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

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## 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.

## 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. In the case of the ash content, a number of authors selected samples for experiments with an ash content of 15% or less, followed by recalculation of the data to an ash-free basis (Mavor *et al.*, 1990; Yee *et al.*, 1993). For coals with Gondwana-like characteristics, often manifesting marked temporal and lateral variations in organic composition and mineral content, such 'selectivity' in sampling and sample representation is considered to be inappropriate, especially when the coal basin is being investigated for a number of potential uses other than gas potential.

The coals in the present study were analysed for their chemistry and petrographic composition. In many instances, for practical reasons, the study of a coal basin involves compositing samples to represent particular areas, seam or seam combinations. For analytical purposes, this process consists of blending coal samples with different ash contents so as to achieve a theoretical reserve average. In some cases, the basin investigation may consider assessing for other potential requirements besides gas sorption, such as washability behaviour of the coal and the quality characteristics of the resulting products with a view to establishing their potential utilization.

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.

*Table I*

**Gas composition used in the experimental tests**

| Sample | Gas composition | | |
| --- | --- | --- | --- |
| | Methane (%) | Carbon dioxide (%) | Nitrogen (%) |
| A | 70.00 (±0.01) | 25.00 (±0.01) | 5.00 (±0.01) |
| B | 70.00 (±0.01) | 25.00 (±0.01) | 5.00 (±0.01) |
| C | 88.52 (±0.01) | 6.99 (±0.01) | 4.49 (±0.01) |

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| Table II | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Proximate analyses (%, dry basis) of raw coals and float fractions, and washability yields (%) at rd 1.80** | | | | | | | | |
| Coal | Raw | | | Float fraction @ rd 1.80 (wt %) | | | Sink fraction | | |
| | Volatile matter | Ash | Fixed carbon | Yield | Volatile matter | Ash | Fixed carbon | Yield | Ash |
| A | 32.1 | 28.7 | 39.2 | 71.4 | 38.4 | 10.9 | 50.7 | 28.6 | 73.3 |
| B | 27.6 | 30.4 | 42.0 | 81.6 | 29.1 | 24.7 | 46.2 | 18.4 | 55.7 |
| C | 29.8 | 36.2 | 34.0 | 83.9 | 31.3 | 30.8 | 37.9 | 16.1 | 60.6 |

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 $CO_2$ 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

| Table III | | | | | |
|---|---|---|---|---|---|
| **Petrographic analyses and volatiles (dry, ash-free basis) of float fractions** | | | | | |
| Sample | Petrography (%, mmf) | | | | |
| | Volatiles (%) | Rr (%) | Vitrinite | Liptinite | Inertinite |
| A | 43.0 | 0.71 | 85 | 8 | 7 |
| B | 38.6 | 0.75 | 46 | 11 | 43 |
| C | 45.2 | 0.69 | 81 | 7 | 12 |

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ash content. In this study, each coal sample was washed at relative density of 1.80, using a mixture of perchloroethylene and benzyne.

## 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).
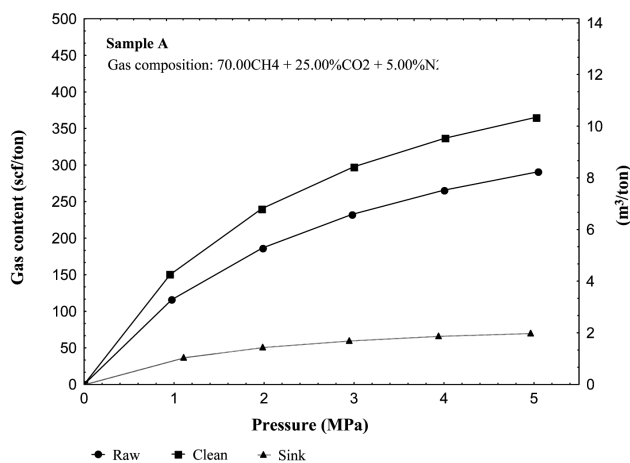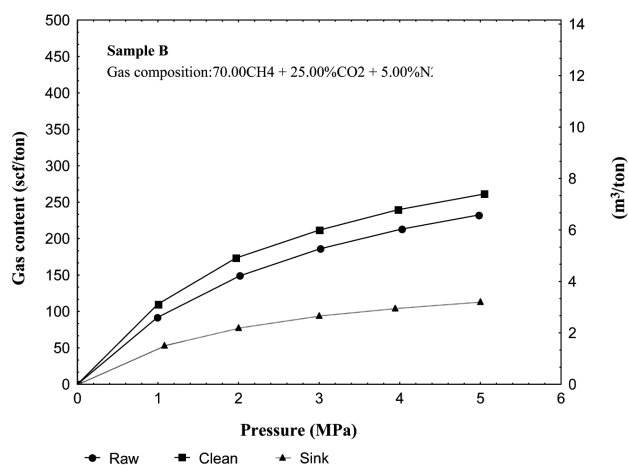


Figure 2—Sample B : sorption isotherms of raw coal, float and sink fractions



Figure 1—Sample A : sorption isotherms of raw coal, float and sink fractions



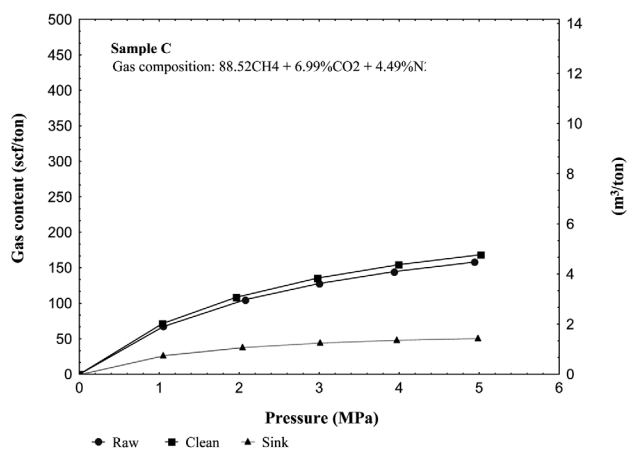Figure 3—Sample C : sorption isotherms of raw coal, float and sink fractions

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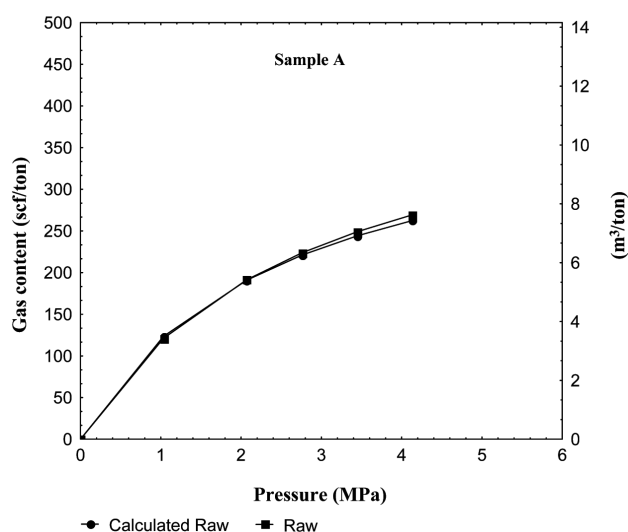| Rank | Sample | Max adsorption (scf/ton) | Calc max adsorption (scf/ton) | Ash % (dry) | Calc ash % (dry) | Vitrinite % (mmf) | Comment |
|------|--------|--------------------------|-------------------------------|-------------|------------------|-------------------|---------|
| 1 | Float A | 350 |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

*Table IV*

**Ranking of maximum adsorption and ash content**



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

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.
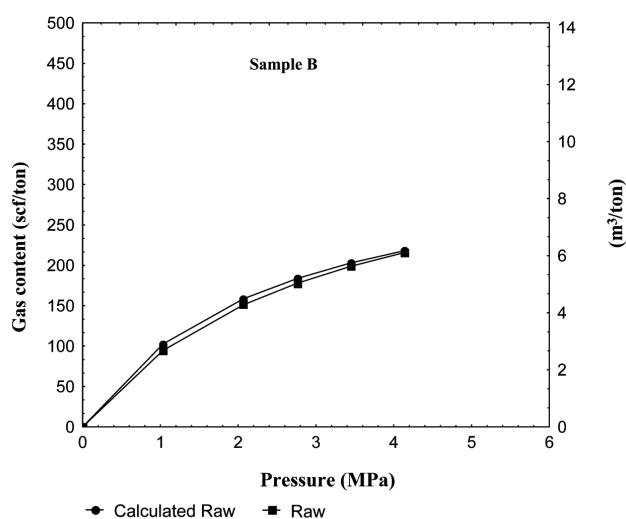


Figure 6—Sample B: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data
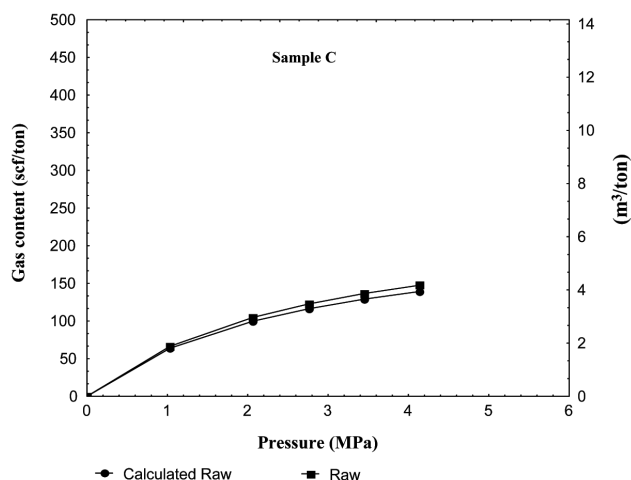
# Comparative study of the influence of minerals in gas sorption isotherms
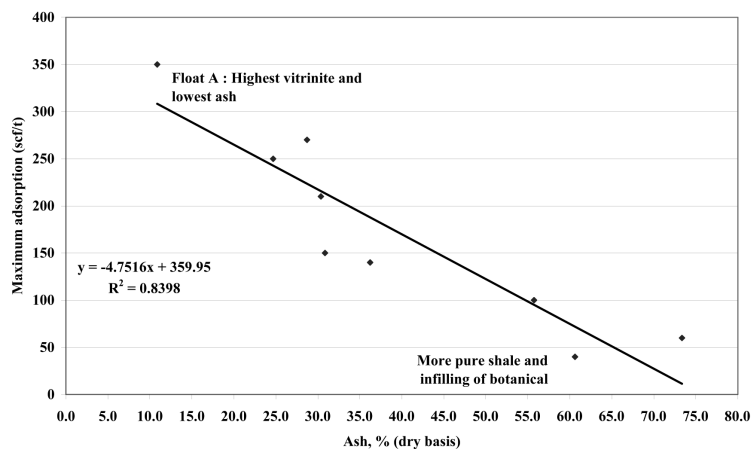


**Figure 7—Sample C: comparison between isotherm of the raw coal with calculated weighted isotherm using float and sink sorption data**

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 semifusinite 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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