Contrasts in Methane Sorption Properties Between New Zealand and Australian coals

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ABSTRACT

High pressure microbalance investigations have produced results for both New Zealand and Australian coals which show fundamental differences in their methane sorption properties. New Zealand high volatile bituminous C rank coals have a methane adsorption capacity of 38 cc/g(daf) which decreases to a minimum of 23 cc/g(daf) at medium volatile bituminous rank and increases to 31 cc/g(daf) at low volatile bituminous rank. Vitrinite-rich coal samples from Australia display a similar trend, but, the methane adsorption capacity is approximately 8 cc/g higher than for New Zealand coals at low volatile bituminous rank increasing to 20 cc/g higher at high volatile bituminous A rank. From these differences it is implied that New Zealand coals contain a lower proportion of microporosity than Australian coals, most likely due to the presence of volatile components blocking the micropore structure making them unable to sorb as much methane.

INTRODUCTION

Little published data exists on the methane sorption properties of New Zealand coals, making it difficult to assess the likely potential of both methane recovery from coal seams and resulting emissions from underground mining. Methane adsorption studies were recently conducted on these coals using high pressure microbalances. The same equipment and technique has been used to study Australian coals. This paper compares the results obtained for coals from both countries and assesses the influence of coal rank and type on methane adsorption capacity.

EXPERIMENTAL

Coal samples

The New Zealand coal samples studied were obtained from the Coal Research Ltd sample bank in Wellington, New Zealand. Two sets of samples were analysed:

1. a rank suite of run-of-mine coals covering the range from high volatile bituminous C to low volatile bituminous (Table 1); and

2. a lithotype suite of high volatile bituminous C rank from the Greymouth Coalfield (Table 1). This lithotype suite is distinguished by increasing amounts of vitrain bands present: bright non-banded (752-5), bright <25% vitrain (55/382), bright 25-30% vitrain (55/381) and pure vitrain (752-8). All New Zealand coal samples were supplied as splits from samples prepared for proximate analysis.

The Australian coal samples were obtained from underground in-seam borehole cores in the Sydney Basin and vertical surface boreholes from across the Bowen Basin. Bright, vitrinite-rich fractions covering the rank range from high volatile bituminous A to low volatile bituminous (Table 1), were used for direct comparison in this study, as the New Zealand coals are predominantly vitrinite-rich with subordinate amounts of liptinite. To show the effects of coal type, two Australian inertinite-rich, high volatile bituminous A rank samples (Table 1) were also analysed for comparison with the New Zealand high volatile bituminous coal type suite. The Australian samples were crushed to <212 mm and a separate split of this product was used

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for thermogravimetric proximate analysis (Beamish, 1994).

Table 1 - Coal properties and Langmuir volumes for New Zealand and Australian coals

Sample No.	Moisture (%, ar)	Ash (%, db)	Volatile matter(%, daf)	Langmuir volume(cc/g, daf)	ASTM Rank
New Zealand coal rank suite					
54/920	5.6	9.3	45.7		hvCb
54/921	4.5	3.1	42.8	34.8	hvCb
54/804	4.9	2.6	39.6	32.1	hvCb
53/680	2.7	4.1	41.5	30.2	hvBb
54/918	2.5	4.	44.	30.3	hvBb
55/508	3.2	2.	38.9	30.	hvBb
55/617	1.4	1.6	33.2	25.5	hvAb
54/800	0.8	14.4	30.5	23.	mvb
57/205	0.7	9.6	27.8	25.6	mvb
54/923	0.7	8.0	21.8	31.1	lvb
New Zealand high volatile bituminous C coal type suite (see text for descriptions)					
752-8	7.8	.4	37.2	39.8	hvCb
55/381	6.6	3.4	40.1	41.9	hvCb
55/382	5.9	1.3	42.9	39.2	hvCb
752-5	6.0	1.2	46.6	35.4	hvCb
Australian vitrinite-rich coal rank suite					
G102/14CTBR	5.4	0.5	33.	46.3	hvAb
G102/15CTBR	5.4	.2	34.6	46.0	hvAb
NM1-04BR	1.6	9.4	27.4	38.6	mvb
NM1-21BR	.5	5.3	22.0	38.1	mvb
PH1-03BR	1.5	16.2	19.0	38.0	mvb
RS1-02BR	1.2	3.8	18.1	38.0	lvb
SM1-05BR	1.4	6.6	15.0	39.4	lvb
Australian high volatile bituminous A inertinite-rich coal types					

| G102/14CTDU | 3.3 | 8.8 | 30.1 | 38.2 | hvAb |
| G102/15CTDU | 3.5 | 12.1 | 34.1 | 37.4 | hvAb |

Methane adsorption determinations

High pressure microbalances were used to measure the methane adsorption by the samples. All coals were initially dried to avoid effects of moisture and enable direct comparisons of the maximum methane adsorption capacities (Langmuir volumes as determined from the Langmuir equation) of each coal. Methane volumes adsorbed at approximately, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, and 9.0 MPa were recorded. Calculations used to determine the methane adsorbed are reported in Crosdale and Beamish (1995).

RESULTS AND DISCUSSION

A comparison of the Langmuir volumes of the two suites of coals is shown in Figure 1, plotted against volatile matter (%, daf). There is a pronounced minimum in methane adsorption capacity (Langmuir volume) at medium volatile bituminous rank for both Australian and New Zealand coals. This minimum is quite sharp for the New Zealand coals, but appears to be rather broad for the Australian coals. There is a shift in the position of the minimum (based on volatile matter), which is partly real and partly due to the New Zealand coals having a higher volatile matter content than Australian coals for any given rank (based on vitrinite reflectance). The shift in position of the minimum in Fig. 1, which is partly real and partly due to the New Zealand coals having a higher volatile matter content than Australian coals of equivalent rank should be noted.
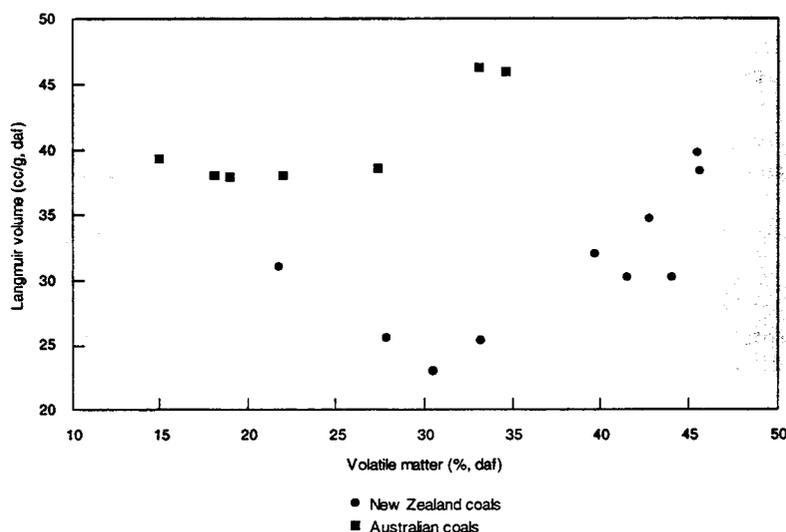

Fig. 1 - Variation in Langmuir methane volumes for Australian and New Zealand coals. Both suites of coal show a minimum in Langmuir volume at medium volatile bituminous rank

The Australian coal trend is very similar to that obtained by Griffith and Hirst (1944) for coal internal surface areas, whereas the New Zealand coal trend is similar to that obtained by Kini (1964). In absolute terms the Australian coals at high volatile bituminous rank adsorb as much as 20 cc/g more methane than the New Zealand coals. This difference in adsorption capacity

appears to decrease with increasing rank, such that at low volatile bituminous the difference is as much as 8 cc/g. Measured CO_2 internal surface areas for these coals are 70 m^2/g for the New Zealand high volatile bituminous A rank coal (Clemens, Matheson
and Rogers, 1991) and 200 m^2/g for a similar rank coal from the Sydney Basin.

A direct implication of this difference in adsorption capacity between the Australian and New Zealand coals of equal rank is that lower gas contents could be expected for New Zealand coals at equivalent depths. Gas contents as high as 10 cc/g have been recorded for New Zealand high volatile bituminous coals at depths of 700 m. The same gas contents are found in high volatile bituminous Australian coals at depths as shallow as 130 m in the Bowen Basin and 400 m in the Sydney Basin. Conversely, New Zealand coals with equivalent gas contents to Australian coals would have substantially higher seam pressures. This has serious consequences for trying to apply gas content threshold limits to New Zealand conditions.

There is a general increase in the methane adsorption capacity of the high volatile bituminous C New Zealand coal with increase in vitrain content, ranging from 35.4 cc/g to 41.9 cc/g (Table 1). A similar relationship exists for the high volatile bituminous A Australian coal, which ranges from 37.4 cc/g to 46.0 cc/g for one lithotype pair, and 38.2 to 46.3 cc/g for the other (Table 1).

It is well documented that the majority of the methane adsorption takes place in the micropores of the coal. The observed decrease in methane adsorption capacity from high volatile bituminous C to medium volatile bituminous rank has been attributed to "plugging" of the micropore system by "low boiling" hydrocarbon constituents (Thomas and Damberger, 1976). As coalification continues, cracking of the occluded oils during debituminization re-opens the micropore system increasing the availability of adsorption sites (Levine, 1993). Levine (1991) also points out experimental and field evidence indicating that methane adsorption capacity of coal is diminished by the presence of entrapped oils. He states that, "Hypothetically, molecules of occluded volatile constituents occupy molecular sites that would otherwise be accessible to methane, thus decreasing the methane sorption capacity". Toda et al. (1971) came to a similar conclusion suggesting that the decrease in micropore volume was strongly influenced by the concentration of hydrogen atoms bound directly to carbon atoms on the pore walls. The marked contrast in the methane adsorption capacity between the New Zealand and Australian coals in the high volatile bituminous rank (Figure 1) support this view, with the New Zealand coals for a given rank having a higher volatile component.

While both coal type suites showed the same trend of increasing methane adsorption capacity with increasing vitrain content (Table 1), the mechanisms for the trends appears to be different. The New Zealand coal type suite shows a consistent decrease in volatile matter with increasing vitrain content, and hence the increase in methane adsorption as discussed above. However, the Australian coal type suites shows a consistent increase in volatile matter content with increasing vitrain content. In this case the difference is due to a greater increase in the proportion of the macropores present in the coal, not a loss of micropores.

CONCLUSIONS

The methane adsorption capacity of New Zealand coals is much less than Australian coals. At low volatile bituminous rank the difference is 8 cc/g and increases to 20 cc/g at high volatile bituminous A. These differences are primarily due to decreased microporosity in the New Zealand coals from the presence of volatile components blocking the micropore structure. The same mechanism accounts for the rapid decrease in methane adsorption capacity from high volatile bituminous C to a minimum at medium volatile bituminous rank for the New Zealand coals. The Australian coals show a similar trend, but the decrease is not as rapid.

Coal type also shows a significant effect on the methane adsorption capacity of the high volatile bituminous coals from both countries. Generally, there is an increase in methane adsorption capacity with increase in vitrain content of the coal. However, the mechanism for this increase is different for New Zealand coals compared to Australian coals. The New Zealand coal type trend is controlled by the presence of volatile components producing a similar effect to the rank trend, whereas the Australian coal trend is a result of increased macroporosity relative to microporosity in the coal.

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REFERENCES

Beamish, BB, 1994. Proximate analysis of New Zealand and Australian coals by thermogravimetry. *New Zealand Journal of Geology and Geophysics*, 37: 387-392.

Clemens, AH, Matheson, TW and Rogers, DE, 1991. Low temperature oxidation studies of dried New Zealand coals. *Fuel*, 70: 215-221.

Crosdale, PJ and Beamish, BB, 1995. Applications of coal petrography and microstructure to gas emissions, outburst-proneness indications and alleviation in underground coal mines. Joint Coal Board Health and Safety Trust Final Report. Coalseam Gas Research Institute, James Cook University of North Queensland, March, 1995, 121pp.

Griffith, M and Hirst, W, 1944. The heat of wetting of coals in organic liquids. *Proceedings of Conference on the Ultra-fine Structure of Coals and Cokes*, 80-94.

Kini, KA, 1964. Measurements of the surface area of coals and cokes by adsorption of xenon, krypton, argon and methanol. *Fuel*, 43: 173-180.

Levine, JR, 1991. The impact of oil formed during coalification on generation and storage of natural gas in coalbed reservoir systems. *The 1991 Coalbed Methane Symposium Proceedings*, 307-315.

Levine, JR, 1993. Coalification: The evolution of coal as source rock and reservoir rock for oil and gas. *Hydrocarbons from Coal*, BE Law and DD Rice editors, 39-77, (AAPG Studies in Geology #38).

Thomas, J Jr and Damberger, HH, 1976. Internal surface area, moisture content, and porosity of Illinois coals: Variations with coal rank. Illinois State Geological Survey Circular 493, 38pp.

Toda, Y, Hatami, M, Toyoda, S, and Honda, H, 1971. Micropore structure of coal. *Fuel*, 50: 187-200.