Moisture Readsoption Performance of Air-Dried and Hydrothermally Dewatered Lignite

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ABSTRACT: Lignite is a kind of coal that has high moisture content and needs to be dried before being utilized. The dried lignite will readsopt moisture during its storage. In this work, a typical Chinese lignite was dried by air at 120–180 °C and hydrothermally dewatered at 200–320 °C. The moisture adsorption isotherms of treated coal and the parent coal were obtained at 30 °C to investigate the essential moisture adsorption properties. Then the moisture readsoption performance of the studied coal in the real storage was simulated by placing the samples in the atmosphere and monitoring the evolution of the sample masses. The experimental results indicated that the moisture readsoption capacity of the air-dried lignite was lower than the parent coal and decreased with increasing drying temperature. For the hydrothermally dewatered coal, the moisture readsoption capacity increased with increasing dewatering temperature to 240 °C and then decreased significantly as dewatering temperature rose to 320 °C. The inhibiting effects of both air drying and hydrothermal dewatering at 280 and 320 °C on the moisture readsoption performance were more remarkable in winter than in summer due to the lower relative humidity. The evolution of the lignite pore structure and functional groups after the air drying and hydrothermal dewatering were also examined to understand the changes in moisture readsoption properties.

1. INTRODUCTION

Coal is one of the most important energy sources, fueling around 40% of the power stations around the world.1,2 For a long time, lignite had not been used as widely as anthracite and bituminous coal in power stations because of its high moisture content, lower heating value, great tendency to combust spontaneously, and high degree of weathering. This situation is being changed. Lignite is now being exploited more and more intensively due to the increasing demand for electricity. However, high moisture content, which gives rise to high transportation cost, potential safety hazard in transportation and storage, and low thermal efficiency obtained in power plant, critically restrict the widespread use of lignite. Therefore, it is of great importance to reduce the moisture of lignite before industrial applications.3

Numerous technologies have been developed for lignite drying, and the drying properties of lignite have been studied by many investigators. However, attention should also be paid to the moisture adsorption properties of lignite, which are important to lignite storage. It is known that the dewatered lignite could readily readsopt moisture from the atmosphere, which brings difficulties to the storage of lignite after drying. Therefore, it is necessary to understand the moisture readsoption properties of dewatered lignite.

The moisture adsorption of lignite is mainly caused by its rich porous structure. In the drying process, the pore structure may collapse, shrink, or become cross-linked, which gives rise to significant changes in the moisture adsorption properties of lignite. Yang et al.4 dried a typical Chinese lignite at 60–160 °C and investigated the readsoption performances of dewatered samples and the changes in pore structure. The results showed that the mesopore (5–50 nm) was the main factor that influenced the readsoption of the coal. Choi et al.5 investigated the moisture readsoption behavior of upgraded lignite produced by a coal-oil slurry dewatering process. The moisture readsoption of the dewatered lignite is reduced by the coating of asphalt on both the outer and inner surfaces of lignite, which covers the pores and suppresses the active functional groups. Surface functional groups also play roles in the moisture adsorption on coals. Previous studies indicate that the oxygen functional groups on the coal surface can adsorb water molecules.6,7 Hydrogen bonds may be formed between water molecules and oxygen functional groups such as carboxyl, carbonyl, phenolic, and hydroxyl groups.8–11 The changes in the pore structure and surface functional groups due to the dewatering treatment will result in changes in the moisture adsorption property of the coal.

The moisture adsorption isotherm represents the relationship between the equilibrium moisture content (EMC) of the porous material and the corresponding relative humidity (RH) at constant temperature and pressure. Since the moisture adsorption isotherm can provide the essential moisture adsorption properties of porous materials, it has been widely applied in the research of hygroscopic materials, including lignite. Allardice and Evans12 investigated adsorption and desorption isotherms of Yallourn lignite from Australia at 30, 40, 49, and 60 °C. Fei et al.13 obtained adsorption isotherms of Victorian lignites at 30 °C by three different measurement methods. Comparisons show that the rate of approaching the final relative vapor pressure has an insignificant effect on the adsorption isotherms. Allardice et al.14 and Fei et al.13,15 measured the adsorption isotherms of water-washed, acid-
washed, and ion-exchanged lignites and found that the presence of inorganic cations increases the EMC values of lignites.

As mentioned above, most previous studies focus on the moisture adsorption properties of raw lignites or chemically treated lignites. However, the conclusions of these studies may be not suitable for the dried or dewatered lignites. Most drying processes could change the physical and chemical structures of the lignite so that the moisture adsorption properties of the lignite will be changed after drying. Therefore, the moisture adsorption property of the dried or dewatered lignite should be redetermined to provide the theoretical guidelines for its storage conditions.

In this study, a typical Chinese lignite was treated by packed bed air drying and hydrothermal dewatering, which are, respectively, the representative evaporative and nonevaporative drying technologies. The moisture adsorption isotherms of the treated coals were obtained and analyzed. The treated lignites were then placed in the atmosphere to investigate the readsorption performance in summer and winter. All the results were compared with those of the parent coal to identify the effects of air drying and hydrothermal dewatering on the lignite’s moisture adsorption properties. The pore structures and functional groups of the treated coals and parent coal were measured to understand the mechanism of these changes.

### 2. EXPERIMENTAL SECTION

#### 2.1. Coal Preparation.

In this study, lignite from Pingzhuang Mine, Inner Mongolia, China, was selected as the parent coal. The proximate and ultimate analyses of the lignite are shown in Table 1. The raw coal was ground and sieved to 1−7 mm and treated by two different methods: packed bed air drying and hydrothermal dewatering. In the packed bed air drying, the raw coal (as received basis lignite) was dried in a lab-scale packed bed dryer with the height of 300 mm and the inner diameter of 30 mm, as shown in Figure 1.

The coal samples of 30 ± 0.1 g were located in the packed bed at different heights above the gas distributor to monitor the temperature, and the other five were located in the packed bed at different heights above the gas distributor to monitor the temperature inside and above the bed. The raw coal was dried until the mass and the temperature did not change any more. To study the effect of drying temperature on the moisture readsorption performance, the packed bed air drying experiments were carried out at four temperatures (120, 140, 160, and 180 °C). Notice that treating processes above 160 °C are not exactly drying processes; Yang et al. have pointed out that this kind of lignite will release CO₂ during the air drying processes above 160 °C, representing the decomposition of volatile matter in the lignite. However, for convenience, the treating processes with the temperature above 160 °C are still expressed as drying processes.

The hydrothermal dewatering of lignite was carried out in the experimental system shown in Figure 2. The lignite samples (30 ± 0.1 g) were mixed with water, and the slurry was placed in an autoclave. The autoclave was then sealed and heated to the desired temperature. The hydrothermal dewatering experiments were conducted at 200, 240, 280, and 320 °C for 60 min. Then the autoclave was cooled, and the dewatered coal was taken out and dried at 105−110 °C for 2 h. As the calibrator sample, the raw lignite was also dried at 105−110 °C for 2 h, which is called the parent coal. The parent coal, air-dried lignite, and hydrothermally dewatered lignite, were ground and sieved to.

### Table 1. Proximate and Ultimate Analyses of Pingzhuang Lignite

<table>
<thead>
<tr>
<th>proximate analysis (wt %, ad)</th>
<th>ultimate analysis (wt %, ad)</th>
<th>Q_{net,ar} (MJ·kg⁻¹)</th>
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<td>M&lt;sub&gt;ar&lt;/sub&gt;</td>
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<td>8.55</td>
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Figure 1. Schematic diagram of the experimental packed bed dryer system. (1) Air pump, (2) mass flow controller, (3) electrical heater, (4) temperature controller, (5) packed bed, (6) thermocouples, (7) gas distributor, (8) gravity sensor, (9) data acquisition unit, (10) computer.

Figure 2. Schematic diagram of hydrothermal dewatering system. (1) Pressure gauge, (2) thermocouple, (3) autoclave, (4) electrical heater, (5) coal sample, (6) water.

g) were mixed with water, and the slurry was placed in an autoclave. The autoclave was then sealed and heated to the desired temperature. The hydrothermal dewatering experiments were conducted at 200, 240, 280, and 320 °C for 60 min. Then the autoclave was cooled, and the dewatered coal was taken out and dried at 105−110 °C for 2 h. As the calibrator sample, the raw lignite was also dried at 105−110 °C for 2 h, which is called the parent coal. The parent coal, air-dried lignite, and hydrothermally dewatered lignite, were ground and sieved to.
100−125 μm and dried at 105−110 °C to obtain the dry base samples, which were prepared for further analyses.

2.2. Analytical Methods. 2.2.1. Pore Structure and Functional Group Analysis. The pore structures of studied coals were investigated. The pore volumes and specific surface areas of the samples were determined by the nitrogen Brunauer−Emmett−Teller (BET) surface method. Prior to the BET surface analysis, vacuum degasification at 373 K for 4 h was conducted for all the samples. Every measuring experiment was repeated three times.

Infrared spectra of the parent coal and the treated coals were analyzed using a Fourier transform infrared (FTIR) spectrometer. KBr pellets were prepared by mixing ∼2.0 mg of coal with 200 mg of KBr. Infrared spectra of the lignite samples in the 4000−3900 cm−1 region were obtained. The assignment of the functional groups in the infrared spectra was made according to literature.16−18 Every measuring experiment was repeated twice.

2.2.2. Adsorption Isotherm Measurements. Moisture adsorption isotherms of the studied coals were measured at 30 °C. The three kinds of lignite samples (10 ± 0.1 g) were placed in open glass pans and put in desiccators containing selected saturated salt solutions. The salts of KOH, LiCl, CH3COOK, MgCl2, Mg(NO3)2·6H2O, NaCl, KCl, and K2SO4 were selected to maintain the equilibrium relative humidity in the desiccators. The desiccators were placed in a temperature-controlled hot-air oven. Samples were weighed every 3 d until changes in weight loss or gain reached less than 0.001 g for two successive readings. The moisture content of each sample was determined gravimetrically by drying in an oven at 105°C for 2 h. In this study, the moisture content in the lignite was expressed on dry matter basis as follows:

\[
m = \frac{M_w}{M_d}
\]

where \(M_w\) is the mass of the moisture in the lignite, and \(M_d\) is the mass of dry lignite.

2.2.3. Moisture Readsoption Performance. The moisture readsoption performance of the studied coals was investigated. The samples (10 ± 0.1 g) of the raw coal, air-dried coal, and hydrothermally dewatered coal were tiled in a container and placed in the atmosphere. The mass of samples increased because of the moisture readsoption. The mass of the samples was monitored every 2 h in the first 24 h and then monitored with longer intervals in the following days. The experiments lasted for ~10 d, and the mass changes on the coal samples with the time were obtained. During the experiments, the average ambient temperature and relative humidity were recorded every day. The experiments were carried out in summer and winter.

3. THEORETICAL BASIS

3.1. Moisture Adsorption Isotherm Model. Several models have been developed to describe the moisture adsorption on porous materials, such as Langmuir model, BET model, GAB (Guggenheim−Anderson−deBoer) model, Halsey model, Henderson model, etc.19−21 According to the previous studies, the modified BET model is the most suitable for the moisture adsorption on lignite.9,10 In this model, moisture was presumed to be adsorbed on two types of adsorption sites: primary adsorption sites and secondary adsorption sites. The primary adsorption sites have high binding energies with respect to water molecules, which could be represented by oxygen-containing groups such as carboxyl and hydroxyl groups on the coal surface. The secondary adsorption sites could be considered as the water molecules adsorption on the first water-occupied primary sites or previously formed secondary sites, having lower binding energies. The schematic diagram of primary and secondary adsorptions in a pore is shown in Figure 3. For primary and secondary sites, the adsorption capacities can be described as follows:9,10,22,23

\[
m_1 = \frac{m_0 K_1 P_m}{1 - K_1 P_m + K_2 P_m}
\]

\[
m_2 = \frac{m_0 K_1 K_2 P_m^2}{1 - K_1 P_m (1 - K_2 P_m + K_2 P_m)}
\]

where \(m_1\) and \(m_2\) are the adsorption capacities of the primary and secondary sites, respectively, \(K_1\) and \(K_2\) are the constants related to the adsorption energies of the primary and secondary sites, respectively, \(m_0\) represents the monolayer adsorption capacity, \(P\) is the vapor pressure, and \(p\) is the saturation vapor pressure.

Thus, the adsorption capacity \(m\) of the coal can be calculated by adding \(m_1\) and \(m_2\) together and expressed as follows:

\[
m = \frac{m_0 K_1 P_m}{1 - K_1 P_m + K_2 P_m}
\]

4. RESULTS AND DISCUSSION

4.1. Pore Structure. Generally, the moisture adsorption properties of coals are mainly determined by the pore structure. The drying and dewatering processes can give rise to significant changes in the pore structure of the lignites, which will further influence the moisture adsorption properties. The total pore volumes and specific surface areas of the parent coal and treated coals are shown in Table 2. It can be seen that the total pore volume of the lignite decreases slightly, while the specific surface area decreases significantly due to the air drying. As the drying temperature increases from 120 to 180 °C, the decreases of the total pore volume and specific surface area become more and more significant.

For the hydrothermally dewatered coals, the changes of the pore structures are more complex. Both the total pore volume and specific surface area of the coal increased significantly due to the dewatering processes under the dewatering temperatures of 200 and 240 °C, while a decrease takes place at dewatering temperatures of 280 and 320 °C. A similar trend is found for the specific surface area. More detailed information about the pore structures of the studied coals can be obtained and investigated from the pore size distributions of the coals, as shown in Figure 4.
the micropore (\(D_{\text{pore}} < 2\) nm) volume is very small. This is one of the typical characteristics of lignite. As shown in Figure 4a, the mesopore volume decreases significantly, while the micropore volume decreases slightly after the air drying. This is because the shrinkage force caused by the removal of water leads to the shrinkage and collapse of the mesopores and micropores during the drying process.\(^4,24\) Moreover, the macropore volume of air-dried coals becomes higher than that of the parent coal, which indicates that some new macropores are formed by the air heating. The cross-link of mesopores can give rise to the increase of the macropores. Some low molecular mass compounds are released during the air drying, which also causes the formation of macropores.

The evolution of the hydrothermally dewatered coal seems to be more remarkable than that of the air-dried coal, as shown in Figure 4b.\(^{25}\) For the hydrothermally dewatered coals, no macropores are found, and the mesopores account for the vast majority proportion of the pore volume. The changes in the pore structure of the lignite probably result from the competition of two counteracting phenomena, which are the removal of low molecular mass volatile matter and the particle thermal contraction.\(^{24}\) As known to all, the coal particles will contract due to the heating during dewatering, resulting in the shrinkage of macropores. On the other hand, low molecular volatile matter is removed during the dewatering process, giving rise to the formation of new mesopores. At the dewatering temperatures of 200 and \(240 \, ^\circ\text{C}\), the decrease of the pore volume due to the shrinkage of macropores is not as much as the increase in volume of the newly formed mesopores; thus, the total pore volume increased significantly. As the dewatering temperature is raised up to 280 and \(320 \, ^\circ\text{C}\), the particle shrinkage goes on. Moreover, tar begins to generate at this temperature and covers the pores in the coal particles, resulting in the decrease of the total pore volume.

4.2. Functional Group. According to previous studies,\(^8−11\) carboxylic groups have strong interactions with \(\text{H}_2\text{O}\) molecules due to the strong H-bonds, while other functional groups have weaker interactions. The functional groups, including carboxylic and carbonyl groups, on the surface of studied coals were investigated by FTIR spectroscopic analysis. Generally, the aromatic nucleuses are stable enough so that reactions can hardly take place on them under the drying and dewatering conditions in this study. Since the aromatic carbon remains almost invariable, the ratio of oxygen functional groups to the aromatic carbon can provide a quantitative understanding of their changes during the drying or dewatering processes,\(^{27,18}\) and the results are listed in Table 3.

### Table 2. Pore Structure of the Parent Coal and Treated Coals (100−125 μm)

| sample | parent coal | air-dried coal (\(120 \, ^\circ\text{C}\)) | | | | air-dried coal (\(140 \, ^\circ\text{C}\)) | | | | air-dried coal (\(160 \, ^\circ\text{C}\)) | | | | air-dried coal (\(180 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(200 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(240 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(280 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(320 \, ^\circ\text{C}\)) |
| \(V_t\) (mm\(^3\)·g\(^{-1}\)) | 26.30 | 25.96 | 23.49 | 22.63 | 21.68 | 30.33 | 43.99 | 17.66 | 7.77 |
| SD\(^b\) | 1.707 | 1.409 | 0.854 | 0.540 | 0.673 | 1.939 | 2.031 | 0.904 | 0.596 |
| \(S_t\) (m\(^2\)·g\(^{-1}\)) | 13.84 | 6.95 | 6.45 | 6.35 | 5.26 | 16.62 | 30.41 | 12.97 | 3.26 |
| SD\(^c\) | 0.738 | 0.332 | 0.329 | 0.478 | 0.233 | 0.773 | 1.763 | 0.597 | 0.340 |

\(^{a}\)\(V_t\) is the total pore volume. \(^{b}\)SD is the standard error. \(^{c}\)\(S_t\) is the total surface area.

### Table 3. Functional Groups of the Parent Coal and Treated Coals

| sample | parent coal | air-dried coal (\(120 \, ^\circ\text{C}\)) | | | | air-dried coal (\(140 \, ^\circ\text{C}\)) | | | | air-dried coal (\(160 \, ^\circ\text{C}\)) | | | | air-dried coal (\(180 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(200 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(240 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(280 \, ^\circ\text{C}\)) | | | | hydrothermally dewatered coal (\(320 \, ^\circ\text{C}\)) |
| CO/Car | 0.233 | 0.234 | 0.369 | 0.416 | 0.482 | 0.229 | 0.167 | 0.048 | 0.062 |
| SD | 0.0215 | 0.018 | 0.0195 | 0.02 | 0.023 | 0.019 | 0.014 | 0.011 | 0.009 |
| COOH/Car | 0.652 | 0.651 | 0.646 | 0.748 | 0.866 | 0.597 | 0.520 | 0.454 | 0.354 |
| SD | 0.026 | 0.03 | 0.015 | 0.036 | 0.0315 | 0.03 | 0.0225 | 0.021 | 0.024 |

Figure 4. Pore size distribution of the parent coal and treated coals (micropore: \(D_{\text{pore}} < 2\) nm; mesopore: 2 nm < \(D_{\text{pore}} < 50\) nm; macropore: \(D_{\text{pore}} > 50\) nm).
For the air drying, the ratios of carboxyl/aromatic (COOH/Car) and carbonyl/aromatic carbon (CO/Car) stay almost unchanged at the drying temperature of 120 °C and start to increase at 140 and 160 °C, respectively. At the drying temperature of 180 °C, both the ratios of (COOH/Car) and (CO/Car) show significant increase, compared to those of the parent coal. These observations suggest that oxidation reactions take place between the coal and the drying air and result in the formation of oxygen functional groups. Since the aromatic carbon of the coal seems unaffected by the oxidation, the increase of oxygen functional groups is probably caused by the oxidation of aliphatic parts.

For the hydrothermally dewatered coals, it can be observed that the ratios of carboxyl/aromatic (COOH/Car) and carbonyl/aromatic carbon (CO/Car) are lower than those of the parent coal and decreased with the dewatering temperature, which indicates that some of the carboxyl and carbonyl groups were removed during the hydrothermal dewatering. The changing trend of the functional groups due to the hydrothermal dewatering agrees with previous studies.26−28

4.3. Moisture Adsorption Isotherms. The moisture adsorption isotherms of the studied coals, which can provide the essential moisture adsorption properties, are obtained at 30 °C.

4.3.1. Air-Dried Coal. The EMC of the parent coal and air-dried coals at different vapor pressures are plotted in Figure 5.

![Figure 5. Moisture adsorption isotherms of air-dried coals at 30 °C.](image)

The moisture adsorption isotherms are then obtained by fitting the series of points in Figure 5, using the modified BET model. The fitted parameters are listed in Table 4. It can be observed that the parent coal has higher EMC than the air-dried coals, regardless of the vapor pressure. This is mainly because the total pore volume of the coal decreases due to the air drying.

In detail, the EMC of dried coals are lower than that of the parent coal. The gaps increase with the increasing vapor pressure at low vapor pressure (p/psat < 0.5) and then decrease at higher vapor pressure (p/psat > 0.5). This is because the primary adsorption, representing the adsorption on the coal surface, plays a major role in the moisture adsorption at low vapor pressure. The primary adsorption capacity becomes lower after the air drying.

The primary adsorption content of the air-dried coals under different p/psat are shown in Figure 6a. The primary adsorption content increases with the increasing vapor pressure and approached the limiting value of m0, which represents the monolayer adsorption capacity of the coal. The primary adsorption capacity decreases significantly due to the air drying. Since the primary adsorption takes place on the coal surface, the primary adsorption capacity is mainly determined by the specific surface area and the concentration of primary adsorption sites on the coal surface. As mentioned above, hydrophilic oxygen-containing functional groups act in the primary adsorption sites, so it is reasonable that higher specific surface area and more oxygen functional groups will give rise to a higher primary adsorption capacity. As shown in Table 2, the specific surface areas of the air-dried coals are much lower than those of the parent coal. The oxygen functional groups increase after air drying, as shown in Table 3. However, the increase of oxygen functional groups is not as much as the decrease of specific surface area. The competition of the two changes finally results in a decrease in the primary adsorption capacity.

The secondary adsorption content of the air-dried coals are shown in Figure 6b. The secondary adsorption content increases with the increasing vapor pressure for all the coals. It is interesting to notice that the air drying processes have weak effect on the secondary adsorption content of the coal. This is mainly because the secondary adsorption is mainly determined by the pore volume, and the changes in the pore volume of the coals due to the air drying are slight. Besides, M. Švábová et al.30 have pointed out that the secondary adsorption may be affected by the concentration of the primary adsorption sites, because the modified BET model presumes that the secondary adsorbed water molecules are adsorbed on the water-occupied primary sites or the previously formed secondary sites. As shown in Tables 2 and 3, the pore volume of the air-dried coals decreases slightly, while the oxygen functional groups increase slightly; the competition results in a small decrease in the secondary adsorption content. In summary, the EMC of the lignite decreases after the air drying. The primary adsorption content decreases significantly, while the secondary adsorption content decreases slightly due to the air drying.

4.3.2. Hydrothermally Dewatered Coal. The experimental data and fitted moisture adsorption isotherms of the parent coal and hydrothermally dewatered coals are shown in Figure 7. The fitted parameters are listed in Table 4. The moisture adsorption capacity of the coal is changed by the hydrothermal dewatering. However, different from the air-dried coals, changes in the moisture adsorption capacity with the dewatering temperature are relatively small.

<table>
<thead>
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<th>Table 4. Fitting Parameters of the Moisture Adsorption Isotherms</th>
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* R² = coefficient of determination
are not monotonous. The EMC of the lignite increases with the increasing dewatering temperature up to 240°C and then decreases significantly, which conforms with the trend of pore volume evolution of the coal.

It can be observed from Figure 8a that the primary adsorption content of the coal is increased with increasing dewatering temperature up to 240°C and is then decreased. The primary adsorption is determined by the specific surface area and the concentration of primary adsorption sites. At the dewatering temperatures below 240°C, the specific surface area of the coal increases significantly with increasing temperature. Contrarily, the oxygen-containing functional groups are decreased, representing the decrease of primary adsorption sites. However, since the dewatering temperature is not high enough, the decrease of oxygen-containing functional groups is slight, and thus its effect on the primary adsorption capacity is not as great as the increase of the specific surface area. Therefore, the primary adsorption content of the coal is increased with the dewatering temperature up to 240°C. As the dewatering temperature is increased to 280 and 320°C, both the specific surface area and oxygen-containing functional groups are decreased to even lower levels than those of the parent coal. Therefore, the primary adsorption content of the lignite decreases with increasing dewatering temperature above 240°C and becomes lower than that of the parent coal.

The secondary adsorption content of the hydrothermally dewatered coals and the parent coal are shown in Figure 8b. The secondary adsorption content of 200 and 240°C dewatered coals are almost the same with the parent coal. Although 200 and 240°C dewatered coals have higher pore volumes, their primary adsorption site concentrations, which also influence the secondary adsorption content, are lower than those of the parent coal. The net effect of the two counteracting evolutions results in negligible change on the secondary adsorption content of the 200 and 240°C dewatered coals, compared to the parent coal. For the 280 and 320°C dewatered coals...
dewatered coals, both the pore volume and the concentration of the primary adsorption sites are much lower than those of the parent coal, resulting in the significant decrease of secondary adsorption content.

4.4. Moisture Readsorption Performance. To estimate the moisture readsorption performance of the studied coals in the real storage, the coals are tiled in a container and placed in the atmosphere. The mass of samples and the relative humidity are recorded. The moisture readsorption performances of air-dried coals and the parent coal are shown in Figure 9. According to the moisture adsorption isotherms, the moisture adsorption content of the air-dried coals is lower than that of the parent coal and decreases with the drying temperature. Higher moisture readsorption contents are obtained in July compared to those in December, which results from the higher relative humidity in July. It is interesting to notice that the differences between the moisture readsorption content of dried coals and the parent coal in December are larger than those in July. This can be explained by the moisture adsorption isotherms. Figure 6 shows that the primary adsorption content decreases more significantly than the secondary adsorption content due to the air drying. The experiments in December are conducted under lower relative humidity (~60%), compared to the higher relative humidity of ~80% in July. The primary adsorption takes a larger proportion of the total adsorption under lower relative humidity, so the decrease of the moisture readsorption content is greater than that under higher relative humidity. Therefore, the air drying treatment can reduce the water absorption of the lignite, and it is more effective under a lower relative humidity.

Figure 10 shows the moisture readsorption performance of hydrothermally dewatered coals and the parent coal. Also according to the moisture adsorption isotherms, the moisture readsorption content of the lignite increases with the increasing dewatering temperature up to 240 °C and then decreases significantly. This suggests that the moisture readsorption is reduced only if the hydrothermal dewatering is carried out above 240 °C. Moreover, the moisture readsorption content obtained in December is much lower than those in July for all the coals due to the lower relative humidity, suggesting that it is easier to reduce the moisture readsorption of hydrothermally dewatered coals in winter than in summer.

5. CONCLUSIONS

In the present work, a typical Chinese lignite was treated by packed bed air drying and hydrothermal dewatering. The moisture readsorption properties of treated coals was investigated and compared with those of the parent coal. The pore structure and functional groups of the studied coals were measured. The main conclusions of the current studies are as follows: (1) Both the pore volume and the specific surface area of the lignite decrease after air drying, while the oxygen functional groups increase. The moisture readsorption capacity of the air-dried coals is lower than the parent coal and decreases with increasing drying temperature due to the evolution of pore structure and oxygen functional groups. (2) The pore volume and the specific surface area of the lignite increase significantly due to the dewatering process under the dewatering temperature of 200 and 240 °C, while a decrease takes place under 280 and 320 °C. The oxygen functional groups of the lignite decrease monotonically with increasing dewatering temper-
ature. As a result, the moisture readsorption capacity of the lignite increases with increasing dewatering temperature up to 240 °C and then decreases significantly up to 320 °C. (3) The inhibiting effects of both air drying and hydrothermal dewatering at 280 and 320 °C on the moisture readsorption performance are more remarkable in winter than in summer due to the lower relative humidity.

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

\[ D_{\text{pore}} = \text{pore diameter, nm} \]
\[ K_1, K_2 = \text{constants} \]
\[ m = \text{moisture content, g·g}^{-1} \]
\[ m_0 = \text{monolayer adsorption capacity, g·g}^{-1} \]
\[ m_1 = \text{adsorption capacity of primary sites, g·g}^{-1} \]
\[ m_2 = \text{adsorption capacity of secondary sites, g·g}^{-1} \]
\[ M_d = \text{mass of the dry lignite, g} \]
\[ M_w = \text{mass of the moisture in the lignite, g} \]
\[ p = \text{vapor pressure} \]
\[ p_s = \text{saturation vapor pressure} \]

■ REFERENCES