

## Coalbed methane sorption related to coal composition

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### Abstract

Gas sorption by coal is closely related to its physical and chemical properties, which are, in turn, governed by coal type and rank. The role of coal type (*sensu* maceral composition) is not fully established but it is clear that coal type may affect both adsorption capacity and desorption rate.

Adsorption capacity is closely related to micropore (pores < 2 nm) development, which is rank and maceral dependent. Adsorption isotherms indicate that in most cases bright (vitrinite-rich) coals have a greater adsorption capacity than their dull (often inertinite-rich) equivalents. However, no differences, or even the opposing trend, may be observed in relation to coal type.

Desorption rate investigations have been performed using selected bright and dull coal samples in a high pressure microbalance. Interpretation of results using unipore spherical and bidisperse pore models indicate the importance of the pore structure. Bright, vitrinite-rich coals usually have the slowest desorption rates which is associated with their highly microporous structure. However, rapid desorption in bright coals may be related to development of extensive, unmineralised fracture systems. Both macro- and micro-pore systems are implicated in the more rapidly desorbing dull coals. Some dull, inertinite-rich coals may rapidly desorb due to a predominance of large, open cell lumina. Mineral matter is essentially nonadsorbent to coal gases and acts as a simple diluent. However, mineral-rich coals may be associated with more rapid desorption.

Coal rank and type (maceral composition) *per se* do not appear to be the critical factors in controlling gas sorption, but rather the influence they exert over pore structure development. © 1998 Elsevier Science B.V.

**Keywords:** adsorption isotherm; bidisperse pore model; desorption rate; maceral composition; methane

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## 1. Introduction

Sorption of gas by coal is an ongoing and extremely important area of research to enhance successful gas recovery from coal seams and to assist the understanding of gas-related problems in underground coal mining. Methane ( $\text{CH}_4$ ) normally dominates seam gases but many other gases may also be present (e.g.  $\text{C}_2\text{H}_6$  and other hydrocarbons,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$  and noble gases).

Despite the large quantities of  $\text{CH}_4$  and  $\text{CO}_2$  generated during coalification, other processes may be dominant in the production of adsorbed seam gases. Isotopic studies indicate that bacterial activity may be important in methane (biogenic) generation at shallow depths (< 400 m). Carbon dioxide is usually only common in areas of igneous intrusion, generated by interactions between the coal, water and the intruding body (Rice, 1993). However, significant concentrations of  $\text{CO}_2$  may occur unrelated to igneous activity.

A variety of mechanisms have been proposed for the storage of gases in coal as follows: (1) as a free gas compressed in the pore spaces, (2) condensed as a solid or liquid, (3) dissolved in the coal structure and (4) adsorbed on the internal surface. Storage as a compressed gas is precluded as the seam pressures are too low to account for the large gas volumes present. Methane adsorption by coal is dominated by physical adsorption onto the pore surfaces. Physical adsorption for methane, rather than chemical adsorption, is indicated by the reversibility of the equilibrium between the gas and solid, the relatively rapid sorption rate when temperature or pressure are changed and low heat of adsorption.

Many parameters influence the gas sorption characteristics of a coal seam (e.g. type, rank, moisture content, temperature, in situ stress, degree and type of secondary mineralisation, fracture development). Coal type variations can be expressed in terms of many physical and chemical properties (e.g. ultimate analysis, proximate analysis, maceral content, mineral matter composition). Here, we restrict our discussion to the influence of maceral composition.

Coal type effects are poorly understood in terms of gas emission and outbursting, and have generally been overshadowed by the inferred relationships with coal rank. Most work has focused on bulk sample testing, which confuses the issue of the effect of coal rank and type. Recent investigations of small, hand-picked samples and using high pressure microbalances (Beamish and O'Donnell, 1992; Crosdale and Beamish, 1993; Levine et al., 1993) are providing more clear distinctions between the two parameters of coal rank and coal type.

## 2. Maceral composition effects on adsorption characteristics

### 2.1. Gas adsorption characterisation

The most widely used technique to describe gas adsorption by coal is the adsorption isotherm. Coals generally exhibit a type I (Brunnauer et al., 1940) isotherm and do not have a significant hysteresis when pure gases are used. Type I isotherms are typical of

microporous solids in which it is assumed that a monomolecular layer is adsorbed on the pore walls and that the isotherm plateau corresponds to completion of the monolayer (Gregg and Sing, 1967). The isotherm may be modelled by the Langmuir equation (Eq. (1) see Appendix A for notation), which represents a special form of the multilayer BET (Brunnauer–Emmett–Teller) adsorption equation:

$$V = \frac{abP}{1 + bP} = V_L \frac{P}{P_L + P}. \quad (1)$$

The Langmuir isotherm describes monolayer adsorption on open surfaces freely exposed to gas (Langmuir, 1918) and its extrapolation to include microporous solids may be questioned. Despite this, it is frequently applied to, and usually adequately models, the coal adsorption isotherm.

## 2.2. Gas adsorption mechanisms

Gas storage by coals occurs predominantly by adsorption on the walls of the micropore network. At high vapour pressures, multilayer adsorption probably occurs after the micropores are filled, resulting in condensation to a bulk liquid; a process not uncommon in microporous solids (Gregg and Sing, 1967). The gas content is maintained by the hydrostatic head of water on the seam or simply by gas pressure if the seam is dry. This differs markedly from conventional gas reservoirs where an impermeable seal is required and the gas occurs either as a free gas in the pore system or dissolved within other hydrocarbons. The pore structure and distribution, and not the total porosity, of coals is therefore critical in understanding how gas content may vary in relation to coal type and rank.

Pore structure development during coalification underpins the increase in adsorption capacity observed with increasing coal rank. During coalification, the total porosity of the coal structure progressively decreases from about 20% at 82% carbon to a minimum of 3% at 89% carbon and again increases with rank increase (King and Wilkins, 1944 cited by van Krevelen, 1993).

However, total porosity trends are not reflected by individual pore categories. Pores may be subdivided into macropores (> 50 nm), mesopores (50–2 nm) and micropores (< 2 nm) (IUPAC, 1982). During coalification, the relative importance of the micropores increases at the expense of macropores and mesopores. For low rank bituminous coals, inertinite is more macroporous and less microporous than their rank equivalent vitrinite (Unsworth et al., 1989). With rank increase, the mesoporosity of vitrinite decreases considerably compared to that of inertinite.

## 2.3. Coal type (maceral) effects

Many workers have indicated that coal type influences gas adsorption by coal (e.g. Ettinger et al., 1966; Faiz et al., 1992; Lamberson and Bustin, 1993; Crosdale and Beamish, 1993, 1995; Bustin et al., 1995). Most agree that vitrinite-rich coals have a greater methane adsorption capacity than inertinite-rich, rank-equivalent coals. However, poor or no correlation may be found between adsorption capacity and maceral composi-

tion (e.g. Faiz et al., 1992). In some cases, inertinite-rich coals have been found to have the greatest methane adsorption capacity (Ettinger et al., 1966).

Relationships between maceral composition and Langmuir volume have been determined using a variety of experimental techniques and sample preparations. Sample preparations have been either: (1) the use of bulk coal samples followed by a statistical treatment of maceral composition and methane content (e.g. Faiz et al., 1992) or (2) the use of hand picked samples to concentrate vitrinite and inertinite (e.g. Ettinger et al., 1966).

Experimental techniques are also divided into 2 main categories: (1) much early work used large samples (up to 150 g) and volumetric techniques in which a fixed volume of gas was added to the sample chamber and the pressure drop monitored (e.g. Ettinger et al., 1966) and (2) more recently, small samples (up to 1 g) and gravimetric techniques using high-pressure microbalance technology in which weight change is monitored at constant gas pressure (e.g. Beamish and O'Donnell, 1992; Levine et al., 1993).

Studies on gas sorption in relation to coal type from the Bowen Basin, Australia (Beamish and Gamson, 1993; Crosdale and Beamish, 1993) show both rank and compositional trends. Bright coals are shown to have significantly higher methane adsorption capacities than their dull coal equivalents from the same seam in many cases (Fig. 1). The bright coals are vitrinite-rich (Table 1), especially in collotelinite, whereas the dull coals are dominated by inertinites, particularly semifusinite. Pore structure analysis of these coals (Table 2) shows greater total pore volumes for dull coals compared to their equivalent bright coal pair. In contrast, the bright coals have larger surface area (Table 3). These contrasting trends suggest that the bright coals are more highly microporous than their equivalent dull coal pair.

In the southern coalfield of the Sydney basin, Australia, little correlation of gas sorption properties to coal maceral content has been observed (Faiz and Cook, 1991;

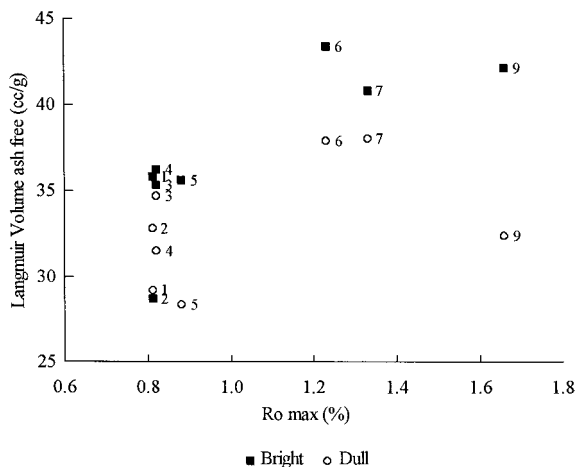


Fig. 1. Relationship between Langmuir volume (for methane) and rank (expressed as mean maximum reflectance of vitrinite-Romax) for selected Bowen basin coals on an air dry, ash-free basis. Bright and dull coal pairs show vitrinite-rich bright coals have greater capacities to adsorb methane.

Table 1

Coal properties of selected Bowen basin coals used in methane sorption studies. Pairs of bright and dull coal were selected from single seams

Sample	Proximate analysis			CSN	Maceral-group analysis (%)				Romax (%)	$V_L$ (cm <sup>3</sup> /g)
	moisture (%adb)	ash (%db)	VM (%daf)		vit	lipt	inert	MM		
1 Bright	3.5	3.7	36.9	3	72.9	3.2	23.7	0.6	0.81	35.8
1 Dull	2.6	3.6	32.9	1	32.8	3.9	63.2	0.8	0.81	29.2
2 Bright	4.0	1.7	34.1	6	96.3	0.0	2.6	0.8	0.81	28.7
2 Dull	2.6	10.6	31.1	$\frac{1}{2}$	18.7	3.7	74.3	3.4	0.81	32.8
3 Bright	2.3	4.5	38.0	$5\frac{1}{2}$	82.7	3.3	12.7	1.2	0.82	35.3
3 Dull	2.3	7.0	32.1	1	23.6	2.3	69.5	4.6	0.82	34.7
4 Bright	2.8	2.1	37.3	$6\frac{1}{2}$	86.1	1.6	11.7	0.6	0.82	36.2
4 Dull	3.1	4.6	31.0	1	18.9	1.5	78.9	0.7	0.82	31.5
5 Bright	3.1	1.8	31.3	$5\frac{1}{2}$	99.4	0.0	0.0	0.6	0.88	35.6
5 Dull	2.3	17.2	26.2	$\frac{1}{2}$	1.9	8.5	78.4	11.2	0.88	28.4
6 Bright	1.3	3.7	24.3	9	84.3	0.5	14.7	0.5	1.23	43.4
6 Dull	1.6	15.7	24.8	1	26.7	0.0	70.8	2.4	1.23	37.9
7 Bright	1.5	0.7	21.9	9	100.0	0.0	0.0	0.0	1.33	40.8
7 Dull	1.6	9.9	21.3	$1\frac{1}{2}$	20.1	0.0	73.4	6.4	1.33	38.0
9 Bright	1.0	0.5	16.8	8	99.4	0.0	0.0	0.6	1.66	42.1
9 Dull	1.0	18.9	14.9	$\frac{1}{2}$	9.7	0.0	83.5	6.7	1.66	32.4

adb = air-dry basis; db = dry basis; daf = dry, ash-free; csn = crucible swelling number; vit = vitrinite; lipt = liptinite; inert = inertinite; Romax = mean maximum reflectance of vitrinite in oil;  $V_L$  = Langmuir volume.

Faiz et al., 1992; Crosdale and Beamish, 1994). However, other workers in this coalfield (e.g. Bartosiewicz and Hargraves, 1985) have concluded that bright coals generally adsorb more gas than dull coals in the pressure range of 0–1 MPa.

A fundamental difference in the relationship between gas adsorption and maceral content is therefore found between coals of the Sydney and Bowen basins. Detailed petrography of inertinites of coals in the southern coalfield show they contain fewer

Table 2

Density and porosity data for selected Bowen basin coals

Sample	Helium density (g/cm <sup>3</sup> , mmcb)		Mercury density (g/cm <sup>3</sup> , mmcb)		Total pore volume (cm <sup>3</sup> /g, mmcb)		Porosity (% , mmcb)	
	dull	bright	dull	bright	dull	bright	dull	bright
1	1.39	1.29	1.20	1.27	0.11	0.01	13.7	1.6
2	1.42	1.31	1.26	1.29	0.09	0.01	11.3	1.5
5	1.48	1.29	1.35	1.28	0.07	0.01	8.8	0.8
7	1.39	1.32	1.24	1.25	0.09	0.04	10.8	5.3
9	1.53	1.30	1.34	1.27	0.09	0.02	12.4	2.3

Total pore volume =  $(1/\rho_{Hg} - 1/\rho_{He})$ ; %Porosity =  $100\rho_{Hg}(1/\rho_{Hg} - 1/\rho_{He})$ ;  $\rho$  = density; mmcb = mineral matter containing basis.

Table 3  
Surface area measurements for selected Bowen basin coals

Sample	Carbon dioxide surface area (m <sup>2</sup> /g, mmcb)	
	dull	bright
1	209	237
2	194	247
3	200	228
4	209	245
5	175	277
6	213	269
7	150	196
9	187	261

mmcb = mineral matter containing basis.

macropores as cell lumina and are more inertodetrinite-rich than the Bowen basin coals. However, no detailed pore structure analysis is available to better understand these differences.

The only report of fusinites having substantially greater methane adsorption capacities than vitrinites is the study of Ettinger et al. (1966), who used hand-picked vitrinites and fusinites. They found no influence of maceral content at low pressure (0.1 MPa) but at higher pressures (> 2 MPa) fusinites (their F<sub>3</sub> and F<sub>1</sub>) could adsorb twice as much methane as vitrinites. These results are puzzling compared to those of other workers, but the solution may lie in the type of fusinite analysed. Inertinites are derived by oxidation and may be divided into degrado- and pyro-types. Fusain (fossil charcoal) results from combustion (Scott, 1989). Coal chars have surface areas 3 to 5 × greater than coals and open porosities up to 35% (Kamishita et al., 1977). These characteristics, if applied to charcoal, may help explain the apparently anomalous results of Ettinger et al. (1966).

### 3. Maceral composition effects on gas desorption

The effects of maceral composition on gas emission rates are less well appreciated than their relationship to gas content. Studies in the Bowen Basin have indicated possible relationships of petrographic composition to outburst-proneness and gas emission rates (Hunt and Botz, 1986; Beamish and Crosdale, 1995; Crosdale and Beamish, 1995; Beamish and Crosdale, 1998). Inertinite-rich (especially fusinite and semifusinite) coals exhibit high gas emission rates whereas vitrinite-rich coals show slower emission rates and are implicated in increasing outburst-proneness. However, it has also been suggested that coal type has little influence on gas emission rates (Faiz and Cook, 1991).

#### 3.1. Gas desorption mechanisms

Gas movement through coal is a three-stage process: (i) free flow (Darcy flow) in sufficiently large pores out of the coal system in response to a pressure gradient allows (ii) gas diffusion (Knudsen diffusion) through the micropore structure towards the larger

pores in response to a concentration gradient and (iii) finally gas desorbs off the internal surfaces (King and Ertekin, 1989a,b; Harpalani and Schraufnagel, 1990a,b).

Since methane is physically adsorbed on coal, the time required for desorption is negligible compared to the diffusion step (Ruppel et al., 1972, 1974). According to this model, gas migration is governed by two main factors. First, the diffusion distance depends upon the fracture spacing, which delineates the matrix block size of the coal. Second, gas flow volume through the fractures depends on fracture width, length, continuity and permeability. This model of gas transport through coal may best apply to predominantly vitrinite-rich coals in which fracture systems are open and unmineralised. However, complexities may arise due to secondary mineralisation inhibiting gas flow and the presence of other macropore systems, especially phytal porosity predominant in some inertinites, enhancing gas flow (Gamson et al., 1993).

### 3.2. Gas diffusion in coal

Three different techniques have been applied to determine of gas diffusion parameters of coals: (1) passing gas through a solid coal disc and from the measured pressure drop and flow rate, a diffusion coefficient may be calculated (Thimons and Kissell, 1973; Smith and Williams, 1984a), (2) the gas solid chromatography method (Olague and Smith, 1989) and (3) after undergoing a step-change in surface concentration, the rate of sorption from small particles is used to determine a diffusion coefficient (Bolt and Innes, 1959; Sevenster, 1959; Bielicki et al., 1972; Beamish and Gamson, 1993).

Diffusion of gas through coal is usually described using a spherical unipore diffusion model (Sevenster, 1959; Airey, 1968; Walker and Mahajan, 1978) (Eq. (2) see Appendix A for notation), which provides a simple form for comparison of diffusion data:

$$\frac{V}{V_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D_e n^2 \pi^2 t). \quad (2)$$

For short times ( $< 600$  s) and when the fraction desorbed is less than 0.5, the diffusion equation may be simplified (Eq. (3) see Appendix A for notation) to give an estimate of the effective diffusivity (Smith and Williams, 1984a,b). However, the unipore spherical model often fails to describe the desorption adequately for the entire timescale of coal desorption and an alternative, bidisperse pore model has been proposed:

$$\frac{V}{V_{\infty}} = \frac{6}{\sqrt{\pi}} \sqrt{D_e t}. \quad (3)$$

Application of a bidisperse pore model (Ruckenstein et al., 1971) leads to better estimation of long-term coal desorption trends (Smith and Williams, 1984a,b). The sorption behaviour is modelled by a macrosphere comprised of microspheres. Two phases of gas movement are described: firstly by movement of the gas to the outside of the microsphere and secondly by gas movement in the spaces between the microspheres until the gas reaches the outside of the macrosphere. These two phases simulate the diffusion and flow stages (stages (ii) and (iii) of Section 3.1) of gas desorption.

Rigorous mathematical description of the sorption (Ruckenstein et al., 1971; Eq. (4) see Appendix A for notation) may be simplified if either macropore or micropore diffusion is a rate limiting step, which may be evaluated from the parameter  $\alpha$ . Three cases occur: (i) when  $\alpha < 10^{-3}$  then macropore diffusion is much faster than by the micropores, indicating the micropores are rate controlling, (ii) when  $10^{-3} < \alpha < 10^2$  then both macropore and micropore diffusion are important and (iii) when  $\alpha > 10^2$  then the macropore diffusion process is the rate limiting step:

$$\frac{V_t}{V_\infty} = \frac{\sum_{k=1}^{\infty} \sum_{q=1}^{\infty} \frac{k^2 [1 - \exp(-\alpha \xi_{qk}^2 \tau)]}{\xi_{qk}^4 \left[ \frac{\alpha}{\beta} + 1 + \cot^2 \xi_{qk} - \left( 1 - \frac{k^2 \pi^2}{\beta} \right) \frac{1}{\xi_{qk}^2} \right]}}{\sum_{k=1}^{\infty} \sum_{q=1}^{\infty} \frac{k^2}{\xi_{qk}^4 \left[ \frac{\alpha}{\beta} + 1 + \cot^2 \xi_{qk} - \left( 1 - \frac{k^2 \pi^2}{\beta} \right) \frac{1}{\xi_{qk}^2} \right]}} \quad (4)$$

For  $\alpha$  less than about  $10^{-3}$ , the uptake may be considered a two-stage sorption process (Ruckenstein et al., 1971). In this case, macropore diffusion and sorption is much faster than in the micropores and equilibrium is essentially achieved before any appreciable micropore uptake occurs. Initially, only macropore diffusion occurs, followed by a much slower second stage of micropore sorption with macropore sorption at equilibrium.

Further information on the relative importance of the microsphere versus the macrosphere is given by the parameter  $\beta/\alpha$ , which reflects the ratio of the microsphere and macrosphere uptakes at equilibrium. Very small values of  $\beta/\alpha$  indicate negligible microsphere uptake while large values show macrosphere uptake is negligible.

### 3.3. Application of gas diffusion models

Both the unipore and the bidisperse pore models have been applied to a range of coal ranks and types from the Bowen Basin, Australia (Beamish and Gamson, 1993; Beamish and Crosdale, 1995) (Table 1). Solid coal blocks approximately 0.8 mm in size were selected from bright and dull coal types and characterised by proximate analysis, pore distribution, petrography and methane sorption properties (Tables 1–4).

Methane desorption rate testing was carried out using a high pressure microbalance (Beamish and O'Donnell, 1992; Crosdale and Beamish, 1993; Levine et al., 1993). Following regassing of the coal samples, desorption to atmosphere was recorded as a weight loss with respect to time. Diffusion coefficients are calculated from the rate data using the models described above. Desorption testing and modelling from two pairs of bright and dull coals indicate the spectrum of results obtained (Fig. 2).

The unipore model does not describe the long term desorption for all samples. Coals fitting this model are typically vitrinite-rich bright coals, although the model also applied to a sample high in inertodetrinite (Fig. 2). Gas release from sheared coal is also



Table 4

Diffusivity data for selected Bowen Basin coals using unipore and bidisperse pore models. A single parameter of effective diffusivity ( $D_e$ ) is derived for the unipore model. Two parameters are derived for the bidisperse pore model: the effective macropore ( $D_a$ ) and effective micropore ( $D_i$ ) diffusivity.  $\alpha$  and  $\beta$  (Eq. (4); Appendix A) are dimensionless rate parameters which describe the relative importance of macropore and microsphere diffusion processes

Sample	Unipore model $D_e$ ( $s^{-1}$ )	Bidisperse pore model				
		$D_a$ ( $s^{-1}$ )	$D_i$ ( $s^{-1}$ )	$\alpha$	$\beta$	$\beta/\alpha$
1 Bright	$3.0 \times 10^{-6}$	$6.7 \times 10^{-7}$	$1.2 \times 10^{-6}$	$1.8 \times 10^{-2}$	0.3	16.8
1 Dull	$8.3 \times 10^{-5}$	$1.6 \times 10^{-4}$	$9.2 \times 10^{-7}$	$5.8 \times 10^{-3}$	0.008	1.4
2 Bright	$2.0 \times 10^{-6}$	described by unipore model				
2 Dull	$1.0 \times 10^{-4}$	$1.7 \times 10^{-4}$	$1.1 \times 10^{-4}$	$6.5 \times 10^{-1}$	0.006	$9.3 \times 10^{-3}$
3 Bright	$2.0 \times 10^{-6}$	described by unipore model				
3 Dull	$4.5 \times 10^{-5}$	$1.0 \times 10^{-4}$	$1.0 \times 10^{-6}$	$1.0 \times 10^{-2}$	0.02	1.6
4 Bright	$1.0 \times 10^{-6}$	described by unipore model				
4 Dull	$5.4 \times 10^{-5}$	$1.0 \times 10^{-4}$	$1.0 \times 10^{-6}$	$1.0 \times 10^{-2}$	0.01	0.6
5 Bright	$9.2 \times 10^{-7}$	described by unipore model				
5 Dull	$4.5 \times 10^{-6}$	described by unipore model				
6 Bright	$3.8 \times 10^{-6}$	described by unipore model				
6 Dull	$9.0 \times 10^{-5}$	$1.7 \times 10^{-4}$	$8.3 \times 10^{-5}$	$4.9 \times 10^{-3}$	0.01	1.2
7 Bright	$1.5 \times 10^{-6}$	described by unipore model				
7 Dull	$2.7 \times 10^{-5}$	$1.0 \times 10^{-4}$	$1.0 \times 10^{-6}$	$1.0 \times 10^{-2}$	0.027	2.7
9 Bright	$5.0 \times 10^{-6}$	described by unipore model				
9 Dull	$8.3 \times 10^{-5}$	$1.2 \times 10^{-4}$	$5.0 \times 10^{-6}$	$4.2 \times 10^{-2}$	0.04	1.0

described by this model. Sheared coals typically have very high diffusion rates, related to microstructural rather than petrographic controls.

Coals not fitting the unipore model can be described by the bidisperse pore model, especially banded or dull samples with complex pore distributions. Petrographically,

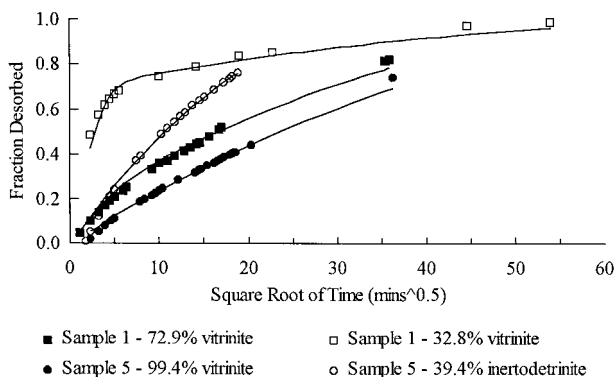


Fig. 2. Desorption modelling of selected Bowen basin coals illustrating the range of results. Vitrinite-rich samples (solid symbols) show a uniform desorption rate and are modelled using a unipore spherical model. A two-phase desorption of initially rapid followed by slow desorption is exhibited by the semifusinite-rich sample 1, which is described by a bidisperse pore model. A dull, inertodetrinite-rich sample shows similar desorption characteristics to the vitrinite-rich samples and is also described by the unipore spherical model. Other samples have been modelled in a similar fashion (Table 4) but are omitted for clarity.

these coals contain a variety of maceral types and usually include mixtures of vitrinites and inertinites. The parameter  $\alpha$  is usually in the range  $10^{-3} < \alpha < 10^{-1}$  (Table 4), suggesting both macropore and micropore diffusion process are important. However, many values are near the limiting case of  $\alpha < 10^{-3}$ , which suggests macropore diffusion is more rapid than micropore diffusion and that micropore diffusion is the rate controlling step.  $\beta/\alpha$  values are typically large ( $10^{-1} < \beta/\alpha < 10$ ) (Table 4), indicating negligible macrosphere uptake, i.e. most gas uptake is by the micropore network.

These models suggest that gas desorption from coal is complex. Different desorption rates can be expected related to coal type (bright, dull or banded) (Crosdale and Beamish, 1993). Practical application of this has been found at the Collinsville underground coal mine, Australia at Collinsville, bright (vitrinite-rich) lower portion of the seam has retained higher gas contents than the duller (inertinite-rich) upper part. The lower part of the seam has a greater tendency for outbursting (Beamish and Crosdale, 1995; Beamish and Crosdale, 1998).

#### 4. Conclusions

Maceral composition significantly affects both adsorption and desorption properties of coals. Vitrinite-rich coals usually have greater adsorption capacities than their rank equivalent, inertinite-rich counterparts. However, significant variations may occur to this generalisation, even at regional scales. Variations in adsorption capacity are related to pore structure development, especially micropores, which is both type and rank dependent.

Modelling indicates that bright and dull coals behave differently during gas desorption. The applicability of the unipore spherical model to bright coal desorption suggests a dominant role is played by the micropore system. A two phase desorption is indicated for dull, inertinite-rich (particularly semifusinite) coals and may be modelled using a bidisperse pore system. Initial desorption is strongly influenced by mesopores and macropores from which gas rapidly escapes; longer term desorption is governed by the micropores.

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#### Appendix A. Notation

$D_e$	the effective diffusivity ( $\text{cm}^2/\text{s}$ )
$P$	pressure (in atm in Eq. (2))
$P_L = 1/b$	Langmuir pressure
$t$	time (s)

$V$	volume of the sorbed gas
$V_L = a$	maximum sorptive capacity (Langmuir volume)
$V_t$	volume of the desorbed gas at time $t$
$V_\infty$	total desorbed volume
$\alpha$	dimensionless rate parameter
$\beta$	dimensionless rate parameter
$\tau$	dimensionless time
$\xi$	$\sqrt{-s/\alpha}$

## References

- Airey, E.M., 1968. Gas emission from broken coal. An experimental and theoretical investigation. *Int. J. Rock Mech. Min. Sci.* 5, 475–494.
- Bartosiewicz, H., Hargraves, A.J., 1985. Gas properties of Australian coal. *Proc. Aust. Inst. Min. Metall.* 290, 71–77.
- Beamish, B.B., Crosdale, P.J., 1995. The influence of maceral content on the sorption of gases by coal and the association with outbursting. In: Lama, R.D. (Ed.), *Int. Symposium-Cum-Workshop on Management and Control of High Gas Emissions and Outbursts in Underground Coal Mines*. National Organising Committee of the Symp., Wollongong, pp. 353–361.
- Beamish, B.B., Crosdale, P.J., 1998. Instantaneous outbursts in underground coal mines: an overview and association with coal type. In: Flores, R.M. (Ed.), *Coalbed Methane*. *Int. J. Coal Geol.* 35, 27–55, this volume.
- Beamish, B.B., Gamson, P.D., 1993. Laboratory Studies: Sorption Behaviour and Microstructure of Bowen Basin Coals. In: Oldroyd, G.C. (Ed.), *Final Report ERDC Project 1464. Prediction of Natural Gas Production from Coal Seams*. Energy Res. Develop. Corp., Canberra, vol. 2, pp. 128.
- Beamish, B.B., O'Donnell, G., 1992. Microbalance applications to sorption testing of coal. *Symp. Coalbed Methane Research and Development*, vol. 4. Dept. Earth Sci., James Cook Univ., Townsville, pp. 31–41.
- Bielicki, R.J., Perkins, J.H., Kissell, F.N., 1972. Methane diffusion parameters for sized coal particles. *US Bur. Mines Rep. Invest. RI 7697*, Washington, 12 pp.
- Bolt, B.A., Innes, J.A., 1959. Diffusion of carbon dioxide from coal. *Fuel* 38, 333–337.
- Brunnauer, S., Demming, L.S., Demming, W.S., Teller, E., 1940. *J. Am. Chem. Soc.* 62, 1723.
- Bustin, R.M., Clarkson, C., Levy, J., 1995. Coalbed methane adsorption of coals of the Bulli and Wongawilli seams, southern Sydney Basin: Effect of maceral composition. *Proc. 29th Newcastle Symp. on Advances in the Study of the Sydney Basin*. Dept. Geol., The Univ. of Newcastle, pp. 22–28.
- Crosdale, P., Beamish, B., 1993. Maceral effects on methane sorption by coal. In: Beeston, J.W. (Ed.), *New Developments in Coal Geology: A Symposium*. Coal Geol. Group, Geol. Soc. of Aust., Brisbane, pp. 95–98.
- Crosdale, P.J., Beamish, B.B., 1994. Methane sorption studies at South Bulli (NSW) and Central (Qld) collieries using a high pressure microbalance. *Proc. 28th Newcastle Symp. on Advances in the Study of the Sydney Basin*. Dept. Geol., The Univ. of Newcastle, pp. 118–125.
- Crosdale, P.J., Beamish, B.B., 1995. Methane diffusivity at South Bulli (NSW) and Central (Qld) Collieries in relation to coal maceral composition. In: Lama, R.D. (Ed.), *Int. Symposium-Cum-Workshop on Management and Control of High Gas Emission and Outbursts in Underground Coal Mines*. National Organising Committee of the Symp., Wollongong, pp. 363–367.
- Ettinger, I., Eremin, I., Zimakov, B., Yanovskaya, M., 1966. Natural factors influencing coal sorption properties. I. Petrography and sorption properties of coals. *Fuel* 45, 267–275.
- Faiz, M.M., Cook, A.C., 1991. Influence of coal type, rank and depth on the gas retention capacity of coals in the southern coalfield, NSW. In: Bamberry, W.J., Depers, A.M. (Eds.), *Gas in Australian Coals*. *Symp. Proc.*, vol. 2. Geol. Soc. of Aust., pp. 19–29.

- Faiz, M.M., Aziz, N.I., Hutton, A.C., Jones, B.G., 1992. Porosity and gas sorption capacity of some eastern Australian coals in relation to coal rank and composition. *Symp. Coalbed Methane Res. and Develop.*, vol. 4. Dept. of Earth Sci., James Cook Univ., Townsville, pp. 9–20.
- Gamson, P.D., Beamish, B.B., Johnson, D.P., 1993. Coal microstructure and micropermeability and their effects on natural gas recovery. *Fuel* 72, 87–99.
- Gregg, S.J., Sing, K.S.W., 1967. *Adsorption, Surface Area and Porosity*. Acad. Press, London. 371 pp.
- Harpalani, S., Schraufnagel, R.A., 1990a. Measurement of parameters impacting methane recovery from coal seams. *Int. J. Min. Geol. Eng.* 8, 369–384.
- Harpalani, S., Schraufnagel, R.A., 1990b. Shrinkage of coal matrix with release of gas and its impact on permeability of coal. *Fuel* 69, 551–556.
- Hunt, J.W., Botz, R.W., 1986. Technical note-outbursts in Australian coal mines: A petrographic factor. *Bull. Proc. Aust. Inst. Min. Metall.* 291, 59–63.
- IUPAC, 1982. *Manual of symbols and terminology*. Appendix 2, Part 1, Colloid and surface chemistry. *Pure Appl. Chem.*, 52, 2201.
- Kamishita, M., Mahajan, O.P., Walker, P.L. Jr., 1977. *Fuel* 56, 444–450.
- King, G.R., Ertekin, T.M., 1989a. A survey of mathematical models related to methane production from coal seams, Part I. Empirical and equilibrium sorption models. *Proc. 1989 Coalbed Methane Symp. The Univ. of Alabama, Tuscaloosa*, pp. 125–138.
- King, G.R., Ertekin, T.M., 1989b. A survey of mathematical models related to methane production from coal seams, Part II: Nonequilibrium sorption models. *Proc. 1989 Coalbed Methane Symp. The Univ. of Alabama, Tuscaloosa*, pp. 139–155.
- King, J.G., Wilkins, E.T., 1944. The internal structure of coal. *Proc. Conf. Ultrafine Structure of Coals and Cokes. British Coal Utilisation Res. Assoc., London*, pp. 46–56.
- Lamberson, M.N., Bustin, R.M., 1993. Coalbed methane characteristics of Gates Formation coals, northeastern British Columbia: Effect of maceral composition. *Am. Assoc. Petrol. Geol. Bull.* 77, 2062–2076.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40, 1361.
- Levine, J.R., Johnson, P.W., Beamish, B.B., 1993. High pressure microgravimetry provides a viable alternative to volumetric method in gas sorption studies on coal. *Proc. 1993 Int. Coalbed Methane Symp. Univ. of Alabama, Tuscaloosa*, pp. 187–195.
- Olague, N.E., Smith, D.M., 1989. Diffusion of gases in American coals. *Fuel* 68, 1381–1387.
- Rice, D.D., 1993. Controls of coalbed gas composition. *Proc. 1993 Int. Coalbed Methane Symp. Univ. of Alabama, Tuscaloosa*, pp. 577–582.
- Ruckenstein, E., Vaidyanathan, A.S., Youngquist, G.R., 1971. Sorption by solids with bidisperse pore structures. *Chem. Eng. Sci.* 26, 1305–1318.
- Ruppel, T.C., Grein, C.T., Bienstock, D., 1972. Adsorption of methane/ethane mixtures on dry coal at elevated pressure. *Fuel* 51, 297–303.
- Ruppel, T.C., Grein, C.T., Bienstock, D., 1974. Adsorption of methane on dry coal at elevated pressure. *Fuel* 53, 152–162.
- Scott, A.C., 1989. Observations on the nature and origin of fusain. *Int. J. Coal. Geol.* 12, 443–475.
- Sevenster, P.G., 1959. Diffusion of gases through coal. *Fuel* 38, 403–418.
- Smith, D.M., Williams, F.L., 1984a. Diffusion models for gas production from coal-Determination of diffusion parameters. *Fuel* 63, 256–261.
- Smith, D.M., Williams, F.L., 1984b. Diffusion models for gas production models from coals-application to methane content determination. *Fuel* 63, 251–255.
- Thimons, E.D., Kissell, F.N., 1973. Diffusion of methane through coal. *Fuel* 52, 274–280.
- Unsworth, J.F., Fowler, C.S., Jones, L.F., 1989. Moisture in coal. 2. Maceral effects on pore structure. *Fuel* 68, 18–26.
- van Krevelen, D.W., 1993. *Coal*. Elsevier, Amsterdam, 979 pp.
- Walker, P.L.J., Mahajan, O.P., 1978. Methane diffusion in coals and chars. In: Karr, C.J. (Ed.), *Analytical Methods for Coal and Coal Products*. Vol. 1. Academic Press, New York, pp. 163–188.