Porosity and gas sorption capacity of some eastern Australian coals in relation to coal rank and composition

by

M.M. Faiz, N.I. Aziz, A.C. Hutton and B.G. Jones

Department of Geology, University of Wollongong

ABSTRACT

The porosity, pore-size distributions, methane sorption and carbon-dioxide sorption capacities of a suite of coals selected from the southern Sydney and Bowen Basins were studied. The total open pore volumes of these coals range from 2.9 to 7.4 × 10⁻² cm³/g with mineral matter causing a relative increase in the macro-pore volume. Most of the gas uptake in coals appears to take place in meso- and micro-pores which are the dominant porosity in the coals.

At a temperature of 25°C and pressure of approximately 4000 kPa the volume of CH₄ and CO₂ sorbed by the southern Sydney and Bowen Basin coals studied ranges from 10.7 to 16.9 cm³/g and 22.6 to 29.7 cm³/g respectively. The sorption capacity shows a positive correlation with coal rank and surface area, and a negative correlation with the minerals content. Fixed carbon content of the coal is linearly related to the sorption capacity and can be used to model sorption isotherms at a given temperature. Variations in maceral composition do not show any significant influence on the gas sorption capacity.

INTRODUCTION

Coal has a capacity for storing large volumes of gas relative to conventional clastic or carbonate reservoirs. Permian coals along the eastern coast of Australia are no exception and contain up to 30 m³/t methane and carbon-dioxide gas. The amount of gas retained in a coal seam is controlled by many geological factors including coal rank, maceral and ineral composition, porosity, pressure, temperature, tectonic history and geological structure. The aim of this study was to determine the influence of coal rank, composition, porosity, type of gas and pressure on the gas storage capacity of a suite of coal samples selected from the Southern Sydney and Bowen Basins. Samples for this study were obtained from the Bulli and Wongawilli seams of the southern Sydney Basin and Castor, Dysart, Garrick and German Creek seams of the Bowen Basin. Petrographic and chemical properties of these samples are summarised in Table 1.

GAS RETENTION IN COAL

The three modes of gas retention in coals (Rightmire, 1984) are as:

1. sorbed molecules on pore surfaces;
2. free gas held within the matrix porosity (macro-and micro-porosity); and
3. gas dissolved in groundwater within the coal seam.

The first of these modes, sorption, accounts for more than 90% of the gas held in coal.

It has been well established that the gas sorption capacity of coal increases with increasing pressure and coal rank, and decreases with increasing temperature (Kim, 1978). The influence of the maceral composition of coal on the sorption capacity, however, is poorly understood. Previous work carried out in this area by various workers has indicated contradictory results. Ettinger et al. (1966) concluded that at low and medium ranks, inertinite-rich coals have a higher CH₄ sorption capacity than vitrinite-rich coals, whereas at higher ranks, both coal types sorb similar amounts. In contrast to works of Patteisky and Coppens (1961; cited in Ettinger et al., 1966), and Creedy (1979) concluded that CH₄ sorption capacity of vitrinite is greater than inertinite. To further complicate matters, the
work of Swietoslawsicy (1942) and Schwarzer and Byrer (1983) indicated that the quantity of CH\textsubscript{4} sorbed does not vary in any systematic manner relative to the maceral composition. It is worth noting all of these works were concentrated on coals of the Northern Hemisphere. Such work on coals of the Southern Hemisphere, more importantly Gondwana coals, is lacking and extrapolation of Northern Hemisphere data to Gondwana coals may be erroneous.

POROSITY, SURFACE AREAS AND PORE SIZE DISTRIBUTIONS

Electron microscopic studies have indicated the presence of a wide range of pores in coals and the size range categories as defined by the IUPAC (1972) are; macro-pores (> 50 nm), meso-pores (2-50 nm) and micro-pores (< 2 nm). An estimation of the porosity and pore volumes of coal is conveniently made using fluid displacement methods (Mahajan and Walker, 1978) and the total open pore volume of coal is determined from the difference in the reciprocal values of the densities between He (d\textsubscript{He}) and Hg (d\textsubscript{Hg}):

\[
V_t = \frac{(1 - \frac{d_{He}}{d_{Hg}})}{d_{He}}
\]

total porosity,

\[
P = \frac{100d_{Hg}(1 - \frac{d_{He}}{d_{Hg}})}{d_{Hg}}
\]

In these calculations it is assumed that the He molecule does not react with the surface of the coal and does penetrate the open pores; that is, pores of greater than 0.42 nm.

Table 2 summarises He and Hg densities and estimated porosities of the coals tested.

Pore size distributions in the coal samples were estimated by the intrusion of Hg at increasing pressures up to 41.3 MPa (6000 psi). Two typical curves showing the pore size distributions of coals as determined by Hg intrusion are shown in Figure 1. All the samples tested show similar patterns of pore-size distributions. This pattern indicates: a very high frequency of pores with a size less than 10 nm, a very low frequency of pores in the range between 10 nm and 500 nm and a moderate number of pores with a size greater than 500 nm.

The use of Hg intrusion to estimate micropores and the smaller range of meso pores by applying very high Hg pressures is not reliable for two reasons (Deblek and Schrodlt, 1979; Unsworth et al., 1989):

- opening up of closed pores due to high pressures, and
- volume reduction due to coal compressibility at high pressures.

Micro- and meso-pore volumes in coals and coal surface areas are more reliably estimated by the gas adsorption-desorption techniques and in this study pore volumes of the coal samples were determined by CO\textsubscript{2} adsorption at 0°C using the Dubinin-Radushkevich equation. The surface area was then determined by multiplying the pore volume by the CO\textsubscript{2} cross-sectional area (0.253 nm\textsuperscript{2}).

On the basis of the pore volume distributions obtained from Hg intrusion and CO\textsubscript{2} adsorption data, it is possible to differentiate pore volumes according to their size ranges. A summary of these values are shown in Table 3.

The volume of macro-pores (50 nm) of the coals studied varies between 0.007 and 0.024 ml/g. For the majority of the coals, percentage of macro-pores accounts for less than 25% of the total pore volume although some samples gave values outside this range. Macro-pore volume of the samples CK-1 and T-2 accounted for about 35% of the total open pore volume. In contrast, the lowest macro-pore volumes were observed in samples TH-1 and GK-1. It is interesting to note that of the coals studied TH-1 and GK-1 had the lowest mineral matter content and CK-1 and T-2 had the highest. The relationship between the mineral matter content and the macro-pore volumes (Fig. 2a) indicates that the volume of macro-pores increases with increasing mineral matter content. This relationship, therefore, clearly indicates that the occurrence of mineral matter contributes to the abundance of large pores in the suite of coals studied. However, porosity and pore sizes in mineral-rich layers in coal could vary significantly with the type of mineral matter and this needs further study.
Plots of the volumes of different pore sizes (that is, \( V_{50} \), \( V_{(T-50)} \) and \( V_{(T-10)} \)) against the pore volume determined by CO\(_2\) adsorption (\( V_{(CO2)} \)) are shown in Figures 2b, 2c and 2d. These plots indicate that \( V_{(CO2)} \) shows strong positive correlations with meso- and finer sized pores (\( V_{(T-50)} \) and \( V_{(T-10)} \)) while it shows no significant correlation with macro-pores (\( V_{50} \)). Therefore, indications are that no significant CO\(_2\) uptake occurs in macro-pores and most of it occurs in the pores of much finer dimensions, that is, in meso- and micro-pores.

\[ V = \frac{V_m b P}{(1+bP)} \]

where,

\[ P = \text{pressure}, \]

\[ V = \text{volume of adsorbate adsorbed at pressure P}, \]

\[ V_m = \text{monolayer saturation volume (quantity of gas adsorbed per gram of coal to form a saturated monomolecular layer)}, \]

\[ b = \text{constant}. \]

The plot of \( P/V \) against \( P \) for the experimentally-derived data form a least squares straight line and the slope of this line gives the reciprocal of the Langmuir volume (\( V_m \)).

According to the Langmuir theory the value of \( V_m \), ideally, represents the maximum gas holding capacity of the coal. For the coals studied the calculated \( V_m \) values for CH\(_4\) varies from 16.7 to 22.7 cm\(^3\)/g and for CO\(_2\) from 27.8 to 36.2 cm\(^3\)/g.

**EFFECT OF COAL COMPOSITION AND RANK ON SORPTION CAPACITY**

To investigate coherence patterns among gas sorption capacity, porosity and coal properties, an R-mode cluster analysis technique was used. According to the dendrogram shown in Figure 4 it is evident that the Langmuir volumes are strongly positively related to vitrinite reflectance (\( R_{mv} \)), fixed carbon content (\( FC_\% \)), surface area and porosity of coal. As shown Figures 5a and 5b Langmuir volumes also show strong negative correlations with ash content (\( M_\% \)) and mineral content (\( M_\% \)). These relationships, therefore, indicate that mineral matter does not contribute significantly to the amount of gas sorbed in coal. As noted previously the occurrence of mineral matter in coal mainly contributes to its macro-pore (50 nm) volume and the amount of gas stored in these pores is relatively small and mainly occurs as free gas. Therefore, it is postulated an increase in mineral matter in coal causes a relative decrease in the meso- and macro-pore volumes and consequently decreases the gas sorption capacity of the coal.

Langmuir volumes show the strongest correlation with fixed carbon content (Figs. 4 & 5c). As fixed carbon is a measure of the material (mainly C) that is devoid of volatile
matter, mineral matter and moisture (i.e. FC = 100-IM-A-VM) it is virtually a measure of the combined effects of rank, moisture and mineral matter content of coal. Thus, the strong positive correlation between FC% and Langmuir volumes reflects the combined effects of rank, moisture and ash contents on the gas sorption capacity.

As the inorganic phase of the coal suggested a negative effect on the sorption capacity, to gain a better understanding of the effect of maceral composition and rank it is necessary to compare these variables on a basis independent of inorganic matter. For this purpose, Langmuir volumes and volatile matter were converted to a dry ash free basis whereas coal maceral volumes were converted to a minerals free basis. Bivariate plots showing the relationships between Langmuir volumes (daf, dry ash free basis), $R_{\text{max}}$, VM% (daf) and inertinite (mf), minerals free basis) are shown in Figures 5d - 5f. Relationships indicated in these graphs clearly show that the gas sorption capacity linearly increases with increasing rank. The relationship between the Langmuir volumes and inertinite contents shown in Figure 5f indicates a vague negative correlation, but, it is not significant enough to suggest that inertinite has a lower gas sorption capacity than vitrinite. It is worth noting, however, that due to the strong dependence of the sorption capacity on coal rank, the effect of the maceral composition, if any, could be masked.

As discussed previously, of all the coal properties, fixed carbon is most strongly related to the sorption capacity of raw coals. Therefore, using least squares regression technique sorption isotherms for CH4 and CO2 are modelled (Fig. 6) showing the sorption capacities of these coals at 25°C and varying pressures.

CONCLUSIONS

Approximately 75% of the pores in the suite of coals studied fall into the size range of meso- and micro-pores (< 50 nm). The presence of mineral matter in coal mainly contributes to the volume of macro-pores, hence the macro-pore volume increases with increasing mineral matter content.

Micro- and meso-porosity accounts for most of the gas retained in coal. The CO2 sorption capacity of the coals studied is approximately two times higher than that of CH4 and the quantity of CH4 sorbed by coal increases with increasing rank and decreases with increasing mineral matter content. The decrease in the volume of gas sorbed with increasing mineral matter content could be attributed to the relative decrease in the meso- and micro-porosity.

For the suite of Australian coals studied, no significant variations in the gas sorption capacity of different coal types were observed. Due to the combined effects of rank and mineral matter, the gas sorption capacity is proportional to the fixed carbon content of the coal and the volume of gas in the coal can be modelled with a reasonable degree of confidence using the fixed carbon content at any nominated pressure and temperature conditions.

ACKNOWLEDGMENTS

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REFERENCES


Table 1. Results of petrographic and proximate analyses of the samples tested.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>V (%)</th>
<th>I (%)</th>
<th>L (%)</th>
<th>M (%)</th>
<th>R_max (%)</th>
<th>IM (%)</th>
<th>ASH (%)</th>
<th>VM (%)</th>
<th>FC (%)</th>
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<td>T-2</td>
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<td>57.6</td>
<td>0.5</td>
<td>8.5</td>
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<td>21.7</td>
<td>60.8</td>
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<td>70.8</td>
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<td>8.2</td>
<td>20.0</td>
<td>70.8</td>
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<td>21.6</td>
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<td>68.4</td>
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<td>54.4</td>
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<td>2.9</td>
<td>20.2</td>
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<td>6.1</td>
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<td>1.1</td>
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<td>16.6</td>
<td>72.2</td>
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<td>PD-1</td>
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<td>37.1</td>
<td>0.2</td>
<td>7.6</td>
<td>1.32</td>
<td>1.2</td>
<td>9.7</td>
<td>22.9</td>
<td>66.2</td>
</tr>
</tbody>
</table>

V - vitrinite  I - inertinite  L - Liptinite  M - minerals  
IM - inherent moisture  A - ash content  VM - volatile matter  FC - fixed carbon  
tr. - trace amounts  R_max - mean maximum reflectance of vitrinite  

Note: Proximate analyses data on air dried basis.
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>( d_{\text{He}} ) (g/cm(^3))</th>
<th>( d_{\text{Hg}} ) (g/cm(^3))</th>
<th>( V_r \times 10^3 ) (cm(^3)/g)</th>
<th>P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-2</td>
<td>1.42</td>
<td>1.35</td>
<td>3.65</td>
<td>4.93</td>
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<td>CD-1</td>
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<td>-</td>
<td>-</td>
</tr>
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<td>W-1</td>
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<td>1.27</td>
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<tr>
<td>G-1</td>
<td>1.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GK-1</td>
<td>1.32</td>
<td>1.23</td>
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<td>6.84</td>
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<tr>
<td>PD-1</td>
<td>1.36</td>
<td>1.28</td>
<td>4.60</td>
<td>5.88</td>
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</table>

\( d_{\text{He}} \) - helium density, \( d_{\text{Hg}} \) - mercury density, \( P \) - porosity, \( V_r \) - open pore volume estimated from He and Hg densities

*Table 2. Densities, pore volumes and porosities of selected coals.*

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>( S_{\text{CO}_2} ) m(^2)/g</th>
<th>( V_{\text{CO}_2} ) (cm(^3)/g)</th>
<th>( V_T ) (cm(^3)/g)</th>
<th>( V_{\text{He}} ) (cm(^3)/g)</th>
<th>( V_{\text{He}} ) (cm(^3)/g)</th>
<th>( V_{(T-50)} ) (cm(^3)/g)</th>
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<tbody>
<tr>
<td>T-2</td>
<td>161</td>
<td>0.0408</td>
<td>0.0365</td>
<td>0.012</td>
<td>0.019</td>
<td>0.025</td>
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</tr>
<tr>
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<td>0.0289</td>
<td>0.007</td>
<td>0.014</td>
<td>0.022</td>
</tr>
<tr>
<td>CK-1</td>
<td>183</td>
<td>0.0463</td>
<td>0.0680</td>
<td>0.024</td>
<td>0.035</td>
<td>0.044</td>
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<tr>
<td>GK-1</td>
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</table>

\( S_{\text{CO}_2} \) = surface area estimated from CO\(_2\) adsorption
\( V_{\text{CO}_2} \) = pore volume estimated from CO\(_2\) adsorption
\( V_T \) = volume of total open pores (accessible to He) > 0.42nm
\( V_{\text{He}} \) = volume of pores > 50nm
\( V_{(T-50)} \) = volume of pores between 0.42 and 50nm

*Table 3. Pore volumes estimated from different methods.*
Figure 1. Pore size distributions in coal determined by mercury intrusion.

Figure 2. Relationships between volumes of various pore-sizes and minerals content.
Figure 3. CH₄ and CO₂ sorption isotherms at 25°C.

Figure 4. R-mode cluster analyses dendogram showing the similarity levels between the variables.

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Figure 5. Relationships between the gas sorption capacity, coal composition and rank.
Figure 6. Modelled CH₄ sorption isotherms as a function of fixed carbon content.