Measurements and Analysis of Water Adsorption and Desorption by Coals and Chars

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MEASUREMENTS AND ANALYSIS OF WATER ADSORPTION AND DESORPTION

BY COALS AND CHARS

by

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Abstract

An investigation was carried out on the adsorption and desorption of moisture in chars of low rank coal. Equilibrium moisture sorptions of dry and moist chars were measured at room temperature and relative humidity of 30% and 80%. Based on these measurements, a novel mathematical model was developed to predict both the rate and the level of hydration for coals and chars. The formulation uses a shrinking core model which required only the measurement of the adsorbing material's equilibrium moisture content at different temperatures and humidities. The model was validated against experimental and literature data. It accurately and reliably predicted both the rate and extent of hydration and dehydration for coals and char. Using this model, the effects of varying temperatures, relative humidities, and size of the particles and coal pile were simulated. The sensitivity study demonstrated that, as expected, relative humidity and temperature had strong effects on both the rate of hydration and the equilibrium moisture of coal or char. The particle size dramatically influenced the rate of hydration, but had no affect on the equilibrium moisture content. This model can be used effectively to simulate the impact of moisture on drying, storage, and spontaneous combustion of coals and coal-derived chars.
Introduction

According to the United States Geological survey, a large proportion of the total fuel reserve in the United States is in high moisture, low rank coal. These coals have been found to be expensive and difficult to transport. Drying and partial pyrolysis of coals minimizes these problems but raises another by increasing the susceptibility of the char to auto-ignition.

The Department of Energy has been actively engaged in a program toward understanding the spontaneous combustion of coal/char in storage. It has been reported in the literature [1-4] that the presence of moisture in a humid climate is a major cause of auto-ignition. Therefore, a part of that program is devoted to developing a technique for predicting the rates of adsorption and desorption of moisture by stored char and coal. A study of moisture adsorption and desorption characteristics in both dry and moist coal and char was undertaken to provide a fundamental basis for such prediction.

Moisture has several potential effects on the self-heating of coals and chars. Foremost is the heat released upon hydration of dried coals which can liberate sufficient heat to raise the coal temperature. Schmidt [3] reported that the condensation of enough water to raise the moisture content of coal 1% is sufficient to raise its temperature 17 °C. This, in turn,
increases the rate of oxidation more than fivefold. Drying coals also dramatically effects the heat capacity of the coal such that reduced moisture content leads to a lower heat capacity [5]. The effect is that dried low rank coals have significantly increased tendencies to self-heat. Such physical and chemical effects were directly incorporated into the model of coal hydration and drying presented here.

For low rank coals, moisture also plays an integral role in the structure of the coal which are considered to be "colloidal" or "gel-like" in nature [3]. Upon drying and removal of "inherent" moisture, the gel-structure is disrupted and shrinkage or "slacking" is observed [3,6]. The Fleissner process [7] uses steam to maintain an open structure during heating and drying to avoid such particle decrepitation. In addition, moisture interacts with oxygenated coal species and intermediates in the oxidation process. This interaction may alter the stability of the carbon oxygen complexes and thus the rate of the weathering process. The model presented here will describe the projected water sorption behavior in the absence of such structural and mechanistic effects.

Since all the coal and char storage piles are exposed to air with some relative humidity, a quantitative knowledge of the rate of moisture adsorption and desorption is important. The present study describes a unique mathematical model that uses the
relationships for equilibrium moisture content within a shrinking core model. This model predicts the rate of moisture adsorption and desorption by coal and/or char at various environmental conditions.

Experimental

The Piceance basin Wyodak coal was used to prepare char samples by heating 2" by 1/8" inch coal in a packed bed. The heating was done in two stages. In the first stage the coal bed was heated by passing a hot flue gas stream through the bed to raise the temperature and remove moisture without initiating pyrolysis. In the second stage a hot recycle gas stream from an external combustor was passed through the dried coal bed to further increase the temperature gradually up to 1000 F, before quenching. Dried char samples were taken from an indirectly cooled section and sealed in air tight steel cans, while moist char samples were removed downstream after passing through a rotating drum heat exchanger with direct water spray to introduce the desired amount of moisture. These were also sealed in air-tight steel cans.

The rate of water adsorption and desorption for various coal and char samples were determined gravimetrically. A 10-gram aliquot of each sample (mean diameter of 1 mm) was weighed into a petri dish having a diameter of 82 mm. This provided a thin
layer of sample only about 3 mm thick. The samples were placed
in a constant humidity chamber consisting of a 10-liter
desiccator and a constant humidity solution. The rate of
evaporation of the solution was increased by using paper towels
as wicks around the circumference of the container. Different
relative humidities (RH) were attained in the chamber using the
following materials: anhydrous calcium sulfate (RH = 0%),
saturated calcium chloride solution (30%), saturated calcium
nitrate solution (50%), and saturated sodium chloride solution
(80%).

The Petri dishes were removed from the chamber periodically,
immediately covered with lids, weighed using a 3-place analytical
balance, and returned to the chamber. The rates were measured at
room temperature.

At the conclusion of water sorption, the sample was dried in
an oven at 110 °C with flowing nitrogen to determine the
equilibrium moisture and initial moisture contents of the sample.

In a few experiments the solution in the desiccator was
agitated using a magnetic stirrer. The result splashing of the
solution and air current did not increase the rate of adsorption.
This indicated that the rate of adsorption was not being limited
by the rate of mass transfer of the moisture from the solution
through the atmosphere to the coal.
Description of the Model

The modelling of the rate of sorption of moisture by a coal or char particles is a complicated process and involves consideration of physicomechanical and physicochemical aspects of the moisture. In 1906 Gibbs [8] proposed the following relationship as a basis for adsorption:

\[ \Gamma = -(\frac{\partial \sigma}{\partial \mu})_T \]  

(1)

Where \( \Gamma \) is the "surface concentration" of the absorbed gas in mole/cm\(^2\), \( \mu \) its chemical potential, \( T \) absolute temperature, and \( \sigma \) the work required to form 1 cm\(^2\) of new surface under the environmental conditions defined by \( T \) and \( \mu \).

For an adsorbate of perfect gas, one can replace:

\[ \partial \mu = RT \partial \log P \]  

(2)

Bangham [9,10] used equations (1) and (2), and derived an expression for the adsorption of vapor on coal char as:

\[ \sigma - \sigma = CRT \ln \frac{P_s}{P} \]  

(3)

Where \( C \) is the concentration of the adsorbed liquid in moles per cm\(^2\) of wetted surface, and \( P_s \) is the saturated pressure of water at temperature \( T \).

Henderson [11] applied equation (3) to the equilibrium moisture content curves of a number of material and found to have
the mathematical characteristic:

\[ 1 - RH_e = \exp(-KTM_e^n) \]  

(4)

Where \( RH_e \) is equilibrium relative humidity, \( M_e \) is equilibrium moisture content, dry basis, factor \( K \) and exponent \( n \) vary for different materials.

It is well known that there are three dominant types of water-coal linkage: chemically bonded water; water adsorbed by physicochemical forces; and free water held by physicomechanical forces \([4,12]\). Coal and char are considered to be hygroscopic materials \([13]\) with micropores smaller than 1 \( \mu m \) in radius which filled with moisture with weak bond energy (100 j/mol) to confining capillary walls. On the other hand, chemically attached moisture, such as water of crystallization, can have a bond energy of 5000 j/mol. The adsorption or desorption of lightly bound moisture will not change the material's form and properties significantly, but adsorption or desorption of strongly bound moisture will induce changes in the character of the solid. In this study, for modelling purpose, it is assumed that the rate of sorption of adsorbed and free water are dominant and may happen simultaneously and related to the gradient of vapor density between the saturation liquid at the evaporation/condensation surface and the gas phase. Bangham et al. \([10]\) described the adsorbed film formed by the vapor as a Langmuir Monolayer in which the molecules have fixed points of attachment. Based on this vapor existing within the material can be
considered as a concentric sphere. Therefore, with spherical geometry assumption, as portrayed in Fig. 1, the rate of water sorption can be written as:

\[
\frac{3r_v^2}{R_o^3} M_o \rho_s \frac{dr_v}{dt} = r_v
\]

(5)

Where \( r_v \) is the radius of the water sorption surface (Bangham's evaporation/condensation surface) at any time \( t \). The rate of movement of the sorption surface can be obtained by a vapor balance at \( r=r_v \);

\[
\frac{dr_v}{dt} = \frac{D_w \partial \rho_v}{M_o \rho_s \partial r}
\]

(6)

For the moisture vapor profile within the particle in the region \( r_v < r < R_o \), is provided by the solution of:

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 D_w \frac{d\rho_v}{dr} \right) = 0
\]

(7)

with the boundary conditions;

at \( r=R_o \)

\[
D_w \frac{d\rho_v}{dr} = K_g (\rho_v^R - \rho_v^G)
\]

(8)

and at \( r=r_v \)

\[
\rho_v = \rho_v^{r_v}
\]

(9)
By combining the equations (6) through (9), the following equation can be derived:

\[
\frac{dV}{dt} = \frac{R_0^2 K_g (\rho_v^g - \rho_v^r)}{M_p \rho_p R_v (1 + BI_m (R_0^g - 1))}
\]

(10)

Where BI_m, K_g, D_w are the mass transfer Biot number, mass transfer coefficient (cm/sec), and water diffusion (cm^2/sec) through the particle, respectively.

The equation (10) was also used by Arisory et al. [14], and McIntosh [15] in their modelling efforts on spontaneous combustion and drying process.

Finally, the differential equation for mass diffusion of moisture through the layer of coal/char sample in the petri dish of the experiment can be written as:

\[
\epsilon \frac{\partial \rho_v^g}{\partial t} = D_g \epsilon \frac{\partial^2 \rho_v^g}{\partial y^2} - \nu_g \frac{\partial \rho_v^g}{\partial y} + (1-\epsilon) V_v
\]

(11)

where \( \epsilon \) is void fraction between the particles. The boundary conditions are:

at \( y=0 \)

\[
\rho_v^g(0) = \rho_v^{ginlet}
\]

(12)
and at y=L

\[ \frac{\partial \rho_y}{\partial y} = 0 \]  

(13)

The moisture in the coal particle was calculated by;

\[ \rho_p \frac{\partial M}{\partial \lambda} = \lambda \]  

(14)

where M is the coal moisture content (kg/kg).

Solution procedure

The way in which moisture is adsorbed or desorbed by its host material, the knowledge of the moisture-solid equilibria is essential to the solution of these phenomena. Therefore, an attempt was made to measure the equilibrium moisture content of each sample as a function of relative humidity. However, in order to ease the experimental tasks, first the reliability of equation (4) was tested against the equilibrium moisture data of coal obtained by Glanville et al. [16] and Nordon et al. [17]. Their experimental data was limited to a temperature of approximately 25 °C. In order to obtained the values for K and n in equation (4), the knowledge of equilibrium moisture content at two relative humidities is necessary. In Fig. 2, prediction of equation (4) is shown to fit the experimental data. Therefore, if equilibrium moisture contents are known for two different relative humidities, equation (4) can be used to predict the equilibrium moisture content at any relative humidity.
In Fig. 3 the equilibrium moisture content is presented for two Wyoming chars based on two measured points (equilibrium moisture content at 80% and 30% RH). If a dry solid is exposed to an atmosphere of fixed relative humidity, it will gain moisture until equilibrium is reached. Increasing the relative humidity of the surroundings will then cause the solid to gain more moisture to reach another equilibrium state.

The water vapor at the core was assumed to be in equilibrium with the particle moisture content at all time, with it value as:

$$\rho_{v}^{r=\text{RH}_{e}} \rho_{s}$$  \hspace{1cm} (15)

where the RH$_{e}$ is the relative humidity within the particle and is at equilibrium with particle moisture content, and $\rho_{s}$ is the saturation density at the particle temperature. The relative humidity at equilibrium (RH$_{e}$) was obtained by equation (4) which was pre-determined based on experimental measurements for the specific particle.

Equation (10) was solved using the fourth order Runge-Kutta method with $BI_{n}=K_{n}R_{p}/D_{n}=1$.

Equation (11) was transformed into the appropriate difference form for solution using an implicit Crank-Nicholson scheme and was solved numerically using Thomas'algorithm method.
Results and Discussion

The values of vapor density at the vapor core, eq. (10), is the major factor in determining the movement of water vapor within the particle. In a study of coal drying, Evseev et al. [12] suggested that the vapor density on the sorption surface depends on the temperature and the energy of the water-coal bonding. Due to the lack of information on the energy of the water-coal bonding a second approach was considered in which the sorption behavior at this surface was interpreted using the BET equation [18]. Both of these approaches were tested in our initial analysis; however, the driving forces for hydration were found to be independent of the coal's moisture content. As a result, high levels of water adsorption, unbounded by the coal's ability to adsorb moisture, were observed during hydration simulations.

In this study, the sorption surface was defined based on thermodynamic relationship between the equilibrium moisture content and relative humidity as applied to agricultural materials [11]. Therefore, an attempt was made to measure the equilibrium moisture content at different relative humidities for each sample under study. Based on these measurements a relationship between the equilibrium moisture content and RH was obtained (eq. 4). This approach included the dependence of the sorption surface on temperature, an effective water-coal bonding,
and the equilibrium water capacity.

For the initial analysis of the hydration rate tests, the 3 mm thick layer was assumed to be a single particle with radius of 3 mm and the rate of adsorption or desorption was predicted. The rate of water vapor movement within the single particle was obtained (eq. 10) using a value of 0.0225 cm$^2$/sec for the water diffusion ($D_w$) through the coal or char particle. The comparison between the model (as a single particle) and the experimental measurements is displayed in Figures 4 and 5. Good agreement was obtained for each sample studied.

Then, the hydration tests were analyzed considering the experimental petri dish as a fixed bed with 3 mm thickness, a particle size of 1 mm in diameter, and zero gas velocity through the bed. Using combinations of equations (10), (5), (11) and (14), the rate of adsorption or desorption was predicted and compared with the experimental data. The comparison of model prediction and test data demonstrated good agreement if the value of diffusion coefficient of water through the bed was the same as diffusion coefficient of water through the particle (0.0225 cm$^2$/sec) (Figures 6 and 7). These simulations were performed assuming a void fraction of 0.35.

However, literature [14] suggests that the diffusion coefficient of water through the air is about 0.25 cm$^2$/sec. This
diffusion coefficient is about 11 times greater than the value required by the model to match the test data. On the other hand, Nordon et al. [19] measured the diffusion coefficient of water through the bulk char of 60% voidage to be 4.9 times less than diffusion coefficient of water through the air. Therefore, the results obtained from this study are consistent with Nordon et al. [19] measured values.

The model was also used to predict the rate of adsorption of water vapor by Yallourn-Briquette char published by Nordon et al. [19]. A comparison between the model and experimental data was found to be in very good agreement as displayed in Fig. 8.

Sensitivity Study

In order to test further the utility of the model, the sensitivity of the rate of hydration was examined for its response to some key physical parameters in the model. Parameter sensitivities were chosen to include the effect of particle size, temperature, and relative humidity on the rate of hydration for dry Wyoming char. For the sensitivity analysis a baseline condition was selected. The base conditions included a particle size of 6 mm, temperature of 25 °C, and relative humidity of 80%. The rate of hydration for each of the model input parameters of interest was then examined by holding others constant, while varying the value of the parameter under study.
The effect of changing particle diameter on the resulting rate of hydration is illustrated in Fig. 9. These prediction illustrated that the rate of hydration was a strong function of diameter. The observed functional dependence arose from the fact that the rate of hydration is inversely proportional to diameter (Eq. 5).

The dependence of the rate of hydration on temperature is illustrated in Fig. 10. These results show that the rate of hydration increased and the equilibrium moisture content decreased at a given relative humidity as the temperature increased. A strong dependence of temperature on the rate of hydration is understandable because the rate (Eq. 10) is proportional to the core's equilibrium relative humidity. Upon inspection of equation (4) it is also clear that with increasing temperature the relative humidity increases and the equilibrium moisture content at a given relative humidity decreases.

Variation of the relative humidity had a significant impact on rate of hydration. This point is illustrated in Fig. 5. These results are a direct consequence of Equation 5, which indicate that the rate of hydration is proportional to the relative humidity.

Conclusion
A new mathematical approach was applied to predict the rate of adsorption or desorption of water vapor by char or coal particles. The model was based on measured equilibrium moisture content for specific coal or char at two different relative humidities. Excellent agreement between the model predictions and measurements on the rate of adsorption and/or desorption demonstrated that the model was accurate and reliable for calculating the rates of both hydration and drying.

The model was validated against experimental and literature data. It was found that the diffusion coefficient for water through the coal pile was the same order of magnitude as the diffusion of water within the particle.

A sensitivity analysis was performed on the rate of hydration. This rate depended on three essential parameters: the particle size, temperature, and relative humidity. As expected, the particle size strongly affected the rate of hydration, such that the rate was greater for smaller particles, but had no impact on the equilibrium moisture content. The relative humidity strongly affected both the equilibrium moisture content and the rate of hydration. Higher humidity resulted in faster rate and higher moisture content. The temperature also had a strong impact on both the rate and the equilibrium moisture content of the coal or char. As temperature was increased, the rate of hydration increased, but equilibrium moisture content
decreased.
Nomenclature

BI_a  mass transfer Biot number
D_wg  diffusivity of water into the gas (cm² s⁻¹)
D_w  diffusivity of water into the particle (cm² s⁻¹)
K_g  mass transfer coefficient (cm s⁻¹)
L   bed length (cm)
M  equilibrium moisture content (kg kg⁻¹)
P   Pressure (g cm⁻¹ s⁻²)
P_s   saturation pressure (g cm⁻¹ s⁻²)
r_v vapor radius within the particle (cm)
r_w rate of adsorption/desorption of moisture (g cm⁻³ s⁻¹)
R_p  particle radius (cm)
R   universal gas constant
RH_e equilibrium relative humidity
t  time (s)
T   temperature (K)
V_g gas velocity (cm s⁻¹)
y  distance in the Y-direction (cm)

Greek Symbols

Γ surface concentration of the absorbed vapor (mole cm⁻²)
ε   bed voidage
µ   chemical potential
ρ_p particle density (g cm⁻³)
\[ \rho_s \] saturation density \( (g \text{ cm}^{-3}) \)

\[ \rho_v \] vapor density \( (g \text{ cm}^{-3}) \)

\[ \rho_{v^g} \] vapor density in the gas phase \( (g \text{ cm}^{-3}) \)

\[ \rho_{v^v} \] vapor density at the vapor radius \( (g \text{ cm}^{-3}) \)

\[ \rho_{v^p} \] vapor density at the particle surface \( (g \text{ cm}^{-3}) \)
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References


Figure Captions

Figure 1. Schematic diagram of the shrinking core model showing the moisture vapor densities at different radii.

Figure 2. Comparison of the predicted (using eq. 4) and experimental equilibrium moisture contents at 25 °C for different relative humidities. Data from: (*) Glanville et al. [16], (■) Nordon et al. [17].

Figure 3. Solution of the equilibrium moisture equation (eq. 4) for dry (•) and moist (+) Wyoming chars based on data at different relative humidities (30 and 80%) at 25°C.

Figure 4. Single particle model prediction of the rate of hydration for a moist Wyoming char at 25 °C, R_e=3 mm, and different relative humidities: 30% (•) and 80% (+).

Figure 5. Single particle model prediction of the rate of hydration for a dry Wyoming char at 25 °C, R_e=3 mm, and different relative humidities: 30% (•) and 80% (+).
Figure 6. Fixed bed model prediction of the rate of hydration for a dry Wyoming char at 25 °C, \( R_0 = 0.5 \) mm, \( L = 3 \) mm, and different relative humidities: 30% (\( * \)) and 80% (+).

Figure 7. Fixed bed model prediction of the rate of hydration for a moist Wyoming char at 25 °C, \( R_0 = 0.5 \) mm, \( L = 3 \) mm, and different relative humidities: 30% (\( * \)) and 80% (+).

Figure 8. Fixed bed model prediction of the rate of hydration for a dry Yallourn-Briquette char from Nordorn et al. [19] at 25 °C, \( R_0 = 0.5 \) mm, \( L = 3 \) mm, and different relative humidities: 38% (\( * \)) and 74% (+).

Figure 9. Sensitivity test of the single particle model for rates of hydration using different particle sizes: \( R_0 = 0.5, 1.5, \) and 3 mm.

Figure 10. Sensitivity test of the single particle model for equilibrium moisture content as a function of relative humidity for different temperatures \( T = 25, 35, \) and 50 °C.
Fig. 3.
Fig 4.

Char Moisture Content (%) vs. Time (hr)

Time (hr):
0  10  20  30

Char Moisture Content (%):
0  1  2  3  4  5  6  7  8  9  10  11