

# Microbalance applications to sorption testing of coal

by

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## ABSTRACT

Sorption testing of coals from the Bowen Basin has been performed using a high pressure microbalance. The gravimetric method is applied, enabling adsorption isotherms to be determined at different coal moisture states. The apparatus is ideal for testing of side-wall material, drill cuttings or maceral concentrates, as well as core material.

No single coal parameter can be used to accurately predict the sorption capacity of the Bowen Basin coals tested. A general positive correlation with coal rank and a negative correlation with ash content is observed. Bright coals have a higher sorption capacity than dull coals of equivalent rank (up to 30 %), related to their greater degree of microporosity.

At 4 MPa gas pressure and 23.5°C the sorption capacity of the dried coals tested ranged from 20-29 scc/g (daf) of methane. Methane sorption capacity decreases with increasing moisture content and the relationship with the Langmuir Volume of  $V_w/V_d = 1/(1.02 + A_m)$  applies, where  $A = 0.35$ .

## INTRODUCTION

Major research on methane gas production from coal seams to date has been conducted in the United States, with limited investigations in Australia being related to shallower coals for mine safety purposes. Methane production from coal seams faces several technology gaps, which require research and fresh ideas, particularly for developing new basins, deeper coals, and geologically complex settings (Schraufnagel *et al.*, 1990). The Bowen Basin of Queensland poses a major challenge in this context.

Sharer (1992) states that besides gas content and permeability effects, two other characteristics are critical in understanding the nature of fluid flow through coal. These are the

adsorption/desorption isotherm which defines the relationship between pressure and sorption capacity of the coal, and the diffusion parameters (diffusivity) of the coal, which control the gas flow rate through the main coal matrix. Sorption testing of coal is therefore a major component of coalbed methane assessment. Mavor *et al.* (1990) provide a review of sorption testing procedures applied in the US.

The transport of methane through coal is generally considered a two-stage process:

- diffusion of methane through the pore structure of the coal to naturally occurring cracks followed by
- the simultaneous flow of water and gas through the crack structure.

Smith and Williams (1984), conducted numerous tests on American coals, looking at the rate effects and assessing the current accepted physical models. They pointed out investigators studying the relative magnitudes of the above two steps, including Kissell (1972) and Kuuskraa *et al.* (1979), ignored the coupling of the diffusional and laminar flow processes. This same finding has been emphasised by the work of Beamish *et al.* (1991), particularly in the case of dull and bright coal behaviour, which will be addressed by a further paper by Gamson and Beamish in these proceedings. The work on coal microstructure at the CGRI adds a further dimension to the complexities of gas flow behaviour through coal, whereby the macropore system is seen as more than just a cleat network.

Previous studies on gas sorption capacities have revealed that the methane is primarily stored as an adsorbed layer on the internal surface of the coal pores (Curl, 1978). The amount of gas stored is pressure, temperature and moisture content dependent (Patching, 1970). Kim (1977) reported that the

sorption capacity of coal generally increases with rank and depth. Limited data reported to date on Australian coals (Bartosiewicz and Hargraves, 1985) have not been able to substantiate a rank dependence of sorption capacity. Coal type effects on sorption capacity have shown conflicting results as indicated by Ettinger *et al.* (1966).

Recently, a new approach to gas sorption studies has been advocated by Levine (1991) and Beamish *et al.* (1991). The apparatus used, in work performed independently in the US and Australia, is a high pressure microbalance. The gravimetric method (Daines, 1968; Lama and Bartosiewicz, 1982) is applied to coal samples down to milligram size. This allows detailed comparison of coal type sorption behaviour. Core samples are no longer a pre-requisite for analysis. The apparatus is ideal for testing of side-wall material, drill cuttings or maceral concentrates.

As part of an ERDC funded project, samples from the Bowen Basin have been tested with the microbalance sorption technique.

## LABORATORY SORPTION TESTING

### Equipment for Adsorption/Desorption Tests on Coal

There are two main methods to consider in selecting the equipment for adsorption/desorption testing of coal samples. These are Volumetric (Ruppel *et al.*, 1972) and Gravimetric (Daines, 1968; Lama and Bartosiewicz, 1982). Other factors to be considered are, the purpose of testing, sample size fraction and quantity to be used. The majority of testing for gas storage capacity uses fine coal size ( $< 250 \mu\text{m}$ ). Bulk quantities are often used (80 - 150 g), which normally provides broad relationships between parameters. To obtain a closer understanding of the coal type and microstructure influence there is a need to use pieces of coal which can be used for sorption testing and SEM work. Approximate 1 g solid samples are ideal for this purpose.

After reviewing the techniques being applied overseas and previously used in Australia, the gravimetric technique was selected with two options to be considered to meet CGRI's research objectives.

Option 1: Custom build a system along the lines of Daines (1968) or Lama and Bartosiewicz (1982).

Option 2: Purchase a ready made unit from a reputable manufacturer which is capable of accurate and efficient adsorption/desorption testing.

Constructing equipment in-house as per option 1 was considered time consuming and requiring a major debugging period. The accuracy of data measurement is reasonable (with multiple sampling), but manually time intensive. Recent developments to computerise results have been made by Siahaan *et al.* (1989) using a high precision balance, but the manual component of disconnecting and re-connecting vessels to the system still remains.

Off-the-shelf equipment existed, namely Sartorius high pressure microbalances, which fulfilled the requirements of option 2. These are fully self-contained units capable of highly accurate measurements of weight changes in samples associated with adsorption/desorption under a wide range of pressure and temperature conditions. The unit is amenable to automated measurement and provides possibilities of future flexibility. This equipment had previously been used in Australia by:

- (i) CSIRO, Division of Coal and Energy Technology for adsorption testing on activated carbon.
- (ii) Griffiths University, Department of Science and Technology for adsorption testing of hydrogen in hydrides.

Consultation with both these institutions indicated that a Sartorius M 25D-P microbalance would produce the results to satisfy the requirements of the research work at CGRI.

### Equipment Operation

The microbalance arrangement is illustrated in Figure 1. Methane was introduced to the coal samples at stepped pressures varying from 0.5 MPa to 1 MPa up to a maximum of 7 MPa, and the sorption capacity measured at each step. Two particle size ranges were used, crushed ( $\sim 212$  microns) and solid (5-10 mm), with approximately 1 g of sample being used in each case. A fixed temperature of 23.5 °C was used for all tests and the mois-

ture content of each test run was controlled by evacuation. The crushed samples were dried and the solid samples were partially dried.

Due to the volume differences on either side of the balance point of the beam, one side of the unit will be more buoyant than the other and a correction is therefore required for this effect. This has been determined by calculating the volume difference between the two sides, and converting this volume difference to a weight factor which is pressure dependent.

#### Particle Size Effects on Storage Capacity

Reducing coal particle size to speed up the sorption process has often been confused as a possible source of falsely increasing storage capacity. Experimental results by Ruppel *et al.* (1974) and Bielicki *et al.* (1972) have shown that storage capacities of coals tested at particle sizes ranging from 3.36 mm - 44  $\mu\text{m}$  and 12.7 mm - 74  $\mu\text{m}$  respectively, do not differ with any degree of statistical significance. This comes as no surprise when the sum of the external surface area of progressively smaller coal particles is compared to the internal surface area of the pores available for sorption.

Take for example  $n$  grams of bituminous coal made up of  $m$  spherical particles of radius  $r$  (cm) and density  $\rho$  (g/cc), then

$$n = \frac{4\pi r^3}{3} m \rho \quad (1)$$

$$m = \frac{3n}{4\pi r^3 \rho} \quad (2)$$

The external surface area of these particles is given by

$$SA = 4\pi r^2 m \quad (3)$$

substituting for  $m$  from equation (2) into equation (3) gives

$$SA = \frac{4\pi r^2 3n}{4\pi r^3 \rho} \quad (4)$$

$$= \frac{3n}{r\rho} \text{ cm}^2 \quad (5)$$

Consider the normal isotherm testing crushed fraction of 60 mesh (250  $\mu\text{m}$ ),  $r = 0.0125$  cm. From equation (5), 100 g of this coal with a density of 1.35 g/cc would have an external surface area of:

$$SA = \frac{3 \times 100}{0.0125 \times 1.35}$$

$$= 178 \times 10^2 \text{ cm}^2$$

The range of internal surface areas measured for bituminous coals are 100 - 300  $\text{m}^2/\text{g}$  (1,000,000 - 3,000,000  $\text{cm}^2/\text{g}$ ). Using the lower end of the internal surface area values gives

$$SA = 100 \times 10^6 \text{ cm}^2$$

Therefore the percentage change in surface area by crushing is of the order of 0.02% at most.

#### METHANE SORPTION CAPACITIES

##### Effects of coal rank, surface area and ash content

The sorption capacity data for all coals tested are contained in Table 1. The standard coefficients for the Langmuir Isotherm equation are used for comparison. There is a general increase in sorption capacity with increasing coal rank (Figures 2 and 3), and a general decrease in sorption capacity with increasing ash content (Figure 4). The scatter in the data would suggest that other parameters affect the sorption capacity, and no simple relationship is possible for prediction.

The test results also show a clear distinction exists between dull and bright coals. The bright coal has a higher sorption capacity than the dull coal (Figure 5). This is consistent with the surface area data for the coal. Jolly *et al.* (1968) found a similar relationship with a "Brights" and "Hards" sample taken from the Top Hard seam, Welbeck Colliery in the United Kingdom. The carbon contents of the two coals on a dry, ash-free basis were similar, but the isotherms were very different. The "Brights" sample had a maximum sorption capacity of 850  $\text{ft}^3/\text{ton}$  (23.7  $\text{cc/g}$ ), whereas the "Hards" sample had a maximum sorption capacity of 570  $\text{ft}^3/\text{ton}$  (15.9  $\text{cc/g}$ ).

Levine (pers comm) using a similar methodology to CGRI has observed the same relationship in US coals.

However, these results are in contrast to those reported by Ettinger *et al.* (1966), who found that fusinite rich coals had a higher sorption capacity than vitrinite rich coals above 20 atmospheres. Also, the results of this study appear to contrast with the findings of Faiz and Cook (1991), namely, inertinite-rich coals tend to store relatively more gas than vitrinite-rich coals. However, Faiz and Cook (1991) were comparing desorbable gas contents with the coal types in their paper and not sorption capacities. Their results in fact are as expected from the desorption behaviour exhibited by dull and bright coals (see Gamson and Beamish, these proceedings).

#### Moisture Reduction Factor

An indication of moisture reduction effects on sorption capacity is provided by comparing the results of the dull solid samples and the crushed samples (Table 1). It can be seen that an increase in the coal moisture content significantly reduces the gas sorption capacity of the coal (Figure 6). These effects were studied by both Ettinger *et al.* (1958) and Joubert *et al.* (1973, 1974). From the limited data set, a linear regression yields a reasonable fit and produces an equation of the form  $V_w/V_d = 1/(1.02 + Am)$ , where  $A = 0.35$ . This equation is similar to the one proposed by Ettinger *et al.* (1958).

#### CONCLUSIONS

A technique for sorption testing of coals has been developed at the Coalseam Gas Research Institute which uses a high pressure microbalance. The key function of performing sorption testing with a microbalance is the ability to provide results for the direct comparison of effects of:

1. coal type (band selection or maceral concentrates)
2. coal microstructure
3. particle size (micron sized to centimetre).

Tests performed on Bowen Basin coals indicate that there is a general positive correla-

tion between sorption capacity and coal rank, and a negative correlation with ash content. The variation in sorption capacity with rank is most likely related to the coal microstructure, in particular, the pore size distributions. Two other factors appear to affect sorption capacity of coals. Firstly, the coal type where bright coals have a higher sorption capacity than dull coals. This is essentially related to the greater internal surface area displayed by bright coals (196-277 m<sup>2</sup>/g, db) as compared to the dull coals (150-213 m<sup>2</sup>/g, db). Secondly, the coal moisture, where an increase in moisture greatly reduces the sorption capacity. A reasonable linear fit is obtained for coal moisture effect on sorption capacity, namely  $V_w/V_d = 1/(1.02 + Am)$ , where  $A = 0.35$ .

#### ACKNOWLEDGMENTS

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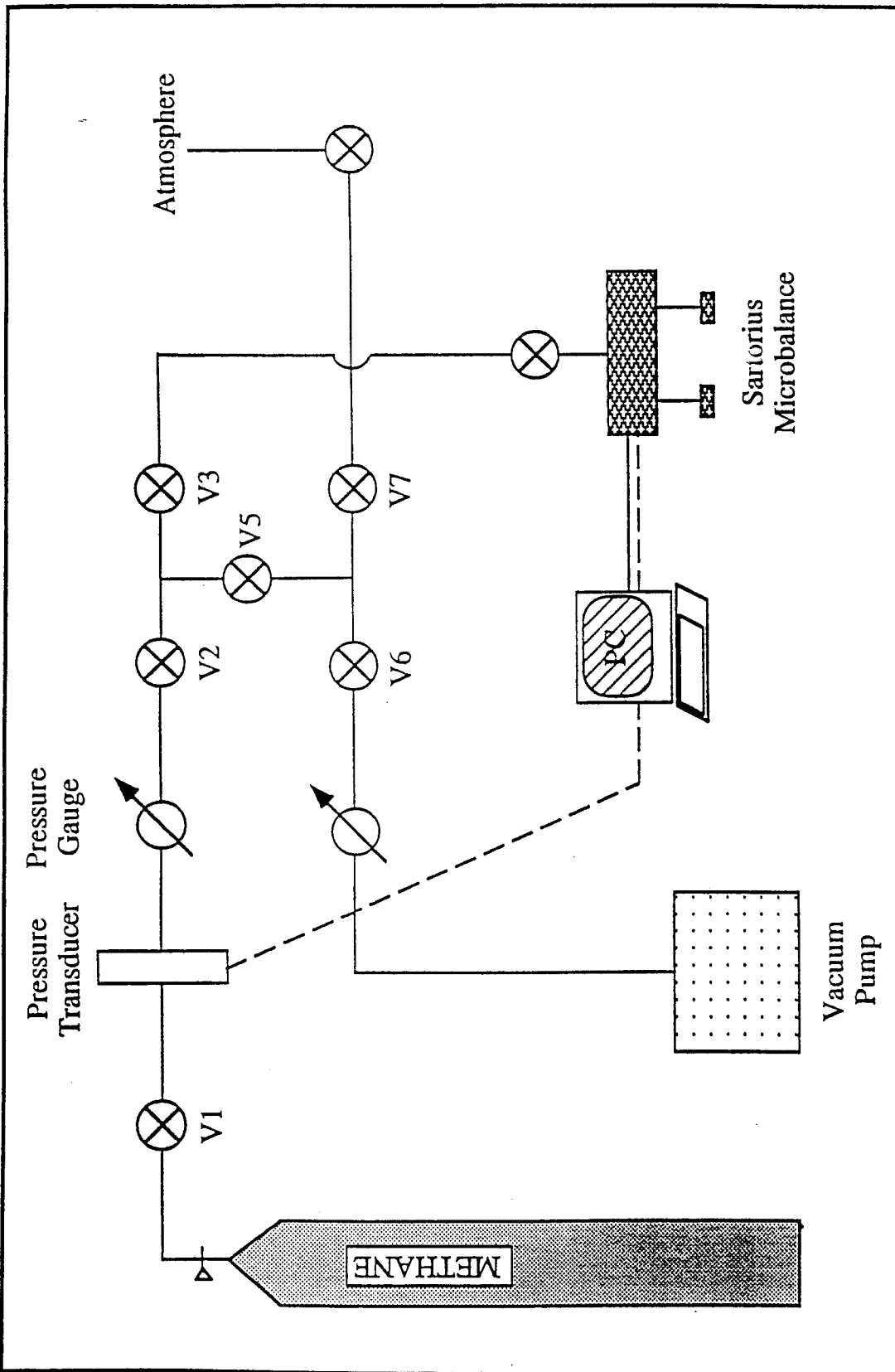


Figure 1. Schematic of microbalance set up.

Sample	Coal Group	Rank	Sample State	Test Moisture (%)	Ash Content (% db)	Volatile Matter (% db)	Fixed Carbon (% db)	Surface Area (m <sup>2</sup> /g db)	Total Porosity (%)	Langmuir Volume (cc/g db)	Langmuir Pressure (MPa)
1 Bright	BAR	0.81	Crushed	0	2.1	33.3	64.6	237	1.6	32.8	1.8
1 Dull			Crushed	0	4.2	29.2	66.5	209	13.7	26.9	1.4
2 Bright	BAR	0.81	Solid	0.7						19.5	1.5
2 Dull			Crushed	0	5.2	34.2	60.7	247	1.3	25.2	1.2
			Crushed	0	10.1	27.3	62.6	194	11.1	27.8	1.7
3 Bright	BAR	0.82	Solid	1.0						20.9	1.5
3 Dull			Crushed	0	4.1	33.1	62.8	228	N/A	30.9	2.1
			Crushed	0	5.6	30.8	63.6	200	N/A	30.7	1.6
4 Bright	BAR	0.82	Solid	1.1						27.2	1.9
4 Dull			Crushed	0	2.3	34.0	63.7	245	N/A	32.2	1.7
			Crushed	0	4.7	30.8	64.5	209	N/A	28.1	1.3
5 Bright	BAR	0.88	Solid	1.1						19.5	1.3
5 Dull			Crushed	0	3.7	30.4	65.8	277		30.9	1.4
			Crushed	0	13.8	20.9	65.3	175	9.0	24.4	1.4
6 Bright	RGL	1.23	Crushed	0	5.7	24.1	70.2	269	N/A	36.9	1.4
6 Dull			Crushed	0	10.9	20.1	69.0	213	N/A	31.5	1.3
			Solid	0.6						26.1	1.5
7 Bright	BAR	1.33	Crushed	0	4.2	21.0	74.8	196	5.4	35.6	1.4
7 Dull			Crushed	0	7.1	19.4	73.5	150	10.5	33.6	1.6
			Solid	1.0						25.3	1.7
8 Bright	RGL	1.65	Crushed	0	9.7	22.8	67.5	213	2.1	35.5	1.9
8 Dull			Crushed	0	17.1	14.6	68.3	173	5.9	28.8	1.9
9 Bright	FTC	1.66	Crushed	0	1.9	16.8	81.6	261	2.6	37.9	2.5
9 Dull			Crushed	0	24.5	13.8	61.7	187	12.4	24.7	1.3
			Solid	0.5						20.9	1.1

Table 1. Summary of coal data and isotherm test results.

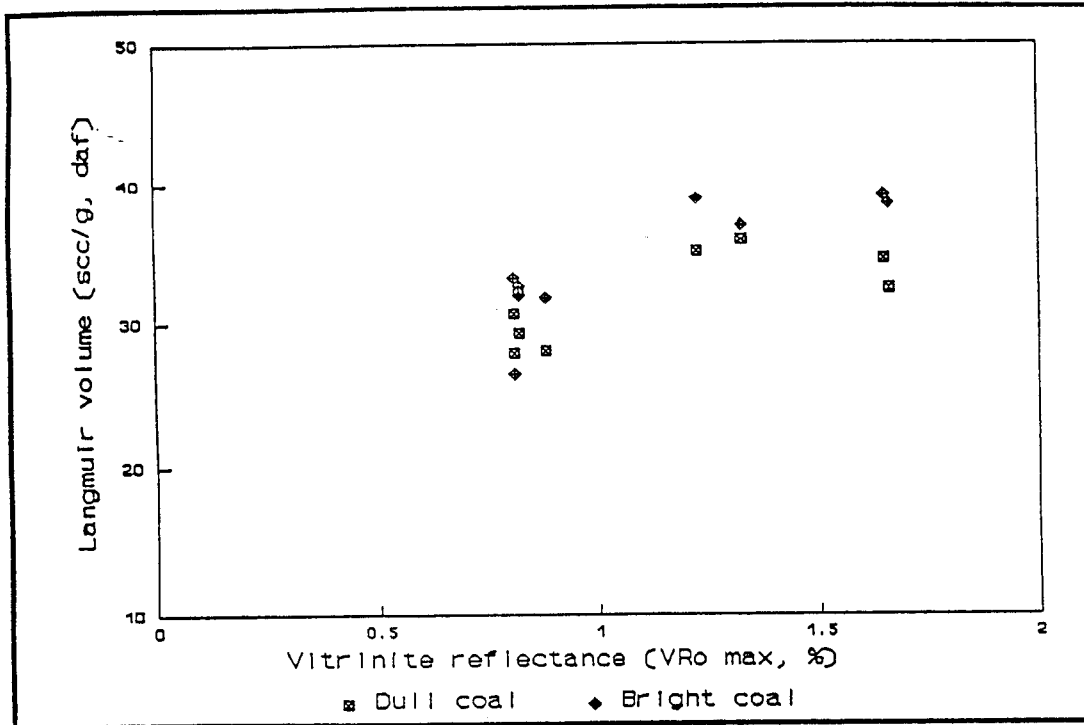


Figure 2. Variation in gas sorption capacity with vitrinite reflectance for dull and bright coals from the Bowen Basin.

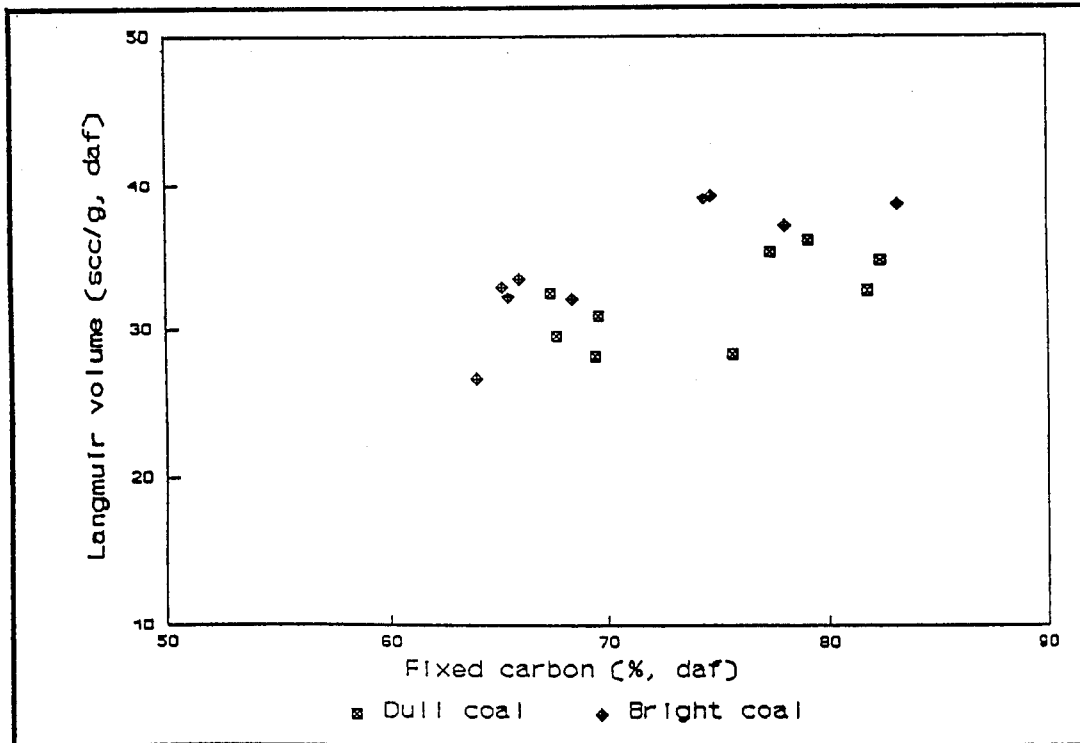


Figure 3. Variation in gas sorption capacity with fixed carbon content for dull and bright coals from the Bowen Basin.

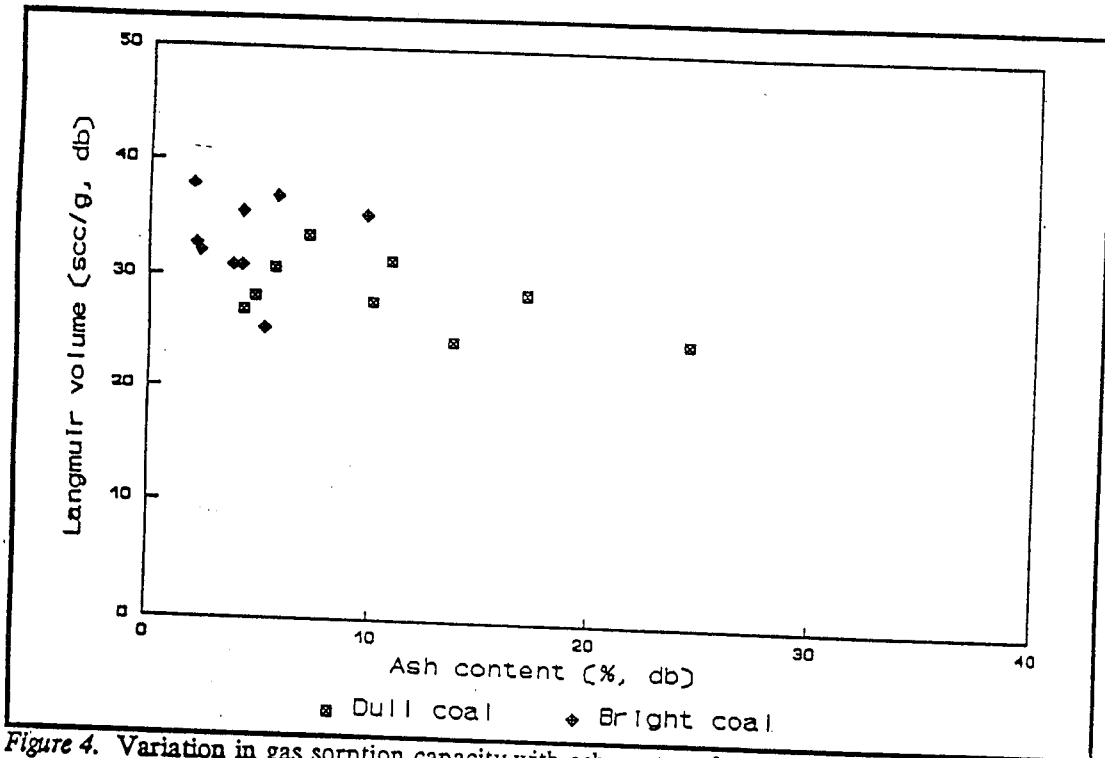


Figure 4. Variation in gas sorption capacity with ash content for dull and bright coals from the Bowen Basin.

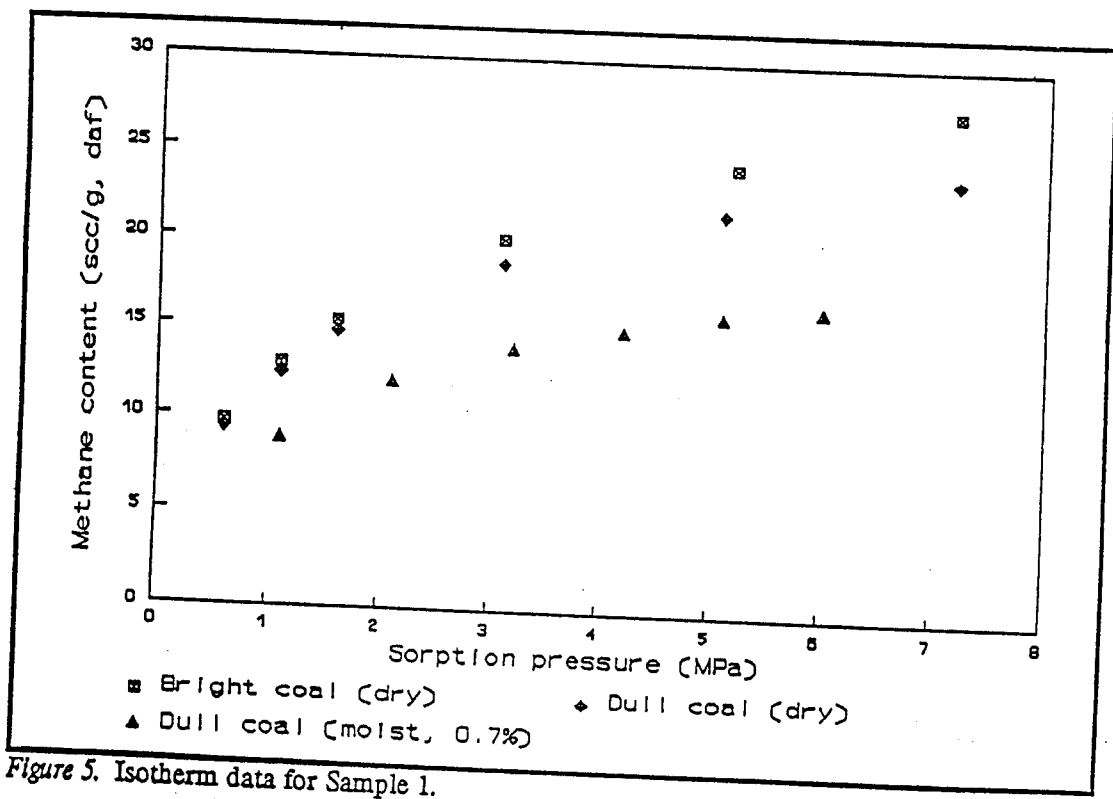


Figure 5. Isotherm data for Sample 1.

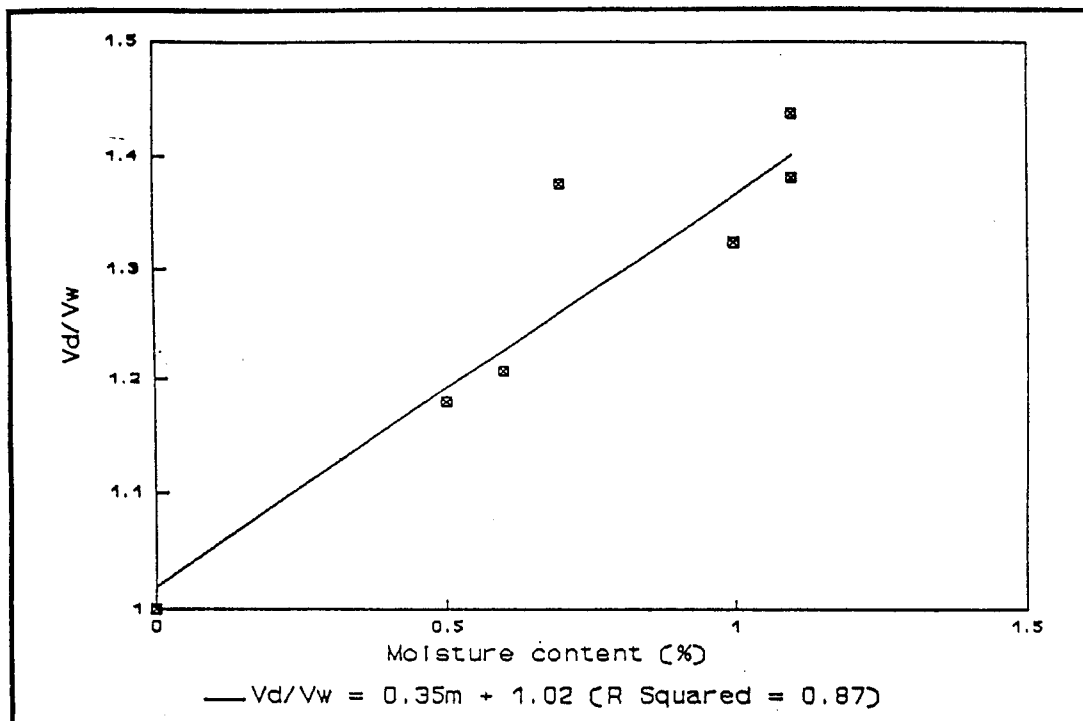


Figure 6. Moisture content effect on gas sorption capacity of coal.