

Thermodynamical Studies of Irreversible Sorption of CO₂ by Wyodak Coal

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ABSTRACT: Differential scanning calorimetry (DSC), temperature programmed desorption mass spectrometry (TPD-MS) and small angle neutron scattering (SANS) were used to investigate CO₂ uptake by the Wyodak coal. Adsorption of carbon dioxide on Wyodak coal was studied by DSC. The exotherms evident at low temperatures are associated with the uptake of CO₂ suggesting that carbon dioxide interacts strongly with the coal surface. Reduction in the value of the exotherms between the first and second runs for the Wyodak coal suggests that some CO₂ is irreversibly bound to the structure even after heating to 200 °C. DSC results also showed that adsorption of CO₂ on the coal surface is an activated process and presumably at the temperature of the exotherms there is enough thermal energy to overcome the activation energy for adsorption. The adsorption process is instantly pursued by much slower diffusion of the gas molecules into the coal matrix (absorption). Structural rearrangement in coal by CO₂ is examined by change in the glass transition temperature of coal after CO₂ uptake at different pressures. The amount of gas dissolved in the coal increases with increasing CO₂ pressure. TPD-MS showed that CO₂ desorption from the Wyodak coal follows a first order kinetic model. Increase in the activation energy for desorption with pre-adsorbed CO₂ pressure suggests that higher pressures facilitate the transport of CO₂ molecules through the barriers therefore the amount of CO₂ uptake by the coal is greater at higher pressures and more attempts are required to desorb CO₂ molecules sorbed at elevated pressures. These conclusions were further confirmed by examining the Wyodak coal structure in high pressure CO₂ by SANS.

KEY WORDS: Coal, CO₂, Adsorption, Desorption, Storage, Structural change.

INTRODUCTION

Among different CO₂ sequestration options such as depleted oil and gas fields, deep saline aquifers, gas-rich hales, methane hydrate formations, salt caverns, other geological formations, or the ocean disposal of CO₂, long-term storage of CO₂ within coal seams is known as one of the best options under investigation [1].

Study of sorption of CO₂ by coal is an ongoing and very important area of research for permanently storing CO₂ into coal seams and reducing the rate of accumulation of this greenhouse gas in the atmosphere. Oceanic sequestration may be a viable option for the storage of CO₂ from large, stationary sources near the coast; however,

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it is probably not the best option for CO₂ from sources in the continental interior. Furthermore, the biological effects of CO₂ disposal on the deep aquifers and deep-sea floor are not known yet and considering these sites as potential geological hosts for long-term CO₂ storage is ecologically under question [1, 2].

Sequestration of CO₂ in coal is a storage process, which allows the production of a value-added product such as methane (CH₄). This value-added process includes sequestration of CO₂ in gassy coalbeds with the simultaneous recovery of CH₄ with CO₂ [1].

In fact knowledge of coal/CO₂ interactions contributes to the understanding of the possible effects of CO₂ on the structure and behaviour of the coal in order to predict the ability of coal seams to sequester CO₂ for long time period.

Coal is a chemically heterogeneous solid containing mainly carbonaceous material with very lower amount of mineral matter [3]. It is a three dimensionally crosslinked macromolecular structure with a wide range of highly reactive chemical functional groups [4]. The coal molecules are closely packed in coal particles by different intermolecular forces such as London and van der Waals forces, hydrogen bonds, π - π and charge transfer interactions [4, 5].

Diffusion of gasses or organic molecules through the internal surface and internal structure of coal influences its structure and properties. By measuring the rate of toluene uptake by a pyridine extracted bituminous coal, *Hsieh and Duda* [6] showed that the solvent molecules first rapidly adsorb on the coal surface and diffuse immediately but breaking apart of these intermolecular forces between coal molecules occurs at a much slower rate. As the solvent molecules make their way into the solid coal, the relaxation and rearrangement of the macromolecular structure of coal occurs. There is some evidence that coal can swell in high pressure CO₂ [7], presumably due to the quadrupolar nature of the molecule disrupting weak electrostatic bonds within the coal structure. Dilatometric studies on coals in contact with CO₂ also showed significant increase in sample size [8].

Coal surface areas have been determined by CO₂ adsorption. It is believed that CO₂ gives higher surface area values, because it is able to induce swelling in coal and through imbibition it is available to both open and close porosity [9]. In the most significant study of coal behaviour in high pressure CO₂ atmospheres *Reucroft*

and *Sethuraman* [7] have shown that coals swell after exposure to CO₂ and the amount of swelling increases with increasing pressure. These studies show that CO₂ behaves similar to organic solvents in its interactions with coal.

Many workers have investigated the use of coal beds as the geologic host for sequestration of CO₂. An extensive review on the storage of captured CO₂ in coal seams is reported by *Withe et al.* [10]. This review shows that the thermodynamics of CO₂ adsorption on coal concerning the irreversibility of the adsorption and binding of carbon dioxide molecules to the coal structure is not well studied yet and there is a dearth of information on the irreversibility of coal/CO₂ interactions.

This paper considers the adsorption / desorption behaviour of the Wyodak coal for CO₂ storage. The coals of the Tongue River Member in the Powder River Basin of Wyoming consist of approximately 32 coal seams with a combined thickness in excess of 300 ft. One of the major coal seams within the Tongue River Member is the Wyodak coal. This coal seam contains the largest coal resource in the Powder River Basin and is the largest coal producing bed in the United States. It is subbituminous with an average BTU of 8, 220, ash of 6.0 %, and sulfur of 0.50 % [11].

In this study the thermodynamics and mechanism of CO₂ sorption by the Wyodak coal in terms of the strength and irreversibility of the interactions and structural changes caused by imbibition of the gas in the coal matrix at pressures up to 30 bar are examined. The sorbed coal was then desorbed to check how tightly stored gas is bound to the coal structure. The experimental desorption data were fitted to a first order kinetic model to determine the binding energy of CO₂ for the Wyodak coal. SANS technique was applied to investigate adsorption and diffusion of CO₂ into the coal structure at pressures up to 30 bar. Significant decrease in the scattering intensities upon exposure of the coal to high pressure CO₂ showed that high pressure CO₂ rapidly adsorbs on the coal and reaches to all pores in the structure. In situ small angle neutron scattering on coal at high pressure CO₂ atmosphere showed an increase in scattering intensities with time suggesting that high pressure CO₂ diffuses into the coal matrix, swells the matrix and probably creates micro-porosity by extraction of volatile components from coal.

SANS theory

Small angle scattering from porous solids arises from

the changes in scattering density due to the interface between the solid and the pores [12]. In a SANS experiment, the intensity of scattered neutrons $I(q)$ is measured as a function of scattering angle from the incident beam, or alternatively, as a function of the scattering wave vector q . The scattering wave vector, q , is the difference between the vectors of incident beam and scattered neutrons and is defined by:

$$q = \frac{4\pi}{\lambda} \sin(\theta) \quad (1)$$

Where, λ is the neutron wavelength, and θ is half of scattering angle. The general equation for determining the intensity of scattering is:

$$I(q) = I_0(\lambda) \Delta\Omega \eta(\lambda) T(\lambda) V_s \frac{d\Sigma}{d\Omega}(q) \quad (2)$$

Where I_0 is the incident flux, $\Delta\Omega$ is the solid angle element, η is the detector efficiency, T is the neutron transmission of the sample and V_s is the volume of the sample exposed to the neutron beam [13]. The first three terms in equation (2) are instrument specific, whereas the last term is sample dependent and is known as the differential cross section. Because the differential cross section contains all the information on the size, shape, and interactions between the scattering centres in the sample, the objective of a SANS experiment is to determine differential cross section. A generalized expression for the SANS from a sample can be written as follows [14]:

$$\frac{d\Sigma}{d\Omega}(a) = (\rho_p - \rho_m)^2 \int N_0 G(q, R) [V(R)]^2 F(R) dR \quad (3)$$

Where N_0 is the number density of scattering centres, $G(q, R)$ is the scattering kernel, $V(R)$ is the volume of the scattering centres and $f(R)$ is the normalized size distribution of scattering centres.

The term $(\rho_m - \rho_p)^2$ is the square of the difference in neutron scattering length density of the two phases (particles or pores and matrix). This term is known as contrast and is the key parameter to determining the intensity of scattering.

EXPERIMENTAL

Coal sample

Wyodak coal obtained from Argonne sample bank

Table 1: Analysis of the coal sample.

Coal	Approximate analysis (wt %)				Elemental analysis (wt %)				
	MC	FC	VM	Ash	C	H	O ^a	N	S
Wyodak	19.9	38.4	35.7	5.9	75.1	5.35	18.05	1.12	0.7

MC: Moisture content, FC: Fixed carbon, VM: Volatile Matter, a) By difference.

received in sealed 5 g ampoules was used in this study. Wyodak coal is a sub-bituminous coal. The complete analysis of the coal sample such as proximate analysis, elemental analysis and Pore analysis are given in table 1 and in the BET analysis section.

BET analysis

Adsorption-desorption isotherms of nitrogen on the Wyodak coal sample are shown in Fig. 1. The isotherms show a hysteresis loop with type-IV isotherm which is representative of the filling and emptying of mesopores in the P/P_0 region of 0.2 - 0.9 by capillary condensation of the adsorbate in the mesopores of the solid. This suggests the mesoporosity in the solid [15]. The lower part of the hysteresis loop represents the filling of the mesopores while the upper part represents the emptying of the mesopores.

Shown in Fig. 2 is pore size distribution (PSD) for the coal sample calculated using the BJH method. The obtained PSD indicates that the coal structure is dominated by mesopores with pore width of 8 nm. Specific surface area S_{BET} , total pore volume V_t and average pore diameter for the coal sample under study are 3.7 m²/g, 0.015 cm³/g and 17.13 nm respectively.

DSC measurements

The DSC measurements were performed with a Mettler DSC 30 instrument using standard aluminium pans with two pinholes in order to minimize 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 of 10 °C/min. Cooling of the furnace between consecutive heating scans was carried out using a liquid nitrogen cooling accessory directly beneath the furnace.

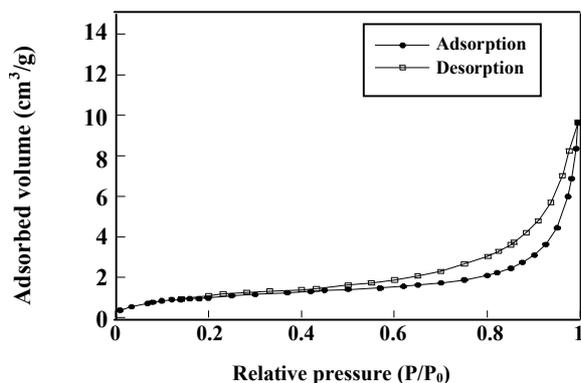


Fig. 1: Adsorption / desorption isotherms of N_2 (77 K) on Wyodak coal.

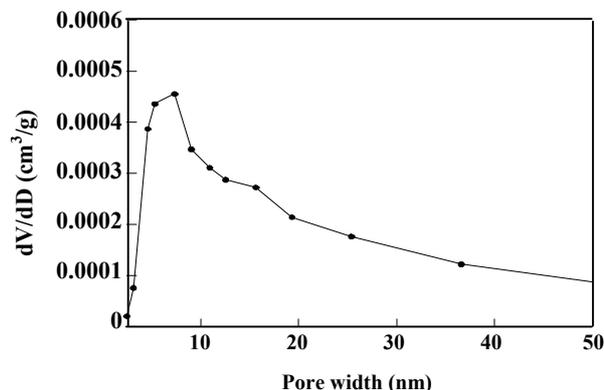


Fig. 2: Pore size distribution of Wyodak coal sample.

Adsorption tests

A sample of fresh Wyodak coal was purged with N_2 flowing at 10 ml/min for 10 min in the DSC chamber. Then heated to 110 °C at 10 °C/min and held for 30 min, cooled at nominal rate of 100 °C/min to -60 °C under N_2 flowing at 10 ml/min. At this point DSC was performed under either 1 bar N_2 or CO_2 from -60 °C to 200 °C three times in succession.

Structural change tests

Effect of high pressure CO_2 on the macromolecular structure of the wyodak coal was investigated by DSC as follows: A sample of fresh wyodak coal was placed in a high pressure cell and purged with 20 bar Ar three times in succession to flush adsorbed gases present in the pores in coal and also oxygen from high pressure cell. The sample was dried at 110 °C for 30 min and cooled down to 30 °C under Ar in the high pressure cell. Then the dried sample was exposed to CO_2 at the desired pressure for 24 hours. After that the CO_2 pressure was rapidly released and the sample was purged with 20 bar Ar and transferred to the DSC chamber. Prior to the DSC scans the sample was purged with N_2 flowing at 10 ml/min for 10 min in the DSC chamber and DSC was performed from 30 °C to 200 °C at 10 °C/min under N_2 flowing at 10 ml/min three times in succession.

TPD-MS measurements

CO_2 desorption tests

The desorption experimental data were collected by a Hiden Analytical HAL/HPR20 Quadrupole Mass Spectrometer (QMS). The mass spectrometer was set up to continuously monitor the evolution of CO_2 from the

sample. The CO_2 partial pressure and temperature data were collected by a computer via the HAL temperature interface and the mass spectrometer interface. Flowing helium with a flow rate of 100 ml/min was used to flush evolved gas into the mass spectrometer. Approximately 100 mg of the sample was placed in a sample holder 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, the 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, prior to the TPD run. To perform a TPD 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 QMS.

SANS measurements

Small angle neutron scattering experiments were performed at the ISIS spallation neutron source at the Rutherford Appleton Laboratories, Chilton, Didcot in the UK. This is a time-of-flight source and the small angle instrument (LOQ) and uses neutrons over the wavelength range 2.2-10 Å. With this wavelength range, LOQ offers a very wide range of scattering wave vector q . The sample holder consisted of two optically transparent windows made from sapphire with a path length of 0.2 cm. This assembly was placed in a high-pressure cell. Typical SANS experiments were as follows: In the first experiment, a sample of fresh coal (no CO_2) was contained in the high pressure optical cell and SANS performed with transmission time of 15 min, and scattering time of 10 min. In second experiment the coal

sample was placed in the high pressure optical cell and CO₂ was transmitted from a high pressure CO₂ cylinder within the cell. The pressure was controlled by a pressure transducer at a desired pressure and sample was under this pressure for 24 hours prior to the SANS experiment. Then SANS was performed with transmission time of 15 min, and scattering time of 10 min. This experiment was repeated for different CO₂ pressures. In the third set of experiments, SANS was performed *in situ* on the coal sample at high pressure CO₂ atmosphere. The high pressure CO₂ was introduced rapidly on the fresh coal sample contained in the high pressure optical cell at a desired pressure controlled by pressure transducer and $I(q)$ was immediately measured every 10 min with transmission time of 15 min, and scattering times of 10 min. In each experiment data were collected and then reduced. Data reduction consists of the correction of the scattering data for scattering from empty cell or gas filled cell, transmitted beam and other instrumental backgrounds.

RESULTS AND DISCUSSION

DSC

CO₂ adsorption on the Wyodak coal

Figs. 3 and 4 show the results of calorimetric measurements of the adsorption process for nitrogen and carbon dioxide on the Wyodak coal respectively. The exotherms evident at low temperatures are absent when the experiment was conducted under nitrogen and are associated with the uptake of CO₂ by the coal sample. The DSC results show that CO₂ adsorption on the coal is an activated process and presumably at the temperature of the exotherms there is enough thermal energy to overcome the activation energy for diffusion.

The integrated values for the exotherms are given in table 2. These values are indicative of the total amount of CO₂ adsorbed during the experiment. The reduction in the integrated values for the exotherms between the first and second runs suggests that some CO₂ is irreversibly bound to the structure even after heating to 200 °C. The energy value associated with the irreversible sorption capacity of the Wyodak coal for CO₂ was obtained in terms of difference between integrated values of exotherms for the first and second runs. This energy value is also given in table 2 and indicates that CO₂ molecules interact with the highest binding energy sites available on the coal surface to form strong bonds

Table 2: Differential enthalpies of CO₂ adsorption on Wyodak coal.

	1 st scan	2 nd scan	3 rd scan	Irreversible sorption capacity
ΔH (J/g)	27.40	20.60	18.72	6.8

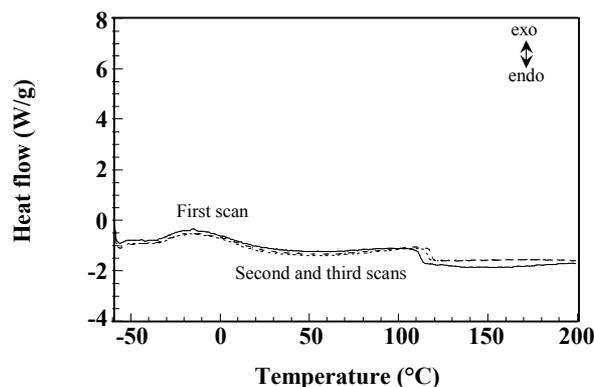


Fig. 3: DSC scans for adsorption of N₂ on Wyodak coal sample.

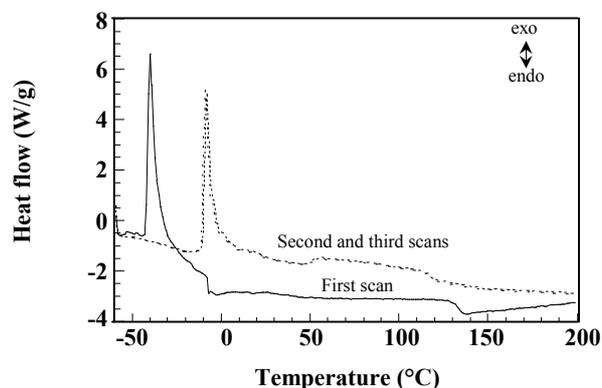


Fig. 4: DSC scans for adsorption of CO₂ on Wyodak coal sample.

with the surface active sites like carboxylic and hydroxylic functional groups [16]. Table 2 shows that the heats of adsorption of CO₂ in second and third scans are almost the same and lower than the heat of adsorption in the first scan.

This suggests that high-energy binding sites are saturated with CO₂ during the first scan and pre-adsorbed active sites can affect the CO₂ adsorption energy. Steep exotherms observed on the DSC scans suggest that CO₂ adsorbs rapidly on the coal and accesses entire pores. Once the gas enters the pores, it may interact strongly with some sites on the coal surface and

may not be removed totally after the second heating. This irreversible CO₂ adsorption may be evidence of "permanent" sequestration.

Structural change in the coal caused by high pressure CO₂

Fig. 5 shows the DSC thermograms for dried Wyodak coal from 30 °C to 200 °C. The first scan shows an irreversible process, which might be attributed to the structural rearrangement and relaxation in the coal when heated above its glass transition temperature [17]. Subsequent two scans after the first scan show a reversible second order process. This process has the characteristics of glass transition [18]. 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 [19]. These results show the occurrence of the glass transition process in the Wyodak coal by heating in N₂ atmosphere before exposure to CO₂.

Fig. 6 shows the DSC thermograms for dried Wyodak coal held under 30 bar CO₂ atmosphere for 24 hours prior to DSC measurements. In this case, the first scan illustrates two endothermic effects. The first one is related to the continuous release of sorbed CO₂ since desorption process is endothermic. The second effect might be attributed to the fast release of sorbed CO₂ 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 CO₂. 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. The second and third scans in Fig. 6 are reversible and show the glass transition process in the Wyodak coal after exposure to 30 bar CO₂. It can be seen that the temperature at which glass transition happens is decreased significantly.

Fig. 7 shows the variations of the glass transition temperature of Wyodak coal at different CO₂ pressures. Depression in the glass transition temperature of the coal with increase in CO₂ pressure might be in part due to the additional solubility of CO₂ in the macromolecular structure of the coal.

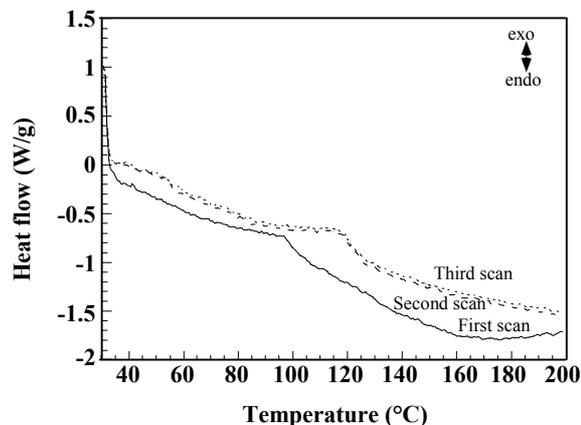


Fig. 5: DSC for dried Wyodak coal from 30 °C to 200 °C in N₂ atmosphere.

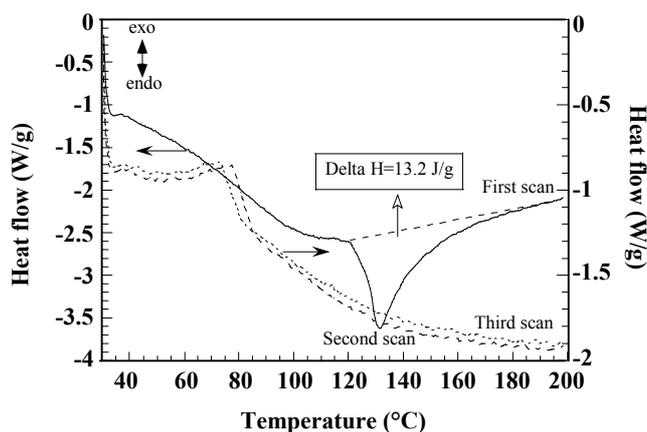


Fig. 6: DSC for dried Wyodak coal (held in 30 bar CO₂ for 24 h) from 30 °C to 200 °C in N₂ atmosphere.

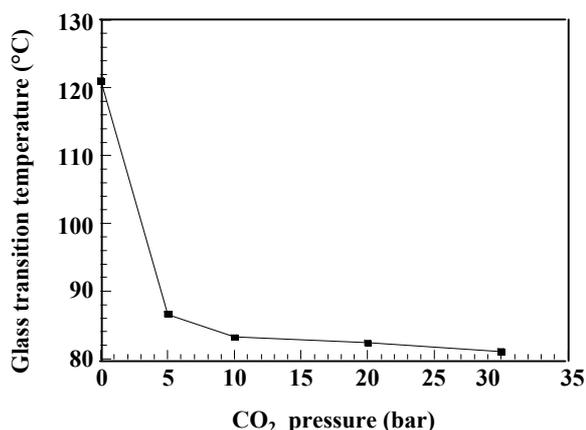


Fig. 7: Depression in the glass transition temperature of Wyodak coal with CO₂ pressure.

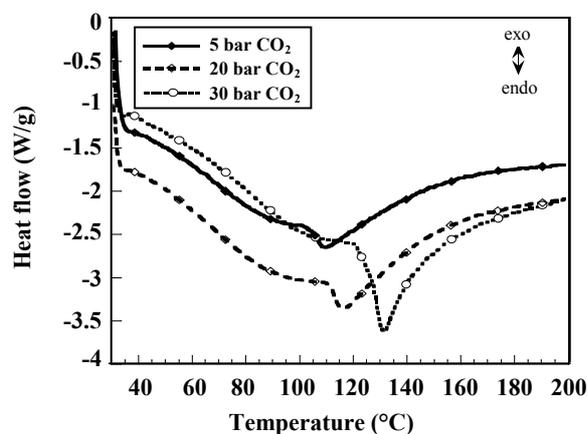


Fig. 8: DSC thermograms for desorption of CO₂ from Wyodak coal adsorbed at different CO₂ pressures.

DSC thermograms for desorption of CO₂ pre-adsorbed at different pressures on the Wyodak coal are shown in Fig. 8.

Increase in the intensity of the endothermic peaks with pre-adsorbed CO₂ pressure suggests that the amount of CO₂ sorbed into the coal matrix increases with CO₂ pressure as a result larger amount of gas would be desorbed and significant heat effect can be detected at higher pressures. The solubility parameter is defined in terms of the molar enthalpy of vaporization (ΔE) and the molar volume (V) as $\delta = (\Delta E / V)^{1/2}$ [8]. The solubility parameter of CO₂ will increase with pressure due to the decrease in its molar volume. Therefore the further solubility of the gas into the coal matrix at higher pressures may be partly due to the solubility parameter of CO₂ approaching to a value closer to that of the coal [7,8].

TPD-MS

Desorption of CO₂ from the coal

TPD-MS spectrum of CO₂ desorption from Wyodak sample is shown in Fig. 9. The coal was loaded with 5 bar CO₂ prior to the desorption experiment. The thermodesorption spectrum shows that the rate of desorption increases with temperature, goes through a maximum and drops to zero as adsorbed molecules desorb from the coal. This shows that the desorbing molecules must pass through an activated state and CO₂ desorption from coal is an activated process.

The experimental desorption data were fitted to a first

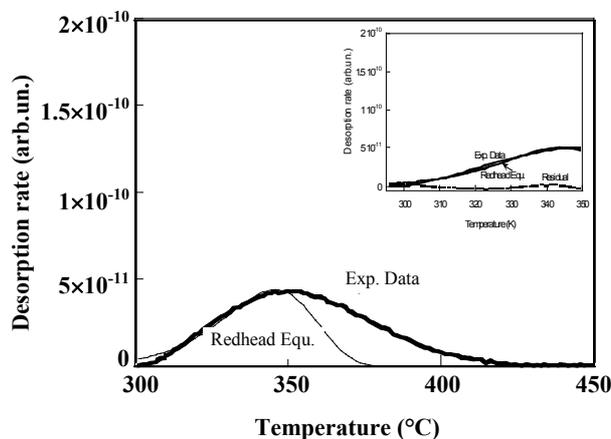


Fig. 9: TPD-MS spectrum of CO₂ adsorbed on Wyodak coal at 5 bar.

order kinetic model to determine the binding energy of CO₂ for the Wyodak coal.

$$\frac{E_{des}}{RT_p^2} = \left(\frac{k_{des}}{\beta} \right) \exp\left(\frac{E_{des}}{RT_p} \right) \quad (5)$$

Where N is the number of gas molecules desorbed from the surface, E_{des} is the activation energy for desorption and A is the pre-exponential factor for desorption. It can be considered as the attempt frequency at the overcoming the barrier to desorption.

At the maximum desorption rate the desorption parameters are related by the Redhead equation [20] as follow:

$$-\frac{dN}{dt} = AN \exp\left(\frac{-E_{des}}{RT} \right) \quad (4)$$

T_p is the peak temperature or the temperature at which the maximum active desorption occurs. A normalized expression for the first order desorption is given by equation (6) [21]:

$$\ln\left(\frac{N'_p}{N'} \right) = \frac{E_{des}}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) + \left(\frac{T}{T_p} \right)^2 \times \exp\left[-\frac{E_{des}}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) \right] - 1 \quad (6)$$

N'_p is the maximum desorption rate at peak temperature and N' is the rate of desorption at any temperature.

Embedded graph in Fig. 9 shows that the first order kinetic model provides a good fit to the desorption

spectrum in the range of 300-350 K. The value of the activation energy for desorption of CO₂ from the Wyodak coal at this temperature range is estimated as $E_{des} \approx 15$ kcal/mole. This value is in agreement with the value of ~ 11 kcal/mole for desorption of CO₂ from the pittsburgh # 8 coal, measured by Mirzaeian and Hall [22] and shows that CO₂ is strongly bound to the structure of the Wyodak coal. The high temperature part of the thermodesorption spectrum shows that desorption data deviate from the first order kinetic model. The existence of different adsorption sites on the coal surface and also diffusion of CO₂ into the structure of the coal could be the source of the deviation from the first order model. Desorption of CO₂ from coal is an activated process and involves several elementary processes.

These processes may include diffusion through macropores, mesopores and micropores and also diffusion through the coal matrix [23]. It is assumed that the rate of desorption is the rate at which CO₂ molecules pass through the activated state and overcome the energy barriers for desorption [24]. At lower temperatures the surface coverage is high, diffusivity is high and desorption happens from the low energetic physisorbed sites. As temperature increases high energy sites will desorb and due to the large energy barriers the activation energy for desorption is sufficiently high and desorption from these sites is very slow [25]. This will lead to more benefit on the storage of CO₂ into the coal.

TPD-MS spectra of CO₂ adsorbed on Wyodak coal at various pressures are compared in Fig. 10. The total area under a TPD-MS spectrum is proportional to the amount of adsorbed CO₂ [26]. The values of E_{des} and the integrated areas under the spectra of CO₂ for various pressures are given in table 3. It can be noted that the desorption intensities increase with pressure indicating the amount of CO₂ sorbed in the coal is greater at higher pressures. Consequently at higher pressures the relatively larger amount of CO₂ would be desorbed.

SANS

CO₂ uptake by coal at different pressures

Fig. 11 shows the small angle neutron scattering patterns of the Wyodak coal at various CO₂ pressures. The drastic reduction in the scattering intensities for coal at high pressure CO₂ compared with the intensities for fresh coal might be attributed to the reduction in the

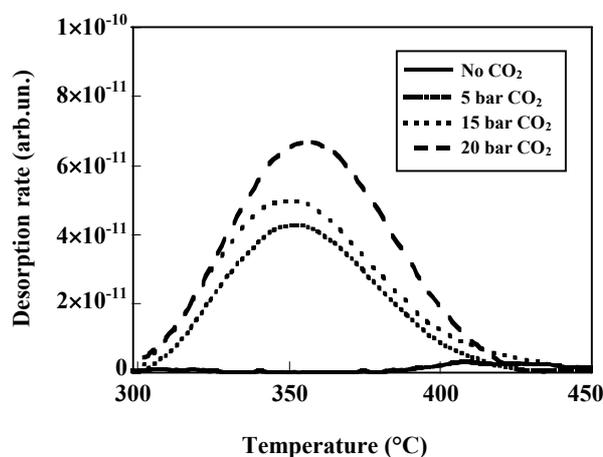


Fig. 10: TPD-MS spectrum of CO₂ adsorbed on Wyodak coal at various pressures.

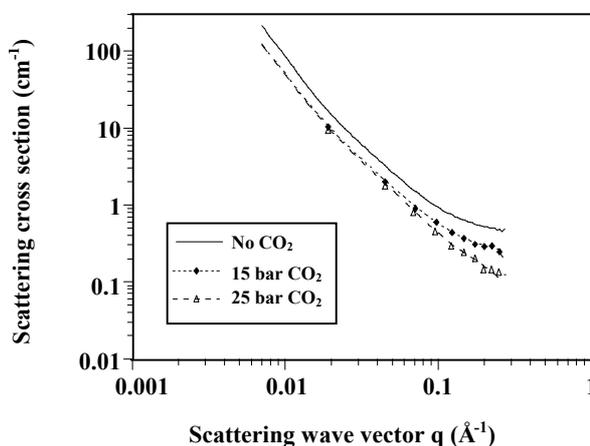


Fig. 11: SANS patterns for Wyodak coal loaded with CO₂ at various pressures for 24 hours.

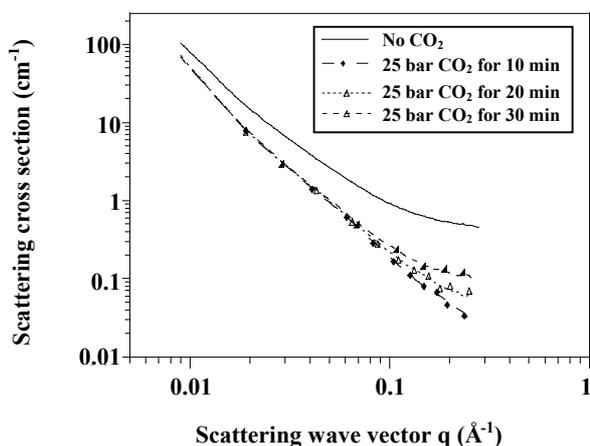


Fig. 12: SANS patterns for Wyodak coal under 25 bar CO₂ for various times.

Table 3: Desorption parameters for CO₂ adsorbed on Wyodak coal at various pressures.

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

scattering contrast between pores and coal matrix due to the adsorption of CO₂ within the pores.

It can be observed that the scattering intensities decrease with CO₂ pressure in the entire q range. This suggests that as CO₂ is adsorbed into pores the scattering contrast between pore and coal, $[(\rho_m - \rho_p)^2]$, will decrease and the amount of reduction in the scattering contrast will increase with CO₂ pressure due to increase in the scattering length density of CO₂ with pressure.

SANS results also show that the amount by which scattering is reduced varies as a function of scattering wave vector q . This might be related to the variations of the density of adsorbed CO₂ with pore size. It has been suggested that the density of CO₂ is a function of pore size and as CO₂ is adsorbed in pores, it interacts with two pore walls and will be subjected to a large interaction energy or an effectively large pressure [27]. The amount of the interaction energy increases with the reduction in the size of pores.

Structure changes in the coal by high pressure CO₂

Small angle neutron scattering patterns for fresh Wyodak coal and the coal in contact with 25 bar CO₂ for various times are shown in Fig. 12. As it can be observed, the effect of 25 bar CO₂ is to reduce the scattering intensity considerably in a very short time (<10 min). This shows that CO₂ can diffuse into the pore structure and access the entire pores quickly. If small micropores were still being filled, they would become more transparent to the neutrons as the difference in scattering length density of two phases decreases, and the scattering patterns would continue decreasing with time. This is not observed suggesting all pores are filled with CO₂. It is also clear that the amount by which scattering is reduced changes with q that might be due to the variations of the density of CO₂ with pore size.

The scattering curves for Wyodak coal at 25 bar CO₂ at different times show an increase in scattering

intensities with time for $q > 0.06 \text{ \AA}^{-1}$. There are two possible explanations for increase in the scattering intensities with time. One can be the swelling of coal caused by high pressure CO₂ dissolved in the coal matrix [7]. CO₂ is a fluid that can dissolve in the organic matrix and modify the physical and possible chemical structure of the coal matrix. This physical modification is associated with the relaxation and rearrangement of the macromolecular structure of coal and changes the pore structure of the coal [19]. An alternative explanation is that as CO₂ is adsorbed in micropores, it interacts with two pore walls and will be subjected to a large interaction energy or effectively a large pressure and behaves as a supercritical fluid [27]. Since the supercritical fluids have unique solubilizing and extracting properties, the increase in the scattering intensities might be attributed to the creation of additional microporosity in the structure and increase in micropore volume due to the extraction of organic matter from coal by supercritical CO₂. Hall et al. [28] have also observed the formation of microporosity in Pittsburgh # 8 coal following solvent treatment.

CONCLUSIONS

It has been found that CO₂ binds to the structure of Wyodak coal strongly and irreversibly even after heating to 200 °C. The strong and steep exothermic peaks on the DSC scans for adsorption of CO₂ on the Wyodak coal show that CO₂ rapidly adsorbs on the coal surface. Decrease in the Glass transition temperature of coal with CO₂ pressure suggests that after adsorption CO₂ diffuses through the coal matrix, causes significant plasticization effects and changes the macromolecular structure of the coal. Desorption characteristics of coal loaded with high pressure CO₂ show that CO₂ desorption from the coal is an activated process and follows a first order kinetic model at temperatures in the range of 300-350 K. The amount of CO₂ uptake increases with increasing CO₂ pressure. Increase in activation energy for CO₂ desorption from coal with pre-adsorbed CO₂ pressure suggests that high pressure interactions will demand more energy to desorb from coal probably due to the further access of CO₂ to the coal microporous structure. Significant decrease in the scattering intensities upon exposure of the coal to high pressure CO₂ also showed that high pressure CO₂ rapidly adsorbs on the coal and reaches to all pores in the structure. *In situ* small angle neutron scattering on

coal at high pressure CO₂ atmosphere showed an increase in scattering intensities with time suggesting that high pressure CO₂ diffuses into the coal matrix, swells the matrix and probably creates microporosity by extraction of volatile components from coal. The results of this study prove that Wyodak coal have a great affinity and high irreversible sorption capacity for CO₂ and could be excellent for CO₂ sequestration.

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