Chapter 5

Moisture Adsorption

5.1 Moisture Isotherms

Moisture uptake by Puxtrees coal samples was measured at 10, 20, 30, 40 and 60 °C for four particle sizes ranging from 0.125 to 9 mm mean particle diameter and at seven relative humidities between about 10 and 100 percent. The results of a typical experiment are plotted in Figure 5.1.
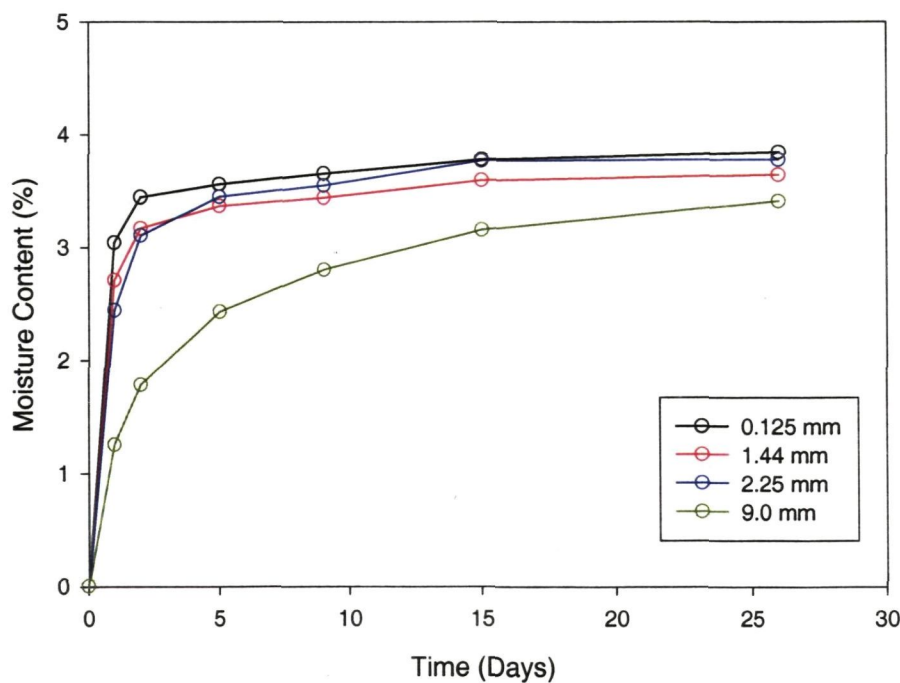

Figure 5.1. Moisture uptake of coal samples (at 10 °C and 76 percent relative humidity) as a function of time

For a given relative humidity and temperature, the total amount of moisture adsorbed by the coal (i.e. the equilibrium moisture content) was about the same for each particle size fraction, although the rate of moisture uptake was faster in small particle size fractions than in the 9 mm material (Figure 5.1).

Isotherms were constructed for each temperature by plotting the equilibrium moisture content as a function of relative humidity (Figure 5.2). Note that since the equilibrium moisture content of the samples was unaffected by particle size, the moisture contents shown in Figure 5.2 are the average of the four particle size fractions for each temperature and relative humidity.
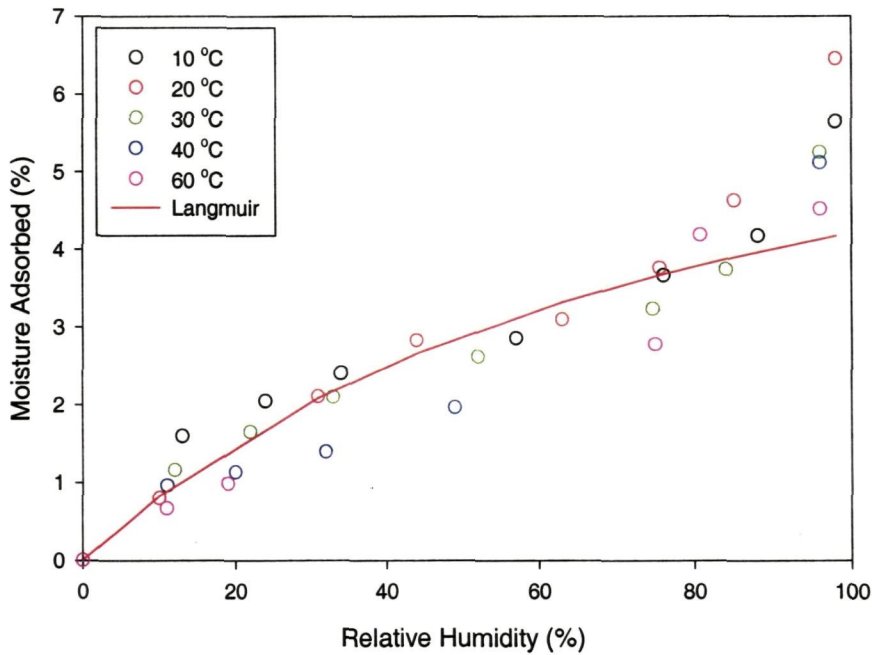

Figure 5.2. Moisture isotherms for Puxtrees coal at 10, 20, 30, 40 and 60 °C. The solid line is the calculated Langmuir isotherm for the 20 °C data

The shapes of the isotherms were found to be similar across the temperature range examined. As well, for a given relative humidity, the final equilibrium moisture content of each sample was about the same over the temperature range. For example, at 76 percent relative humidity, the equilibrium moisture content at 10 °C was 3.5 percent compared to about 2.8 percent at 60 °C. The mean value over this temperature range and relative humidity was 3.3 percent. These results compare with those of Allardice, 1968, who also found that temperature did not substantially influence the equilibrium moisture content in Victorian brown coal.

Various theoretical models have been applied to describe adsorption isotherms and one commonly used in relation to coal is the Langmuir model (Killingley, 1990). The Langmuir equation, which relates the amount of adsorbed gas (in this case water vapour) to the partial pressure (i.e. relative humidity), is often written as:

$$\frac{P}{V} = \frac{P_L}{V_L} + \frac{P}{V_L}$$ (5.1)

where V is the amount of water adsorbed at pressure P, V_L is the amount of water required for complete monolayer coverage and P_L is a constant. A plot of P/V versus P will yield a straight line with a slope of $1/V_L$ and intercept of P_L/V_L if the Langmuir model is applicable.

The solid line in Figure 5.2 is the Langmuir isotherm calculated for the 20 °C data and it can be seen that it closely follows the experimental points up to about 80 percent relative humidity. At higher relative humidities, however, it substantially underestimates the equilibrium moisture content. Similar results were found for the other temperatures.

One of the fundamental assumptions of the Langmuir isotherm is that the adsorbate molecules attach to the surface as a single layer. It may be, however, that 80 percent relative humidity corresponds to the point where all of the adsorption sites become fully occupied and at higher relative humidities, multiple layers of water molecules develop so the monolayer requirement for the Langmuir model breaks down.

In an attempt to predict the equilibrium moisture content of coals over the full relative humidity range, Henderson, 1952, (cited in Monazam et al., 1998) developed the following empirical relationship:

$$1 - RH = \exp(-KTM_e^n)$$ (5.2)

where *RH* is the relative humidity, M_e is the equilibrium moisture content, *T* is the absolute temperature and *K* and *n* are coal specific constants. The constants *K* and *n* can be evaluated by plotting *log(-ln(1/RH)/T)* against *log(M_e)* to give a straight line with a slope of *n* and intercept of *log(K)*.

For this coal, the values of *K* and *n* were found to be 7.39 and 2.21 respectively. Substituting these values into Equation 5.2 to calculate the equilibrium moisture content at each relative humidity and temperature yielded very good agreement with the experimental data as shown in Figure 5.3.
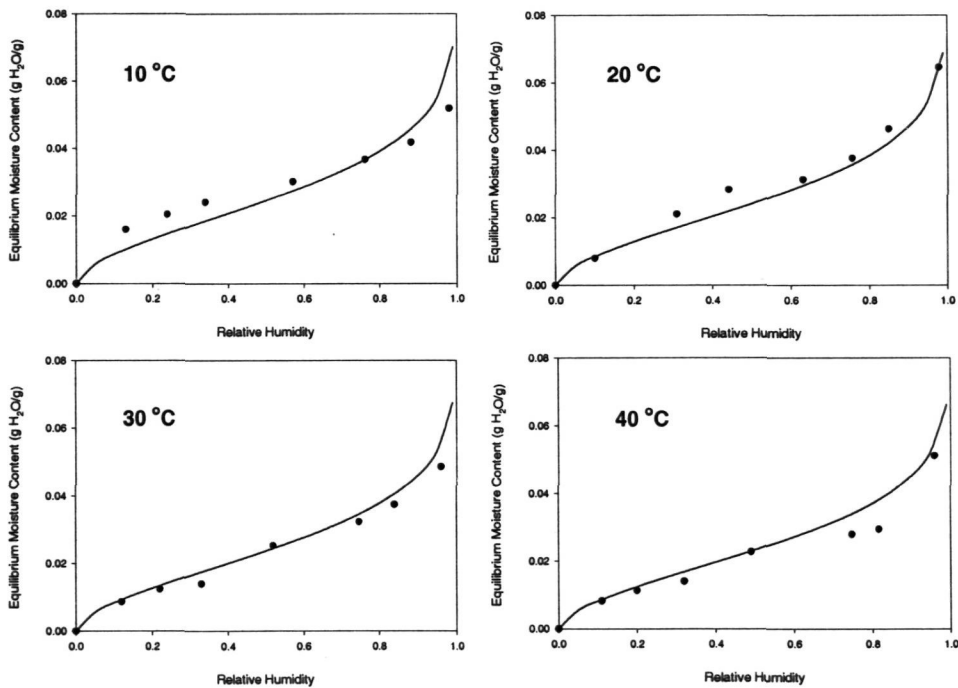

Figure 5.3. Measured isotherms at 10, 20, 30 and 40 °C compared with the corresponding modelled isotherms calculated using Equation 5.2

5.2 Rate of Adsorption

Figure 5.1 shows some plots of the moisture content of the coal as a function of time for various particle sizes. The examples shown are at 10 °C at 76 percent relative humidity, but the forms of the curves are typical of all of the other results. The rate of moisture uptake was initially fast but slowed as it approached the equilibrium moisture content. Replotting

these data in terms of rate of moisture adsorbed (as g H_2O/g coal/s) versus time yielded
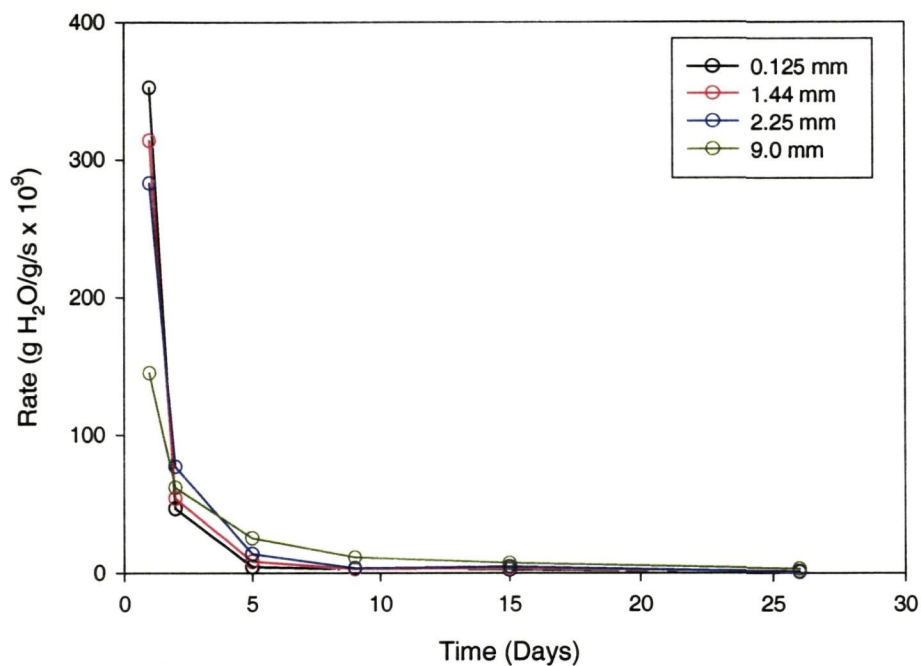
the curves in Figure 5.4.

Figure 5.4. Rate of moisture adsorption (at 10 °C and 76 percent relative humidity) as a function of time

The rate of moisture adsorption eventually dropped to zero as the coal reached its

equilibrium moisture content. This was the case for all of the conditions examined except

that the rate of moisture uptake was found to depend upon the relative humidity to which

the sample was exposed, the temperature of the sample and the particle size of the sample.

These effects are discussed below.

5.2.1 Effect of Relative Humidity

The rate of moisture adsorption was in all cases found to increase with increasing relative

humidity. This effect is shown in Figure 5.5 where the rate of adsorption measured at two

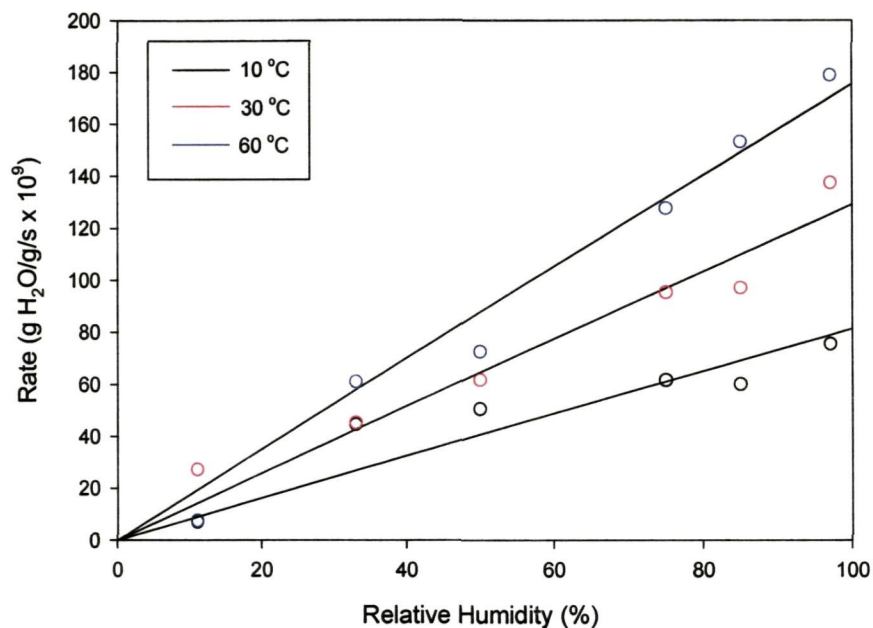days is plotted as a function of relative humidity.

Figure 5.5. Effect of relative humidity on rate of adsorption. Rates were measured after two days of exposure

At all temperatures examined, the rate of moisture uptake was taken to be a linear function of the relative humidity. The rate of moisture uptake at 97 percent relative humidity was approximately six to eight times higher than at 10 percent humidity.

The range of relative humidities corresponds to a range of reactant concentrations, hence the order of reaction can be determined. Plotting *log(Rate)* against *log(RH)* will give a straight line the slope of which is equal to the order of reaction (Equation 1.7).

In the initial stages of adsorption (i.e. within the first two days), the order was between about 0.95 to 1.05 indicating that the order of the reaction is first order with respect to the partial pressure of water.

5.2.2 *Effect of Temperature*

As shown in Figure 5.5, the rate of moisture adsorption at a given relative humidity increased with increasing temperature. At 97 percent humidity, for example, the rate at

10 °C was approximately 60 x 10^{-9} g H_2O/g/s compared to about 170 x 10^{-9} g H_2O/g/s at 60 °C. These data obeyed the Arrhenius relationship and plots of *ln(rate)* versus *1/T* yielded straight lines as shown in Figure 5.6. The slopes of the lines plotted for the range of relative humidities were similar. Converting the slopes of these lines gave activation energies ranging from about 3 to 11 kJ/mol with an average value of approximately 8 kJ/mol.
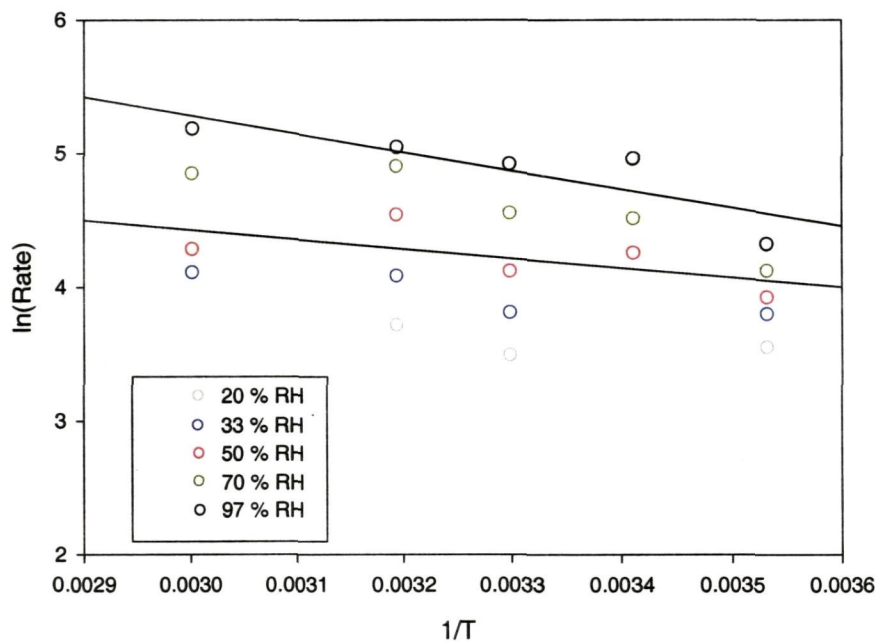

Figure 5.6. Arrhenius plots for moisture adsorption at various relative humidities

Compared to the oxidation kinetics measured for this coal, the kinetics of water adsorption are much less sensitive to temperature. In the case of the oxidation results, a 10 °C increase in temperature approximately doubled the rate of reaction. However, for moisture adsorption, a temperature rise of about 50 °C would be required to increase the rate by a similar amount.

The range of activation energies found for the Puxtrees coal is somewhat lower than those reported by Huang and Bodily, 1993, who measured the rates of moisture desorption for a

series of American coals of varying ranks using a TGA technique. They found that the activation energy of the desorption process increased with increasing equilibrium moisture content and was in the range of about 27 kJ/mol at 0.6 percent water to 78 kJ/mol at 32 percent water. More recent work by Harding *et al.*, 1998, has shown that the porosity of the sample may affect the activation energy of moisture adsorption and desorption. This group measured activation energies for water uptake by activated carbons in the range of about 6 to 41 kJ/mol for adsorption and 3 to 24 kJ/mol for desorption, a range which includes the values measured for the Puxtrees coal. These authors suggested that lower activation energies were associated with lower diffusive barriers to moisture movement in particles with higher porosity. Given the relatively high porosity of the Puxtrees coal sample used in the current study, this suggestion is consistent with the low activation energy determined for this sample.

5.2.3 Effect of Particle Size

The rate of moisture adsorption was always fastest in the 0.125, 1.44 and 2.25 mm fractions (Figures 5.1 and 5.2). These fractions usually adsorbed more than 90 percent of their final equilibrium moisture content within the first two or three days of exposure whereas the 9 mm particles required much longer (depending on the temperature and relative humidity) to reach the same moisture content.

For the three smallest fractions, the rates of moisture adsorption were generally very similar, and at temperatures above 10 $^{\circ}$C, were usually about the same. At 10 $^{\circ}$C where the rates were slowest, there was some particle size effect apparent over the full range of particle sizes. This effect is illustrated in Figure 5.7 where the rate is plotted as a function of the mean particle diameter.
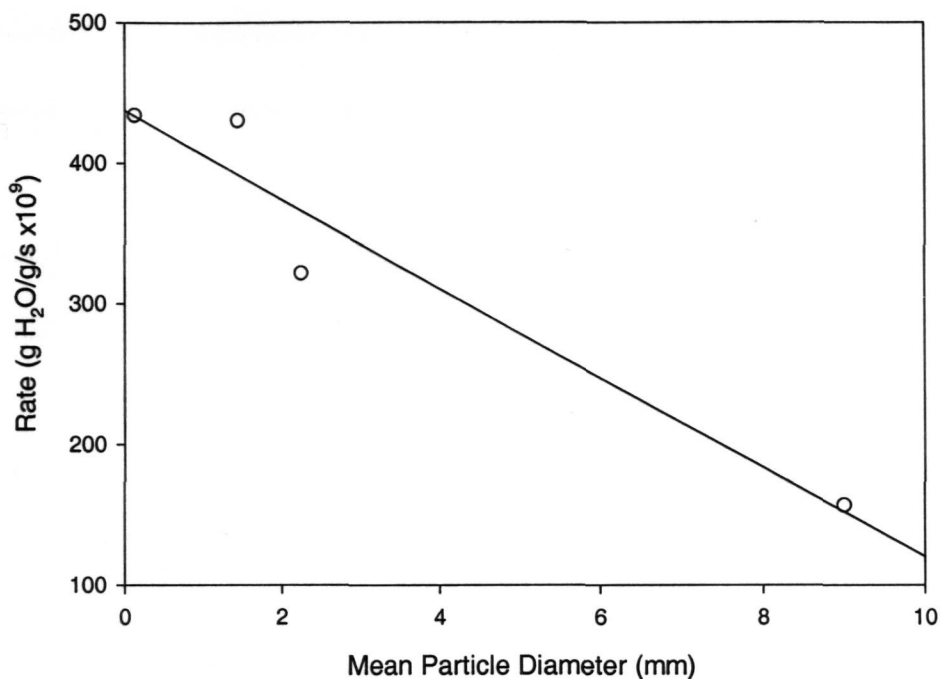
Figure 5.7. The dependence of the rate of moisture uptake on particle size. Rates were measured after one day at 10 °C and 76 percent relative humidity

The data in Figure 5.7 show that the rate of moisture uptake decreases with increasing particle size. This relationship probably holds at the other experimental conditions but it would require a more sophisticated technique (such as a continuously reading microbalance) to confirm this.

5.3 Moisture Adsorption Kinetics

Despite the masses of literature relating to water in coal, there has been relatively little investigation of the kinetics of moisture uptake by coal. In one study, Mazumdar and Bhattacharya, 1989, conducted desorption measurements at room temperature on wet coal varying in rank from lignite to anthracite. They found that desorption for all coals proceeded in three distinct steps corresponding to (1) the removal of free water, (2) desorption from 100 to 60 percent relative humidity and (3) desorption from 60 to zero percent relative humidity. They proposed that the second step represented the removal of physically bound water while in the final phase, more tightly held, hydrogen bonded, water was lost. The kinetics of desorption of the last two stages were examined and both were

found to follow first order kinetics with stage 2 always being faster than stage 3 by about an order of magnitude. The kinetics of the initial phase were not reported.

In the study by Huang and Bodily, 1993, rates of moisture desorption were fitted to a kinetic expression of the form:

$$r_d = k(W_{H2O}/W_c)^n \qquad\qquad (5.3)$$

where r_d is the rate of desorption, k is the rate constant, W_{H2O} is the moisture content, W_c is the weight of coal and n is the order of reaction. For the coals examined, n varied from 1.8 to 2.7 with most being close to 2. Harding *et al.*, 1998, examined the kinetics of water vapour uptake by a range of activated carbons and found that both adsorption and desorption followed what they termed a linear driving force mass-transfer rate law (which is equivalent in form to first order kinetics).

One of the aims of the current study was to find an expression that could describe the kinetics of moisture uptake by Puxtrees coal. Initial attempts involved applying some common solid-state reaction models. Numerous such models exist and they have been successfully applied to many solid state reactions (e.g. Sharp *et al.*, 1966; Harrison, 1969), although generally not to coal. The reason for this is that all of these models require that the end of the reaction be identified, since they rely on being able to measure the extent of reaction as a function of time. Thus, for low temperature oxidation of coal, where the reaction continues seemingly indefinitely, it is difficult to determine how far the reaction has progressed at any instant. Adsorption of moisture by coal, on the other hand, does proceed to completion so the application of these models becomes feasible.

In testing these models against the experimental data, only the results from the 9 mm particles were considered. This was because the rate of adsorption was quite fast compared

to the frequency of measurement used in this set of experiments. Hence for the smaller particles, most of the moisture adsorption took place within the first day of exposure. However, for the 9 mm particles the rate was slow enough so that points at relatively low moisture contents could be collected thus giving a greater insight into the rate over the full adsorption period. It was not practical with this method of measurement (i.e. removing samples from their chambers and weighing on a balance) to increase the frequency of measurement because of the time required for the system to re-establish equilibrium after each disturbance.

In relation to coal, it seemed reasonable to expect moisture adsorption would proceed via a diffusion process and, since the diffusion would occur over the entire surface of each particle, a three-dimensional model would seem appropriate. Accordingly, the so-called "D3" model which represents diffusion in a sphere (Sharp *et al.*, 1966) was compared to the measurements of moisture adsorption rate over the range of experimental conditions examined. The integrated D3 equation is:

$$D_3(x) = [1 - (1 - x)^{1/3}]^2 = kt \qquad (5.4)$$

where x is the fraction of the total moisture adsorbed at time, t. To test the fit of the model, plots of x versus t were made and compared to those prepared from standard tabulated data such as those provided by Sharp *et al.*, 1966.

Agreement of this model with the experimental results was quite good for all conditions which suggests that moisture uptake is indeed controlled by diffusion. The model, however, is quite simple and limited in its application. For example, it does not include particle size effects nor can it be used to model the effect of relative humidity on the rate of adsorption.

Monazam *et al.*, 1998, developed a much better model based on the shrinking core geometry described in Chapter 4. Their model includes the effect of temperature, particle size and the relative humidity to which the coal is exposed. In addition, it includes the empirical expression of Henderson (Equation 5.2) to determine the final equilibrium moisture content of the coal. To test their model, they compared it to some limited data reported in the literature as well as some of their own experiments and reported very good agreement. The range of temperatures and relative humidities tested, however, were limited so it was decided to test the Monazam model against the wider range of experimental conditions used in this study. The model is described in detail in Monazam *et al.*, 1998, but it is described briefly below.
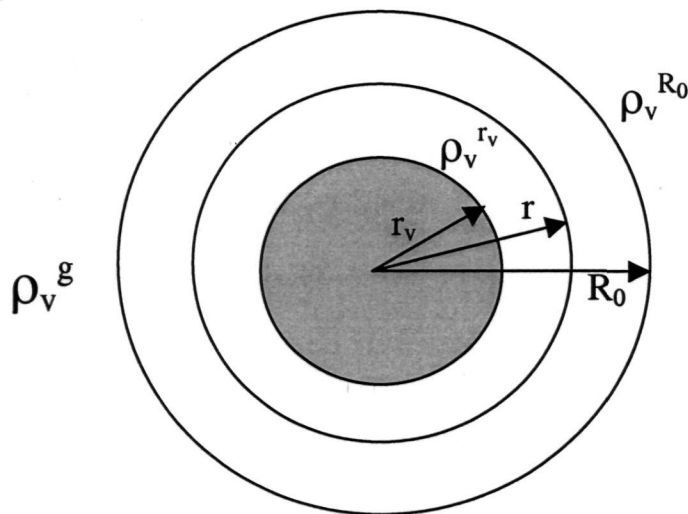

Figure 5.8. Shrinking core geometry of moisture in a single coal particle (from Monazam *et al.*, 1998)

Figure 5.8 represents a single, spherical coal particle of radius R_0 with a contracting core of dry coal presenting a sorption surface of radius r_v. The vapour density at the exterior surface of the particle and the sorption surface are ρ_v^{R0} and ρ_v^{rv} respectively. In the bulk gas the vapour density is ρ_v^g.

The rate of water uptake by the particle, r_w, is given by:

$$r_w = \frac{3r_v^2}{R_0^3} M_e \rho_p \frac{dr_v}{dt}$$

(5.5)

where M_e is the equilibrium moisture content of the particle, ρ_p is the density of the coal

particle and r_v is the radius of the sorption surface at any time, t.

The rate of movement of the sorption surface was shown by Monazam *et al.* to be given

by:

$$\frac{dr_v}{dt} = \frac{R_0^2 K_g \left(\rho_v^g - \rho_v^{r_v} \right)}{M_e \rho_p r_v^2 \left(1 + BI \left(\frac{R_0}{r_v} - 1 \right) \right)}$$

(5.6)

where D_w is the diffusivity of water into the particle, K_g is the mass transfer coefficient and

BI is the mass transfer Biot number. The Biot number is defined as:

$$BI = K_g R_0 / D_w = 2$$

(5.7)

Monazam *et al.*, 1998, included in their model expressions to account for the mass transfer

of water vapour through the layer of coal in the weighing jar. In the experiments on the

Puxtrees coal, however, the 9 mm diameter particles were completely exposed to the test

atmosphere since there were only about 4 to 5 particles in each weighing jar. Hence the

mass transfer expressions derived by Monazam *et al.* were not used.

Equation 5.6 cannot be solved analytically because $\rho_v^{r_v}$ also varies with time so a

numerical solution is necessary. This was achieved by rearranging Equation 5.6:

$$dr_v = \frac{R_0^2 K_g \left(\rho_v^g - \rho_v^{r_v} \right)}{M_e \rho_p r_v^2 \left(1 + BI \left(\frac{R_0}{r_v} - 1 \right) \right)} dt$$

(5.8)

and, using a Visual Basic routine, solving for dr_v at small time steps. At each step, the rate

of moisture uptake, and hence moisture content of the particle, was calculated. Using this

moisture content, the relative humidity at the sorption surface for the next time step was

determined using Equation 5.2. This process was repeated until the program converged. Plots of moisture content versus time could then be prepared from the model output.

The program was tested by comparing its output to some of the results presented by Monazam *et al.* for single, 3 mm radius, char particles of char made from a Wyoming coal. Their results were for relative humidities of 30 and 80 percent and at a temperature of 25 °C. The value of D_w they used was 0.0225 cm^2 s^{-1}. The empirical constants K and n in Equation 5.2 were not reported directly but some experimental data were provided from which these parameters could be calculated for the char and were found to be 6.41 and 2.70 respectively.

Running the program yielded moisture content versus time curves which were virtually identical to those reported by Monazam *et al.*, 1998, confirming that the program used here was indeed the same model used by this group.

Figure 5.9 shows some selected moisture uptake measurements made on Puxtrees coal at various conditions of temperature and relative humidity compared to the corresponding model predictions. In general, the model was able to predict the actual moisture content of the coal with a reasonable degree of accuracy for most conditions.
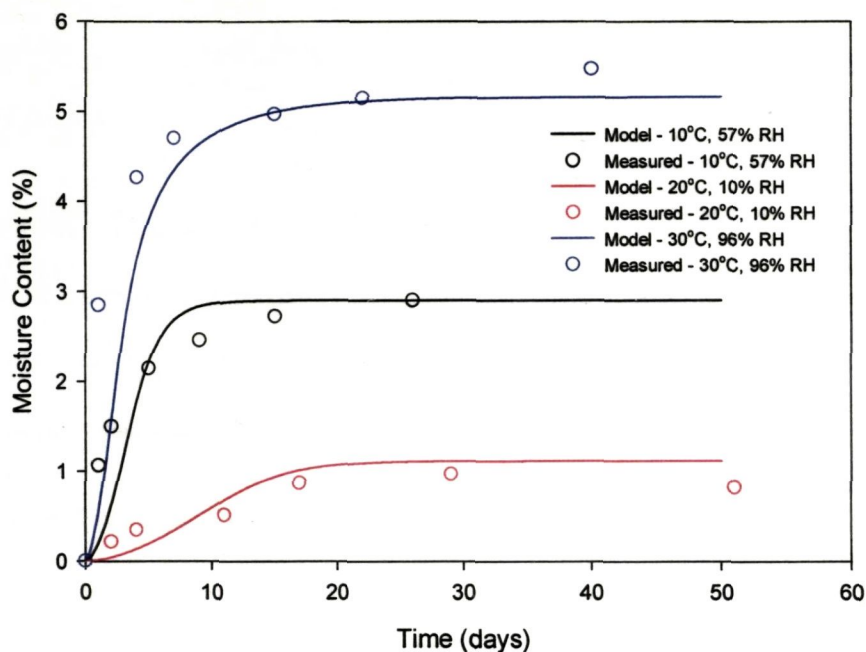
Figure 5.9. Comparison of model predictions with measured moisture contents as a function of time for Puxtrees coal

The equilibrium moisture content estimated by the model was usually very close to the measured value, which is to be expected given that Henderson's equation (Equation 5.2) used to model the isotherm, yielded very good agreement with the actual isotherms (Figure 5.3). In all instances where the estimated final moisture content differed from the measured value, it corresponded to a region where Equation 5.2 did not fit the isotherm particularly well, e.g. the top end of the 10 °C isotherm.

To achieve the best fit to the measured moisture data, it was necessary to adjust the value used for the diffusivity of water vapour. Monazam *et al.*, 1998, found that a value of 0.0225 cm^2 s^{-1} gave the best fit in their modelling. However, this group was attempting to model moisture uptake by char, which is likely to have significantly different properties to coal.

Recent work by Liu *et al.*, 2000, found that the intruded volume (measured by mercury porosimetry) of chars made from Australian bituminous coals was of the order of 1 mL/g. This is about 20 times higher than the result obtained for the Puxtrees coal suggesting that access to the interior of coal by water vapour is much more restricted than in char. In view of this result it was not surprising to find that the value of 0.0225 cm^2 s^{-1} used by Monazam *et al.* was too high when applied to the Puxtrees coal and resulted in the predicted moisture content reaching the equilibrium content much faster that was observed in practice. A value of about 0.0005 cm^2 s^{-1} was found to give the best fit when applied to the Puxtrees coal. The effect of varying the value of diffusivity is shown in Figure 5.10.
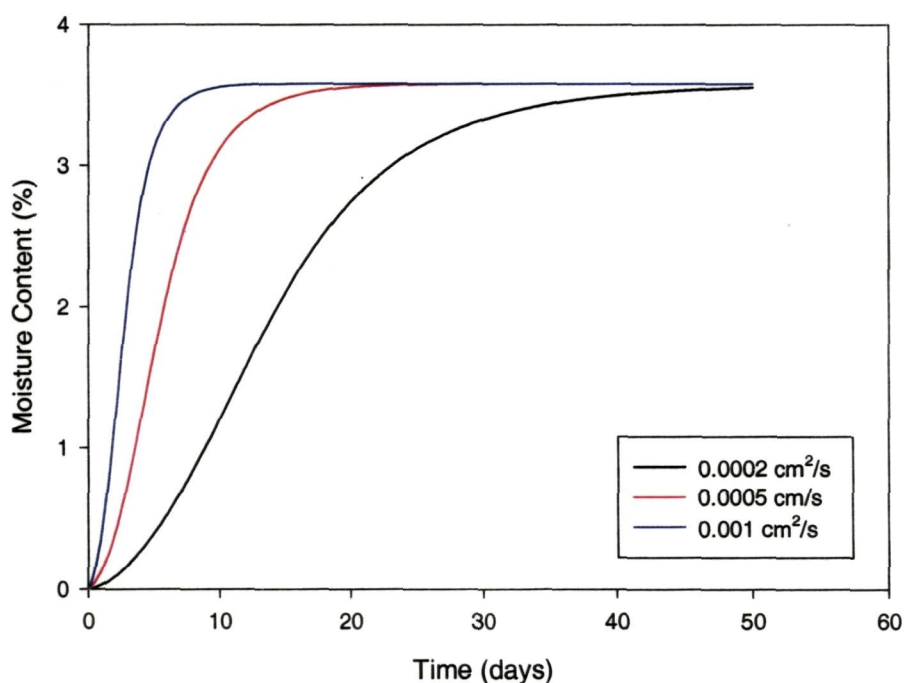

Figure 5.10. The dependence of the model output on the value used for D_w

In the example shown in Figure 5.10, the radius of the particle was set to 5 mm with a temperature and relative humidity of 20 °C and 75 percent respectively. When D_w was set to 0.001 cm^2 s^{-1} the equilibrium moisture content was reached after about 10 days, but with

a value five times lower at 0.0002 cm^2 s^{-1}, the final moisture content was not reached until about 50 days. A higher value of D_w implies greater access to the interior of the particle.

Once a reasonable value of D_w was established, the model was be used to make predictions for a range of conditions of temperature, relative humidity and particle size. The trends predicted by the model were then compared to those observed in the experimental results. In the following examples, a value of 0.0005 cm^2 s^{-1}, was used for D_w.

The effect of temperature predicted by the model is illustrated in Figure 5.11.

**Figure 5.11. The dependence of predicted moisture content on temperature as a function of time.
Particle size = 5 mm, relative humidity = 75 %**

The model predicted that the rate of moisture uptake increases with increasing temperature. This is the same effect that was observed in the experimental results. The model also shows that the final equilibrium moisture content of the coal is slightly higher at lower temperatures. At 10 ^{o}C the moisture content predicted by the model was 3.63 percent

compared to 3.47 percent at 40 $^{\circ}$C. This trend is also consistent with the experimental results although the scatter in the results obscures the small differences in moisture content.

The effects of relative humidity on the rate of adsorption and final moisture content are clearly demonstrated by the model. Figure 5.12 shows the predicted rate curves for 25, 50 and 75 percent relative humidity.

Figure 5.12. The dependence of predicted moisture content on relative humidity as a function of time. Particle size = 5 mm, temperature = 20 $^{\circ}$C

The rate of moisture uptake increased with increasing relative humidity although the time taken to reach the equilibrium moisture content was about the same in each case. The curves shown in Figure 5.12 are entirely consistent with the experimentally results obtained for the Puxtrees coal.

Finally, the effect of particle size was examined by setting the temperature to 20 $^{\circ}$C and the relative humidity to 75 percent (Figure 5.13).
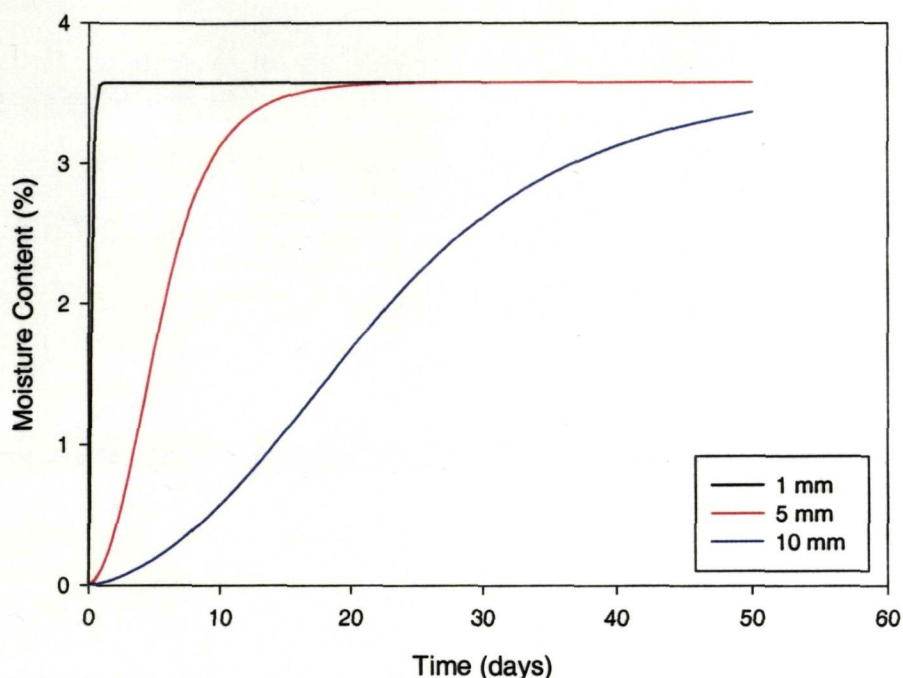
Figure 5.13. The dependence of predicted moisture content on particle size as a function of time. Relative humidity = 75 %, temperature = 20 °C

A particle with a radius of 1 mm is predicted to reach its final moisture content within about two days which was generally the case for the measured rates.

5.4 References

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Chapter 6

Conclusions

6.1 Coal Characterisation

The chemical composition of the high volatile bituminous coal from the Puxtrees seam in the Hunter Valley examined in this study did not vary significantly with particle size over the range of 0.125 to 9 mm particle diameter. In the finest fraction (125 μm average diameter particles) there was, however, a slight enrichment in mineral matter. This was probably due to differences in the density of the mineral matter and the organic material. As the coal is crushed and sieved, the heavier mineral matter is released from the organic matrix and tends to separate and concentrate in the finer material.

The petrology of this coal was also relatively unaffected by particle size range up to about 2.25 mm diameter but above this size, the vitrinite content increased with a corresponding increase in the inertinite content. Despite the significant difference in maceral composition between the coarse and fine material, the inherent reactivity of the coal was unaffected. This, combined with the fact that the chemical composition was essentially the same across all particle size fractions confirms that the differences in the oxidation rate observed between particle size fractions were the result of physical effects rather than differences in the chemistry of the process.

6.2 Pore Structure

The total volume of the coal pores measured by mercury porosimetry (i.e. those with radii above about 3.75 nm) increased with decreasing particle diameter, varying by a factor of about 50 percent over the particle size range of 0.303 to 7.3 mm. The reason for this is that most of the larger pores accessible to the mercury are on or near the surface of the particles. Towards the interior of the particles, these pores are not accessible because they

are either not connected to the surface (i.e. blind pores) or the interconnecting pore network is too small for mercury to penetrate. For smaller particles, the external surface area per unit mass is much higher so there is a proportionally higher number of relatively large accessible pores in small particles. In this particular coal, more than 35 percent of the accessible pores in the 0.303 mm particles were more than 100 nm in radius whereas for 5.73 mm material, only about nine percent were above 100 nm.

Helium pycnometry results also showed a particle size dependence, with the apparent density increasing with decreasing particle size. The apparent drop in density with particle size suggests that some of the internal void space in the larger particles is not accounted for by the measurement technique. Consequently, the volume of the sample is overestimated which results in the measured density being lower than the true density. Taken with mercury porosimetry, these results indicate that a large proportion of the internal porous structure, particularly in larger particles, is even inaccessible to helium and presumably, oxygen.

In contrast to the mercury porosimetry and helium density results, surface area measurements of the microporous region of the coal (< 2 nm in radius) using CO_2 adsorption showed essentially no particle size dependence. Given that CO_2 molecules are larger than helium atoms it seems improbable that the very fine pores should be more accessible to CO_2 than helium. A possible explanation to this apparent anomaly may be that, unlike most other gases, CO_2 can dissolve into solid coal thus enabling it to reach blind pores, which would otherwise be inaccessible.

The measurement technique used for determining CO_2 surface areas on coal appears to have an effect on the results obtained. Results from this study indicated that the CO_2

adsorbate must be allowed to remain in contact with the coal sample for periods of many hours or even days to enable equilibrium to be established and thus determine the entire microporous surface area. In a commonly used measurement technique where a flowing stream of adsorbate gas flows over the sample, contact times are typically less than one hour. This method was found to yield low surface areas because there was insufficient time for the adsorbate to fully access the pore network.

The porosity of the coal, measured by mercury porosimetry, appears to be an indirect measure of the reactive surface area of the coal. External surface areas calculated from spherical geometry underestimate the reactive area by a very large factor because they do not include the internal pore structure of the coal. Internal surface area measurements made using CO_2 adsorption, at least using the method employed in this study, overestimated the available reactive area because the blind pores (which are not available for reaction) are apparently included in these measurements. Mercury porosimetry, on the other hand, provided a measure of the relatively large pores which connect to the exterior of the particle and this seems to be related to the active surface area.

6.3   Effect of Particle Size on the Rate of Oxidation

The results presented in this thesis show that the oxidation rate of Puxtrees coal is affected by the particle size in some circumstances, but not in others. At 75 °C, the rate of oxidation was barely affected by the particle size over the range of 0.125 to 9 mm, but at higher temperatures, the rate began to decrease with increasing particle diameter. When the diameter of the particles was less than about 1 mm, however, the rate remained unaffected by particle size to at least 120 °C.

The rate of oxygen consumption, R_O, was found to be proportional to particle diameter, d, according to the expression:

$$R_O \propto d^{-m} \tag{6.1}$$

where m is an empirical constant.

In the regions where there was no particle size effect, m was equal to zero. In other regimes where the rate decreased with increasing particle diameter, m was found to vary from 0.04 at 75 °C to 0.23 at 120 °C.

The results of this work show that oxidation occurs within some fraction of the pore network near to the external surface, forming a diffuse oxidation layer around the particle. The overall rate of oxidation within this layer can be controlled by the intrinsic chemical rate of oxidation or the rate of diffusion of oxygen molecules to reaction sites. Since any increase in the reactive surface area of a coal particle due to reduced particle size is small compared to the internal area, it follows that the rate of chemical reaction should be relatively unaffected by changes in particle size. Hence, in regimes where the rate of oxidation is not affected by particle size, the overall reaction must be predominantly under chemical control.

The radius of the particle where particle size effects start to become apparent probably corresponds to the depth to which oxygen can penetrate the particle. At this radius, or less, the entire internal surface area is accessible to oxygen, however, above this radius access to the interior of the particle is restricted and the flow of oxygen to the reaction sites is no longer enough to supply the chemical reaction. As a result, the limiting process shifts to diffusion and the overall rate of oxidation decreases with increasing particle diameter.

At lower temperatures, or for coals with low intrinsic reactivity, the rate of chemical reaction will be slow so that oxygen can diffuse further into the particle before being

consumed by the reaction. In this situation the oxidation layer will be thicker so that the range where the rate is unaffected by particle size will extend to larger particle sizes.

6.4 Kinetic Modelling

The effect of temperature on the oxidation rate of coal was well described by the Arrhenius equation. For the Puxtrees coal, the Arrhenius equation was applicable over the temperature range of 22 to120 °C and yielded an average activation energy of about 45 kJ/mol.

To attempt to model the effects of other variables, particularly time and particle size, on the rate of low temperature oxidation several other models were applied. Each of these is discussed below.

6.4.1 Elovich Model

This simple, empirical model underestimated the oxidation rate by as much as a factor of two at $t = 0$, but after about two to three days the rate estimated by the model agreed quite well with the measured rates. A significant disadvantage with the Elovich model, apart from its inability to accurately predict the initial rate, is that it takes no account of the effects of temperature or particle size. An attempt was made to extend the model to accommodate these effects by developing relationships to predict the two Elovich parameters as functions of temperature and particle size. The uncertainties associated with estimating these parameters were, however, quite high and resulted in modelled rates that did not compare well with experimental data.

6.4.2 Shrinking Core Model

The shrinking core model, unlike the Elovich equation, is based upon physical properties of the coal and oxidation environment rather than empirical constants and it explicitly includes the reaction temperature, particle radius and time. This model could be made to fit all of the experimental rate measurements almost perfectly, but to achieve this fit it was

necessary to adjust the parameters representing the rate constant and diffusion coefficient for each condition of temperature and particle size. A consequence of this adjustment was that the values of k and D_e required by the model to achieve the desired fit increased substantially with increasing particle size. In reality, the rate constant should not be affected by particle size. The diffusion coefficient should also be constant with particle size although the presence of cracks in larger particles may lead to a real increase in diffusivity.

The apparent increase in these values with increasing particle diameter is related to the assumption in the model that the chemical reaction between oxygen and coal is confined to a sharp reaction front on the surface of a shrinking sphere. It seems that the excellent fit to the measured rates afforded by this model was due to the values selected for the rate constant and diffusion coefficient containing some undefined factor which compensated for the assumption that the reactive surface is spherical. This compensation had the effect of making the rate constant and diffusion coefficient appear to increase over a very wide range with increasing particle size.

An extension to the shrinking core model (suggested by Carras), in which each coal particle was considered to be made up of many, much smaller, spherical particles which themselves behaved as shrinking cores, proved to largely overcome the problem of increasing diffusivity and rate constant with increasing particle diameter. In this model, the diffusivity was found to be constant over the entire particle size range. The rate constant increased slightly with increasing particle size but the effect was much less than was the case if the basic shrinking core model was used. In its present form, the extended model can only be applied to oxidation regimes where there is no particle size effect because it does not yet include an expression to calculate the oxygen profile within the particle.

Inclusion of such an expression would significantly improve this model and make it generally applicable for a wide range of conditions.

6.4.3 *Pore Tree Model*

The pore tree model is a complex, semi-empirical model developed in an attempt to model the porous structure of coal. The pore tree model did not fit the measured rates well. A trend of decreasing rate with increasing particle diameter was successfully predicted, however, the extent of this effect was substantially more than reflected in the experimental results. One of the problems associated with using this model was the large number of input parameters required to run it. Some of these parameters can be measured but most must be estimated or simply adjusted to yield the best fit to the data.

The other, and probably more important, shortcoming of this model is that the predicted rated does not decrease with time. It therefore is unable to model the ageing effect on coal. This limits its application to oxidation regimes that have reached approximate steady-state conditions and for this reason the pore tree model cannot be used as a general model for low temperature oxidation of coal.

6.5   Moisture Adsorption

Moisture uptake by Puxtrees coal was examined over a temperature range of 10 to 60 °C and at relative humidities from about 10 to 100 percent. The effect of the particle size on the amount and rate of moisture adsorption was also studied.

For coal particles with diameters within the range of about 0.1 to 9 mm the amount of water adsorbed (at a given temperature and relative humidity) was independent of the particle size. Temperature also had little effect on the final equilibrium moisture content.

Adsorption of moisture onto Puxtrees coal was well described by the Langmuir isotherm for relative humidities up to about 80 percent. Beyond this, however, the amount of water taken up by the coal was considerably higher than predicted by the Langmuir model. An empirical model developed by Henderson provided a much better fit to the experimental data over the entire relative humidity range and was applicable at temperatures between 10 and 60 °C. The disadvantage of Henderson model is that it requires two curve-fitting parameters that must be determined from experimental measurements made on the material to which it is applied.

The rate of moisture adsorption was characterised by being initially rapid but tapering off to zero as the equilibrium moisture content was approached. The rate was found to:

- Increase with increasing relative humidity. At 97 percent relative humidity, the rate of moisture uptake was about 6 – 8 times faster than at 10 percent.

- Increase with increasing temperature according to the Arrhenius relationship. The activation energy of the adsorption process was approximately 8 kJ/mol.

- Decrease with increasing particle size.

The rate of moisture adsorption was found to fit a solid state reaction model of diffusion in a sphere. This model provided a reasonable fit to the data over most of the adsorption process, however, a much more sophisticated model developed by Monazam et al. resulted in a better fit to most of the experimental data. Monazam's model had the advantage that the input parameters included temperature, relative humidity and particle size so that the rate of adsorption could be predicted for any combination of experimental conditions. The effect of each of these variables on the rate of adsorption predicted by the model agreed very well with the trends observed in the measured rates. Monazam's rate model used

Henderson's isotherm equation and consequently, the final equilibrium moisture contents predicted by the rate model also agreed closely with the measured values.

A problem with this rate model is that it requires a value for the diffusion coefficient of water vapour in the coal particle, which is not readily available and cannot be easily measured. Additionally, since it also relies on the Henderson model to predict the equilibrium moisture content, the coal-specific parameters required by that model are also needed.

Appendix

Summary of Previous Research into the Effect of Particle Size on the Rate of Oxidation

Table A.1. Summary of research into the effect of particle size on the rate of low temperature oxidation.

Authors	Type of Coal	Temperature Range (°C)	Particle Size Range (mm)	Type of Reactor	Results
Carpenter and Sergeant, 1966	South Wales	37-105	0.036-1.866	Isothermal, Fixed Bed	• Oxidation rate increased with decreasing particle size until a critical size was reached • Activation energies increased with increasing particle size (11.7-23.4 kJ/mol).
Sondreal and Ellman, 1974	North Dakota lignite	65	2-9.5	Isothermal	• Rate was dependent on particle size according to: $$r = c/m(1 - e^{-km})$$
Karsner and Permutter, 1981	7 US coals of various ranks	150-300	0.7-2.3	Isothermal fixed bed	• Oxidation is diffusion controlled for most coals, however, for very porous coals, the rate is chemical controlled • Activation energies were between 39-63 kJ/mol • Particle size did not affect activation energy
Karsner and Permutter, 1982 (a)	Illinios hvC bituminous (one of the coals used in the 1981 study)	150-160	0.84-2.79	Isothermal fixed bed	• Particle size had no effect on rates of production of CO_2, CO or water at these temperatures • Activation energies were determined for each reaction: 105 kJ/mol for carbonic gas formation, 42 kJ/mol for O_2 adsorption, 76 kJ/mol for O_2 desorption and 139 kJ/mol for O_2 chemisorption
Karsner and Permutter, 1982 (b)	7 US coals of various ranks (same coals as used in their 1981 study)	150-300	0.297-2.36	Isothermal fixed bed	• All samples exhibited particle size effects • Developed model by incorporating an effectiveness factor to account for diffusive effects
Polat and Harris, 1984	Loy Yang brown coal	35	0.039-0.10	Microbalance	• Particle size had no effect on oxidation rate
Kaji, Hishinuma and Nakamura 1985	Wyoming, Queensland, Hokkaido, China and Vietnam	30-250	0.074-1.0	Fixed bed isothermal	• Particle size had no effect on oxidation rate • Activation energies 51.5-59.4 kJ/mol for CO and CO_2 formation
Rahman, Hasan and Baria, 1986	Montana sub-bituminous	?	?	?	• Oxidation rate was affected by particle size • Rate was controlled by surface (chemical) reaction in smallest particles • Reactivity was proportional to 1/5 power of particle size

Kaji, Hishinuma and Nakamura 1987	Wyoming, Queensland, Hokkaido, China and Vietnam	20-65	0.074-1.0	Fixed bed isothermal and calorimeter	- Heat generation independent of particle size - Activation energy for oxidation ranged from 51 to 54 kJ/mol for all coals tested - Heat of oxidation 313-397 kJ/mol
Itay, Hill and Glasser, 1989	South African coal	25-140	0.045-0.710	adiabatic	- Smaller particles reacted faster (but not in proportion to internal surface area) - Heat of reaction ~450 kJ/mol
Palmer, Cheng, Goulet and Furimsky, 1990	3 Canadian and Illinios No 6 coals	150-250	-0.038-2.0	isothermal microbalance	Rate of oxidation increased with decreasing particle size until about 50 μm
Akgün and Arisoy, 1994	Turkish coal	above 75	2-50	adiabatic	- Activation energies of 33.0 to 52.6 kJ/mol reported - Activation energy decreased with increasing particle size - Rate controlling mechanism determined to be pore diffusion
Pànek and Tabara, 1996	60 different coals	30-50	0.075-1.125	pulsed flow calorimetry	- There was a particle size dependence - Activation energies in the range of 15-48 kJ/mol - Highest activation energies associated with coals of highest porosity - thus diffusion decreases apparent activation energy
Krishnaswarmy, Gunn and Ararwal, 1996	Wyoming sub-bituminous coal	27-60	0.297-2.0	isothermal fixed bed	- Rate decreased with increasing particle size - Activation energies found to be 57.5 kJ/mol for burn off reaction, 53.1 kJ/mol for sorption and 90.4 kJ/mol for decomposition of oxy-coal compounds