Influences of temperature and moisture on coal sorption characteristics of a bituminous coal from the Sydney Basin, Australia

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Abstract: Accurate testing of coal isotherms plays a significant role in the areas of coal seam gas drainage, outburst control, CO₂ geo-sequestration, coalbed methane (CBM) and enhanced coalbed methane recovery (ECBM). Coal isotherms were tested with CO₂ and CH₄ gases with a modified indirect gravimetric method in the University of Wollongong (UOW), Australia. The adsorption capacity of coal shows a linear decrease with increasing temperature. The decreasing rate of adsorption capacity is greater for CO₂ than CH₄, and which is also higher for dry coals. The moist coal sample isotherms for both CO₂ and CH₄ demonstrate a much lower sorption capacity. The average reduction ratio of coal adsorption capacity of CO₂ and CH₄ with moisture is 11.1% and 14.0%, respectively in the testing temperature range. The experimental results show that moisture content in coal has greater effect on the adsorption capacity of CH₄ than that of CO₂. [Received: August 23, 2013; Accepted: December 13, 2013]

Keywords: temperature; moisture; indirect gravimetric method; coal sorption; isotherm; adsorption capacity; particle size; CO₂; CH₄; Australia.


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1 Introduction

Gas sorption in coal has been studied over the years by many researchers (Briggs and Sinha, 1933; Moffat and Weale, 1955; Joubert et al., 1973; Lingard et al., 1984; Wu, 1994; Gode and Pehlivan, 2005; Busch and Gensterblum, 2011), and different types of apparatus were evolved for isotherm tests, and correspondingly, different calculation methods were used to obtain coal sorption isotherms. In general, these can be categorised into either volumetric or gravimetric methods. The general principle in determining the volume of gas being adsorbed by a particular type of coal is calculated by subtracting the void gas from the total gas.

Lama and Bodziony (1996) reported that the term ‘sorption’ consists of two parts: adsorption and absorption. Adsorption refers to the accumulation of gas on the surfaces of pores and cracks, and absorption means the penetration of gas into the internal structure of coal. A summary of the various adsorption measurements in recent years is provided in Table 1. Siemons and Busch (2007) measured CO₂ sorption isotherms on both dry and moist coals of various ranks from coal basins from around the world and these measurements were made at a temperature of 45°C. Day et al. (2008a) carried out experiments on supercritical gas sorption of carbon dioxide on moist coals at temperatures of 21°C and 55°C and pressures up to 20 MPa. Coal samples for the experiment were prepared by crushing and screening fresh air-dried lumps of coal to a particle size range of 0.5–1.0 mm.

The coal sorption characteristics of moist coal at higher temperatures (>25°C) is recognised as being an attractive option for in situ sorption study. With the improvement in coal production, underground coal mines are facing the operational realities of increased risk of gas explosion or outburst. Accurately identifying coal’s sorption characteristics in changing environmental conditions will shed light on the behaviour of gas sorption from in situ coal, especially when mining is to take place in deeper deposits. Thus, the sorption capacity of coal due to different temperatures and moisture content needs to be tested and compared.
<table>
<thead>
<tr>
<th>Author</th>
<th>Gas</th>
<th>Location</th>
<th>Coal rank</th>
<th>Method</th>
<th>Grain size (mm)</th>
<th>Dry/moist</th>
<th>T(°C)</th>
<th>p(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gruszkiewicz</td>
<td>CO₂, CH₄, CO₂/CH₄</td>
<td>Black Warrior Basin, USA</td>
<td>h.v.b.</td>
<td>Manometric</td>
<td>0.045–0.15; 1.2–2; 5–10</td>
<td>Dry, moist</td>
<td>35,40</td>
<td>1.4–6.9</td>
</tr>
<tr>
<td>Busch</td>
<td>CO₂, CH₄</td>
<td>Upper Silesian Basin, Poland</td>
<td>h.v.b.</td>
<td>Manometric</td>
<td>&lt;0.063; 0.063–0.177; 0.177–0.354; 0.354–0.707; 0.707–3</td>
<td>Dry, moist</td>
<td>32,45</td>
<td>CO₂ &lt; 6; CH₄ &lt; 10</td>
</tr>
<tr>
<td>Charriere</td>
<td>CO₂, CH₄</td>
<td>Loraine Basin, France</td>
<td>l.v.b.</td>
<td>Gravimetric</td>
<td>0.5–1</td>
<td>Dry</td>
<td>10–60</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Li</td>
<td>CO₂, CH₄</td>
<td>Inner Mongolia, Henan, Shanxi, China</td>
<td>Subbituminous, m.v.b., anthracite</td>
<td>Manometric</td>
<td>0.354–1</td>
<td>Dry</td>
<td>35, 45, 55</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Poste</td>
<td>CO₂, CH₄</td>
<td>Western Kentucky Coalfield, USA</td>
<td>h.v.b.</td>
<td>Manometric</td>
<td>&lt; 0.25; cylindrical: d 2.5–6.2</td>
<td>Moist</td>
<td>20</td>
<td>3.1</td>
</tr>
<tr>
<td>Pan</td>
<td>CO₂, CH₄</td>
<td>Sydney Basin, Aus</td>
<td>m.v.b.</td>
<td>Flow experiment</td>
<td>cylindrical: d 25.4–182.6</td>
<td>Dry, moist</td>
<td>26</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>Marecka</td>
<td>CO₂, CH₄</td>
<td>n.a.</td>
<td>Semianthracite</td>
<td>Volumetric</td>
<td>&lt; 0.032; 0.30–0.30; 0.75–0.49; 1.56–1.60</td>
<td>n.a.</td>
<td>20,30</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ciembroniewicz</td>
<td>CO₂</td>
<td>Poland</td>
<td>Anthracite</td>
<td>Manometric</td>
<td>0.49–0.75</td>
<td>n.a.</td>
<td>16–35</td>
<td>&lt; 0.065</td>
</tr>
<tr>
<td>Siemons</td>
<td>CO₂</td>
<td>Great Britain</td>
<td>Anthracite; semi-anthracite</td>
<td>Manometric</td>
<td>0.04–0.06; 0.06–0.18; 0.35–0.71; 0.71–2.0</td>
<td>Dry, moist</td>
<td>45</td>
<td>&lt; 12</td>
</tr>
<tr>
<td>Clarkson</td>
<td>CO₂, CH₄</td>
<td>Lower Cretaceous Gates Formation, Canada</td>
<td>m.v.b.</td>
<td>Volumetric</td>
<td>&lt; 0.25; &lt; 4.76</td>
<td>CH₄ dry; CH₄ dry; CH₄ dry</td>
<td>30</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Cui</td>
<td>CO₂, CH₄, N₂</td>
<td>h.v.b.</td>
<td>Manometric</td>
<td></td>
<td>&lt; 0.25</td>
<td>Moist</td>
<td>30</td>
<td>&lt; 7</td>
</tr>
<tr>
<td>Seeswald</td>
<td>CH₄</td>
<td>Ruhr Basin, Germany</td>
<td>h.v.b.; m.v.b.; anthracite</td>
<td>Volumetric</td>
<td>0.04 to 1 in 9 fractions</td>
<td>Dry, moist</td>
<td>0, 15, 50</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Kelleman</td>
<td>CO₂, CH₄</td>
<td>Argonne Coals, US</td>
<td>h.v.b., l.v.b.</td>
<td>Gravimetric</td>
<td>~ 7mm²</td>
<td>Dry</td>
<td>30,75</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Notes: h.v.b, m.v.b. and l.v.b are high, medium and low volatile bituminous coals.
Source: After Busch and Gensterblum (2011)
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Most of the above relevant papers were focusing on the sorption studies of a particular coal seam, either for the purposes of outburst control, CO₂ geo-sequestration or coal reservoir assessment relevant to coalbed methane (CBM) area. As giving an indication of coal sorption capacity of different gases to benefit those mentioned areas, this paper reports the experimental results on the influences of temperature and moisture on coal sorption characteristics of a bituminous coal from the Sydney Basin in Australia. The tests were conducted using a particular apparatus developed at the University of Wollongong based upon indirect gravimetric method. This paper describes the experimental setup, operation procedures and calculation methods of isotherms. The Langmuir model is used to analyse the experiment results for both dry and moist coal samples.

2 Experimental methods and procedures

2.1 Sample preparation

Coal samples tested in this experiment were collected from a longwall, panel (520) extracting from the Bulli Seam of the Sydney Basin, Australia. The coal samples used in this study included the borehole cores and samples obtained by coring from large coal lumps freshly collected from development headings and delivered to the laboratory. Coal fragments were later crushed and sieved to obtain the appropriate particle sizes for the tests. Pulverised coal samples of 150–212 µm (150 µm) and these with particle size ranges of 1.2–2.36 mm (1.2 mm), 2.36–3.35 mm (2.4 mm), 8–9.5 mm (8 mm) and 16–19 mm (16 mm) were used in this study. The preliminary information about this type of coal was shown in Tables 2 and 3, reported by Saghafi and Roberts (2008) from CSIRO.

Table 2 Coal density and proximate analysis

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Depth (m)</th>
<th>Moisture (%)</th>
<th>Volatile matter (%)</th>
<th>Fixed carbon (%)</th>
<th>Volatile matter (%daf)</th>
<th>Coal density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>450</td>
<td>1.3</td>
<td>21.7</td>
<td>71.4</td>
<td>23.3</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Table 3 Coal petrography

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Vitrinite reflectance (%)</th>
<th>Maceral (%)</th>
<th>Maceral (%), mineral free (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vitrinite</td>
<td>Liptinite</td>
<td>Inertinite</td>
</tr>
<tr>
<td>520</td>
<td>1.28</td>
<td>41.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Prior to sorption testing, the coal samples were dried in a desiccator containing water sorbing material. The desiccator was kept in a heated oven at 60°C under vacuum to keep the coal from the air to prevent sample oxidation. The coal sample moisture content was checked regularly to achieve a total dry condition (zero moisture content).

A number of studies reported on the process of adding moisture to the coal (Joubert et al., 1974; Clarkson and Bustin, 2000; Busch et al., 2003; Day et al., 2008b). The method of adding moisture to the coal sample as reported by Day et al. (2008b), was used in this study. The dry coal samples were vacuumed in the desiccator containing the
saturated solution of potassium sulphate at 25°C. The objective was to achieve 97% relative humidity. The consistency of maintaining sample humidity was monitored by repeated weighing till the weight of coal samples became almost constant, indicating the moisture equilibrium.

Figure 1 shows the moisture content equilibrium test in terms of different coal particle size. It can be seen that the moisture content added to the sample was influenced by the sample fragment size. The 150 µm particle size achieved the highest level of moisture content at 2.12% and the largest particle size of 16 mm had the lowest at 1.40%. The smaller particle coal samples could achieve a higher moisture content within shorter saturation time, it took around 24 hours for 150 µm particle size coal get fully saturated, but more than 120 hours for the other larger particle size coal. The total dry and moisture equilibrium coal samples were used in the following sorption tests.

In comparison, to obtain higher moisture content coal samples, the following steps were followed: at first different particle size coal samples were prepared, using a crusher and then oven dried. The sample was then immersed in distilled water for two hours to achieve moisture saturation. Finally the mixture was filter drained. Table 4 shows the moisture content of coal samples at different coal particle sizes. It is obvious that the level of moisture in coal is strongly dependent on coal particle size, i.e., the smaller the particle size, the higher of moisture.

**Figure 1**  Moisture content of coal samples with water equilibrium method (see online version for colours)

![Figure 1](image)

**Table 4**  Moisture content of coal samples with water immersion method

<table>
<thead>
<tr>
<th>Coal size</th>
<th>16 mm</th>
<th>8 mm</th>
<th>2.4 mm</th>
<th>1.2 mm</th>
<th>150 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>3.97%</td>
<td>4.53%</td>
<td>7.78%</td>
<td>10.95%</td>
<td>35%</td>
</tr>
</tbody>
</table>
It is believed that through both sample preparation tests that the water molecule is prone to firstly adsorbed on the surface of coal and remained near the surface of the particle, rather than penetrating deep into the coal structure. This is clearly evident from the high rate of moisture content in fine particles in comparison with coarse samples. Actually, the interaction of carbon materials like natural coal with water is more complex than with non-polar gases like helium, argon, nitrogen, methane, or carbon dioxide (Busch and Gensterblum, 2011). This complexity is due to the weak dispersion interaction of water with coal, the tendency of water to form hydrogen bonds with other sorbed water molecules and surface chemical species, and the chemisorptive interaction with the coal mineral matter. Busch and Gensterblum (2011) also stated that up to a sample-specific limit additional water is only present as free water on the surface of coal without occupying sorption sites.

2.2 Sorption apparatus

The gravimetric method with single sample cell, also referred to the indirect gravimetric method, was first reported by Lama and Bartosiewicz (1982), and later by Aziz and Li (1999) and Sereshki (2005). Figure 2 shows the modified version of the apparatus currently being used in the gas laboratory, University of Wollongong. A new and more accurate sorption testing and calculation method was recently developed for this apparatus in this study.

Figure 2  Schematic diagram of the modified gravimetric method with sample cells (see online version for colours)
In this apparatus, each cell known as a ‘bomb’, has its own pressure transducer connected to the data logger so that the sorption process and pressure changes in the bomb can be readily determined. These bombs are immersed in the automatic temperature-controlled water bath, which allows testing for coal isotherms at different temperatures. Approximately 200 g of coal ranging from powder size to standard coal core size can be used in the test. A high accuracy balance is used to weigh the bomb. The equipment has recently been modified to accommodate increases in temperature up to 100°C. The addition of a heat isolation jacket outside the water bath as well as the insulation cover enabled the sample bombs to maintain the desired experimental temperature with an accuracy of 0.1°C.

2.3 Experiment procedure

1. Weigh the empty adsorption isotherm bomb.
2. Enclose coal in the bomb and weigh.
3. Place the bomb with coal sample in the water bath, which is maintained in the desired test temperature.
4. Evacuate the bomb to ensure no air is inside the bomb.
5. Charge the bomb with Helium and allow to equilibrate until the pressure becomes constant.
6. After equilibrium, record the constant pressure and weigh the bomb again.
7. Repeat Steps 5 and 6, charging at different pressure steps of approximately 1, 2, 3, 4 MPa; this data is used to calculate the free volume (void volume) of the bomb and consequently the helium density of the coal.
8. After determination of the void volume, the bomb is evacuated.
9. Introduce the test gas into the bomb and allow to equilibrate until the pressure becomes constant.
10. Record pressure at equilibrium, and weigh the bomb again.
11. Repeat Steps 9 and 10 at different pressure steps to obtain final isotherm at approximate pressures of 0.5, 1, 2, 3, 4 MPa.
12. The isotherm results are calculated as adsorbed volume per mass of coal at normal temperature and pressure condition (NTP) which is 20°C and 1 atm (101.325 kPa), the Australia standard condition.

2.4 Isotherm calculation method

In the indirect gravimetric method, at each of the pressure step, the total mass of gas in the bomb is directly weighed and the total gas in the bomb is calculated:

\[ n_{\text{total}} = \frac{M_{\text{total}}}{M_{\text{gas}}} \] (1)
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where \( n_{\text{total}} \) is the total amount-of-substance of gas, \( M_{\text{total}} \) is the total gas weight in bomb and \( M_{\text{gas}} \) is the mole mass of gas. The amount-of-substance of gas in the void space can thus be calculated using the following SRK equation:

\[
P V_{\text{void}} = n_{\text{void}} Z_{\text{SRK}} RT
\]

where \( n_{\text{void}} \) is the void volume of the bomb, \( V_{\text{void}} \) is the void volume, calculated with the helium expansion, \( P \) is the equilibrium gas pressure inside the bomb, which can be measured with the transducer, \( T \) is the experiment temperature, \( R \) is the universal gas constant, \( Z_{\text{SRK}} \) is the compressibility factor of the tested gas calculated with SRK equation at the pressure \( P \) and temperature \( T \). Using \( n_{\text{total}} \) and \( n_{\text{void}} \), the Gibbs (excess) amount of adsorbed gas can be calculated as (Saghafi et al., 2007; Busch and Gensterblum, 2011; Zhang, 2013):

\[
\text{n}_{\text{adsorbed}} = n_{\text{total}} - n_{\text{void}}
\]

The adsorption isotherm is expressed with volume in standard condition, hence the adsorbed volume is:

\[
\text{n}_{\text{adsorbed}} = \text{n}_{\text{adsorbed}} V_m
\]

where \( V_{\text{adsorbed}} \) is the adsorbed volume of gas and \( V_m \) is the mole volume of gas at standard condition (NTP). For each of the pressure steps, the Gibbs adsorbed gas for the isotherm is calculated by dividing Gibbs \( V_{\text{adsorbed}} \) by the mass of coal in the cell.

3 Results and discussions

3.1 Influence of temperature on coal adsorption isotherms

The adsorption tests of totally dry and at moisture equilibrium (2.12% moisture content) 150 µm coal samples were carried out following the above test procedure for determining the coal adsorption isotherm. All samples were enclosed in bombs and systematically subjected to \( \text{CO}_2 \) and \( \text{CH}_4 \) gas pressurisation at various temperatures of 35°C, 45°C and 55°C respectively. The level of gas pressurisation of the samples was carried out initially at 500 kPa steps until reaching 1,000 kPa and later increased at 1,000 kPa steps until reaching a maximum of 4,000 kPa. Some of the important operational procedures were specially noted, for both dry and moist samples, the same coal sample was tested at 35°C, 45°C and 55°C at each pressure step, in order to avoid the samples’ variation and extra errors. The equilibrium at different temperatures (35°C, 45°C and 55°C) was achieved by changing the bath water temperature to avoid possible hysteresis due to repeated high pressure charging processes.

Figures 3 and 4 show the adsorption isotherm at three temperatures for dry and moist coals (2.12% moisture content). At every pressure step, from 0 to 4 MPa, the adsorbed volume of \( \text{CO}_2 \) and \( \text{CH}_4 \) decreased with increasing temperature in each step. The sorbed volume achieved the highest level at 35°C and the lowest at 55°C. Results indicate clearly the exothermic nature of the adsorption process; higher temperature has a negative influence on the surface tension and results in decreased adsorption capacity of coal samples.
3.2 Influence of temperature on coal adsorption capacity

In the Langmuir equation, shown in equation (5), the inverse of the slope of the Langmuir plot provides the Langmuir volume ($V_L$). The product of the Langmuir volume within the Y intercept gives the Langmuir pressure $P_L$. When the sorbed volume is half of the Langmuir volume, the pressure value is referred to as the Langmuir pressure $P_L$. Both $V_L$ and $P_L$ are important parameters for economic assessment of CBM resources. While $V_L$ is the maximum sorption capacity of the coal, which is the value of gas content at high pressure, $P_L$ represents the pressure to which the coalbed reservoir has to be depleted to obtain a 50% recovery (Harpalani et al., 2006).

\[
\frac{P}{V} = \frac{1}{V_L} \times P + \frac{P_L}{V_L}
\]  

(5)

Figure 5 shows the CO$_2$ and CH$_4$ adsorption capacity of dry and moist coals (2.12% moisture content) at different temperatures are represented by their Langmuir volume.
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It is apparent that the Langmuir volume for CO₂ and CH₄ adsorption decreases with increasing temperature. The decreasing coal sorption capability of CO₂ and CH₄ with increasing temperature was confirmed by other researchers (Sakurovs et al., 2008; He et al., 2010; Busch and Gensterblum, 2011). In this analysis, all the raw Langmuir volume constant results are adjusted based on the same average Langmuir pressure constant value from the results of three temperatures’ tests. The Langmuir volume of CO₂ adsorption for dry coal follows the trend line: \( y = -0.5449x + 54.3400 \) (\( R^2 = 0.894 \)), and for CH₄ \( y = -0.2818x + 28.3890 \) (\( R^2 = 0.908 \)). Similarly, the Langmuir volume of CO₂ adsorption for moist coal follows the trend line \( y = -0.4529x + 46.7810 \) (\( R^2 = 0.936 \)), and for CH₄ \( y = -0.2329x + 23.9340 \) (\( R^2 = 0.916 \)). Apparently, coals’ adsorption capacity shows a linear decrease with increasing temperature. For both tested dry and moist coal samples, the decreasing rate of adsorption capacity was greater for CO₂ than CH₄, and for each tested gas, the decreasing rate was higher for dry coals.

**Figure 5** CO₂ and CH₄ adsorption capacity of dry and moist coals at different temperature (see online version for colours)

For tested coals at three temperature levels, the average adsorption capacity of dry coal for CO₂ was reduced by 5.45 cc/g with every 10°C temperature increase. The adsorption capacity of CO₂ in moist coal was reduced by 4.53 cc/g. However, under similar situation the adsorption reduction capacity for CH₄ was in the order of 2.82 cc/g for dry coal and 2.33 cc/g for moist coal. From Figure 5, it is clear that there is a greater drop in the adsorption capacity of coal for CO₂ than CH₄ with increasing temperature.

Several studies have been reported on CO₂ and CH₄ sorption characteristics, using the same coal sample under different moisture conditions, in order to obtain information on the selectivity of the coal for either gas types (Busch et al., 2003; Harpalani et al., 2006; Day et al., 2008a; Li et al., 2010). Higher sorption values for CO₂ were observed as compared to CH₄ while the CO₂/CH₄ sorption ratio (the ratio of maximum sorption volume) varied from 1.1 to 9.1 (Figure 6). A relative decrease in sorption ratio with coal rank was observed for moist coal, with CO₂/CH₄ ratio of around 9 for low coal rank, decreasing to 1.2–1.5 for anthracite coals (Busch and Gensterblum, 2011). Busch and Gensterblum (2011) explained that the high CO₂/CH₄ sorption ratios for low coal maturity could (partly) be due to a much high solubility of CO₂ in water as compared with CH₄, considering the large moisture content for low rank coal (Figure 6). For dry
coal such a relationship with coal rank was not observed and the data scatter for CO₂/CH₄ varied around 1–3 for different coals maturities (Busch and Gensterblum, 2011). It should be noted from sorption measurements that some Sydney Basin coals can store twice as much CO₂ as CH₄ (Saghafi et al., 2007).

In this study, the adsorption ratios of CO₂ versus CH₄ were 1.90 for dry coal and 1.96 for moist coal. This indicates that the coal was the medium volatile bituminous type (m.v.b), with CO₂/CH₄ ratio being higher for moist coal than dry coal and no apparent relationship was found between CO₂/CH₄ sorption ratio and temperature increase.

**Figure 6** CO₂/CH₄ sorption ratio for different moist and dry coal samples at various temperatures as a function of coal rank

Note: Values were picked between 1 and 5 MPa. Data fit for moist samples only.

*Source:* after Busch and Gensterblum (2011)

3.3 Influence of moisture on coal adsorption isotherms

Figure 7 shows the CO₂ and CH₄ adsorption isotherm curves at 35°C, 45°C and 55°C of moist 150 µm coal sample with a moisture content of 2.12%. In each test with different environment temperature, the moist coal sample isotherms for both CO₂ and CH₄ demonstrate a lower sorption capacity. This clearly indicates that the moisture in the coal reduces the adsorption capacity of coal.

This is in agreement with the previous study carried out by Mohammad et al. (2008), inferring that water was treated as ‘pacifying’ the coal matrix; i.e., water occupies part of the coal pore surfaces, thus limiting the accessible space for adsorbing gases. In actuality, the adsorption on wet coal was less than that on dry coal, partly because water competes with gas molecules for the available coal surface, impeding gas molecules from accessing this surface. Based on the study of Mohammad et al. (2008), the model parameter ‘gas
The reduction of coal’s adsorption capacity in this experiment reflects the effect of water on gas adsorption on wet coals, implicitly assuming that the water is strongly adsorbed that it denies access by CO₂ or CH₄ to a portion of the surface area throughout the pressure range of the measurements.

Figure 7  Dry and moist coal adsorption isotherms in terms of different temperature: (a), (b) and (c) is CO₂ at 35°C, 45°C and 55°C respectively; (d), (e) and (f) is CH₄ at 35°C, 45°C and 55°C respectively (see online version for colours)
3.4 Influence of moisture on coal adsorption capacity

Figure 8 shows the CO$_2$ and CH$_4$ adsorption capacities of dry and moist coals (2.12% moisture content) at different temperatures. It is apparent that the Langmuir volume for CO$_2$ and CH$_4$ adsorption decrease almost linearly with the moisture content. The decreasing coal sorption capability with the moisture content was also reported by other researchers recently (Day et al., 2008a; Mohammad et al., 2008; He et al., 2010; Busch and Gensterblum, 2011).

The average value of coal adsorption capacity of CO$_2$ reduces by 3.42 cc/g from dry samples to moist samples, while the average value of coal adsorption capacity of CH$_4$ reduces by 2.26 cc/g. For the tested three temperatures, the average reduction ratio of coal adsorption capacity of dry to moist coal for CO$_2$ is 11.3% and for CH$_4$ is 14.3%.

Moist coal has a lower maximum sorption capacity for both CO$_2$ and CH$_4$ than dry coal (Joubert et al., 1974; Levy et al., 1997; Clarkson and Bustin, 2000; Mohammad et al., 2008), ranging from 15% (Joubert et al., 1974) to 60% (Levy et al., 1997), however, the extent to which the capacity is reduced has been found to be dependent upon the rank of the coal (Day et al., 2008a; He et al., 2010). Higher rank coals are less affected by the presence of moisture than low rank coals. All coals exhibit a certain moisture content beyond which further increase of moisture does not appear to affect the sorption capacity (Day et al., 2008a; Joubert et al., 1973, 1974). Day et al. (2008a) reported that in the case of the similar coal type from the same region, no further reduction in sorption capacity occurred beyond about 0.9% moisture.

The experimental results also show that the equilibrium moisture content of 2.12% in coal has more effect on CH$_4$ than CO$_2$, indicating a significant competition for the sorption sites between methane and water molecules. As confirmed by other researchers (Day et al., 2008a; Busch and Gensterblum, 2011), although the general trend of reducing CH$_4$ capacity was similar to that for CO$_2$, comparatively, the effect was greater for methane and this effect was less pronounced in higher rank coal. However, the CH$_4$ capacity was still more affected than CO$_2$. Alcañiz-Monge et al. (2002) found that the process of water sorption was due to both physical sorption and chemical interaction with surface groups and that micropore filling remains progressive with the narrow micropores
being filled first, and subsequently, water being sorbed in the remaining greater range of microporosity.

Figure 9 shows schematically, the total set of sorption sites for CO₂, CH₄ and water on coal at a constant temperature and pressure. CO₂ has the largest number of sorption sites, followed by CH₄ and then water (Busch and Gensterblum, 2011). The ratio of sorption capacity or sorption sites of CO₂ and CH₄ is in the range of 1 to 9 and changes strongly to lower ratios when moisture content decreases or coal rank increases (Busch et al., 2003; Harpalani et al., 2006; Day et al., 2008a; Li et al., 2010). The intersection area of water and methane (γ) is smaller than the intersection area of water and CO₂ (β), as illustrated in Figure 9. Intersection δ represents the primary sorption sites of water. If there is water present in the system, these sorption sites will be occupied by water molecules because of its higher heat of sorption.

According to the above isotherm results in the experiment, the gas adsorption isotherms are in general less sensitive to changes in temperature than to variations in moisture content which is also confirmed by other studies (Joubert et al., 1974; Day et al., 2008a; Ozdemir and Schroeder, 2009). However, in in situ condition, an increase in temperature results in a decrease in moisture-saturation. Lower equilibrium moisture contents will increase the gas sorption capacity; higher temperature will decrease the sorption capacity (Joubert et al., 1974; Day et al., 2008a; Ozdemir and Schroeder, 2009).

4 Conclusions

Using a modified indirect gravimetric method in UOW, isotherm tests of CO₂ and CH₄ were carried out at 35°C, 45°C and 55°C on dry and moist coals obtained from the Bulli Seam of the Sydney Basin. Two methods including moisture equilibrium with high humidity and liquid water immersion to add the moisture content into the coal were both
adopted, it was found that coal could achieve different moisture content levels with two methods. Moisture content added to coal samples varies with coal particle size and saturation time, smaller particle coal samples achieved higher moisture content within shorter time.

The adsorption capacity analysis of the tests shows a linear decrease with increasing temperature, the decreasing rate of adsorption capacity is greater for CO₂ than CH₄, and for each gas test, the decreasing rate is higher for dry coals. Greater reduction rate for CO₂ than CH₄ is observed with increasing temperature on the adsorption capacity of coal.

The adsorption ratio of CO₂ versus CH₄ for this type of medium volatile bituminous coal is 1.90 for dry sample and 1.96 for moist sample. The CO₂/CH₄ ratio is higher for moist coal than dry coal. No apparent relationship is found between CO₂/CH₄ sorption ratio and temperature increase.

The isotherms for moist coal sample of CO₂ and CH₄ demonstrated a much lower coal sorption capacity for both CO₂ and CH₄. This clearly indicates that the moisture content in coal reduces its adsorption capacity. For the coal sample tested at various temperatures (35°C, 45°C and 55°C), the average reduction ratio of coal adsorption capacity with moisture of CO₂ and CH₄ was 11.1% and 14.0%, respectively. The experimental result showed that moisture content in coal has more effect on CH₄ than on CO₂.

As the adsorption isotherm of coal varies significantly with different temperatures and with moisture, it is important to identify the sorption capacity of coal according to in situ condition, to benefit coal seam gas drainage for either underground outburst control, CBM exploitation or CO₂ geo-sequestration purposes.

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References


Influences of temperature and moisture on coal sorption characteristics


