Comparative study of the influence of minerals in gas sorption isotherms of three coals of similar rank

by C. Rodrigues*, H.J. Pinheiro†, M.J. Lemos de Sousa*

Introduction

In previous studies, Levine (1993), Yee et al. (1993), Lemos de Sousa et al. (2003) and Rodrigues et al. (2000) discussed the influence of several factors on the sorption isotherm processes in coals (such as pressure, temperature, moisture content, mineral matter content, gas composition, rank, and petrographic composition). Moisture and ash are known to inhibit the gas sorption capacity of a coal (Rodrigues and Lemos de Sousa, 1999), thus reducing its gas storage capacity. The study demonstrated that the clean fraction of a coal has the highest capacity to retain gas in the sorbed state, followed by raw coal, and lastly the sink fraction, and re-confirmed previous investigations that showed minerals to be inhibitors of gas adsorption and retention.

Synopsis

This investigation compares the gas adsorption behaviour and capacity of three bituminous coals from South Africa, of similar rank, by assessing the characteristics of the raw coal, as well as the resulting float and sink fractions (at 1.80 cm³/g) obtained by density separation of crushed coal samples. Calculations were also made to obtain the raw coal gas storage capacity from the weighted contribution of both float and sink fractions results, thereby permitting comparison with the analysed results of the raw coal. The study demonstrated that the clean fraction of a coal has the highest capacity to retain gas in the sorbed state, followed by raw coal, and lastly the sink fraction, and re-confirmed previous investigations that showed minerals to be inhibitors of gas adsorption and retention.

Table I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methane (%)</td>
</tr>
<tr>
<td>A</td>
<td>70.00 (±0.01)</td>
</tr>
<tr>
<td>B</td>
<td>70.00 (±0.01)</td>
</tr>
<tr>
<td>C</td>
<td>88.52 (±0.01)</td>
</tr>
</tbody>
</table>

Several researchers use pure methane gas for testing sorption capacity of a coal. However, it is most prudent and preferable to select the gas composition as close as possible to that of the gas present in the basin under investigation. In some instances, the gas composition in the basin may vary from area to area and for the sake of simplicity, one may decide to use the average of the basin only. In order to investigate eventual effects and/or different sample behaviours due to varying gas composition, two different gas mixtures were used in the tests, as shown in Table I.

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In this study, emphasis is given to the influence of the amount of impurities (minerals), which are conveniently quantified as ash content, in the sorption process. However, it is wise to use Parr’s formula to calculate the amount of minerals in a coal, especially for those with sulphur and carbonate minerals, which are known to be driven off during high temperature combustion (ashing), thereby leading to underestimating the ash content (Alpern et al., 1984).

Minerals occur in coal due to their accumulation with the organic matter during deposition in the peat swamp (syngenetic minerals), or by secondary formation (epigenetic minerals) due to circulation of fluids and precipitation of certain elements, normally in cleats, fractures and cellular structure of the organic matrix. (Mackowsky, 1968).

Methodology and samples

Sorption isotherms

The use of gas sorption (adsorption and desorption) isotherms is one of the main tests in any methodology aimed at investigating CBM, and more recently also in studying CO2 geological sequestration in coals.

Gas sorption isotherms are currently used to:

➤ determine the maximum gas storage capacity of a coal in situ
➤ estimate the actual volume of gas in situ
➤ estimate the gas saturation degree of a coal by the difference between the maximum gas storage capacity and the actual volume of gas
➤ estimate the gas diffusion coefficients at different pressures
➤ determine the critical desorption pressure
➤ estimate the composition of the gas stored at different pressures
➤ estimate the gas formation volume factor at different pressures
➤ estimate the volume of gas that will be released from the coal as reservoir pressure decreases
➤ determine the coal density
➤ determine the coal volume.

The apparatus used to perform sorption isotherms was constructed to allow the use of volumetric techniques and gas expandability to perform measurements of adsorbed gas. Volume determination is based on Boyle’s Law for ideal gases. The isotherm model adopted was that of Langmuir, which describes the existing equilibrium between stored and free gases in microporous structures such as those present in coal (Lemos de Sousa et al., 1999; Levine, 1993; van Krevelen, 1993).

Experimental conditions of the sorption process must be well controlled since a slight change in the conditions will influence significantly the sorption process, i.e. depending on the experimental conditions sorption results can be underestimated or overestimated (Rodrigues et al., 2000; Lemos de Sousa et al., 2003). All experiments were performed under the following conditions:

➤ temperature in the bath 35ºC, corresponding to the temperature of the coal seam reservoir (the test vessel is placed in a tank filled with water so as to maintain the temperature constant throughout the sorption testing; see Lemos de Sousa et al., 1999)
➤ moisture content of the sample equal to, or greater than, the moisture-holding capacity (Rodrigues and Lemos de Sousa, 1999)
➤ particle size of sample less than 212 µm
➤ mass ca. 100 g.

Samples

Three coals of Permian age from South Africa, designated A, B and C, were used in the present investigation. Each raw coal was subjected to float and sink separation, resulting in their respective float and sink fractions. In all, nine samples were assessed (Tables II and III).

Float-sink density separation

The washability yield of a coal at a given size fraction and a given density, is a function of, and dependent on, the ash content and organic composition of the coal, as well as their association. Float and sink laboratory tests as described in ISO 7936 are used to obtain float fractions with the desired properties.
ash content. In this study, each coal sample was washed at relative density of 1.80, using a mixture of perchloroethylene and benzene.

Results
Proximate analyses were carried out on all samples, i.e. raw coals (A, B, and C) and on their float (≤ rd 1.80) and sink fractions (rd > 1.80), whereas petrographic analyses (maceral composition and vitrinite reflectance) were performed only on the float fractions of each coal.

The results indicate that the clean coal fractions, with the lowest ash contents, reported the highest capacity to store gas, followed in decreasing order, by the raw coal and the sink fractions (Figures 1, 2 and 3; Tables II and III). It is simple to deduce that the absence of minerals in the coal, especially those intimately associated with the organic matrix and filling voids and cavities, allowed the gas to be adsorbed into any free space available. On the other hand, the sink fractions, mostly composed of non-porous minerals, is the fraction with the lowest available free space and hence less space for gas to be adsorbed. The low amount of organic matter present in the sink fractions still retains the ability to store gas, hence the adsorption shown for these samples, albeit low.

As expected, the float and sink densimetric separation resulted in lower ash contents in the float fractions. However, the relation between yield and ash clearly indicates that in sample C the organic and inorganic portions are more intimately mixed, resulting in poor liberation of the minerals from the organic matrix. In contrast, sample A with a lower yield at 71.4% reported the lowest ash (10.6%) at the cut-off density, indicating that the coal sample comprised of distinctly separated coal lithotypes and shale bands, with the latter reporting to the sink and the former to the float.

All three coals are virtually identical in rank (as measured by vitrinite reflectance, medium-rank bituminous C), but while the floats of Samples A and C are vitrinite-rich (>80%), that of Sample B contains only moderate vitrinite (46%). As a result, the volatiles (dry, ash-free) of Float B are lower than those for Floats A and C, once again supporting the value and application of petrographic composition for rank determination rather than chemical parameters such as volatiles, which are commonly used (see Table III).

Figures 1 to 3 illustrate the sorption curves obtained from testing the three raw coals, and corresponding floats and sinks. In all cases, the float reported the highest maximum adsorption, followed by the raw and finally the sink fraction. The maximum gas content adsorbed is attributed to the float of sample A (lowest ash, highest vitrinite). In ranking the maximum gas adsorption, it is possible to illustrate that an increase in ash is accompanied by a decrease in adsorption and that the presence of the latter appears to be more influential than the petrographic composition in coals of the same or similar rank. Also, the weighted calculated ash for the raw coals, using the yield and ash of the corresponding float and sink fractions, are very close to the analysed ash in the raw coal (Table IV; see also Figure 4).
Comparative study of the influence of minerals in gas sorption isotherms

Table IV

<table>
<thead>
<tr>
<th>Rank</th>
<th>Sample</th>
<th>Max adsorption (scf/ton)</th>
<th>Calc max adsorption (scf/ton)</th>
<th>Ash % (dry)</th>
<th>Calc ash % (dry)</th>
<th>Vitrinite % (mmf)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Float A</td>
<td>350</td>
<td>10.9</td>
<td>85</td>
<td></td>
<td></td>
<td>Lowest ash, highest adsorption</td>
</tr>
<tr>
<td>2</td>
<td>Raw A</td>
<td>270</td>
<td>267</td>
<td>28.7</td>
<td>28.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Float B</td>
<td>250</td>
<td>24.7</td>
<td>46</td>
<td></td>
<td></td>
<td>In spite of lowest vitrinite of the floats, its ash is lower than in float C</td>
</tr>
<tr>
<td>4</td>
<td>Raw B</td>
<td>210</td>
<td>222</td>
<td>30.4</td>
<td>30.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Float C</td>
<td>150</td>
<td>30.8</td>
<td>81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Raw C</td>
<td>140</td>
<td>132</td>
<td>36.2</td>
<td>35.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Sink B</td>
<td>100</td>
<td>55.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Sink A</td>
<td>60</td>
<td>73.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Sink C</td>
<td>40</td>
<td>60.6</td>
<td></td>
<td></td>
<td></td>
<td>More pure shale and less intermixing with coal matrix? or more intermixing and more filling of botanical and other structures?</td>
</tr>
</tbody>
</table>

When the gas adsorption is calculated by using the weighted contribution of the float and the sink analyses, the resulting curves are very close to those obtained on the raw coal samples, as are the calculated maximum sorption for the raw coals. This is illustrated in Figures 5 to 7 (see also Table IV).

Discussion and conclusions

The present studies confirm that the quantity of impurities present in a coal (conveniently expressed as the ash content) is an impediment to the ability of the coal to adsorb gas (Yee et al., 1993; Rodrigues et al., 2000). In summary, minerals have two major effects on the sorption capacity:

- they are almost non-porous and consequently cannot store gas, and
- they occupy space that could otherwise be occupied by gas or other fluids.

Figure 4—Relation between maximum adsorption and ash percent (dry basis)

Figure 5—Sample A: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data

Figure 6—Sample B: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data

Figure 7—Sample C: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data
Moreover, in the examples used, it appears that the presence and amount of impurities is a greater impediment to gas adsorption than the amount of vitrinite (versus inertinite), although in the case of these samples, compact inertodetrinite-rich inertinites are predominant and more common than the banded inertinite macerals such as semifiusinite and fusinite, where open or closed cellular structures are common features.

The differences between calculated and measured maximum sorption are not considered to be significant, especially if this type of investigation is carried out during the prospecting phase of a project—in all three cases the difference is below 6% of the measured value.

In such cases where a planned multi-disciplinary investigation of a coal basin requires that analyses for gas adsorption, along with other characterisation requirements need to be carried out, especially when core samples are limited in quantity for tests, such as densimetric ones, it seems plausible that the calculated weighted adsorption curves and maximum sorption faithfully approximate those of the raw adsorption curve. This means that a split of the raw sample for adsorption tests is not necessary, and that adsorption can be carried out on float and sink fractions that are also being tested for other characteristics.

Acknowledgements
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References


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Errata


The following are the correct legends for Figures 4 to 7:

Figure 4 – Sample A: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data.

Figure 5 – Sample B: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data.

Figure 6 – Sample C: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data.

Figure 7 – Relation between maximum adsorption and ash percent (dry basis).

The correct Table II is as follows:

<table>
<thead>
<tr>
<th>Coal</th>
<th>Volatile matter</th>
<th>Ash</th>
<th>Fixed carbon</th>
<th>Yield</th>
<th>Volatile matter</th>
<th>Ash</th>
<th>Fixed carbon</th>
<th>Yield</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>32.1</td>
<td>28.7</td>
<td>39.2</td>
<td>71.4</td>
<td>38.4</td>
<td>10.9</td>
<td>50.7</td>
<td>28.6</td>
<td>73.3</td>
</tr>
<tr>
<td>B</td>
<td>27.6</td>
<td>30.4</td>
<td>42.0</td>
<td>81.6</td>
<td>29.1</td>
<td>24.7</td>
<td>46.2</td>
<td>18.4</td>
<td>55.7</td>
</tr>
<tr>
<td>C</td>
<td>29.8</td>
<td>36.2</td>
<td>34.0</td>
<td>83.9</td>
<td>31.3</td>
<td>30.8</td>
<td>37.9</td>
<td>16.1</td>
<td>60.6</td>
</tr>
</tbody>
</table>