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Isotherms, gas contents and diffusion coefficients of coals and shales

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Abstract

The measurement of gas content of coals has been dominated by the standard methods of core desorption described by ASTM D7569 and AS3980 (1999). In this paper the limitations of these procedures are discussed with particular reference to the partial gas pressure the gas content is being referred to. Because the gas content is always quoted as an absolute value measured to an undefined gas partial pressure as opposed to a value at atmospheric pressure it brings into question the nature of the isotherm model being used at pressures below atmospheric. The generally accepted Langmuir model is found to be lacking at these lower pressures and alternative options are considered.

The current practise of measuring isotherms is also questioned, particularly with respect to mixed gas types where the extended Langmuir or IAS models are found wanting.

To overcome these deficiencies the process of measuring gas contents to known partial pressures of seam gas is used. So too is the process of measuring native isotherms on initial desorption of core. This is extended to the measurement of laboratory isotherms at reduced pressures.

The results of isotherm testing indicate that the native isotherms are generally not the same as isotherms derived from laboratory testing though they are more similar where the seam gas is of a single composition. By undertaking isotherm tests to lowered pressures we can see that there are shortcomings in the Langmuir equation and that gas storage at lowered pressures may vary substantially from this model. The measurement of gas content by conventional desorption needs to be measured to a known partial pressure and this needs in turn to be related to the isotherm.

This paper uses some basic science to produce better solutions to gas content analysis. Along with these developments comes the analysis of desorption of a sample and how this relates to the diffusion coefficient and core fracturing. This leads in turn to an improved process to determine the lost gas on core retrieval for coals and shales.

Gas content measurement from coal core

The measurement of coal seam gas contents within Australia is currently defined by AS3980-1999, with a review due to be released in 2015. The American standard for the same process is ASTM D7569/D7659M-10 (2015). It is based on the work of the USBM (Kissel, McCulloch and Elder, 1973). The process generally involves taking coal core and bringing it to the surface as quickly as possible. The

core is then placed in canisters and allowed to desorb. The volume desorbed is monitored with respect to time. At the end of this period the core is withdrawn from the canister, weighed and its apparent relative density determined. The core should also be geologically logged, though this important part of the process is frequently ignored. Subsections of core are broken off, weighed and then crushed. The crushing process speeds desorption. Broadly the gas content of the core is calculated for the three parts of the process:

- 1) Before measurement of gas release takes place Q1
- 2) During measurement of gas release Q2
- 3) From gas released by crushing Q3

Process 2, the measurement of gas release, involves keeping a record of gas release with time. It is fairly straightforward, at least in concept. The gas volume can be measured, the time, barometric pressure and temperature can be noted. From these a plot of gas release at standard conditions (20°C, 101.325 kPa) or other conditions can be derived. By measuring the coal mass it is then possible to work out the gas release per unit mass with time.

Process 3, the measurement of gas release from crushing, is normally simply a process of measuring how much gas is evolved from the mass of coal per unit time.

Process 1, the measurement of the gas lost before measurement commences, involves extrapolation through the time period before measurements were undertaken. The basis of this is the straight line plot of cylindrical diffusion and the nearly straight line plot of spherical diffusion each with respect to the square root of time from the commencement of desorption as shown in Figures 1 and 2 respectively.

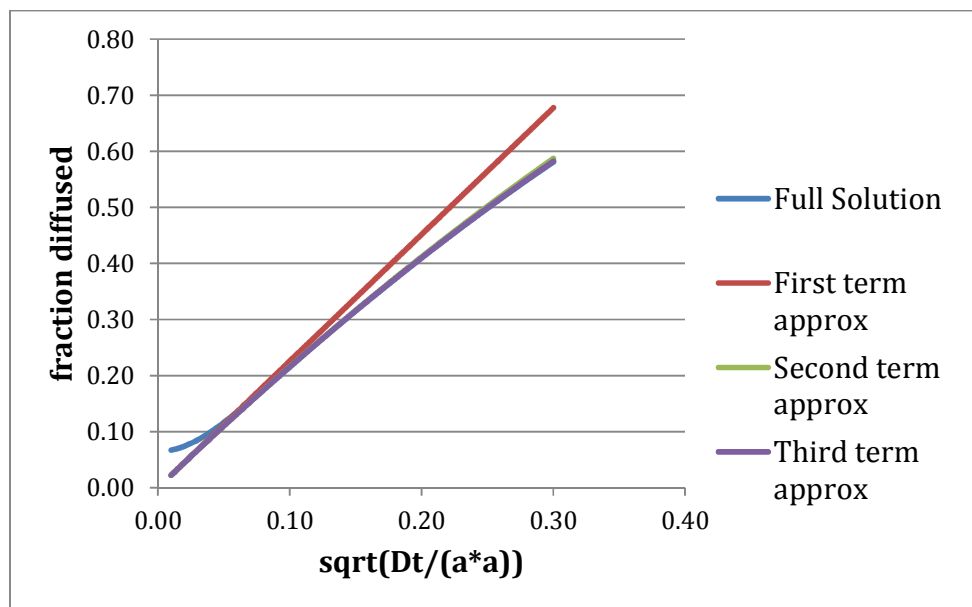


Figure 1 Plot of Fickian diffusion of a cylinder in early time showing various solutions

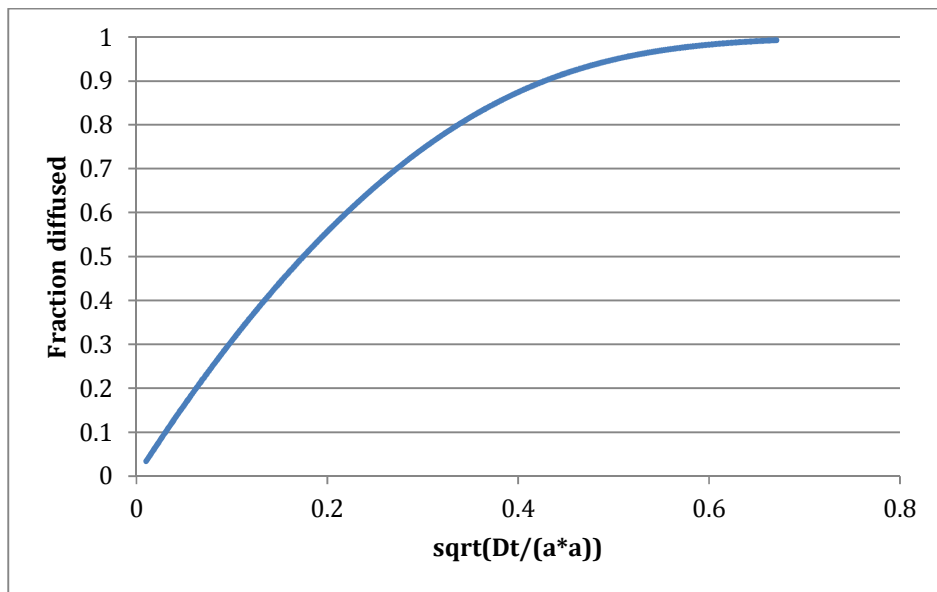


Figure 2 Fickian spherical diffusion: The fraction of total available material diffused versus $\sqrt{Dt/a^2}$.

As an alternative to long term desorption, the quick crush method forms part of the AS3890-1999. In this the initial desorption takes place. The core is then sealed into the canister, which is a pressure vessel and transported to the laboratory. Desorbed gas from the cylinder is then measured and the core taken out and weighed. Subsamples are then taken for the determination of Q3 by crushing.

Measurement error

Volume measurement error: This is just the error in determining the desorbed volume. It is associated with the nature of the measurement instrumentation. Specifically in manual measurement it is the error in reading a measuring cylinder.

Time measurement error: The prime part of this error is in knowing at what time desorption commenced. This is more straightforward in underground boreholes where there is not significant water pressure. However in holes drilled from surface using a drilling mud there is a significant fluid pressure. This means that at some depth as the core is withdrawn from the hole desorption will commence. However it does not commence immediately but gradually and increases as the core is lifted to surface.

Pressure at time measurement error: This error is related to knowing what pressure actually exists on the core and applies particularly to that period of core withdrawal to surface.

Measurement at varying temperature: The effect of temperature on the isotherm characteristic of the coal is very significant. This means that as the temperature of the core changes so will its gas retention capability. Cores therefore need to be kept at seam temperature during the period of desorption, or at least returned to that temperature towards the end of the test.

Procedural error

Failure to measure gas contained in pore volume: The entire core desorption procedure fails to take into consideration gas that is readily available for desorption from pore space. This is simply lost before the core ever gets into a canister and currently there is no basis for calculating this loss. This is only a problem if free gas exists in pore space. If the core is water saturated the only gas loss from pore space will be solution gas, a small component of the total. If however the coal sorption pressure is at or above reservoir pressure and a gas cap exists there is a real problem as the pore volume is unknown.

Measurement under vacuum or back pressure: The measurement of gas content under partial backpressure or vacuum affects the desorption rate. It also changes the mass of gas held in the dead volume of the canister. It is generally associated with the use of an inverted measuring cylinder with the gas water contact in the cylinder being at a different level to the air water contact outside the cylinder.

Measurement to an unknown partial pressure: This is the error which occurs in the determination of most Q3 samples. The sample is placed in the crusher which is either air filled or is frequently filled with helium. The crushing process takes place and gas is desorbed. However the question needs to be answered as to what partial pressure this is being measured to. This can be calculated from knowledge of the crusher container volume, the volume of coal being crushed, and the volume of gas generated.

Depending on the isotherm behaviour at low pressures, something which is generally not known, the volume of gas stored below atmospheric pressure may be 1.5 to 3 m³/t. What fraction of this is actually being measured in the gas content value?

Measurement at incorrect temperature: This occurs because the core is not kept at reservoir temperature. This is particularly the case where the core is placed in a canister which sits in the sun and gets very hot. The opposite can occur in cold conditions but heating is usually easier to arrange than cooling. It can also affect the residual gas content measurement in the crusher, as these are not usually held at seam temperature.

Calculation error

Lost gas: This is calculated from an extrapolation of the initial gas desorption with respect to the square root of time and is extrapolated back to some zero time. The problems with this are linked to the assumption of zero time. It is generally taken as the mean cutting time underground or the mid time between starting to pull a core from surface to the time of actually getting it there. This has little basis, as the surface concentration of gas on the core will vary as it comes to surface and only when the drilling mud pressure has dropped below the sorption pressure will the gas start to be desorbed. The rate of desorption will then be controlled by the pressure at the surface of the core.

The other big problem with lost gas estimation is that the initial desorption curves frequently deviate from a straight line. This may be due to temperature change but is more likely to be due to the fact that the fracture system in the core is making it behave as though it has a much smaller effective size than the core. As a result the smaller blocks between fractures have reached values of time where the straight line approximation is no longer valid. Most operators simply fit a straight line to the initial part of the curve without thought as to why this may not be a valid process.

Failure to take account of the dead volume in the canister: If the measurement procedure involves fluctuating pressures, such as changing pressure in an inverted measuring cylinder, then the gas mass held in the dead volume of the canister will vary too.

Failure to take account of humidity: A portion of the space in the canister and the gas volume measurement system will be occupied by water vapour. This is small at low temperatures. However at 40°C this will account for 7% of the total gas volume.

Failure to take account of partial pressure: Proper calculation procedures are needed to deal with the partial pressure effects of different gases including water vapour. Failure to account for these can easily lead to an error in gas content of 2-3 m³/t.

One of the key problems with the current system is that it does not quote gas content to a defined partial pressure. In our view this should be one atmosphere pressure of seam gas, not some variable and undefined partial pressure, as is currently the case.

One gas content does not fit the entire seam section: Different coal plies have different sorption capacities. Variations will be due to different macerals and varying mineral matter proportion. The

assumption that mineral matter simply displaces coal and reduces its sorption capacity is not quite true. It can be applied over about a 10% mineral matter range but beyond this the mineral matter seems to affect the sorption capacity of the remaining coal.

The use of ash values from proximate analysis may lead to significant error because carbonate rocks and clays will disassociate at the temperature of the ash measurement. It is more reliable to determine mineral matter composition by apparent relative density though this is not totally without compromise.

Isotherm testing

The isotherm of gas content in coal or shale is by definition the relationship between gas content of a coal sample and gas pressure obtained at a constant temperature, logically that of the seam. Isotherms are known to vary markedly with temperature. The hotter the coal, the less gas it will hold for a given pressure. Salmachi and Haghghi (2012) report a 50 percent reduction in methane storage of coal between 35°C and 75°C.

The measurement of isotherms for coal may be conducted gravimetrically or more commonly volumetrically. In the former case a precise balance is used to measure the uptake of gas onto coal in a pressurised environment. This process is undertaken on small samples. The volumetric method may be undertaken on any size sample but is typically in the range of a few hundred grams to several kilograms, depending on the size of test equipment employed. The volumetric process enables a large enough sample to be blended to represent an entire seam rather than making a number of measurements of small samples and trying to numerically combine the results at a later stage.

In the laboratory volumetric process, the gas and ground coal are put in a vessel. This is then evacuated and filled with helium and then pressurised and then de-pressurised. The dead volume is then determined from the pressure and volume of gas released. Helium is used because it does not adsorb readily onto coal. The vessel is then evacuated again and pressurised with a single gas type. A single gas type is used because a mixed gas will not generally adsorb in proportion to the gases it contains. The volume of gas input into the pressure vessel may be measured and the pressure determined as the gas adsorbs into the coal for the adsorption isotherm. The desorption isotherm is determined from volume of gas released as the pressure is lowered in the vessel. The test pressure steps are normally only above atmospheric pressure because it is inconvenient to work at a vacuum. This process is described by Mavor, Owen and Pratt (1990).

At low pressures the majority of gas in the vessel is adsorbed into the coal but at higher pressures the dead volume component becomes far more important. Any errors in dead volume measurement or the equations of state may lead to gross errors in the calculation of the isotherm at higher pressures. Vessel and valve leakage will also occur, however correct design of the apparatus will minimise this to diffusional behaviour through the seals. This level of diffusion should also be known and can thus be accounted for.

Because the isotherm is very seldom measured below 150 kPa absolute pressure, its real value below this range is not known. However isotherms are invariably quoted as a volume adsorbed above absolute zero pressure. There is no sound basis for doing this and it has important consequences in gas content assessments.

The most common equation used to characterise the pressure-volume relationship of an isotherm is the Langmuir equation (Langmuir and Irving, 1918). This is presented in equation 1. The equation was derived for monolayer adsorption on flat surfaces and it has theoretical shortcomings when multilayer

adsorption occurs or the surfaces are rough or indeed capillary condensation occurs. The theoretical extension of the Langmuir equation is the multilayer version by Brunauer, Emmett and Teller (1938). This too has shortcomings.

$$V = \frac{PV_L}{P + P_L} \quad (1)$$

Where P is the absolute pressure
 P_L is the Langmuir Pressure at which half V_L is stored
 V is the volume of gas at STP conditions for a given mass or volume
 V_L is the Langmuir Volume which V approaches at high pressure for a given mass

The values of P_L and V_L are obtained by plotting the value of P/V against P as in Figure 3 when the slope is theoretically $1/V_L$ and the intercept is $\frac{P_L}{V_L}$. In this case the fit is very good. The volume of gas stored below this pressure is not measured but comes from an extrapolation based upon the Langmuir equation. The isotherm associated with this is shown in Figure 4.

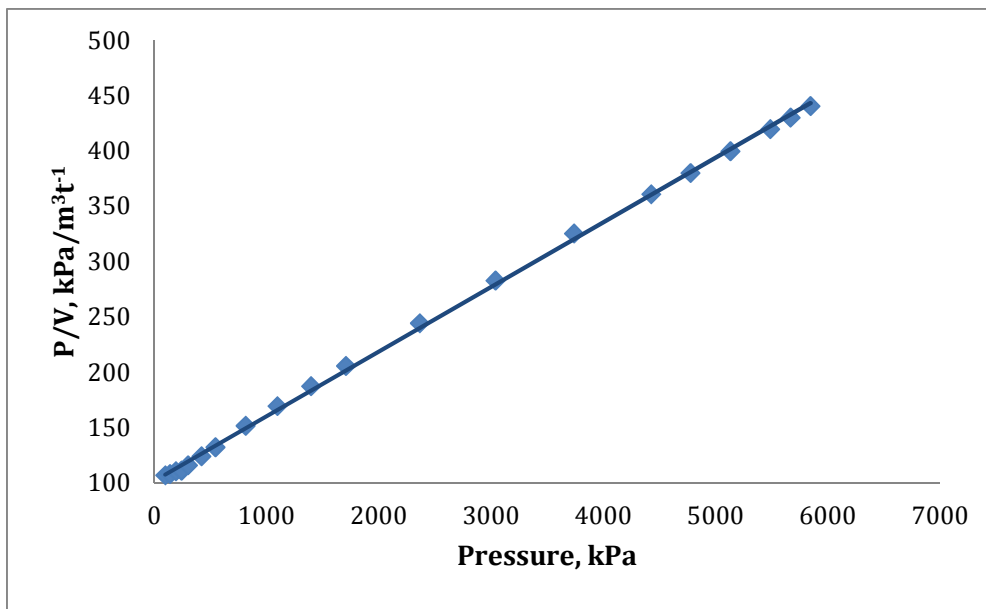


Figure 3 Langmuir Isotherm Regression Methane Sorption Test. Seam combined sample (mm free)

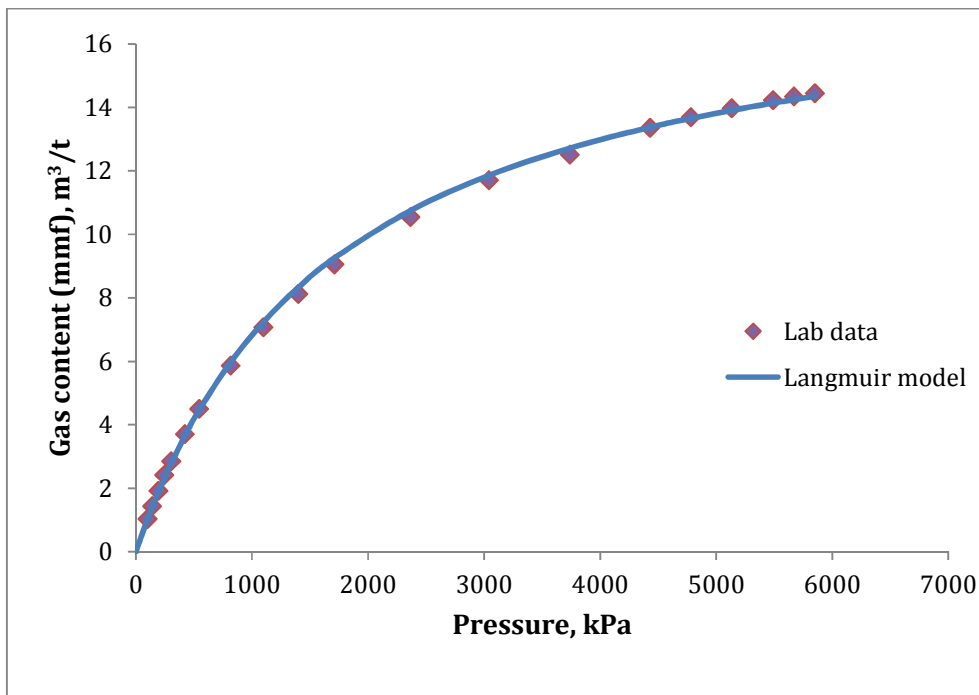


Figure 4 Langmuir Isotherm Curve Methane Sorption Test. Seam combined sample (mm free)

As a practical alternative to the Langmuir equation Gray (1983) used a logarithmic form to describe isotherms. The equation has the form shown in equation 2 and is derived from plotting the inverse slope of the experimental isotherm curve (volume at standard conditions versus absolute pressure) against pressure as shown in Figure 5. The data is the same as used for the Langmuir isotherm. In the case in Figure 5 there are two straight lines that fit experimental data extremely well. We think that the change in slope may be related to a change in adsorption behaviour. This may be the change from monolayer to multilayer adsorption or the onset of capillary condensation.

$$V = \frac{1}{a} \ln \left(\frac{a}{b} P + 1 \right) \quad (2)$$

Where P is the absolute gas pressure
 a is the slope of the plot (units of mass/volume)
 b is the intercept of the plot (units of pressure x mass/volume)
 V is the volume of gas at STP conditions for a given mass

In reality we have found from experience that some laboratory derived isotherms fit the Langmuir equation well while others fit the log equation.

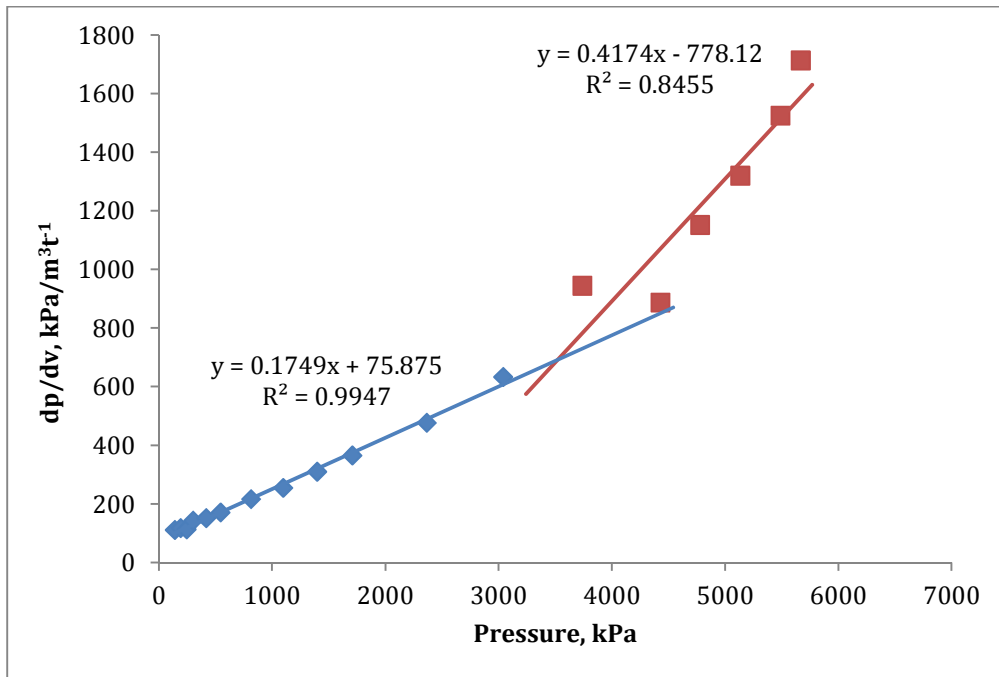


Figure 5 Logarithmic Isotherm Regression Methane Sorption Test. Seam combined sample (mineral matter free)

The reason for presenting the logarithmic form of the equation is not principally to show that it fits the data better but rather to show the consequence of extrapolation of the isotherm down to zero absolute pressure. Figure 6 shows the same experimental data with a logarithmic fit. In this case the isotherms of Figures 4 and 6 are virtually identical. In many cases there may be a difference of one or two cubic metres per tonne in the extrapolated volume between atmospheric and zero absolute pressure. There is also an uncertainty in the isotherm anywhere below the lowest pressure reading of the test. This is of extreme importance as the isotherm is the relation between the gas content and pressure.

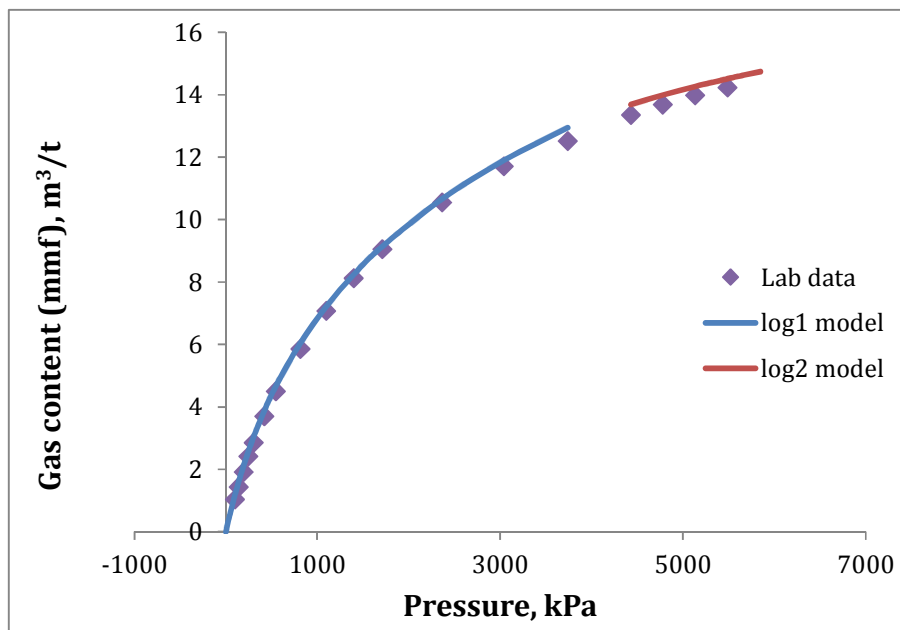


Figure 6 Logarithmic Isotherm Curve Methane Sorption Test. Seam combined sample (mineral matter free)

Mixed gas isotherms

In many cases coal seam gases are of mixed composition. The isotherm cannot in this case be measured by pressurising the coal with a gas mixture of the seam gas composition because some gases such as carbon dioxide are preferentially adsorbed over methane. This means that the results of individual isotherm tests have to be combined using some theory. The theories that are in use are the extended Langmuir model (ELM) (Ruthven, 1984) or the Ideal Adsorbed Solution (IAS) approach (Clarkson and Bustin, 2000). Figure 7 shows the result of combining the Langmuir based equations for methane and carbon dioxide to a mixed gas situation using ELM and IAS theory.

Extended Langmuir model (ELM) is the simplest model for prediction of multicomponent adsorption isotherms. It is reasonably accurate and works well for binary mixtures.

The Langmuir isotherm can be alternatively expressed as:

$$V(P) = V_L \times \frac{bP}{1 + bP}$$

where $b = \frac{1}{P_L}$

Thus, using the above form of the equation, the extended Langmuir isotherm is as follows:

$$V_i = \frac{V_{Li} \times b_i \times P_i}{1 + \sum_{j=1}^n b_j \times P_j}$$

Ideal Adsorption Solution (IAS) model is based upon the assumption that the adsorbed mixture behaves like an ideal adsorbed solution and the gas phase behaves like an ideal gas. Activity coefficients of the adsorbed solution are therefore assumed to be unity and the equilibrium between the gas phase mole fraction of a component and the adsorbed phase mole fraction is given by:

$$Py_i = P_i^o(\pi)x_i$$

Where P_i^o is the gas pressure of the pure component adsorbed at the same temperature and spreading pressure as the solution. The spreading pressure for the pure components may be determined through integration of the Gibbs adsorption isotherm to the vapour pressure of the pure component, P_i^o :

$$\pi_i^* = \frac{\pi_i A}{RT} = \int_0^{P_i^o} \frac{n(P)}{P} dP$$

Where $n(P)$ is the pure component adsorption isotherm. The spreading pressure (π) may be defined as the reduction in surface tension of a surface due to the spreading of the adsorbate over the surface (Ruthven, 1984).

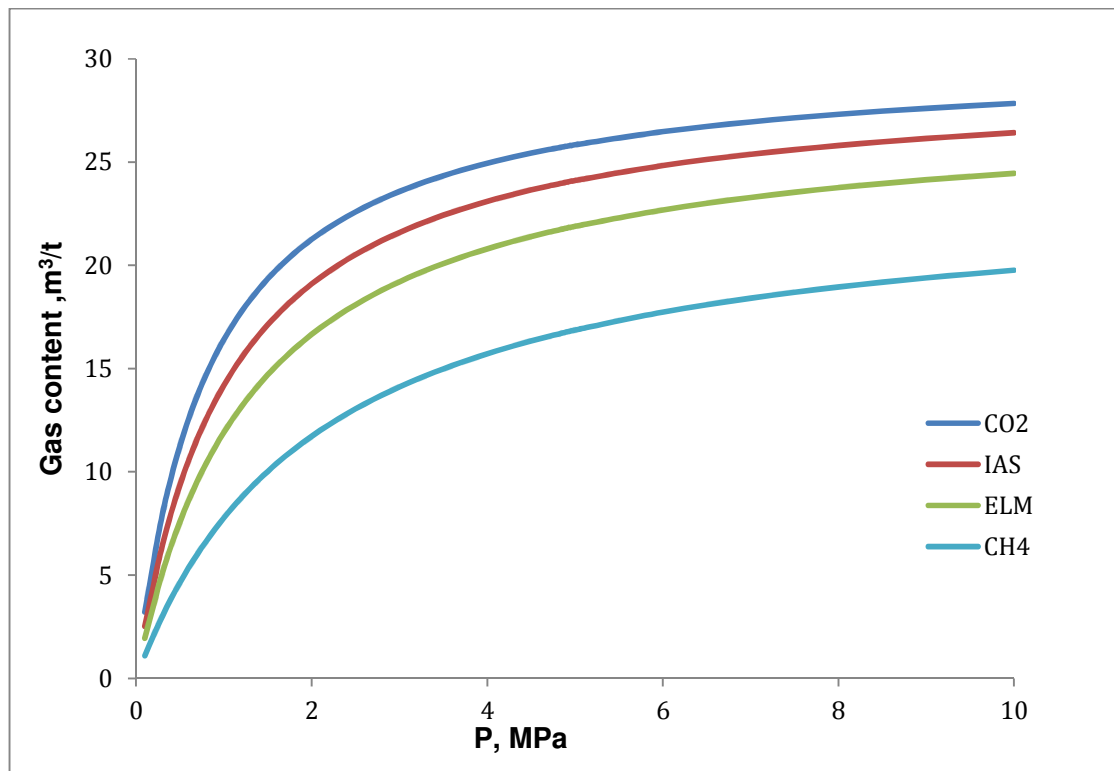


Figure 7. Mixed gas sorption isotherm combined using ELM and IAS theories for a Bowen Basin seam (mineral matter free).

Native Isotherms

Unfortunately coals do not necessarily adhere to any adsorption theory and it is highly desirable to actually measure their behaviour on initial desorption. This applies particularly to cases of coals where mixed gas types are present. For this reason we conduct native sorption isotherm tests.

The Native isotherm procedure involves placing a length of freshly cored coal seam directly into a water filled pressure vessel immediately after the core reaches the surface. The vessel is then sealed and allowed to reach equilibrium pressure. It is then sent to the laboratory to undergo the normal isotherm pressure drop procedure at a controlled temperature.

The advantage of this procedure is that it uses the native gas mixture within the coal to conduct the test so the isotherm generated is consequently a mixed gas isotherm determined on the desorption phase. This eliminates the necessity to combine the two separate methane and carbon dioxide pure gas isotherms. Upon completion of this test the coal is crushed and subjected to the normal pure gas isotherm testing regime.

The disadvantages of the Native isotherm test are that it takes a long time and it requires high quality seals and possible compensation for diffusion through the seals. Also unless a pressurised core barrel is used the initial gas content and sorption pressure are lower than the in seam condition as gas is lost in recovery.

It is then possible to compare the Native mixed gas isotherm with the combined mixed gas isotherm results. As can be seen from Figure 8 the results are not always the same. Figure 9 shows another example of a mixed gas system with results of a native isotherm test. This does not appear so precise as the real experimental points are shown. They also fall outside of the extended Langmuir model.

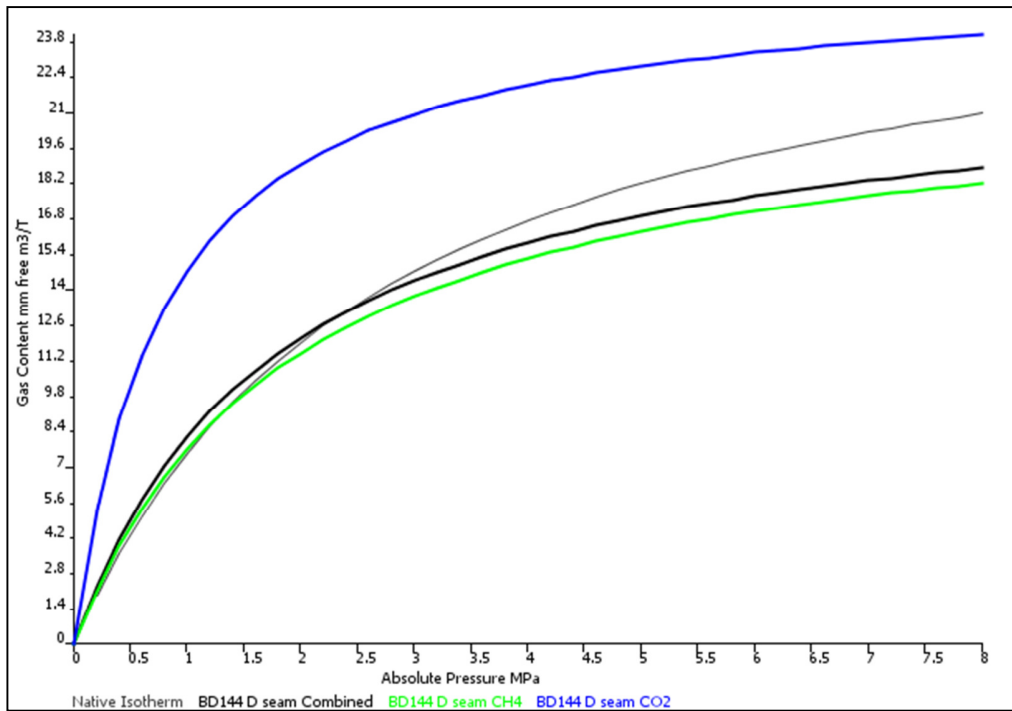


Figure 8 Sorption isotherm results for a Bowen Basin seam (mineral matter free basis). The native isotherm is in grey, the laboratory derived isotherm for methane is in green while the laboratory isotherm for carbon dioxide is in blue. The IAS combined isotherm is in black

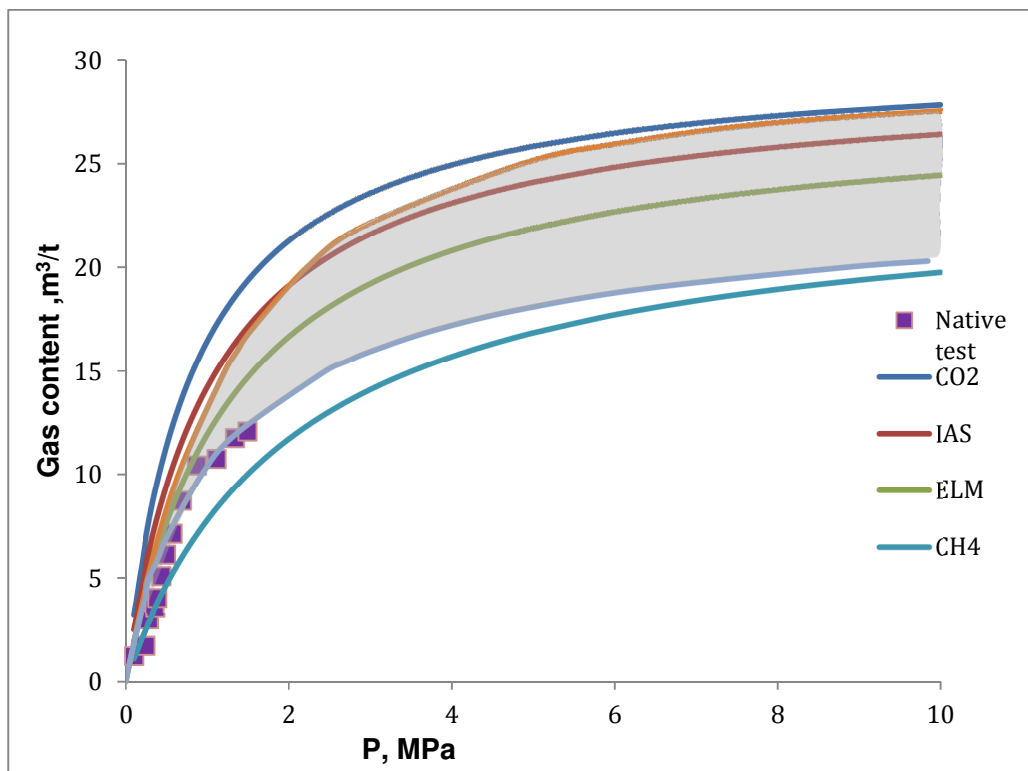


Figure 9. Native sorption isotherm superimposed on IAS, ELM and alternative models.

In fact they lie closer to an alternative, very simple model used by the authors to gain an idea of the range in which an isotherm may lie and which is shown by the light grey shaded zone. This is based on the big assumption that the order in which the gas type came into the system makes a difference to the isotherm. The fact that some coals with mixed gases will not always produce methane preferentially to carbon dioxide (with a higher affinity to coal) on desorption suggests that this may be the case.

This very simple model considers that for a given volume of type A gas the resultant pressure may be determined by its isotherm. The volume of second gas type B may then be considered to be absorbed. The differential pressure required to take this from volume A to volume A+B on the isotherm of gas B is added to the pressure reached after component A. This process can be repeated for varying proportionate volumes to arrive at an isotherm. The process may then be repeated using gas type B first and gas type A second to arrive at an alternative isotherm. The result is considered to provide upper and lower bound ranges for the mixed isotherm. It should be borne in mind that the water as well as gasses competes for storage within the coal and this will complicate the isotherm further. This model comes out of observations of areas where methane existed, was replaced by carbon dioxide due to igneous events and probably had some more methane generated by thermogenic process. The carbon dioxide tends to be preferentially desorbed from these coals despite its apparently greater affinity for the coal.

Conclusions

The first conclusion is that mixed isotherms are uncertain. This is borne out experimentally. The best way to measure them is to conduct a native sorption isotherm test on freshly retrieved core. Without this resort can be made to extended Langmuir or Ideal Adsorption Solution models. These however give different answers and the data from native isotherms would suggest that the range may be even larger. A simple model to gain an idea of the potential range of an isotherm is presented without any theoretical proof but with an empirical correlation.

The second conclusion is that because the extent of the isotherm into the pressure range below atmospheric pressure is generally not known, isotherms should be quoted from atmospheric pressure rather than some theoretical low pressure value which is not measured.

The third conclusion applies to gas contents. These should also be referred to atmospheric pressure of the seam gas rather than some indeterminate partial pressure.

Finally many of the error inducing limitations of gas content measurement are outlined.

Because shales have so much lower sorption characteristic than coals, the measurement of gas content and isotherm is much more difficult. The gas content may however be determined by direct measurement that avoids the problems of pressure measurement and dubious isotherms based on organic content of the rock. This method is outlined by Gray, Singh and O'Brien (2013) and is called gas content without coring or alternatively gas content while drilling.

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