A DISCUSSION ON MOISTURE IN COAL IMPLICATIONS FOR COALBED GAS AND COAL UTILIZATION

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ABSTRACT

There are a profusion of terms describing water in coal. The terms do not necessarily help in understanding the association of coal and water. Water isotherms provide the best way of indicating what component of total water in coal may interfere with gas adsorption. Most coals are saturated with water, but for coals that are under saturated with water it is important to understand the interplay of water and gas adsorption within the coal.

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INTRODUCTION

This note summarized existing data on moisture in coal and may make some new connections but does not add any new data. As such it has no pretensions to be anything more than a useful summary.

Coal as an industry and as a science appears to alternately shine and fade over time rather than develop consistently and this has implications for those with persistence or long memories. There is a wealth of coal science literature, almost forgotten, which predates the development of the coal export market and the coalbed gas industry (coalbed methane, CBM). Much of the science, though conducted to answer questions of interest of the day, is still very useful today. This is true for a lot of the studies on coal moisture and coal surface characteristics, an understanding of which helps, for example, in attaining an in-depth understanding of methane isotherms. There are many other examples where this resource of older literature is very useful to understanding today's challenges.

MOISTURE, FRACTURE POROSITY AND IN SITU SPECIFIC GRAVITY

It is important, before discussing moisture in coal, to make sure that the reader and writer are on the same page. There are a profusion of moisture terms some of which are conceptual and some measurable. Some of these terms overlap and are probably redundant (Table 1). Total moisture in coal is broken down into a number of components with different significance (Figure 1).

The first moisture measurement made in a laboratory is the as-received moisture (ARM). This value can provide interesting information, based on how fresh outcrop or core samples were collected and handled prior to arriving at the laboratory. Samples should be collected and placed in a sealed bag so that none of the as-received moisture is lost. Laboratories report as-received moisture and air-dried moisture; the percent difference of the two is nearly equivalent to the volume of water that was removed from the sample by air-drying (air-dried moisture loss). Because of the way as-received and air-dried moisture measurements are calculated in the laboratory, the percent of air-dried moisture loss (free moisture) is slightly more than the difference of the two measurements (Table 2). In some situations where the sample is not finely crushed coal, the free moisture is an estimate of water filling fractures in the sample and can be expressed as fracture porosity, if the air-dried specific gravity (SG adb) of the sample is measured. Also it is possible to calculate the in situ SG using the SG adb and free moisture content. The relationship between the moisture terms, as-received, air-dried moisture and air-dried moisture loss, fracture porosity, SG air-dried basis and in situ SG are depicted in Figure 2. In situ SG is essential for calculating in situ coal and gas resources.

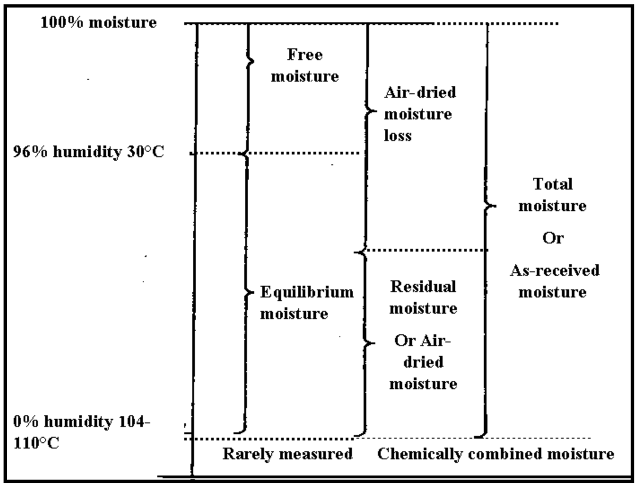


Figure 1. Moisture components in coal.

TABLE 1. SOME MOISTURE TERMS

Name	Reality		Preferred or equivalent term
Equilibrium moisture	measured in lab	EQ	
Air-dried moisture	measured in lab	ADM	
Air-dried moisture loss	measured in lab	ADL	
As-received moisture	measured in lab	ARM	
Free moisture	conceptual	?	Surface moisture
Surface moisture	conceptual	?	
Total moisture	measured in lab	TM	As-received moisture
Inherent moisture	conceptual	IM	Air-dried moisture ?
Bed moisture	conceptual	?	Equilibrium moisture ?
Residual moisture	conceptual	RM	Air-dried moisture ?

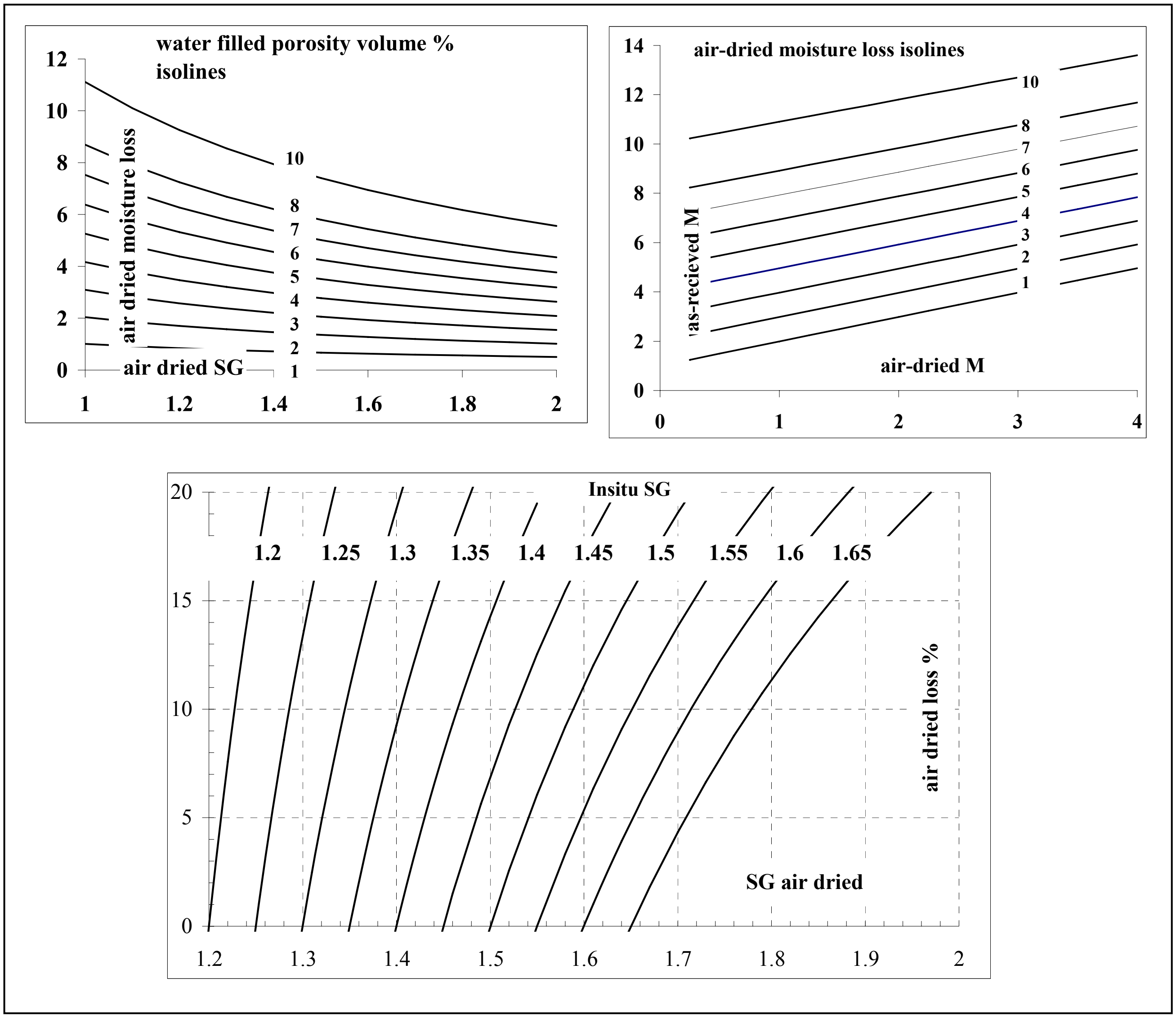


Figure 2. Relationship between measured moisture contents, SG air-dried basis and in situ fracture porosity.

TABLE 2. CALCULATION OF GAS AND MOISTURE CONTENTS AT DIFFERENT BASES

It is very important to know how various water contents are calculated

Example calculations		enter	
Enter As Received weight	W1	115	
Enter weight after air drying	W2	102	
Enter weight after drying at 110°C	W3	100	
Weight after heating air-dried sample to 750°C	W4	25	
Gas cc stp total	V	1000	
		result	**formula**
As received moisture	ARM	**13.04**	(W1-W3)/W1
Air dried loss	ADL	**11.30**	(W1-W2)/W1
Air dried moisture	ADM	**1.96**	(W2-W3)/W2
Free moisture as % of total sample	FM	**11.30**	(W1-W2)/W1
Free moisture	FM	**11.30**	1-(1-ARM)/(1-ADM)
Ash content adb %	Aadb	**24.51**	W4/W2*100
gas content arb	G arb	**8.70**	V/W1
Gas content adb	G adb	**9.80**	V/W2
Gas content db	G db	**10.00**	V/W3
Gas content daf basis	G daf	**13.33**	V/W3/(1-Aadb/(100-(W2-W3)/W2*100))
Gas content daf basis	G daf	**13.33**	Gadb/(100-Aadb-ADM)*100

The water that is dried off samples before measuring air-dried moisture contains total dissolved solids (TDS) that are precipitated onto coal surfaces during drying. It is possible to calculate the chemistry of TDS in the free water associated with the coal, if a sample is weighed then air-dried to calculate weight of free water and then soaked in a known volume of distilled water to re dissolve the TDS. This may indicate the quality of water that might drain into an open pit coal mine and flag possible handling procedures. Based on sulphate contents it can indicate the degree of oxidation of the associated coal. If samples are collected from depth, then the water chemistry may indicate CBM potential (Van Voast, 2003) based on the chemical finger print of the TDS in the water.

MOISTURE *VERSUS* ASH RELATIONSHIPS

Moisture content is generally considered to decrease as the amount of ash (or mineral matter) increases. For equilibrium moisture (EQ) or air-dried moisture (adm or inherited moisture), which are high for low rank coals, the negative correlation is strong. The plot indicates that at the equivalent of 100% mineral matter there is still some moisture in the sample. The amount can only be determined once the mineral matter/ash ratio is know, as this defines the 100% mineral matter point on the X = ash axis. For example if the ratio is 1.15, then 100% mineral matter is equivalent to 87% ash. Results indicate that EQ moisture ranges from 1% to 4% at 100% mineral matter (Roberts, 1991). This is the moisture on the sample that is lost once it is dried to 110°C and must represent capillary and or adsorbed moisture because the EQ measurement is conducted at 96% humidity in order to remove surface moisture. Roberts (1991) estimates adm of mud rocks to be in the range 0.4% to 3.2% (this is not structural water). This value should vary somewhat with rank because of increased maturity of the mineral matter (clays) and with changes in composition. It provides information about the composition of the mineral matter and possibly about gas adsorption potential, if shale gas potential is being considered.

There are a lot of data sets of air–dried moisture (adm) *versus* ash for different rank coals (Figure 3). The adm of zero ash coal is rank dependent and varies from over 6% for low rank coals to a minimum of less than 1% for medium rank coals increasing to about 2% for high rank coals. The moisture content at 100% mineral matter (87% ash assuming a 1.15 mineral matter/ash ratio) is an indication of the moisture remaining in the mineral matter after air-drying that is subsequently lost when the sample is dried at 110°C. This probably represents adsorbed moisture. Plots of adm *versus* ash for low rank coals (Rmax 0.67%) have a negative slopes indicating that the zero ash coal adsorbs water more strongly than the included mineral matter. Plots for higher rank coals (Rmax 1.3% to 1.8%) indicate very little change in adm with increasing ash content. They also have lower adm contents for the full range of ash contents. It appears that these ranks of coal have the same amount of tightly adsorbed water as mineral matter and generally lower adsorption than low rank coals. The adm for zero ash anthracite is higher than that for medium rank coals. Surprisingly the adm for 100% mineral matter is also high and this may reflect changes in the type of clays that make up the ash present in high rank coals.

Drying coal samples to 110°C does not remove structural water from clays. This water is only apparent in the volatile matter content of mineral matter. In fact the slope of line in an ash *versus* volatile matter (VM) plot gives information about the volatility of the ash and a line on a CV *versus* ash plot gives information about the heat steeling or heat generating capacity of the ash, which is related to its composition.

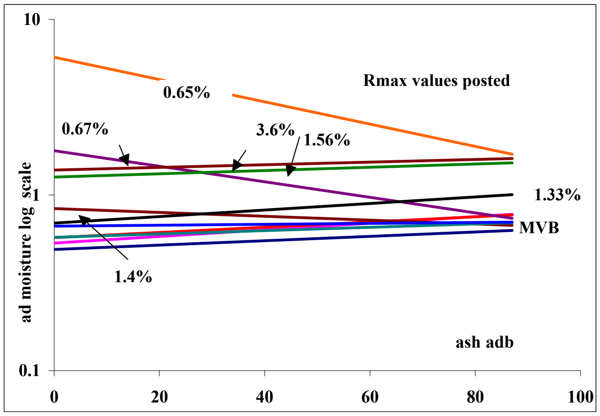


Figure 3. Plots of air-dried moisture *versus* ash for different rank coals.

MOISTURE AND PETROGRAPHY

Air-dried and EQ moisture contents vary based on maceral composition of samples. Generally vitrinite contains the most moisture and inert macerals the least (Figure 4). This is not always the case and Roberts (1991) found a weak positive correlation of inertinite content with “inherent moisture”, which based upon the way he sampled, is an estimate of bed moisture. The variation in EQ and adm contents probably mimics the ability of macerals to adsorb methane. For fresh, low-ash samples, of the same rank, higher adm probably correlates with greater methane adsorption ability.

EQUILIBRIUM MOISTURE AND GAS ADSORPTION

Equilibrium Moisture (EQ) is a laboratory measured property of coal that is intended to, and may be an approximation of immobile water in coal at situ conditions; i.e. what is often referred to as bed moisture. In that EQ moisture is the moisture coal can hold in a humid atmosphere, it is effectively the sum of adsorbed moisture filling micro pores and moisture filling large pores by capillary action. The test is on wetted 16 mesh (1 mm diameter) coal fragments held at 30°C, at 96% humidity and at a pressure of 30 mm mercury (atmospheric pressure is 760 mm mercury). Based on the procedure there are a number of concerns. EQ moisture may be influenced by grain size. The temperature of 30°C does not necessarily reflect the in situ temperature of all samples. The low pressure may cause complete degassing of methane and carbon dioxide and aid infusion of water into pores. This would increase EQ moisture above the equivalent in situ EQ moisture.

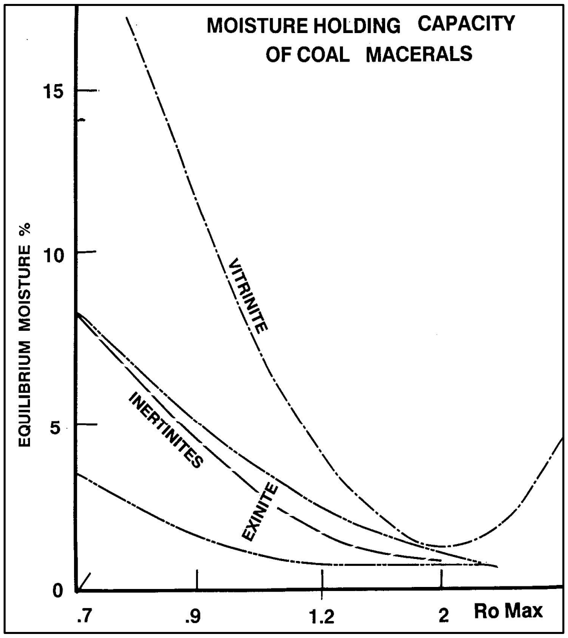


Figure 4. Variation in EQ moisture with rank and maceral content; plot from Shell internal publication.

The reason for equilibrating samples at EQ moisture (especially when the temperature is changed from 30°C to in situ temperature) is to mimic the in situ moisture content of coal during isotherm experiments and therefore to able to predict the true saturated gas capacity of coal at in situ conditions or at conditions that match in situ temperature but not necessarily pressure. If isotherms are run on coal with inappropriate moisture contents, then it will be difficult to determine whether desorbed coal samples are saturated or under saturated. If EQ moisture is higher than in situ moisture, then under saturated samples will appear to be saturated and some samples may appear to be “over saturated”. If the EQ moisture is too low, compared to in situ conditions, then adsorption ability is increased and desorbed samples will appear to be under saturated. It is important to have the correct estimate of the degree of gas saturation of samples because it has a major influence on production economics.

Many papers, for example Joubert *et al.* (1973) and Bustin and Clarkson (1998) indicate that gas capacity is very dependent on water content and can increase by 30% for low rank coals if they are dried below EQ moisture. However, the difference in adsorption based on moisture content is much less for medium rank coals. It is obviously very important to perform isotherm measurements at the correct moisture content. It is not clear that the ASTM EQ moisture value, even if modified for different temperatures, provides a good estimate of the in situ moisture content that should be used to model in situ gas capacity.

Bed moisture probably decreases with increasing depth of burial for iso rank coals because of increasing temperature, but also possibly because of increasing pressure. Increasing effective stress will cause compaction of the coal based on the compressibility of coal, which can be calculated using Poisson’s Ratio and Young’s Modulus. Based on average values coal will compress (volume decrease) by about 0.3% for a 1000 metres equivalent increase in effective stress. This would decrease the volume available for capillary moisture but the effect is not large enough cause large changes in EQ moisture. Equilibrium moisture decreases with increasing temperature (Figure 5). In that part of EQ moisture is adsorbed moisture this is not unexpected as the Langmuir Pressure is temperature sensitive increasing as temperature increases.

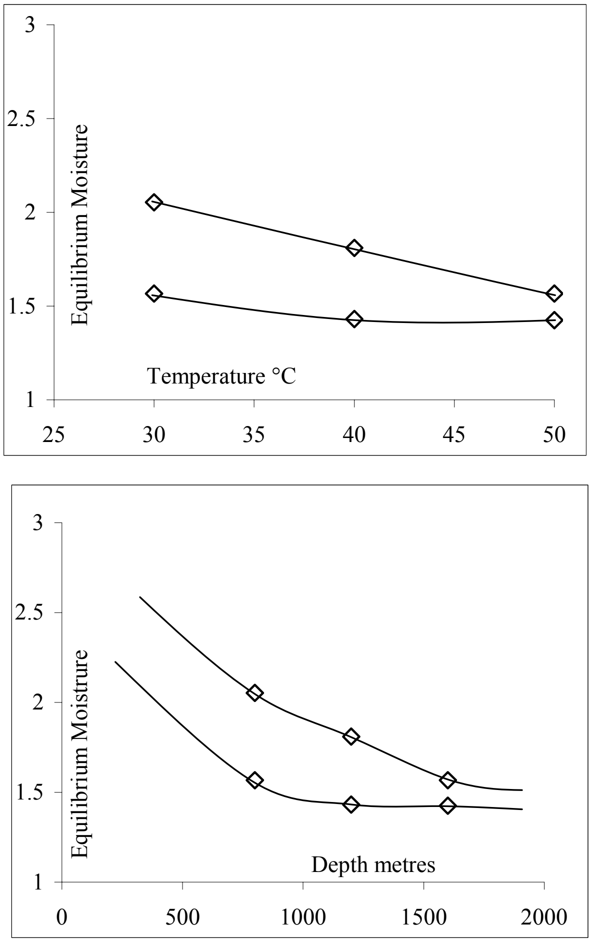


Figure 5. Changes in EQ moisture with increasing temperature (data from Bustin and Clarkson, 1998). Data calculated to indicate depth based on a geothermal gradient of 25°C; surface temperature 10°C.

Low rank coals with larger pores may experience evaporation from pores at humidities greater than 96% and therefore EQ moisture may be considerably less than bed moisture (Luppens, 1988). This may result in isotherms over estimating gas-saturated capacity, if this evaporate moisture is occupying adsorption sites also available for methane. The problem extends to medium-volatile bituminous coals and the percent difference between bed moisture and EQ moisture is actually larger for medium-volatile coals, despite the fact that the actual difference is much lower than for low rank coals (Figure 6).

If increasing temperature is the major effect decreasing EQ, then it is probably accompanied by a decrease in methane adsorption ability, rather than an increase that would be expected if the sample were dried below its EQ moisture without increase in temperature. If bed moisture varies with effective stress because of compression and if this variation changes the saturated gas capacity of coal, then saturation conditions will change during de-pressuring caused by production. As production proceeds effective stress increases and the coal becomes more compressed. This may decrease saturated gas capacity and initiate or stimulate desorption but slow diffusion.

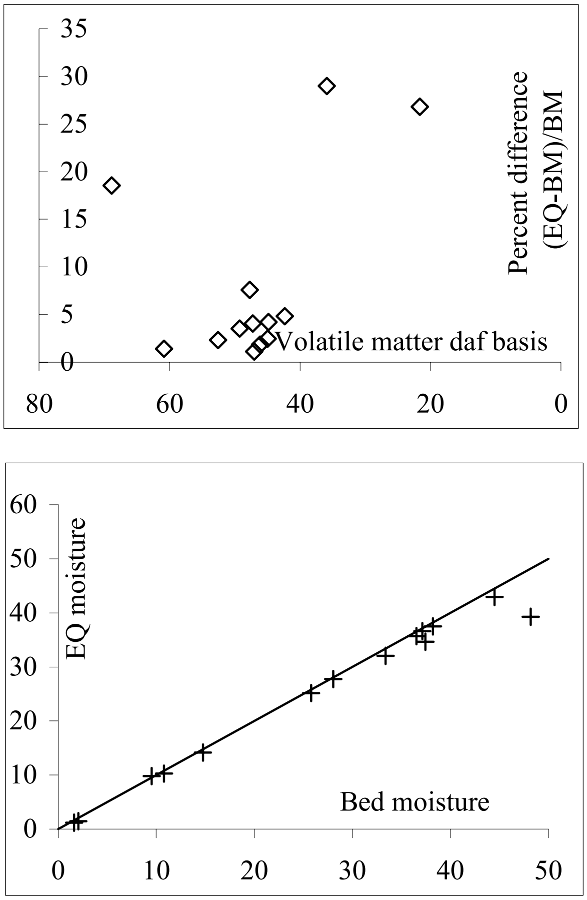


Figure 6. Relationship between bed moisture and equilibrium moisture; data from Luppens, (1988).

WATER ISOTHERMS

Allardice and Evans (1978) provide an in depth discussion of water adsorption in coal and provided an example of a water isotherm for a low rank coal The steep part of the curve of a water isotherm (Figure 7) at high humidities indicates loss of surface moisture. For this reason EQ moisture is measured at 96%-97% humidity because this ensures that surface moisture is evaporated and not included in the measurement. The amount of surface moisture on in situ coal is in part related to the amount of fracturing (amount of surface area available). However, this moisture will have minimal effect on gas adsorption (it may be significant in adsorption of gas on clays).

It is possible to measure a water isotherm by measuring the amount of water lost as the relative humidity decreases (Allardice and Evans, 1978). The shape of the resulting water sorption isotherm indicates at what relative humidity the various forms of water evaporate from coal. These include capillary water (steeper part of the curve, Figure 7), water in macro pores (central flatter part of the curve), multi layer adsorbed moisture and monolayer adsorbed water (steep part of the curve close to the origin). Capillary and macro pore moisture are removed at vapour pressures that range from 0.96 P/P_o to 0.5 P/P_o (Figure 7). From 0.5 P/P_o to about 0.1 P/P_o (i.e. the flat part of the curve) water from multiplayer adsorption sites is lost and monolayer adsorbed water is lost below 0.1 P/P_o.

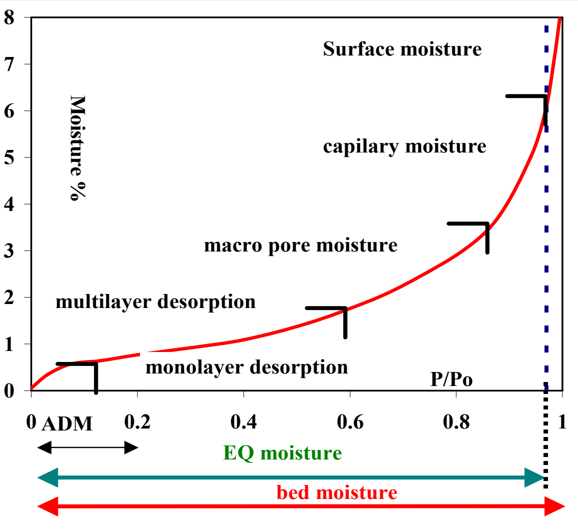


Figure 7. Water isotherm for a low rank coal. Figure adapted from Allardice and Evans (1978).

The energy released during adsorption or required for desorption of various gases is important in situations where various gases are competing for adsorption sites. Allardice and Evans (1978) document the isoteric heat of adsorption of the various forms of water. The energy released or required to evaporate water in capillaries is 2.43 Mj/kg (580 cal/g or 10.4 Kcal/mole). The energy increases by 1-2.43 Mj/kg for water adsorbed as monolayers (Allardice and Evans, 1978) i.e. in the range 3.43 to 4.86 Mj/Kg (14.7 to 20.8 Kcal/mole). When comparing gases it is better to use units of Kcal/mole as this compares similar numbers of molecules. The heat of adsorption of water is similar to the heat of condensation (10.6 Kcal/mole) this compares to the heat of adsorption of methane, which is 4 to 6 Kcal/mole (Anderson *et al.,* 1964). The heat of adsorption of CO_2 (5.5 to 6.5 Kcal/mole; Ozdemir, 2004) is slightly higher than for methane and this in part explains its stronger adsorption.

Water isotherms are constructed by decreasing relative pressure (desorption isotherm) or by increasing relative pressure (adsorption isotherm). The two curves do not overlap i.e. there is marked hysteresis, suggesting that the process of desorption from mono and multiplayer adsorption sites is not the same as adsorption. The desorption curve is always higher (Figure 8) than the adsorption curve indicating that for a fixed relative pressure more water remains during desorption than is adsorbed during adsorption. The two curves do not always meet at the end points indicating that sometimes there is permanent damage to the coal during desorption and drying caused by shrinkage and the swelling resulting from adsorption does not overcome the damage. The amount of hysteresis for coals, which increases as rank decreases, indicates the degree of risk resulting from handling coals prior to conducting methane isotherm analysis. If a sample is over dried prior to conducting an EQ measurement then the value will be too low especially for low rank coals.

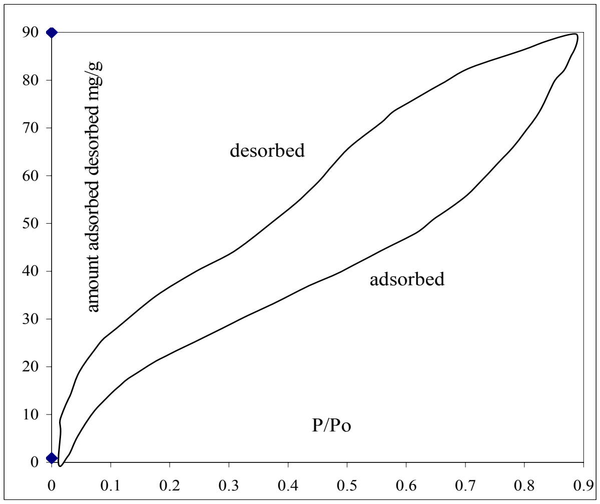


Figure 8. Hysteresis effect for desorption and adsorption; data from Mahajan and Walker (1971).

Water isotherms vary based on rank (Figure 9). The total amount of water adsorbed is high for low and high rank coals and low for medium rank coals. However, subbituminous and bituminous coals adsorb more water at relative low vapour pressures (multi and monolayer adsorption) than high rank coals. Increasing temperature causes evaporation of capillary moisture because the saturated partial pressure of water vapour in air increases and water will evaporate to try to reach the new partial pressure. The adsorbed moisture content decreases but the form of water sorption isotherms stay the same for samples (Mahajan and Walker, 1971).

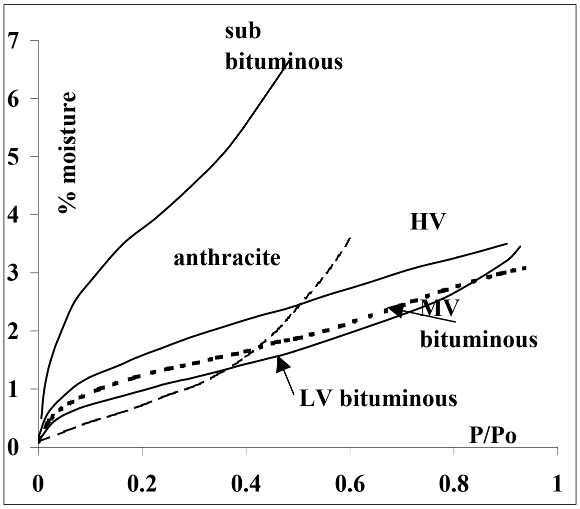


Figure 9. Water isotherms for different rank coals; data from Mahajan and Walker (1971).

Water molecules held by multi or monolayer adsorption are attracted to hydrophilic sites on the coal surface that are oxygen-containing functional groups (Allardice and Evans, 1978). Mahajan and Walker (1971) found that the proportion of the surface area of coal that contains these sites varies from 60% in low rank coals to 12% in low-volatile bituminous coals. These sites have a preference for adsorbing water rather than methane or other gases. Mahajan and Walker (1971) measured CO$_2$ surface areas of coals and used water isotherms to measure the amount of monolayer adsorbed water. They then calculated the surface area occupied by this water and were able to estimate the percentage of surface area occupied by monolayer adsorbed water in coals of different rank (Figure 10).

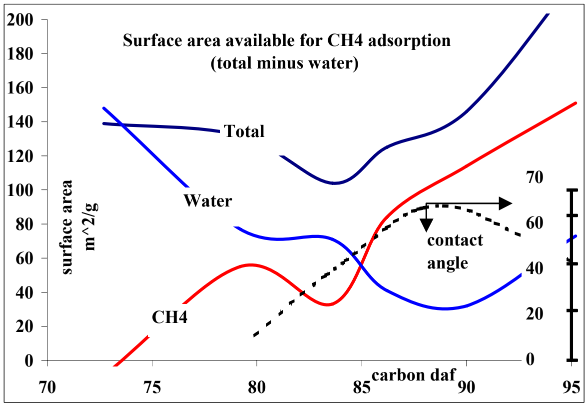


Figure 10. Percent surface area in coal occupied by monolayer adsorbed water; data from Mahajan and Walker (1971).

Their data indicate that the absolute surface area that appears to be hydrophilic is high for low rank coals decreases for medium-rank coals and increases slightly for high rank coals. Subtracting the area saturated by monolayer adsorbed water from the total surface area provides the area available for methane adsorption on water saturated coals. The area increases with rank but goes through a minimum at intermediate ranks (Figure 10). The plot is very important because it provides the basis for understanding the influence of water on methane adsorption on coals of different rank and different degrees of drying below EQ moisture.

There is no direct relationship between any component of a water isotherm and air-dried moisture content. However, adm may well be an estimate of the amount of multi and monolayer adsorbed water. A curve of air-dried moisture *versus* rank is similar in form to the curve of adsorbed water *versus* rank (Figure 11).

The minimum adsorbed water saturation outlined (Figure 10) is mirrored by the behavior of the water contact angle to a coal surface (an inverse measure of wetability) that also goes though a maximum for medium rank coals (i.e. beading). Large contact angles indicate a resistance to wetting for medium rank coals and this has implications for relative permeability and the ability to approach absolute permeability during production and dewatering. The results also agree with the data from Joubert *et al.* (1973) that indicate the high degree of sensitivity of gas adsorption to moisture content in low rank coals.

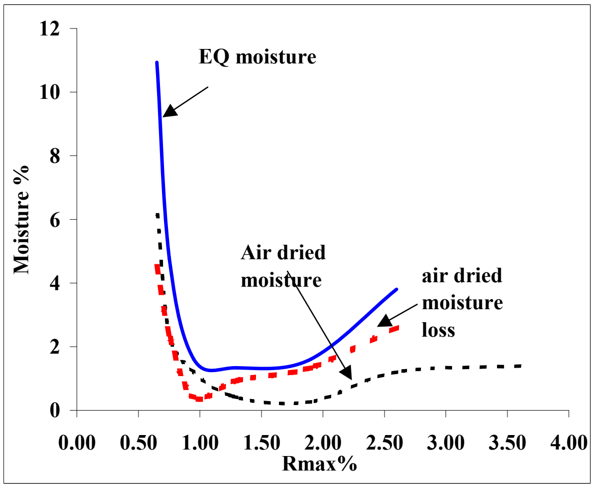
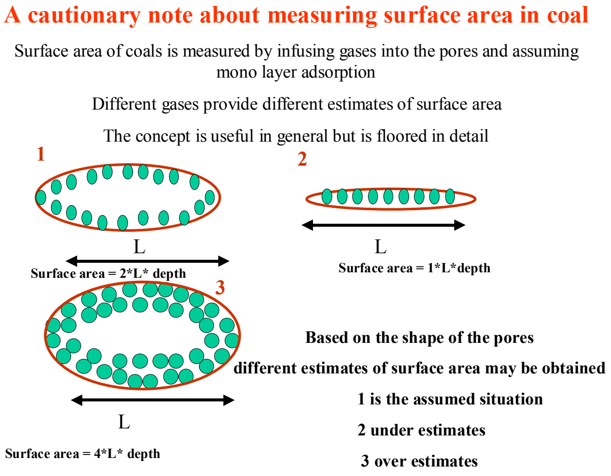


Figure 11. Air-dried and EQ moisture *versus* rank.

SURFACE AREA OF WATER IN COALS

The concept of surface area of coals should be treated with caution as Marsh (1987) pointed out. It is a calculated rather than a physical property and may be misleading; for example if pores are slit shaped with widths approaching that of the diameter of one molecule, then the surface area will be two times the area covered by adsorbed molecules (Figure 12**).** In comparison to larger pores these molecules are bonded to two surfaces and this will increase heat of adsorption and decrease diffusivity.


A cautionary note about measuring surface area in coal

Surface area of coals is measured by infusing gases into the pores and assuming mono layer adsorption

Different gases provide different estimates of surface area

The concept is useful in general but is floored in detail

Based on the shape of the pores different estimates of surface area may be obtained

1 is the assumed situation

2 under estimates

3 over estimates

Figure 12. Schematic figure indicating relationship between surface area and adsorption.

It is possible to, very roughly, estimate the minimum surface area occupied by adsorbed water. For example, if 1% water is adsorbed, then this is equivalent to 0.01 cc/gm. Using Avagadro's Number (6*10^23) this is 3.3*10^20 molecules of water. If the water molecules, which have a diameter of about 4 Angstroms are arranged one layer deep in a square packing pattern then the length of one side is (3.3*10^20)^1/2*4*10^-8 cm = 7.3 metres so that the surface area covered is 53 square metres. Mahajan and Walker (1971) used a surface area for molecular water of 10.6 angstroms squared, which would result in a smaller surface area. These surface areas are less than but in the same order of magnitude as surface areas calculated using CO_2 adsorption.

A number of authors have measured surface area of coals (one of the earliest studies was by Walker and Kini, 1965). Surface area of coals ranges from 200m^2/g for low rank coals to 100m^2/g for medium rank coals to 250m^2/g for high rank coals. It is easy to see that for low rank coals with 60% hydrophilic surface area and high equilibrium moisture contents that there is the potential for none to nearly all of the surface area to be occupied by adsorbed water. This will result in a wide range in adsorbed gas concentrations based on how much the coal is dried below EQ moisture.

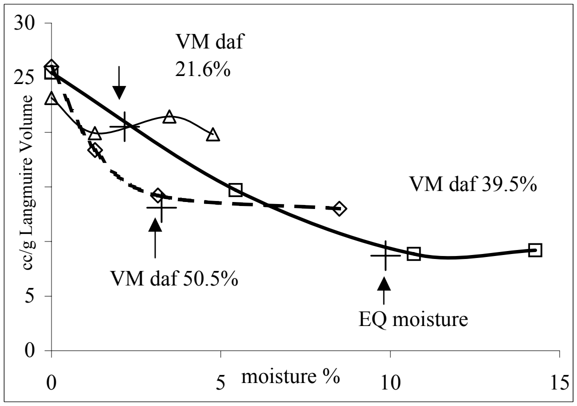
For high rank coals with 12% of the surface area hydrophilic and lower equilibrium moisture contents there is much less potential for degree of water saturation to change adsorbed gas concentrations. The EQ moisture content of anthracites is higher than for medium rank coals (Figure 11). However, based on the shape of water isotherms, the increased moisture is capillary moisture (not monolayer adsorbed water) and therefore it will not effect the gas adsorption capacity. This means that drying anthracite below EQ moisture may not produce a marked increase in gas adsorption. The increase in capillary moisture in some situations may be related to macro pores or vesicles produced by rapid de-volatilization related to a thermal event that affected the anthracite.

INFLUENCE OF WATER ON METHANE ADSORPTION

The relationship between water content below EQ moisture and Langmuir Volume for methane is close to linear (Figure 13) (Jouber*t et al.* (1974). It appears that as water vacates sites, they are occupied by methane and that water does not block access to additional sites. However, the replacement is not one for one. A 1% loss of water is equivalent to a loss of 0.01/18 moles of water; the weight of the same number of methane molecules is 16*0.01/18 and this mass of methane as a gas (stp) occupies 12.45 cc. Therefore for a one to one replacement of methane for evaporated water the gradient on a cc/g *versus* moisture plot should be 12.45 in fact the gradient is much less and is rank dependent (Figure 13). This means that for low rank coals approximately 1 methane molecule replaces 3 water molecule sites but for medium rank coals the ratio has increased to 1 methane molecule replacing 11 water molecule sites.

The relationship of Langmuir Pressure (Pl) to moisture content is ambiguous; for low rank coals it appears to decrease as moisture deceases for higher rank coals there is no consistent change. A decrease in Pl implies easier adsorption of methane as moisture contents decrease.

Jouber*t et al.* (1974) provide an equation (Vd/Vw=Co*M+1); where M is moisture content below EQ moisture and Co is a constant; Vw is adsorption on wet coal (the variable with M<EQ moisture) and Vd is adsorption on dry coal (a constant). The ratio Vd/Vw is linearly related to moisture not the value Vw as implied by Killingley *et al.* (1995). Their data re plotted provides a value of Co of 0.58 which is higher than the value 0.2 for the same pressure predicted by Joubert *et al.* (1974). The term Co is pressure dependent and decreases slightly as pressure increases.



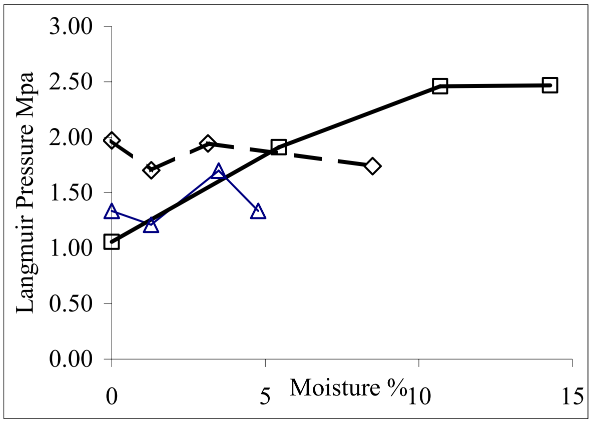


Figure 13. Langmuir Volume and Langmuir Pressure *versus* moisture content below EQ moisture; data from Joubert *et al.* (1974).

The equation (Vd/Vw=Co*M+1) implies that the gradient of cc/g *versus* moisture varies and increases as moisture decreases but does not increase to 12.45 even at very low water contents. This can be interpreted in terms of the location of water in coal as defined by water isotherms. At moisture levels a little below EQ water is held by multi layer adsorption. Methane with less polarity than water tends not to occupy multi layer adsorption sites and therefore methane does not occupy many vacated water sites, i.e. low gradient. At low moistures where water is vacating mono-layer adsorption sites methane replacement is closer to one to one, i.e. the gradient is steeper. The gradient (Figure 13) is steeper for low rank coals indicating, in agreement with water isotherms, that there is more replacement of monolayer adsorbed water by methane than in higher rank coals. Because the interchange between water and methane molecules is not one to one there will be a shrinkage as coal is dried below EQ moisture and water is replaced by methane and there will be a swelling when dry coal methane saturated is wetted and methane is released and water adsorbed. This may in part explain the hysteresis seen in water isotherms (Figure 8).

Based on the difference in heats of adsorption, in a situation where coal is dried below EQ moisture, if water and methane become available then coal will re adsorb water in preference to methane until the water adsorption sites are filled. Coal with less than EQ moisture in a dry environment will contain more gas than if it contained EQ moisture. If the environment becomes water saturated, then coal will re attain EQ moisture and in the process will release methane even if there is no decrease in pressure. This sequence of events may take place where a coal zone is subjected to regional or local, temporary heating caused by intrusions. Heating decreases both EQ moisture and adsorbed gas content and based on heats of adsorption may reduce gas adsorption more than water adsorption. However, the expelled gas may, if a trap situation exists, produce a level in a coal bearing section where the coal is gas saturated and a lower level where the coal is water saturated. On cooling the gas saturated area will have a moisture content below EQ moisture and an adsorbed gas content that recognizes this. Under normal conditions of increasing temperature, saturation of water and methane will both decrease and methane will not have the opportunity of occupying vacated water adsorption sites.

OXYGEN CONTENT AND COAL PETROGRAPHY

Joubert *et al.* (1974) introduce an equation that relates Vw/Vd to oxygen content, EQ moisture and to three constants that are pressure dependent. The equation does not predict how absolute gas adsorption levels change with rank, it only predicts how EQ moisture and oxygen content (maceral or rank dependent) influence relative adsorption behavior (Vw/Vd) below EQ or critical moisture contents. The equations do not incorporate temperature, because experiments were all done at the same temperature.

A number of authors provide plots of oxygen *versus* carbon content of coal and of EQ moisture *versus* carbon content (Berkowitz, 1979). These diagrams are re arranged to provide EQ moisture ranges *versus* carbon content with the EQ moisture prediction of Joubert *et al.* (1974) (Figure 14). The equations predict that EQ moisture increases slightly as pressure increases (no change in temperature) and that as depth and rank increase the difference between adsorption on dry and water saturated coal decrease (Vw/Vd→ 1) (Figure 15).

Water molecules bond to the coal on oxygen functional groups (OH and COOH) using oxygen in the coal and hydrogen bonds in the water molecules (Allardice and Evans, 1978). Analyses by Ladner and Stacey (1962) and Mastalerz and Bustin, (1993) indicate that vitrinite has higher O/C ratios than inert macerals of the same rank. This explains the positive correlation of EQ moisture with vitrinite content in coal. Data from both papers plotted into a Krevelin Diagram (Figure 16) indicate the deceptive way macerals of the same rank plot into the diagram. Oxygen/Carbon ratios are high for low rank coals and decrease for high rank coals and for most ranks the O/C ratio is greater for vitrinite than inert macerals (Figure 17). Despite an increase in EQ moisture, the O/C ratio for anthracite does not increase and this is the reason that for high rank coals there is not a decrease in methane adsorption. The increase in EQ moisture is related to an increase in capillary moisture not monolayer adsorbed water as indicated by the shape of anthracite water isotherms (Figure 9).

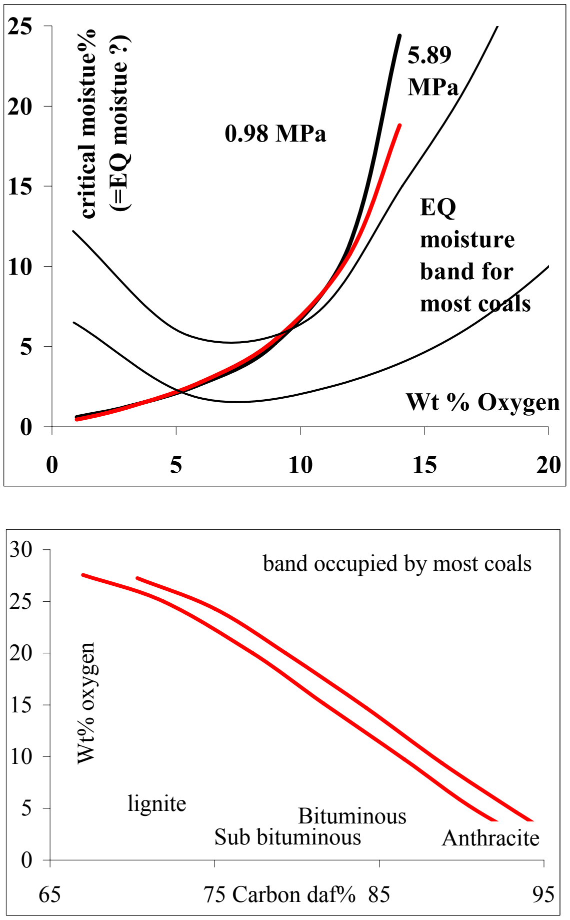


Figure 14. EQ moisture *versus* oxygen content (modified from Berkowitz, 1979) with the relationships developed by Joubert *et al.* (1974).

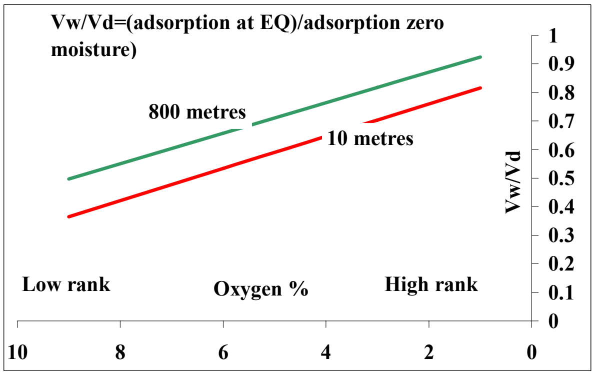


Figure 15. Variation of Vw/Vd with depth and rank as represented by oxygen content. Data from Joubert, *et al.* (1974).

The importance of available adsorption sites for water in influencing gas adsorption is indicated by a comparison of Australian Permian coals and Gates Cretaceous coals (Bustin and Clarkson, 1998). These coals have similar ranks and CO_2 surface areas, yet the Gates coals have 20% lower adsorption capacities. They have higher EQ moistures than Bulli coals for similar vitrinite contents (Figure 18). They also have a positive correlation of vitrinite content to EQ moisture content. The EQ moisture content of Bulli coals does not change much with changes in vitrinite content and has a weak negative correlation to EQ moisture.

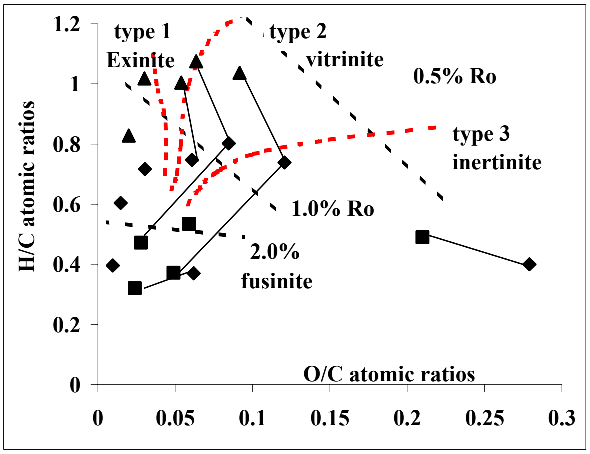
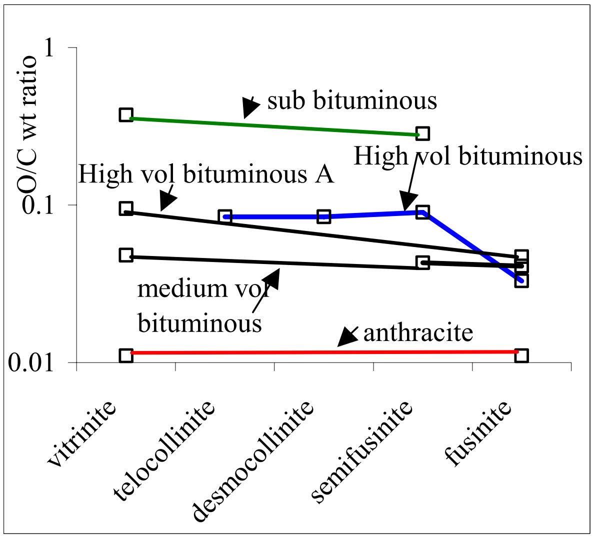


Figure 16. Maceral data from Mastalerz and Bustin (1993) and Ladner and Stacey (1962) plotted into a Van Krevelen Diagram. Square=fusinite or semifusinite, diamonds=vitrinite and triangle=exinite. Lines join macerals from same coal sample.

The explanation for the lower gas contents in Gates coals may be related to lower O/C ratios for vitrinite from Bulli compared to vitrinite from Gates coals indicating less adsorption sites stolen by monolayer adsorbed water. Also part of the explanation may lie in different shapes of water isotherms for inert macerals from the two areas. Like the Bulli data (Figure 18), Roberts (1991) found a negative correlation of EQ moisture with vitrinite content for South African coals. In this situation vitrinite probably has more sites for multi or monolayer adsorption than semifusinite and fusinite, but fusinite and semi fusinite have more macro pore and capillary moisture so on balance they have greater EQ moisture contents than vitrinite. This emphasizes the importance of the shape of water isotherms for different coals or macerals. In the Bulli coals with similar vitrinite and EQ moisture contents to Gates coals less of the moisture in the Bulli coal is occupying multi or monolayer adsorption sites and therefore less methane is displaced by water. The difference in EQ moisture contents may also be related to a difference in over burden pressure Roberts (1991) found that some Permian South African coals have lower inherent moisture contents than northern hemisphere coals of similar rank and petrographic composition.

MULTIGAS COMPETITION FOR ADSORPTION SITES

Much of the above discussion considers the competition between methane and water for adsorption sites in the coal. There is very little information in the literature that provides light on the situation where there are a number of gases for example, CH_4, CO_2 and water competing for adsorption sites. No papers were located that investigate adsorption of CO_2 on partially dried coals.



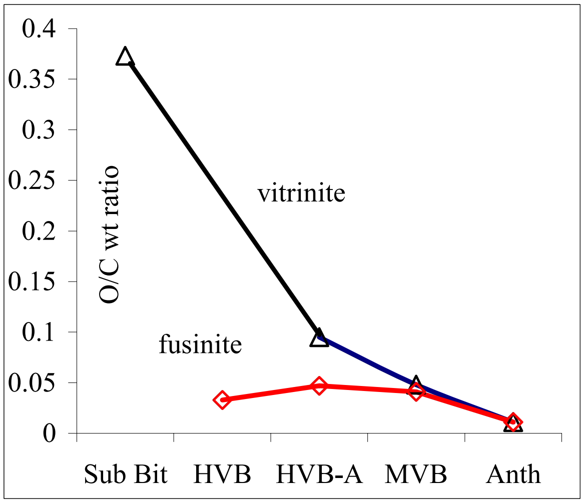


Figure 17. Variation of O/C wt ratio by rank and maceral type data from Mastalerz and Bustin (1993).

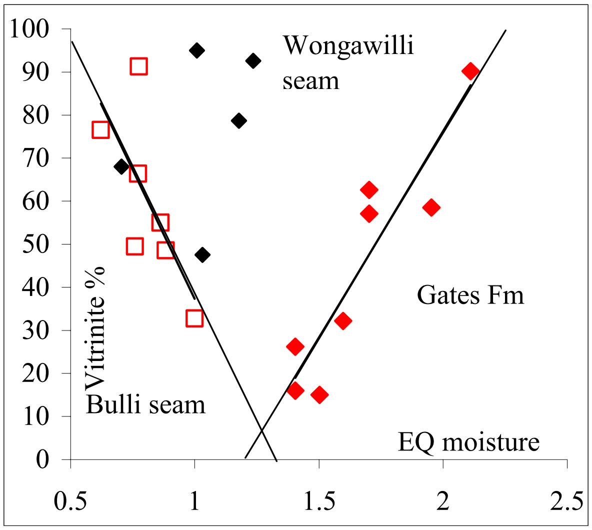


Figure 18. Variation of EQ moisture *versus* vitrinite content for Bulli (Australian) and Gates (British Columbia) coals; Data from Bustin and Clarkson (1998).

A study by Busch *et al.* (2006) measured selective adsorption of CO_2 from a CO_2/CH_4 gas mixture on wet and dry coal; their results indicate that compared to CH_4, CO_2 is preferentially adsorbed on dry coal. This may indicate that in contrast to CH_4, CO_2 can compete with water for sites not available to CH_4. Coals in contact with a gas rich in CO_2 may in fact have lower EQ moistures than coals in contact with air.

CONCLUSIONS

Apart from a few people intimately involved in coal analyses, the intricacies of moisture in coal are not well understood. There are a profusion of terms often used with variable definitions. Even before considering the inter relationship of coal moisture and gas adsorption, there is useful information buried in moisture analyses. With some careful sampling, water analyses can provide information on coal fracture porosity and in situ SG. In some cases it is possible to estimate the quality of interstitial water using a process of drying and leaching coal samples.

There is generally a poor understanding of the effect of water on gas adsorption. Some papers not directly dealing with CBM provides valuable insights. Water isotherms provide information on the various ways water is held in coal and this indicates how the water will affect gas adsorption.

The weight of EQ water can be roughly expressed as the equivalent area of adsorbed water; comparing this to the surface area predicted by CO_2 adsorption indicates that water can only adsorb on a limited percentage of adsorption sites and the percentage varies with rank. The combination of an understanding of how water is adsorbed and the percentage area occupied provides a better understanding of the way it influences gas adsorption.

Non-surface water (EQ moisture) occupies capillaries, multi layer adsorption sites and mono layer adsorption sites all with different heats of adsorption as indicated by changing slope of water isotherms. The sites that are available for water or gas adsorption correlate with the oxygen content of the coal, which varies by rank and maceral content. These sites are oxygen functional groups COOH.

Methane molecules do not replace water molecules on a one to one basis. They prefer mono layer adsorption sites to multi layer adsorption sites but even there the ratio of replacing methane molecules to water molecules is less than 1 to 3.

REFERENCES

Allardice, D.J. and Evans, D.G. (1978): Moisture in Coal; *in* Analytical Methods for Coal and Coal Products, Volume 1, Academic Press New York 1978.

Anderson, R.B., Bayer, J. and Hofer, L.J.E. (1964): Equilibrium sorption studies of methane on Pittsburgh Seam and Pocahontas No.3 Seam coal; pages 386-399.

Berkowitz, N. (1979): An Introduction to coal technology; Academic Press.

Busch, A., Gensterblum, Y., Kroos, B.M. and Siemons, N. (2006): Investigation of high pressure selective adsorption/desorption behavior of CO_2 and CH_4 on coals: an Experimental study; International Journal of Coal Geology, Volume 66, pages 53-68.

Bustin, R.M. and Clarkson, C.R. (1998): Geological controls on coalbed methane reservoir capacity and gas content; International Journal of Coal Geology, Volume 38, pages 3-26.

Diessel, C.F.K. (1992): Coal-bearing depositional systems; Springer-Verlag.

Joubert, J.I., Grein, C.T. and Bienstock, D. (1974): Effect of moisture on the methane capacity of American coals; Fuel, Volume 53, pages 186-191.

Killingley, J., Levy, J. and Day, S. (1995): Methane adsorption on coals of the Bowen Basin, Queensland Australia; Intergas 95 Conference, May 14-20, University of Alabama, pages 401-412.

Ladner, W.R. and Stacey, A.E. (1962): The hydrogen distribution in macerals; Fuel, pages 75-83.

Luppens, J.A. (1988): The Equilibrium moisture problem; Journal of coal Quality, Volume 7, pages 39-44.

Luppens, J.A. and Hoeft, A.P. (1991): Relationship between inherent and equilibrium moisture contents in coals by rank; Journal of Coal Quality, Volume 10, pages 133-141.

Mahajan O.P. and Walker Pl, Jr. (1971): Water adsorption on coals; Fuel, Volume 50, page 308.

Marsh, H. (1987): Adsorption methods of study micro porosity in coals and carbons - a critique; Carbon, Volume 25, Number 1, pages 49-58.

Mastalerz, M. and Bustin, R.M. (1993): Variation in elemental composition of macerals an example of application of electron microprobe to coal studies; International Journal of Coal Geology, Volume 22, pages 83-99.

Ozdemir, E (2004): Chemistry of the adsorption of carbon dioxide by Argonne premium coals and a model to simulate CO2 sequestration in coal seams; Ph.D. University of Pittsburgh.

Roberts, D.L. (1991): The inherent moisture content of South African Permian coals; International Journal of Coal Geology, Volume 17, pages 297-311.

Van Voast, W.A. (2003): Geochemical signature of formation waters associated with formation water; American Association of Petroleum Geologists, Bulletin 87, pages 667-676.

Walker, P.L. and Kini, K.A. (1965): Measurement of the Ultrafine surface area of coals; Fuel, Volume 44, pages 453-459.