EFFECTS OF PARTICLE SIZE ON THE DESORPTION KINETICS OF
WATER FROM BEULAH-ZAP LIGNITE COAL:

Differential Scanning Calorimetry Results

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ABSTRACT

The drying kinetics of water from three particle-sized Beulah-Zap lignite coal samples were probed using the differential scanning calorimetry technique at $295 < T < 480$ K. The measurements undertaken under flowing N_2 gas environment indicate that water is lost from this coal by two independent but simultaneously operative kinetic mechanisms. Our results suggest that the unimolecular decay kinetics are obeyed by those water molecules which are near the mouths of large pores and/or surround the coal particles. Most of the water, about 80% of the water lost in our experiments, was removed via a 2nd-order diffusion mechanism. As expected, the desorption activation energies of the 2nd-order diffusion kinetics were much larger than the decay mechanism's activation energies. Our results also suggest, at least for particle sizes $< 841 \mu m$, $< 106 \mu m$, and $< 37 \mu m$, that the coal particle size has little effect on the desorption activation barriers.

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Low-rank coals' high moisture content presents a substantial problem with their effective utilization. Not only does high moisture content waste energy in transportation and coal combustion, but it may also impede secondary utilization reactions¹⁻⁴. Therefore, an effective dewatering technology is required to make low-rank coals economically more attractive. Before this technology can be developed though, it is essential to understand how low-rank coals hold water and how water interacts with coal.

Coal-water interactions are complex because coal not only lacks long-range structural order but also has considerable heterogeneity in the short-range order. This lack of order in coal inhibits the application of mathematical tools, which have been developed to describe the physical structure of materials, to coal. However, it is generally recognized that coal is composed of an organic matrix in which minerals and pores of various sizes are randomly distributed. It is also believed that the pore network usually contains water in "as-mined" coals. Mraw and Silbernagel⁵ suggested that the amount of water present in coal provides a measure of pore volume. On the other hand, Kaji et al.⁶ found no correlation between the water-holding capacity of 13 coals (of various ranks) and their pore volume. They argued that there is a monotonic relationship between the hydrophilic sites in coal and coal's water-holding capacity. They reached this conclusion based on the assumption that the total oxygen of the coal is uniformly distributed in coal. However, the conclusion of Kaji et al. is surprising since the presence of minerals and various cations will alter the coal-water interactions.

Efforts have been directed towards understanding the coal-water interactions by measuring the desorption or adsorption kinetics of water from coal. The most frequently used approach is gravimetric measurements⁷⁻⁹. Vorres et al.^{7,8} adopted the approach of ascertaining the kinetics of vacuum drying of coal as a means to understand complex coal-water interactions. From isothermal desorption experiments, Vorres et al. contended that the dehydration of Illinois No. 6 coal obeys a first order kinetics. They also argued that the rate controlling mechanism is governed by the surface of the coal. Abhari and Isaacs⁹ studied the drying kinetics of water of six coals from the Argonne coal-sample bank by thermogravimetric (TGA) technique and explained their results in terms of bulk moisture/pore moisture model. More recently, Mu and Malhotra¹⁰ demonstrated the capability of the in-situ transmission FTIR technique to probe the desorption kinetics of water from deep cleaned Homer City bituminous coal.

To further our understanding of coal-water interactions, we undertook the differential scanning calorimetry (DSC) measurements on a lignite coal with a view (a) to demonstrate the effectiveness of DSC technique to measure the desorption kinetics of water from coal, and (b) to determine how the particle size affects the kinetic parameters. Also, possible physical models for the desorption of water from lignite coal are discussed.

EXPERIMENTAL TECHNIQUES

To probe the desorption kinetics of water from high-moisture coal, we chose Beulah-Zap lignite coal from the Argonne Premium Coal Sample Program. The received ampule, sealed under

nitrogen, had $< 841 \mu\text{m}$ particle-sized coal. The ampule was broken, and the sample was divided into three fractions. Two of the fractions were ground in a Brinkmann rapid-micro mill to reduce their particle sizes. After grinding the coal samples, two particle sizes of the coal were extracted by sieving the ground coal, i.e., $< 106 \mu\text{m}$ and $< 37 \mu\text{m}$. All three particle-sized samples, i.e., $< 841 \mu\text{m}$, $< 106 \mu\text{m}$, and $< 37 \mu\text{m}$, were transferred to a humidity-controlled chamber, kept at 93% relative humidity. After equilibrium for 96 hours, about 20 mg of the coal samples, accurately weighed on a micro-balance, were loaded in Al DSC sample pan holders. The sample pans were sealed with the help of Al lids. Efforts were made to ensure that the coal samples were loosely packed in the pans so that the mechanical compaction of the particles did not control the overall desorption kinetics of water¹¹. A number of holes were drilled in the Al lids for easy escape of water vapors from the DSC pans. Prior to inserting the pans in the platinum sample pan holder of the DSC system, the samples were again weighed to ascertain if any weight loss or gain had occurred. The elapsed time from when the holes were drilled to when the sample was loaded in the DSC system was minimized.

The desorption of water from $< 841 \mu\text{m}$, $< 106 \mu\text{m}$, and $< 37 \mu\text{m}$ particle-sized lignite coal was determined with the help of a well calibrated¹¹⁻¹³ Perkin-Elmer DSC7 system. The procedures adopted for the calibration of the temperature and of the specific heat have been described elsewhere¹³. Our calibrated DSC system had a temperature precision of $\pm 1 \text{ K}$. The desorption kinetics of

water from Beulah-Zap coal was determined at $295\text{ K} < T < 480\text{ K}$ using a heating rate of 10 K/min under a controlled N_2 purge environment ($30\text{ cm}^3/\text{min}$). After the DSC runs, the sample pans were again weighed to determine the weight loss due to the thermal treatment.

RESULTS AND DISCUSSION

Experimental Results

The non-isothermal techniques, such as thermal gravimetry (TG), differential thermal analysis (DTA), and DSC, have been applied to the study of many chemical reactions in solid state. Applications of non-isothermal measurements have ranged from the qualitative estimation of reaction temperature to the quantitative determination of kinetic parameters¹⁴. Janikowski and Stenberg¹⁵, Elder and Harris¹⁶, and Suuberg et al.⁴ have reported that when coals are subjected to DSC measurements, under an inert environment, a broad endothermic peak is produced at $323 < T < 423\text{ K}$. They argued that this broad peak can be associated with the water loss from coal. Therefore, the non-isothermal DSC scans can impart information on the water's desorption kinetics from coal¹⁷.

Figure 1 reproduces the recorded DSC curves for the three sized particles, i.e., $< 841\text{ }\mu\text{m}$, $< 106\text{ }\mu\text{m}$, and $< 37\text{ }\mu\text{m}$. As can be seen from this figure, all three particle sizes produce a broad endothermic peak centered at around 373 K . It should also be noted that the endothermic peak occurs in the same temperature range as has been previously reported for Beulah-Zap lignite coal^{4,18}. Since we do not observe any endothermic peak for the

vacuum dried sample at $300 < T < 423$ K, we believe that the broad peak at around 373 K is due to the loss of water from coal.

Non-Isothermal Kinetics

The general expression for the decomposition of a solid is given by

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

and

$$k = A \exp(-E/RT). \quad (2)$$

In Equations (1) and (2), α is the fractional conversion at time t , k is the rate of reaction, E is the activation energy (in J mol⁻¹), R is the gas constant (in J mol⁻¹ K⁻¹), A is the frequency factor, and T is temperature. The expression for the isothermal kinetics can be obtained by integrating Equation (1), i.e.,

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt. \quad (3)$$

Depending upon the decomposition kinetic mechanism^{17,19}, $F(\alpha)$ has twelve different expressions. The decomposition models are listed in Table 1. In order to obtain non-isothermal kinetic expressions, Equation (1) can be modified by introducing heating rate, i.e.,

$$\frac{d\alpha}{dT} \frac{dT}{dt} = A \exp(-E/RT) f(\alpha). \quad (4)$$

Substituting for $dT/dt = B$ in Equation (4), we can rewrite it as

$$\frac{d\alpha}{dT} = \frac{A}{B} \exp(-E/RT) f(\alpha). \quad (5)$$

It should be noted that B ($= dT/dt$) is a constant heating rate and is known for DSC experiments. Rearranging and integrating²⁰ Equation (5), we obtain

$$F(\alpha) = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E}\right) \exp(-E/RT). \quad (6)$$

From Equations (3) and (6) the fractional conversion α can be solved mathematically as a function of temperature. The appropriate non-isothermal expressions for $F(\alpha)$, representing twelve different kinetic models, were solved and are listed in Table 1. To extract the activation energy from the experimental data, Equation (6) should be further simplified by taking logarithms, i.e.,

$$\ln\left(\frac{F(\alpha)}{T^2}\right) = \ln\frac{AR}{BE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT}. \quad (7)$$

Thus, from a plot of $\ln\left(\frac{F(\alpha)}{T^2}\right)$ versus $1/T$, the activation energy E and frequency factor A can be obtained.

Kinetic Parameters

To determine the mechanisms of desorption of water from coal, the experimentally determined parameters, i.e., temperature and the fractional loss of water ($\alpha(T)$), are fitted to appropriate kinetic equation(s). However, before the desorption kinetic models can be tested for the DSC data, whether the enthalpy of the evolution of water is proportional to the amount of water lost needs to be established. To answer this, we undertook the following experiments: the as-received coal sample (particle size $< 841 \mu\text{m}$) was saturated with distilled water for 48 hours. The sample was then dried for different amounts of time. This enabled us to produce coal samples with different moisture contents. The DSC curves of these samples were recorded, and the enthalpy of the evolution of water (ΔH) was calculated. The ΔH has been graphed in Fig. 2 as a function of moisture content. As can be seen from

this figure, an excellent linear relationship exists between ΔH and the moisture content of coal.

The experimental $\alpha(T)$ values²¹ were obtained from the DSC curves shown in Fig. 1., i.e.,

$$\alpha(T) = \frac{\int_{T_0}^T \Delta H_T dT}{\int_{T_0}^{T_1} \Delta H_T dT}, \quad (8)$$

where T_0 is the temperature at which the endothermic curve begins and T_1 is the temperature at which the curve ends. The α values obtained from Equation (8) were fitted to 12 non-isothermal kinetic models listed in Table 1. A least square computer procedure, in conjunction with Equations (5), (6) and (7), was adopted to ascertain the kinetic mechanism of water's desorption from lignite coal.

Our calculations suggest that the unimolecular kinetic model and the 2nd-order diffusion kinetic model are simultaneously operative for the desorption of water from all three particle sized coal. The activation energies for unimolecular decay and 2nd-order diffusion models were determined from Equation (7) and are listed in Table 2. The individual contributions of the fore-said kinetic models to the overall desorption of water from lignite coal were determined by fitting the experimental data to the temperature dependence of $\alpha(T)$, i.e.,

$$\alpha(T) = C_1 \{1 - \exp[-Y(T)]\} + C_2 \left\{1 - \frac{1}{Y(T) + 1}\right\}, \quad (9)$$

and

$$Y(T) = \frac{ART^2}{BE} \left\{1 - \frac{2RT}{E}\right\} \exp\left(-\frac{E}{RT}\right).$$

In Equation (9) the first term on the right hand side depicts the unimolecular decay, while the second term represents 2nd-order diffusion kinetics. The contributions of C_1 and C_2 ($C_1 + C_2 = 1$) for three particle sized lignite coal were determined and listed in Table 2. In Fig. 3 we graph both the experimentally observed and the theoretically calculated $\alpha(T)$ values. An excellent agreement between the calculated values and the experimentally observed values was discerned.

An interesting feature of our DSC results is the main endothermic peak which shifts to higher temperatures as the particle size of coal increases, i.e., peak is observed at 372 K, 376 K, and 382 K for $< 37 \mu\text{m}$, $< 106 \mu\text{m}$, and $< 841 \mu\text{m}$ particle size, respectively (see Fig. 1). This observation indicates that higher thermal energy was required for a larger particle sized sample to desorb water. In order to understand this surprising observation, we need to examine the factors which determine the value of heat energy flow towards the sample.

For a power-compensated DSC system, when heat is absorbed, the heat flow rate dH/dt is dictated by^{21,22}

$$\frac{dH}{dt} = \frac{dq}{dt} + (C_s - C_r) \frac{dT}{dt} + RC_s \frac{d^2q}{dt^2}. \quad (10)$$

In Equation (10), q is the heat of transformation per unit of volume, C_s is the sample heat capacity, C_r is the reference heat capacity, and R is the effective thermal resistance. The reference heat capacity C_r is the same for all three samples. The heat of the transformation should remain constant considering that the three different particle sized samples were prepared from the same

coal. However, two factors can affect the heat flow rate, i.e., the sample's heat capacity and the effective thermal resistance. It is reasonable to argue that the C_s value of the dry coal should be independent of particle size. However, according to Table 2 the total moisture content of coal decreases as the particle size decreases. Therefore, C_s value will be largest for $< 840 \mu\text{m}$ sized particles. This fact suggests that the peak temperature should shift towards higher temperatures for larger sized particles. However, we estimate that the heat capacity alone can not explain the observed peak temperature shifts.

The effective thermal resistance (R) depends on how well the sample contacts the sample pan and how good the thermal conductivity of the sample is. In our experiments, we packed the coal samples loosely in the aluminum sample pans to minimize mechanical diffusion barriers created by the dense packing¹¹. Barrall and Rogers²³, using glass beads of various sizes, examined the effects of particle size on the thermal resistance. From their experimental data, they argued that the large beads did not transmit heat as well as the smaller beads. The ground coal particles have different shape and sizes. Therefore, quantitative estimation of the effective thermal resistance, as a function of particle size range, is difficult if not impossible. Qualitatively, the greater the particle size the larger will be the average interstices between the coal particles. This will effectively raise the thermal resistance of a packing of larger sized coal particles relative to a packing of smaller sized coal

particles. Hence, the thermal resistance will increase as the particle size increases. If such is the case, then Equation (10) predicts that the larger sized particles will need higher thermal energy (kT) for water to desorb. In view of the above discussion, we argue that the endothermic peak shifts observed (see Fig. 1), for larger sized coal particles relative to smaller sized particles, are due to larger thermal resistance of the sample packing. Similar shifts have been reported for the dehydration reaction of the kaolinite clay mineral. Langer and Kerr²⁴ reported that an increase in the particle size of kaolinite increased the peak temperature of the dehydration reaction.

The results presented in Table 2 indicate that the activation energies for desorption of water decrease as the particle size of the sample decrease. The effective thermal resistance of various sized particle packing and the time taken for the evolved water to diffuse to the particle surface will affect the activation energies computed. Since the variation in the activation energies of various sized coal samples is small, it is difficult to separate the contributions of thermal resistance from the particle size. However, for larger particles the surface area-to-mass ratio is relatively small, and consequently, the desorption of the water will be slower. Similar behavior has been reported by Pope and Sutton²⁵ for the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ particles.

Kinetic Mechanisms

As discussed in the previous section, our DSC results indicate that the desorption of water from Beulah-Zap lignite coal

obeys the unimolecular decay and 2nd-order diffusion kinetics. The unimolecular decay mechanism is applicable for a system where each molecule has an equal probability of undergoing decomposition reaction^{1,26}. In the coal-water system, the bulk-type water is expected to display evaporation like characteristics¹, if present. A simple, but excellent, description of the physical process involved in water's evaporation has been presented by Feynman et al.²⁷. In our case it implies the existence of an effective water-nitrogen interface where the water molecules at the interface have an equal chance of leaving the interface. This leads us to believe that bulk-type of water is located around the coal particles and/or is near the mouths of large pores. Similar drying behaviors have been reported for gunpowder and some polymers²⁸ where initial water, about half of the total moisture, is lost via first order decay law. However, once the initial water has been lost from coal the mechanism of drying is expected to shift to a moving phase boundary mechanism, e.g., contracting sphere model^{17,19}. As initial water vaporizes, the water below the interface will vaporize and the rate of reaction will be controlled by the speed with which interface moves into the coal particle. On the other hand, if, as suggested by Suuberg et al.⁴, the low rank coals have colloidal gel-like structure, then the initial water loss will induce cross-linking in the coal. For water to desorb, especially at the later stages, it must diffuse to the surface. Hence, one would expect diffusion controlled kinetics once the initial water has been desorbed. Our previous results do not

indicate that water is lost from lignite coal either by moving phase or 1st-order diffusion mechanism^{1,18}.

Second-order diffusion kinetic is described as a recombination or non-dissociative process. For example, product molecules can be produced with an excess of energy which can re-energize reactant molecules. This kinetic has been observed for a number of systems²⁹, where desorption is non-dissociative. The non-dissociative desorption may result from the existence of a mobile precursor state, i.e., the adsorbed species must involve a transfer through this precursor (intermediate) state to gas phase. In coal-water system, the first layer of water is hydrogen bonded to the hydrophilic sites on the surfaces¹⁰. Since coal has a heterogeneous structure and the hydrophilic sites in coal are not uniformly distributed, the water adsorbed on the surface is in the form of patches (or clusters). Therefore, it is argued that the water molecules which follow the aforementioned diffusion kinetics are those water molecules which are on the coal surface or close to the coal surface. For these water molecules to desorb, they must hop from one site to another (i.e., in the mobile precursor state) along the surfaces of pores before they reach the outer surface of the particles and desorb. The possible models by which water desorbs from coal, obeying the 2nd-order diffusion mechanism, are shown in Figs. 4 and 5. As can be seen, it is possible for some water monomers to become dimers by re-energizing the water molecules on the surfaces. Some water monomers, having different velocities, can recombine to form dimers, and some water molecules having attained thermal energy kT can hop directly as

water dimers. The water molecules following this kinetic are mostly in the narrow pores (> 0.5 nm), as shown in Fig. 4, or on the surfaces of large pores (> 5 nm), as shown in Fig. 5.

Based on the data presented in Table 2, a question is raised: why do bulk water and surface water desorb simultaneously? It would be natural to expect bulk water to desorb first and then surface water. However, it should be kept in mind that in a DSC experiment the coal is heated under a flowing dry nitrogen condition. The effective humidity around the sample is expected to be extremely low. Evans³⁰ from his thermodynamic calculations has shown that under very low humidity conditions water can be lost from large and narrow pores simultaneously. In view of this, it is not surprising that two independent desorption mechanisms, operating simultaneously, are observed since water in narrow pores is largely surface water.

The values of the fractional constant C_1 , associated with unimolecular decay model, decreased from 0.29 to 0.14 as the particle size of the sample decreased from < 841 μm to < 37 μm (see Table 2). It seems that the main contribution to the bulk type of water, which obeys unimolecular decay kinetics, comes from those water molecules which are held near the mouth of large pores. On grinding the coal, it is reasonable to expect that fractures will occur at large pore sites. Hence, as the particle size decreases, the concentration of large pores decreases. This will lead to the reduced value of C_1 .

Abhari and Isaacs⁹ reported the drying kinetics of water of six coals from the Argonne coal-sample bank by TGA technique. Their calculated activation energy was 11.5 kJ mol^{-1} , which is much less than the activation energy of 40.6 kJ mol^{-1} for water vaporization¹. Vorres et al.¹ probed the drying kinetics of Beulah-Zap lignite coal at $293 < T < 360 \text{ K}$ under N_2 gas flow using the isothermal TGA technique. They used gas flow velocities from 20 to $160 \text{ cm}^3/\text{min}$ (in comparison to the present rate of $30 \text{ cm}^3/\text{min}$) and obtained activation energies, depending on the sample size, ranging from 30.6 to 41.9 kJ mol^{-1} . A direct comparison of our results with results reported by Vorres et al. is not feasible since the drying kinetics strongly depend on the temperature, gas flow velocities, and sample size. Malhotra et al.¹⁹ examined the water's desorption kinetics from the microporous KBr pellets by undertaking isothermal desorption measurements at 340, 350, 360, and 390 K with the help of the transmission-FTIR technique. They obtained a desorption activation energy of 37 kJ mol^{-1} at $P=0.13 \text{ Pa}$. Burroughs²⁸ monitored the drying kinetics of water from gun-powder by TGA technique and determined an activation energy of 63.2 kJ mol^{-1} . Activation energies of 46 kJ mol^{-1} to 170 kJ mol^{-1} have been reported for the dehydration of crystalline hydrates¹⁴. In view of the above discussion, we believe our activation energy values of about 52.4 kJ mol^{-1} for the unimolecular decay kinetics and of about 91.4 kJ mol^{-1} for the 2nd-order diffusion kinetics seem reasonable.

CONCLUSIONS

From the constant heating rate differential scanning calorimetry measurements at $295 < T < 480$ K on the Beulah-Zap lignite coal, the following is concluded:

(A) The drying kinetics of water, under the flowing N_2 gas environment, from the lignite coal are governed by two independent but simultaneously operative mechanisms, i.e., the unimolecular decay and the 2nd-order diffusion mechanisms.

(B) The bulk-type of water, which largely is confined near the mouths of large pores and/or surrounds the coal particles, is removed from coal via the unimolecular decay kinetics. The surface adsorbed water, including those physically confined in pores, is purged from coal via 2nd-order diffusion kinetics.

(C) The desorption activation energies of water are strongly affected by the physical process of desorption, but the energies are little affected by the particle size of coal.

(D) The water, which dries via 2nd-order diffusion, is the largest fraction of water in Beulah-Zap lignite coal.

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Table 1

Kinetics equations used to determine the
desorption kinetics of water from Beulah-Zap lignite coal

Model	Isothermal $F(\alpha) = kt$	Non-isothermal $\alpha(T)$
1) Contracting cylinder movement	$1 - (1 - \alpha)^{1/2} = kt$	$1 - (1 - y(T))^2$
2) Contracting sphere movement	$1 - (1 - \alpha)^{1/3} = kt$	$1 - (1 - y(T))^3$
3) Unimolecular decay	$-\ln(1 - \alpha) = kt$	$1 - \exp(-y(T))$
4) 2-dimensional growth of nuclei	$(-\ln(1 - \alpha))^{1/2} = kt$	$1 - \exp(-y(T)^2)$
5) 3-dimensional growth of nuclei	$(-\ln(1 - \alpha))^{1/3} = kt$	$1 - \exp(-y(T)^3)$
6) Arrami-Erofeev equation for nuclei growth	$(-\ln(1 - \alpha))^{1/4} = kt$	$1 - \exp(-y(T)^4)$
7) 2-dimensional diffusion	$(1 - \alpha)\ln(1 - \alpha) + \alpha = kt$	$(2y(T))^{1/2*}$
8) 3-dimensional diffusion	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3} = kt$	$(9y(T))^{1/2*}$
9) Second order diffusion	$(1 - \alpha)^{-1} - 1 = kt$	$1 - \frac{1}{y(T)+1}$
10) Power law	$\alpha^{1/2} = kt$	$(y(T))^2$
11) 1-dimensional diffusion	$\alpha^2 = kt$	$(y(T))^{1/2}$
12) Exponential law	$-\ln \alpha = kt$	$\exp(-y(T))$

$$y(T) = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E} \right) e^{-\frac{E}{RT}}$$

* Approximation has been made by series expansion.

Table 2

The kinetic parameters reflecting the desorption of water from Beulah-Zap lignite coal. The parameters were obtained from non-isothermal differential scanning calorimetry measurements.

Sample particle size (μm)	Activation energy (kJ/mol)		Moisture content (%)	Fractional constant	
	Unimolecular decay	2nd-order diffusion		C_1	C_2
< 841	54.99	95.54	30.31	0.29	0.71
< 106	51.76	90.09	26.86	0.20	0.80
< 37	50.55	87.78	22.38	0.14	0.86

FIGURE CAPTIONS

- Fig. 1 The DSC curves show the endothermic peak due to the desorption of water from Beulah-Zap lignite Coal.
- (A) < 841 μm particle size, (B) < 106 μm particle size, and (C) < 37 μm particle size.
- Fig. 2 This graph shows the linear dependence between the enthalpy of the evolution of water and the moisture content of the coal.
- Fig. 3 Graphs compare the experimentally observed desorption kinetics data with the calculated values of Equation (9) for three sized particles, i.e., (A) < 841 μm , (B) < 106 μm , and (C) < 37 μm . $\alpha(T)$ values were normalized so that $C_1 + C_2 = 1$ for each particle size.
- Fig. 4 The proposed desorption model of water in coal displays 2nd-order diffusion mechanism. The water is being removed from narrow pores.
- Fig. 5 The desorption model of water which obeys the 2nd-order diffusion kinetics is shown. The water is lost from the surfaces of large pores.

● Oxygen functional group
 — O-H group

⊗ Water (hopping)
 ○ Water

⊗ Water (hopping)

○ Water

• Oxygen functional group

— O-H group