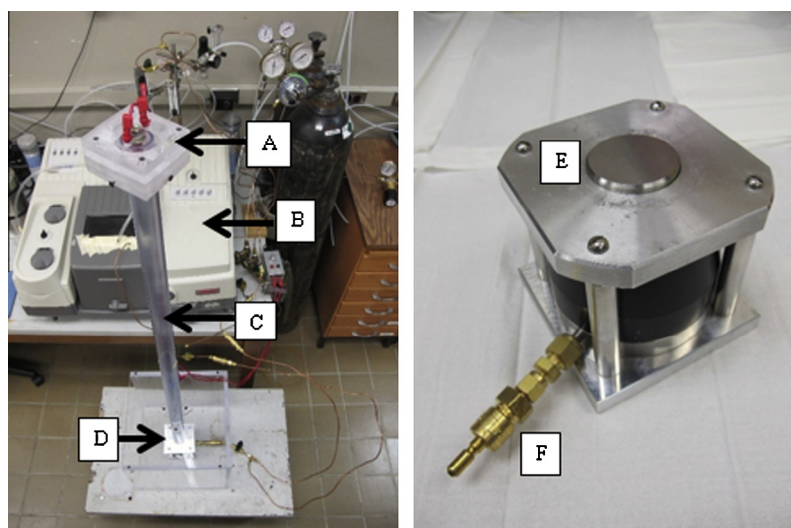


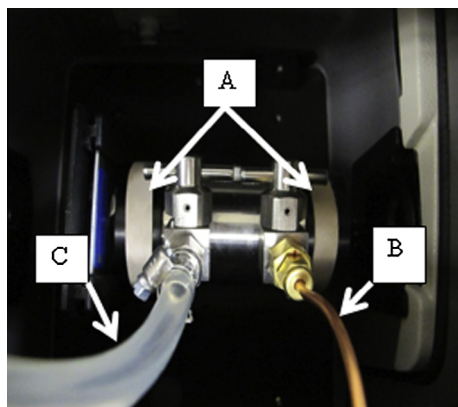
Fig. 2. Photographs of the high pressure cell system for subjecting the coal cores to shockwaves. A: Electromagnetic trigger, B: FTIR spectrometer, C: Plexiglas guide tube, D: High-pressure die, E: 4 cm piston, and F: High-pressure fittings.

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 CO<sub>2</sub>:** 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 N<sub>2</sub> gas to the high pressure line just as the gases were being ejected from the high pressure die. Because N<sub>2</sub> gas has no vibrational modes in the frequency range 4000–400 cm<sup>−1</sup>, only the CO<sub>2</sub> 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



**Fig. 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, and C: Exhaust line.

vapor bands do not interfere with the measurements of the CO<sub>2</sub> vibrational modes. If a CO<sub>2</sub> pressurized coal core degasses with or without the impact of sudden shockwaves, then CO<sub>2</sub> vibrational bands in our FTIR system would be observed. Carbon dioxide produces strong stretching oscillators at  $\sim 2345\text{ cm}^{-1}$  and bending vibrational modes at  $\sim 667\text{ cm}^{-1}$ . It is difficult to control the amount of CO<sub>2</sub> emitted from the coal cores, especially CO<sub>2</sub> pressurized cores, when subjected to shockwaves. The amount of emitted CO<sub>2</sub> gas in the optical cell may saturate the MTC detectors even though the emitted gas is continuously being diluted by the injection of N<sub>2</sub>. 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<sub>2</sub> emitted.

### 2.3. CO<sub>2</sub> 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 (ambient  $\leq P \leq 27\text{ MPa}$ ) with CO<sub>2</sub>. A SFT-10 supercritical fluid CO<sub>2</sub> 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<sub>2</sub> injection pressure was limited to 6.9 MPa. The high pressure vessel was maintained at the desired CO<sub>2</sub> pressure for 72 h. After 72 h of adsorption and/or absorption of CO<sub>2</sub>, 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<sub>2</sub> in the high pressure vessel. However, no fluids were observed being extracted from the coal samples when they were pressurized with CO<sub>2</sub>. 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 CO<sub>2</sub> at 10.35 MPa. Again, no fluids were observed when the samples were extracted during the pressurization experiments. After recovering CO<sub>2</sub> 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 CO<sub>2</sub> in bituminous coal cores, which were pressurized with CO<sub>2</sub>.

## 3. Results and discussion

The main focus of this research is on how shockwaves may affect the fate of sequestered CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> induced activity. It is known that CO<sub>2</sub> 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 CO<sub>2</sub> would stay sequestered in coal seams.

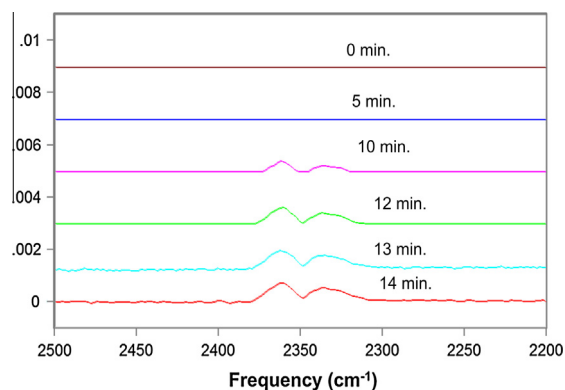
### 3.1. Effects of shockwaves on non-pressurized samples

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. Figs. 4 and 5 show the FTIR spectra of emitted CO<sub>2</sub> 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 min in the shockwave setup prior to subjecting them to shockwaves. It should be noticed that no CO<sub>2</sub> bands were observed prior to 10 min, 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  $2400\text{--}2100\text{ cm}^{-1}$ , indicating that some CO<sub>2</sub> was emitted from the coal. Because this coal core was not pressurized

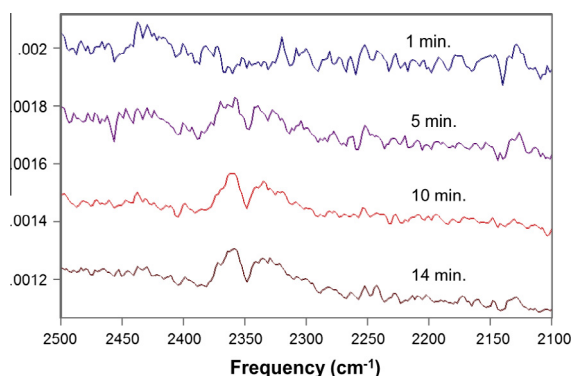
**Table 1**  
Parameters used for shockwave experiments on CO<sub>2</sub> pressurized Cottage Grove Illinois bituminous coal cores. The cores were subjected to a compressive shock of 0.374 MPa under atmospheric pressure in a high pressure die.

Sample ID	Pressurized with CO <sub>2</sub>	CO <sub>2</sub> Pressure (MPa)	Time under CO <sub>2</sub> Pressure (h)	Shockwave application after degassing at atmospheric pressure in high pressure die (min)
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)

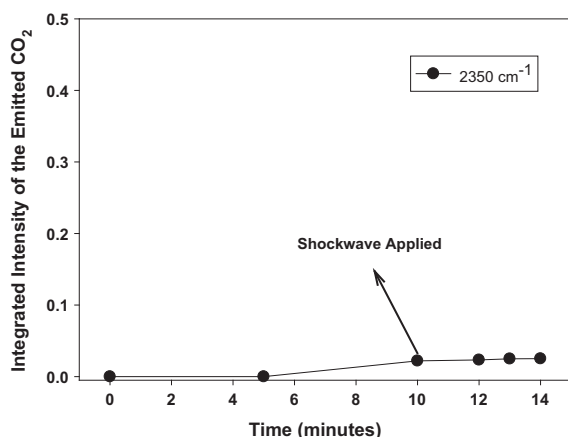




**Fig. 4.** Effects of the shockwaves on the emission of CO<sub>2</sub> from an un-pressurized Cottage Grove coal core (CGC-CS). Shockwaves were applied at 10 min. The spectra have been displaced along the y-axis (absorbance) for easy comparison.



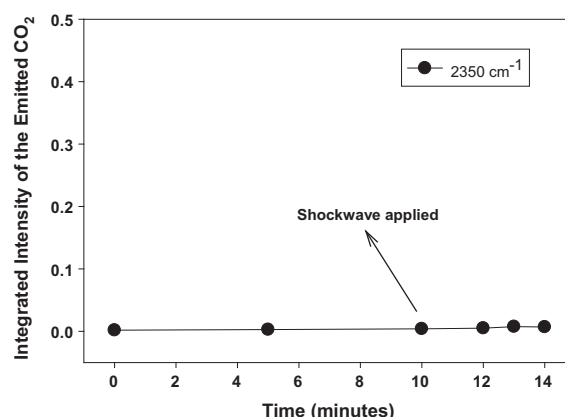
**Fig. 5.** Effects on the emission of CO<sub>2</sub> from an un-pressurized porous pumice stone (PPS) core. The shockwaves were applied at 10 min. The spectra have been displaced along the y-axis (absorbance) for easy comparison.



**Fig. 6.** Effects of shockwaves on the integrated intensity (arbitrary units) of the stretching mode of the emitted CO<sub>2</sub> from an un-pressurized Cottage Grove coal core (CGC-CS) core.

with CO<sub>2</sub>, the potential sources of the observed CO<sub>2</sub> 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 CO<sub>2</sub> 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

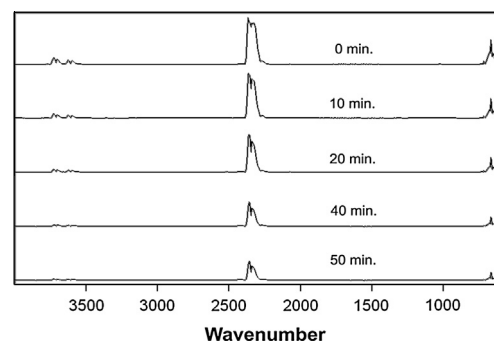


**Fig. 7.** Changes in integrated intensity (in arbitrary units) of the vibrational bands of CO<sub>2</sub> as a function of exposure time for an un-pressurized pumice stone (PPS) core. The shockwaves to the core were applied at 10 min.

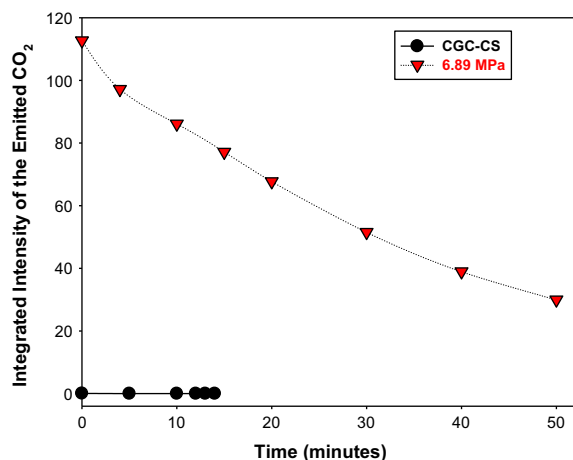
vibrational bands of CO<sub>2</sub> gas were observed, suggesting no CO<sub>2</sub> emission. The fact that no CO<sub>2</sub> gas was emitted from the PPS core further supports the argument that the CO<sub>2</sub> bands observed from non-pressurized Cottage Grove are due to most likely inherent CO<sub>2</sub> in the coal.

### 3.2. Effects of shockwaves on CO<sub>2</sub> pressurized samples

To understand how CO<sub>2</sub> 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 min. This degassing was in addition to ~1 h of degassing required for extracting the coal core from the high pressure (6.9 MPa) CO<sub>2</sub> vessel and transferring it to the closed cell system. Fig. 8, which shows the intensity of the vibrational bands of emitted CO<sub>2</sub>, indicates how much and how fast CO<sub>2</sub> 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 CO<sub>2</sub> pressurized coal cores were exposed to atmospheric conditions, massive amounts of CO<sub>2</sub> were emitted from the Illinois bituminous coal during the first 50 min. Fig. 9 shows a comparative



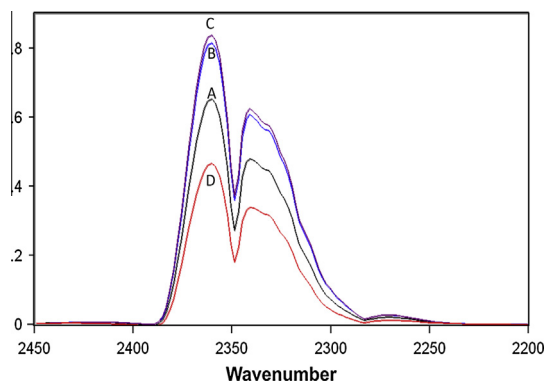
**Fig. 8.** The FTIR spectrum of the gases emitted from the pressurized coal (CGC-S1) core under atmospheric pressure conditions. The spectra have been displaced along the y-axis (absorbance) for easy comparison.



**Fig. 9.** Changes in the integrated intensity (in arbitrary units) of the vibrational bands of CO<sub>2</sub> as a function of exposure time for (a) the control (CGC-CS) core (non-pressurized) and (b) the pressurized (CGC-S1) core.

behavior of the intensity as a function of time of the observed vibrational CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> are ejected. The results presented in Figs. 8 and 9, however, do not answer whether coal, which is known to react with CO<sub>2</sub> physically and chemically, still continues to hold significant amounts of CO<sub>2</sub> even if leakage pathways have been established.

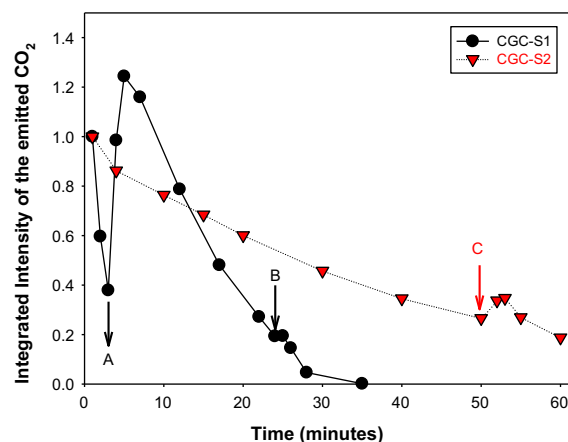
After allowing the CO<sub>2</sub> pressurized CGC-S1 core to emit gas under atmospheric conditions for 50 min, the core was subjected to a 0.374 MPa (54 psi) shockwave at the 51 min mark. As can be seen from Fig. 10, on the application of the shockwave, additional CO<sub>2</sub> was ejected from the coal core. The intensity of the emitted CO<sub>2</sub> jumped in the gas cell on the application of the shockwave



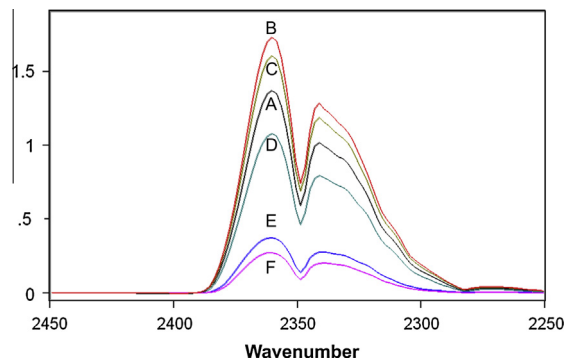
**Fig. 10.** Effects of the shockwave on the emission of CO<sub>2</sub> from pressurized coal (CGC-S1) core. A: Spectrum after 50 min of degassing at atmospheric pressure, prior to the applied shockwave. B: Spectrum at 51 min when the shockwave was applied. C: Spectrum from 1 min after shockwave application. D: Spectrum from 8 min after shockwave application. The y-scale represents absorbance.

at the 51 min, and the intensity of the emitted gas further increased at the 52 min. Thereafter, the intensity of the CO<sub>2</sub> 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 CO<sub>2</sub>, which was either adsorbed or absorbed in the sample, was emitted when the shockwaves were applied to the coal core.

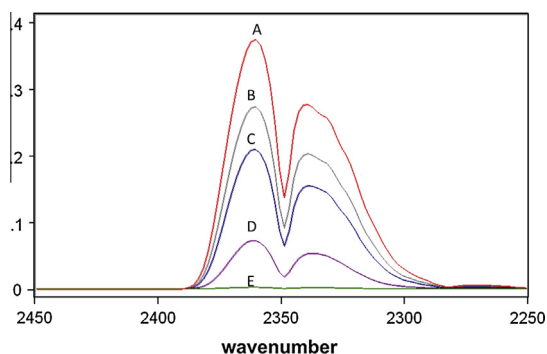
In a second experiment, the Cottage Grove coal core (hereafter listed as CGC-S2), which was pressurized with CO<sub>2</sub> at 6.9 MPa, was allowed to emit CO<sub>2</sub> for 5 min in the closed cell system at atmospheric pressure before a 0.374 MPa shockwave was applied to the sample. Again, the 5 min 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 CO<sub>2</sub> 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 CO<sub>2</sub> were observed from the core (see Figs. 11–13). However, this is



**Fig. 11.** Changes in the integrated intensity (in arbitrary units) of the vibrational bands of the emitted CO<sub>2</sub> as a function of exposure time for cores pressurized to 6.9 MPa of CO<sub>2</sub>. Pressurized coal (CGC-S1) core was allowed to emit CO<sub>2</sub> for 50 min at atmospheric pressure prior to the application of shockwave at the minute 51 (point C). Pressurized coal (CGC-S2) was allowed to emit CO<sub>2</sub> at atmospheric pressure for 4 min before first shockwave was applied (point A). A second shockwave (point B) was applied after 20 min of the first shockwave.



**Fig. 12.** Effects of the shockwave on the emission of CO<sub>2</sub> from coal (CGC-S2) core. A: Spectrum after 1 min of degassing at atmospheric pressure. B: Spectrum at minute 5 when the shockwave was applied. C: Spectrum from 2 min after shockwave application. D: Spectrum from 7 min after shockwave application. E: Spectrum from 17 min after shockwave application. F: Spectrum from 19 min after shockwave application. The y-scale represents absorbance.



**Fig. 13.** Effects of the shockwave on the emission of CO<sub>2</sub> from coal (CGC-S2) core. A: Spectrum from 17 min after shockwave application. B: Spectrum from 20 min after a first shockwave was applied. C: Spectrum from 1 min after the second shockwave application. D: Spectrum from 3 min after the second shockwave application. E: Spectrum after 10 min of the second shockwave application. The y-scale represents absorbance.

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 min mark, observations showed a massive ejection of CO<sub>2</sub> 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 min. 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 min, almost all the sequestered gas in the coal core was emitted. Fig. 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 CO<sub>2</sub> from the coal core during shockwave experiments. However, there was no evidence that CO<sub>2</sub> molecules remained trapped in the coal pores after the application of the shockwaves.



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

## 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 CO<sub>2</sub> sequestration could occur. Nevertheless, the public acceptance of the large-scale geological CO<sub>2</sub> sequestration would require evidence that it is safe. One potential source for CO<sub>2</sub> sequestration is unmineable coal seams. Therefore, experiments were undertaken to identify the fate of CO<sub>2</sub> 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 CO<sub>2</sub> from the coal cores could be simultaneously monitored. The following is concluded from the experiments: (i) Non-CO<sub>2</sub> pressurized coal and porous pumice stone cores showed no significant emission of CO<sub>2</sub> when they were subjected to 0.374 MPa shockwaves. (ii) A massive loss of CO<sub>2</sub> occurred rapidly and exponentially from the coal cores, which were pressurized with 6.9 MPa of CO<sub>2</sub>, when they were exposed to atmospheric pressure in the system. Thereafter, the rate of emission of CO<sub>2</sub> decreased though CO<sub>2</sub> 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 CO<sub>2</sub>, and this CO<sub>2</sub> was not emitted by simply exposing the CO<sub>2</sub> pressurized coal to atmospheric pressure conditions in the closed system. However, all the adsorbed/absorbed CO<sub>2</sub> 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 CO<sub>2</sub> would be emitted in less than 60 min 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 CO<sub>2</sub> in Illinois bituminous coal during seismic activity cannot be discounted.

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