ADSORPTION CHARACTERISTICS OF COALS WITH SPECIAL REFERENCE TO THE GETHING FORMATION, NORTHEAST BRITISH COLUMBIA

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INTRODUCTION

There are two major coal-bearing formations in the Peace River Coalfield in northeastern British Columbia, The Gates and the Gething. The younger Gates Formation hosts to the two major coal mines that have operated in the area; therefore there is some coalbed methane (CBM) information available for the formation. In contrast there is very little CBM information available for the older Gething Formation. This paper presents some coal adsorption data for the Gething Formation.

The two major coal-bearing formations in northeast British Columbia (Figure 1) outcrop extensively throughout the Peace River coalfield. The Gates Formation is separated from the older Gething Formation by the marine Moosebar Formation. Coal seams of economic interest in the Gates Formation and Gething formations occur in the southern and the northern parts of the coalfield respectively, which roughly coincides with the north and south of Mount Spieker (Figure 2).

THE GETHING FORMATION

The Gething Formation, which is late Jurassic to early Cretaceous, overlies the Cadomin Formation (Table 1). Therefore it is slightly younger than the Mist Mountain Formation, which underlies the Cadomin in the southeast British Columbia coalfields. The type section for the Formation is in the Peace River Canyon where it is 550 metres thick (Gibson, 1985). It thins to the south and at the Saxon property at the southern end of the coalfield is only 7 metres thick. In the area around the Sukunka property (Figure 2) the upper and lower coal-bearing part of the Gething is separated by a marine tongue (Duff and Gilchrist, 1981 and Legun, 1986) and economic coal seams are found in the upper and lower non-marine sections. The extent of the upper Gething coal-bearing zone is limited to the Sukunka River, Mt. Spieker area, but it has been suggested that there are other marine tongues in the Gething that wedge out to the south (Broatch, 1987). Leckie and Kalkreuth (1990) have suggested that Lower Cretaceous coals formed in a strand plain environment that was distant and protected from the shoreline and storm/tidal inundations. The Formation extends at depth to the east into the Western Canadian Sedimentary Basin, where it hosts a number of gas plays. The Formation has been extensively explored, from Mount Spieker in the south to Williston Lake in the north (Figure 2), for its potential to host surface and underground coal mines as documented by numerous coal assessment reports from the Ministry of Energy and Mines.

There has been very limited mining in the Gething Formation despite the fact that it hosts the first coal to be discovered in British Columbia by Mackenzie in 1793. More recently the Pine Valley Coal Corporation has obtained permits for a mine in the Willow Creek area located 40 kilometres west of Chetwynd (Figure 2). To date they have mined, screened and sold about 70 000 tonnes of coal probably to be used for pulverized coal injection (PCI) and hope to expand into full-scale production soon.

For this study a number of samples were collected in the summer of 2001 from a single seam in the Pine Valley Coal test pit representing a range of petrographic composition. The adsorption characteristics of these seven sam-

TABLE 1 GENERALIZED LOWER CRETACEOUS STRATIGRAPHY, PINE RIVER AREA





Figure 1. Gething and Gates formations outcrop pattern northeastern British Columbia.



Figure 2. Location of coal mines and deposits in northeastern British Columbia.

ples were measured and attempts made to correlate the results with various coal parameters.

PETROGRAPHY

Ryan (1997) has summarized the coal quality and petrography of the Gething Formation. Coal from the Formation is characterized by variable reactives content and low wash ash values. Reactive maceral contents can range from approximately 80% to less than 50%. This variation can explain some of the range of free swelling index (FSI) values seen in exploration coal quality data, but it does not explain the washing characteristics of the coal. The coal samples from Willow Creek have a high content of collodetrinte, which contains fragments of non-structured inert macerals such as macrinite and inertodetrinite. Structured macerals, such as semifusinite and fusinite are less common. Some of the collotelinite could be classified as semifusinite depending on the reflectance cut off. There is a lot of pseudo vitrinite (Photo 1), characterized by small lenses shaped holes, present in some samples. It may be evidence of partial desiccation of partially coalified material. In this temporary dry environment in the coal swamp any forest fires would char partially rotten vegetation, which having lost its cell structure would become macrinite rather than semifusinite after coalification.

The limited amount of structured inert macerals (semifusinite and fusinite) restricts the amount of dispersed mineral matter, which often fills cell lumen in these macerals. There also are few bands of carbonaceous shale in the samples, composed of finely dispersed ash and vitrinite particles, in the coal. These two factors probably explain the low raw ash and very low wash ash concentrations of seams in the formation. Wash-ash contents of Gething coals are consistently lower than those of Gates or Mist Mountain coals.

Preliminary observations of the 7 samples collected from the Willow Creek property indicate that samples contain a lot of particles made up of more than one maceral. Groundmasses of collodetrinite contain fragments of macrinite, collotelinite and occasionally semifusinite (Photo 2). There is little dispersed mineral matter in collodetrinite. In fact most of the finely dispersed mineral matter is associated with telinite or gelovitrinite (Photo 3). Generally compared to coals from the Mist Mountain Formation there is less fusinite and semifusinite and consequently less preserved cell structure

The generation of collodetrinite and macrinite often indicates a prolonged period of humification and destruction of biomass, which is accompanied by a concentration, in the remaining biomass, of the inherent mineral matter derived from the original vegetation. This finely dispersed mineral matter may affect the adsorption characteristics of the coal. The amount of inherent mineral matter in vegetation varies but can be as much as 8% (Renton *et al.*, 1979). It contains high concentrations of base oxides, which may be partially lost during coalification. It is estimated that from 1.5% to 2.5% of the mineral matter in bituminous coals may be derived from the original vegetation. The relationship of the amount of



Photo 1. Psuedo vitrinite in Gething coal showing elliptical cavities. Width of photo approximately 0.2 mm.



Photo 2. Groundmass of collodetrinite containing fragments of macrinite, collotelinite and semifusinite. Width of photo approximately 0.2 mm.

biomass destroyed to the volume percent of inherent mineral matter in the remaining coal indicates that very high amounts of biomass must be destroyed to produce significant increases in the volume of inherent mineral matter.

Many post Carboniferous coals are enriched in inertinite with respect to Carboniferous coals. One possible explanation (Taylor et al., 1989) is that the high inertinite content of Permian Gondwana coals is caused by a cool climate with wet summers and dry cold winters, during which the coal swamp dried out and inertinite developed. This environment might produce a fine layering of lithotypes similar to varves seen in clays. Possibly the cool climate and lack of ground covering vegetation also allowed dust to blow into the swamp which would explain the high contents of dispersed mineral matter found in some of these coals. Hunt and Smyth (1989) suggest that Australian Permian coals with high inertinite, and low ash contents formed in cratonic basins in fresh water mires, with low subsidence rates, allowing for extensive oxidation. Lamberson et al. (1991) emphasize the importance of fires in forming inertinite in Gates coals. There is no obvious explanation for the variable and sometimes high content of inertinite in Gething coals. Gething coal swamps may have experienced more episodes of drying and a greater frequency of forest fires than Gates swamps.

RANK

Karst and White (1979) Kalkreuth and McMechan (1988) and Kalkreuth *et al.* (1989) have all discussed coal rank in the Gething Formation. Rank varies from semi anthracite to high-volatile bituminous. Along the outcrop belt in the foothills the rank is high, in places reaching



Photo 3. Finely dispersed dark mineral matter associated with telinite. Width of photo approximately 0.2 mm.

semi anthracite. To the north and east it decreases to high-volatile bituminous. There is some evidence that outcrops at the western outcrop edge of the formation have lower ranks. Rank was established prior to deformation and variations are related to changes in the thickness of the Gething plus post Gething sedimentary package. Ref Leckie, 1983).

The rank at Willow Creek, where the samples were collected ranges from medium to low-volatile bituminous. The rank of 7 seam, which is in the lower part of the section is low-volatile bituminous (WC001-6 Rmax = 1.70% and WC001-4 Rmax=1.73%). Some of the samples have pseudo vitrinite and using this maceral to measure Rmax produced a value that was 0.02% high.

WILLOW CREEK SAMPLE DATA

SAMPLE COLLECTION

Samples were collected from the Pine Valley Coal test pit in the Willow Creek property located on the south side of the Pine River about 40 kilometres west of Chetwynd (Figure 2). In this area the Gething Formation has 8 coal seams ranging in thickness from 1 to over 5 metres and numbered downwards from the top of the formation. Samples were collected from seam 7-0 and seam 7-2 (Figure 3). A mudstone parting (30 cm thick), which separates seam 7-0 from 7-2, was used as a reference plane for sample location. Two samples (WC001-1 and WC001-2) representing a total of 2.74 metres were collected above the parting and a third sample representing 0.7 metres of 7-2 seam was collected adjacent to and below the mudstone parting. The base of seam 7-2, which is 1.1 metres thick, was not exposed. Four grab samples, 2 of bright and 2 of dull coal, were taken from seam 7-0.

Total apparent thickness of 7-0 seam, based on a density log from a nearby hole, is about 3.6 metres; 2 metres of buff-coloured sandstone immediately overlies 7-0



Figure 3. Stratigraphic section of the Gething Formation from the Willow Creek property.

TABLE 2
COAL QUALITY DATA FOR ADSORPTION SAMPLES

						8_	
Sample	Sm	Description	length	$H_2O\%$	H ₂ O	⁵ 5	
WC001			cm	ar	ac		
-1	7-0	channel	163	4.3	0.9		
-2	7-0	channel	111	3.1	0.8	0+	
-3	7-2	channel	70	5.1	ع.و	12.0	4
-4	7-0	grab/bright	comp	2.7	0.7	14.9	1
-5	7-0	grab/dull	1.35	3.6	0.7	13.1	1
-6	7-0	grab/bright	20	6.7	0.7	14.8	13
-7	7-0	grab/dull	comp	2.9	0.6	12.7	3

seam, and a 30-40 cm thick coal marker lies just above the sandstone. Seam 7-0 coal is dominantly dull with numerous mm-scale bright coal laminas and one 20 cm thick bright band just above a lower mudstone parting.



 TABLE 3
 PETROGRAPHY FOR SAMPLES 300 POINT COUNT

	VOLUME PERCENTS													
sample	telinite	collotelinite	collodetrinite	vitrodetrinite	liptinite	total reactives	semifusinite	fusinite	inertodetrinite	macrinite	micrinite	total inerts	mineral matter	weight ash%
WC001-1	1	21	39	1	0	62	12	3	11	5	3	33	5	8.3
WC001-2	0	20	39	2	0	61	10	2	9	6	2	28	10	16.3
WC001-3	8	5	32	1	0	47	23	2	6	19	0	51	2	4.0
WC001-4	27	1	48	0	0	76	7	0	4	9	1	22	1	2.3
WC001-5	4	17	36	0	1	58	23	2	4	9	2	40	2	4.0
WC001-6	24	21	34	1	0	81	1	1	1	0	2	6	13	20.5
WC001-7	2	7	44	0	0	53	14	0	9	20	2	44	3	4.5



Figure 4. Histogram of random reflectances for sample WC001-4.

COAL QUALITY AND PETROGRAPHY OF SAMPLES

Proximate analyses were performed on all samples of seam 7-0 and 7-2 (Table 2). With the exception of two samples, ash contents are very low (Table 2) and VM daf concentrations indicate a rank of low-volatile bitumi-

 TABLE 4

 SUMMARY OF RANDOM REFLECTANCE DATA

Sample WC001-	calculated Rmax%	vitrinite %	random reflectance	reactive semifusinite %	maceral boundary reflectance	inert inertinite %	mean random reflectance inertinite
1	1.67	8.0	1.56	41.7	1.82	50.3	1.82
2	1.66	38.2	1.55	0.1	1.55	61.7	1.84
3	1.66	14.8	1.55	17.3	1.80	67.9	1.88
4	1.65	54.8	1.54	4.8	1.70	40.4	1.54
5	1.67	18.8	1.56	28.6	1.74	52.6	1.80
6	1.65	93.7	1.54	0.8	1.54	5.5	1.65
7	1.67	12.6	1.56	10.7	1.76	76.7	1.90

nous, which is supported by 2 Rmax determinations of WC001-6 = 1.7% and WC001-4 = 1.73%.

The petrography of the samples (Table 3) indicates a wide range in total reactives contents from 48% to 81% of sample. Some of the samples contain a lot of pseudo vitrinite (Photo 1), the reflectance of which was checked and found to be similar to, or slightly higher than, that of collodetrinite. As previously discussed semifusinite and fusinite with good cell structure makes up less of the inert material than in coals from many other formations.

Coal petrography tends to be a somewhat subjective process that is hard to standardize. For this reason, random reflectance histograms were constructed for each sample to see if they might provide a better estimate of variations of petrography as defined only by reflectance. The histograms are produced using a computerized scanning process in which maceral fragments are scanned for random reflectance under the microscope. The computer is able to extract measurements of minerals or measurements influenced by edge effects from the data. For most samples clear vitrinite and inertinite peaks can be interpreted from the original distribution of random reflectance data (Figure 4). The data (Table 4) indicate that there is a very wide range of total vitrinite contents as recognized by random reflectance (8% to 94% on a dry



Figure 5. Total reactives by petrography and random reflectance histograms.

mineral matter free basis, dmmfb) and that Rmax values calculated from random reflectance (1.65%-1.67%) are some what lower than Rmax values measured on samples WC001-4 and WC001-6.

A comparison of total vitrinite by random reflectance histograms versus microscope examinations (Figure 5) provides a good correlation though the best-fit line does not go through the origin because microscope identification has tended to identify more vitrinite in the low vitrinite samples. The reason appears to be that the low vitrinite samples contain more reactive semifusinite as identified by reflectance profile and this material is identified as telinite during microscope petrography. The vitrinite macerals have a higher volatile content than the inert macerals and both methods of identifying vitrinite contents produce data that correlate well with VM daf (Figure 5). This means that once the quality of a coal seam is understood, VM daf gives a good and very cheap estimate of reactivity and can be used to correlate with adsorption characteristics.

TABLE 5SUMMARY OF ADSORPTION DATA

	isotherms at 25º C									
	ash%	$H_2O\%$	VI cc/g	Vlcc/g	PI					
sample	ad	equil	ar	daf	Мра					
WC001-1	1.3	5.0	30.2	32.3	2.08					
WC001-2	15.6	2.6	24.0	29.4	2.44					
WC001-3	2.0	6.2	30.8	33.5	2.57					
WC001-4	1.6	3.4	37.1	39.0	3.25					
WC001-5	1.1	5.0	33.4	35.6	2.73					
WC001-6	13.7	3.6	25.0	30.2	3.63					
WC001-7	2.6	3.8	32.5	34.7	3.27					

VI Langmuir volume PI Langmuir pressure.



Figure 6. Comparison of Gething coal desorption curves to the curve predicted by the Ryan Equation for a reflectance of 1.7%.



Figure 7. Total reactives versus langmuir volume dmmf basis; filled data points have high ash contents.

ADSORPTION DATA

Adsorption isotherms were measured at 25°C, which probably corresponds to crustal temperatures at a depth of about 1000 metres. This means that using Langmuir volumes (VI) and Langmuir pressures (PI) to calculate adsorption at shallower depths will under estimate adsorption capacity and if the depths are greater than 1000 metres adsorption capacity will be over estimated. Adsorption results (Table 5) indicate that in general terms the samples have high adsorption capacities (Figure 6). This is not surprising and is in agreement with the high rank, though based on the Eddy *et al.*, (1982) curves and the equation derived from Ryan (1992), they are somewhat higher than the norm. It should be noted that the Ryan Equation was set up to model the Eddy curves and at the same time to be somewhat conservative.

Langmuir volumes (Vl) of the samples do not have a clear relationship to petrography based on a plot of Vl dmmf concentrations *versus* total vitrinite by random



Figure 8. Plot of VM daf versus Langmuir pressure data from Olszewski (1992), and this study.

reflectance histogram (volume percent basis) (Figure 7). The two samples that have distinctly higher ash contents are highlighted (Figure 7) and if these 2 samples are removed from the data set, then there is a moderate correlation between total vitrinite and adsorption contents. The adsorption versus vitrinite content (by random reflectance histogram) relationship is more diffuse if reactive semifusinite is added to vitrinite, implying that reactive semifusinite is not acting as a vitrinite maceral in terms of its adsorption ability. The fact that there is a moderately good relationship between adsorption and vitrinite content as defined by random histograms indicates that in this data set the structure of maceral sub types may not play a major part in influencing adsorption ability. It has been suggested that collodetrinite may have a higher adsorption capacity than telinite and collotelinite (Gurba, 2001).

There is nothing obviously anomalous about the two high ash samples in terms of their petrography or VM daf contents. If there had been a problem with equilibrating the samples back to equilibrium moisture the VI values would generally increase. It is possible that the low VI values are caused by ash acting as a more than a simple dilutent.

The Langmuir pressure (Pl) is independent of ash content and may be a better indicator of the effect of petrography on adsorption characteristics. It is dependent on rank, generally decreasing as rank increases (Figure 8) (Olszewski, 1992). Olszewski data were obtained on dry coal and indicate that dry coals of equivalent rank have increased adsorption capacities and reduced Langmuir pressures. There is no obvious relationship between Pl and petrography in this study (Figure 8). If the two high ash samples are removed, then there is weak positive correlation of Pl with total reactives, which would imply that the effect of increased reactives is similar to a decrease in rank. Part of the reason for the weak or absent correlation of Pl to petrography may be the high rank of the samples. The physical properties of macerals, including porosity, tend to converge at higher ranks.

Moisture content, below equilibrium moisture, has a profound influence on adsorption capacity. Joubert (1974) investigated the effect of moisture on the adsorptive capacity of coals of different ranks and found that it increased as the moisture decreased below equilibrium moisture. The equilibrium moisture of individual macerals varies and vitrinite of low to medium rank has higher equilibrium moistures than inertinite. There is no correlation of equilibrium moisture with petrography in this study. However for many British Columbian coals. air-dried and equilibrium moisture correlate positively with vitrinite content and negatively with ash content. This means that, at constant rank, equilibrium moisture may be an indicator of adsorption ability. It appears that iso-rank coals from different basins are characterized by different average equilibrium moisture contents. In fact there is a rough trend for data suites with lower equilibrium moisture to contain more gas (Bustin and Clarkson, 1998). It is not clear if changes in equilibrium moisture



Figure 9. Schematic plot of rank versus adsorption as coal is buried and uplifted.

content for different suites are related to variations in the vitrinite sub-types, the history of the coal or the original vegetation source. Equilibrium moisture varies by rank and maceral content going through a minimum at the boundary between high and medium-volatile bituminous. Above this rank the difference in equilibrium moisture contents of the various macerals is less pronounced. It is also probably pressure dependent. In coal seams that are pressured by free gas, it is possible that moisture contents of coals are below equilibrium moisture. This would increase the coals ability to adsorb gas and would make it look over saturated, based on desorption data, depth and rank. Just as water movement has been used to explain under saturated coals, free gas movement in seams might re-

move water and increase the adsorption capacity and gas content of seams.

DISCUSSION

EFFECT OF TEMPERATURE AND PRESSURE ON ADSORPTION CAPACITY AND POTENTIAL GAS CONTENT

This paper discusses adsorption ability, but it is the actual volume of adsorbed gas that is available for recovery that is important. It is revealing to construct a schematic plot (Figure 9) outlining the tract of coal on a downward coalification curve with a number of upward branches representing uplift tracts for coals, which have attained different ranks. The plot does not attempt to exactly reproduce temperatures, depths and adsorption characteristics of coals of different ranks, though numbers are probably within a moderate margin of error. Both Kim (1977) and Olszewski (1992) have developed empirical equations predicting gas contents at varying coal ranks and temperatures. However, they were using data derived from dry coals tested over a temperature range of 0 to 50 degrees. The equations are therefore probably not reliable at the higher temperatures at which bituminous coals form. As vegetation is progressively buried, rank, pressure and temperature all increase. Initially adsorption capacity also increases, but eventually increasing temperature causes it to decrease. Over a temperature range of 20 to 65°C Levy et al. (1997) found that adsorption decreased by 0.12 cc/g per C. During most of their burial tract coals are producing CH4 in excess of their adsorption capacity and the excess is expelled into the surrounding rocks. Upon uplift, rank is fixed and temperature and pressure decrease. At depths considerably greater than those equivalent to Pl, adsorption capacity is generally not pressure dependent and adsorption capacity increases as temperature decreases. It is only at depths equivalent to about Pl x 2 that the effect of decreasing pressure becomes dominant and adsorption capacity decreases with uplift. This means that most coals must scavenge CH₄ during uplift in order to achieve saturation. The plot (Figure 9) indicates that higher rank coals probably have to scavenge large amounts of CH₄ during uplift if they are to achieve saturation at shallow depths. Therefore one should not be surprised that many coals are either under saturated or contain biogenic CH4. In fact, based on the importance of biogenic CH₄, which may provide the only viable way of re-saturating coals during uplift, there might well be a negative correlation of degree of saturation with depth in some coalfields.

Coal generates much more gas during coalification than it can adsorb and the excess is expelled into the surrounding rocks. If it is contained in these rocks at depth then the rocks become gas saturated rather than water saturated. It is possible to estimate the amount of gas charged into surrounding rocks. This has been done by Meissner (1984) and by the authors. Estimates need to take account of the effect of increasing temperature and its effect on the adsorption ability of the coal. As an approximate calculation, a coal buried such that its rank reaches 1.5% Rmax will generate enough excess gas to saturate about 5 times its volume of surrounding rock. based on a porosity of 4%. During uplift to 500 metres the gas will expand to fill over 40 times the coal volume. If coals are buried to greater depths, reach higher ranks, and generate more excess gas, then the volumes of surrounding rock that they can saturate are even larger. These calculations require estimates of a number of relationships including, the amount of gas generated by coal during coalification, the effect of temperature on adsorption, temperature gradients, and a relationship between rank and temperature. Obviously only order of magnitude estimates can be made of the effect of coal gas on the surrounding stratigraphy. Oh the other hand if the stratigraphy is gas saturated it is probable that the coal will remain saturated, in terms of adsorption, during uplift. Also it is possible that gas saturation could lead to a reduction in the moisture content of the coal below equilibrium moisture, producing apparent adsorption over saturation when compared to an isotherm run at equilibrium moisture.

RELATIONSHIP BETWEEN COAL COMPOSITION AND ADSORPTION CAPACITY

Different macerals have different adsorption capacities and generate different amounts of gas. Vitrinite generates much more gas during coalification than inertinite, but based on the work of Ettinger *et al.* (1967) may have lower adsorption capacities at high temperatures in conditions where moisture has less influence on adsorption. In banded coals, at high temperatures, inertinite may retain more gas than vitrinite. On uplift a banded or inertinite rich coal would have to scavenge less methane to achieve saturation. Coals in which inertinite has similar adsorption capacities to vitrinite may have a better chance of being saturated during uplift.

There are a number of papers in the literature that study the influence of coal composition on the adsorption ability of coal. Early literature generally dealt with coals dried below equilibrium moisture and is therefore difficult to compare to more recent data. Some of the earlier papers include the work of Ettinger et al. (1966). They found distinct differences in the adsorption capacity of vitrinite-rich versus inertinite-rich coals. Both types of coals exhibit a minimum adsorption capacity at a rank of about Rmax=0.8%. The minimum increased in intensity with increasing pressure and temperature. Levine (1993) suggests that hydrocarbons generated at about this rank block micro pores and reduce adsorption capacity, especially that of vitrinite, but not necessarily that of inertinite. Ettinger et al. (1966) indicated that inertinite rich coals had higher adsorption capacities than the vitrinite rich coals. They do not indicate the moisture contents of samples analyzed and they may have been below equilibrium moisture. The samples studied by Ettinger generally had low ash contents (less than 10%), which is important because it tends to remove the added confusion of ash as a variable when interpreting the results. Based on

their results, for coals of medium or low-volatile rank the ratio of adsorptive capacities inertinite/ vitrinite was 1.5 to 2 at high pressures. The ratio decreased at low pressures, but remained greater than 1. Ettinger *et al.* also state that the rate of desorption was faster from inertinite than from vitrinite. Levy *et al.* (1997) found that where as the adsorption capacity of coals at equilibrium moisture contents increased moderately consistently with rank the same was not true for coals dried below equilibrium moisture.

Ulery (1988), studying coals from Pennsylvania, found that desorbed gas content was related to vitrinite reflectance and not maceral content. Gas contents were also influenced by local geological factors such as roof lithology and local folding. Most of his samples contained over 75% vitrinite on a mineral matter-free basis so that it is difficult to use his database of 88 samples to test for any maceral influence on gas content, especially because of the wide range in mean maximum reflectance values (Rmax 0.6% to 1.1%) which strongly influence gas content.

Faiz and Cook, (1992) found that depth of cover had an overriding effect on gas content but that inertinite rich coals of Permian age from southern part of the Sydney Coalfield in Australia tended to contain more gas than vitrinite rich coals. They studied samples collected from the Bulli, Cape Horn and Wongawilli seams with ranks ranging from 1.1% to 1.5%. Within this range and for a wide range of ash contents they derived the following relationship:

 m^{3} /tonne gas = -19.4 + 0.0383 x depth(m) + .0292 x inerts% - 0.153 x MM + 7.63x Rmax% (R²=0.65).

A review of earlier literature does not indicate a clear maceral control on adsorption capacity or desorbed gas content, possibly because researchers were analyzing coals below equilibrium moisture. More recent literature tends to indicate that vitrinite has a greater adsorption capacity than inertinite. Levine and Johnson (1993) found that over a range of ranks, vitrinite-rich coals from the Bowen Basin, Australia had higher adsorption capacities than inertinite-rich coals. The data were not collected at equilibrium moisture and moisture probably suppresses the adsorption of vitrinite more than inertinite.

Lamberson and Bustin (1993), studied coals from the Gates Formation in northeast British Columbia and found that adsorption capacity correlated with the amount of vitrinite in the ash-free samples of medium-volatile bituminous coals ranging in rank from 1.02% to 1.14% Rmax. Variations in vitrinite content caused greater variation in adsorption capacity than a wide range of rank. Based on their plot of gas versus vitrinite %, on a dry mineral matter-free basis (dmmfb), gas concentrations of 0.25 cc/g per 1% vitrinite and 0.1 cc/g per 1% inertinite can be derived. The equivalent values for the Gething samples are 0.45 cc/g for 1% vitrinite and 0.32 c/g for 1% inertinite. They also report adsorption values for CO₂, which have similar relationships to maceral content as CH₄. This is interesting because an argument can be made that inertinite may preferentially adsorb CO₂ where as vitrinite preferentially adsorb CH_4 . This is because CH_4 may volume fill the smaller micro pores in vitrinite, where as CO_2 may layer fill the larger meso pores in inertinite.

The maceral influence on adsorption varies with increasing pressure. Bustin *et al.* (1995) studied the Bulli and Wongawilli coals from the Sydney Basin and found that the maceral control of adsorbed gas for these coals was less apparent than for the Gates coals studied by Lamberson and Bustin (1993). Bustin *et al.* looked at the correlation of differential adsorbed gas volume with maceral content at different pressures and found that at low pressure there was a correlation of differential adsorbed gas volume with vitrinite content but at higher pressures the correlation was with inertinite content. The cross-over was at about 2.5 MPa (or about 250 metres).

The data from Bustin et al. (1995) plotted in terms of total adsorbed gas at different pressures (Figure 10) emphasizes the lack of maceral influence on adsorption for coals from the Bulli seam. A similar analysis is applied to the Gething and Lamberson and Bustin (1993) data sets (Figure 10). As pressure increases the positive correlation factor for vitrinite versus adsorbed gas content improves for the Gething and Gates data suites and the difference in adsorption abilities of the end member macerals increases. The correlation factors are very dependent on the slope of the line and are not reliable for flat lines. The plot is a bit miss leading because the data does not reflect the effect of increased temperature with increased pressure in that the data were acquired at a constant temperature of 25°C. The Gething data set comes from 5 samples so that not a lot of confidence can be placed in the conclusions.

Bustin and Clarkson (1998) indicated that medium-volatile Permian coals from Australia have higher adsorption capacities than Gates Formation coals of similar rank from northeast British Columbia. It is apparent from Figure 10 that the reason may be that, though the vitrinite from the 2 coals has similar adsorption capacities, inertinite in Australian coals has a higher adsorption capacity than inertinite in Gates coals. This difference may also be apparent in the rheology of the two coals. Australian coking coals tend to have higher Giesler fluidities and FSI values than British Columbian coking coals of similar rank and petrography.

If the type of plot in Figure 10 is valid, then it is possible to pick a depth and therefore a pressure line and predict the adsorption capacity of a coal by sliding along the line to the correct vitrinite percentage. Changes in the maceral influence on adsorption capacity with depth opens the possibility, that depending on depth, coals of high vitrinite or high inertinite content may be better exploration targets. Inertinite is stronger than vitrinite, diffuses gas better (Beamish and Crosdale, 1993) and may retain permeability at depth better, however it would probably under go less matrix shrinkage as gas is produced. Vitrinite on the other hand may have better cleat permeability but may tend to loose gas (Bustin and Clarkson, 1998) and be under saturated.



Figure 10. Effect of increasing pressure on vitrinite and inertinite adsorption with R^2 correlation factors for lines. Data from this study, Lamberson and Bustin, (1993) and Bustin *et al.* (1995).

EFFECT OF MINERAL MATTER ON ADSORPTION CAPACITY

Most of the authors mentioned, used maceral content *versus* adsorption or desorbed gas content plots to support their arguments. Data were corrected either to an ash-free basis or a mineral matter free basis. Although



Figure 11. Tertiary plot of vitrinite, inertinite and mineral matter in volume percents. Posted numbers are gas contents. Data from this study, Dawson and Clow (1992), Lamberson and Bustin (1993), Bustin *et al.* (1995) and walker *et al.* (2001).

most data indicate that mineral matter acts simply as a dilutent, this may not always the case. It is possible that in some cases a component of the mineral matter may have a negative adsorption capacity. This may be the case for the two samples in this study. Even if this is rare, a useful way of avoiding any confusion about the effect of mineral matter is to plot data into triangular plots. This removes any uncertainty generated by correcting for ash or mineral matter. It is also probably best to use mineral matter volumes determined by microscope work, if available, as they may better estimate the volume of mineral matter that acts as a dilutent.

A number of data suites are re plotted into triangular plots (Figure 11). The plot contains medium-volatile coals from northeast British Columbia (Lamberson and Bustin, 1993), southeast British Columbia (Dawson and Clow, 1992), Australia (Bustin et al, 1995 and Walker et al., 2001) and low-volatile Gething coals from this study. There is a trend for adsorption to decrease as mineral matter content increases and to increase as vitrinite content increases. Though there also appears to be a tendency for adsorption capacity to be a maximum for a low mineral matter samples that contain a mixture of a lot of vitrinite and some inertinite. The relationship between gas capacities per unit volume of vitrinite versus inertinite should be apparent by looking at data that plots along a single mineral matter concentration line. An adsorption maximum at a specific vitrinite/inertinite ratio rather than at a 100% vitrinite content may indicate that collotelinite, which predominates in mixed maceral coals, may contain more gas than telinite, which predominates in high reactive coals. This is counter to the results from the reflectance histogram data, which seems to indicate that adsorptio is dependent on total vitrinite content only.

It is interesting to consider the effect of mineral matter in a little more detail. It is probably important to differentiate between dispersed mineral matter, which may not act strictly as a dilutent and the discreet crystalline mineral matter, which on a weight or volume basis probably acts only as a dilutent. Therefore attempting to correct data for the effects of mineral matter may be difficult. Dry ash-free corrections will under estimate the weight of mineral matter while mineral matter free corrections such as the Parr equation may over correct the data in terms of the dilutent effect of the mineral matter. It is then important to consider whether dispersed mineral matter directly influences adsorption characteristics of coal by effectively having a negative adsorption capacity. This is similar to the argument made by Thomas and Dam Berger (1976) and Levine (1993) who suggest hydrocarbons generated in the high-volatile bituminous coal block micro pores and reduce adsorption capacity.

It is difficult to determine the proportion of total mineral matter that is dispersed in coal. Generally it is in the range of 2% and comes in part from the original vegetation (equivalent to the ash left after burning clean wood) and in part from salts in solution in the inherent water or adsorbed onto the coal. The amount of dispersed mineral matter decreases as rank increases because some is dis-



Figure 12. Ash versus gas content plots for southeast British Columbia. Data (Dawson, 1993) and Walker et al. (2001) ash versus gas content and from Walker *et al.* (2001) ash% dab versus vitrinite/inertinite ratio.

pelled with the inherent water and some leaves the organic matrix and crystallizes as discreet mineral phases. Ward *et al.* (2001) used low temperature aching and detailed analysis of RED traces to identify the proportion of oxides present in crystalline minerals and the proportion present in amorphous form. They were working with Late Permian seams from the Gloucester Basin in Australia. In low rank coals some Ca, Mg, Na, K and Fe may be dispersed in the coal matrix and some may be in solution. In either case these elements may be able to block micro pores acting to decrease the adsorption ability of the coal.

The dispersed mineral matter probably has the same weight as the resultant ash because it is represented by dispersed elements rather than formed minerals that may contain loose CO or OH, which is lost during aching. There does not need to be a miff type correction for this material and as the amount increases in coal there might be a decrease in gas content of more than would be expected based on a weight dilutent effect. At increased ash concentrations represented by the addition of crystalline mineral matter gas contents will decrease based on the dilutent effect of the additional mineral matter. This would imply a 2 stage desorbed gas *versus* ash plot consisting of a line with steep negative slope at low ash and a line with negative slope representing the dilutent effect of ash at higher ash concentrations.

There are a number of data sets that illustrate a progressive decrease in gas contents as ash increases. They usually predict an ash content of less than 100% at zero ash content indicating that mineral matter has a greater weight than the resultant ash, usually by 5% to 20%. However these plots often steeper at low ash contents (Figure 12) (data from Dawson, 1993 and Walker et al., 2001) and a single line does not provide the best fit to the data. This could indicate a negative adsorption effect of dispersed ash or that samples with low ash concentrations have increased vitrinite/inertinite ratios. In some cases the effect is related to petrography as is possibly the case with the desorption data from New lands coals from Queens land Australia (Walker et al., 2001). The desorbed gas versus ash indicates a two-slope trend (Figure 12) and at low ash concentrations the reactives/inerts ratio increases. In these cases the two-component line can be taken as more evidence that vitrinite often contains more gas than the inertinite.

There is limited evidence, that in some data suites, ash has a negative adsorption effect. Some medium-volatile Mist Mountain Formation coals from southeast British Columbia (Dawson and Clow, 1992) range in rank from 1.14% to 1.2% Rmax. The four samples are generally enriched in inertinite and have a limited range of vitrinite/inertinite ratios of 1.05 to 1.52, which are not correlated with ash content. The gas contents corrected for ash using the Parr Equation are correlated with ash content implying that the ash may be negatively affecting the gas more than would be expected if it were acting as a dilutent. This is similar to the effect seen by Faiz and Cook whose equation implies that ash has a negative adsorptive capacity of about 0.45 cc/g per 1% ash. Inherent ash contents are probably higher in vitrinite that inertinite, which generally has mineral matter filling cells but in which dispersed mineral matter was probably expelled during charring.

It is possible that some trace elements can be used to estimate dispersed mineral matter. A trace element correlation matrix for the seven Gething samples in this study shows that a number of trace metals correlate negatively with VI miff and positively with ash. This could imply that they have a direct effect on the adsorption ability of coal. Organic sculpture might also indicate if non-coal elements effect the desorption ability of coal. Unfortunately IMP-MS does not measure organic S and concentrations detected are very low.

CONCLUSIONS

Seven adsorption isotherms of Gething Formation coal have high adsorption capacities. The samples have a rank of 1.7% Rmax and come from a single seam in the mid part of the formation. The data therefore cannot be applied to the formation as a whole, especially considering the wide variation in rank. However it is encouraging that, based on their rank, the samples have, expected or higher than expected adsorption capacities. The adsorption capacity of the five samples with low ash concentrations correlates moderately well with vitrinite content. This is similar to, though not as strong as, the correlation seen between vitrinite and adsorption capacity for the Gates Formation (Lamberson and Bustin, 1993) but better than that seen for some samples from the Bulli seam (Bustin *et al.*, 1995).

Vitrinite measured by conventional petrography and by random reflectance histograms correlate and both correlate with adsorption capacity, as does VM daf. Of the three measures, VM daf is by far the easiest to obtain. A plot of MV daf *versus* adsorption capacity is probably the fastest and easiest way to check for a maceral control on adsorption capacity.

The adsorption capacity of two of the samples seems to be strongly affected by ash content. It is possible that, in some data sets, finely dispersed ash originating from the original vegetation may inhibit adsorption. Based on the expectation that vitrinite adsorbs better than inertinite, a number of data sets imply either an increase in the vitrinite/inertinite ratio at low ash or an ash effect. This ash effect would be greater than the dilution effect of the ash based on its mass or volume.

The adsorption capacities of vitrinite and inertinite change independently as pressure increases and vary between coal seams and fields. Vitrinite/indefinite adsorption ratio is high in Gates coals and increases at high pressure. The ratio is lower for Gething coals but behaves similarly. The ratio is close to 1 for coals from the Bulli seam in the Sydney Basin in Australia and does not vary much with change in pressure.

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REFERENCES

- Beamish, BIB., and Crosdale, P.J. (1993): Characterizing the methane sorption behavior of banded coals in the Bowen Basin Australia; *Proceedings of the International Coalbed Methane Symposium* 1993, pages 145-150.
- Broatch, J. C. (1986): A Summary of the results of a palynological investigation of the British Columbia's northeast coalfield; *Paper 1988-1* pages 451-457.
- Bustin, R.M., Clarkson, C. and Levy, J. (1995): Coalbed methane adsorption of coals of the Bulli and Wongawilli seams southern Sydney Basin: Effects of maceral composition, 29th Newcastle Symposium on Advances in study of the Sydney Basin.
- Bustin, R.M. and Clarkson, C.R. (1998): Geological controls on coalbed methane reservoir capacity and gas content; *International Journal of Coal Geology*, Volume 38, pages 3-26.
- Diessel, C.F.K. (1992): Coal bearing depositional systems; Springer-Verlag
- Dawson, F.M. and Clow, J.T. (1992): Coalbed methane research Elk Valley Coalfield; *Canadian Coal and Coalbed Methane Geoscience Forum*, Parkesville, British Columbia February 1992, pages 57-72.
- Dawson, F.M. (1993): Fording Joint Venture Project, *Geological Survey of Canada*, Summary Report.
- Duff, P, Mc, L and Gilchrist, R.D. (1981): Correlation of Lower Cretaceous coal measures, Peace River Coalfield British Columbia; *Paper 1981-3*.
- Eddy, G.E., Rightmire, C.T. and Byren, C.W. (1982): Relationship of methane content of coal rank and depth: theoretical vs. observed; *Proceedings of the Society of Petroleum Engineers*, Department of the Interior, Unconventional Gas Recovery Symposium, Pittsburgh, Pennsylvania, SPE/DOE 10800, pages 117-122.
- Ettinger, I., Eremin, B., Zimakov, B. and Yanovskaya, M. (1966): Natural factors influencing coal sorption properties 1-petrography and the sorption properties of coals; *Fuel*, Volume 45 pages 267-274.
- Faiz. M.M. and Cook, A.C. (1991): Influence of coal type, rank and depth on the gas retention capacity of coals in the Southern Coalfield N.S.W. Gas in Australian Coals, *Geological Society of Australia*, Symposium Proceedings 2, pages 19-29.
- Gibson, D.W. (1985): Stratigraphy and sedimentology of the Lower Cretaceous Gething Formation, Carbon Creek Coal Basin, northeastern British Columbia; *Geological Survey of Canada*, Paper 80-12.
- Gurba, L.W., and Weber, C.R. (2001): The relevance of coal petrology to coalbed methane evaluation, using the Gloucester Basin Australia as a model; *International Coalbed Methane Symposium 2001*, Proceedings, May 14-18, 2001, pages 371-382.
- Hunt, J.W. and Smyth, M. (1989): Origin of inertinite-rich coals of Australian cratonic basins; *International Journal of Coal Geology*, Volume 11, pages 23-44.
- Joubert, J.I., Grein, C.T. and Beinstock, D. (1973): Sorption of methane in moist coal; *Fuel*, Volume 52, pages 181-185.
- Kalkreuth, W. and McMechan, M. (1988): Burial history and thermal maturation, Rocky Mountains foothills and foreland east central British Columbia and adjacent Alberta; *Bulletin, American Association of Petroleum Geologists*, Volume 72, pages 1395-1410.
- Kalkreuth, W., Langenberg, W. and McMechan, M. (1989): Regional coalification pattern of Lower Cretaceous coal bearing strata, Rocky Mountain Foothills and Foreland, Canada -Implications for future exploration; *International Journal of Coal Geology*, Volume 13, pages 261-302.

- Karst, R. and White, G.V. (1979): Coal rank distribution within the Bluesky-Gething stratigraphic horizon of Northeast B.C.; *Ministry of Energy Mines and Petroleum Geology*, Paper 80-1, pages 103-107.
- Kim, A.G. (1977): Estimating methane content of bituminous coalbeds from adsorption data; U.S. Bureau of Mines, Report of Investigations 8245.
- Lamberson, M.N., Bustin, R.M., and Kalkreuth, W.D. (1991): Lithotype maceral composition and variation as correlated with paleo-wetland environments; Gates Formation northeastern British Columbia, Canada; *International Journal of Coal Geology*, Volme18, pages 87-124.
- Lamberson, M.N. and Bustin, R.M. (1993): Coalbed methane characteristics of the Gates Formation coals, northeastern British Columbia: effect of maceral composition; *American Association of Petroleum Geologists Bulletin* Volume 77, pages 2062-2076.
- Leckie, D.A. (1983): Sedimentology of the Moosbar and Gates Formations (Lower Cretaceous); Ph.D Thesis, McMaster University.
- Leckie, D.A. and Kalkreuth, W. (1990): Formation of coals on wave -dominated strand plains; *International Journal of Coal Geology*, Volume 16, pages 161-162.
- Legun. A. (1986): Relation of Gething Formation coal measures to marine paleo shorelines, (93P,93I); *BC Ministry of Energy, Mines and Petroleum Resources*, Paper 1987-1, pages 369-372.
- Levine, J.R. (1993): Coalification: the evolution of coal as source rock and reservoir rock for oil and gas; Chapter 3, *American Association of Petroleum Geologists*; Studies in Geology Series, Number 38, pages 39-77.
- Levine, J.R., and Johnson, P. (1993): High pressure microbalance sorption studies; *Proceedings of the International Coalbed Methane Symposium*, 1993, pages 187-196.
- Levy, J.H., Day, S.J., and Killingley, J.S. (1997): Methane capacities of Bowen Basin coals related to coal properties; *Fuel*, Volume 76, pages 813-819.
- Meissener, F.F. (1984): Cretaceous and Lower Tertiary Coals as sources for gas accumulations *in* the Rocky Mountain area; in, Hydrocarbon Source Rocks of the Greater Rocky Mountain Region, Woodward J., Meissener F.F. and Clayton, J.L., Editors, *Rocky Mountain Association of Geologists*, 1984 Symposium, pages 401-431.
- Olszewski, A.J. (1992): Development of formation evaluation technology for coalbed methane development; *Quarterly Review of Methane from Coal Seams Technology*; Volume 9, Number 2, January 1992, pages 32-34.
- Renton, J.J., Blaine, C.C., Stanton, R., and Dulong, F. (1979): Compositional relationships of plants and peats from modern peat swamps in support of the chemical coal model; Carboniferous Coal Guide, *Department of Geology and Geography West Virginia University*; pages 57-102.
- Ryan, BD (1992): An equation for estimation of maximum coalbed-methane resource potential; *BC Ministry of Energy, Mines and Petroleum Resources*, Geological Fieldwork 1991, Paper 1992-1, pages 393-396.
- Ryan, BD (1997): Coal quality variations in the Gething Formation northeastern British Columbia; *BC Ministry of Energy*, *Mines and Petroleum Resources*, Geological Fieldwork 1996, Paper 1997-1, pages 373-397.
- Taylor, G.H., Liu, S.Y. and Diessel, C.F.K. (1989): The cold-climate origin of inertinite-rich Gondwana Coals; *International Journal of Coal Geology*; Volume 11, pages 1-22.
- Thomas, J. and Damberger, H.H. (1976): Internal surface area moisture content and porosity of Illinois coals variations with coal rank; *Illinois State Geological Surve*, Circular 193.

- Ulery, J.P. (1988): Geologic factors influencing the gas content of coalbeds in southwestern Pennsylvania; *United States Department of the Interior*, Bureau of Mines, Report RI 9195.
- Walker, R., Glikson, M. and Mastalerz, M. (2001): Relations between coal petrology and gas content in upper Newlands

Seam central Queensland, Australia; *International Journal of Coal Geology*, volume 46, pages 83-92.

Ward, C.R., Taylor, J.C., Matulis, C.E. and Dale, L.S. (2001): Quantification of mineral matter in Argonne Premium coals using interactive Rietveld-based X-ray diffraction; *International Journal of Coal Geology*, volume 46, pages 67-82.