

**PRELIMINARY CHARACTERIZATION OF CO₂ SEPARATION AND STORAGE
PROPERTIES OF COAL GAS RESERVOIRS**

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ABSTRACT

An attractive alternative of sequestering CO₂ is to inject it into coalbed methane reservoirs, particularly since it has been shown to enhance the production of methane during near depletion stages. The basis for enhanced coalbed methane recovery and simultaneous sequestration of carbon dioxide in deep coals is the preferential sorption property of coal, with its affinity for carbon dioxide being significantly higher than that for methane. Yet, the sorption behavior of coal under competitive sorptive environment is not fully understood. Hence, the original objective of this research study was to carry out a laboratory study to investigate the effect of studying the sorption behavior of coal in the presence of multiple gases, primarily methane, CO₂ and nitrogen, in order to understand the mechanisms involved in displacement of methane and its movement in coal. This had to be modified slightly since the PVT property of gas mixtures is still not well understood, and any laboratory work in the area of sorption of gases requires a definite equation of state to calculate the volumes of different gases in free and adsorbed forms.

This research study started with establishing gas adsorption isotherms for pure methane and CO₂. The standard gas expansion technique based on volumetric analysis was used for the experimental work with the additional feature of incorporating a gas chromatograph for analysis of gas composition. The results were analyzed first using the Langmuir theory. As expected, the Langmuir analysis indicated that CO₂ is more than three times as sorptive as methane. This was followed by carrying out a partial desorption isotherm for methane, and then injecting CO₂ to displace methane. The results indicated that CO₂ injection at low pressure displaced all of the sorbed methane, even when the total pressure continued to be high. However, the displacement appeared to be occurring due to a combination of the preferential sorption property of coal and reduction in the partial pressure of methane.

As a final step, the Extended Langmuir (EL) model was used to model the coal-methane-CO₂ binary adsorption system. The EL model was found to be very accurate in predicting adsorption of CO₂, but not so in predicting desorption of methane. The selectivity of CO₂ over methane was calculated to be 4.3:1. This is, of course, not in very good agreement with the measured values which showed the ratio to be 3.5:1. However, the measured results are in good agreement with the field observation at one of the CO₂ injection sites.

Based on the findings of this study, it was concluded that low pressure injection of CO₂ can be fairly effective in displacing methane in coalbed reservoirs although this might be difficult to achieve in field conditions. Furthermore, the displacement of methane appears to be not only due to the preferential sorption of methane, but reduction in partial pressure as well. Hence, using a highly adsorbing gas, such as CO₂, has the advantages of inert gas stripping and non-mixing since the injected gas does not mix with the recovered methane.

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EXECUTIVE SUMMARY

This research study started in September 2001 at the University of Arizona to investigate the feasibility of using carbon dioxide (CO₂) to displace methane in coalbed methane reservoirs resulting in enhanced gas recovery, and simultaneous sequestration of CO₂. Due to the move of the Principal Investigator, the work was sub-contracted to the Southern Illinois University (SIU). Hence, a major part of the work was carried out at SIU. Also, due to a delay in the sub-contract paperwork, DOE granted a no cost extension of one year.

The original objective was to study the preferential sorption property of coal for methane, nitrogen and carbon dioxide, and how it impacts the displacement of methane and its subsequent movement in the reservoir. The objective of the study had to be modified after a few months due to a computational complexity when calculating volumes of gases in free and adsorbed states in multi-gas environments at high pressures. Researchers at Oak Ridge National Laboratory and other institutions currently involved in conducting PVT studies were contacted for assistance. Since this is not a well understood phenomenon, it was decided that the ability of CO₂ alone to enhance the recovery of methane from coal reservoirs, both total recovery and rate of recovery, will be investigated.

This research study started with establishing gas adsorption isotherms for pure methane and CO₂. The amount of gas in the adsorbed state was determined for different pressure steps up to 10.35 MPa (1500 psi). The results were analyzed first using the Langmuir theory. As expected, the Langmuir analysis indicated that CO₂ is more than three times as sorptive as methane. This is in agreement with the laboratory studies completed in the past, and field observations. This was followed by carrying out a partial desorption isotherm for methane, and then injecting CO₂ to displace methane. The purpose of this experiment was to replicate the conditions where CO₂ is injected after partial depletion of a coalbed methane reservoir for additional recovery of methane which is otherwise left behind. The results clearly showed that CO₂ injection at low pressure displaced all of the sorbed methane, even when the total pressure remained high. However, the displacement appeared to be occurring due to a combination of the preferential sorption property of coal as well reduction in the partial pressure of methane. This was not expected since it is generally accepted that injection of an inert gas like nitrogen enhances the recovery of methane by the mechanism of partial pressure reduction, whereas injection of CO₂ does so by displacement due to its higher affinity for coal.

Using the experimental results, the Extended Langmuir model was used to model the coal-methane-CO₂ binary adsorption system. The model was found to be very accurate in predicting adsorption of CO₂, but not so in predicting desorption of methane. This is in agreement with the field observation where EL was found to be more accurate for the higher adsorbing gas. Again, using the experimental results, the selectivity of CO₂ over methane was calculated to be 4.3:1 which is not in very good agreement with the measured values which showed the selectivity to be 3.5:1.

Based on the findings of this study, it was concluded that low pressure injection of CO₂ can be fairly effective in displacing methane in coalbed reservoirs although this might be difficult to achieve in field conditions. Although the displacement of methane appears to be not only due to the preferential sorption of methane, but reduction in partial pressure as well, using a highly adsorbing gas, such as CO₂, has the advantages of inert gas stripping, and non-mixing, since the injected gas does not mix with methane. Injection of CO₂, therefore, combines the advantages of inert gas stripping and displacement, with the major economic advantage of negligible or slow breakthrough – injected gas showing up with the recovered methane – necessitating separation of the gases at the downstream end. Based on these conclusions, it is recommended that a thorough study of PVT properties of gas mixtures be conducted so that injection experiments can be carried out using nitrogen and CO₂ at all pressure levels.

INTRODUCTION

The increasing atmospheric CO₂ (a greenhouse gas) is a cause of concern because of its serious environmental consequences. Various technologies are being developed to contain the atmospheric CO₂ concentration. Carbon sequestration, employed to reduce the atmospheric carbon dioxide level, is a relatively new concept in the practice of carbon management. It is the method of capturing and permanently storing CO₂ in various sinks such that it would remain isolated and not contribute to global climate change. The probable sinks for CO₂ disposal are the terrestrial biosphere, subsurface formations or the geo-sphere, and the ocean. In the geo-sphere, the different potential sinks for carbon sequestration are coal, oil and gas reservoirs, and deep, saline aquifers. Coals or coalbed methane (CBM) reservoirs have good potential to sequester CO₂ because of large deposits all over the world, and their proximity to CO₂ generating coal-fired power plants. CO₂ sequestration in coal is considered advantageous over other subsurface sequestration options because it has both environmental and economic benefits. Firstly, injected CO₂ replaces the adsorbed methane at the internal coal surface, adsorbing firmly to the coal at a near-liquid density. Since the process of gas adsorption has proven its stability through geological time periods, the probability of future CO₂ release from unmineable coal is minimal (1). Secondly, the injected CO₂ not only speeds up, but also increases the production of methane. The technique, known as enhanced coalbed methane recovery (ECBM), thus has the potential to offset some of the costs associated with carbon sequestration, making it more economically attractive. Lastly, ECBM has the ability to increase the life of some of the gas producing wells which would otherwise be abandoned due to low production rates, and recover a resource which is usually wasted.

Unlike conventional gas reservoirs, where the gas is in free state, CBM is stored as an adsorbed phase in the coal pores. Coal has a complex pore-size distribution with pores ranging from the macroscale (>50 nm) to the microscale (<2 nm) (2). The adsorbed gas accounts for 98 percent of the total gas within the coal seams. The most common method to recover CBM is by means of reservoir pressure depletion, also known as the primary recovery method (3). This technique involves pumping off large volumes of water, thus reducing the reservoir pressure and making coal less capable of retaining the gas in adsorbed form. The gas molecules start detaching themselves from the surface of the pores and microfractures by the process of desorption. The released gas diffuses through the coal matrix toward the cleats and fractures. Although this method is simple and effective, it is not an efficient one and can only recover only 50 percent of the gas-in-place (3). Some of the other disadvantages of this method are the long delay in methane production, and large amount of water produced that must be disposed.

Two different ECBM technologies have been proposed to improve the CBM recovery and the rate of recovery. One method is based on the principle of inert gas stripping, where a lower-adsorbing gas such as N₂ is injected. This reduces the partial pressure of methane thus causing it to desorb, since sorption of methane depends on the partial pressure, not the total pressure (3). The second technique utilizes injecting a higher adsorbing gas such as carbon dioxide, which is preferentially sorbed thus displacing the methane from coal (4). The basic principle behind the latter ECBM technique is that the

coal releases the adsorbed methane when it comes in contact with the more sorptive CO₂. The injected CO₂ displaces methane from the site of adsorption in coal, thus resulting in increased production of methane, while getting adsorbed itself and staying there, thus getting sequestered permanently. This ECBM technique is, therefore, of interest from the carbon sequestration point of view. Laboratory experiments and preliminary field tests have suggested that for every methane molecule produced, two CO₂ molecules are sequestered (1). Furthermore, this exchange ratio could be even higher at pressures at super-critical CO₂ condition (5), and for lower rank coal (6). Finally, the technique results in the recovery going up to 90 percent of the gas-in-place (7).

Carbon sequestration by injection of CO₂ in to deep coal is still in its primary stage and, as of now, the process is not fully understood. For successful implementation of this technology, it is critical to understand the mechanism of binary adsorption of methane and carbon dioxide on coal, the preferential sorption property of coal, and the ability of carbon dioxide to displace methane from coal. Understanding the chemical interaction between methane, carbon dioxide, and coal in a competitive environment, and one that is similar to field condition, is very important and critical for the successful implementation of the sequestration technology. There have been some laboratory scale experiments to study the enhanced methane recovery, and a few filed pilot-scale projects to study its implementation in the actual field conditions. Several researchers have studied the adsorption of methane and CO₂ mixture at different composition, temperature and pressure conditions to understand the sorption mechanism. Although these studies have all demonstrated the ability of CO₂ to improve methane recovery from coals, there are still several uncertainties regarding multi-component sorption behavior of coal.

The primary objective of the present work was to understand the sorption mechanism of coal in the presence of binary mixture of gases, i.e., to investigate whether coal exhibits preferential adsorption of CO₂ and desorption of methane. The second objective of the study was to investigate whether methane recovery with CO₂ injection is, in fact, enhanced. The third objective was to fit the sorption data of the resulting gas mixture to the Extended Langmuir (EL) model and assess its accuracy in predicting the gas mixture adsorption equilibria.

LITERATURE REVIEW

Several researchers have studied the effect of injection of CO₂ on the desorption behavior of methane from different coals. Every *et al* (8) conducted experiments to find the ability of carbon dioxide, helium and air to displace methane from crushed coal. Their data showed that carbon dioxide was able to displace 90 percent of methane under laboratory conditions. CO₂ was three times more effective than air, and five times more effective than helium, in displacing methane from coal. Moreover, it was observed that doubling of the injection rate and increasing the injection pressure had little effect on the total amount of methane displaced. The study concluded that at a certain pressure, for a particular coal, carbon dioxide could be retained only at a finite rate. Fulton *et al* (9) conducted experiments with dry and water saturated coal cores of 3 ½ inches in diameter. The coal cores were saturated with methane to a certain degree of saturation. The adsorbed methane

was then produced by desorption by the process of depletion of pressure, i.e., venting out to atmosphere. After natural desorption stopped producing methane, CO₂ was injected in a cyclic fashion, i.e., CO₂ injection followed by a short period of CO₂ adsorption and methane production. The injected CO₂ was able to completely strip the adsorbed methane. Reznik *et al* (10) carried out a set of experiments and injected CO₂ at different pressures into large cores to methane and water-saturated bituminous coal, and further conducted a simulation study to calculate the increase in recovery of methane. CO₂ injection increased the recovery of methane by a factor of two to three times that achieved by pressure drawdown. Also, higher injection pressure achieved greater methane recovery. Presence of even a small amount of N₂ greatly reduced the methane recovery. Puri *et al* (3) carried out a laboratory and simulation study of nitrogen injection, and observed that the recovery and rate of recovery of methane can be increased by stripping the methane off coal by N₂ flooding. Chaback *et al* (21) undertook a simulation study for ECBM with pure CO₂, N₂ and their mixtures. In all three cases, it was observed that cumulative methane production was enhanced by more than a factor of two, and the bulk of the methane was produced much earlier compared to the primary method (7). Wolf *et al* (11) conducted laboratory experiments and simulation to study the improvement of methane production by carbon dioxide injection using methane saturated cylindrical cores of Belgian and German coal. Different carbon dioxide injection rates were used. Both, experiment and reservoir simulation exercise produced promising results concerning methane production and carbon dioxide storage. Manik (12) developed a three-dimensional, two-phase, dual porosity, fully implicit compositional coalbed simulator and, using the thermodynamically consistent ideal adsorbed solution theory and non-equilibrium sorption condition, modeled the injection of nitrogen and carbon dioxide. The conclusion of the study was that it was possible to yield an ultimate methane recovery of 100 percent in a relatively short period of time.

Some field investigations for ECBM recovery and carbon sequestration have already started. In 1995, Meridian (now Burlington Resources) started a CO₂ pilot test in the San Juan Basin in New Mexico. A micro-pilot field test for ECBM and CO₂ injection is currently being carried out in Alberta (Canada) by the Alberta Research Council (7). The first one is considered the only large-scale CO₂ injection field demonstration pilot test in the US (13). Reeves simulated the field condition of the Allison unit in the San Juan Basin using a three-layer reservoir model and matching the field data (14). The results of the simulation study indicated that approximately 2 BCF of incremental methane would be recovered as a result of injecting 6.3 BCF of carbon dioxide. The CO₂/methane ratio of 3.2:1 is consistent with the CO₂/methane sorptive capacity ratio, based on isotherms at the abandonment pressure of about 0.34 MPa (50 psi).

Many researchers have conducted sorption experiments and analyzed the sorption behavior of different coals on binary mixture of gases. Ruppel *et al* (15) studied the adsorption of methane and ethane on dry Pennsylvanian coal to pressures of 40 atmospheres (588 psi) and at temperatures of 0, 30 and 50⁰C, and calculated the binary adsorption equilibria from the pure isotherm data using the ideal adsorbed solution theory of Myers and Prasunitz (16). The IAS theory was able to describe the methane and ethane binary adsorption on coal realistically. Saunders *et al* (17) used a static system to study the

adsorption of H₂-CH₄ mixture on Pittsburgh bituminous coal at temperatures varying from 22 to 207⁰C, and pressures up to 4.1 MPa (594 psi). The ideal adsorbed solution theory failed to predict the binary adsorption from the pure component isotherms. Stevenson *et al* (18) measured adsorption isotherms for binary and ternary mixtures of methane, carbon dioxide and nitrogen on dry Australian coal at 30⁰C and pressures to 5.23 MPa (754 psi). It was observed that equilibrium gas and adsorbate phase composition differ significantly, and the total amount of gas mixture adsorbed is strongly dependent on composition and system pressure. The IAS theory was able to provide good predictions for binary adsorption equilibria, while the Real Adsorbed Solution theory could not do so accurately. Arri *et al* (4) studied the binary sorption of methane-nitrogen and methane-carbon dioxide mixtures on Fruitland coal of the San Juan Basin at 46.1⁰C (115⁰F) and pressures of 3.45, 6.9 and 10.35 MPa (500, 1000, and 1500 psi). The results showed that each gas did not sorb independently. Instead, gases were competing for the same sorption sites. The Extended Langmuir model provided reasonable correlation of the data. Harpalani *et al* (19) studied the adsorption of pure methane, carbon dioxide and a three-component gas mixture consisting of 93 % methane, 5 % carbon dioxide, and 2 % nitrogen on moist Fruitland coal from the San Juan Basin at 112⁰F and up to pressures of 10.35 MPa (1500 psi) (5.52 MPa/800 psi for pure CO₂). Experimental data for the mixture was compared with the theoretical prediction by a numerical method and the Extended Langmuir (EL) model. While, the theoretical predictions were in good agreement with the experimental data for both the models, the EL was better than the numerical technique. Greaves *et al* (20) studied the adsorption of pure methane, carbon dioxide, and their mixtures (90% CH₄ + 10 % CO₂ and 75 % CH₄ + 25 % CO₂) with Sewickley coal at 22.7⁰C (73⁰F) and up to 6.9 MPA (1000 psi). Their results showed that the affinity of coal for CO₂ was much greater than that for methane. Significant sorption hysteresis was also observed during the desorption cycle for both gases. Hall *et al* (5) conducted an extensive experimental adsorption study of pure nitrogen, methane, carbon dioxide and their binary mixture on wet Fruitland coal at 115⁰F and pressures up to 1800 psi. The Ideal Adsorbed Solution theory and various two-dimensional equations of state (EOS) models described the pure component and mixed-gas adsorption data with reasonable accuracy and were better than the traditional Langmuir model. Chaback *et al* (21) presented sorption data for N₂, CH₄, CO₂ and their mixtures on several bituminous coals and used those data to investigate the applicability of the Langmuir sorption isotherm to coals. Langmuir isotherm gave satisfactory representation of sorption behavior for use in reservoir engineering studies including mixtures of two and three components. Clarkson *et al* (22) studied the effect of coal moisture content and composition on methane/CO₂ mixed gas adsorption characteristics. While there was no clear relationship between coal composition and carbon dioxide selectivity, the latter had an inverse relationship with coal composition. The IAS theory and EL model differed substantially in their ability to predict binary gas adsorption behavior. Binary gas adsorption prediction using the IAS theory, in conjunction with the Dubinin-Astakhov single component isotherm equations, were more accurate than using the EL model (23). Busch *et al* (24) carried out adsorption studies with mixtures of methane and carbon dioxide on dry and moisture equilibrated coals of different rank, composition of different European coals. All measurements did not show preferential adsorption of carbon dioxide and desorption of methane. The preferential sorption behavior varied with the pressure range.

EXPERIMENTAL WORK

Sample Preparation

As is the common practice, powdered samples were used for the sorption experiments in order to reduce the experimental duration by minimizing the distance that the gas molecules must diffuse through the matrix. Powdered samples were prepared from well preserved bituminous coal blocks from the San Juan Basin coal in New Mexico. The sample was first broken into small lumps approximately one cm in size. The small lumps were ground in a ball mill and the resulting powdered coal was sieved to obtain the desired sample size of 40-100 mesh (0.425-0.149 mm). The samples so prepared were kept in air-sealed bags. Prior to sorption experiments, approximately 80 grams of the sample was taken and placed in the environmental chamber, which was maintained at 45⁰C (113⁰F) and 96% relative humidity for moisture equilibrium. It took approximately 24 hour for the sample to become fully saturated with moisture. After the sample attained equilibrium moisture, one gram was taken out for moisture and ash analysis, while the rest was used for the sorption experiment. The standard ASTM procedures D 3173 – 87 and D 3174 – 97 were followed for moisture and ash analysis respectively.

Setup and Procedure

The experimental setup design is based on the method of mass balance, utilizing the volumetric analysis method. It uses the gas expansion technique to measure the quantity of sorbed gas. Real gas equation is used to calculate the gas volumes for a single gas. The experimental setup consists of a stainless steel fixed volume cylinder (FV) with a standard volume, and another stainless steel sample container (SC) which holds the powdered coal sample. The two cylinders are separated by a valve. The schematic diagram of the setup is shown in the Figure 1. Since the process of sorption is very sensitive to temperature, the setup is placed in a constant temperature bath which maintains temperature to within 0.2⁰C (0.36⁰F) of the set value. A pressure transducer is attached to the fixed volume cylinder. A filter is placed between the two cylinders to prevent the fine coal sample from being blown away from the sample container in to the fixed volume. Gas is allowed to expand from the fixed volume in to the sample container, or from the sample container to the fixed volume. By monitoring the pressure before and after the expansion, the volume of the gas moving into and out of the SC is calculated. Before each sorption experiment, the calibration of the setup is carried out to determine the void volume (V_v) in the sample container. Calibration involves expanding helium gas from FV to SC, and measuring the equilibrium pressure. Helium gas is used since it is not adsorbed on coal. Ideal Gas Equation is used to calculate all the volumes. The calibration step is repeated three times in order to minimize experimental error.

To establish the adsorption isotherm with a pure gas, the sequence of steps was fairly standard as used in the gas expansion volumetric technique. The constant temperature bath was set to 45⁰C (113⁰F) to simulate the reservoir temperature. Gas was then let in to the FV and pressure, P_1 , was recorded. The gas in FV was allowed to expand

into the sample container. Once the gas pressure stabilized, pressure, P_2 , was recorded. For single component isotherms, minimum equilibrium time of 16 hours was allowed. Using P_1 , P_2 , volume of FV and the Void volume in SC, the adsorbed gas volume was calculated using the real gas equation. The above step was repeated for increasing pressure steps up to a final pressure of 10.35 MPa (1500 psi) for methane and 5.52 MPa (800 psi) for CO_2 . Once the highest pressure for the adsorption isotherm was reached, the desorption isotherm was obtained using the process in reverse, the principle remaining the same. The FV was first bled out partially. After recording the pressure of gas in FV, the gas in SC was allowed to expand in to the FV. The gas pressure was recorded after attaining equilibrium. This procedure was repeated for decreasing pressure steps until the pressure in the sample container was reduced to approximately 6.9 MPa (100 psi), at which time the experiment was terminated.

For the second phase of the experimental work involving CO_2 injection, the adsorption procedure was completed following the steps described above up to a pressure of 10.25 MPa (1500 psi) for pure methane. The usual desorption steps were performed until the SC pressure came down to ~ 3.45 MPa (500 psi). The FV cylinder was then evacuated and CO_2 was filled in to it at a pressure of 2.1 to 3.45 MPa (300 - 500 psi). After the pressure stabilized in FV, the valve between FV and SC was opened and the gas in the two containers was allowed to mix. After equilibrium, the final pressure was recorded and a part of the gas was passed through the GC to determine its molar composition. Using the measured molar composition, the partial pressures of the two gases were calculated. This allowed further calculation of the volume of each gas adsorbed/desorbed.

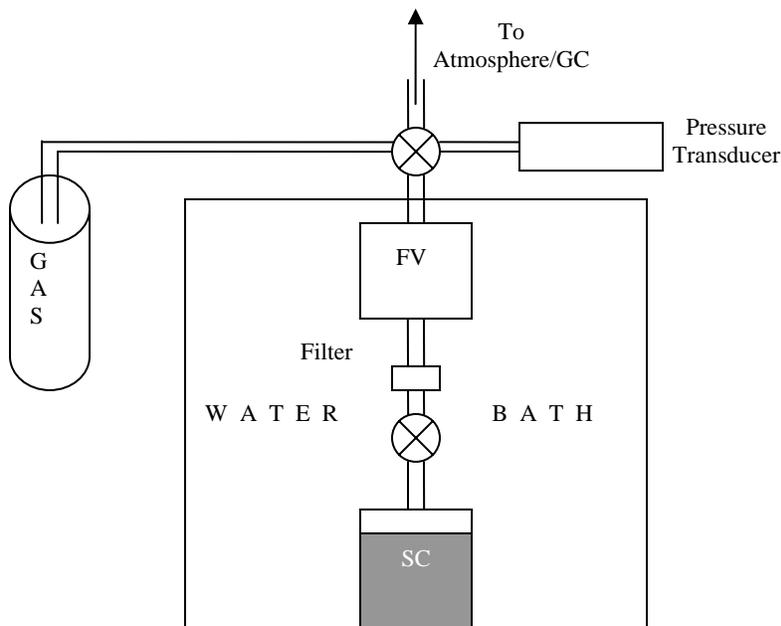


Figure 1. Schematic diagram of the experimental setup to establish adsorption isotherms.

Calculation Principle

The principle for the volumetric measurement of gas sorption is discussed in Mavor *et al* (25). It considers that the process of adsorption removes the sorbate gas molecules from free gas phase and thus results in a decrease of gas pressure within the experimental system. The amount of adsorbed gas (n_{sorbed}) is defined as the difference between the total amount of gas (n_{total}) present in the system and the amount of free gas occupying the void volume (n_{free}). The total amount of gas introduced into the system is computed from the amounts of gas transferred successively through the fixed volume (FV) into the sample cell (SC). The amount of free gas in the void volume is calculated knowing the void volume and the pressure of the system by using an appropriate equation of state (EOS) for that gas. The real gas equation used to calculate the amount of free gas present in the system is given as:

$$n = \frac{PV}{RTZ} \quad (1)$$

where, P = Pressure (psi), V is volume of gas (ml/g), R is Universal Gas Constant (1205.9 psi.ml.K⁻¹.mol⁻¹), T is temperature in Kelvin, and Z is the compressibility factor. To calculate the amount of individual gas components in free state in a gas mixture, Z is replaced by Z_{mix} , the compressibility factor for the gas mixture. The total pressure, P, is replaced by P_i , the partial pressure of each gas. The volumetric calculations require accurate determination of the density and compressibility factor of the free gas phase under experimental pressure and temperature conditions. For this study, the Peng-Robinson EOS was used to calculate the density and compressibility factors for methane, carbon dioxide and their mixture.

RESULTS AND DISCUSSIONS

Pure Gas Sorption

The Langmuir theory (26), the one most commonly used model for the study of adsorption of gases on coal, was used for this study. The main assumptions of the Langmuir theory are:

1. Every adsorbed molecule is held at definite, localized site.
2. Each site can hold one and only one molecule.
3. The surface of the adsorbent is energetically homogeneous.

The adsorption isotherm derived by Langmuir is given as:

$$V = \frac{V_L P}{P + P_L} \quad (2)$$

where, V = Sorbed volume at pressure P , and V_L and P_L are the Langmuir coefficients known as Langmuir Volume and the Langmuir Pressure respectively. Both Langmuir Volume and Langmuir Pressure have important physical significance from the coalbed methane recovery point of view. The Langmuir constants, V_L and P_L , are determined by plotting experimental pressure (P) versus pressure/volume (P/V) results and calculating the slope and intercept of the best fitting lines.

The experimental data for methane and CO_2 were analyzed using the Langmuir Equation and adsorption and desorption isotherms were established. It was observed that adsorption and desorption followed the same path, i.e., there was no hysteresis in the adsorption and desorption isotherms. This reversibility of the adsorption process shows that adsorption of methane and CO_2 on coal are physical in nature. The equilibrium adsorption isotherm of methane and carbon dioxide along with the experimental results are shown in Figure 2. It is apparent that the sorption isotherms for methane and carbon dioxide exhibited Type I behavior according to the Brunauer classification of isotherms (27). As expected with this type of isotherm, adsorption of methane and CO_2 on coal approaches a limiting value of gas as the free gas pressure increases and reaches the saturation pressure. This is logical since the adsorption on coal takes place in micropores and attains the limiting value as the micropores fill. As a common practice, the sorption results presented here are on a dry and ash free basis. The V_L and P_L values based on the tests completed were 14.4 and 15.2 ml/g, and 8.52 and 8.3 MPa (1235 and 1204 psi) respectively. The P_L and V_L values for CO_2 were calculated to be 43 ml/g and 4.07 MPa (590 psi) respectively. Figure 2 also clearly shows that the Langmuir model provides a very good fit to the experimental data. The coefficient of correlation (R^2 value) for methane was 0.98 to 0.97. For carbon dioxide, the coefficient of correlation was calculated to be 0.96. It can be seen from the isotherms that coal has a greater sorption affinity for CO_2 than methane. It can adsorb three times more CO_2 than methane. The CO_2 /methane adsorption ratio is higher than 2:1 ratio reported by Arri *et al* for Fruitland coal sample from the San Juan Basin (4). But such higher adsorption ratios have been reported earlier by Stanton *et al* (28) who studied different samples across the US. The higher adsorption ratio has good implications for ECBM and carbon sequestration. It may be possible to sequester as much as three times more CO_2 than methane produced by ECBM. The P_L value for CO_2 is less than half of that for methane suggesting that coal adsorbs bulk of its CO_2 at pressures below 500 psi. It may, therefore, be possible to sequester large amounts of CO_2 at relatively low pressure.

CO₂ Injection

CO_2 injection was performed at pressures between 2.07 and 3.45 MPa (300 and 500 psi) for two tests. Experimental data for the CO_2 injection tests are presented in Tables 1 and 2. In the first test, adsorption of methane was first completed to a pressure of 1487 psi. This was followed by desorption to a pressure of 3.45 MPa (499 psi) in five steps. The amount of sorbed methane for this pressure change decreased from 8.6 to 5.0 ml/g. At this stage, CO_2 was injected in to the sample container at a pressure of 3.48 MPa (504 psi). After attaining equilibrium, the total pressure decreased to 493 psi, with methane partial pressure at 205 psi and CO_2 partial pressure at 1.99 MPa (288 psi). The sorbed methane

reduced to 2.1 ml/g. The amount of desorbed CH₄ as a result of injection was, therefore, 2.9 ml/g, while the amount of adsorbed CO₂ was 10.3 ml/g. In the subsequent step, CO₂ was injected at 3.37 MPa (489 psi). After injection, the total pressure remained at 3.35 MPa

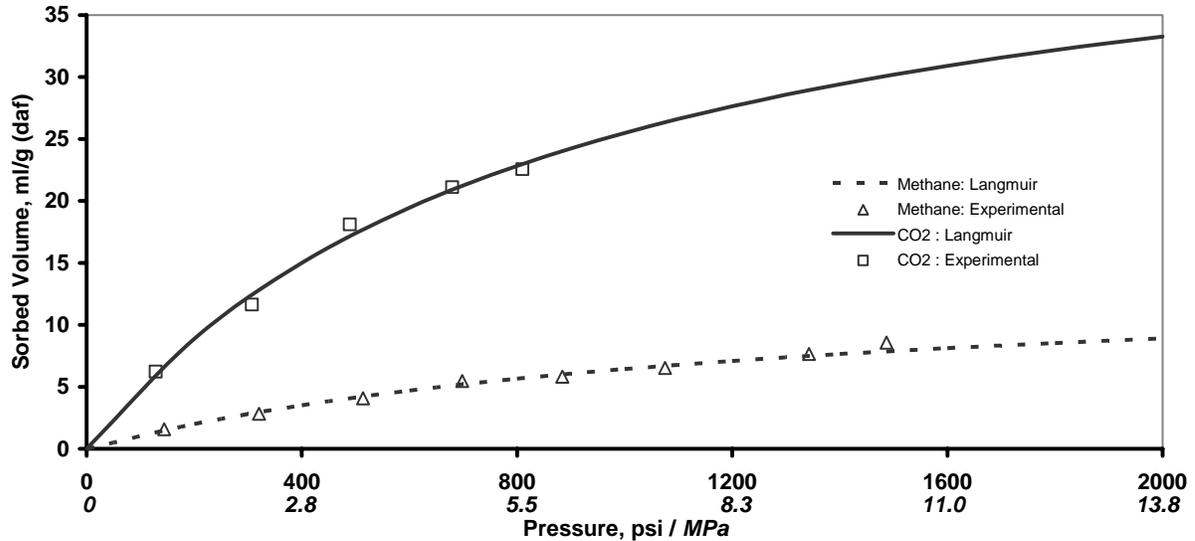


Figure 2. Langmuir isotherms for methane and carbon dioxide.

Table 1. Experimental data of the first injection test.

| Methane Pressure/Partial Pressure (psia) | CO ₂ Partial Pressure (psia) | Sorbed Methane (ml/g) | Sorbed CO ₂ (ml/g) |
|--|---|-----------------------|-------------------------------|
| 1332 | - | 8.5 | - |
| 1107 | - | 7.9 | - |
| 900 | - | 6.8 | - |
| 640 | - | 5.7 | - |
| 499 | - | 5.0 | - |
| 204 | 288 | 2.1 | 10.3 |
| 83 | 403 | 1.0 | 13.9 |

Table 2. Experimental data of the second injection test.

| Methane Pressure/Partial Pressure (psia) | CO ₂ Partial pressure (psia) | Sorbed Methane(ml/g) | Sorbed CO ₂ (ml/g) |
|--|---|----------------------|-------------------------------|
| 1356 | - | 8.2 | - |
| 1125 | - | 7.6 | - |
| 905 | - | 6.3 | - |
| 487 | - | 5.0 | - |
| 204 | 165 | 3.7 | 6.4 |
| 86 | 244 | 1.2 | 9.9 |

(486 psi), while the partial pressures of methane and CO₂ changed to 0.57 MPa (83 psi) and 2.78 MPa (403 psi). The amount of additional desorbed methane at this stage was 1.1 ml/g, while additional CO₂ adsorbed was 3.6 ml/g. The methane sorption results for this test are shown in Figures 3 and 4. It can be seen that for 4 ml/g of methane desorbed, 14 ml/g of CO₂ was adsorbed by the coal. The ratio of CO₂ adsorbed to methane desorbed for this coal is, therefore, approximately 3.5: 1.

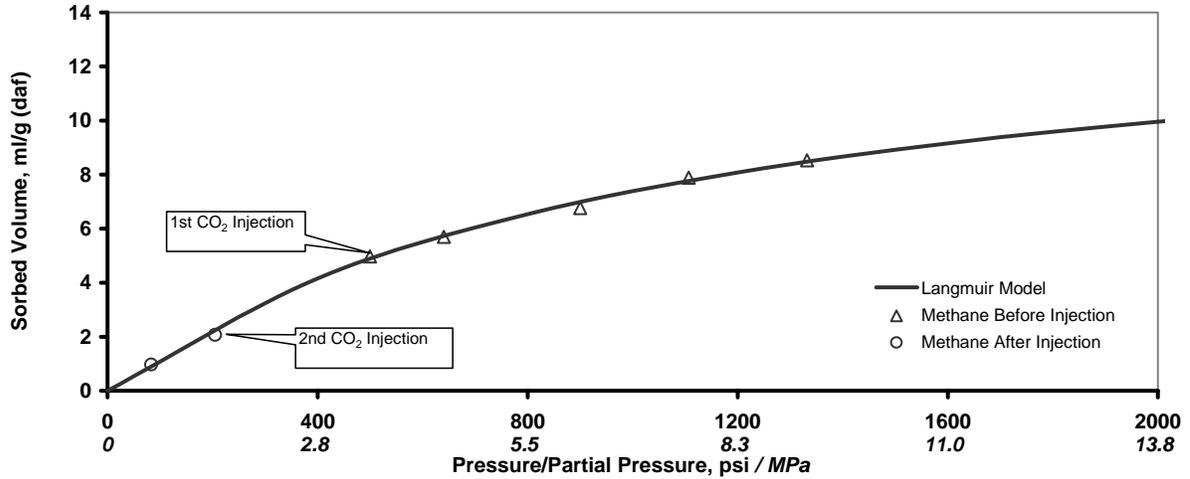


Figure 3. Displacement of methane as a result of CO₂ injection for the first test (partial pressure).

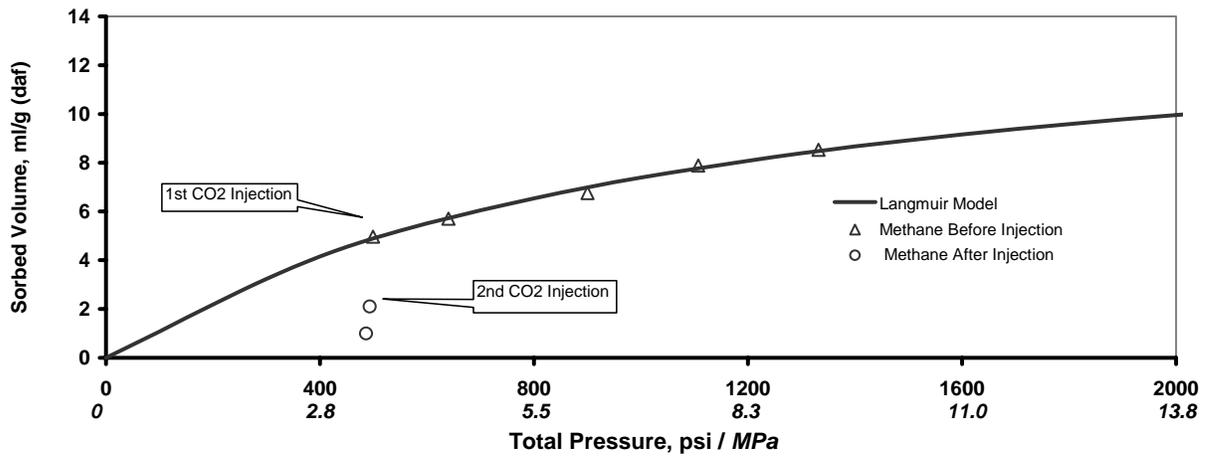


Figure 4. Displacement of methane as a result of CO₂ injection for the first test (total pressure).

In the second test, adsorption of methane was completed to a pressure of 9.35 MPa (1356 psi). The pressure was then reduced to 3.36 MPa (487 psi) in four steps. The amount of sorbed methane went down from 8.2 to 3.7 ml/g of coal. At this stage, CO₂ was injected in to the sample container at a pressure of 2.09 MPa (303 psi). At equilibrium, the total pressure decreased to 2.54 MPa (369 psi) while the partial pressures of methane and CO₂ were calculated to be 1.41 MPa (204 psi) and 1.14 MPa (165 psi). The corresponding amount of sorbed methane reduced to 1.2 ml/g, while adsorbed CO₂ was 6.8 ml/g. In the subsequent step, CO₂ was injected again at 2.15 MPa (312 psi). After injection, the total pressure remained 330 psi and the partial pressures of methane and CO₂ were 0.59 MPa (86 psi) and 1.68 MPa (244 psi) respectively. The sorbed methane, however, came down to nearly zero, while the additional sorbed CO₂ was 4.4 ml/g. The methane sorption results, i.e., sorbed volume versus methane partial pressure and the sorbed volume versus total pressure for the second test are shown in Figures 5 and 6. Thus, for 3 ml/g of additional methane produced, the amount of carbon dioxide sorbed was 11.2 ml/g resulting in a sorbed CO₂/methane ratio of 3.7:1. The average of the two CO₂/methane ratios is, therefore, 3.6:1. This is fairly close to the simulation results of the pilot project in the Allison unit (14). Reeves had reported that approximately 2.0 BCF of incremental methane would be produced by injecting 6.3 BCF of CO₂, i.e., a ratio of 3.2:1.

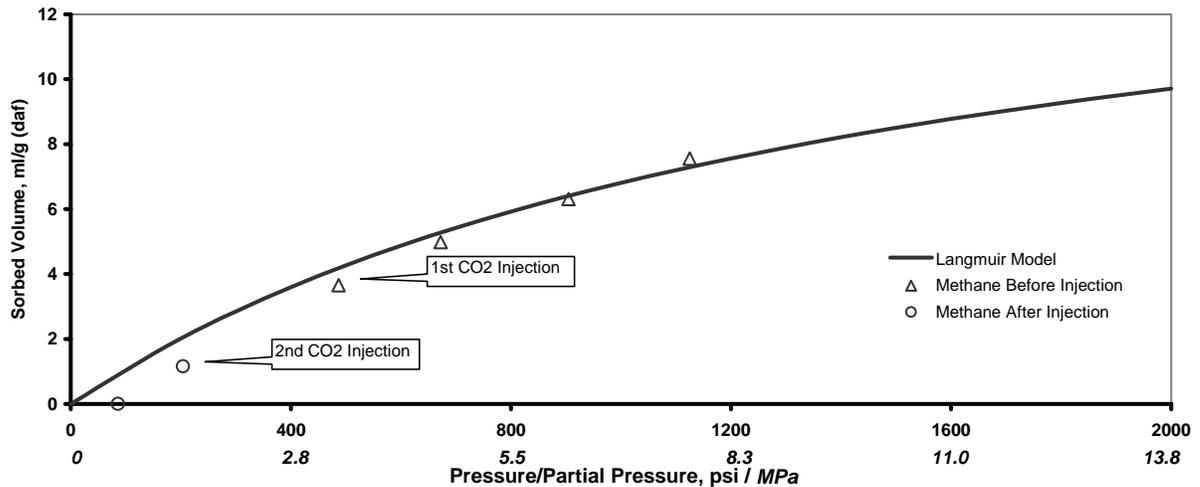


Figure 5. Displacement of methane as a result of CO₂ injection for the second test (partial pressure).

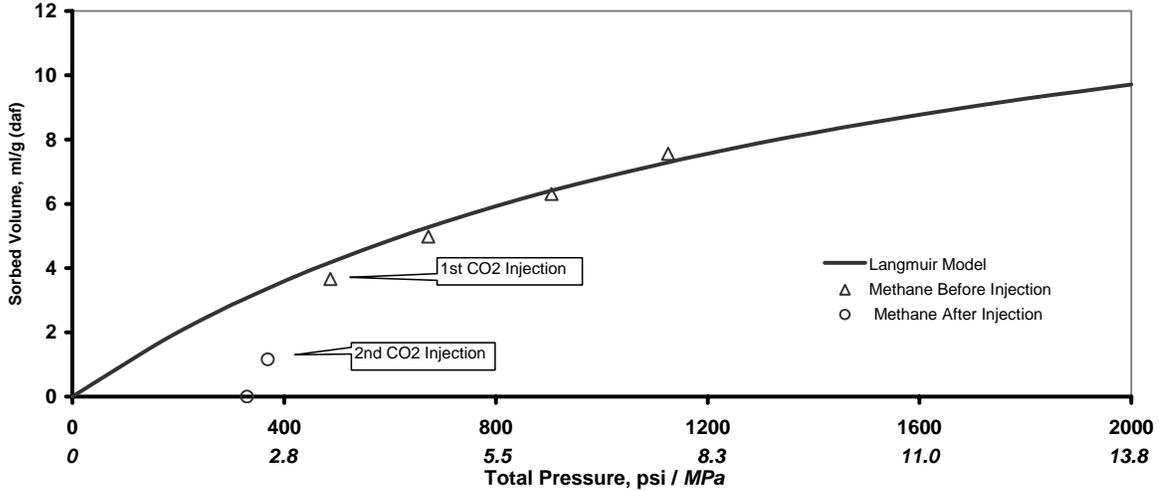


Figure 6. Displacement of methane as a result of CO₂ injection for the second test (total pressure).

It is obvious from Figure 4 that with two injections of CO₂ at approximately 3.45 MPa (500 psi), almost all of the sorbed methane was released even when the total system pressure was still fairly high, i.e., 2.07-2.76 MPa (300-400 psi). However, Figure 3 suggests that the adsorption of methane still followed the Langmuir isotherm and depended only on the partial pressure of methane. Hence, the desorption of methane was only due to reduction in the partial pressure of methane and not because of any preferential adsorption of CO₂, and preferential desorption of methane in the presence of carbon dioxide, as suggested by Arri *et al* (4). However, the results of the second test (Figure 6) indicate that the actual amount of methane desorbed is greater than the desorption resulting from the reduction of partial pressure of methane, as determined by the Langmuir isotherm. This clearly shows that the incremental methane produced is because of methane getting preferentially desorbed due to the presence of CO₂. Hence, based on the results of these two tests, it cannot be conclusively said that methane is preferentially desorbed and CO₂ is preferentially adsorbed. Moreover, it is not clear whether the observed enhanced methane recovery is due to partial pressure reduction, or due to preferential adsorption of CO₂. It is likely that the two mechanisms complement each other in enhancing the recovery of methane.

Extended Langmuir Model

The Extended Langmuir (EL) equation is the simplest and most commonly used model for the prediction of mixed gas adsorption on coal (29). In order to predict the binary adsorption equilibria, it requires pure component isotherm data. The EL equation is given as:

$$V_i = \frac{(V_L)_i b_i P_i}{1 + \sum_j b_j P_j} \quad (3)$$

where, V_L and $b (=1/P_L)$ are the pure gas isotherm Langmuir constants, and $P_{i,j}$ are the partial pressures of individual gas in free-gas phase. The partial pressure is related to the total pressure by the relation:

$$P_i = P y_i \quad (4)$$

where, y_i is the gas phase mole fraction of the component i . The relative adsorption of the two components is calculated by estimating the separation factor or the selectivity ratio. The selectivity ratio of a binary gas adsorption system is defined as:

$$\alpha_{ij} = \frac{(x/y)_i}{(x/y)_j} \quad (5)$$

where, x and y are the molar composition of a component gas in the adsorbed and free phase respectively. For the EL isotherm, the separation factor is simply the ratio of the adsorption equilibrium constants (4, 30):

$$\alpha_{ij} = \frac{(V_L b)_i}{(V_L b)_j} \quad (6)$$

The EL equation was used in order to predict adsorption equilibria of binary mixture of methane and carbon dioxide resulting from the injection of carbon dioxide into the coal-methane system. The predicted values were compared with the actual experimental value. Figure 7 shows the sorption isotherm of methane along with the predicted adsorbed phase equilibria of methane and CO₂ mixture, and compares it with the actual experimental results of the first test. The adsorbed CO₂ is within 3 percent error band of the EL predicted value. The measured adsorbed CH₄ is within 10 percent error band of the predicted value. Also, it can be observed that EL model is under-predicting the methane sorbed value, and over-predicts the sorbed CO₂ value. The selectivity of carbon dioxide over methane is 4.3:1. Figure 8 compares the actual experimental binary adsorption equilibrium data with EL predicted data for the second test. The measured sorbed CH₄ value lies within 20 percent error band of the predicted sorbed value. EL again over-predicted the sorbed methane value. For carbon dioxide, the actual sorbed CO₂ is within 3 percent error band of the predicted value. The selectivity of carbon dioxide over methane is 4.7:1. Thus the EL model is very accurate in predicting sorbed CO₂, while it is only moderately accurate in predicting sorbed methane. This is consistent with the observation of Reeves (13) that the EL model predicts more accurately the more strongly adsorbed component. The average selectivity ratio for both tests is 4.5:1, which is not very accurate as compared to the experimental CO₂/methane sorbed ratio.

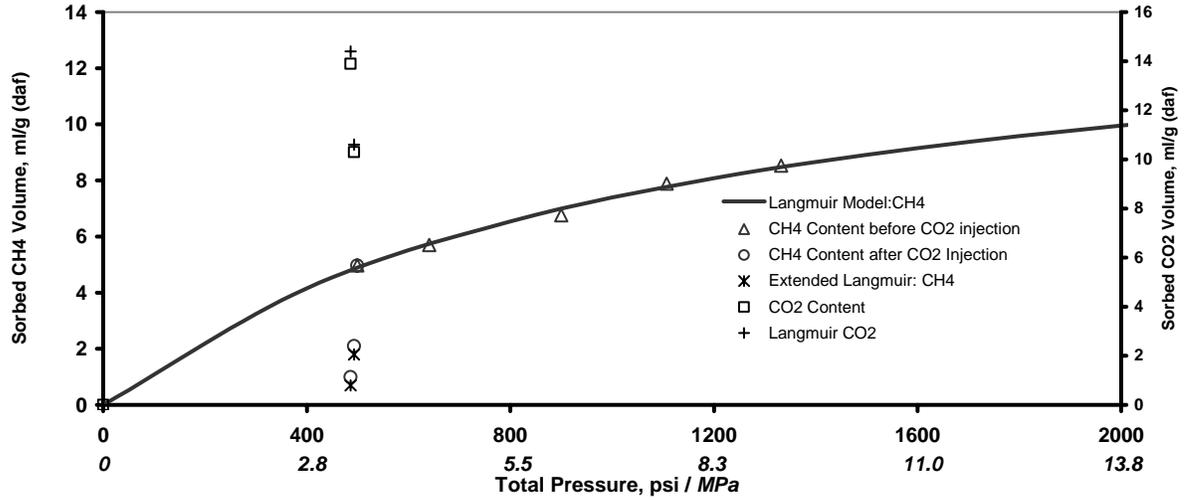


Figure 7. Binary equilibrium adsorption for the first test.

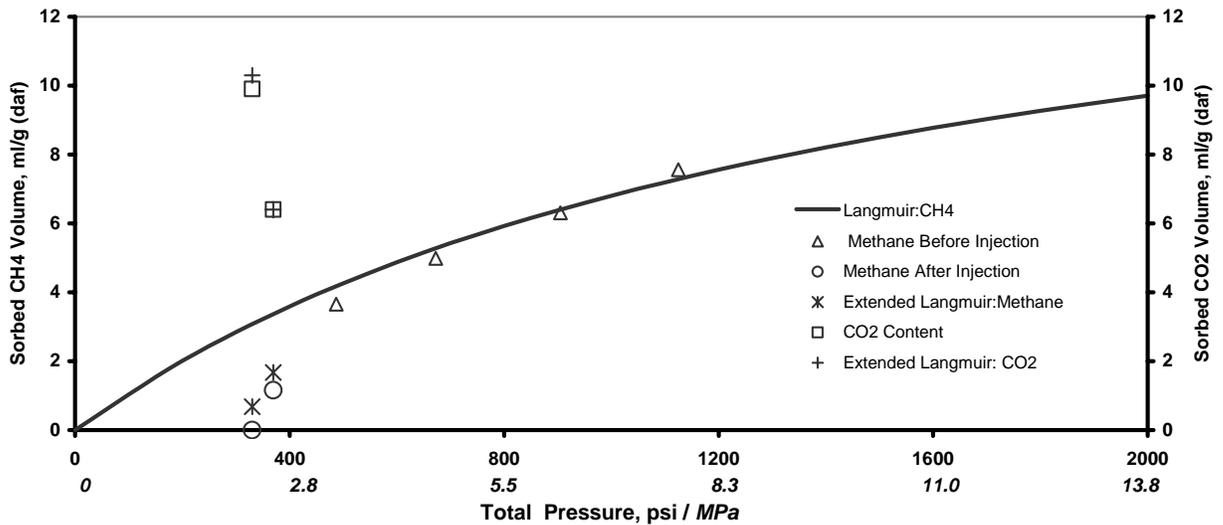


Figure 8. Binary equilibrium adsorption for the second test.

CONCLUSIONS AND RECOMMENDATIONS

Sorption isotherms were established for coal using pure methane and carbon dioxide. Carbon dioxide was injected into coal partially saturated with methane to investigate preferential sorption behavior of coal and to figure out the enhancement in methane recovery. Also, the equilibrium binary adsorption of methane and CO₂ on coal

was analyzed in order to examine the validity of the commonly used Extended Langmuir Model.

Based on the experimental results and analysis of the experimental data the following conclusions were made:

1. The recovery of methane can be enhanced by injecting CO₂ into partially saturated coal. Although relatively low pressure injection was found to be fairly effective in the laboratory, this might be problematic under field conditions.
2. The exact mechanism of methane recovery is not very clear. The enhancement is probably due to a combination of the effects by partial pressure reduction and preferential sorption. Hence, when a highly adsorbing gas is injected, it has all the advantages of inert gas stripping (nitrogen), and the added benefit of non-mixing since the injected gas does not mix with the recovered methane.
3. The EL model is very accurate in predicting sorbed carbon dioxide, but it is not so accurate in predicting sorbed methane.

Based on the above conclusions, the authors believe that further rigorous experimental studies should be conducted to better understand the phenomena involved in CO₂ injection as a means to enhance the recovery of CBM.

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