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## Temperature effect on sorption amount and sorption kinetics of CO<sub>2</sub> in coal

### Abstract

CO<sub>2</sub>, an anthropogenic greenhouse gas can be reduced from the atmosphere by sequestering in coal seams. Sequestered CO<sub>2</sub> displaces Coal Bed Methane (CBM), thus enhancing CBM production. Secondary CO<sub>2</sub> enhanced CBM (CO<sub>2</sub>-ECBM) recovery process involves the adsorption of CO<sub>2</sub> in the pores of the coal bed where the temperatures are elevated. The effect of temperature on CO<sub>2</sub> adsorption thus poses relevance in the development and implementation of CO<sub>2</sub>-ECBM.

The present work presents CO<sub>2</sub> adsorption in Jharia coals at three different temperatures (28°C, 35°C, 45°C) with pressures varying up to 4 MPa. CO<sub>2</sub> is in subcritical state at 28 °C while at 35°C and 45°C CO<sub>2</sub> is in supercritical state; thus the temperature range investigated in the present study covers subcritical to supercritical CO<sub>2</sub> adsorption in porous coals. The present work infers that the gas adsorption in coals varies inversely with temperature. The experimental data is modelled using two theoretical equations, namely, Langmuir and Dubinin-Radushkevich equations, both of which fit the experimental data in a satisfactorily. Average relative error in curve fitting for both the equations are computed for the three temperatures, and the values indicate that the D-R equation is a better predictor of the experimental adsorption isotherm data. Our study also demonstrates that sorption rate of CO<sub>2</sub> in coals increases with temperature. The diffusion coefficient calculated from the isotherm data shows an increasing trend with increasing pressure and temperature, for our experimental range.

### Introduction

Global temperature rise due to increase in anthropogenic emissions of greenhouse gases is a significant concern in today's society. One of the proposed mitigation measure of global temperature rise involves storing the greenhouse gases in deep geological formations, thus separating them from atmospheric circulation pattern. The storage mechanism of CO<sub>2</sub>, one of the major greenhouse gases, in deep coal seams is adsorption of CO<sub>2</sub> in the porous coal structure. Storage of CO<sub>2</sub> in coals come with an added benefit, i.e. recovery of methane gas (CH<sub>4</sub>). The recovered methane gas is a potential source of clean fuel. In the present era of declining production of natural gas and conventional petroleum, CBM is gaining importance and successful commercial production have been carried out in countries like USA, Canada, Australia, China and Russia over the last decade. Thus for technical development of Coal Bed Methane (CBM) and secondary CO<sub>2</sub> enhanced CBM (CO<sub>2</sub>-ECBM) in terms of production from coal seam, detailed knowledge of storage of CO<sub>2</sub> and CH<sub>4</sub>, and the subsequent release of CH<sub>4</sub> from porous structure is essential.

Storage and release of gas from porous coal structure is controlled by the processes of adsorption and desorption, respectively. The volume of gas adsorbed/desorbed is described by plotting adsorbed volume against the corresponding equilibrium pressure at a constant temperature, which is called the adsorption/desorption isotherm. CO<sub>2</sub> and CH<sub>4</sub> sorption isotherms in coals have been experimentally generated by various researchers globally to determine the volume of gas uptake and released in order to better understand the processes of coal bed methane production and CO<sub>2</sub> sequestration. A detailed review on experimental research of CO<sub>2</sub>-ECBM is published by Mukherjee & Misra, 2018<sup>[1]</sup>. CBM and CO<sub>2</sub>-ECBM sorption process and its kinetics along with influencing parameters of sorption process were reviewed by Busch & Gensterblum, 2011<sup>[2]</sup>. Sorption kinetics of CH<sub>4</sub> and CO<sub>2</sub> diffusion in coals from

Lorraine basin, France was studied by Charriere et al., 2010<sup>[3]</sup>. A recent study with similar objective on Indian coals from Jharia coalfields were published by Naveen et al., 2017<sup>[4]</sup>. CO<sub>2</sub> and CH<sub>4</sub> sorption isotherms on Permian Indian coals have been experimentally determined and further modelled using theoretical equations by Dutta et al., 2008<sup>[5]</sup> & Dutta et al., 2011<sup>[6]</sup>. The temperatures of coal seam vary with depth, and thus to have a comprehensive understanding of sorption processes at deep seam conditions adsorption isotherms needs to be generated for varying temperatures.

The present work presents adsorption isotherms of CO<sub>2</sub> on coal collected from Jharia coalfield, India, at three different temperatures. The temperatures are so chosen that it represents sub to super critical CO<sub>2</sub> adsorption on coal beds at depths of 400-700 meters. The experimental data is modelled using the Langmuir and Dubinin-Radushkevich (D-R) equations. Comparison of average relative error of the theoretical equations in explaining the experimental data has also been performed. Effect of temperature on sorption rates of CO<sub>2</sub> in coals have also been presented. Further, the diffusion coefficients are determined from adsorption isotherm data at three different temperatures. The variation of determined diffusion coefficient with pressure at a particular temperature have also been reported.

## Methodology

Fresh coal samples in large blocks (approximately 100 x 80 x 70 mm<sup>3</sup>) were collected from seam number 12<sup>th</sup> of South Balihari colliery located in Jharia coalfields from 350 to 360 meter depths. The samples are of Washery I, II grade and macroscopically characterized by strong depositional planar fabric (bedding planes) and occasional randomly oriented fractures. Fragments of the coal block were pulverized to less than 63micron grain size for adsorption measurement. A part of the coal dust was used to analyze moisture, ash and volatile matter contents following the ASTM Standards 3173, 3174 and 3175 respectively. The analysis shows the coal samples contain 0.85-0.91% moisture, 15.9-17.77% ash, and 24.87-29.15% volatile matter.

The adsorbed amount at variable pressure at a particular temperature with time was measured using a standard Sievert's apparatus (Figure 1). Before the onset of data recording samples were activated by heating at 80 °C for 24 hours under vacuum. A K-type thermocouple was used to measure the temperature of the system with an accuracy of ±0.2 °C and with a stability of better than ±0.05 °C. Pressure transducer was used to measure pressure, with a resolution of 0.001MPa. A fixed amount of gas is injected from the Sievert's apparatus known volume reservoir chamber to the attached sample chamber and the drop in pressure within the total connecting line is recorded. The drop in pressure occurs due to removal of adsorbate gas from free gas phase. The value of drop in pressure is incorporated in Real Gas Law equation to determine the adsorbed amount.

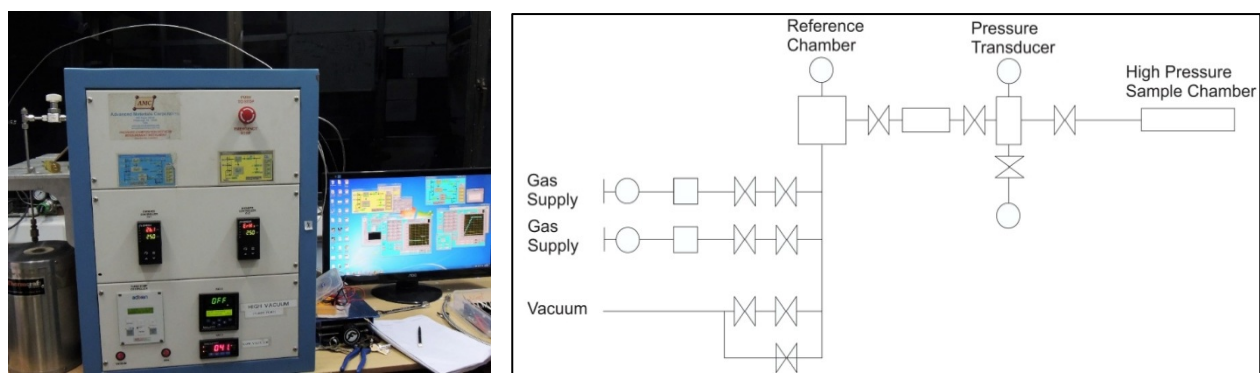


Figure 1- Sievert's apparatus and its schematic diagram used to measure sorption isotherms of CO<sub>2</sub> in coal.

The experimental data was modelled using two theoretical equations. The first model is known as Langmuir model and is based on the concept of dynamic equilibrium between rate of adsorption and

desorption of gas on solid surface. The equation used to fit experimental data with Langmuir model is expressed as

$$\frac{VP}{V_{LL} P + P} \dots\dots\dots (1)$$

where,  $V$  and  $P$  denotes adsorbed amount and equilibrium pressure, respectively.  $V_L$  (Langmuir volume) denotes the maximum monolayer capacity of adsorbing gas at infinite pressure, while  $P_L$  indicates pressure (Langmuir pressure) at which  $V$  is equal to half of  $V_L$ . Another theoretical equation i.e. D-R equation is based on a theory called Dubinin-Polyanyi's theory which assumes existence of a potential field around the pores that attracts the adsorbate molecules and fills up the pore of adsorbent. D-R equation is expressed as

$$V = V_0 \exp\left\{-D \left(\frac{P}{P_0}\right)^2\right\} \dots\dots\dots (2)$$

where,  $V_0$  is the volume of micropores,  $D$  is a constant depending on the adsorbent-adsorbate system and  $P_0$  is the saturation vapor pressure at the concerned experimental temperature. The average relative error which indicates the quality of fitting experimental data with mentioned model equations, and is calculated using the following formula

$$AR(\%) = \frac{100}{N} \sum_{i=1}^N \frac{|V - V_{EXP}|}{V_{EXP}} \dots\dots (3)$$

where,  $V_{EXP}$  is experimentally measured adsorbed amount corresponding to predicted adsorbed amount  $V$ .

The diffusion coefficient ( $D$ ) from adsorption isotherm at a particular temperature is obtained using the following equation

$$\frac{V}{V_T} = \frac{D}{6r^2} \left(\frac{t}{\pi}\right)^{1/2} \dots\dots\dots (4)$$

where,  $r$  is the diffusion path length,  $V_T$  and  $t$  denotes total amount of adsorption and time, respectively.

## Results

CO<sub>2</sub> adsorption isotherms at three different temperatures and fitted using Langmuir and D-R equation is depicted in Figure 2. The absolute value of the adsorbed amount of CO<sub>2</sub> decreases with increase in temperature and the amount of reduction in CO<sub>2</sub> sorbed volume for each temperature step increases at higher temperatures. Temperature increases the kinetic energy of gases, thus at higher kinetic energies and more randomness, the gas molecules tend to prefer free state over being adsorbed on the surface of the adsorbent. Hence, at higher temperatures more energy is required to convert the gas molecules from free phase to adsorbed phase. Figure 3 represents the deviation of Langmuir and D-R models in predicting experimental adsorption amount values as a function of pressure at three different temperatures. It is seen that D-R model predicts the experimental values better than the Langmuir model. Langmuir model fits the experimental adsorption data points of CO<sub>2</sub> at sub critical phase (28 °C) to a reasonable extent but the deviation increases in super critical phase of CO<sub>2</sub> (35 °C, 45 °C). On the other hand, D-R model is consistent in predicting the experimental values of adsorption throughout the experimental temperature range. Table 1 enlists the average relative error of Langmuir and D-R equations in fitting the experimental values of adsorption of CO<sub>2</sub> in three different temperatures. The Langmuir model assumes energy equivalence and structural homogeneity at the pore spaces, which may not hold true in actual coal samples, thus introducing errors in the Langmuir model predictions.

Accounting for the pore geometry and adsorption potential gives D-R model the edge in predicting experimental adsorption values.

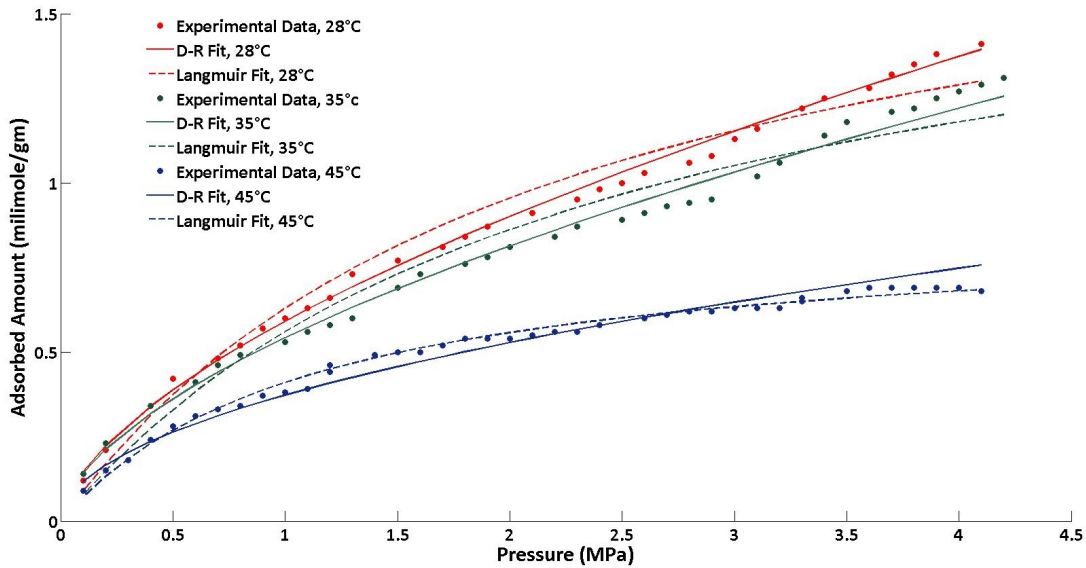


Figure 2- Sorption isotherms of CO<sub>2</sub> in Jharia coal at three different temperatures and modelled using Langmuir and D-R equation

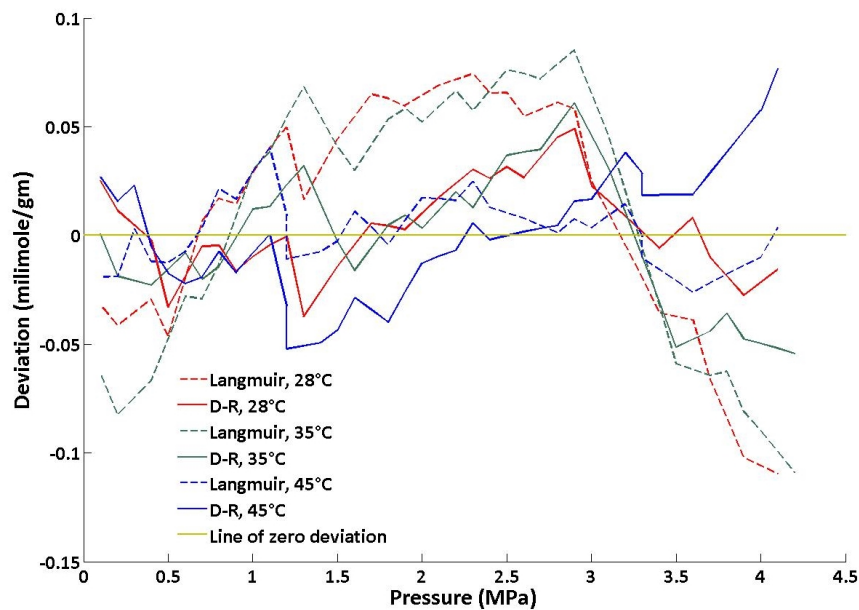


Figure 3- Deviation of Langmuir and D-R equations in predicting experimental adsorption amount at three different temperatures

Table 1- Average relative error in fitting of experimental adsorption isotherm using Langmuir and D-R equations at three different temperatures

Temperature (°C)	Average relative error	
	Langmuir	D-R
28		
35		
45		

28	0.48	0.52
35	6.58	0.63
45	2.18	0.90

Effect of CO<sub>2</sub> sorption kinetics with temperature is performed and is depicted in Figure 4. The percentage of total adsorption with time for three different temperature indicates that sorption rate of CO<sub>2</sub> increases with temperature and rate of increase accelerates at higher temperatures. Diffusion coefficient of CO<sub>2</sub> is plotted against pressure at three different temperatures and the result is illustrated in Figure 5. It is evident that diffusion of CO<sub>2</sub> increases with increase in temperature. As rate of diffusion is higher at higher temperatures it is clear that sorption should also increase with temperature. Figure 5 also depicts that with increase in pressure diffusion coefficient increases at a particular temperature. The present findings are somewhat contrary to the results of Cui et al., 2004<sup>[7]</sup> but similar to the findings of Charriere et al., 2010<sup>[3]</sup>. Cui et al., 2004<sup>[7]</sup> opined that gas molecule-molecule collision and adsorption induced coal matrix swelling increases with pressure, thus lowering the diffusion coefficient with increase of pressure. The study of Busch et al., 2004<sup>[8]</sup> shows that effect of adsorption induced coal matrix swelling is prominent at high pressures (>5 MPa) and high surface coverages. In the present study, the pressure range investigated should have low surface coverage and coal matrix swelling. Thus, our results indicate that effect of coal matrix swelling is negligible in our results and diffusion coefficient increases with pressure at constant temperature.

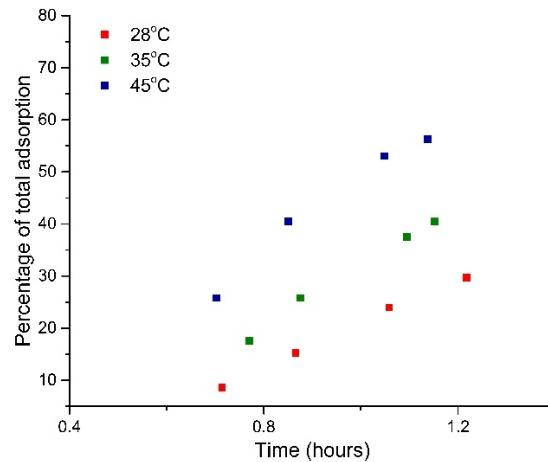


Figure 4- Sorption rate i.e., percentage of total adsorption against time at three different temperatures.

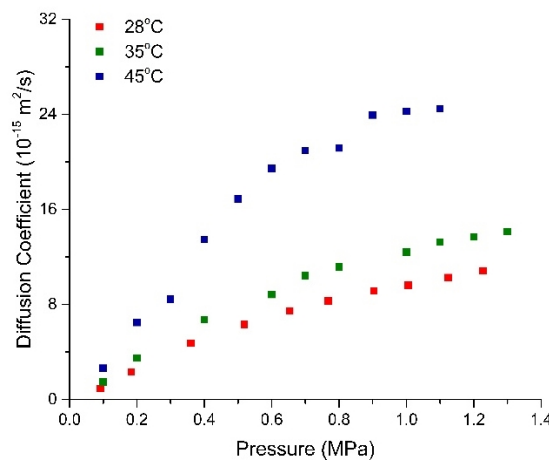


Figure 5- Variation of diffusion coefficient of CO<sub>2</sub> in coals with pressure at three different temperatures.

## Conclusions

The present study investigates the effect of temperature on CO<sub>2</sub> adsorption in Indian coals. The major conclusions of this study includes:

Sorption volume varies inversely with the temperature.

Langmuir and D-R equations are reasonably suited to model adsorption, with D-R equation showing a better fit to the experimental adsorption values.

Sorption rate increases with increase in temperature.

The value of diffusion coefficient increases with temperature as well as with pressure.

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