Sorption Characteristic of Coal, Particle Size, Gas Type and Time

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ABSTRACT: Sorption characteristics of Bulli seam coal samples were examined with respect to coal particle size, gas type and time. Sorption tests were carried out by the indirect gravimetric method for determining gas content in coal. Various coal particle sizes were tested in addition to 54 mm diameter coal core. The other coal sizes were ±15 mm (-5/8+0.530 mesh) cubical blocks and coal fragments of ±1.18 mm (-0.256+16 mesh), ±6.70 mm (-5/16+0.256 mesh), and ±8.00 mm (-5/8+5/16 mesh). The samples were maintained in specially designed pressure vessels, at constant temperature of 24 °C and subjected to gas pressures up to maximum of 4000 kPa with incremental increasing steps of 500 kPa. All samples were tested with CH_4, and CO_2. The first group of ±1.18 mm size coal fragments achieved the highest gas adsorption, and the lowest was 54 mm size. Adsorption of carbon dioxide was typically the highest and that of methane was lowest. Furthermore, the tests also showed that the longer it takes to reach the pressure equilibrium the higher the gas adsorption. This study suggests that the gas content in coal depends strongly on gas type, sorption time, and particle size. Sorption time however, appears to be independent of particle size.

INTRODUCTION

The phenomenon of gas sorption has been studied over a long period of time spanning over two centuries and as early as 1773 by C.W. Scheele. Later on in 1777, A.F. Fontana described the adsorption of gases, mostly in charcoal. Brunauer (1945) reported on the work of De Saussure in 1811 and his systematic measurement of gas adsorption on several adsorbents. One particular reference is rather significant from the sorption point of view, in that De Saussure refers to easily condensable gases being absorbed in largest quantities by the adsorbent. This agrees with the concept that the adsorption is due to the condensation of gases on the surface of the adsorbent while desorption is the evaporation of gases.

More recently gas sorption has been the subject of intense study Seidle and Huitt (1995), Moffat and Weale (1955), Jolly et al. (1968), and Harpalani and Chen (1995), Lama (1988) , and many more. Singh (1968) observed that coal could hold 1.4 to 2 times more carbon dioxide than methane at about 345 kPa (50 psi) pressure and with nitrogen achieving only 0.4 of methane under the same conditions. However, Gunther (1965) reported that at a higher pressure these figures could be less.

While there appears to be enough information about the behaviour of gas adsorption mainly in pulverised coal samples, most of these studies were made on particles sizes up to a few hundred of microns and only few tests were made in sizes larger than a millimetre. Therefore, the aim of this study is to examine gas sorption in coal of particle sizes larger than one millimetre and to evaluate isotherms for a better understanding of gas sorption in coal. Accordingly, various particles sizes were prepared and tested.

PARTICLE SIZE, GAS TYPE AND DURATION

There are different opinions regarding test sorption duration. Seidle and Huitt (1995) used coal matrix strain equilibrium for gas saturation measurement. The test was carried out using coal matrix shrinkage method with the coal samples (core samples of unknown size) being subjected to pressures up to 13,790 kPa (2,000 psi). They reported that when coal adsorption was carried out in methane, the coal matrix strain took about three months to stabilise. However, when in desorption it took about ten days. The process of desorption from the sample was carried out in steps of 1,379 kPa (200 psi). In helium however, the equilibrium time at each step was about three days and in carbon dioxide it took around four days. As a result Seidle and Huitt concluded that longer equilibrium times would be required for matrix shrinkage test.

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Harpalani and Chen (1995) swelling/shrinkage test found that methane took nearly four month to reach strain equilibrium at increasing pressure, but it took about a month in decreasing pressure. They suggested using smaller samples sizes instead of 89 mm diameter cores to reduce the duration of the experiment. Harpalani (2005) reported adsorption measurements of methane and carbon dioxide using pulverised samples of coal 0.420-0.149 mm (40-100 mesh) size from the Illinois basin. Harpalani reported very long desorption times for most Illinois coal, suggesting low diffusion rates.

Moffat and Weale (1955) using only methane gas, found that both powdered coal and lumps of about 12.5 mm (½ in.) size requires the same time to reach the equilibrium pressure. At 100 MPa (1000 atm.) gas pressure, the coal sample took less than one hour to reach equilibrium state. Moffat and Weale also observed that the same sample, previously saturated, when the methane was released in a given amount took almost two hours to reach the new equilibrium pressure state. All the coal particles tested in gas adsorption were 0.211 mm (72 B.S. mesh) size.

Recently, Van Bergen et al. (2009) carried out swelling test in unconfined coal samples of 1.0-1.5 mm^3 exposed to each of CO_2, CH_4 and Ar. The test was run for between 17 and 24 hours for each coal samples.

In the present study carried out on Bulli coal seam, it was found that in adsorption, it took a minimum of three days for carbon dioxide and four days for methane to reach the equilibrium pressure level, as long as the suggested concept of pressure duration was applied, which is defined as the minimum period of gas sorption in coal in reaching the pressure equilibrium. However, it took more than 30 days to reach the equilibrium state at decreasing pressures (testing induced desorption characteristics), for both in carbon dioxide and methane gas environment.

EXPERIMENTAL

The indirect gravimetric method was used to determine the volume of gas adsorbed in coal. Using different coal particle sizes the volume of gas adsorbed in coal was determined at different gas pressures up to 4000 kPa. Gases used in the test were carbon dioxide and methane. The apparatus used for the test is described by Lama and Bartosiewicz (1982) and later by N.I. Aziz and W. Ming-Li (1999). This apparatus has since been modified adding a pressure transducer to each pressure vessel, commonly known as bomb. A total of 17 bombs were used in the test. Seven of these bombs were run with carbon dioxide and another seven with methane. The remaining bombs were used to evaluate the volumetric strain changes in 54 mm diameter coal core samples.

Coal Samples

The adsorption characterisation study was centred on coal samples collected from West Cliff Colliery and longwall panel 520-B3. Details of the coal samples are shown in Tables 1 and 2. Particle fragment sizes of ±1.18 mm (-0.256+16 mesh), ±6.70 mm (-5/16+0.256 mesh), ±8.00 mm (-5/8+5/16 mesh), and ±15.00 mm cubical blocks (-5/8+0.530 mesh) were tested in addition to 54 mm diameter coal core samples as shown in Figures 1 to 3.

Table 3 shows the details of fourteen bombs with the corresponding particle size and gas type. The samples were dried at 105 °C for 18 hours and were then maintained at 24 °C room temperature and atmospheric pressure for about 18-24 hours to achieve moisture equilibrium prior to sorption testing. Each bomb was filled with coal to approximately 85 % of its capacity. Prior to gas pressurisation, all bombs were vacuumed as much as practically possible to remove any residual air or gas from coal. The vacuuming was carried out for one hour, in three 20 minutes steps, down to about -51 kPa. The bombs were maintained at constant temperature in water bath, and the room temperature was acclimatised to a desirable temperature of 24 °C. The room temperature was monitored continuously through thermocouples, located on each sorption apparatus. A data logger was used to record room temperature, water bath temperature, atmospheric pressure, bombs equilibrium pressure and weight on a regular basis. The bomb weight measurements were made both at the initial and final pressure levels and at each incremental increasing step of 500 kPa. Any gas pressure leakage could easily be detected by differences in bomb weight.

Figure 1- 54 mm diameter core size

Figure 2- ±15.00 mm cubical blocks

Table 1 - Coal density and proximate analysis

Sample code	Depth (m)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash Yield (%)	Volatile Matter (%, daf)	Coal density
520-B3	450	1.3	21.7	71.4	5.6	23.3	1.43

(Saghafi & Roberts, 2008)

Table 2 – Petrography

Sample code	Vitrinite Reflectance (%)	Maceral (%)			Maceral (%, mineral free)			
		Vitrinite	Liptinite	Inertinite	Mineral	Vitrinite	Liptinite	Inertinite
520-B3	1.28	41.6	0.1	55.3	3.0	42.9	0.1	57.0

(Saghafi & Roberts, 2008)

Table 3 - Particle size and gas type

Bomb	Particle size	Mesh size	Gas type
B1G	1.18 mm	-0.256+16	CH_4
BB	1.18 mm	-0.256+16	CH_4
B4	6.70 mm	-5/16+0.256	CH_4
BC	6.70 mm	-5/16+0.256	CH_4
BL	15.00 mm	-5/8+0.530	CH_4
BH	15.00 mm	-5/8+0.530	CH_4
BD	54 mm core	54 mm	CH_4
B2	1.18 mm	-0.256+16	CO_2
B5	1.18 mm	-0.256+16	CO_2
BA	8.00 mm	-5/8+5/16	CO_2
BF	8.00 mm	-5/8+5/16	CO_2
B6	15.00 mm	-5/8+0.530	CO_2
BK	15.00 mm	-5/8+0.530	CO_2
B3	54 mm core	54 mm	CO_2

Figure 3- ±1.18 mm size

Results and analysis

Figures 4a and 4b show the rate of gas pressure drop due to adsorption of either CH_4 or CO_2. The rate of gas pressure drop is a clear indication of how the sample is being saturated. In the initial 360 minutes the pressures drop in CO2 gas were about 70-80% in fragments of 1.18 mm, 70% in

fragments of 8.00 mm, 50-80% in cubical blocks of 15 mm, and 40% in 54 mm diameter coal core. In summary, in fragments between 1.18 mm and 15.00 mm, the pressure drop was on average 70% while in 54 mm, it was about 40%.

In CH4, the pressure drop was about 30-40% in fragments of 1.18 mm, 20-30% in fragments of 6.70 mm, 30-40% in cubical blocks of 15.00 mm, and 30% in 54 mm diameter coal core. In summary, in fragments between 1.18 mm and 15.00 mm, the pressure drop was on average 30% and it was 30% in 54 mm coal core. 100% represents the total pressure drop to reach equilibrium pressure for a given gas. Note, the initial confining pressures were different for different particle sizes tested. Post analysis of the data clearly indicated the need to start the test under similar confining pressure.

The concept of sorption duration on vacuumed coal sample was defined according to the data collected over a period of 12 months sorption tests using different gases and in different particle sizes carried out at the University of Wollongong. The concept of duration was studied with respect to the minimum test sorption duration and pressure rate. The minimum sorption duration is defined as the minimum sorption time for coal to reach the equilibrium pressure. This minimum duration was found to be three days for CO_2, and four days for CH_4, irrespective of particle size.
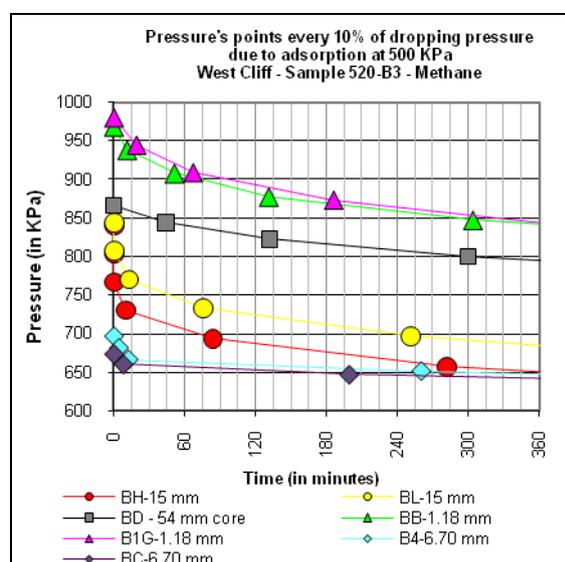

Figure 4a – Dropping of saturation pressure at 500 kPa in adsorption - Methane
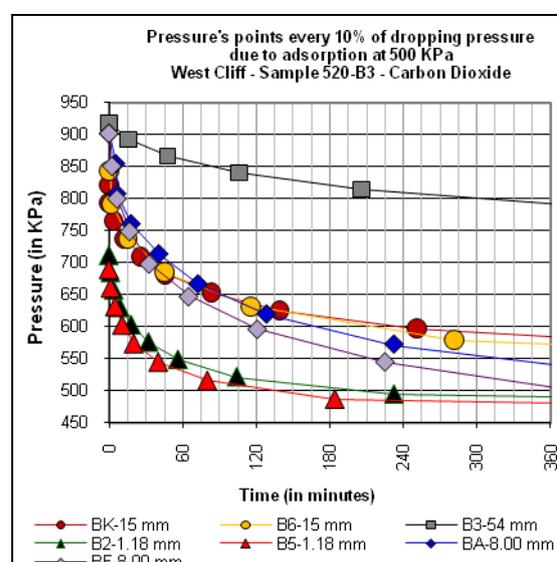

Figure 4b – Dropping of saturation pressure at 500 kPa in adsorption – Carbon dioxide

These finding was in agreement with Moffat and Weale (1955) regarding the particle size and with Seidle and Huitt (1995) with regard to sorption in different gas environment (that is, adsorption in carbon dioxide was occurred faster than in methane). Further to the minimum pressurisation time and the rate of pressure change (which is the pressure change over a given period of time against the total pressure change), the study examined the last 18 hrs of monitoring before the equilibrium pressure reached. The last observed pressure was considered as the equilibrium pressure, once the rate of pressure fluctuation was not greater than 5%. These two requirements (minimum duration and rate of pressure change) guarantee that the change of the gas pressure was stabilised over the time as indicated by the asymptotic profile of the graph to the time axis as depicted in both Figures 5a and 5b.

Figures 5a and 5b show gas adsorption equilibrium path at 500 kPa pressure for two different gas types. The CO_2 curves show a sudden and steep decrease in pressure (Figure 5a), much faster than the CH_4 curves (Figure 5b), which are characterised by relatively slow and gradual tapering graphs to reach the equilibrium state.
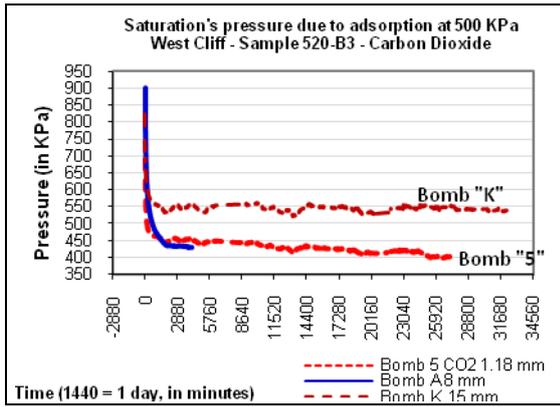
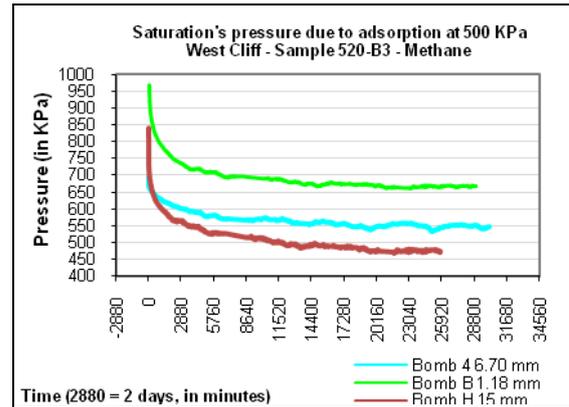**Figure 5a – Saturation pressure due to adsorption – CO$_2$**

Figure 5b – Saturation pressure due to adsorption – CH$_4$

An interesting example of the adsorption duration is the graph of bomb K, shown in Figure 5a. The equilibrium pressure (or saturation pressure) once reached did not change even though the sample was maintained under adsorption for longer period (33120 minutes or about 23 days). That is due likely to low diffusion rates and/or large cleat spacing, particularly at low pressure (in this case 500 kPa). This may even change slower in samples with much smaller (fine) pores. It should be noted that, over the same period however, the pressure in Bomb 5 decreased by 50 kPa (about 11% of the final equilibrium pressure). It is clear that all the three bombs containing particles sizes ranging between 1.18 and 15 mm took around three days to reach equilibrium pressure (Figures 5c and 5d).
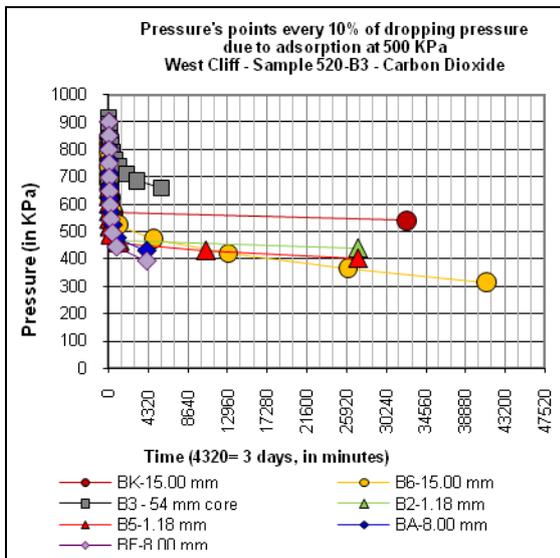

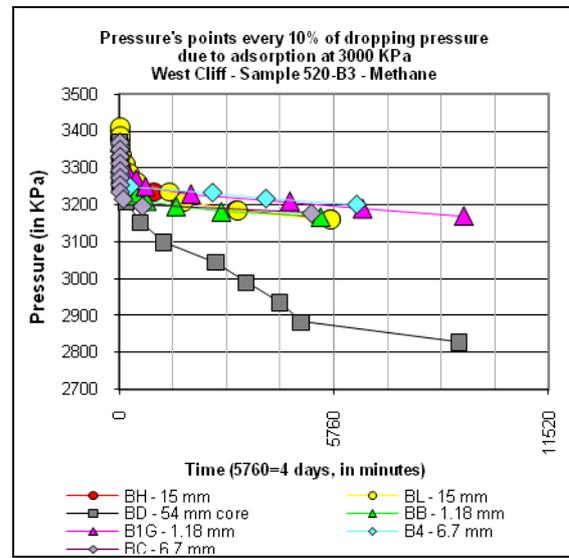**Figure 5c – Saturation pressure due to adsorption – CO$_2$**

Figure 5d – Saturation pressure due to adsorption – CH$_4$

Figures 6a and 6b show how long the gas takes to reach the equilibrium pressure at low confining pressures and with repeated charges spanning over a period of around two days. The behaviour is similar for both gases, methane and carbon dioxide, and depend more on the physical characteristic of the coal and the surface attraction and repulsion forces. The same phenomenon explains why at low gas pressures the coal adsorbs much more gas than at high pressure.
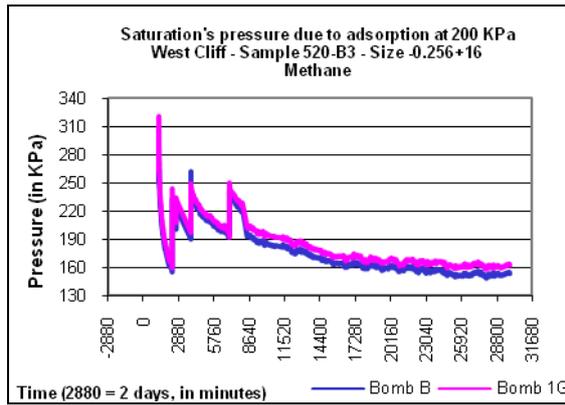
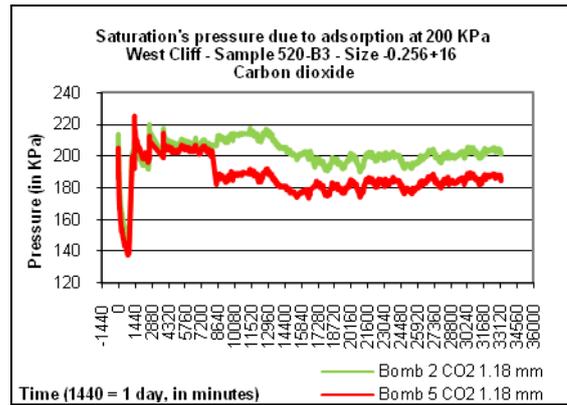**Figure 6a – Saturation pressure due to adsorption – CO₂**

Figures 7a and 7b show the equilibrium pressure due to induced desorption (in reverse process) in three different coal sizes in both methane and carbon dioxide (e.g. at 3,500 kPa). The changes in pressure levels along the time line in all the samples behave similarly with respect to pressure fluctuation and

Figure 6b – Saturation pressure due to adsorption – CH₄

sorption process. Methane desorbs easily but re-adsorbs slowly, which is different to carbon dioxide sorption behaviour. In the case of CO_2, the adsorption is the dominant process, rather than desorption as one expects.
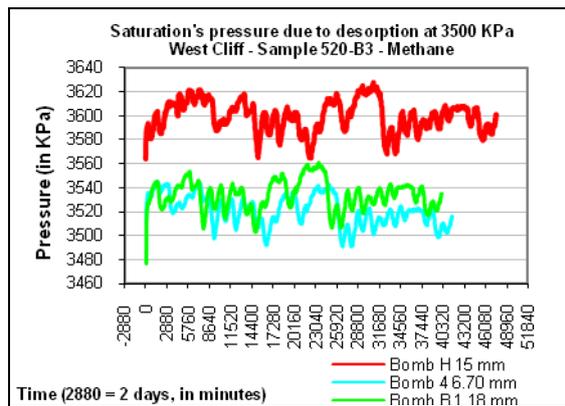

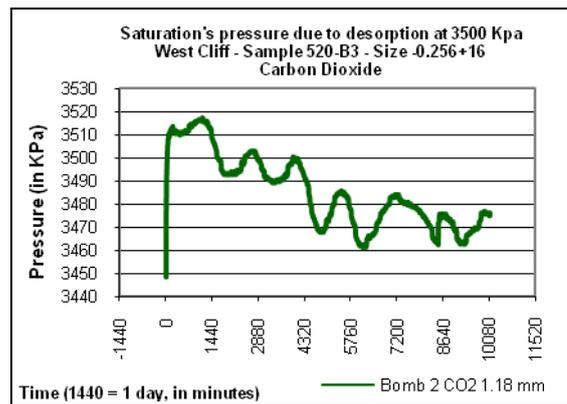**Figure 7b – Saturation pressure due to desorption – CO**

Figure 7a – Saturation pressure due to desorption – CH₄

This gradual drop in bomb pressure as indicated in Figure 7b is a clear indication that gas is continually being readsorbed in coal, and that the process of desorption occurs for very short times and intermittently. In CH_4, the desorption process seems to be predominant with the pressure being gradually increased. In other words, the sorption behaviour and interpretation of the graphs in Figures 7a and 7b is that coal is more prone to adsorb carbon dioxide than methane. These finding are in agreement with the finding of others researchers such as Deitz, Carpenter, and Arnold (1964), Sereshki (2005), and others. St. George and Barakat (2001) stated that the adsorption of carbon dioxide in coal is easier than methane. This differential behaviour is commonly known as the "affinity" of carbon dioxide to the coal. The preferential sorption of CO_2 in coal as compared to CH_4 and coal affinity to carbon dioxide is explained in terms of gas molecular weight and gas thermodynamics. The higher the molecular weight of the gas the lower the rate of vaporization, which means the lower rate of desorption. Thus, the evaporation rate of CO_2 will be lower than of CH_4. The same conclusion can be made by considering the amount of the heat of vaporization. The lower the heat of vaporization the easier the desorption process. Also Harpalani (2005) reported the same affinity in three different coal seams from Illinois basin.

The influence of the adsorption duration on isotherms calculation can be seen in both Figures 8a and 8b. The graph in Figure 8a shows three isotherms for saturated and less than saturated samples. They are: (a) Bomb 1G isotherm profile of full saturation and in accordance with the minimum sorption duration time, (b) an under saturated isotherm profile for 48 hr (2 days) test duration (obtained from data of Bomb 1G), and (c) a simulated profile, termed Sim T profile, calculated based on the changes in pressures of about 50 kPa less than full saturation isotherm profile (a) and for comparison with (b).

The graphs in Figure 8b include two isotherm profiles consisting of (a) full saturation test result isotherm profile of Bomb 1G, containing 250 grams of coal crushed to about -0.256+16 mesh and measured at 24 °C, from Westcliff panel 520-B3 (the result is produced for coal 'as received' and no correction for moisture or ash content was made), and (b) the isotherm (A) measured by Saghafi and Roberts (2008) from 300 gms of West Cliff Colliery coal (panel 520-B3), crushed to 150 µm particle size. The test was carried out at 27 °C and the results were produced for coal 'as received', and no corrections were made for moisture or ash content. Saghafi (2009) reported that, every points of the isotherm (A) reached equilibrium pressure after 4-6 hours, though generally after 2 hours the equilibrium was virtually reached.
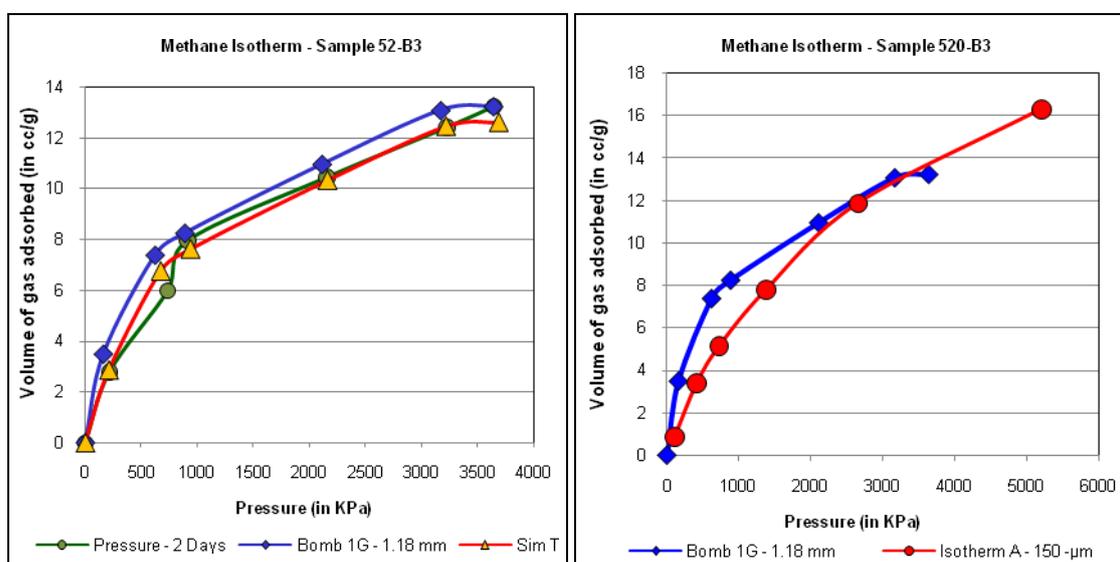

Figure 8a – Saturation at 48 hours   **Figure 8b – Saturation at minimum duration**

It was found that (Figure 8a), in 1.18 mm size coal, and at under saturation adsorption condition (sorption duration below that the minimum suggested sorption time), there was 18% less gas adsorbed in coal at exposed pressures below 500 kPa. However, at pressures up to 4000 kPa the change was 5%. The adsorption duration for 48 hours was also reported by Day, Fry and Sakurovs (2008).

In comparing the isotherms shown in Figure 8b and named as 1G and A, it can be seen that at low pressures, the gas content of the vessel (1G) is higher than the A graph, but at high pressure (at about 4000 kPa), it was quite similar. Clearly under saturation test has its draw backs which, if not addressed properly may lead to errors in the determination of the gas content in coal, thus influencing the production potential of a mine.

CONCLUSIONS

The following conclusions were drawn from this study:

- Coal charged with CO_2 to a confining pressures of up to 4000 kPa;
    - It takes at least three days to reach the equilibrium pressure in coal fragments and four days in 54 mm coal core samples;
    - In coal fragments, around 70% of the equilibrium pressure was reached during the first 360 minutes, while in coal core sample was reached 30% of the equilibrium pressure in the same period.

- The equilibrium pressure behaviour due to the CH_4 was similar to CO_2 but takes longer;
    - It takes at least four days to reach the equilibrium pressure in coal fragments and six days in 54 mm coal core samples.
    - It takes 360 minutes to achieve in average 30% of the equilibrium pressure in coal fragments. In coal core it reached 30% of the equilibrium pressure in the same period of time.

- In general, the higher the initial charged confining pressure at any step the faster is the adsorption for the same particle sizes. However, at lower initial charged confining pressure, the adsorption process takes longer, and the rate of adsorption appears constant, which may be due to the low process of diffusion to the coal matrix.

- Contrary to general belief, the adsorption duration for a given gas appears not strongly affected by the coal particle size (especially among fragments of coal). Further tests are underway to confirm this finding on different coal samples from different coal seams.

- Irrespective of sorption pressurisation, the level of pressure does not play a role in improving the minimum sorption duration.

- In general, the physical characteristic of coal plays an important role at any pressure, as it drives the sorption process and its duration (for a given gas pressure and temperature).

- The preferential sorption of CO_2 in coal as compared to CH_4 and coal affinity to carbon dioxide is explained in terms of gas molecular weight and gas thermodynamics.

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