Carbon dioxide sequestration in coal: implications for CO_2 disposal and CH_4 displacement from coal seams

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Abstract

The sequestration of CO_2 within unmineable coal seams is one of the most attractive options for reducing atmospheric CO_2 levels. Thus there is currently considerable interest in the interactions of coal with CO_2 for its long-term disposal. This paper reports the analysis of coal / CO_2 interactions at pressures of up to 30 bar. The results obtained from differential scanning calorimetry (DSC) show that the interactions of CO_2 with coal leads to strongly bound carbon dioxide on coal. It was also found that the temperature of the second order phase transition of coal decreases with increase in CO_2 pressure significantly, indicating that high pressure CO_2 diffuses through coal matrix, causes significant plasticization effects, and changes the macromolecular structure of the coal.

Desorption characteristics of CO_2 from coal were studied by temperature programmed desorption mass spectrometry (TPD-MS). It was found that CO_2 binds more strongly to coal and demands more energy to desorb from coal at higher pressures.

Keywords: CO_2 sequestration, coal, irreversible adsorption, high pressure interactions, macromolecular structure.

1 Introduction

Increased atmospheric CO_2 concentrations due to fossil fuel combustion cause entrapment of solar radiation in the atmosphere and induce a gradual warming of the Earth's surface (Greenhouse effect). This problem is now recognized as one of the most important environmental issues facing society. Therefore there is

WIT Transactions on Ecology and the Environment, Vol 89, © 2006 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/GEO060161

currently considerable interest in the permanent disposal of CO_2 and one option is to sequester it into uneconomic coalfields.

Coal is a chemically heterogeneous solid containing mainly carbonaceous material with very lower amount of mineral mater. It is a microporous macromolecular material containing a wide range of highly reactive chemical functional groups [1]. Its porosity results in the entrance of fluids into its structure and its polymeric nature accompanied with the presence of various functional groups, leads to the chemical interactions of fluids with its matrix.

It is well known that coal swells if it is in contact with solvents, such as pyridine, which break hydrogen bonds [2]. There is some evidence that coal can swell in high pressure CO_2 [3], presumably due to the quadrupolar nature of the molecule disrupting weak electrostatic bonds within the coal structure. Dilatometric studies on coals in contact with CO_2 showed significant increase in sample size [4]. It was suggested that CO_2 swells coal because the solubility parameter of CO_2 is close to the solubility parameter of coal. In the most significant study of coal behaviour in high pressure CO_2 atmospheres Reucroft and Sethuraman [3] have shown that coals swell after exposure to CO_2 and the amount of swelling increases with increasing pressure. It is supposed that the increased swelling effect with increased pressure might be due to the solubility parameter of CO_2 approaching a value closer to that of the coals.

In the present study we have applied differential scanning calorimetry (DSC) for the first time to the investigation of coal/ CO_2 interactions and the effect of high pressure CO_2 on the coal structure. Temperature programmed desorption mass spectrometry (TPD-MS) has been also applied to the study of the desorption characteristics of CO_2 from coal at pressures of up to 30 bar.

2 Experimental

Wyodak coal obtained from the Argonne sample bank was used in this study.

2.1 The DSC procedure

The DSC measurements were performed with a Mettler DSC 30 instrument in conjunction with Mettler software TA72PS for data acquisition and processing. Standard aluminium pans were used, with two pinholes in order to minimise mass transfer limitations in evaporation of water or contact of gas with sample during DSC scans. Nitrogen flowing at 10 ml/min was used as a carrier gas to keep the cell free of oxygen during measurements. Typically 10 mg of sample was used in an experiment. The DSC measurements were performed at a heating rate 10°C/min. Cooling of the furnace between consecutive heating scans was carried out using a liquid nitrogen cooling accessory directly beneath the furnace.

2.1.1 Adsorption of N_2 and CO_2 on Wyodak coal

To study the irreversible adsorption of CO_2 on the coal two different series of scans were conducted on the Wyodak coal sample.

1- A sample of fresh coal was purged with N_2 flowing at 10 ml/min for 10 min in DSC chamber then heated to 110ºC at 10ºC/min and held for 30 min, cooled at nominal rate of 100ºC/min to -60ºC. The sample was then heated from -60 to 200°C at 10ºC/min three times in succession with a cooling rate of 10ºC/min between heating runs. In all scans the sample always remained in the DSC chamber under nitrogen flowing at 10 ml/min.

2- A sample of fresh coal was purged with N_2 flowing at 10 ml/min for 10 min in DSC chamber. then heated to 110ºC at 10ºC/min and held for 30 min, cooled at nominal rate of 100ºC/min to -60ºC under N_2 flowing at 10ml/min. At this point gas was switched to CO_2 and the sample was then heated from -60 to 200ºC under CO_2 flowing at 10 ml/min at 10ºC/min three times in succession with a cooling rate of 10ºC/min between heating runs.

2.1.2 Effect of high pressure CO_2 on the coal structure

Differential scanning calorimetry was also employed to study the effect of high pressure CO_2 on the macromolecular structure of Wyodak coal:

1- A sample of Wyodak coal was purged with N_2 flowing at 10 ml/min for 10 min in DSC chamber. Then heated from 30ºC to 110°C at a heating rate of 10ºC/min, held at 110ºC for 30 min and cooled to 30ºC in N_2 atmosphere at a flow rate of 10 ml/min. This was performed to remove water from coal sample before determining its glass transition temperature. The dried sample was heated from 30ºC to 200ºC at 10°C/min in N_2 atmosphere flowing at 10 ml/min three times in succession. This experiment was carried out to determine the phase transitions of Wyodak coal in N_2 atmosphere.

2- A sample of Wyodak coal was purged with 20 bar Ar three times in succession, to flush adsorbed gases present in the pores in coal and also oxygen form the high pressure cell. Then heated to 110°C, held for 30 min at 110ºC, and cooled to 30ºC at 10°C/min under Ar atmosphere in the high-pressure cell. The sample was loaded with CO_2 to the desired pressure at room temperature. It was exposed to this CO_2 environment for 24 h. After that, the CO_2 pressure was rapidly released, the sample was purged with 20 bar Ar and transferred to the DSC chamber. The sample was purged with N_2 with a flow rate of 10 ml/min for 10 min in the DSC chamber and DSC was carried out from 30°C to 200°C at 10°C/min in N_2 atmosphere three times in succession. The purpose of this sequence was to determine the effect of high-pressure CO_2 atmospheres on the phase transition of the coal sample.

2.2 The TPD-MS procedure

Approximately 150 mg of sample was placed in a sample tube and loaded with CO_2 to the desired pressure at room temperature in a high-pressure cell. The sample was exposed to this high-pressure CO_2 atmosphere for a certain period of time. Then CO_2 pressure was rapidly released and the sample was transferred to the desorption chamber and purged with high purity helium for 10 min at 298 K, before commencing the TPD run. The gas flow rate was 100 ml/min. To perform a TPD –MS scan, the sample was heated by linearly increasing the temperature, 20 K/min, and the evolution of CO_2 from the sample was monitored by a Hiden Analytical HAL/HPR20 Quadrupole Mass Spectrometer (QMS).

3 Results and discussion

3.1 Irreversible adsorption of CO_2 on Wyodak coal

The results of the calorimetric measurements of the adsorption process for nitrogen and carbon dioxide on Wyodak coal are shown in figures1-2.

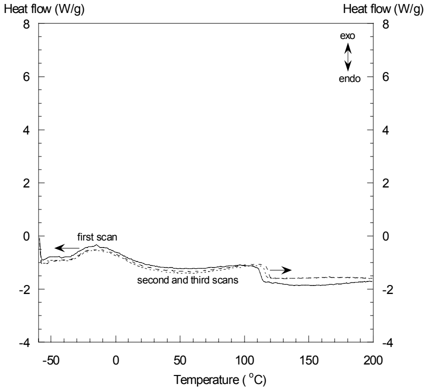

Figure 1: DSC scans for adsorption of N_2 on Wyodak coal sample.

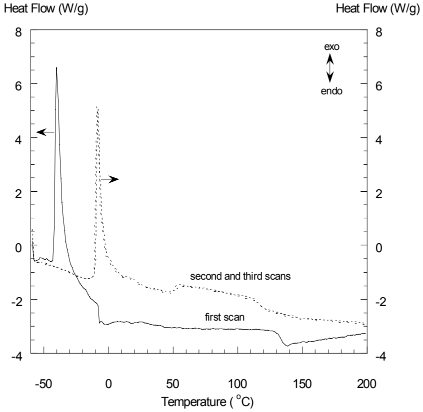

Figure 2: DSC scans for adsorption of CO_2 on Wyodak coal sample.

DSC results for the adsorption of N_2 on coal sample in figure 1 show that coal/N_2 interactions are very weak and the adsorption of N_2 on coal occurs physically and reversibly.

Exothermic peaks for the adsorption of CO_2 on coal in figure 2 are associated with the uptake of CO_2. This is an activated process and presumably at the temperature of the exotherms there is enough thermal energy to overcome the activation energy for diffusion. A comparison between figure1 and figure 2 shows that exotherms evident at low temperatures are absent when the experiments were conducted under N_2. This suggests that interactions between coal and CO_2 are much stronger than those between coal and N_2.

The integrated values for the exotherms associated with the adsorption of CO_2 on Wyodak coal are given in table 1. These values are indicative of the amount of CO_2 sorbed during the experiment. The reduction in the value of the exotherm between the first and second runs suggests that some CO_2 is irreversibly bound to the structure even after heating to 200ºC.

Table 1: Differential enthalpies of the adsorption of CO_2 on Wyodak coal.

	First scan	Second scan	Third scan	Irreversible Sorption capacity
Δ H (J/g)	27.40	20.60	18.72	6.8

3.2 Structural change in coal caused by high pressure CO_2

Figure 3 shows the DSC thermograms for dried Wyodak coal from 30ºC to 200°C. The first scan show an irreversible process, which might be attributed to the structural rearrangement and relaxation in the coal when heated above its glass transition temperature. Subsequent two scans after the first scan show a reversible second order process. This process has the characteristics of glass transition [5]. Before the transition coal is a glassy solid with severely restricted macromolecular motions and diffusion of gases and liquids in its structure is slow. When heated to a certain temperature which is called glass transition temperature, a significant increase in coal's macromolecular motions happens. Above the transition coal becomes rubbery and diffusion into its structure becomes much faster.

Figure 4 shows the DSC thermograms for dried Wyodak coal held under 30 bar CO_2 atmosphere for 24 hours prior to DSC measurements. In this case, the first scan illustrates two endothermic effects. The first one might be related to the evaporation of moisture adsorbed by sample during transferring from the high pressure cell to the DSC chamber and also continuous release of sorbed CO_2 since desorption process is endothermic. The second effect might be attributed to the fast release of sorbed CO_2 from the coal sample at the vicinity of its glass transition temperature. As the coal in the DSC chamber is heated it will continuously release CO_2. At the vicinity of glass transition temperature the desorption rate may suddenly be accelerated since the chain mobility of the coal suddenly increases. This process is irreversible and has disappeared on the second and third scans.

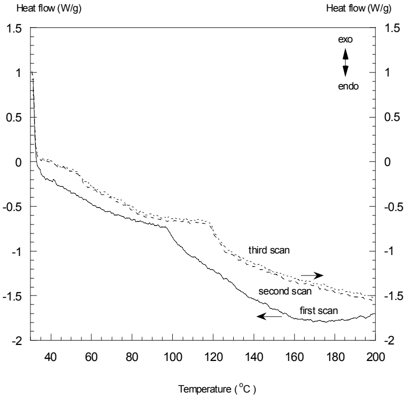

Figure 3: DSC for dried Wyodak coal from 30°C to 200°C in N_2 atmosphere.

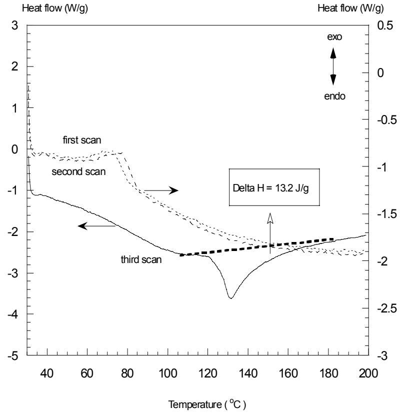

Figure 4: DSC for dried Wyodak coal (held under 30 bar CO_2 atmosphere for 24 hours) from 30°C to 200°C in N_2 atmosphere.

Figure 5 shows the change in the glass transition temperature of the coal with CO_2 pressure. Depression in glass transition temperature of coal at CO_2 atmosphere might be due to the solubility of CO_2 into the coal matrix and plasticization of coal by CO_2.

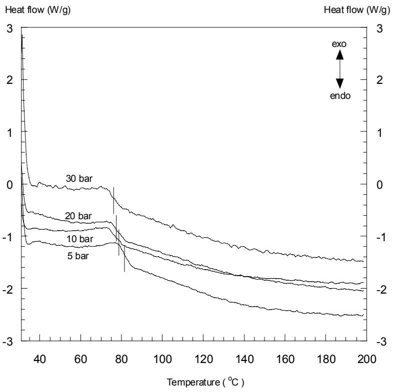

Figure 5: The dependence of glass transition temperature of Wyodak on the pressure of CO_2.

Characteristics of the glass transition of Wyodak coal at various pressures of CO_2 are given in table 2. The further decrease in the glass transition temperature with CO_2 pressure might be due to the further solubility of gas into the coal which is partly due to the solubility parameter of CO_2 approaching to a value closer to that of the coal at higher pressures.

It is supposed that the acidic and basic properties of CO_2 which allow it to form hydrogen bonds or other acid-base bonds play a major role in its solubility in coal [3]. It dissolves in the organic coal matrix, thus modifying the physical and possibly the chemical structure of the coal matrix by disrupting hydrogen bonds in the coal structure during its interaction with coal [6].

Table 2: Glass transition temperature of Wyodak coal at different pressures of CO_2.

P_{CO2} (bar)	Second scan	Third scan
	T_g (°C)	T_g (°C)
0	121.1	121.6
5	86.6	81.7
10	83.2	78.2
20	82.4	77.8
30	81.1	75.7

3.3 Desorption characteristics of CO_2 from Wyodak coal

Figure 6 shows the TPD-MS spectrum of CO_2 desorption from Wyodak coal. The coal sample was held at 5 bar CO_2 atmosphere for 24 hours prior to the

TPD-MS measurements. The spectrum has two regions of interest. The first one at low temperature region (in the range of 300-350 K) and second one after the peak temperature where desorption rates decrease with increasing temperature.

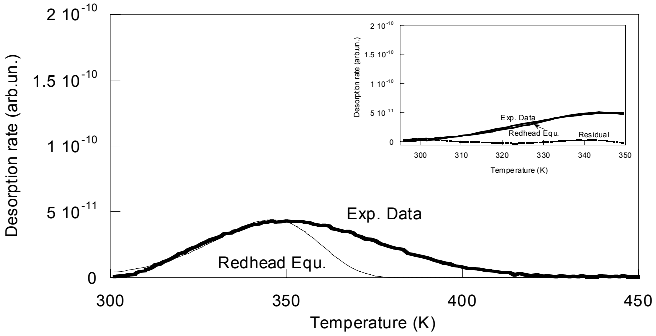

Figure 6: TPD-MS spectrum of CO_2 adsorbed on Wyodak coal at 5 bar.

To analyze the desorption data, the low temperature part of the TPD-MS spectrum has been modelled using the assumption of a first order desorption process with a single activation energy for desorption (Redhead Equation) [7].

$$\ln\left(\frac{N}{N_P}\right)=\frac{E_{des}}{R}\left(\frac{1}{T}-\frac{1}{T_P}\right)+\left(\frac{T}{T_P}\right)^2\exp\left[-\frac{E_{des}}{R}\left(\frac{1}{T}-\frac{1}{T_P}\right)\right]-1$$

N_P is the maximum desorption rate at peak temperature, T_P, and N is the desorption rate at any temperature.

The embedded graph in figure 6 shows that the first order model provides a good fit to the experimental data in the range of 300-350 K. The value of the activation energy for desorption, E_{des}, is calculated from the fitting of the low temperature part of the desorption spectrum to the model. The value of E_{des} for desorption of CO_2 from Wyodak coal is estimated as $E_{des} \approx 15$ kcal/mole. This value is much smaller than the ~ 30 kcal/mol value for activation energy for desorption of pyridine from Illinois #6 coal measured by Hall and Larsen [7]. Pyridine is an excellent hydrogen bound acceptor and a strong organic Lewis base [8], it interacts with coal through strong noncovalent interactions and hydrogen bonding with coal hydroxyls [9]. A comparison between these values shows that the estimated value for activation energy of CO_2 desorption from Wyodak coal is sensible.

The trail of the spectrum after the peak shows that desorption rate does not follow the first order desorption model. The process of CO_2 desorption from coal is a mass transfer process involving several elementary processes. These processes may include diffusion through macropores, diffusion through micropores and diffusion through coal matrix. In small micropores, diffusional resistance limits mass transfer process. The mass exchange can also be limited due to the large energy barrier for desorption. At higher surface coverages, the diffusivity is high and the rate of desorption reaches a maximum. As temperature increases and the desorption process proceeds, high energy sites in the microporous structure are released. Due to the large energy barriers the rare of desorption form these sites is very slow [10]. Therefore the deviation of desorption spectrum from the fist order kinetic model might be due to the contributions of activated diffusion effects, micropore diffusional resistance, barrier resistance of high energetic sites and experimental error in the instrument.

TPD-MS spectra of CO_2 adsorbed on Wyodak coal at various pressures are compared in figure 7. The total area under a TPD-MS spectrum is proportional to the amount of adsorbed CO_2 [11]. The values of E_{des} and the integrated areas under the spectra of CO_2 for various pressures are shown in Table 3. It can be noted that the desorption intensities increases with pressure indicating the amount of CO_2 sorbed in the coal is greater at higher pressures. Consequently at higher pressures the relatively larger amount of CO_2 would be desorbed.

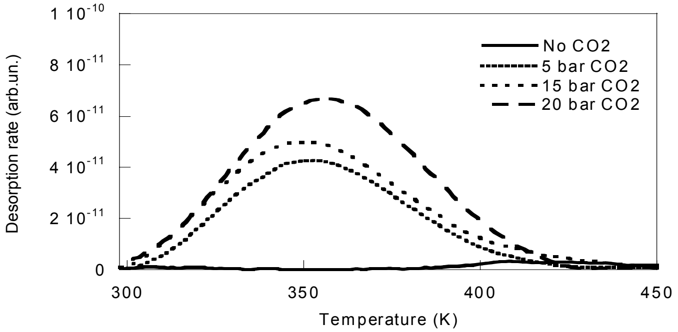

Figure 7: TPD-MS spectra of CO_2 adsorbed on Wyodak at various pressures.

Table 3: Desorption parameters for CO_2 adsorbed on Wyodak coal at various pressures for 24 hours.

P (bar)	E_{des} (cal/mol)	Integrated area
5	14521	1.5744×10^{-9}
15	15210	3.341×10^{-9}
20	15399	4.673×10^{-9}

4 Conclusions

It has been found that CO_2 binds to the structure of Wyodak coal strongly and irreversibly even after heating to 200°C. Glass transition of coal decreases with

CO_2 pressure significantly, so there is a strong suggestion that high pressure CO_2 diffuses through coal matrix, causes significant plasticization effects and changes the macromolecular structure of coal. Desorption characteristics of coal loaded with high pressure CO_2 show that the amount of CO_2 uptake increases with increasing CO_2 pressure. Increase in activation energy for CO_2 desorption from coal with pre-adsorbed CO_2 pressure suggests that high pressure interactions will demand more energy to desorb from coal probably due to the further access of CO_2 to the coal microporous structure.

The results of this study prove that Wyodak coal have a great affinity and high irreversible sorption capacity for CO_2 and could be excellent for CO_2 sequestration.

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