



COALBED METHANE CANISTER DESORPTION TECHNIQUES

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INTRODUCTION

The British Columbia Geological Survey Branch and the Geological Survey of Canada have initiated a joint project to assess the coalbed-methane potential of coal deposits in British Columbia. This project entails participation with private industry to obtain fresh coal samples for desorption from exploration projects throughout the province. Samples are collected from the drill site and undergo a series of desorption measurements that allow an assessment of the *in situ* coalbed methane (CBM) content.

There is a great deal of interest in documenting and exploiting the CBM resource of western Canada both by government agencies and industry. Much of the work involves desorption tests of fresh coal recovered from drill holes. Data from the desorption tests are used to generate resource values that are the starting point for an appraisal of the CBM economic potential of an area. The tests measure the amount of methane released from a coal sample and therefore represent a point estimate of the CBM resource.

The coal sample to be desorbed is sealed in a canister and the incremental desorbed gas is bled off and measured over time. A cumulative gas volume is calculated from the incremental data. In general the procedure is simple and fairly well standardized. There are, however, a number of corrections that must be applied to the measurements and it is not always clear in the literature if they are uniformly applied.

This paper outlines some of the methodologies adopted by the authors for data collection. The paper also presents desorption data from drill-core samples collected from the Quinsam coal mine, 20 kilometres

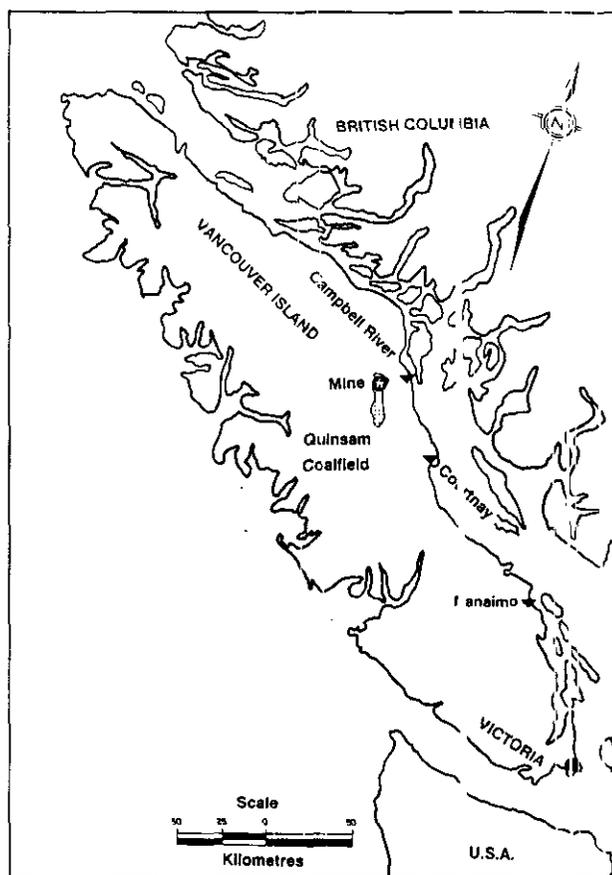


Figure 1: Location map for the Quinsam coal mine on Vancouver Island, British Columbia.

west of the town of Campbell River on Vancouver Island (Figure 1). The data are used to illustrate in more detail the various correction factors that must be applied to the measured data to derive true total desorbed gas contents.

The Quinsam mine has been in operation since 1987, initially as a small surface mine and now as a combined surface and underground operation. It mines high-volatile C bituminous coal for export as a thermal coal. The coal seams are in the Comox Formation of the Upper Cretaceous Nanaimo Group (Kenyon, *et al.*, 1971).

Four seams outcrop in the coal-bearing section. Most of the reserves are in the lowermost seam 1 which averages 2.3 metres in thickness and is mined underground and in surface pits. The overlying seam 2 ranges from 0.30 to 0.55 metre in thickness and is mined at surface only. Seam 3 ranges from 2.4 to 3.4 metres thick and is mined at surface. Seam 4 is thin and is not mined. The stratigraphic separation of seams 1 and 3 is 30 to 60 metres.

Two holes were drilled in 1992 for CBM testing. The first hole (92-34) intersected seam 3 at 141.5 metres and the second hole (92-46) intersected seam 1 at 108.5 metres. Five samples from seam 3 and four samples from seam 1 were desorbed, initially at the mine site and then in Victoria.

FIELD PROCEDURES

The direct method of measuring methane desorbed from coal samples was first described by Bertard *et al.* (1970) and was later adapted by Kissell *et al.* (1973) and Diamond and Levine (1981). The method requires a fresh coal sample to be sealed in a canister. At measured time intervals the gas desorbing into the empty space in the sample canister is released into a manometer and the volume measured at ambient temperature and pressure. The canister is resealed and more gas allowed to desorb. A series of measurements that may span months provides data for a gas desorption *versus* time plot and an estimate of the total desorbed gas in the coal. Samples are usually drill core or drill chips. Both types of samples can be used for gas content determination, although the collection techniques are different.

CORE SAMPLE COLLECTION

Core samples provide the best samples for desorption testing. In order to determine the volume of gas lost prior to sealing the sample in the canister it is important to record five critical times:

- Time of intersection of coal seam with core bit.
- Time of completion of coring of coal seam.
- Time of tripping off bottom of borehole with core barrel.
- Time of core barrel reaching surface.
- Time of coal being sealed in canister.

These times are used in the various procedures for correcting for the lost gas. Details of these correction procedures are presented later in the paper.

When the core is brought to surface the depth of the coal sample should be accurately determined using geophysical logs, core descriptions and driller's logs.

Before putting the core into canisters, broken and fractured core should be reconstructed to represent as best as possible the true core length. The core is striped using a felt marker to provide a record of core piece position. A lithological description of the core is quickly completed to determine sample intervals and to delineate obvious rock partings.

A problem often associated with core samples from conventional oil and gas drilling rigs is the long trip time, which may be up to 2 to 3 hours, required to bring the core barrel to surface. In some coals with fast diffusion rates the lost gas may equal or exceed the cumulative amount of gas desorbed into the canister. Wireline drilling allows the core to be brought to surface much quicker and decreases the impact of the lost-gas correction on the total desorbed gas measurement. Field programs in western Canada using wireline systems have yielded trip times of less than 10 minutes for depths of 600 metres.

CHIP SAMPLE COLLECTION

Chip samples can be used for CBM testing when core samples are not available. This may be because the borehole is being drilled to test a deep conventional hydrocarbon target and coal core samples from shallow horizons are not required. The collection of the chips does not incur additional drilling cost and can provide information about the CBM potential of the seams penetrated by the borehole.

It is difficult to obtain representative chip samples. Chip samples are often contaminated with extraneous non-coal material which can increase as-received ash contents to over 45%. Unrepresentative and high ash contents will lower the measured gas contents. Even when the data are corrected to the accepted *in situ* ash content the gas contents may be too low. This is because inherent ash often appears to decrease gas contents more than would be expected based on dilution effect.

Extraneous rock material can be removed from the sample by floating it in a 1.6 S.G. liquid. The sample can then be air-dried and weighed to determine the true sample weight that theoretically provided the methane gas measured during desorption. This correction takes into account the extraneous non-coal diluant material but it assumes that no material with a specific gravity greater than 1.6 contributed methane to the total gas content of the sample. Current work by the authors addresses the adsorptive capability of coal and coaly material at differing specific gravities, to determine a specific gravity threshold that may be used for chip samples.

Another problem associated with chip samples is the small and variable grain size of the sample. Drilling

processes often produce chip samples that are less than 20 mesh in size. In order to collect a representative sample all the coaly material, including the fine particles, must be collected. The fine particles are often held in suspension in the drilling fluids and do not arrive at the surface at the same time as the chips. Collection of drilling fluids and the suspended fine-coal produces a sample with a high water content. Excess water in the sample tends to inhibit the desorption process.

Corrections for "as-received" sample weight versus "air-dried" sample weight can be made to correct for the excess moisture, but the significance of the presence of excessive amounts of water in the canister on the desorption rates and overall desorption volumes has yet to be quantified. Because chip samples as collected may contain excess water, it is critical that an accurate air-dried weight is obtained after desorption by carefully removing all the sample from the canister.

Determination of sample depth for chip samples is often difficult. Although the depth of penetration of the coal seam can usually be determined accurately using drilling breaks or marker horizons, the actual source of the coal chips may be unknown. If parts of the coal seam are friable or sheared, then these parts may cave into the hole increasing the proportion of coal collected from the intervals, consequently the sample may not be representative of the whole seam. Similarly, if multiple seams are drilled, caving from upper seams can contaminate lower seam samples. These effects can be minimized by drilling fixed short intervals and cleaning the hole of cuttings between each interval. These techniques have been successful in ensuring less contamination of the sample recovered from the shale shaker. Selecting the proper drill bit to maximize the chip size may improve the grain size of the sample but the cost of tripping in and out of the hole to change bits may be costly.

DATA COLLECTION TIME INTERVALS

It is important to make sufficient measurements in the early stages of desorption in the canister in order to accurately determine lost-gas volumes and to define the shape of the desorption curve. The optimum time increments used by the authors to measure desorbed gas are:

- Initially every 2 minutes for the first 30 minutes;
- every 5 minutes from 30 to 60 minutes;
- every 10 minutes from 60 to 120 minutes;
- every 30 minutes from 120 to 360 minutes;
- every 60 minutes from 360 to 720 minutes;
- further times are defined by desorption rate.

These measurement increments are defined for coals from the Mist Mountain Formation, which have high

diffusion rates. For coals from other formations the time increments may be adjusted to reflect the amount of gas being desorbed; *i.e.* if less than 10 cubic centimetres of gas are desorbed for any time increment, the interval between readings can be lengthened.

DATA PROCESSING

There are a number of important corrections and estimations that have to be made during and after data collection in order to estimate the true amount of gas desorbed from the coal.

LOST-GAS CORRECTION

The first correction estimates the amount of gas that escapes from the coal sample by desorption prior to sealing it in the canister. Generally samples are freshly drilled core or chips that are placed in the canister as soon as they reach surface. Unfortunately some gas desorbs from the coal as it is brought up the hole and more desorbs at surface before it is sealed.

There is also gas in the macroporosity and fractures in the coal. This is the free gas component which exists either as a gas or as gas in solution in water. Free gas is compressed by an amount dependent on the hydrostatic pressure in the coal seam. The amount of gas in solution increases with pressure but the solubility of methane in water is generally low. The volume of free gas at surface can be estimated using the universal gas law. Free gas is released into the drilling fluid as the pressure decreases. It is usually a minor component of the total gas. Rightmire (1984) provides some data referred to as free-gas estimates that range from 5 to 17% of the total gas in the samples. Generally the amount of free gas, which will increase with hydrostatic pressure and void porosity and decrease with increasing temperature, can only be estimated from production wells. If the gas-filled porosity is 2% then at 1000 metres the free gas is about 1 cubic centimetre per gram.

There is an important distinction between free gas and lost gas. Lost gas is estimated using desorption theory applied to desorption data measured on the coal after it is placed in the canister. Measurements of lost gas may be influenced by the amount of free gas in the *in situ* coal but generally they do not include an estimate of the amount of free gas. The presence of evolving free gas in the coal as it is brought to surface will have minimal effect on the pressure acting on the coal. It will therefore have minimal effect on the desorption that is also occurring as the coal is brought to surface

Diamond and Levine (1981) provide an empirical method for estimating the amount of lost gas, now generally referred to as the U.S. Bureau of Mines method. They plot the square-root of time (X axis) against cumulative gas desorbed (Y axis) for the first few measurements. The data usually plot on a straight line, implying that a linear projection backward in time for the appropriate time prior to sealing the sample (lost time) will provide an estimate of the lost gas. This method is most applicable for short holes recovering core samples that tend to desorb more slowly than chip samples. In this situation the lost time is generally less than 30 minutes and the lost gas makes up a small percentage of the total desorbed gas volume (<20%).

It is an assumption of the U.S. Bureau of Mines method that the desorption behavior of the coal is similar before and after sealing it in the canister. This may be true for the period, "coal at surface to coal in canister", but is unlikely to be true for the period, "coal cut by drill bit to coal reaching surface".

A more complicated method of measuring the lost gas was introduced by Smith and Williams (1984). They used the unipore diffusion model originally derived by Wheeler (1951), which is applicable to the early stages of desorption, and adapted it to take account of a range of depths (pressures). This model predicts that for the initial stages of desorption the gas desorbed is proportional to the square-root of time. Obviously the unipore model is assumed to apply in the U.S. Bureau of Mines method though it is not emphasized in its reports. Smith and Williams integrate the unipore model over the range of decreasing pressures affecting the sample as it comes up the hole. They do not consider the effect of the temperature change that the coal experiences as it is brought from *in situ* temperature to surface temperature.

The final calculation of lost gas is made with the help of graphs that use the total lost time and the time at surface prior to sealing as components. It should be understood that if the data do not plot on a straight line on a cumulative "gas" *versus* "square-root time" plot then the unipore model is not describing the desorption process and neither the U.S. Bureau of Mines nor the Smith and Williams method is likely to give an accurate estimate of the lost gas. Even if the data obtained after the coal is sealed in the canister plot on a straight line, indicating that desorption in the canister can be modelled by the unipore model, this still does not mean that diffusion before entering the canister obeyed the unipore model.

The Smith and Williams and U.S. Bureau of Mines methods both appear to under-estimate the amount of lost gas based on laboratory experiments (Olszewicki and McLennan, 1992). The Smith and Williams method provided the best predictions, but the predicted lost-gas values had to be multiplied by factors ranging from 1.2 to 1.7 to bring them up to the actual lost-gas values.

Desorption is faster at higher temperatures, therefore a sample that cools as it is brought to surface will lose less gas than one that arrives at surface without cooling. Neither of the two lost-gas estimation methods considers varying temperatures and it is not clear if varying temperature will cause them to over or under-predict the amount of lost gas.

Once the sample is in the canister it should be desorbed at reservoir temperature to simulate the conditions of a production well. This means keeping the canister in a temperature controlled box which may be difficult if the canisters have to be moved sometime during the weeks or months that they take to desorb.

In general it appears that any lost-gas measurement is an under-estimation of the sum of the gas desorbed from the sample and free gas lost from the macroporosity in the sample prior to sealing it in the canister.

The cumulative gas values used for predicting the lost-gas component should be corrected back to standard temperature and pressure conditions (STP) as described in a subsequent section. This may not be as simple as it seems for the first few measurements. If the canister is moved from the drill site to a base camp then there may be significant changes in temperature and pressure. The interior of the canister equilibrates to atmospheric pressure quickly once the canister is opened for a measurement. The same is not true for temperature. It may take tens of minutes before the temperature of the coal in the canister and of the gas bled from the canister are the same as room temperature (or heat controlled box temperature), which is the temperature recorded. Yet measurements are being made at intervals of a few minutes. Ideally the manometer used to measure the gas and the canister should be at the same temperature, otherwise it is difficult to report a true gas volume at STP.

Desorption is an endothermic process which will cool the coal below ambient temperature. When the methane is released into the manometer it expands adiabatically, causing a further drop in temperature. For samples containing a lot of gas desorbing into a canister with very little empty space, care should be taken to ensure that the methane volume released into the manometer is at ambient temperature. In some cases non-linear lost-gas plots may be the result of inappropriate temperature corrections to the initial measurements and not problems with the diffusion model.

Preliminary checks appear to indicate that the internal temperature of the Quinsam coal sample canisters equilibrated quite quickly with the external temperature. The samples were recovered from shallow depth where the rock temperature is probably less than 25°C. For this reason the canisters were not put in a temperature controlled box. The lost-gas corrections for the Quinsam coal samples were calculated using the U.S.

TABLE 1
QUINSAM DATA LOST-GAS CALCULATION AND DESORPTION CURVE-FITTING CONSTANTS

Sample	Initial desorption		Lg(Na)		DX10 ⁻⁴		desorption curve		T(.5)
	To	Na	Lg(Na)	Lg(2)	To	Na	R ²		
92-34-2	48	2.4	156	126	66	2.1	2.0	0.85	11.3
92-34-3	82	3.2	163	132	19	5.3	1.9	0.92	29.8
92-34-4	67	3.2	207	132	21	3.4	2.0	0.95	25.2
92-34-5	65	2.0	176	126	14	6.1	2.0	0.94	30.3
92-34-6	23	4.0	641	N/A	610	7	2.3	0.87	1.7
92-46-1	58	1.3	61	88	2	145	1.9	0.73	82.3
92-46-2	52	1.3	56	96	2	119	2.0	0.83	55.8
92-46-3	35	1.9	120	104	31	36	3.1	0.86	14.7
92-46-4	43	2.2	194	116	36	26	2.3	0.79	12.3

Initial desorption: constants To and Na calculated from linear TNa versus cumulated desorbed gas at STP plot for first few hours

Lg(2) = lost gas calculated using Na=2

T(.5) = total time in hours for half of the gas to be desorbed; calculated using desorption data.

Desorption curve: constants To and Na calculated by fitting Airey equation to desorption curve except for first two and last two points

Airey equation: is $V = V_t \times (1 - \exp\{-T/To\}^{1/Na})$

derivation

$$\text{if } dV/dT = Vr \times \lambda$$

$$\text{where } \lambda = (A \times Tn)$$

Vr = gas remaining at time T where T is time in hours from cutting coal

$$\text{Then } \log_e((dV/dT)/Vr) = \log_e(A) + n \times \log_e(T)$$

intercept of line is $\log_e(A)$ and slope is n

integration gives $V = V_t \times (1 - \exp\{-(A/(1+n)) \times T^{(1+n)}\})$

Airey constants are calculated from $Na = 1/(1 - \text{slope})$

$$To = ((1 + \text{slope}) / (2.718 \log_e(A)))^{Na}$$

Bureau of Mines and Smith and Williams methods applied to cumulative gas volumes corrected to STP.

Most of the data produce reasonably good linear plots of square-root time versus cumulative gas for the first 10 to 15 measurements extending over 2 to 4 hours.

The U.S. Bureau of Mines method predicted lost-gas values ranging from 88 to 132 cubic centimetres with one exception (Table 1). The drilling times used to calculate the lost time are reported in Table 2. Two estimates of lost time are possible for each sample. If the hole is dry then it is assumed that the gas starts to desorb as soon as the coal is cut. If the hole is filled with water then it is assumed that the gas starts to desorb when the core is half way up the hole.

Hole 92-34 was dry and the lost gas was estimated using the dry lost-time estimate (Table 2). Hole 92-46 was water filled and lost gas was estimated using the wet lost-time estimates (Table 2). For comparison purposes the lost-gas calculations for samples from hole 92-34 were made using both dry and wet lost-time estimates. The longer dry lost-time estimates increased the lost-gas calculation by about 15%.

All samples with the exception of 92-34-6 produced reasonably linear cumulative gas (STP) versus square-root time plots. To check the U.S. Bureau of Mines method more closely plots were made where the Y intercept is the projected lost gas and the X axis is the number of points used to define the line (Figures 2 and 3). All predictions started with the first three measurements and then incorporated additional measurements up to a maximum of fourteen. The plots illustrate that for samples 92-34-6 and 92-34-2, the lost-

gas prediction increases as the number of points decreases and for most other samples it decreases as the number of points decreases; only sample 92-34-4 seems to fit the unipore diffusion model closely.

TABLE 2
QUINSAM SAMPLE COLLECTION DATA

HOLE	DATE	SEAM	METRES		ELEVATION
			EASTING	NORTHING	
H92-34	1/10/92	3	32-284	5532297	335
H92-46	16/10/92	1	32-854	5534322	317

HOLE	SEAM	TIMES		LOST TIME	T25%
		FROM-TO	CUT TRIP SURFACE		

HOLE 92-34 SEAM 3 SAMPLES 92-34-2 (TOP) TO 92-34-4 (BOTTOM)

141.9-142.3	14.46	14.50	14.51	14.57	11	4.13
142.3-142.7	14.46	14.50	14.51	14.58	12	8.92
142.7-143.1	14.46	14.50	14.51	14.59	13	8.48
143.1-143.5	14.46	14.50	14.51	14.00	14	8.93
145.3-145.7	15.02	14.09	14.11	14.15	13	0.98

HOLE 92-46 SEAM 1 SAMPLES 92-46-1 (TOP) TO 92-46-4 (BOTTOM)

108.5-108.9	14.57	15.01	15.02	15.10	13	7.16
109.4-109.8	14.57	15.01	15.02	15.08	11	15.2
111.5-111.9	14.09	15.14	15.15	15.19	10	3.95
111.9-112.3	14.09	15.14	15.15	15.20	11	3.75

LOST TIME DRY = Lost-time minutes assuming dry hole

LOST TIME WET = Lost-time minutes assuming water-filled hole

CUT TIME = Time (hours.minutes) drill cuts coal

TRIP TIME = Time (hours.minutes) core starts to surface

SURFACE TIME = Time (hours.minutes) coal reaches surface

SEAL TIME = Time (hours.minutes) sealed in canister

SMITH AND WILLIAMS TERMS

Ts = Cut time to seal time

Td = Cut time to surface time

T25% = Time from cut time to time for 25% desorption into canister

Note this is not time for 25% desorption because it does not

consider the lost-gas component

SURFACE-TIME RATIO = (Ts - Td) / Ts

LOST-TIME RATIO = Ts / T25%

The Smith and Williams method is difficult to apply when the lost time is short. The correction curves in Smith and Williams paper are linear at low values of lost-time ratio and the volume correction factor can be estimated from

$$VCF = (LTR) \times [(STR) \times .127 + .107]$$

where

VCF = volume correction factor

LTR = lost-time ratio

STR = surface-time ratio

These terms are defined in Table 2. In all cases Smith and Williams predicted very low lost-gas volumes.

Another approach to estimating the volume of lost gas is investigated in this paper. Airey (1958) fitted an empirical curve to desorption data. Feng and Lu (1981) fitted the Airey equation to desorption data from coal samples from southeast British Columbia and achieved a good fit. The equation proposed by Airey has the form;

$$V = V_t \times (1 - \exp\{-T/To\}^{1/Na})$$

where V is the gas desorbed up to time T, Vt is the total gas available for desorption, To is a constant with the units of time and Na is a dimensionless constant. This equation has the general form of a radioactive

exponential decay equation in which the decay constant is a time dependent term. Decay equations are based on the premise that the amount of daughter generated in any given time interval is proportional to the amount of parent remaining. The equivalent for desorption data is;

$$dV/dT = D \times V_r \text{ where } D \text{ is a desorption constant at time } T.$$

dV/dT is incremental desorbed gas.

V_r is gas remaining at time T .

If $D = A \times T^n$ then a plot of

$\log_e[(V/dT)/(V_r)]$ versus $\log_e(T)$ will provide a straight line having a slope (sl) whose value is n and Y intercept (in) whose value is $\text{Log}(A)$. This plot can be generated without knowing the lost-gas component because it requires only knowledge of the gas left to desorb.

Integration of $dV/dT = A \times T^n \times V_r$ provides

$$V = V_t \times [(1 - \exp[-K \times T^{(1-n)}])] \text{ where } K = A/(1+n).$$

This is similar to the Airey equation but is developed in a way that makes it easier to derive the constants A and n which can easily be changed to the Airey constants, N_a and T_o .

$$N_a = 1/(1+sl) \text{ and } T_o = [(1+sl)/(2.718^{in})]^{N_a}$$

Figure 4 is a \log (time) versus $\log [(dV/dT)/V_r]$ plot of data from sample 34-6 used to calculate the Airey constants T_o and N_a . The first and last two points were not used in the regression analysis. The constants derived from Figure 4 were used to fit the predicted desorption curve through the measured desorption data for sample 34-6 as illustrated by Figure 5.

Airey states that V_t is proportional to T^{1/N_a} for values of T much less than T_o ($T \ll T_o$). The relationship is

$$V = V_t \times (T/T_o)^{1/N_a}$$

This is based on his empirical equation that fits desorption curves to data from experimental samples with no lost-gas component. The constant T_o is proportional to the square of particle size and inversely proportional to initial methane pressure (depth of burial) (Airey, 1968, Figure 3). Values of T_o in this paper are in the range from 7 to 145 hours (Table 1) and indicate effective particle sizes ranging from about 1 to 5 millimetres. Lost-gas projections are made over the first 7 hours or less to ensure that the condition of $T \ll T_o$ is met.

The fact that V_t is proportional to T^{1/N_a} is important because it means that desorption data will plot on a straight line if the X axis is $(\text{time})^{1/N_a}$. The conventional procedure using the unipore model plots $(\text{time})^{1/2}$ on the X axis for lost-gas estimates. Empirical data indicate

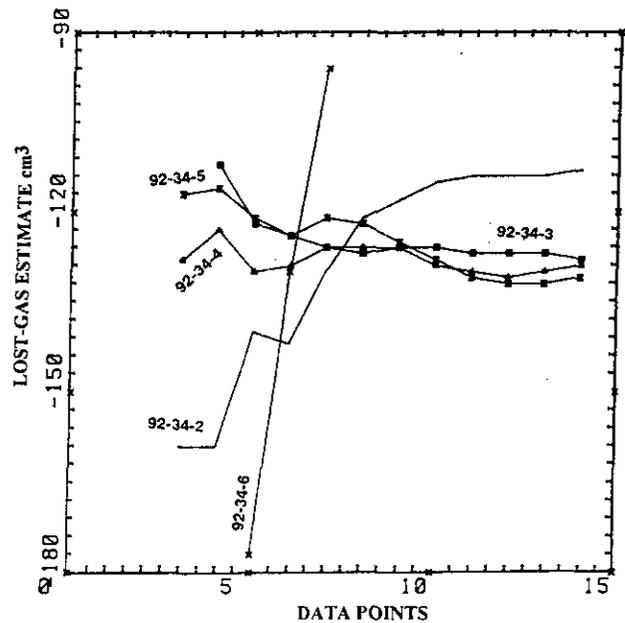


Figure 2: Lost-gas estimate versus number of data points, hole 92-34.

that the power term varies based on the coal. Airey found no relationship between N_a and size, moisture or initial pressure. In this study values of N_a range from 1.3 to 4 (Table 1) and in the study by Feng and Lu (1981) N_a values range from 2.4 to 2.8. Higher values of N_a seem to correlate with shearing and rapid initial desorption.

Figures 2 and 3 indicate that a value of 2 for N_a may not provide the best linear plot. It is easy to adjust values of N_a until the sample tracks in Figures 2 and 3 are horizontal. If the lost-gas predictions decrease as the number of points decreases then the value of N_a is less than 2 and if they increase as the number of points decreases then the value of N_a should be greater than 2. Values of N_a were calculated to achieve this are presented in Table 1 and new lost-gas estimates made. The values of T_o (Table 1) were then calculated using V_t (lost plus desorbed gas) and the slope of the line V versus T^{1/N_a} .

Using values of N_a greater than 2 increases the predicted amount of lost gas and could result in the lost-gas predictions of Olszewicki and McLennan (1992) agreeing more closely with their measured data. A change of N_a from 2 to 3 approximately doubles the lost-gas prediction.

Values of N_a and T_o can also be calculated using plots of $\log(dV/V_r)$ versus $\log(\text{time})$ which exclude the first and last few points. This method provides an easy way of checking the fit of the desorption data to an Airey equation.

For the Quinsam data the linear plots have R^2 values ranging from 0.83 to 0.95 (Table 1). Values of N_a and T_o calculated by this method differ somewhat from

values calculated using the initial part of the desorption curve and V versus T^{1/N_a} plots. This may indicate that a single Airey equation cannot explain the complete desorption curve or that for this particular dataset, the composition of the gas is changing over time and different diffusion constants are coming into play.

An alternate method of predicting lost gas using the Airey equation was tried on the Quinsam data. This method attempts to use the shape of the mid-part of the desorption curve. The total desorbed gas (V_t) is not known because it includes the lost gas but V_t can be calculated by using pairs of data points thus:

$$\begin{aligned} \text{point 1 } & V_1 + L_g = V_t \times (\exp[-(T_1/T_0)^{1/N_a}]) \\ \text{point 2 } & V_2 + L_g = V_t \times (\exp[-(T_2/T_0)^{1/N_a}]) \end{aligned}$$

where L_g is the unknown lost-gas component. Subtracting gives:

$$V_t = (V_2 - V_1) / (\exp[-(T_1/T_0)^{1/N_a}] - \exp[-(T_2/T_0)^{1/N_a}])$$

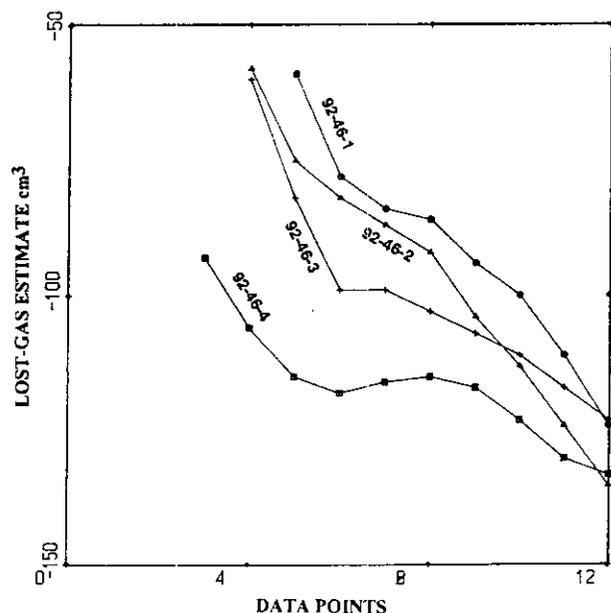


Figure 3: Lost-gas estimate versus number of data points, hole 92-46.

Numerous data pairs can be used to calculate values of V_t and the results averaged. The values of T_0 and N_a are determined from a $\log_e((dV/dT)/(V_t))$ versus $\log_e(T)$ plot. This approach provides an averaged estimation of the total gas desorbed based on the shape of the desorption curve and the amount of gas remaining. The lost-gas component is the difference between V_t calculated and the cumulated desorbed gas measured.

Applying this approach to the Quinsam data, the calculated V_t values were generally greater than the cumulative desorbed gas by an amount similar to the previously calculated lost-gas value. However, the errors associated with the calculated V_t values were large.

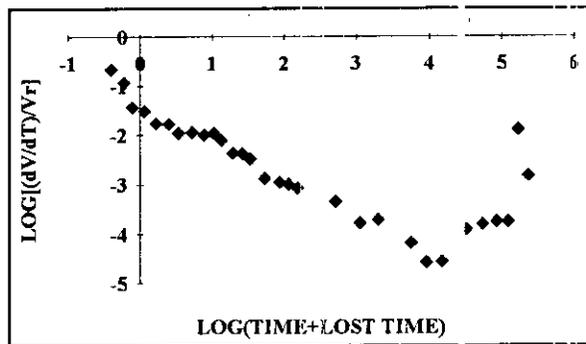


Figure 4: Plot of $\log(\text{time})$ versus \log desorption data for Quinsam sample 34-6 used to calculate Airey constants.

It is not clear if this approach is theoretically sound but it does seem that in some cases the Airey equation may provide a rough estimate of the maximum possible lost-gas component. The approach needs to be tried on a larger data set to see if it will be useful. It is interesting because it may estimate the maximum lost-gas component based on the form of the desorption curve and not on the conditions that existed prior to sealing the sample in the canister. Obviously the sample must be desorbed at a constant temperature.

Fresh coal adsorbs oxygen and this process may influence the initial desorbed methane measurements. When the coal is brought to surface the coal adsorbs oxygen from the empty space in the canister, causing a reduction in pressure. The coal sample is moving towards a new equilibrium based upon the new pressure regime and a more complex mixture of gasses. Methane, oxygen, carbon dioxide and nitrogen all have different adsorption constants on the coal and different distribution coefficients for the gas to solid phases. Methane desorption, in part stimulated by adsorption of oxygen, counters the reduction in pressure. But when the volume of methane is measured in a manometer at atmospheric pressure it will be under-estimated. This problem can be countered by flooding the canister with nitrogen to remove the oxygen, but nitrogen inhibits desorption of methane and may also confuse the results. The Quinsam samples were not flooded with nitrogen because it was felt that all the implications were not understood.

DEAD-SPACE CORECTION

Desorbed gas volumes are usually reported at standard temperature and pressure (288° K and 101.325 kilopascals pressure). The correction from ambient conditions to STP uses standard relationships (Table 3) and the correction is easy if ambient conditions do not

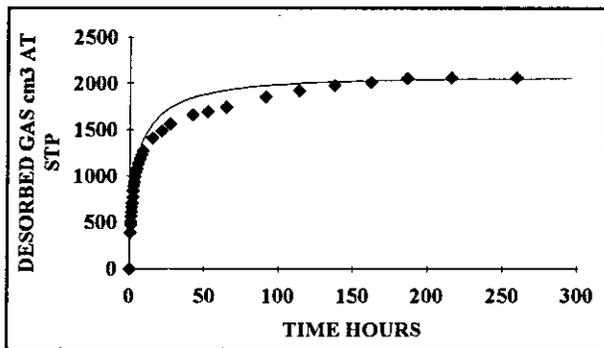


Figure 5: Desorption data for Quinsam sample 34-6 with predicted desorption curve using Airey equation.

change from measurement to measurement. However if conditions change because of change in elevation, weather or temperature, an additional correction must be applied based on the empty space in the canister and the magnitude of the change in ambient conditions. This is referred to as the canister dead-space correction.

It is not clear if all published desorption data are corrected for canister dead space. In simple terms the empty space in the canister is occupied by pre-existing gas and gas desorbed since the last measurement when the canister was opened. If ambient conditions change then the existing gas will occupy a different volume at the new ambient conditions. The change in volume must be added to or subtracted from the volume of new gas measured.

An equation for calculating the dead-space correction is outlined in Table 3. A simple graph to estimate the dead-space correction at ambient conditions, once the dead-space volume is known, is presented on Figure 6. Obviously it is important to minimize and measure the dead space in the canister. The canisters used by the authors have spacer rings to fill in space if the core sample diameter is much less than the inside diameter of the canister.

A number of ways of calculating the dead-space volume (DS) are described here:

1. Weigh the coal sample and use an estimate of specific gravity to calculate its volume. Find the dead-space by subtracting coal-sample volume from canister volume

2. Use a sensitive pressure gauge attached to the canister to measure the pressure (P1) prior to releasing the gas then use the relationship:

$$P1 \times DS = Pa \times (M+DS);$$

where Pa = atmospheric pressure, M = manometer volume displaced by the gas.

3. When the sample has finished desorbing open the canister to the atmosphere; seal it and then cool it in a refrigerator. When cool attach the canister to the

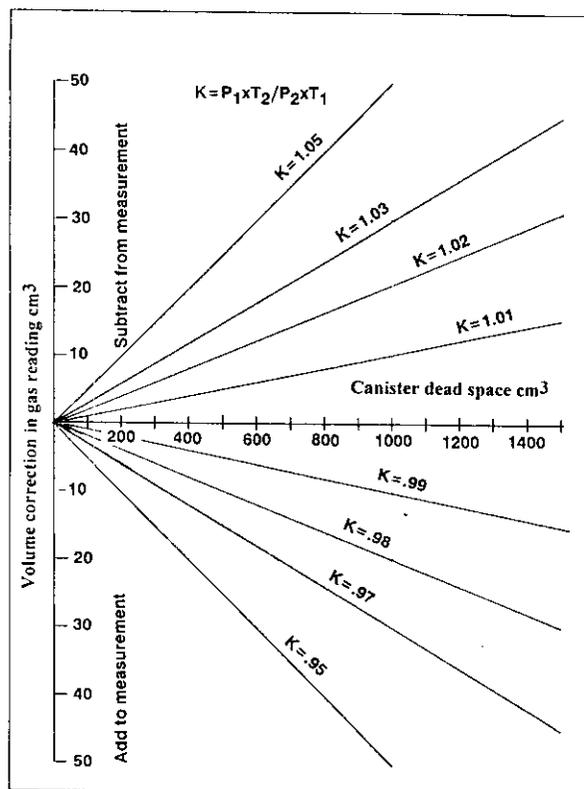


Figure 6: Dead-space correction based on changes in temperature, pressure and volume of dead-space in canister

manometer and measure the decrease in volume at atmospheric pressure. Use the relationship;
 $(DS)/(273 + \text{room temperature}) = (DS-M)/(273 + \text{fridge temperature})$
to calculate the dead-space volume.

4. After making a measurement use the manometer to pressure the canister with methane or air. Raise the water reservoir bulb above the water level in the burette while the manometer is still attached to the canister. This forces the methane or air back into the canister. Measure the difference in water levels (h in cm). This value represents the pressure above atmosphere forcing the methane or air back into the canister. Measure the volume of gas (M) returned to the manometer at atmospheric pressure (Pa). Calculate the dead space using:

$$DS \times (Pa + Ph) = [(DS + M) \times Pa]$$

$$DS = M \times Pa / Ph$$

$$Ph \text{ (millibars)} = 980.62 \times 0.998 \times h / 1000,$$

where 0.998 corrects for the density of water at room temperature.

Method four has a number of advantages. Dead-space calculations can be made after each desorbed gas measurement and a number of measurements averaged. The method requires no additional equipment and is direct. Lastly it measures the same volume as the desorbing gas occupies; rather than measure a liquid-

filled volume or a theoretical volume. The method was used on the Quinsam samples and appeared to work well. If oxygen adsorption is a problem the procedure can be carried out after the coal has finished desorbing and before it is removed from the canister.

WATER VAPOUR CORRECTION

The water vapour correction is required to correct for the presence of water vapour in the canister. In most cases the dead space in the canister is saturated with water vapour because there is excess water in the coal sample. The vapour pressure of water is temperature dependent and ranges from 0.5 to 7.5 kilopascals in the temperature range 0 to 40°C. The volume of gas should be calculated using atmospheric pressure minus partial pressure of water vapour times manometer reading. Applying a water vapour correction reduces the measured gas volume at STP by about 2.5%. The resultant gas volume is dry gas at STP.

TABLE 3
PROCEDURE FOR CORRECTING MEASURED GAS VOLUMES TO DRY GAS AT STP

Conditions
Vc = Canister volume
DS = empty space in canister not occupied by sample (dead-space)
Canister opened to atmosphere at time Tm1
Conditions at Tm1
Atmospheric pressure = Pa1 Temperature = T1
Desorbed gas measured at time Tm2 and canister equilibrated with existing atmospheric conditions Conditions at Tm2
Atmospheric pressure = Pa2 Temperature = T2
Apparent volume of desorbed gas at existing atmospheric conditions = Vg
Dead-Space Correction
$(DS \times Pa1) / T1 = (DS - Vc) \times Pa2 / T2$
This equation expresses the apparent change in volume (Vc) of the pre-existing gas in the canister. This change will affect the value of Vg, the apparent volume of new gas desorbed from Tm1 to Tm2, measured at ambient conditions existing at Tm2.
$DS = (DS - Vc) \times (Pa2 \times T1) / (Pa1 \times T2)$
$DS = (DS - Vc) / K$ Where $K = (Pa1 \times T2) / (Pa2 \times T1)$
$Vc = DS \times (K - 1)$
Vc can be calculated using a simple nomograph (Figure 6)
The actual volume of gas desorbed at Tm2 is $Vgc = Vg - Vc$
STP Correction
Volume Vgc must be corrected to STP conditions
$Vgc(STP) \times P(STP) / T(STP) = Vgc \times Pa2 / T2$
$Vgc(STP) = (Vg - Vc) \times Pa2 \times T(STP) / (T2 \times P(STP))$
P(STP) = 1013.25 millibars T(STP) = 273 + 15 °C
Moisture Correction
If DS in the canister has 100% humidity then a further correction to dry gas at STP must be made
Pw2 = the partial pressure of water vapour at T2 Actual pressure of dry methane at T2 = Pd2
Pd2 = Pa2 - Pw2
$Vgc(STP \text{ dry}) = (Vg - Vc) \times Pd2 \times T(STP) / (T2 \times P(STP))$

CORRECTION TO STP

Finally, the measured gas volume must be converted to the equivalent volume at standard temperature and pressure using the general relationship for ideal gases:

$$P_1 \times V_1 / T_1 = P_2 \times V_2 / T_2$$

The accuracy of the STP correction can be monitored by checking the apparent volume of gas evolved from an empty canister as weather conditions change from day to day. After all corrections are applied the desorbed volume should be zero. If it is not, the corrected gas volumes desorbed from the samples are probably also in error.

SAMPLE WEIGHT AND BASIS FOR REPORTING DATA

The gas contents are expressed in terms of: as-received sample, air-dried sample, dry ash-free sample *in situ* sample or mineral-matter free sample. Data cannot be calculated to any of these bases without using a measurement of sample weight and corresponding moisture content as a starting point.

It is possible to estimate the sample weight by weighing the canister with and without the sample, but without knowing the moisture content of the sample the weight cannot be converted to a dry weight. The as-received moisture reported by an analytical laboratory subsequent to desorption may be similar to the moisture existing in the canister during desorption, when the canister plus sample was weighed, if all the moisture was removed from the canister and the sample did not dry while being shipped to the laboratory. In this case the gas content is calculated on an as-received basis and then adjusted to other bases. The best methods to ensure that all the sample is removed from the canister and shipped to the laboratory and that the laboratory reports a sample weight on an air-dried basis. Gas content can be recalculated to a dry ash-free basis by using the appropriate moisture and the ash content expressed at that moisture.

If the data are to be used for resource calculations, the gas content should be recalculated to an *in situ* base using an estimate of the *in situ* moisture which will be similar to but a little higher than the equilibrium moisture content of the sample.

Often data are reported on a mineral-matter free basis (dmmf). Whereas calculations to the other bases are exact, a calculation to a dmmf basis requires assumptions. Before the data can be corrected the weight loss when the mineral-matter is converted to ash, must be known. Often the weight of mineral matter in the sample

is estimated from the weight of ash using the Parr equation, (Parr, 1932). The equation $[(1.08 \times \text{ash} + 0.55 \times \text{total sulphur})]$ predicts values ranging from 1.08 to 1.25 for the weight ratio (mineral matter/ash) depending on the ash and sulphur content. The Parr equation assumes that all sulphur is present as pyrite and is converted to iron oxide, and that the ash chemistry is constant. The mineral matter to ash ratio can be measured directly using plasma ashing. The results of plasma ashing five samples from Telkwa (Ryan, 1991) indicated that the mineral matter/ash ratio is about 1.16 which is higher than that predicted using the Parr equation.

An alternative method of estimating the ratio is to plot volatile content (daf) versus ash (db). As the ash content increases, VM (daf) values increase because of the addition of volatiles from the ash (H_2O , CO_2 and SO_2). The slope of the plot provides an estimate of the mineral matter/ash ratio. For Quinsam data the slope is 0.18, indicating a mineral matter/ash ratio of 1.18.

The the dmmf gas contents reported in Table 1 are calculated using the Parr equation and are probably low based on the above discussion. As most measured and theoretical adsorption curves are expressed on an as-received or daf basis the dmmf calculation is not critical. Normally, for a coal with 20% ash, a concentration expressed on a dmmf basis will be less than 5% higher than the same concentration expressed on a daf basis. The difference will be greater for samples with a higher ash content. If it is necessary to quote data on a dmmf basis then the method of making the correction should be justified in terms of the chemistry of the particular coal being studied.

DESORPTION CURVES

Nine samples from Quinsam, each consisting of 40 centimetres of core, were desorbed at room temperature. The desorption curves for the samples from hole 92-34 are on Figure 7 and the curves for samples from hole 92-46 are on Figure 8. The gas contents are expressed as cubic centimetres per gram daf and at STP with a water vapour correction applied. The cumulative gas content totals are provided in Table 4. Coal quality information for the samples is in Ryan and Dawson (1994, this volume).

The samples of seam 3 (hole 92-34) were desorbed for 15 days, at which time the canisters were re-used for the seam 1 samples (hole 92-46). At this time only one seam 3 sample had finished desorbing and the last increment of desorbed gas from the other seam 3 samples had to be estimated by projecting the cumulative desorption curves. In all cases the correction was less than 250 cubic centimetres. Seam 1 samples were

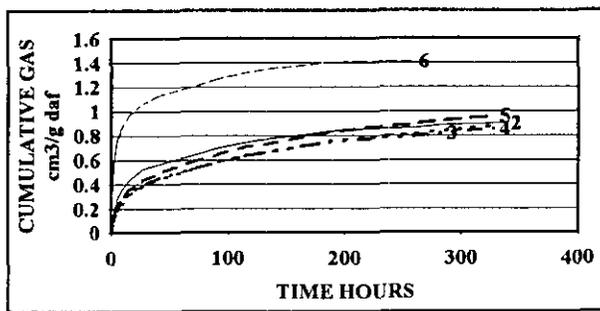


Figure 7: Desorption curves for samples from hole 92-34 (dry ash-free basis).

desorbed for periods ranging from 44 to 54 days. At this time the gas being desorbed after correcting for variations of pressure and temperature between readings was less than 5.0 cubic centimetres per day.

Under ideal conditions, if the coal is saturated, the gas contents of samples on a dry ash-free basis from throughout the seam should be similar. This assumes that the petrography of the samples is similar. Gas contents are similar except for the footwall samples from each seam. These samples contain more gas and are noticeably more crushed than the other samples. Their smaller size-consist probably allowed them to scavenge gas more easily.

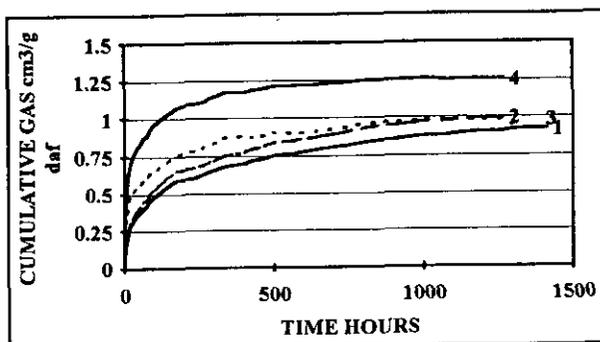


Figure 8: Desorption curves for samples from hole 92-46 (dry ash-free basis).

IN SITU SPECIFIC GRAVITY

Desorption data are often collected as one component of a resource evaluation and the data will probably eventually be expressed as gas content per *in situ* tonne of coal. It is therefore useful to be able to estimate the *in situ* specific gravity versus ash

TABLE 4
SUMMARY DESORPTION DATA CORRECTED FOR CANISTER DEAD SPACE
AND CONVERTED TO STP DRY GAS

SAMPLE	L GAS cm ³ /g	D GAS cm ³ /g	S GAS cm ³ /g	T GAS cm ³ /g	T GAS daf/g
HOLE 34 SEAM 3					
92-34-2	0.0441	0.3919	0.0053	0.441	1.014
92-34-3	0.0516	0.7127	0.0332	0.797	0.978
92-34-4	0.0551	0.7239	0.0676	0.847	0.997
92-34-5	0.0562	0.8694	0.0919	1.018	1.121
92-34-6	0.1482	0.9456	0.0000	1.094	1.632
HOLE 46 SEAM 1					
92-46-1	0.0402	0.7906	0.0000	0.8308	0.971
92-46-2	0.0436	0.8685	0.0000	0.9121	1.068
92-46-3	0.0633	0.8091	0.0000	0.8724	1.057
92-46-4	0.0574	0.9046	0.0000	0.9620	1.331

ABBREVIATIONS

- L GAS = Gas lost prior to sealing sample in canister
- D GAS = Gas desorbed into canister.
- S GAS = Estimate of gas desorbed after samples removed from canister.
- T GAS = Total estimated gas desorbed from samples.
- T GAS daf = Total gas on a dry, ash-free basis per dry gram.

relationship of the coal. The *in situ* specific gravity of core samples can be estimated using the dead-space volume, canister volume, and weight of sample in the canister. If there is not much excess water in the canister this provides sufficient information to calculate a specific gravity for the sample which will be a reasonable estimate of the *in situ* specific gravity. If the samples have a range of ash contents then an ash *versus in situ* specific gravity calibration curve can be constructed.

The specific gravities of the Quinsam samples were calculated using this method and they varied from 1.44 for a 54% ash to 1.2 for an 8% ash sample.

DIFFUSION RATES

The desorption curves provide information on the diffusion characteristics of the coal. Quantifying the rate of desorption is important as one of the parameters used to estimate the productivity of a potential coalbed methane well.

Airey introduced the constants T_0 and N_a . Smith and Williams (1983) quantify the rate of desorption using the effective diffusivity constant (D_f) calculated from the slope of the lost-gas plot using:

$$D_f = (\text{slope}^2 \times \pi) / (Vt^2 \times 36)$$

The effective diffusivity constant of Smith and Williams is derived from the diffusion equation of Barrier and Brook (1953) in which $D_f = D/R_0^2$; D is the diffusion constant in Ficks equation and R_0 is a particle size term that does not necessarily correspond with the visual particle size.

Values of T_0 , N_a and D_f are reported in Table 1 for the Quinsam data set. The T_0 and D_f values decrease

and the N_a values increase as the amount of shearing in the coal increases. There is also an increase in Hardgrove index with shearing.

Another measure of diffusion is the time taken for the coal to diffuse half or one quarter of its methane, including the lost-gas component. This value can be derived from the desorption data or estimated from the Airey equation fitted to the data using:

$$T_{1/2} = -T_0 \times \log_e(.5^{N_a}) \text{ or } T_{1/4} = -T_0 \times \log_e(.25^{N_a})$$

The values in Table 1 were calculated from the desorption data. Values of $T_{1/2}$ decrease as the Hardgrove index and amount of shearing increase.

CONCLUSIONS

There are a number of corrections that must be made to the desorbed gas measurements before a true total desorbed gas content can be calculated.

- There is no foolproof way of making lost-gas corrections, but there are ways of checking the appropriateness of the correction method.
- The Airey equation indicates that it might not always be appropriate to estimate lost gas using a cumulative gas *versus* (time)^{1/2} plot. The value 2 should be replaced by the Airey constant calculated from the desorption data. A limited data set indicates that the value N_a may vary from 1.3 to 4. The Airey equation may also provide a way of estimating the maximum possible lost gas based on the shape of the desorption curve.
- The distinction between free gas and lost gas is important. Free gas occupies the macro-pores in the coal. The term lost gas generally refers to gas that desorbs prior to sealing the sample in the canister.
- Cumulative gas volumes should be reported as dry methane at standard temperature and pressure conditions. The concentrations can be expressed in terms of dry coal, dry ash-free coal *in situ* coal or dry mineral-matter free coal based on a knowledge of the weight of the sample and its corresponding moisture content.
- Useful information on *in situ* specific gravity can be obtained at the same time that the desorption data are collected.

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